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CHEMICAL AND PHYSICAL PROPERTIES OF METHYL IODIDE AND ITS OCCURRENCE UNDER REACTOR ACCIDENT CONDITIONS

(A Summary and Annotated Bibliography)

L. F. Parsly

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L. F. Parsly

Reactor Division

DECEMBER 1971

OAK RIDGE NATIONAL LABORATORY
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FOREWORD

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PREFACE

In the analysis of light water reactor accidents, the existence of part of the radioiodine in a persistent, volatile form, which has been identified as methyl iodide, has been found to limit the effectiveness of iodine trapping systems. While carrying out a research and development program on containment spray technology, I became aware that a rather large body of published information about methyl iodide exists. This includes many research results on its chemical behavior and on the effects of light and ionizing radiation on it. Also there is a substantial and growing body of data on the occurrence of methyl iodide under real or simulated accident conditions. This report brings together and summarizes the published material.

ACKNOWLEDGMENTS

The writer has been helped in many ways by a number of people in assembling this work. G. W. Keilholtz of the Nuclear Safety Information Center has been most helpful in providing a search of the NSIC files and in furnishing a number of the open literature references. He also contributed in several useful discussions. Dr. E. J. Hoffmann of the Division of Technical Information Extension, USAEC, furnished a print-out of the subject index material on methyl iodide in Vols. 22 and 23 of Nuclear Science Abstracts, which was not available in collective index form at the time. Discussions with B. A. Soldano and H. E. Zittel provided valuable leads. Critical reviews of the early drafts by W. B. Cottrell, T. H. Row, and H. E. Zittel have been helpful. H. Kubota and A. Fukuda translated several of the articles written in Japanese.

ABSTRACT

An extensive annotated bibliography on methyl iodide is presented that covers physical and chemical properties, chemical reactions, behavior under radiation, absorption, and trapping. The occurrence of methyl iodide in containment experiments and accidents is discussed.

1. INTRODUCTION

Among the fission products expected to be released from nuclear power reactor fuel in the unlikely event of a major loss-of-coolant accident, radioiodine is of most concern because it is highly volatile and is readily taken up by living organisms. Early studies of the behavior of iodine in containment buildings indicated that iodine existed in several forms in the containment atmosphere.[1] One form, which remained airborne for long periods of time and was difficult to remove from the atmosphere, was identified as methyl iodide by Eggleton and Atkins.[2]

Because it persists in the containment atmosphere and thus remains available to leak to the environment, methyl iodide becomes the limiting factor in determining the dose reduction attainable by some engineered safety systems. If some fraction $\underline{f}$ of the iodine released into a containment building is converted to methyl iodide and if the methyl iodide cannot be removed at a significant rate, the maximum dose reduction attainable is $1/\underline{f}$ (the actual dose reduction will be less, since the other iodine forms are removed at a finite rate). Thus both the yield of methyl iodide and the possibility of removing it at a significant rate are of concern to reactor accident analysts.

In the course of studying the behavior of methyl iodide in connection with the reactor containment spray technology program,[3] we became aware that methyl iodide had been studied extensively by workers outside the field of reactor safety. Although it seems to be practically stable in containment experiments, methyl iodide is reactive enough to be a useful material for fundamental chemical kinetic studies. It is also affected by light and ionizing radiation, and its photolysis and radiolysis have been studied extensively. We also discovered that when all the data were assembled, there was an impressive list of observations on the occurrence of methyl iodide in fission-product release, transport, and containment experiments.

Several reviews have been published on the behavior of methyl iodide that are limited to reactor safety aspects.[4-6] Mishima[4,5] reviewed work up to 1966, and Cejnar[6] presented a brief summary of work up to 1969.

The present work was undertaken with three goals in mind:

1. To draw attention to the extensive knowledge of methyl iodide represented by the material published in the open literature and to indicate the content of this material.

2. To assemble and make conveniently available data on the chemical and physical properties of methyl iodide.

3. To assemble all known data on the occurrence of methyl iodide in fission-product release, transport, and containment experiments and in reactor accidents.

The report discusses physical and physico-chemical properties of methyl iodide (Chap 2), chemical reactions of methyl iodide (Chap. 3), effects of radiation on methyl iodide (Chap 4), methyl iodide absorption and trapping (Chap 5), and identification and occurrence of methyl iodide (Chap 6). These discussions are then summarized and conclusions are set forth.

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2. CHEMICAL AND PHYSICO-CHEMICAL PROPERTIES OF METHYL IODIDE

Most chemical and physico-chemical properties of methyl iodide have been measured and can be found in standard sources.[1,2] A summary of the properties of methyl iodide is given in Table 2.1 (Refs. 1–4), and the vapor pressures are listed in Table 2.2 (Refs. 5,6).

Several measurements and calculations of thermodynamic properties of methyl iodide have been reported, and a tabulation of properties calculated by Gelles and Pitzer[7] is given in Table 2.3 (data from Refs. 8–10). Morgan and Lielmezs[11] and Kennedy and Lielmezs[12] have published values covering the range 100 to 600°K that agree with the data of Table 2.3. Li and Rossini have reported constants for the Antoine equation for calculating vapor pressure for a number of organic halides, including methyl iodide.[13] Thompson and Linnett have reported vapor pressures for several compounds, including methyl iodide.[6] They recommend the equation

$$\log_{10} p_{mm} = -\frac{1475}{T} + 7.56 \ .$$

A number of workers have reported the heat of formation of methyl iodide in the gas phase. Carson and his co-workers reported several values, with the most recent being 3.6 kcal/mole for $\Delta H_{298.16}$ (Refs. 8, 9,14,15). Goy and Pritchard[16] reported 3.40 ± (0.05 + x), where x is the uncertainty in the heats of formation of CH_3, I_2 (g), and HI. Golden and Benson[17,18] reported 3.28 ± 0.16. Long[19] used the data of Carson and his associates[15] to calculate the energy of the $I-CH_3$ bond.

Swain and Thornton[20] have reported the thermodynamic quantities for the reaction

$$CH_3I \text{ (gas)} \rightarrow CH_3I \text{ (solution)} \ .$$

These are given in Table 2.4 (data from Ref. 21).

Spencer and Flannagan have reported the following equation for the heat capacity of methyl iodide for the temperature range 298.1 to 600°K:[22]

$$C_p^\circ = 4.105 + 24.487 \times 10^{-3} T - 9.733 \times 10^6 \ T^2 \ ,$$

where C_p° is in cal/mole·°K.

Table 2.1. Physical Constants of Methyl Iodide

		References
Formula	CH_3I	
Alternate names	Iodomethane; methane, iodo-	
Molecular weight	141.95	1
Form and color	Colorless liquid	1
Specific gravity at 20°C relative to 4°C	2.279	1
Freezing point, °C	-64.4	1
Boiling point, °C	42.4	1
Critical temperature, °C	255	1
Critical pressure, atm	54.6	1
Solubility, g/100 g		
Water at		
20°C	1.42	2
22°C	1.38	3
Ethanol	Infinite	2
Ether	Infinite	2
Surface tension at 20°C, dynes/cm	30.14	4
Viscosity at 20°C, cP	0.46	4

Table 2.2. Vapor Pressure of Methyl Iodide (From Ref. 5)

Below Atmospheric Pressure		Above Atmospheric Pressure	
p (mm)	T (°C)	p (atm)	T (°C)
1	Solid	1	42.4
5	-55.0	2	65.5
10	-45.8	5	101.8
20	-35.6	10	138.0
40	-24.2	20	176.5
60	-16.9	30	206.0
100	-7.0	40	228.5
200	+8.0	50	248.0
400	25.3	66.3	255[a]
760	42.4		

[a]From Ref. 6.

Table 2.3. Thermodynamic Properties of Methyl Iodide (From Refs. 8–10)

T (°K)	C_p° (cal/mole·°K)[a]	$H^\circ - H_0^\circ$ (kcal/mole)[a]	$-(\frac{F^\circ - H^\circ}{T})$ (cal/mole·°K)[a]	S_0 (cal/mole·°K)[a]
100	8.01	0.796	42.88	50.84
150	8.34	1.203	46.11	54.14
200	8.94	1.634	48.44	56.62
250	9.71	2.100	50.29	58.69
298.16	10.55	2.587	51.79	60.47
300	10.58	2.607	51.84	60.53
400	12.36	3.754	54.44	63.83
500	13.95	5.072	56.61	66.76
600	15.31	6.537	58.44	69.72
700	16.48	8.128	60.27	71.88
800	17.51	9.828	61.95	74.15
900	18.40	11.63	63.34	76.26
1000	19.20	13.51	64.73	78.24
1100	19.89	15.46	66.05	80.10
1200	20.50	17.48	67.29	81.86
1300	21.04	19.56	68.48	83.53
1400	21.50	21.69	69.61	85.10
1500	21.92	23.86	70.69	86.60

[a]At standard conditions of ideal gas at 1 atm pressure.

Table 2.4. Thermodynamic Quantities for Solution of Methyl Iodide in H_2O and in D_2O (From Ref. 21)

	CH_3I-H_2O	CH_3I-D_2O
$\Delta F^\circ_{29.43°}$, cal/mole	1119.4 ± 2.8	1178.6 ± 6.2
$\Delta H^\circ_{29.4-40.3°}$, cal/mole	-5916 ± 80	-5547 ± 179
$\Delta S^\circ_{29.43°}$, cal/mole·°K	-23.25 ± 0.27	-22.22 ± 0.61

Lapidus, Seifer, and Nisel'son have reported calculations of the heat capacity of methyl iodide vapor over the range 400 to 1000°K.[23]

Heukelom calculated the critical constants for a number of substances, including methyl iodide.[24] He gives

Critical temperature, °K	528
Critical pressure, atm	66.3
Critical volume, cm^3/mole	171
Heat of vaporization at normal boiling point, cal/mole	
Calculated	6560
Observed	6510

These data are quoted by Seifer, Nisel'son, and Lapidus.[25]

A tabulation by O'Hara and Fahien includes the latent heat of vaporization of methyl iodide over a range of temperatures.[26]

Vogel[27] has reported values of surface tension and parachor, P, as given in Table 2.5. Parachor[28] is defined as

$$P = \frac{M\gamma^{1/2}}{\rho_L - \rho_G},$$

where M is molecular weight, γ is surface tension, ρ_L is liquid density, and ρ_G is vapor density.

Margrave has reported the appearance potentials of CH_3^+, CH_2^+, CH^+, and C^+ from CH_3I.[21] He has also shown that heats of formation calculated from appearance potentials agree well with those from thermochemical data.

Dyson and Littlewood made measurements of the effect of organic vapor molecules on the viscosity of H_2 and He.[10] From these they could determine the collision diameter of the organic molecule. They have reported the collision diameter of CH_3I as 5.73 Å. The collision diameter is used in calculating the diffusion coefficient.

Holland and Moelwyn-Hughes have reported the partial molar volumes of the methyl halides in water.[29] Their results are presented in Table 2.6. The measurements could not be made at temperatures above 35°C because the hydrolysis reaction became fast enough to interfere.

Table 2.5. Surface Tension and Parachor for Methyl Iodide (From Ref. 27)

Temperature (°C)	Surface Tension (dynes/cm)	Parachor
16.5	31.38	146.8
22.9	30.59	146.6

Table 2.6. Partial Molar Volume of CH_3I in Water (From Ref. 29)

Temperature (°C)	Partial Molar Volume (cm^3/g.mole)
0	64.0 ± 0.2
5	63.1
15	60.1
25	63.7
35	63.1

One of the most important properties from the standpoint of gas absorption calculations is the partition coefficient. Measurements of this have been reported by Glew and Moelwyn-Hughes,[30] Hasty,[31] Postma,[32] and Nishizawa and his co-workers.[33]

Glew and Moelwyn-Hughes recommend the following equation for calculating the solubility of methyl iodide in water:

$$\log_{10} (C_{sat}) = -110.278 + 37.621 \log_{10} T + 4823/T ,$$

where C is in moles/liter and T is in °K. From this, partition coefficients can be calculated for saturated solutions if the vapor is considered to be an ideal gas.

Hasty measured the partition coefficient over the range 4.8 to 68.5°C, He recommends the equation

$$\log_{10} H = -4.82 + 1597/T ,$$

where H is the partition coefficient (dimensionless) and T is in °K. He found that the rate of hydrolysis of methyl iodide was too high to permit accurate measurements at higher temperatures.

Postma reported a value of approximately 1.1 at 121°C. He is preparing a report describing the technique and results. His value is over six times that which would be obtained by extrapolating Hasty's data but agrees rather well with results from Glew and Moelwyn-Hughes.

Nishizawa and his associates have reported partition coefficients for methyl iodide at 25, 50, and 80°C. Their values are given in Table 2.7. They indicate a slight concentration effect, and they agree more closely with values calculated from the solubility data of Glew and Moelwyn-Hughes[30] than with values calculated with the equation recommended by Hasty.[31]

Table 2.7. Gas-Liquid Partition Coefficient for Methyl Iodide (From Ref. 33)

Temperature (°C)	C_L, Concentration in Water (μg/liter)	C_G, Concentration in Gas (μg/liter)	Partition Coefficient (C_L/C_G)
25	0.58	0.089	6.5
	3.80	0.795–0.770	4.78–4.93
	396–423	88.6–88.7	4.47–4.-7
50	2.93–3.30	1.43–1.31	2.05–2.52
	196–378	110–115	1.96–3.29
80	0.30–0.24	0.21–0.13	1.4–1.8
	1.9–1.4	1.75–0.97	1.1–1.4
	16.2–10.2	15.5–7.8	1.04–1.31

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3. CHEMICAL REACTIONS OF METHYL IODIDE

Although it has appeared to be almost inert in many containment experiments, methyl iodide is a relatively reactive substance. It is known as a methylating agent in organic chemistry,[1] and it has been used in a variety of fundamental chemical studies. Both descriptive and kinetic studies of the chemical reactions of methyl iodide are discussed here. The effects of light and ionizing radiation on the reactions are discussed in later sections.

Gas-Phase Reactions

The gas-phase reactions of methyl iodide are of interest in explaining its formation in reactor containment systems.

Ogg studied the gas-phase reaction between CH_3I and HI at temperatures of 270 to 320°C and found that thermal decomposition was negligible.[2] He proposed the following mechanisms:

$$CH_3I + HI \rightarrow CH_4 + I_2 + 16 \text{ kcal} \quad (1)$$

$$CH_3I \rightarrow CH_3. + I. - 43 \text{ kcal} \quad (2)$$

$$CH_3. + HI \rightarrow CH_4 + I. + 24 \text{ kcal} \quad (3)$$

$$CH_3. + I_2 \rightarrow CH_3I + I. + 8 \text{ kcal} \quad (4)$$

$$2I. + M \rightarrow I_2 + M \quad (5)$$

Sullivan[3] and Benson and O'Neal[4] published reinterpretations of Ogg's data. They stated, on the basis of more recent data, that Ogg's value of 43 kcal for reaction (2) was too low. Instead they propose

$$I_2 + M \rightleftarrows 2I + M \quad (6)$$

$$I + CH_3I \rightleftarrows CH_3 + I_2 \tag{7}$$

$$CH_3 + HI \rightleftarrows CH_4 + I \tag{8}$$

Flowers and Benson reinvestigated the kinetics over the temperature range 260 to 316°C.[5] They used total pressures (initial CH_3 + HI) of 10 to 200 mm and CH_3I:HI ratios ranging from 0.5 to 3. They generally agreed with the above model, and found that the A-factors in

$$k = Ae^{-E/RT}$$

were in excess of collision frequencies for the iodine-atom reactions [forward reaction of (7) and reverse reaction of (8)]. This is stated to indicate the formation of very unique transition state complexes and to be unique for iodine.

Benson and his co-workers have carried out extensive studies of the gas-phase reactions of iodinated methanes.[6-11] Golden, Walsh, and Benson[6] and Goy and Pritchard[12] published measurements on the equilibrium

$$CH_4 + I_2 \rightleftarrows CH_3I + HI$$

at almost the same time. Their data for the equilibrium constant are presented graphically in Fig. 3.1 and appear to be in good agreement. Attainment of equilibrium in these experiments was slow and required several hours. The other reactions are not of significant interest with respect to methyl iodide formation but are indicative of the thoroughness with which the reactions of the iodinated methanes have been investigated.

Barnes and his associates conducted a program of study of the formation of methyl iodide under postulated nuclear reactor accident conditions.[13-16] This was largely a theoretical study, although a few experiments were done on formation of methyl iodide by irradiation of mixtures of methane and iodine. The calculations showed that chemical equilibrium in the system carbon-hydrogen-oxygen-iodine could not account for the concentrations of methyl iodide observed in containment

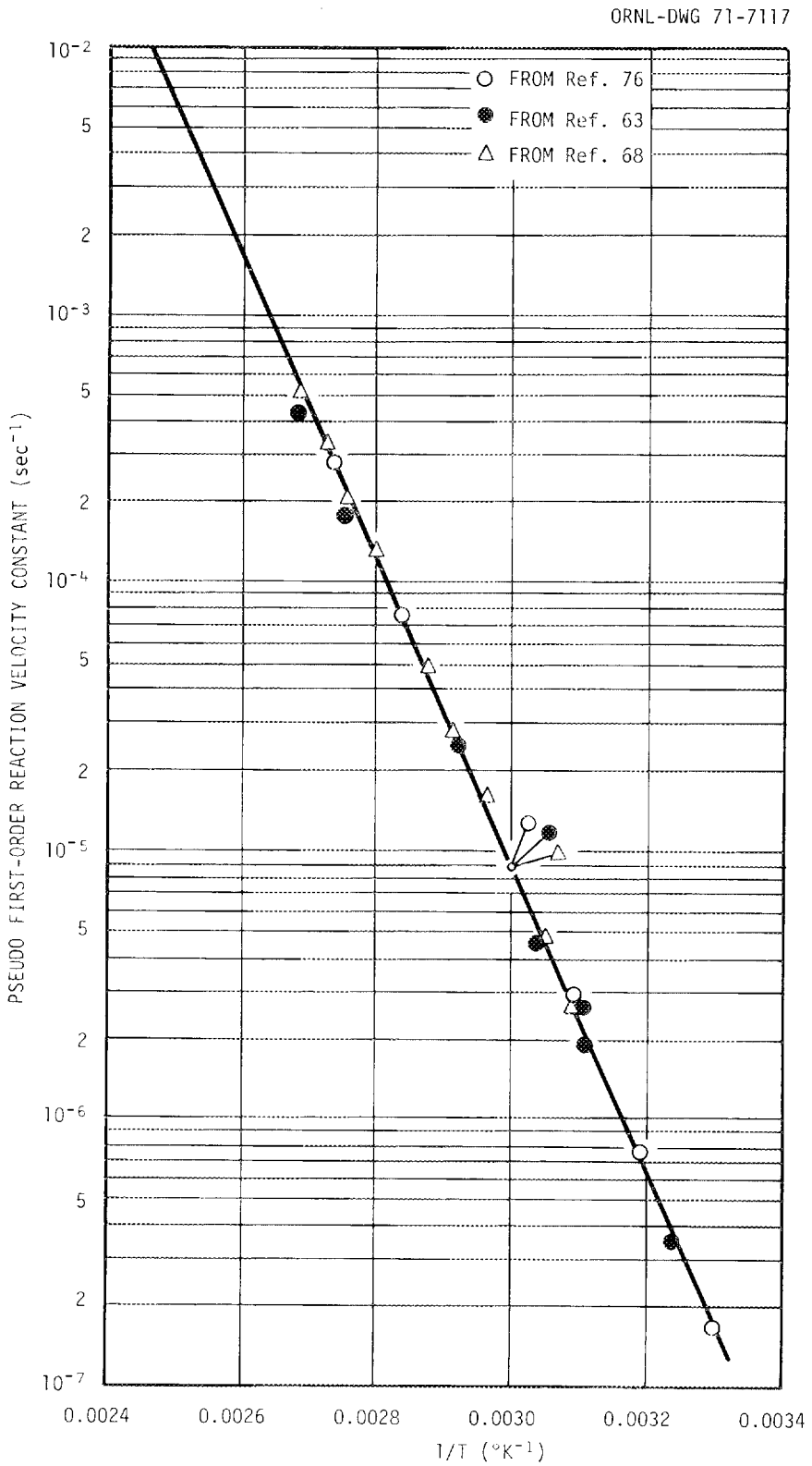

Fig. 3.1. Equilibrium Constant for $CH_4 + I_2 \rightleftharpoons CH_3I + HI$.

experiments. The calculated equilibrium concentrations were several orders of magnitude lower than the levels reported for experiments. Accordingly consideration was given to kinetic effects, and it was shown that fairly high maximum methyl iodide concentrations could be calculated at elevated temperatures (e.g., 800°C).

The experiments were carried out with $CH_4:I_2$ mole ratios ranging from 87 to 490. These are high, since the standard atmosphere contains 1 ppm (4.5×10^{-8} mole/liter) of methane, and the expected iodine concentration in a 1000-MW(e) PWR containment vessel following a loss-of-coolant accident at end of core life is of the order of 2×10^{-7} moles/liter (based on TID-14844, Ref. 17, assumptions). The experiments showed that under the conditions used, CH_3I was formed. At the $CH_4:I_2$ ratio of 490, over 50% conversion of I_2 to CH_3I had occurred at a dose of 5×10^7 rad. At lower ratios, there were indications of an equilibrium concentrations of CH_3I being attained. A few experiments were done on the effects of diluents (air, O_2, H_2O) but probably not enough to draw any conclusions.

Tang and Castleman[18] and Zittel[19] have reported the decomposition of methyl iodide by radiation. It appears that radiation can promote either the formation or destruction of methyl iodide, depending on the relative concentrations of the several reactants and products.

Kassmann and Martin carried out experiments on the exchange of iodine between CH_3I and I_2, using ^{131}I tracer, at temperatures of 870 to 1105°K in the hope of eliminating interference by surface reactions.[20] They reported that their results are consistent with the model proposed by Benson and his co-workers.[4-9] Clark and his associates had attempted to study the same reaction at much lower temperatures by using ordinary thermal reaction methods and had found a dominant surface effect — adding packing, which was estimated to increase the surface by a factor of 8, increased the reaction rate 30-fold.[21]

Schmied and Fink also studied the exchange of iodine between ^{131}I-labelled I_2 and CH_3I.[22] They found that the reaction was surface catalyzed and therefore sensitive to the nature and condition of the surface of the reaction vessel. The experiments were done in the dark to eliminate possible photochemical effects.

Charamathieu and his associates have reported results of five experiments on the effect of radiation on methyl iodide formation.[23] All experiments were conducted with 7×10^{-5} g/cm^3 of CH_4 (approximately 4×10^{-3} mole CH_3I/liter), and 10^{-10} to 10^{-8} g/cm^3 of I_2 (0.1–10 mg/m^3 of vessel). In one experiment 7×10^{-6} g/cm^3 of H_2O was also present. Air was excluded from the ampoules. The results are presented in Table 3.1, which shows that some conversion to methyl iodide occurred in all cases and that there was some enhancement due to irradiation. The authors expressed some concern over the methyl iodide conversion found in the control ampoules and suggest that cracking of the methane may have occurred when the ampoules were sealed. Since the methane concentrations are much higher than should exist under reactor conditions, the results are not directly applicable to containment structures.

Vilenchich and Venter[24] and Vilenchich and Hodgins[25] published related papers on gamma irradiation of methane-iodine mixtures. The first paper deals with techniques for determining the composition of the product mixture from ultraviolet absorption data, while the second reports the results for the radiation-induced reactions. The experiments were done to demonstrate potential commercial production of iodinated methanes by this process. The starting mixture contained I_2 and CH_4 only (no air, etc.); the pressure was 1200 mm Hg; CH_4:I_2 ratios of 1 to 6 were used; temperatures were varied from 80 to 230°C. G-values were found to be very high (7×10^7 for methyl iodide and 1.4×10^8 for methylene iodide under optimum process conditions). Yields of up to 60 wt. % methyl iodide were obtained.

A number of studies of the reaction of methyl iodide with alkali metals in crossed molecular beams have been reported.[26-29] This technique enables the energies of the reacting molecules and the orientation of the asymmetric CH_3I molecule to be controlled. Thus the effect of energy and orientation on the probability that a collision will result in a reaction can be evaluated.

Steacie and McDonald have reported measurements of the thermal decomposition of methyl iodide in a Pyrex bulb at temperatures of 400 to 510°C.[30,31] They found that measurable reaction occurred only at

Table 3.1. Effect of Radiation on Methyl Iodide Formation

Mixture	Irradiation Time (hr)	Radiation Dose (rad)	Iodine Concentration (g/cm^3)	CH_4 Concentration (g/cm^3)	H_2O Present (g/cm^3)	$CH_4:I_2$ Mole Ratio	I_2 Crystal Temperature (°C)	Mass of CH_3I in Ampoule (g)	Percentage of I_2 Converted to CH_3I	Conversion Due to Radiation (%)
$I_2 + CH_4$	0	0	1×10^{-8}	7×10^{-5}		5.5×10^4	-35	7.6×10^{-8}	1.6	
	64	3×10^6	1×10^{-8}	7×10^{-5}			-35	1.89×10^{-7}	3.95	2.35
	128	6×10^6	1×10^{-8}	7×10^{-5}			-35	2.08×10^{-7}	4.33	2.73
$I_2 + CH_4 + H_2O$	0	0	5×10^{-9}	7×10^{-5}	7.5×10^{-6}	2.7×10^5	-35	2.45×10^{-8}	1	
	64	3×10^6	5×10^{-9}	7×10^{-5}	7.5×10^{-6}		-35	2.82×10^{-8}	1.22	0.22
	128	6×10^6	5×10^{-9}	7×10^{-5}	7.5×10^{-6}		-35	3.15×10^{-8}	1.31	0.31
$I_2 + CH_4$	0	0	1×10^{-8}	7×10^{-5}		5.5×10^4	-35	2.3×10^{-8}	0.48	
	64	3×10^6	1×10^{-8}	7×10^{-5}			-35	3.7×10^{-8}	0.77	0.29
	128	6×10^6	1×10^{-8}	7×10^{-5}			-35	6.7×10^{-8}	1.4	0.92
$I_2 + CH_4$	0	0	1×10^{-9}	7×10^{-5}		5.5×10^5	-54	1.8×10^{-8}	3.8	
	64	3×10^6	1×10^{-9}	7×10^{-5}			-54	1.13×10^{-7}	26.6	21.8
	128	6×10^6	1×10^{-9}	7×10^{-5}			-54	7.9×10^{-8}	16.4	12.6
$I_2 + CH_4$	0	0	1×10^{-10}	7×10^{-5}		5.5×10^6	-72	1.8×10^{-8}	37	
	64	3×10^6	1×10^{-10}	7×10^{-5}			-72	2.95×10^{-8}	61.4	24.4
	128	6×10^6	1×10^{-10}	7×10^{-5}			-72	2.85×10^{-8}	59	22

450°C and above in an empty bulb, but if the bulb was packed with powdered Pyrex, measurable reaction was observed at 400°C. They state that the reaction was too complicated to be of value in kinetic studies.

Butler and Polanyi[32] used a flow method for studying pyrolysis of methyl iodide, rather than the static method used by Ogg. They claim that this permits a less complex process to be studied. They reported five measurements on the decomposition of methyl iodide in nitrogen at 493 to 495°C, total pressures of 5 to 7 mm Hg, and methyl iodide partial pressures of 0.003 to 0.012 mm Hg. They found that methyl iodide decomposed about one-third as fast as ethyl iodide but did not obtain reproducible results.

Horrex and Lapage have reported work on the nitrogen-methyl iodide system with toluene added as a radical acceptor.[33] They conclude that the reaction becomes second-order at low total pressures. That is, if a CH_3I molecule is to decompose it must first be activated either by a collision with another CH_3I molecule or by one with an N_2 molecule. At 600-mm Hg total pressure, they state that CH_3I decomposition is first-order.

Liquid-Phase Reactions

Reactions of methyl iodide in the liquid phase are important in its absorption by sprays, etc. For convenience, we have divided the liquid-phase reactions into the following groups: (1) bimolecular nucleophilic substitutions, (2) hydrolysis, (3) electrophilic substitutions, and (4) others.

Bimolecular Nucleophilic Substitution (S_N2) Reactions of Methyl Iodide

An important class of reactions in which methyl iodide participates is known as the bimolecular nucleophilic substitution (or displacement) reaction.[34-37] The abbreviation S_N2 is often used to designate reactions of this type.

The reactions are of the form

$$N + R\text{-}S \rightarrow R\text{-}N + S \ ,$$

where N is the nucleophile and R-S is called the substrate. N and S are electron donors (Lewis bases) and R is an electron acceptor (Lewis acid), so S_N2 reactions are often viewed as generalized acid-base reactions.

Significant systematic studies of the reactivities of nucleophiles toward various substrates have been made. The first paper of importance was that of Swain and Scott, who proposed the equation

$$\log (k/k^{\circ}) = sn ,$$

where k is the reaction rate of the substrate with the nucleophile, k° is its reactivity with water, n is a measure of the nucleophilic reactivity of N, and s is a measure of the discrimination of S among different N reagents.[38] This relationship was found to correlate 47 reactions.

Subsequently Edwards proposed a relationship of the form

$$\log (k/k_0) = \alpha P + \beta H ,$$

where P is a measure of the polarizability of the molecule and H is a measure of its basicity.[39] However, a group of nucleophiles was found that reacted at rates invariably higher than can be accounted for by the above.[35,40] These nucleophiles can be represented by the formula YN, where N is the nucleophilic atom and Y is an electronegative atom that contains one or more pairs of unshared electrons. Examples are NH_2OH, ClO^-, and $R_2C{=}NO^-$. This is known as the "alpha effect" by reference to the unshared electrons on the alpha atom.

Davis suggested a modified equation:

$$\log (k/k_0) = \alpha E + \beta H ,$$

where E is the oxidation potential.[41] He also suggested this be called the <u>oxibase</u> scale.

Davis and his co-workers have published a series of papers on the application of the oxibase scale. The most recent discusses the reaction of methyl iodide with mercaptoethylamine (MEA).[42] MEA is under consideration as an antiradiation drug.

Pearson groups Lewis acids and bases into two groups: "hard" and "soft."[36] Bases which are easily polarizable are "soft"; nonpolarizable bases are "hard." For acids he points out small size and high positive oxidation state as features leading to hard behavior. Soft behavior tends to be associated with low oxidation state and large size. He states that hard acids associate preferentially with hard bases; soft acids with soft bases.

A number of reactions between nucleophiles and methyl iodide in aqueous systems have been investigated.[42-62] The results are summarized in Tables 3.2 and 3.3. Table 3.2 lists reaction rates obtained with 16 nucleophiles of various types, while Table 3.3 presents results for ten amines. Several of the references (47, 49, 52–54, 60) report on the effect of isotope mass (e.g., deuterium vs hydrogen) on the reaction rate.

Table 3.2. Reaction Rates of CH_3I with Nucleophiles in Aqueous Solution at 25°C

Nucleophile	k_2 (liters/mole.sec)	References
Mercaptoethylamine	1×10^3 to 2×10^0, depends on pH	42
SO_3^{--}	3.9×10^{-2}	48
$S_2O_3^{--}$	3.15×10^{-2}, 2.84×10^{-2}, 3.31×10^{-2}	45,46,48
$(CH_3)_3N$	3×10^{-2}	43
$(CH_3)_2NH$	9.4×10^{-3}	43
CH_3NH_2	2.25×10^{-3}	43
N_2H_5OH	1.1×10^{-3}	51
CN^-	5.76×10^{-4}, 5.9×10^{-4}, 6.03×10^{-4}	44,47,52
I^-	4.71×10^{-4}, 4.85×10^{-4}	55,57
SCN^-	3.58×10^{-4}	56
NH_3	1×10^{-4}	43
OH^-	6.52×10^{-5}, 6.36×10^{-5}	45,57
Br^-	4.95×10^{-5}, 4.16×10^{-5}	55
Cl^-	3.30×10^{-6}	55
F^-	7.08×10^{-8}	55
H_2O	1.41×10^{-9}, 7.3×10^{-8}	57

Table 3.3. Second-Order Rate Constants for the Displacement of Iodide Ion from Methyl Iodide at 30°C (From Ref. 58)

Amine	k_2 (liters/mole.sec)	pK_a' (a)
Methylamine	3.08×10^{-3}	10.62
Glycine	2.17×10^{-3}	9.63
Hydrazine	2.17×10^{-3}	8.11
Glycineethyl ester	7.67×10^{-4}	7.75
Hydroxylamine	3.33×10^{-4}	6.05
Trifluoroethylamine	2.50×10^{-4}	5.63
Methoxylamine	1.63×10^{-4}	4.85
Piperidine	1.53×10^{-2}	11.10
Morpholine	5.67×10^{-3}	8.59
Methylhydrazine	8.33×10^{-3}	8.14

[a] pK_a' is the negative logarithm of the dissociation constant.

Frequently, only relative rates are reported. Such data are not included in the tables.

Soldano and Ward investigated the effect of several additives on the reaction of CH_3I with $Na_2S_2O_3$. Increases of up to 35% in the pseudo-first-order reaction rates were reported.[61]

Adams, Bennett, and Slusher measured the rate of reaction of borax and borax—sodium thiosulfate alone and with various combinations of PEI-1000* and HCHO.[62] The additive caused an increase in the reaction rate.

Table 3.4 lists parameters for the Arrhenius reaction rate equation for six of the reactions. From the data of Tables 3.2, 3.3, and 3.4, it appears that sulfite ion might be a good additive for methyl iodide removal.

Because of their importance, the reactions of methyl iodide with water and with hydroxyl ion have been considered separately from the other

*PEI-1000 is a trademark of Dow Chemical Company.

Table 3.4. Arrhenius Constants for Some Reactions of Methyl Iodide in Aqueous Solution[a]

Reaction	Arrhenius Constants		References
	A, Frequency Factor (liters/mole·sec)	E, Energy of Activation (cal/mole)	
$CH_3I + OH^- \rightarrow CH_3OH + I^-$	1.24×10^{12}	22,220 ± 230	45
	5.6×10^{12}	19,400 ± 900	48
$CH_3I + S_2O_3^{--} \rightarrow CH_3S_2O_3^- + I^-$	2.01×10^{12}	18,880	45
	2.29×10^{12}	18,880	46
	2.73×10^{14}	20,380	49
$CH_3I + CNS^- \rightarrow CH_3CNS + I^-$	1.49×10^{11}	19,950 ± 400	56
$CH_3I + CN^- \rightarrow CH_3CN + I^-$	6.31×10^{10}	19,200	52
	5.1×10^{12}	21,750	47
$CH_3I + N_2H_4 + OH^- \rightarrow CH_3NHNH_3OH + I^-$	1.7×10^{12}	20,200	51
$CH_3I + SO_3^{--} \rightarrow CH_3SO_3^- + I^-$	2×10^{12}	18,600 ± 600	48

[a] $k = Ae^{-E/RT}$.

Table 3.5. Bimolecular Velocity Constants for the Reaction Between Methyl Iodide and Hydroxyl Ion

Temperature (°K)	k_2 (liters/mole.sec)	References
288.16	1.34×10^{-5}	60
298.16	5.8×10^{-5}	60
303.00	1.16×10^{-4}	39
312.23	3.45×10^{-4}	39
313.16	4.09×10^{-4}	60
314.79	4.52×10^{-4}	45
322.03	1.06×10^{-3}	45
333.03	3.21×10^{-3}	45
333.16	3.4×10^{-3}	65
342.83	8.54×10^{-3}	45
347.96	1.52×10^{-2}	65

S_N2 reactions of methyl iodide. A number of workers have investigated these reactions,[63-75] and the reported experimental results are summarized in Tables 3.5 and 3.6 and are presented graphically in Fig. 3.2 (from

Table 3.6. First-Order Reaction Velocity Constant for the Hydrolysis of Methyl Iodide

Temperature (°K)	k (sec^{-1})	References
303.19	1.73×10^{-7}	67
308.87	3.43×10^{-7}	63
313.26	7.84×10^{-7}	67
321.23	1.93×10^{-6}	63
323.20	2.63×10^{-6}	68
323.32	2.92×10^{-6}	67
323.69	2.70×10^{-6}	63
328.18	4.92×10^{-6}	68
328.72	4.81×10^{-6}	63
333.11	9.07×10^{-6}	67
333.16	8.90×10^{-6}	68
333.88	8.72×10^{-6}	63
338.16	1.60×10^{-5}	68
342.92	2.49×10^{-5}	63
343.16	2.77×10^{-5}	68
343.66	2.85×10^{-5}	67
348.17	4.78×10^{-5}	68
353.16	7.97×10^{-5}	68
353.38	7.84×10^{-5}	67
358.17	1.30×10^{-4}	68
363.00	1.80×10^{-4}	63
363.16	2.09×10^{-4}	68
366.17	2.79×10^{-4}	67
368.18	3.31×10^{-4}	68
371.16	4.30×10^{-4}	68
372.92	4.31×10^{-4}	63
373.19	5.15×10^{-4}	68

Refs. 63, 68, and 76). The data show that sprays should remove methyl iodide at a measurable rate as a result of hydrolysis, although the rate is expected to be too slow to produce a significant 2-hr dose-reduction factor.

S_N2 Reactions in Solvents Other than Water

Many investigations of S_N2 reactions involving methyl iodide in non-aqueous systems have been reported (Refs. 63, 65, 69–121). These reactions generally are of less direct interest to workers in the safety field than reactions in aqueous solutions. However, they are of value in achieving an understanding of the reaction mechanisms.

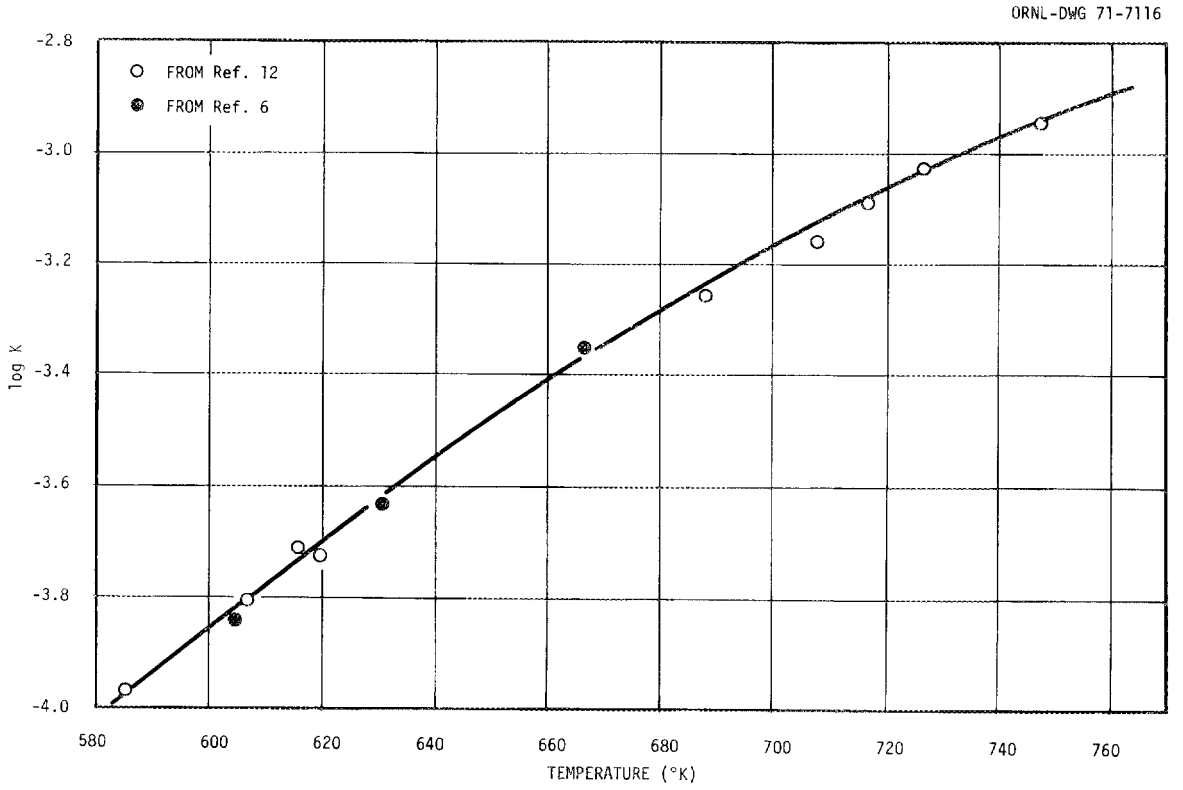

Fig. 3.2. Experimentally Determined Hydrolysis Rate Constants for CH_3I.

Davies and his co-workers have reported reactions of methyl iodide with various tertiary nitrogen, phosphorus, and arsenic bases (amines, phosphines, and arsines).[77-79] They reported that the rate of reaction between mesityldimethylphosphine was 0.89 liters/mole·min in ethanol solution at 25°C.[78] The rate in acetone-water mixtures was too fast to measure by the method used. The corresponding arsine reacted much more slowly.

Bender and Hoeg have discussed the ^{14}C kinetic isotope effect in S_N2 reactions and have reported on the reaction of $^{14}CH_3I$ with triethylamine in benzene hydroxyl ion in 50% dioxane, pyridine in benzene, and silver ion in 70% alcohol.[80] The kinetic isotope effects (k_{12}/k_{14}) were 1.10, 1.14, 1.09, and 1.09, respectively.

Smith and Winstein have described a reaction of methyl iodide with dimethylsulfoxide (DMSO),[81] and Murto has discussed the alkaline hydrolysis and alcoholysis of methyl iodide in dimethylsulfoxide-water and dimethylsulfoxide-alcohol mixtures.[70] The rates increase with increasing

percentages of DMSO in the solution. The reaction with OH^- ion is about 5×10^6 times as fast in pure DMSO as in water at 25°C.

Parker and various co-workers have investigated a number of the S_N2 reactions of methyl iodide in a variety of solvents.[82-90] Their concern has largely been with studying the relationship between solvation of the nucleophile and its rate of reaction with methyl iodide.

Leffek has reported on the deuterium isotope effect on the reaction between alkyl bromides and sodium thiosulfate in 50% ethanol.[91] Unexpectedly it was found that k_H is greater than k_D for this reaction.

Beronius has reported on studies of iodine exchange between CH_3I and iodide ions in ethanol, propanol, and acetone.[92-94] Solvent effects are attributed to solvation of the ions.

Virtanen has reported the activity coefficients and kinetics of hydrolysis of methyl iodide in water-dioxane and water-dimethylsulfoxide mixtures.[95] The first-order rate constant for hydrolysis decreases with increasing organic content in water-dioxane mixtures but increases in water-DMSO mixtures. The effects are related to solvation of the transition state.

Lassau and Jungers have reported on the reaction between methyl iodide and tertiary amines in a large number of solvents.[96] They conclude that the reaction rate depends on both the polarity and the polarizability of the solvent.

Tommilla and Airo have studied the reaction between methyl iodide and cyanide ion in dimethylsulfoxide-water and acetone-water mixtures.[97] The reaction rate increased with increasing organic content with both organic solvents, but more with DMSO than with acetone. Rates in pure DMSO are roughly 10^5 times those in water.

Carlsson and his associates have reported rates of reaction of organo-tin and organo-germanium hydrides with methyl iodide in cyclohexane.[98-100] The reactions occur by a free-radical chain mechanism and are relatively fast (order of 10^9 liters/mole.sec).

Anderson and his co-workers have reported rates of reaction of CH_3I with methoxide in methanoldioxan mixtures.[101] The reaction rate increases with dioxan content of the solvent.

Pearson, Sobel, and Songstad have reported the rates of reaction of 58 nucleophiles toward CH_3I in methanol.[102] Only two of the substances tested ($C_6H_5S^-$ and $C_6H_5Se^-$) reacted faster with methyl iodide than did thiosulfate. They also tabulate the nucleophilicity of 67 nucleophiles toward CH_3I. Only four of these, the two above and $(C_6H_5)_3Ge^-$ and $(C_6H_5)_3Sn^-$ (values for the latter were calculated, not experimental) are higher than $S_2O_3^{--}$.

Jackson and Leffek have investigated the deuterium isotope effect on the reaction between $S_2O_3^{--}$ and methyl iodide in 50% ethanol.[103] The reaction was about 6% slower when deuterated methyl iodide was used.

Farhat-Aziz and Moelwyn-Hughes have reported the kinetics of the reaction between methyl chloride and lithium iodide in acetone.[104] They concluded that the reverse reaction was about 4000 times as fast as the direct reaction.

Davies has reported the rates of reaction of methyl iodide with 9 p-alkyldimethyl anilines in a 90% acetone-water mixture.[105] Rates of the order of 10^{-4} liters/mole.sec are reported.

Chanon and his associates have reported reactions of methyl iodide with thiazoles in acetone.[106,107] The Δ_4-thiazolinethiones-2 showed rates of the order of 10^{-4} liters/mole.sec; methylthio-2 thiazoles gave rates of the order of 10^{-6} liters/mole.sec.

De La Mare and his associates have published a series of papers in which they discuss the Finkelstein reaction (halide replacement in alkyl halides by attacking halide ion).[108-112] Their concern is in examining the mechanism of the substitution reaction and the structural factors influencing the reaction rate.

Hawthorne, Hammond, and Graybill have reported measurements of the reaction rate of cyanide with methyl iodide in 50% aqueous dioxan.[113] The rate at room temperature is of the order of 10^{-3} liters/mole.sec.

Leffek and MacLean examined the deuterium isotope effect on reactions between methyl and methyl-d_3 iodides in benzene.[114] Rates ranging from 10^{-3} to 10^{-6} liters/mole.sec were obtained at 50°C for six different amines. Methyl iodide reacted about 88% as fast as methyl-d_3 iodide in all cases.

Kalliorinne and Tommilla studied the reaction between pyridines and methyl iodide in benzene-nitromethane mixtures.[115] They found that reaction rates increased with nitromethane content of the solvent. Rates were of the order of 10^{-4} liters/mole.sec in pure nitromethane.

Brown and McDonald investigated secondary isotope effects in the reactions of methyl-d_3 pyridines with alkyl iodides in nitrobenzene solution.[116] The reaction was faster for the deuterated forms.

Brown and Cahn have reported rates of reaction of methyl iodide with alkylpyridine in nitrobenzene solution.[117] The fastest rate constant at 30°C ($\sim 10^{-3}$ liters/mole.sec) was observed with 3-t-butyl pyridine.

McCabe, Grieger, and Eckert determined the partial molal volumes of the transition state of the Menschutkin reaction between pyridine and methyl iodide in six solvents.[118] Their results are useful in the interpretation of the structure of the transition state and its intermolecular interactions in solution.

Dessy, Pohl, and King measured rates of reaction of several transition element and main-group-derived anions with alkyl halides in glyme (glycoldimethylether).[119] They have listed nine reactions involving CH_3I. The fastest was with Ph_3Pb^-. The rate constant was 490 liters/mole.sec.

Abraham[120] commented on the results of Okamoto, Fukiu, and Shingu[43] and concluded that the unexpectedly small rate difference in the reaction in benzene and water solution (the reactions are about four times as fast in water as in benzene) can be accounted for because the transition states have the same higher free energy in water as in benzene.

Parker has reviewed the solvent effects of a great many reactions.[88] Twelve reactions of methyl iodide are included in the 56 reactions examined.

Swart and LeRoux examined the exchange reaction between iodide ion and methyl iodide in five solvents.[121] They concluded that the reaction rate was approximately inversely proportional to the dielectric constant.

Evans, Watson, and Williams have reported measurements of the kinetics of the formation of aryltrimethylammonium iodides in methanol solutions.[122,123] The reagents used were variously substituted dimethylanilines and methyl iodide.

Uguagliati and his associates have discussed the reaction of methyl iodide with a rhodium complex.[124] Woolf,[125] Laidler,[126] Raine and Hinshelwood,[127] and Evans[128] have discussed the kinetics of several reactions involving methyl iodide in nonaqueous solvents. Brown and Mihm have discussed the effect of steric strains in displacement reactions,[129] and Anderson and his co-workers have discussed solvent effects on nucleophilic reactions.[101] Radhakrishnamurti and Panigrahi measured nucleophilic reactivity constants for several reagents in nonaqueous systems.[130]

Kacsér used data on several methyl iodide reactions in developing an equation for the "effective shape" of a polar molecule in the field of an ion.[131] This method can be applied to help understand the reaction mechanism.

Okamoto and his associates reviewed the linear free-energy relationships for 35 S_N2 reaction series and obtained excellent correlation of the reaction constant with the linear free energy.[132] They concluded, however, that existing correlations accounting for polar and steric effects are not satisfactory.

An article by Dove and Sowerby presents a relatively up-to-date review of halogen exchange reactions and contains much information about methyl iodide.[133]

Genco and his co-workers have developed coatings containing tertiary amines that are strong nucleophiles toward methyl iodide.[134,135] These are claimed to be highly effective in fixing iodine and thus making it unavailable for leakage to the environment.

Viles and his associates have investigated reagents that might be added to foams.[136] Their list includes hydrazine, unsymmetrical dimethylhydrazine (UDMH), thioacetamide (TA), triethylamine diamine (TEDA), piperazine, and tributyl phosphine (TBP). Of these, the last was found to be the most reactive with methyl iodide. This is in disagreement with the results of Pearson, Sobel, and Songstad,[102] who found that $S_2O_3^{--}$ reacted twice as fast, $C_6H_5S^-$ reacted nearly 20 times as fast, and $C_6H_5Se^-$ reacted over 100 times as fast as TBP in methanol solution at 25°C. Possibly the change of solvent accounts for the difference.

Reactions of Methyl Iodide with Electrophilic Reagents

Another important class of reactions of the alkyl halides is electrophilic attack on the halogen atom. Examples of reactions of this class are

$$CH_3I + AgNO_3 \rightarrow AgI + CH_3NO_3$$

$$CH_3I + Hg^{++} \rightarrow CH_3^{+} + HgI^{+}$$

The first reported work on such reactions was that of Burke, Donnan, and Potts.[137,138] Senter first pointed out that the solid silver halide product had a catalytic effect on reactions between alkyl halides and silver salts.[139]

Roberts and Hammett state that the rate of hydrolysis of an alkyl halide may be increased by several orders of magnitude by the addition of silver or mercuric salts.[140] Benfey has reported reaction rates for mercuric nitrate with ethyl, n-propyl, and isobutyl bromides in 70% dioxane.[141] The rate constants were EtBr, 3×10^{-3}; n-PrBr, 1.75×10^{-3}; and iso-BuBr, 4.8×10^{-4} liters/mole·sec at 25°C.

Colcleugh and Moelwyn-Hughes have reported rates of reaction of methyl iodide with silver nitrate and silver perchlorate in aqueous solution.[142] They state that complex formation must be assumed to account for the observed kinetics.

The use of $Hg(NO_3)_2$ as a catalyst in the nitric acid dissolution of aluminum-clad uranium fuels is well known.[143-145] Rupp, Beauchamp, and Farmakes pointed out that the use of mercury must be avoided if radioiodine is to be recovered.[145] Several workers in the atomic energy program have used Hg^{++} either to retain iodine in process solutions or to remove it from off-gas streams.[146-150] Consequently, since iodine retention factors of 10^7 to 10^8 are required in processing LMFBR fuels, it was decided to try mercuric nitrate—nitric acid solutions for iodine scrubbing. Extensive investigations of the scrubbing of iodine and alkyl iodides by these solutions have been conducted at the Oak Ridge National Laboratory.[151-153] The results indicate that absorbers can be designed that will remove most of the iodine and alkyl iodides with mercuric

nitrate—nitric acid solution; decontamination factors of at least 100 seem attainable. While this is only a small fraction of the desired retention factor, it represents removal of nearly all iodine in the off-gas so that the burden on the rest of the trapping system is considerably reduced. In connection with this work, the reaction rate of alkyl iodides with mercuric nitrate was measured.[152] The second-order rates are given in Table 3.7. The relative reaction rates are in the order expected from experiments on alkyl bromides by Benfey,[141] Dostrovsky and Hughes,[154] and Read and Taylor.[155] The rate for methyl iodide at 30°C (2.17 liters/mole·sec) is over 40 times that for the nucleophilic reaction with thiosulfate at the same temperature.

Table 3.7. Second-Order Reaction Rate Constants of Alkyl Iodides with Mercuric Nitrate at 30°C (From Ref. 152)

Alkyl Iodide	k_2 (liters/mole·sec)
Methyl	2.17
Ethyl	13.7
n-Propyl	8.5
n-Butyl	8.7

Other Reactions

Hasty reported measurements of the rate of reaction of gaseous methyl iodide with alkaline hydrazine solution.[156] It had originally been thought that this was a gas-phase reaction. Hasty's results, however, apparently can best be explained by a model which states that a fraction of the methyl iodide molecules striking the liquid surface react and are retained in the liquid. The rest return to the gas phase.

Tuszynski and Graydon investigated the effect of ultrasound on aqueous solutions of methyl iodide at 18°C.[157] The methyl iodide was decomposed at a zero-order rate of 3.2×10^{-6} liters/mole·sec.

Lieser and Joerchel measured the rate of isotopic exchange between $CH_3{}^{131}I$ and solid $Na^{127}I$ in the temperature range 177 to 255°C.[158] They state that at 177°C only the outermost layer of atoms was involved in the reaction. At 255°C, approximately 30 layers were involved.

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4. EFFECTS OF RADIATION ON METHYL IODIDE

References covering the effects of all forms of radiation on methyl iodide and related compounds are discussed in this chapter. These effects have been studied many years, and as a matter of convenience, we have grouped discussions of the references under the general headings of photolysis (effect of light), radiolysis (effect of other radiation), and hydrated electron effects. However, it should be emphasized that all these effects are interrelated.

Photolysis

We have listed two general reviews,[1,2] and certainly others could be found. The journal references date back to 1920 (Ref. 3), and work was probably done prior to that time. Early papers on photolysis of alkyl halides were written by Job and Emschwiller.[4,5]

Several papers appeared in the decade 1931 to 1940 (Refs. 6–8), and it began to be recognized that the primary process is

$$CH_3I + h\nu \rightarrow CH_3 + I \ , \qquad (1)$$

where h is Planck's constant and ν is frequency of the light.

Ultraviolet light at 2537 Å is required to rupture the C–I bond in CH_3I. Bates and Spence[6] found low quantum yields (about 0.02) in methyl iodide photolysis and attributed this to recombination processes.

Porret and Goodeve[7] deduced that the iodine atoms would be produced in an excited metastable state. West and Schlesinger studied photolysis of methyl and ethyl iodides in the gas phase.[8] They found that at 25°C under 2537 Å light and a methyl iodide vapor pressure of 300 mm, the gaseous products were 80 to 90% methane. The quantum efficiency was about 0.001. About one-third of the iodine decomposed as CH_3I_2. In the presence of silver foil, the rate was about 40 times faster, all the iodine appeared as AgI, and the gaseous products were 55% C_2H_6, 18% C_2H_4, and 28% CH_4. The explanation given is that the basic reaction of Eq. (1) is followed by a series of reactions between iodine atoms,

methyl radicals, and methyl iodide molecules. When silver is present, it collects the iodine atoms.

More work was reported in the period 1941 to 1950 (Refs. 9-11). Iredale and McCartney[9] showed that when excess NO was present, the recombination reaction to reform CH_3I was suppressed and the quantum yield of I_2 became 0.5. Williams and Ogg investigated the photolysis of methyl iodide in the presence of hydrogen halides.[10] By controlling the concentration of hydrogen halides used, it was possible to have essentially all the incident light absorbed by the methyl iodide. The reaction rates appeared to be in the order HI > HBr > HCl, with the last being much the slowest. Also, while CH_4 and I_2 are formed in equal amounts when the halide is HI or HBr, this is not true in the case of HCl. A chain reaction mechanism was postulated for HCl only.

Schultz and Taylor[11] studied the photolysis of methyl iodide vapor, both pure and mixed with CO_2. Experiments were run with and without silver foil to act as an iodine getter. They found that the methane yield was the same whether silver was present or not but was reduced in the presence of CO_2. They believe the effect of the CO_2 is to "cool" "hot" methyl radicals, which otherwise could abstract hydrogen from CH_3I to form CH_4. Methyl radicals not having excess energy will normally combine with I to reform CH_3I; when silver is present to remove the iodine, they combine to form C_2H_6.

A large number of papers on methyl iodide photolysis and photochemical reactions was published in 1951 to 1960 (Refs. 12-20). Hamill and Schuler reported on studies of photolysis of liquid methyl and ethyl iodides that were undertaken in conjunction with a program of radiolysis studies at Notre Dame University.[12] They propose a mechanism involving "hot" alkyl radicals to account for the chemical reactions observed. They found an iodine atom quantum yield of 0.016. Their work was extended by Schuler and Chmiel,[14] who showed that methyl iodide and methyl iodide containing up to 10 wt % dissolved iodine were photolyzed at 2537 Å. Large amounts of dissolved iodine were found to reduce gas yields from the reaction. The results were considered with the "hot" methyl radical mechanism.

Souffie, Williams, and Hamill[16] reinvestigated the photolysis of CH_3I vapor at 2537 Å and emphasized the mode of production of CH_4 and C_2H_6. They attributed methane and ethane production to a hot radical mechanism and found that methane production was not affected by the presence of free iodine; however, ethane production was decreased in the presence of free iodine.

Davidson and Carrington reported iodine inhibition in flash photolysis of methyl iodide—argon mixtures.[13] The flashes were produced by discharging a condenser through a xenon-hydrogen-filled quartz tube. Repeated 5-μsec flashes were used. A spectrograph indicated that the minimum wavelength was 2250 Å. They reported a quantum yield of 0.2 in the presence of 2×10^{-3} mm I_2 and of 0.005 in the presence of 0.54 mm I_2.

Harris and Willard reported a number of studies of the effect of light on methyl iodide reactions.[15] These included exchange of iodine between CH_3I and I_2; photolysis of CH_3I to produce CH_4, CH_2I_2, CHI_3, and I_2; and formation of CH_3I and HI by absorption of 1849 Å light in CH_4-I_2 mixtures. The quantum yield of CH_3I in the last was about 0.1 based on light observed by the I_2. Christie investigated the photolysis of gaseous methyl iodide in the presence of O_2 and NO.[17-19] She found that the reaction of CH_3 with O_2 was third-order. Methyl iodide was about ten times as efficient as CO_2 in accelerating the combination of methyl radicals and oxygen. She also found that the quantum yield of molecular iodine increased to a maximum of 0.5 as the O_2 concentration increased, and then it remained constant with further increase in oxygen concentration.

Nitric oxide was found to react much more rapidly with methyl radicals than oxygen. An NO partial pressure of 3 mm was sufficient to suppress side reactions, whereas 30 mm O_2 was required.

McTigue and Buchanan studied photolysis of methyl iodide in the presence of active silver and copper surfaces at temperatures of 100 to 250°C.[20] They found a sharp drop in ethane production at 145°C, which they attributed to a phase change in AgI. Above 180°C, the yield of methane is enhanced by a thermal reaction between silver and CH_3I.

Meyer carried out flash photolysis of methyl iodide at low pressures, alone and with Ar, O_2, Kr, and H_2 as diluents.[21,22] The photolysis product formation was observed by time-resolved mass spectrometry. It was found that I_2 is formed by two processes — one fast and the other slow. He hypothesizes that the fast reaction involves "hot" iodine atoms:

$$I(^2P_{1/2}) + CH_3I \rightarrow CH_3 + I_2 + 3 \text{ kcal}$$

The slower reaction is iodine atom recombination

$$I + I + M \rightarrow I_2 + M$$

Rebbert and Ausloos carried out photolysis of methyl iodide—hydrocarbon and methyl iodide—alcohol mixtures at 20 and 77°K.[23] The light was filtered so that only the 2537 Å radiation reached the sample. By using systems where one reactant contained only normal hydrogen and the other deuterium and examining the hydrogen isotope makeup of the products, much insight into the reaction mechanism was gained. Quantum yields of the solid-phase reactions were substantially higher than the yields of liquid- or gas-phase reactions. The results appear to confirm the important role of hot methyl radicals in the formation of methane.

Donovan, Hathorn, and Husain[24] confirmed the abstraction of iodine atoms from methyl iodide by hot iodine atoms as the important fast iodine-producing mechanism. Mains and Lewis[25] studied flash photolysis of methyl iodide in the gas phase. Methane, ethane, ethylene, acetylene, and iodine were produced.

Barker, Purnell, and Young report further studies on the photolysis of methyl iodide at 77°K and 253.7 nm.[26] They irradiated films of solid CH_3I for periods ranging from 20 min to 2 hr and found that numerous products were obtained (C_2H_6, C_2H_4, C_3H_8, C_3H_6, C-C_3H_6, I_2, higher hydrocarbons). A material balance deficit for carbon, hydrogen, and iodine that was proportional to the amount of CH_3I consumed indicated that a compound $(CHI_2)_n$ was also being formed. The authors reject a free-radical mechanism and attribute the results to reactions involving an activated CH_3I molecule and several of its neighbors.

It can be concluded that the photolysis of methyl iodide has been thoroughly studied. The publications indicate that ultraviolet light is necessary to rupture the C—I bond. Quantum yields vary over a wide range but tend to be low unless a scavenger is present to react with free methyl radicals.

Radiolysis

The literature on radiolysis of methyl iodide is even more extensive than that on photolysis. The earliest work we found was a paper by Kleeman[27] published in 1910, and Swallow[28] has reviewed work published up to 1958. A few laboratories have been particularly active in studying methyl iodide radiolysis; in particular, the University of Notre Dame under Professors W. H. Hamill and R. R. Williams, Jr.; the University of Wisconsin under Professor J. E. Willard; and Carnegie-Mellon Institute under Dr. R. H. Schuler, who continued earlier work he did at Brookhaven National Laboratory.

Gevantman and Williams used ^{131}I tracer to detect and identify the free radicals formed by e^- and gamma irradiation of alkanes and alkyl iodides.[29] Methyl iodide was irradiated in the liquid phase with ^{60}Co gammas and in the gas phase with a 2-MeV beam from a Van de Graaff generator. The principal products were reported to be methyl radicals.

Schuler and Hamill studied the decomposition of alkyl halides by fast electrons and X-rays over the range 0.5 to 2.0 MeV.[30] G values* were approximately 3 in the absence of dissolved oxygen, and they doubled when the sample was saturated with oxygen. Additional papers in this series are largely concerned with identifying the reactions that take place.[31-35]

Petry and Schuler[36] carried out an investigation of the radiolysis of liquid methyl iodide by 100-keV X-rays for comparison with the photolysis investigation by Schuler and Chmiel.[14] They found relatively much higher iodine yields in radiolysis. In addition, whereas methane is the

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*The G value is the number of molecules formed or decomposed per 100 eV of energy absorbed.

predominant hydrocarbon product of photolysis, higher hydrocarbons are predominant radiolysis products. They report $G(I_2) = 1.26$. A continuation of this work has been reported by Schuler and Petry.[37]

Schuler studied the effect of various solutes, including methyl iodide, on the radiolysis of cyclohexane.[38] He found concentrations as low as 10^{-3} mole fraction can profoundly change the nature of the radiation chemical process; solutes at concentrations of 10^{-4} mole fraction have no measurable effect.

Warman, Ausmus, and Schuler reinvestigated the radical formation by ^{60}Co gamma radiolysis of solutions of CH_3Cl, CH_3Br, and C_2H_5Br in cyclohexane; I_2 was used as a radical scavenger.[39]

Hornig and Willard have reported on the radiolysis of seven alkyl iodides.[40] G values for I_2 of 2.50 at room temperature, 0.94 at -120°C, and 0.64 at -190°C are reported. Hanrahan and Willard investigated the elementary processes in the gamma radiolysis of alkyl halides.[41] They concentrated principally on ethyl iodide but also have reported a few data on methyl iodide. The $G(I_2)$ was increased by added HI and decreased by added I_2.

Jones and his associates investigated phase effects (liquid vs solid) in radiolysis of alkyl halides.[42] They found that $G(I_2)$ was significantly lower in the crystalline state at -190°C than in the liquid state at room temperature.

Geissler and Willard studied solute-solvent interaction in the radiolysis of alkyl halides.[43] They found that the presence of CH_3I and other alkyl iodides significantly increased the yield of radicals on irradiation with ^{60}Co gammas.

Kang reported on the gas-phase radiolysis of CH_3I-n-C_5H_{12}-I_2 mixtures.[44] In discussing his results, he pointed out that when the CH_3I concentration was low, most of the energy was absorbed by the pentane and often led to fragmentation of the pentane molecules. A succession of reactions involving the fragments could then occur.

Claridge and Willard investigated the spectra of several alkyl halides immediately after gamma irradiation in the glassy state at 80°K.[45] Four transient absorption peaks were found in the 3000- to 8000-Å region. Two of these were tentatively identified.

Arnikar and Willard investigated yields of HI and I_2 resulting from ^{60}Co gamma irradiation of ethyl, n-propyl, and n-butyl iodides in the glassy and crystalline states at 77°K and the liquid state at room temperature.[46] G(HI) is higher in the solid state; $G(I_2)$ is lower.

Wilkey, Brensike, and Willard studied the reaction of dilute aqueous CH_3I with iodine activated by nuclear processes.[47,48] Solutions containing $CH_3{}^{127}I$ and $^{129}I_2$ were irradiated and the yields of $CH_3{}^{128}I$ and $CH_3{}^{130}I$ were determined. Significant yields of both were found. The authors concluded that "failure of rupture of C—I bonds in CH_3I does not account for all" the $CH_3{}^{128}I$ from $CH_3{}^{127}I$ and "possibly not for any of it."

Claridge and Willard[45,49] and Egland and Willard[50] have investigated evidence for transient irradiation products in both pure alkyl halides and solutions at 77°K using optical and electron-spin resonance spectra. Evidence for several intermediates has been obtained.

LeGoff and LeTort studied the mechanism of production and disappearance of free methyl radicals on metal surfaces.[51] On tungsten, significant decomposition of CH_3I was observed above 1200°K. They state that the primary decomposition reaction on a carbonized tungsten surface is

$$CH_3I \rightarrow CH_3 + I$$

Papazian reported that a white deposit of frozen methyl iodide becomes yellow-brown when subjected to the discharge from a Tesla coil.[52] This is attributed to free radical formation.

Sturm and Schwarz irradiated liquid methyl iodide with helium ions accelerated by a cyclotron (approximately 40-MeV initial energy).[53] Their purpose was to establish that ethane is formed by combination of methyl radicals in the spurs. They also postulated that HI is produced by

$$H + CH_3I \rightarrow CH_3 + HI$$

and methane by

$$CH_3 + HI \rightarrow CH_4 + I$$

Croft and Hanrahan studied I_2 production by ^{60}Co radiolysis of solutions of methyl iodide in cyclohexane.[54] $G(I_2)$ decreased with increasing cyclohexane in the solution; it was 1.4 for pure CH_3I.

Holroyd and Klein used $^{14}CH_3I$ as a scavenger for determining the yields of radical species in radiolyses of olefins.[55] Millimolar quantities of the methyl iodide were dissolved in the solvents, and the solutions were irradiated. The relative yields of products indicate the corresponding radical yields.

Schroth and Adloff studied the reaction of methane with ^{125}I atoms produced by electron capture by ^{125}Xe.[56] Gas mixtures ranging from 1 to 86% xenon, the balance being CH_4, and some containing the above two plus krypton, argon, or neon as the diluent were irradiated in the EL-2 or the EL-3 reactor. Up to 56% of the ^{125}I formed was found as organic iodine compounds. The yields decreased with increasing xenon content of the binary mixture. When krypton was used as a diluent, the organic iodine yield was reduced; argon and neon appeared not to affect the organic iodine yields. It is assumed that "hot" iodine atoms react with methane to give $CH_3{}^{125}I$.

Breslav, Kotov, and Pshezhetskii have reported studies of the mechanism of the radiation-catalyzed processes occurring on zeolites.[57] Only a small yield of CH_3 radicals was found in radiolysis of CH_3I on NaA zeolite.

Sherman has reported chain dehalogenation of alkyl halides in alkaline alcoholic solution.[58] $G(CH_3)$ from CH_3I jumped from 3 in neutral methanol solution to 64 in 0.1 M KOH in methanol (using 0.1 times the radiation dose) and from 2.9 in neutral 2-propyl to 179 in the alkaline solution.

Sagert, Reid, and Robinson have reported radiolysis of methyl iodide adsorbed on silica gel.[59] They found that energy absorbed by the silica gel, as well as that absorbed by the CH_3I, was effective in decomposing CH_3I. Combined methane-ethane yields indicate decomposition of approximately 1 molecule CH_3I per 100 eV.

Jones reported up to 90% decomposition of methyl iodide flowing through charcoal beds in a 2×10^7-rad/hr radiation field.[60] The test

bed was 1 in. deep, and face velocities of 11 ft/min (0.45-sec residence time) and 55 ft/min (0.09-sec residence time) were used.

Tang and Castleman have reported results on decomposition of methyl iodide in air by radiation.[61,62] Their data indicate that the rate of methyl iodide decomposition is a function of dose to the air and of initial methyl iodide composition. For concentrations of 10^{-8} to 10^{-6} mole CH_3I/liter, the concentration was reduced a factor of 10 by a dose of 2.5×10^{19} eV/g air, or roughly 5×10^5 rads. They report that water vapor has an inhibiting effect on methyl iodide decomposition. A later paper by the same authors presents additional data on the destruction of methyl iodide by the ^{60}Co gamma irradiation of concentrations of 2.8×10^{-9} to 2.4×10^{-4} mole/liter in air at 15°C.[63] The lowest concentration is about the upper limit of methyl iodide concentration expected in a conventional PWR vessel under accident conditions. They propose a mechanism involving active oxygen or nitrogen particles produced by absorption of gamma rays in the air. These partly react with methyl iodide and partly decay in other ways. For the lowest concentrations, the decomposition of methyl iodide was first-order; for the highest it was zero-order. The proposed mechanism explains these observations.

Zittel measured the rate of decomposition of CH_3I by radiation in dilute aqueous solutions and in low concentrations in moist air.[64] He found that $G(-CH_3I)$ in solution decreased with concentration below 1×10^{-3} mole/liter. At the concentrations of 10^{-8} to 10^{-9} mole/liter expected under accident conditions, the G value would probably be extremely small. In air, considerable decomposition of CH_3I was noted. Zittel points out that extrapolation of the data would indicate that a total dose of 10^4 r would destroy all the CH_3I at an initial concentration of 10^{-8} mole/liter. However, he feels there is not enough information (e.g., on simultaneous processes forming CH_3I) at present to warrant using this information to predict the behavior of CH_3I in a containment atmosphere.

Denschlag, Henzel, and Herrmann investigated the reaction of fission-product iodine with methane and found that three processes were involved in methyl iodide formation:[65,66]

1. Reaction of methane with iodine atoms produced directly by fission. The yield of methyl iodide was highly variable, ranging from 3 to 66%.

2. Reaction of methane with iodine atoms produced by beta decay of precursors. The yield was much lower (0 to 2.5%).

3. Reaction of methane (probably methyl radicals) with iodine adsorbed on the walls. This was a first-order process with a half-life of more than 140 d. This reaction is considerably enhanced in a gamma field, presumably because irradiation increases the yield of methyl radicals.

Cross and Wolfgang studied the hot iodine substitution reaction in gaseous methyl iodide.[67] They found that the substitution reaction had very low efficiency.

Buchanan and Hanrahan studied the radiation chemistry of systems containing phosphine.[68,69] This included radiolysis of pure methyl iodide and of mixtures of methyl iodide and phosphine. A maximum $G(CH_4)$ of 12.6 was observed in a mixture containing 3.5 mole % phosphine. This study is probably of little value in accident analysis, because it involves high partial pressures (of the order of 20 cm) of methyl iodide and no air or steam dilution.

Hydrated Electron Effects

Pulse radiolysis is a relatively new experimental technique.[70,71] It involves subjecting a sample to a burst of radiation of very short duration (2 μsec or less) and monitoring the intensity of light of a suitable wavelength by means of a photomultiplier-amplifier-oscilloscope system. The technique allows observation of very fast transient processes and thus gives considerable insight into the mechanisms of radiolysis. A major result of this work was the discovery of the importance of hydrated electrons as reaction intermediates.

Capellos and Swallow subjected liquid alkyl iodides to pulse radiolysis and gamma radiolysis.[72,73] For gamma radiolysis of methyl iodide they found $G(I_2) = 1.33$ in degassed CH_3I, 3.81 in CH_3I saturated with air, 4.92 in the presence of 842 mm of O_2, and 0.37 for the solid at

-196°C. The pulse radiolysis showed a transient absorption of 410 nm. This is a transient substance that decays to iodine.

Shankar, Rama Rao, and Shastri[74] subjected aerated aqueous solutions of methyl iodide to gamma radiolysis at a dose rate of 3.27 eV/liter·min. Hydrogen peroxide, iodine, and methyl hydroperoxide were major radiolysis products. $G(I_2)$ was a function of concentration; it was 0.05 at 10^{-4} M CH_3I and 10^{-3} M KI, the lowest concentration used.

Thomas and his co-workers have studied the radiation chemistry of aqueous methyl iodide solutions by pulse radiolysis.[75-77] They attribute decomposition of methyl iodide partly to reaction with the hydrated electron:

$$e^-_{aq} + CH_3I \rightarrow CH_3 + I^-$$

The second important reaction is formation of an iodine—methyl iodide complex, $I(CH_3I)$, which then decays very rapidly. The initial I_2 yield is given by $G(I_2) = 1.10$. The reaction of the hydrated electron with methyl iodide is very fast ($k = 1.7 \times 10^{10}$ liters/mole·sec).

As may be seen from the above, enough work has been done on the interaction of methyl iodide with various forms of radiation to at least permit some educated guesses as to its behavior. It appears that radiation is likely to promote decomposition of methyl iodide under accident conditions and is especially likely to do so in condensed phases, such as in water solutions and on filters.

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5. METHYL IODIDE ADSORPTION AND TRAPPING

Evidence that a major fraction of the iodine remaining airborne in a containment atmosphere would be in the form of methyl iodide has caused much attention to be given to ways and means of removing it. Three general types of removal systems for containment vessels have been studied: charcoal adsorbers, sprays, and paints containing nucleophilic reagents. In addition, other systems that remove methyl iodide fairly successfully have been used for radiochemical processing plants.

Charcoal Adsorber Systems

The application of charcoal adsorbers for iodine retention in reactor containment systems has been studied for many years, and work in this field through early 1968 has been discussed by Keilholtz and his associates.[1-3] Additional results have been reported by a number of others.[4-21] It has been demonstrated that unimpregnated activated charcoal is ineffective for removing methyl iodide. Charcoals can be made effective by impregnating them with either of two types of reagent. One type is a nucleophilic reagent, such as an amine that reacts with methyl iodide and removes the iodine from the molecule. The second type is a stable inorganic iodine compound. In this case, the radioactive iodine atoms of the methyl iodide exchange with stable iodine atoms of the impregnant, and the methyl iodide that passes through the bed is essentially nonradioactive.

Ferelli, Bocola, and Belardi have reported an extensive series of tests on the performance of charcoal for collecting methyl iodide from humid air.[15] They found that they could correlate penetration under 100% relative humidity conditions against $t(5\ cm)/D$, where $t(5\ cm)$ is the time for the superficial gas flow to penetrate the bed to a depth of 5 cm and D is the time that gas is flowing through the bed. There was considerable data scatter.

Lindeken, Santomassimo, and Nelsen have also reported on the effect of humidity on methyl iodide absorption.[16] Data on retention of methyl iodide on the filters of the Connecticut Yankee Reactor have indicated satisfactory performance.[17]

The reported results indicate that impregnated charcoals remain effective for methyl iodide removal up to 100% relative humidity. Apparently they can withstand weathering but may be poisoned by impurities in the air that flows through them. Probably it is best, if possible, not to expose charcoal in emergency trapping systems to continuous air flow. Also, periodic tests of the charcoal efficiency should be made.

Winter has discussed the engineering design of charcoal filter systems.[22] He states that "cell" filters (canister type) should be used when retention factors of up to 0.999 are required, and "kettle" filters (deep charcoal beds) should be used for retention factors of over 0.999.

Murata and Kamiya report tests of a full-size filter unit (600 × 600 mm).[23] They found no essential difference in performance from that of a smaller filter they had tested previously.[18]

Craig, Adrian, and Bouwer report test results in which they investigated the concentration dependence of charcoal-adsorber efficiency.[24] They found that the efficiency of both unimpregnated and impregnated (with KI) charcoal decreased with iodine concentrations below 1 $\mu g/m^3$ and becomes essentially zero at 0.1 $\mu g/m^3$.

An alternative adsorbent, silver zeolite, has been proposed by Maeck, Pence, and Keller.[25] This was efficient at temperatures up to 500°C.

Adsorbers are an effective means of removing methyl iodide (and iodine) from containment systems. The removal rate constants (λ) for such systems depend on the throughput and on the efficiency (fraction of input concentration removed) of the adsorber. Filter systems are generally sized to give two to three air changes per hour. An efficiency of 50% might reasonably be assigned to an impregnated charcoal adsorber system under accident conditions. Thus the λ for methyl iodide removal might be 1 to 1.5/hr.

Spray Systems

Many present-day plants are being equipped with containment spray systems to remove both heat and airborne fission products from the

containment atmosphere in the unlikely event of a major loss-of-coolant accident. Consequently, a spray technology research and development program was sponsored by the U.S. Atomic Energy Commission to provide technical data needed for evaluating containment spray systems.[26] While the principal emphasis has been on the performance of sprays in removing elemental iodine from containment atmospheres, much attention has been given to methyl iodide removal as well. The program has included measurements of the partition coefficient for methyl iodide between water and air, measurements of the rates of reaction between methyl iodide and proposed solution additives, wind tunnel studies of the uptake of methyl iodide by solution drops, and pilot plant experiments on methyl iodide removal by sprays.

The theory of methyl iodide absorption by sprays has been explored by Schwendiman, Hasty, and Postma[27] and by Parsly.[28] An examination of the process indicates that it consists of liquid-phase controlled absorption with simultaneous chemical reaction. It also becomes evident that chemical reaction can increase the removal rate enough to be of interest only if the reaction time is of the same order as the drop lifetime (the reaction time is defined as the reciprocal of the pseudo-first-order reaction rate constant). There are two models of the hydrodynamic condition of the drop that are the upper and lower bounds of the real case. One is the perfectly mixed drop for which all points in the drop are presumed to be saturated with solute. The removal rate constant is proportional to the reaction rate constant to the first power. For the other limiting case, it is assumed that the drop is a rigid sphere with no internal circulation. The surface layer of the drop is saturated with solute, and the rest is at lower concentration. For this case, the removal rate constant increases as the one-half power of the concentration. Real spray drops show behavior intermediate between these two limits.

Soldano and his associates have carried out an extensive program of studies of the uptake of methyl iodide by water drops suspended in a wind tunnel.[29-32] This work was undertaken to gain a better insight into processes operating in sprays, but in practice it has proved difficult to extrapolate from single drops to sprays. This is true partly because the drops used in the wind-tunnel experiments are much larger (4 to 5 mm diam) than spray drops (1 mm mass mean diam) and partly because the hydrodynamic behavior of the drops is transient.

Devemy and Dickerson analyzed some of the wind-tunnel data and concluded that it was likely that the form of iodine being absorbed in the drops was I_2, rather than CH_3I.[33] There is considerable evidence that methyl iodide is decomposed in the wind tunnel; for example, after a few experiments, elemental iodine is visible as a brown deposit in certain areas of the wind tunnel, and data quoted by Devemy and Dickerson show that the concentration in the gas phase decreases with a half-life of approximately 20 min, although the amount being removed by the solution droplets is negligibly small.

Pilot-plant studies on methyl iodide removal by sprays have been carried out by several groups.[34-42] Parker, Creek, and Horton used a very fine spray of sodium thiosulfate in a laboratory-scale facility.[34] Methyl iodide was removed with a 45-m half-life. Schwendiman and his associates used hydrazine as the solution reagent.[27,35] Methyl iodide was removed at a faster rate than would have been possible for sprays alone, and it was concluded that a film of solution running down the vessel wall made a significant contribution to the overall rate. However, Zittel has shown that hydrazine is readily decomposed by radiation.[43]

Parsly[28] and Hilliard and his associates[36-41] have studied the performance of both borax and borax-sodium thiosulfate solutions in removing methyl iodide. They agree that only the latter solution removes methyl iodide fast enough to be of potential value in the accident case. There is disagreement as to the relative importance of the wall film; Hilliard and his group believe a major part of the absorption occurs in the film.

Nishizawa, Oshima, and Maekawa studied removal of several of the organic iodides with water.[42] They reported half-lives of 3 to 16 hr at 25°C and 9 to 19 hr at 80°C, depending on flow.

Chemically Reactive Paints

Rosenberg and his co-workers have proposed the use of specially formulated paint for trapping methyl iodide.[44] The paint incorporates a nucleophilic reagent to fix the methyl iodide. Good results have been obtained in laboratory tests and in pilot plant tests at the Containment Systems Experiment. However, samples of these coatings failed when exposed to simulated loss-of-coolant conditions in tests at the Carolinas-Virginia Test Reactor.[45]

Methyl Iodide in Radiochemical Processing Plants

The methyl iodide problem is different at radiochemical process plants. Because of the extensive use of solvent extraction, high concentrations of organic vapors are found in many of the off-gas streams. The volumes of gas to be cleaned can be kept quite small. On the other hand, very large decontamination factors (10^7 to 10^8) are needed, especially for processing fast breeder reactor fuels, since it is not economically feasible to store these until the ^{131}I has largely decayed.

Because of the high concentration of organic compounds in the process off-gas streams, charcoal beds rapidly become saturated with organics and lose their ability to trap methyl iodide. Another effect of the high organic concentration is a high conversion of volatile iodine to methyl iodide. To deal with methyl iodide in these gas streams, two general approaches have been followed. One is to destroy all organic compounds by catalytic oxidation and then to collect the resulting inorganic iodine forms on charcoal. The other is to use a highly efficient scrubbing system to remove the methyl iodide.

The problem of organic saturation of charcoal adsorbers was encountered in the Transuranium Processing Facility at the Oak Ridge National Laboratory.[46] The solution adopted was catalytic oxidation of the organics, followed by collection of the iodine on charcoal adsorbers.[47] While processing the first batch of targets after this system was installed, an average ^{131}I decontamination factor of 400 was attained. The operators feel that once the system is debugged, it should give a decontamination factor of 10^4.

Scrubbing with an acid solution of mercuric nitrate has been proposed as the first stage of an iodine removal system for liquid-metal fast breeder reactor fuel-reprocessing plants (Refs. 151-153 of Chap. 3). Experimental data indicate that a decontamination factor of 10^2 is possible with such a system. While this is only a small part of the total required, it represents removal of most of the iodine so that the load to be handled by more efficient elements downstream of the scrubber is greatly reduced.

A number of results on methyl iodide scrubbing, trapping, etc., are reported in Ref. 48. These include results of scrubbing with mercuric nitrate, trapping on solid sorbents, and data on the performance of a composite system tested on the dissolver off-gas of the transuranium (TRU) facility.

Frevel and Kressley have patented a process for scrubbing alkyl halides from hydrocarbon streams using alkanolamines.[49] They cite treating butadiene containing 100 ppm of CH_3I with $NH_2(CH_2)_2OH$-H_2O (90:10) in an 11-plate bubble cap column. The butadiene leaving was essentially free of CH_3I.

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6. OCCURRENCE OF METHYL IODIDE UNDER ACCIDENT CONDITIONS

Identification of Methyl Iodide in Containment Experiments

Following the early DIDO and PLUTO reactor experiments in which evidence was obtained that two iodine compounds were formed that did not plate out on surfaces,[1] Eggleton and Atkins undertook a program to identify these compounds.[2,3] Their initial experiments involved 100- to 200-μCi quantities of carrier-free $Na^{131}I$. Iodine was generated from this by air oxidation at 400°C. The elemental iodine produced was adsorbed by specially activated knit copper mesh, particles were removed by an absolute filter, and the iodine compounds remaining were collected either by absorption in 0.02 M H_2SO_4 or by condensation in a liquid-oxygen-chilled cold trap. The compound fraction was 1 to 2% of the original iodine activity. Four bubblers containing 0.02 M H_2SO_4 in series had an efficiency of 90 to 95% removal.

The activity collected in the bubblers was subjected to a series of solvent extraction treatments, and it was found to consist of two fractions. Fraction A was soluble in benzene and was unreactive, and fraction B partitioned roughly equally between benzene and water. Following a series of chemical treatments, Eggleton and Atkins concluded that fraction B could not be I^-, IO^-, or IO_3^-, and no positive identification of this compound was made.

Fraction A was studied in further ways. For example, its molecular weight was determined to be 152 ± 3 by measuring its rate of effusion through a small hole. The molecular weight of $CH_3{}^{131}I$ is 146, but a molecular weight of 152 ± 2 was also found for synthetic $CH_3{}^{131}I$ by the effusion technique.

Fraction A was also fractionated by gas-liquid chromatography into seven fractions with the compositions given in Table 6.1. This showed that fraction A was composed of alkyl iodides, principally methyl iodide.

Subsequently, Eggleton and Atkins analyzed samples of gas from oxidizing trace-irradiated UO_2 and found methyl iodide. This work gives a sound basis for believing that the iodine compounds which are difficult to remove in trapping systems are alkyl iodides and that methyl iodide is the principal compound present.

Table 6.1. Gas Chromatographic Analysis of Eggleton's Fraction A (From Ref. 2)

Peak No.	Percentage of Total	Identification
1	85	Methyl iodide
2	2.9	Ethyl iodide
3	0.2	2-iodopropane
4	0.7	1-iodopropane
5	1.1	2-iodobutane
6	0.5	1-iodo-2-methyl propane
7	9.6	1-iodobutane

Theoretical Studies of Methyl Iodide Formation

Once it became evident that a major portion of the difficult-to-remove fraction of the iodine airborne in containment vessels was CH_3I, researchers started asking, "where does it come from?" There is no simple answer to this question. The organic material can be oil and grease residues on surfaces, decomposition products of protective coatings, and air pollution. Stern states that "normal dry air" contains 1.0 to 1.2 ppm methane that originates from vegetation.[4] This amounts to 4.5×10^{-8} mole/liter. Pollution could easily increase the methane concentration by a factor of 10.

The amount of iodine airborne will vary, depending on burnup, degree of core melting, etc. Row, Parsly, and Zittel quote a figure of 1.21 g-at. of iodine for 20,000-MWd/MT burnup.[5] Taking the TID-14844 (Ref. 6) assumptions of 50% release and 50% plateout and assuming 100 MT U and a 2×10^6 ft^3 containment volume, the airborne I_2 would be about 2.8×10^{-8} g-mole/liter with no credit for engineered safety systems. Thus there would be a slight excess of methane under the most favorable conditions. With impure air and lower burnup, the $CH_4:I_2$ ratio could easily become 100 or more.

Such quantitative reasoning indicates that it is easily possible for conditions favoring methyl iodide formation to exist. To investigate the possible consequences, a theoretical study was undertaken at Battelle Memorial Institute that was sponsored by the U.S. Atomic Energy Commission as part of its light-water reactor safety research and development program.[7-10]

The first phase of the program was a thermodynamic study of the system H_2O, CO_2, HI, CH_3OH, I_2, CH_3I, H_2, O_2, CO, CH_4, CH_2O, and solid carbon over the temperature range 300 to 1500°K.[7-8] This study showed that at equilibrium the amounts of methyl iodide expected were negligibly small. It is stated that the maximum equilibrium methyl iodide yield is about 2×10^{-3}% of the iodine present.[8] Since much larger conversions to methyl iodide have been observed, attention was then turned to kinetics.

The kinetic studies completed covered the homogeneous gas-phase reaction of CH_4 and I_2 with and without inert gas present.[9] The calculations indicate a maximum in the CH_3I concentration in the absence of inert gases but not when inert gases are present. Thus it does not appear that the kinetics of a homogeneous gas reaction could explain the type of methyl iodide production that has been observed.

Two remaining possibilities are surface-catalyzed reactions and radiation-induced reactions. The former could be important both in experiments and in the accident case. Radiation-induced reactions are likely to occur to a significant extent in only a few of the experiments, but they could be important in the accident situation.

As is discussed in the next section of this report, there is evidence that dry stainless steel surfaces catalyze the formation or destruction of methyl iodide, even at temperatures as low as 100°C. We are not aware of any quantitative investigation of surface catalysis.

The Battelle investigators undertook several experiments to investigate the formation of methyl iodide in a radiation field. They examined the effect of radiation dose, CH_4:I_2 ratio, irradiation rate, steam, and air on methyl iodide formation. They found that for mixtures of CH_4 and I_2 in the absence of inert gases, conversion increased linearly with dose and also increased with CH_4:I_2 ratio for doses up to 4×10^7 rads and

$CH_4:I_2$ ratios up to 500. The maximum conversion observed was over 40%. No effect of dose rate was found. Temperature appeared to have no effect between 100 and 275°C; at higher temperatures the conversion for a given dose increased rapidly. Conversion was increased in the presence of saturated steam but markedly decreased when both steam and oxygen or air were present. It should be noted that very high methane and iodine concentrations were used. The methane was loaded at partial pressures of 100 to 350 mm (5×10^{-3} to 2×10^{-2} mole/liter), and iodine quantities ranged from 1 to 5 mg (5 mg of I_2 in a 250-ml sample bulb is 8×10^{-5} mole/liter). These are orders of magnitude above the concentrations expected in the accident case, but it may be that as a practical matter they represent the lowest concentrations which can be used in experiments.

The overall impact of these studies appears to be that they demonstrated that thermodynamics and homogeneous kinetics cannot explain the methyl iodide formation observed in tests and emphasized the potential importance of radiation-induced reactions.

Occurrence of Methyl Iodide in Real and Simulated Reactor Accidents

A definitive answer to the question of what fraction of the iodine is converted to methyl iodide is needed for accident analysis. Methyl iodide is far more difficult to remove than other iodine forms when using either sprays or charcoal beds and therefore will eventually become the predominant airborne iodine species. The methyl iodide yield can be predicted in two ways: (1) consider all possible formation routes, estimate the contribution from each, and sum; (2) examine all available experimental results and attempt to arrive at an "experience" value for methyl iodide yield.

The first route has been taken by Durant and his associates,[11] Adams and his co-workers,[12] and Burley.[13] Durant and his associates specifically studied the safety problems of the Savannah River Plant (SRP) reactors, which employ uranium metal fuel. They identified the following factors as promoting the formation of organic iodine compounds:

1. In the fuel – organic impurities, high temperatures, and high hydrogen content.

2. Upon meltdown — low radiation field, high temperatures, and CO/CO_2 atmosphere.

3. In the containment building — long residence time, high temperatures, organic impurities, and low gas-phase iodine concentration.

4. On the reactor room surfaces — bare ferrous metal surfaces, high surface-to-volume ratio, and dry surfaces.

They concluded that for the SRP reactors, methyl iodide formation should not exceed 10^{-6}% of the core iodine inventory and stated that 10^{-4}% would be a conservative design value.

Adams and his co-workers reviewed the question of methyl iodide formation in connection with the safety analysis of the high flux isotope reactor (HFIR) at Oak Ridge National Laboratory.[12] They stated that 50% of the core iodine might be released, and 5% of this would be converted to methyl iodide in a maximum credible accident.

Burley reported that by using a "pseudo-theoretical" calculation of methyl iodide yield under water reactor accident conditions, he had arrived at 10% conversion of the free iodine in the containment building to methyl iodide.[13] He considered this figure to be conservative. Since he used TID-14844 criteria[6] for iodine release to the containment structure (25% of the core iodine inventory airborne in the structure), this is equivalent to stating that 2.5% of the core iodine inventory becomes airborne in the containment building as methyl iodide.

Wilhelm stated that based on studying the experimental data he had also arrived at the 10% figure.[14] Holmes stated that 100% conversion to methyl iodide was considered in the safety analysis of CO_2-cooled reactors.[15]

Well over 100 experiments in which the chemical form of iodine released from reactor fuel and/or aged in a containment volume was determined are reported in the literature. These results are assembled in the following sections so that they will be available for examination together.

Characterization of Iodine Forms

Before entering into a discussion of the results it is probably pertinent to review the iodine forms that might be present, as well as the characterization methods in use and their limitations. Iodine airborne in a containment atmosphere may be in one or more of the following six forms: (1) I_2 vapor, (2) HI vapor, (3) HOI vapor, (4) organic iodide vapors, such as CH_3I, (5) iodine vapor adsorbed on particles, and (6) inorganic iodine compounds associated with particles. The forms that may be present are determined by the chemical environment to which the iodine is exposed while it is being released and transported into the containment vessel.

Methods of differentiating iodine forms in experiments include wet chemical techniques, gas chromatography, and collection by May packs. The first two methods have been used primarily in laboratory-scale experiments. The May pack is an assembly of filters and adsorbers originally devised by F. G. May of the United Kingdom.[1] The original version contained specially cleaned copper screens, high-efficiency filters, charcoal-impregnated fiber glass (Whatman ACG/B), and granular charcoal. It was expected that inorganic iodine vapors would be collected by the copper screens, particles by the high-efficiency filters, easily adsorbable iodine compounds by the charcoal paper, and compounds more difficult to adsorb by the charcoal granules. A number of variations of the original device have appeared. Most American workers use silver rather than copper surfaces to collect inorganic iodine vapors, mainly because the copper surfaces have a useful life of only a few hours and are therefore not compatible with installations where samplers are sealed into containment systems several days before the experiment is done. Present May packs generally have more than one charcoal bed.

Experience with May packs[16] has led to the following conclusions:

1. The overall efficiency of the device is very high. Negligible amounts of iodine will penetrate a May pack that has been properly assembled and installed.

2. All the filter media can and probably will collect more than one iodine form.

3. The charcoal has a high efficiency for adsorption of all iodine forms, and any iodine that escapes other collection media will be picked up by the charcoal.

4. There are two iodine forms collected by the silver surfaces; one is collected very quickly and the other more slowly.

5. It is suspected that the silver surfaces lose efficiency in saturated steam-air atmospheres.

These facts lead to the conclusion that May-pack results tend to overestimate the proportion of methyl iodide present in a containment atmosphere. This view is shared by Durant and his associates[11] and is supported by experimental results reported by Collins and his co-workers.[17] The results of the latter group, presented in Table 6.2, give the only published direct comparison of results obtained by gas chromatography and with May packs. They show that the May packs indicated more methyl iodide than the chromatographs in five out of six cases, with the ratio ranging from 0.8 to 20 and averaging more than 4.

Yield of Methyl Iodide in Experiments

Experiments in which the yields of methyl iodide have been studied fall into two principal categories: those in which the yield in a fission-product release has been determined and those in which a fission-product mixture has been introduced into a containment volume and allowed to age.

Methyl Iodide Released from Irradiated Fuel

Experiments in which fission products have been released from irradiated fuel have been reported by Collins and his co-workers,[17] Castleman and his associates,[18] Collins and Hillary,[19] and Taketani and Ikawa.[20]

Collins and his associates[17] performed the series of 22 experiments described in Table 6.2. The data indicate methyl iodide yields ranging from 0.1 to 20% of the iodine in the fuel. There is no obvious pattern to the results.

Castleman, Tang, and Munkelwitz studied the release of fission-product iodine from uranium, UO_2, and U_3O_8 into superheated steam.[18] They reported a 1.6% CH_3I yield when iodine was released from metallic uranium and 10 to 24% when the iodine was released from UO_2. The results reported appear to

Table 6.2. Release of Iodine from Irradiated UO_2 Samples Under AGR Conditions

Run No.	Irradiation Level (MWd/MT)	Fuel Element Temperature (°C)	Gas Composition	Mean Gasborne Iodine ($\mu g/m^3$)	Percentage of Iodine in Sample as CH_3I	
					Determined by May-Pack Analysis	Determined by Gas Chromatography
4	1.5	1400	CO_2/50% air	0.015	6	
6	1.5	~1500	CO_2/50% air			
7	1.5	1700–1800	CO_2/50% CO	0.02	6	
8	1.5	1700–1800	CO_2/50% CO	0.03	6	
9	1.5	1700–1800	CO_2/50% CO	0.05	4	
10	1.5	1700–1800	CO_2/50% CO	0.04	8	
11	15	1700–1800	CO_2/50% CO	0.5	4	
12	15	1700–1800	CO_2/50% air	0.6	0.1	
13	50	1700–1800	CO_2/5% CO	4.5	2	
15	100	1700–1800	CO_2/5% CO	2	0.25	
16	150	1700–1800	CO_2/5% CO	7	0.5	
17	150	1700–1800	CO_2/5% CO	9	1.2	
18	2400	1700–1800	CO_2/50% air	7×10^{-4}	(a)	
19	2000	1700–1800	CO_2/5% CO	980	(b)	
20	2000	1700–1800	CO_2/5% CO	190	1	0.2
21	150	1700–1800	(c)	3×10^{-4}	1	0.5
22	150	1700–1800	CO_2/5% CO	2.5	2	0.5
23	150	>2000	CO_2/5% CO	10^{-5}	4	4
24	150	1700–1800	CO_2/5% CO/0.1 % CH_3	3×10^{-5}	20	1
25	150	2000	CO_2/5% CO	8	10	
26	100	1700–1800	CO_2/5% CO	3×10^{-4}	2	0.7
27	150	1700–1800	CO_2/5% CH_4	6	0.7	0.1

[a]No estimate of the percentage of the iodine in the fuel which reached the trapping system was given for this run; 6% of the iodine collected by the May pack was on charcoal-impregnated paper and 3% on the charcoal bed.

[b]Not reported; however, only 1 part in 10^5 of the iodine originally in the fuel penetrated 4 in. of charcoal in 1 hr and 5 parts in 10^5 in 14 hr; this penetration is roughly twice that found in experiment 20 and indicates that May packs should have shown about 2% of the iodine in the fuel as methyl iodide.

[c]CO_2, 54%; CO, 35%; air, 10%; H_2, 1%; CH_4, 0.02%.

be based on the iodine released. The percentage release is not stated but is probably high, since the uranium oxides were in powder form. The uranium was trace-irradiated, and the mass of iodine involved in the experiments was extremely small. The results are given in Table 6.3.

Collins and Hillary reported on a number of releases of iodine from Zircaloy- and stainless-steel-clad UO_2 into superheated steam. Their results, given in Table 6.4, indicate that the methyl iodide yield increased with irradiation level.[19] Table 6.5 gives the results of another series of experiments in which I_2 or CH_3I was released into steam at 700°C.

Taketani and Ikawa also conducted a series of iodine release experiments in which yields of methyl iodide were obtained.[20] Their results are given in Table 6.6.

Containment Experiments

British Experiments. Megaw and May released ^{132}I into the DIDO and PLUTO containment structures.[1] They conducted ten experiments and found methyl iodide in three. Their results are given in Table 6.7.

Croft and Iles released stable I_2 with ^{132}I tracer into the Zenith reactor containment building.[21] The results are given in Table 6.8. In experiments 1 and 2, with the ventilation system off, 0.2 and 0.03%, respectively, of the iodine released turned up as organic iodides. In experiment 3, with the ventilation system operating, the amount of iodine collected on the second ACG/B paper and charcoal granules was too small to analyze.

Croft, Iles, and Davis have reported on three experiments in which relatively high iodine concentrations were released into a room coated with chlorinated rubber-based paint.[22] The results are given in Table 6.9. They found 0.02% of the iodine in organic form in the dry experiments and 0.01% in the wet experiment.

Croft and Iles[21] also reported on two unpublished experiments by Davis and Rowbury. In the first, iodine was released into the Zenith reactor circuit outside the graphite fuel boxes with air circulating at ambient temperature. After 2 1/2 hr, 0.1% of the iodine was still circulating; this was probably all organic iodides. In the second experiment the iodine was released inside a graphite fuel box, and the primary

Table 6.3. Chemical States of Iodine Found upon Release from Uranium or UO_2 into Steam (From Ref. 18)

Uranium Form	Iodine Chemical State and Fraction Found[a]				
	I°	I^-	I^{+5}, I^{+7}	A	B
Metallic uranium	12.0	83.2	1.8	1.4	1.6
UO_2 to H_2O	76.6	10.5	0.5	2.3	10.1
UO_2 to $H_2O + H_2$	11.0	61.9	9.1	2.0	16.0
UO_2 to ordinary distilled H_2O with no carrier gas	50.6	30.3	0.7	5.8	12.6
UO_2 to ordinary distilled H_2O with carrier gas	20.6	44.2	1.9	8.4	24.6

[a]Fraction A is iodine remaining in aqueous phase after (1) extracting I° with CCl_4, converting to I_2, and extracting with CCl_4 and (2) reducing IO_3^- and IO_4^- to I_2 and extracting with CCl_4. Fraction B is iodine extracted from original solution by CCl_4 but not back-extracted by aqueous $Na_2S_2O_3$. This was identified as CH_3I.

Table 6.4. Quantities of Organic Iodides Found upon Release of Iodine from Irradiated Fuels into Superheated Steam (From Ref. 19)

Irradiation (MWd/MT)	Fuel Cladding	UO_2 Melting	Iodine Released from Fuel (%)	Iodine Released as Organic Iodides (%)
0.5	Zircaloy	No	6.2	0.02
0.5	Zircaloy	No	6.8	0.02
1.0	Zircaloy	No	2.4	0.01
2.0	Zircaloy	No	2.4	0.02
5.0	Zircaloy	No	2.9	0.01
1.0	Zircaloy	Some	13.7	0.1
2.0	Zircaloy	Some	15.4	0.003
7.0	Zircaloy	Some	40.0	0.03
~100	Zircaloy	Some	28	0.04
100	Zircaloy	Some	35	0.5
100	Zircaloy	Some	34	3
100	Zircaloy	No	9	2
100	Stainless steel	Some	27	0.08
100[a]	Stainless steel	Some	60	0.2

[a]Melting in air atmosphere; steam added to off-gas.

Table 6.5. Results of Experiments on Release of Trace Iodine into Steam at 700°C (From Ref. 19)

	Experiment 1	Experiment 2	Experiment 3
Form of iodine introduced	I_2	I_2	CH_3I
Zircaloy and UO_2 present in system	Yes	No	Yes
Iodine released, %	49.6	90.3	70.6
Disposition of released iodine, %			
In hot water	44.5	80.6	66.9
In cold water, including demister water	3.2	8.85	2.45
Fine particulates	0.06	0.15	0.03
Organic iodides	1.7	0.35	0.9

Table 6.6. Yields of CH_3I from Fuel Samples Irradiated to Approximately 10^{16} Neutrons/cm^2 in Experiments of Taketani and Ikawa (From Ref. 20)

Run No.	Fuel	Maximum Temperature (°C)	Carrier Gas	Gas Flow (cc/min)	CH_3I in Released Iodine (%)
1	UO_2	1400	Argon	40	0.2
2	Uranium	1400	Argon	40	
3	Uranium	800	CO_2	100	0.2
4	Uranium	1400	Argon	60	
5	UO_2	1400	Argon	60	0.2
6	UO_2	800	10% CH_4 90% argon	50	2
7	UO_2	600	O_2	50	<1

Table 6.7. Results of Experiments in Which Megaw and May Released ^{132}I into DIDO and PLUTO Containment Structures (From Ref. 1)

Reactor	Experiment Designation	Theoretical Iodine Concentration ($\mu g/m^3$)	Activity (dpm/m^3)	CH_3I Found (fraction of theoretical)	
				Maximum	Final
DIDO	1	1.0	8.2×10^6		
	2	0.14	9.8×10^6		
	3	1.0	9.8×10^6		
PLUTO	A	0.013	8.9×10^6	0.009	0.009
	B	0.14	7.2×10^6	0.0056	0.0025
	C	14.1	9.7×10^6	0.0030	0.0027
	D	14.1	6.7×10^6		
	E	1.0	8.5×10^5		
	F	1.4	1.5×10^7		
	G	1.4	1.2×10^7		

circuit contained air at 130°C. Approximately 7% of the iodine was converted to organic form.

Stinchcombe and Goldsmith have reported on two experiments carried out in DIDO.[23] Their results, given in Table 6.10, show a decreasing concentration of charcoal-seeking iodine during the experiment from 0.2% of the release at the start to about 0.05% after 4 hr. A stream from the containment vessel was taken through a steam condenser. The results showed that 1.5 to 3% of the elemental (copper-seeking) iodine, 30 to 50% of the iodine compounds trapped by charcoal paper, and 80 to 100% of the compounds trapped by granular charcoal passed through the steam condenser.

CMF and CRI Experiments. Parker's group at the Oak Ridge National Laboratory has reported on 20 experiments conducted in the containment mockup facility,[24-30] the CMF, which has a 0.2-m^3 stainless steel containment vessel. The results are given in Tables 6.11, 6.12, and 6.13. Except for four runs in which 0.1% mixed organic vapors was added to the containment atmosphere, the amounts of "penetrating" iodine reported do not exceed 1.3%. This is based on iodine found; no attempt was made to assay the iodine sources and account for all the iodine.

Table 6.8. CH_3I Yields in Experimental Iodine Releases to Zenith Reactor Containment Building (From Ref. 21)

Experiment No.	Iodine Yields (g/m^3)				Final Concentration on Charcoal Grains	Ratio CH_3I Yield to Total Available Iodine (Calculated)
	Calculated Maximum Concentration	Observed Maximum Concentration[a]				
		At SP-1	At SP-2	At SP-3		
1	3.8×10^{-7}	1.9×10^{-8}	1.5×10^{-8}	2.5×10^{-9}	2×10^{-10}	5.3×10^{-4}
2	7.8×10^{-7}	4×10^{-7}			2.2×10^{-10}	2.8×10^{-4}
3	7.7×10^{-7}	3×10^{-7}	3×10^{-8}	2×10^{-8}	Below analytical limit	
	7.2×10^{-7}		7×10^{-8}	4.8×10^{-8}		

[a]SP-1 = point in reactor pit
SP-2 = point in ventilation duct upstream of filter
SP-3 = point in ventilation duct downstream of filter

Table 6.9. Results of Experimental Releases of Iodine into Room Coated with Chlorinated Rubber-Based Paint (From Ref. 22)

Experiment No.	Environmental Conditions[a]	Concentration of Iodine Released (mg/m^3)	Maximum Total Iodine Observed (mg/m^3)	CH_3I Yield	
				mg/m^3	Percent of Iodine
1	85% relative humidity	113	80	0.024	0.021
2	85% relative humidity	237	200	0.057	0.024
3	100% relative humidity, heavy condensation	190	130	0.02	0.01

[a]All temperatures approximately 20°C.

Table 6.10. Results of DIDO Experiments (From Ref. 23)

Run	Iodine Concentration (g/m^3)		Iodine on Charcoal (fraction of theoretical)	
	Theoretical	Maximum Observed	Maximum	Final
A	0.12	0.023	0.0021	0.00056
B	0.12	0.05	0.0028	0.00083

Table 6.11. Results of Experimental Releases of Iodine into Air Atmospheres in the Containment Mockup Facility (From Ref. 24)

Experimental conditions:

Run A. Iodine released from trace-irradiated stainless-steel-clad UO_2 containing ~1 μg I (5 $\mu g/m^3$ in vessel)
Run B. Same as run A, except that filtered air was used
Run C. UO_2 irradiated to a burnup of 7000 MWd/MT U; 20 g U, ~400 μg I (~3 mg/m^3 in vessel)
Run D. Vaporized iodine tracer used; ~200 μg I
Run E. Vaporized iodine tracer used; ~350 μg I

	Run A	Run B	Run C	Run D	Run E
Total iodine release,[a] %	84	64	91	92	100
Iodine found,[a] %					
In hot zone	6.3	11	0.4	0.4	0
In aerosol tank	47	24	25	34	86
Airborne after 3 hr	31	30	62	57	13
Amount of iodine in "penetrating" form, %	3.7	0.4	0.3	0.5	0.3
Iodine loss through 1.5 in. of charcoal, %	1.3	0.1	0.01	0.03	0.003

[a]As percentage of inventory.

Table 6.12. Results of Iodine Deposition and Desorption Experiments in Containment Mockup Facility (From Ref. 25)

	Atmosphere						
	Air	Steam-Air		Steam-Air and Organics			
	Run 6-11[a]	Run 6-25[b]	Run 8-4[c]	Run 7-16[d]	Run 9-10[e]	Run 10-7[e]	Run 10-28[f]
Iodine held in containment tank,[g] %							
Retained on tank walls	79.6	60.8	38.2	19.3	20.9	24.4	18.3
Collected in steam condensate		34.9	54.0	52.9	47.3	58.2	43.5
Total retention	79.6	95.7	92.2	72.2	68.2	82.6	61.8
Iodine removed from tank,[g] %							
By pressure release	3.0	1.1	2.4	12.9	8.5	6.2	14.6
By argon displacement	7.4	1.2	2.4	13.3	15.9	7.2	15.7
By air sweep	2.9	0.3	1.7	0.5	2.6	1.2	1.8
Total removed, airborne	13.3	2.6	6.5	26.7	27.0	14.6	32.1
Iodine removed on test samples,[g] %	6.1	1.7	1.4	0.8	2.2	1.9	0.9
Distribution of airborne iodine from tank,[g] %							
Retained on filters	4.1[h]	0.5	1.5	0.1	0.3	0.03	0.01
Retained on silver-plated screens	5.3	0.8	2.3	6.4	8.5	2.6	9.1
Retained on charcoal papers	3.0	0.4	0.4	2.0	15.8	1.7	16.3
Retained in charcoal cartridges	0.3	0.6	2.0	16.4	2.3	9.1	6.6
Penetration loss through 3/4 in. of charcoal,[g] %	0.01	0.08	0.3	3.8	0.17	0.8	0.5
Penetrating iodine,[g] %	0.3	0.5	1.2	1.6	2.5	7	21[i]

[a]Iodine was released to the containment shell filled with filtered air only at 30 psia; containment time at full pressure, 4 hr.

[b]Iodine released into steam (20 psia) and air (20 psia) mixture under conditions providing a large amount of condensate; containment time at full pressure, 4 hr.

[c]Iodine released into steam (~21 psia) and air (~21 psia) mixture and held in containment shell 18 hr.

[d]An undetermined amount of organic material, acetone, and solid CO_2 was inadvertently included in the iodine tracer preparations; release was into steam (~20 psia) and air (~20 psia); held in containment shell 5 hr.

[e]In runs 9-10 (steam, ~22 psia; air, ~22 psia; containment time, 5 hr) and 10-7 (steam, ~22 psia; air, ~22 psia; 16 hr), containment time, 16 hr), 500 cm^3 of mixed hydrocarbons prepared by hydrolysis of UC-UC_2 was added.

[f]In run 10-28, UO_2 was melted above the iodine tracer which, in turn, was released when the molten UO_2 mixture heated a quartz ampul to its melting or softening point; release into steam (~22 psia) and air (~22 psia); 9 hr containment time.

[g]As percentage of total inventory.

[h]One organic membrane filter probably reacted with and retained some molecular iodine in addition to particulate iodine.

[i]Based on iodine retained on charcoal beds only; 6.6% was penetrating iodine.

Table 6.13. Iodine Behavior in the Containment Mockup Facility (From Refs. 27-30)

	Iodine Released From							
	Stainless-Steel-Clad UO_2		Zircaloy-Clad Simulated Fuel				Zircaloy-Clad High-Burnup UO_2	
	Run 3-5	Run 12-9	Run 2-24	Run 3-25	Run 1008	Run 1007	Run 10-29[a]	Run 4-11[b]
Furnace atmosphere	Air	Air	Air	H_2O-He			Steam-air	Air
Containment tank atmosphere	Air	Steam-air	Steam-air	Steam-air	Steam-air	Steam-air	Steam-air	Steam-air
Iodine released,[c] %	90.6	~100	86.8	92.3			100	90.8
Iodine held in containment tank,[c] %								
Retained on tank walls	25.2	33.7	13.2	8.1	38.9	31	19.8	20.3
Retained on deposition coupons		0.1		1.4			7.2	23.7
Collected in steam condensate		56.0	50.0	71.6	45.1	68	57.6	19.2
Total retention	25.2	89.8	63.2	81.1	84.0	99	84.6	63.2
Iodine removed from tank,[c] %								
By pressure release		1.7	2.3	1.1	8.1[d]		2.9	7.7
By argon displacement	65.2	4.4	3.1	6.0	7.9		4.8	11.5
By air sweep		1.8	0.9	2.6		1.2	1.2	2.6
Total removed, airborne	65.2	7.9	6.3	9.7	16.0	1.2	8.9	21.6
Distribution of airborne iodine from tank,[c] %								
Retained on high-efficiency filters	3.9	0.05	0.1	0.2			0.4	2.1
Retained on silver-plated screens	52.6	4.6	1.6	6.0			5.6	5.0
Retained on charcoal papers	4.1	2.4	0.7	0.2				
Retained in charcoal beds	4.5	0.9	3.2	0.8			2.2	11.7
Amount of iodine in "penetrating" form, %	0.3	1.3	0.7	0.8			0.6	0.6
Amount that penetrated 3/4 in. of charcoal, %	0.08	0.02	0.02	0.02				
Amount that penetrated 1 1/2 in. of charcoal, %	0.01	0.002						

[a]Approximately 1000 MWd/MT burnup.

[b]Approximately 7000 MWd/MT burnup.

[c]As percentage of inventory.

[d]Includes amount removed by sampling.

In view of the experience of workers who have attempted to obtain iodine balances and have found that appreciably less than 100% of the iodine introduced can be accounted for, the methyl iodide yields in these experiments are probably biased on the high side. Also the May-pack techniques used have evolved with time in such a way that the fraction reported as "penetrating" or "organic" iodine would tend to be higher in the earlier runs than in the recent ones.

Parker's group also completed ten experiments in the Containment Research Installation.[29-31] (The CRI has a 3.8-m^3 containment vessel with interchangeable liners; a stainless steel liner was used for the experiments discussed here.) The maximum methyl iodide yield reported was 0.3%. The experimental results are summarized in Table 6.14.

Parker and his associates have also reported on a series of experiments in which very low concentrations of iodine or methyl iodide were released into the CRI containment vessel with an Amercoat-66 liner installed.[32-34] The atmosphere was an unsaturated mixture of air and steam. In the first experiment in the series, approximately 1 μg of carrier-free $^{131}I_2$ was vaporized into the vessel by oxidizing $Na^{131}I$ with $K_2Cr_2O_7$. Initially, approximately 20% of the iodine inventory was found as organic iodides; however, during the 20-hr hold time the amount decreased to 2% of the iodine inventory. In the second experiment an estimated 2 μg of ^{131}I as $CH_3{}^{131}I$ was introduced into the vessel. Over 22 hr, the concentration decreased to about 11% of its initial value.

In the third experiment, 50 μg of I_2 was released into the containment vessel to give the I_2 concentration anticipated for the LOFT experiment. The results indicated that the 5 to 15% of the iodine initially present as organic iodides decreased to 0.5 to 1.3% after 20 hr (the variation represents the spread between the various sampling methods used). Parker and his co-workers have pointed out that the concentration of paint solvents in the vessel atmosphere produced as the result of repeatedly steaming the vessel decreased with time;[33] it was a factor of 50 lower in the third experiment than in the first. In all of these experiments, over 90% of the iodine was found on the paint at the end of the experiment.

Table 6.14. Iodine Behavior in the Containment Research Installation with a Stainless Steel Liner (From Refs. 30-32)

	Run 100	Run 101	Run 104	Run 105	Run 107	Run 108	Run 109	Run 110	Run 111	Run 114
Nature of iodine source	I_2	HI	I_2	HI	Simulant	Simulant	Simulant	Prompt release	Prompt release	Fuel with 6000-MWd/MT burnup
Mass of I_2 released, mg			30	20	15	20	9.2	2.4	0.23	1.2
Iodine distribution, % of inventory										
Washed from walls	97	98.6	84	86.7	83.9	62.6	53.5	77	72.3	84.2
In condensate			15.3	13	14.7	35.9	40.1	20.9	27.3	13.2
In gas samples	0.25	0.067								
Maximum methyl iodide observed, %	0.046	0.12								
Time after release, min	832	842								
Methyl iodide at end of aging period, %	0.034	0.018	0.22	0.04	0.32	0.26	0.04	0.06	0.16	0.12
Total aging period, min	1255	1093								

[a]Prompt release of iodine from overheated fuel simulated by melting a silica ampoule containing iodine in a Zircaloy-2-clad UO_2 dummy fuel element.

The results of these experiments differ noticeably from the results of experiments at comparable concentration levels done in the aerosol development facility (ADF). (See later section on "CSE Experiments.") In the ADF experiments, the charcoal-seeking iodine fraction exceeded 1% in only one of seven irradiated uranium (very low iodine concentration) experiments. There was indication of fairly fast iodine removal during the first 60 min in the ADF experiments, but later the I_2 was removed slowly. The final iodine distribution was significantly different in CRI tests from that in ADF tests. In the ADF experiments 60% of the iodine was found in the condensate and 40% was calculated to be on the surfaces, while in the CRI experiments over 90% was calculated to be on the surfaces and only 3 to 4% in the condensate.

Differences in experimental techniques may account for these differences in observed iodine behavior. The ADF experiments were conducted with saturated air-steam mixtures, and the atmosphere's temperature was controlled by adding steam as the experiment continued. In the CRI, heaters installed around the tank wall were used to control temperature, and the experiments were done with unsaturated air-steam mixtures in the vessel. It seems likely that the CRI technique resulted in some dry painted surfaces being present. Condensation rates were very much lower in the CRI experiments than in the ADF experiments.

NSPP Experiments. The nuclear safety pilot plant group has reported 16 experiments in which the behavior of iodine in the containment vessel was followed.[35-41] (The NSPP has a 38.3-m^3 stainless steel containment vessel.) The experimental results are presented in Tables 6.15 and 6.16. In some of the experiments as much as 10% of the original iodine inventory was found to be present at some point in the aging process; the maximum at the end of an experiment was 1.7%. Most of the very high values were found in early runs when the May-pack assembly for the NSPP was still under development; prior to run 12 the assembly was made so that it was possible for part of the sample gas to bypass the silver-plated screens and for the I_2 in the gas to be collected on charcoal beds. It is questionable whether methyl iodide would really be formed and destroyed as rapidly as indicated.

Table 6.15. Summary of Iodine Behavior in the Nuclear Safety Pilot Plant (From Refs. 35-41)

	Iodine Only			Iodine Released from Simulated UO_2 Fuel					Iodine Released from Trace-Irradiated UO_2		Iodine Released from High-Burnup UO_2	
	Released by Melting		Low-Temperature Release									
	Run 4	Run 5	Run 6	Run 3	Run 7	Run 10	Run 11	Run 12	Run 8	Run 9	Run 14	Run 15
Cladding material	Pyrex	Pyrex	Pyrex	Stainless steel	Stainless steel	Stainless steel	Stainless steel	Stainless steel	Stainless steel	Stainless steel	Zircaloy	Zircaloy
Atmosphere	Air	Air	Air	Air	Air	Air-steam	Air-steam	Air-steam	Air-steam	Air-steam	Air-steam	Air-steam
Initial temperature, °C	Room	Room	Room	Room	Room	108	106	106	108	104	105	
Mass of iodine, mg	100	100	100	100	1000	51	5	76	Trace	Trace	28	28
Distribution of iodine, % of inventory												
In fuel residue					0.4	74	4.1	26	54	37.3	52.7	27.8
In furnace	28.2	5.5	28.5	12.3	18.8	2.2	12	65	5.7	24.6	21.7	45.9
In containment vessel, % of inventory												
In condensate						3.7	20.5	8.4	0.67	7.6	0.40	25.5
On filters			0.9			0.04	15.5	0.2		6.9[a]	0.12	0.28
On walls	29.5	21.5	29.0	43.4	49.9	20.3	46.9	0.2	0.56	18.5	1.21	1.8
Airborne in purge gas	20.9[b]	18.9[b]	2.8[b]	15.6[b]	8.6[b]	0.01	0.84	0.08	0.11	0.4	0.07	0.0026
Total in vessel	50.4	40.4	32.7	64.0	58.5	24	84	8.9	1.34	33.4	1.80	27.6
Maximum methyl iodide observed, % of iodine in sample	9.1	10.2	6.0	0.28	6.3	0.27	7.4	0[c]	0.14	3.0		0.97[d]
Time after release, min	588	1440	23	810	5	540	180		30	60		30
Methyl iodide present at end of aging period, %	0.91	1.7	0.35	NA	0.30	0	0.22	0	0.03	0.04	0.07[e]	0.003[e]
Total aging period, min	1440	2880	2810	1440	2160	1440	1300		2880	1830	1440	1440

[a] In spray water.

[b] Estimated.

[c] Cleanup of containment atmosphere with filters and charcoal adsorbers was started at 2 hr.

[d] Highest value in any May-pack sample; some samples taken at the same time had only one-tenth as much.

[e] Upper limit value based on all iodine purged being in organic form.

Table 6.16. Summary of Iodine Behavior in Nuclear Safety Pilot Plant Runs Involving Release of Elemental Iodine into a Dry-Air Atmosphere (From Ref. 41)

	Run 16	Run 17	Run 18	Run 19
Mass of iodine, mg	400	400	400	400
Distribution of iodine, % of inventory				
In breaker tee	52.1	71.0	30.8	33.8
On MCV walls[a]	47.9	27.8	66.1	65.3
In purge gas	0.01	1.0	3.1	0.9
Total in vessel	58.2	28.8	69.2	66.2
Maximum methyl iodide observed, % of inventory	0.24	0.3	0.77	1.98
Time after release, min	900	(b)	960	720
Methyl iodide present at end of experiment, %	0.098	0.27	0.68	0.71
Total aging period, min	2760	2760	4200	1440

[a]Determined upon decontamination.

[b]Concentration constant throughout run.

CSE Experiments. The staff of the containment systems experiment (CSE) has reported on the results of 21 experiments conducted in the aerosol development facility (ADF).[42] (The ADF is an auxiliary facility set up on the CSE site for development of simulation and sampling techniques.) Two tanks were used in the experiments: the painted aerosol tank (PAT), which was a 1.5-m^3 carbon steel pressure vessel painted with Phenoline 300,* and the stainless steel aerosol tank (SAT), which was a 0.9-m^3 stainless steel pressure vessel. The experiments were done at a temperature of 80°C, and the vessels were maintained nearly isothermal by continuously feeding steam. The total pressure was 0.9 to 1 atm abs. The experimental results, given in Table 6.17, show that the methyl iodide yields ranged from 0.006 to 1% of the sample iodine inventory.

Also the results of two natural effects experiments in the CSE drywell and three in the main CSE vessel have been reported.[43-47] The drywell has a volume of 65 m^3 and is painted with Phenoline 302. The main CSE vessel, including the drywell, has a volume of 596 m^3 and is also painted with

*Carboline Company, St. Louis, Missouri.

Table 6.17. Summary of Results from ADF Experiments (From Ref. 42)

Run	Vessel	CH_3I as Fraction of Initial Gas-Phase Concentration	Initial Gas-Phase Iodine Concentration (mg/m^3)
SA-21	PAT	7×10^{-4}	450
SA-23	PAT	3×10^{-4}	520
IA-26	PAT	2.5×10^{-3}	0.045
SA-28	PAT	1×10^{-2}	0.33
IA-32	PAT	4.5×10^{-3}	0.18
IA-33	PAT	5×10^{-3}	0.16
IA-39	PAT	3.5×10^{-3}	0.30
IA-40	PAT	9×10^{-3}	0.23
IB-41	PAT	7×10^{-3}	0.27
IB-42	PAT	1×10^{-3}	0.27
SA-43	PAT	2.5×10^{-4}	450
SA-44	SAT	6.4×10^{-5}	530
SB-48	SAT	3.5×10^{-4}	540
SB-50	SAT	3.5×10^{-4}	530
SB-53	SAT	2×10^{-4}	1000
SB-60	SAT	2×10^{-4}	780
SB-61	SAT	2×10^{-4}	1500
SB-63	SAT	2×10^{-4}	1×10^5
SB-63	SAT	1.8×10^{-4}	1070
SB-74	SAT	1.08×10^{-3}	51,000
SB-78	SAT	5×10^{-4}	980

Phenoline 302. The experimental results are given in Table 6.18. The reported methyl iodide concentration was low in all these experiments, with the maximum being 0.3% in run A-5. It should be noted that CH_3I was deliberately injected in run A-5, and the final concentration was 28% of that expected as a result of the injection.

In-Pile Experiments. Aging of the aerosol generated in an in-pile fuel meltdown facility has been studied at the Oak Ridge National Laboratory.[48,49] The aging chamber is stainless steel and has a volume of 0.2 m^3. The experimental results are given in Table 6.19. Two of the runs were done with steam-air atmospheres, and in both the CH_3I yield was 0.85%. In one run done in an air atmosphere at ambient temperature the yield was 1.2%, but in the second, done at 103°C, the methyl iodide concentration had attained 14% of the fuel inventory at the end of the aging period and

Table 6.18. Summary of Results from CSE Experiments (From Refs. 43-47)

Run	Vessel Volume (m^3)	C_0, Initial Gas-Phase Iodine Concentration (mg/m^3)	C_{CH_3I}, Methyl Iodide Yield (mg/m^3)	C_{CH_3I}/C_0, Ratio of CH_3I Yield to Initial Iodine Concentration
D1	65	660	0.77 (max)	1.17×10^{-3}
			0.0198 (final)	3×10^{-5}
A-1	850	1.29×10^2	4.8×10^{-1}	3.7×10^{-3}
A-2	850	1.19×10^5	1.2×10^2	1×10^{-3}
A-5	850	1.416×10^5[a]	4.5×10^2	3.2×10^{-3}
D-2	65	940	0.226	2.4×10^{-4}
			0.164	1.7×10^{-4}

[a]Includes 1.6×10^3 mg/m^3 of CH_3I deliberately injected.

Table 6.19. Results of ORNL In-Pile Fuel Meltdown Experiments (From Refs. 48, 49)

	Run 1	Run 2	Run 3	Run 4
Burnup of UO_2	Trace	Trace	16,000 MWd/MT	Trace
Atmosphere	Air	Air	Air-steam	Air-steam
Iodine in sample, mg			0.62	8.1
Iodine in containment vessel, % of I in sample	31.0	71.3	50	50
CH_3I observed at end of aging period, % of I released to containment vessel	4.0	20	1.7	1.7
CH_3I as % of I in sample	1.2	14.3	0.85	0.85

was increasing with a doubling time of about 3.5 hr. Trace-irradiated UO_2 was used for the air-atmosphere experiments.

Discussions with the operators of the in-pile experiment indicated that irradiation of the fuel resulted in 3×10^{17} fissions.[50] If a yield of 0.1 atom of iodine per fission (^{127}I, ^{129}I, ^{131}I, and ^{133}I combined) and 70% transfer to the containment vessel are assumed, a concentration of 9×10^{-11} mole I_2/liter in the containment vessel is obtained. A concentration of 1 ppm CH_4 in the air (Stern[4] indicates that this much is normally found in the atmosphere) is equivalent to 4.5×10^{-8} mole CH_4/liter. Thus the CH_4:I_2 ratio is 500, and high conversion to CH_3I would be expected.

An experience at the nuclear safety pilot plant was significant.[51] In three experiments attempts were made to introduce methyl iodide into the containment vessel through a line that contained a steam-jacketed stainless steel pipe tee. The steam pressure in the tee jacket was sufficient to prevent condensation from the air-steam jacket in the containment vessel on the tee surfaces. The results obtained when sprays were started indicated the presence of significant amounts of I_2, and comparison of the results with those of later experiments made without the hot tee indicated that over 90% of the methyl iodide had been converted to I_2, although contact with the tee should have been momentary.

From these data, we conclude that a dry heated stainless steel surface can act as a catalyst for either the formation or the destruction of methyl iodide. The reaction will doubtless depend on the relative amounts of iodine, organic substances, and methyl iodide present.

Lorenz, Parker, and Hobson have reported on an experiment in which a fuel rod irradiated to 650 MWd/MT in the MTR was ruptured by a 556 MW-sec transient in TREAT.[52,53] They found that 0.17% of the iodine in the fuel was released; 6.7% of this, or 0.01% of the iodine in the fuel, was methyl iodide.

CDE Experiments. Workers at Idaho Nuclear Corporation have conducted several experiments in the Contamination-Decontamination Experiment, and two of their experiments have yielded data significant to this study.[54,55] (The CDE has a stainless steel pressure vessel with a volume of 2.4 m^3.) The experimental results, given in Table 6.20, indicate that 4 to 5% "organic" iodine was present at 1/2 hr after meltdown and approximately 1% after 24 hr. The experimenters have suggested that much of this material is hypoiodous acid (HOI), rather than organic iodides.[56] Recently they succeeded in proving that HOI is a volatile iodine compound.[57]

Other Experiments

Barry has reported the results of an experiment in which the cladding of a fuel element in an in-pile test loop was deliberately ruptured by reducing the coolant flow.[58] A "large proportion" of the UO_2 was dispersed into the loop cooling water, but only 0.2% of the iodine in the UO_2

Table 6.20. Results in CDE Experiments
(From Refs. 54, 55)

	Run 3	Run 4
Iodine in sample, mg/m^3	111	107
Iodine accounted for after release, % of I in sample	19	57
Organic iodides present after 1/2 hr, mg/m^3	3.9	4.8
Organic iodides present after 24 hr, mg/m^3	1.0	1.3

became dissolved in the water. Some of this leaked into a pump room and evaporated. Results of monitoring the ventilation duct from the pump room, presented in Table 6.21, show that the iodine that became airborne was principally I_2 and volatile iodine compounds. The author noted that a 6-m-long sampling line was used and some of the I_2 was probably lost by plateout, so the yield of volatile iodine compounds was probably overestimated. It appears that the methyl iodide yield could not have exceeded 0.04% of the iodine inventory of the fuel and was probably less.

Bennett, Slusher, and Adams[59] conducted tests in which elemental iodine was introduced into stainless steel vessels that had been painted with either Amercoat-66 or Phenoline-302. The vessels were heated and the concentration of organic iodides was determined by gas chromatography. Atmospheres used were dry air, air saturated with water vapor, and air plus 0.5% hydrogen. In order to produce measurable results, fairly large elemental iodine concentrations (1 to 23 g/m^3) were used. The maximum amounts of methyl iodide formed were 3×10^{-4} mg in 1.2 liters at 100°C, 8×10^{-4} mg at 150°C, and 7×10^{-3} mg at 250°C. The investigators express the belief that the methyl iodide was produced by a surface reaction; under the conditions of the experiments, the painted surface probably was dry. In a loss-of-coolant accident, it probably would be covered by a film of water.

Murata, Inoue, and Kobayashi used a mass spectrometer to measure the methyl iodide content of iodine samples prepared by various procedures.[60] The largest amount (0.8%) was found in I_2 prepared by decomposing PdI_2. The least ($<10^{-6}$%) was found in I_2 prepared by oxidizing NaI with H_2O_2.

Releases from Reactors

A deliberately defected fuel rod under test at the Plutonium Recycle Test Reactor (PRTR) failed in such a way as to cause a pressure-tube rupture and release of fission products to the coolant water and containment building. Freshly and his associates described the incident,[61] and Perkins and his co-workers have discussed the fission-product behavior.[62,63] Table 6.22 summarizes the iodine behavior. The organic iodine was estimated by using a May-pack sample taken by the CSE staff 8 1/2 hr after the

Table 6.21. Results of Release of Iodine by Deliberate Overheating of Fuel Rod (Ref. 58)

Time of sampling, min after iodine release	1425–1525	1530–1630	1710–1810	1825–1925	1947–2047	40 days later
Iodine found at end of vent duct from pump room, % of inventory[a]						
On copper screen[b]	57	59	53	52	46	7
On glass fiber	15	3	1	1	1	6
On charcoal paper	20	28	28	36	45	64
On charcoal bed	8	11	17	11	7	22

[a]Only 0.2% of I in fuel dissolved in coolant.

[b]Plateout losses in duct upstream of sampling point would tend to bias copper-seeking species low; hence, others high.

Table 6.22. Iodine and Methyl Iodide Found in the PRTR Incident (From Refs. 61-63)

Iodine, Ci	
Total ^{131}I in the fuel	773
^{131}I found in "340" tanks	205
^{131}I released to reactor atmosphere	7.0
^{131}I removed by cooling coils	4.7
^{131}I remaining in atmosphere	2.3
^{131}I plated out on surfaces	0.05
^{131}I in organic form	0.7
Organic iodine	
Percentage of total fuel rod inventory	0.09
Percentage of iodine released from fuel rod	0.34
Percentage of iodine released to reactor atmosphere	10.0

incident. A 50-ft sampling line was used, and plateout of I_2 could have occurred. Thus the 0.1% of inventory reported represents an upper limit, rather than a definite organic iodine compound yield.

Several French experiments involving pool-type reactors have been reported.[64,65] In these the fraction of the iodine in the defected fuel escaping to the atmosphere above the pool has never exceeded 10^{-4} and has often been an order of magnitude lower. Much of it appears to have been organic compounds.

At the Halden Reactor Project (HBWR) some 22 failures of experimental fuel assemblies have taken place in which quantities of up to 300 Ci of ^{131}I were released to the reactor coolant.[66-72] The quantities of organic iodine compounds formed in these experiments were very small — less than 0.04% of the iodine released to the reactor tank in the most recent work reported. It is also reported that much more carryover to the reactor steam occurred than would be expected. On the basis of wet chemical techniques, this is not organic iodide, and by comparison with the behavior of other soluble fission products, it is not due to entrainment. Thus it appears to be supporting evidence for the HOI hypothesis.

Walke, Sinderman, and Axtell have reported on the composition of the iodine that was circulating in the coolant of a boiling-water reactor as a consequence of operating with defected fuel elements.[73] Only 0.3% of the iodine was in organic form.

Summary of Experience with Respect to CH_3I Formation

In total, the various experiments and incidents discussed above amount to 172 cases in which iodine or one of its compounds has been released and some evidence of the degree of conversion to organic compounds has been sought. The results in general support the list of factors suggested by Durant and his associates.[11] Some further conclusions seem warranted by the data. There seems to be good evidence that negligible methyl iodide formation occurs when the release takes place from the fuel into cooling water, as in the HBWR and PRTR. Also much more CH_3I formation apparently occurs from oxide fuel than from metal fuel.

Formation of methyl iodide has been indicated during aging experiments in the CRI and the ORNL in-pile facility but not in the ADF and CSE experiments. All the experiments in which formation occurred were carried out in stainless steel tanks, with wall heaters being used to delay or prevent cooling. Even in the CRI experiments, where condensation was occurring, it seems likely that the tank walls under the heaters were dry.

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7. SUMMARY AND CONCLUSIONS

This annotated bibliography shows that the chemistry and radiation chemistry of methyl iodide have been studied extensively. Over 350 references are cited. The studies indicate that methyl iodide is a moderately reactive substance that is slightly soluble in water (although surprisingly soluble for an organic compound) and sensitive to ultraviolet light and ionizing radiation.

The bibliography includes reference to over 170 cases in which measurements of methyl iodide have been reported in fission-product release experiments, containment experiments, and accidents. The proportion of the initial iodine measured as methyl iodide ranges from less than 1% to over 20%. A few data are available (from seven experiments) which indicate that the May-pack technique used by most experimenters for studying the behavior of iodine in containment vessels overestimates the amount of methyl iodide present. In the experiments in which the methyl iodide concentration was measured both by May packs and by gas chromatography, the ratio of the percentage of the iodine present as methyl iodide, as measured by the May-pack method to that measured by gas chromatography, ranged from 1 to 20 and averaged about 6. However, the data are too scattered to be used quantitatively.

The data on the percentage of the available iodine converted to organic form are quite scattered. It does seem fairly clear that when the release occurs into water, less than 0.1% of the iodine will be converted to organic form. Release into atmospheres containing large amounts of organic vapors seems to promote conversion of the iodine to organic forms, as would be expected. The only data on release of iodine from fuel under the most probable conditions in a loss-of-coolant accident, namely, a steam atmosphere, were taken by using trace-irradiated UO_2 with no cladding material present. In most experiments the atmosphere at the point of release was either a noble gas or air, since most UO_2 melting techniques will not work if the atmosphere is steam. We emphasize that here we are describing the atmosphere in immediate contact with the fuel at the instant the iodine is liberated, rather than the atmosphere in the vessel to which the iodine may subsequently be transported. At the point of

release the temperatures are very high, reactions go very fast, and the chemical form of the iodine is largely determined.

In well over half the experiments in which the amount of charcoal-seeking iodine was reported as a function of time, the amount was highest immediately after iodine release and decreased with time. We cannot state with certainty that this was or was not methyl iodide. Certainly the information available on the chemical behavior of methyl iodide indicates it should be reactive enough to decompose to some extent.

The methods available for reducing the concentration of methyl iodide in containment building atmospheres include trapping on impregnated charcoals and absorption by sprays. Methyl iodide is reversibly adsorbed on conventional activated charcoal and thus will subsequently be desorbed as air flow through the charcoal is continued. Two general types of impregnants are used. One class consists of nucleophilic reagents that will react with the methyl iodide to tie up the methyl group and convert the iodine to an inorganic form that will be held up by the charcoal. The second consists of inorganic iodine forms. With these the radioiodine in the methyl iodide is exchanged with stable iodine atoms from the impregnant and, although the methyl iodide is not retained by the charcoal bed, most of its radioactivity is removed. The impregnated charcoals lose efficiency under 100% humidity and thus will not perform well under the conditions that will exist after a loss-of-coolant accident.

The study of spray systems for methyl iodide removal from containment atmospheres indicates that only reagents that react fast with methyl iodide are worth considering. Sodium thiosulfate is the best of the reagents known at the present time. It gives reasonably good performance in pilot plants (half-times for removing methyl iodide of 25 min have been observed). However, mathematical modeling indicates that the removal rate constant varies as the ratio of spray flow to vessel volume and indicates appreciably longer half-times in large containment vessels. For typical PWR design conditions, the half-time for methyl iodide removal is calculated to be approximately 2 hr. Hence the dose reduction factor is insignificant. A reagent that will give substantially faster reaction is needed.

Although much information about methyl iodide is available, the study also indicates that there are several areas in which more information is desirable. First, a continuing search for additives to improve the performance of sprays in removing methyl iodide is needed. The review points out that something really new is needed; nothing which has been tried looks much better than sodium thiosulfate. Also, the removal rate constant varies about as the square root of the reaction rate constant, so a new reagent must react several times as fast to yield a real gain. Since the removal rate constant varies directly as the partition coefficient, a reagent that increased the partition coefficient potentially could give a larger gain in performance. However, it does not seem likely that an acceptable reagent will be found that operates by increasing the partition coefficient.

Second, more experiments should be done in which the methyl iodide concentration measured by May packs is compared with that measured by gas chromatography. Enough comparative measurements are needed to enable a statistically valid comparison to be made and to identify the effects of operating conditions. Typical loss-of-coolant accident conditions should be included (saturated air-steam mixtures containing at least 50 vol % steam), since such conditions may reduce the efficiency of the I_2 collection media, and part of the I_2 therefore may penetrate to the activated charcoal and be reported as methyl iodide.

Third, data are needed on the forms of iodine released from clad UO_2 in the presence of steam or steam plus steam-cladding reaction products with iodine-to-uranium ratios in the UO_2 typical of those expected in a loss-of-coolant accident. Such experiments would provide a firmer basis than is presently available for postulating the extent to which iodine released under loss-of-coolant conditions will be converted to methyl iodide.

Experiments of the types listed above could improve confidence in the values of methyl iodide yield assumed in accident analysis. If an improved solution additive for removing methyl iodide is discovered, credit for reducing the dose due to methyl iodide could be claimed, and the overall iodine dose reduction factor could be increased.

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