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The Thermal Gas-phase Decomposition of Methyl Iodide

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The thermal gas-phase decomposition of methyl iodide diluted in Ar has been studied behind shock waves over the temperature range between 1050 and 1500 K and the total density range of 3.5×10^{-6}—3.9×10^{-5} mol cm^{-3}. The decomposition was monitored by means of the UV absorption of CH_3I at 259 or 275 nm. The initiation reaction was found to be the C–I bond fission, and the process proceeded in the low-pressure region under the present experimental conditions. The low-pressure limit rate constant was obtained as:

$$k_{2nd} = 10^{15.40\pm0.26}\exp\{-(42.56\pm1.50\ \text{kcal mol}^{-1})/RT\}\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

Applying the RRKM strong collision theory, the collision efficiency factor was estimated to be 0.018 at 1300 K.

The thermal decomposition of methyl halides is of interest in connection with the decomposition mechanism and is an important test case for the theory of unimolecular reactions.[1] There have been reported many shock-tube studies of the pyrolysis of fluoro- and chloro-methanes.[2–5] In most cases, the decomposition of these molecules is initiated *via* the molecular elimination of HF and HCl.[6] Moreover, the unimolecular process was found in the fall-off region under the conditions available in shock waves.[7] On the other hand, there are few data on the decomposition of bromo- and iodo-methanes, although they are considered to offer proper kinetic data regarding simple bond-fission reactions of the C–Br and C–I bonds. It is important to determine the pressure dependence of the unimolecular process, because it depends on the energy-transfer efficiency in collisions between the reactant and diluent molecules. In the thermal unimolecular processes of relatively small molecules, at low pressures and at high temperatures the collisional activation is rate-determining. This allows us to derive information on the average energy transferred in collisions, which is difficult to describe theoretically. It is, therefore, necessary to accumulate many experimental data on the thermal unimolecular reactions of common molecules.

In the present work, we have studied the pyrolysis of CH_3I in Ar behind shock waves in order to obtain the unimolecular rate constant of the initiation reaction and to discuss the energy-transfer efficiency.

Experimental

The experiments were performed in shock tubes 5 cm and 9.4 cm in inner diameter. Detailed explanations of the equipment and the procedures have been given elsewhere.[8,9] The shocked gas properties were calculated by using the incident shock speed, assuming non-reaction conditions.

Liquid CH_3I (98% stated minimum purity) was purified by trap-to-trap distillation, while Ar (99.998%) was used as the diluent without further purification. Mixtures (0.2, 0.4, 1.25, 2.5, and 3.0 mol% CH_3I in Ar) were prepared in a 30-l glass flask. They were allowed to stand for more than 12 h before use.

Results

Measurements were performed behind incident and reflected shock waves which covered the following ranges: temperature=1050—1500 K; total density=3.5×10^{-6}—3.9×10^{-5} mol cm^{-3}; $[CH_3I]=4.5\times10^{-8}$—3.5×10^{-7} mol cm^{-3}. The disappearance of the shock-heated methyl iodide was followed by observing the absorption at 259 or 275 nm with FWHM=1.65 nm. The absorption due to the X→A transition of CH_3I has a maximum at 259.1 nm.[10] The absorption profiles obtained in a shock-heated mixture at 259 and 275 nm were essentially the same except for a slight difference which was observed at long reaction times. That is, it appeared that the absorption at 259 nm was largely influenced by some products in the later part of the reaction. Figure 1 shows a typical absorption profile at 275 nm and at the mean temperature of all the experimental runs. The absorption coefficient at this wavelength was about 4×10^5 cm^2 mol^{-1}, with a slight temperature dependence in the range of 1000—1500 K. Lambert-Beer's law was ascertained to hold in the concentration range studied. Values of the first-order rate constant were determined by two different procedures; *i.e.*, for the data obtained at 259 nm, the initial slope method was applied as: $k_{1st}=-d[CH_3I]/dt/[CH_3I]_0$, while for the data at 275 nm, the integration method was applied as: $k_{1st}=\ln([CH_3I]_0/[CH_3I])/dt$. As will be shown later, no

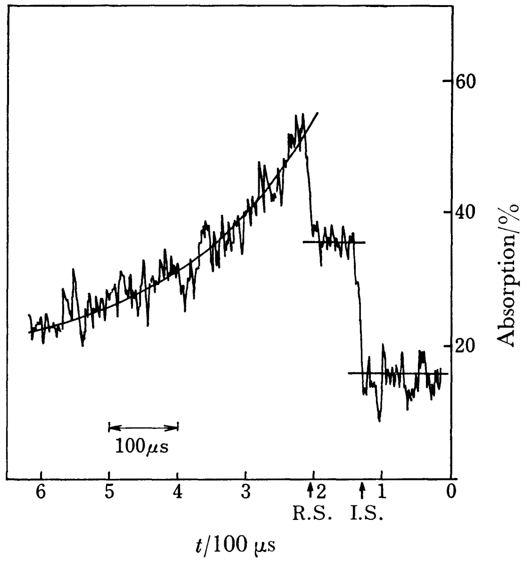

Fig. 1. Typical absorption profile obtained at 275 nm. 1.0 mol% in Ar, $P_1=100$ Torr, $P_5=3.01$ atm, $T_5=1300$ K, total density=2.82×10^{-5} mol cm^{-3}.

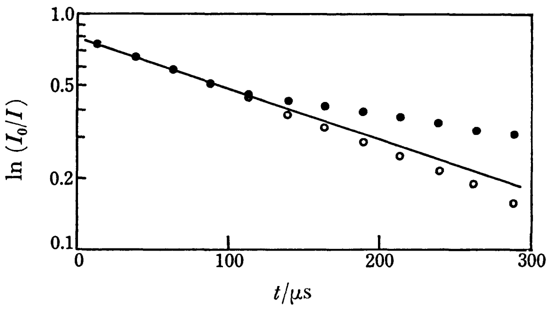

Fig. 2. Logarithmic plot of $\ln(I_0/I)$ *vs.* time for the data in Fig. 1.
● denotes the direct plot of the absorption profile and ○ denotes the corrected profile by substructing the absorption of C_2H_5I (see Ref. 15). The straight line gives $k_{1st}=4.78\times10^3$ s^{-1} and $k_{2nd}=1.71\times10^8$ cm^3 mol^{-1} s^{-1}.

difference is found between the k_{1st} values obtained by the two methods. Figure 2 shows the procedure of the integration method used for the data shown in Fig. 1. In the figure, the closed circles show the data directly obtained from the absorption profile, while the open circles correspond to the data corrected for the absorption of C_2H_5I, which will be discussed later. It appears that the plot (closed circles) shows a straight line at least 100 μs after the shock front passage; *i.e.*, the initial decomposition rate is first-order with respect to [CH_3I] until 35% of the substance decomposes.[11] At higher temperatures, this value decreases slightly, but it is never less than 20%. It was ascertained that k_{1st} was independent of the concentration of CH_3I over the ten-fold range. An Arrhenius expression is given for the data at a total density of 1.6×10^{-5} mol cm^{-3} as:

$$k_{1st} = 10^{10.36\pm0.29}\exp\{-(41.57\pm1.67 \text{ kcal mol}^{-1})/RT\} \text{ s}^{-1},$$

where the error limits are the standard deviations. The value of the preexponential factor obtained is too low for us to consider that the initial process is in the high-pressure region. In fact, from the experiments in which the total density is changed over about ten-fold, k_{1st} was found to be fairly proportional to the total density over the whole range. Figure 3 shows an example of the Arrhenius plots of k_{1st} for three different total densities. They form three pallarel straight lines with the same slope as the above Arrhenius expression. The initial process is, thus, in the low-pressure region under the present experimental conditions. Therefore, the initial decomposition rate is expressed as:

$$-\mathrm{d}[CH_3I]/\mathrm{d}t = k_{2nd}[CH_3I][M],$$

where [M] denotes the total density. From the data of 40 runs, an Arrhenius expression for k_{2nd} is given as:

$$k_{2nd} = 10^{15.40\pm0.26}\exp\{-(42.56\pm1.50 \text{ kcal mol}^{-1})/RT\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

An Arrhenius plot of k_{2nd} is given in Fig. 4, where the data evaluated by the two procedures are in good agreement with each other.

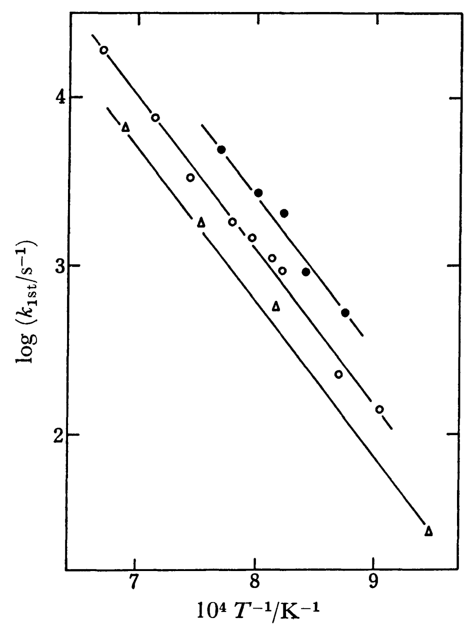

Fig. 3. Comparison of k_{1st} values for different total densities.
△: 0.58×10^{-5} mol cm^{-3}, ○: 1.32×10^{-5} mol cm^{-3}, ●: 2.73×10^{-5} mol cm^{-3}.

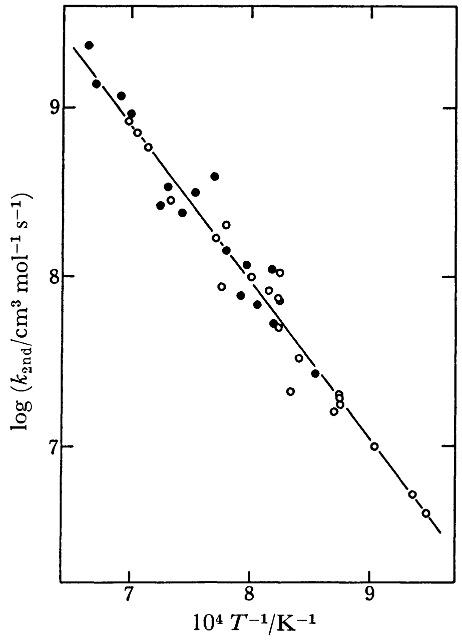

Fig. 4. Arrhenius plot of k_{2nd} evaluated by initial slope (●) and integration method (○).

Discussion

The initiation reaction is the C–I bond fission, not the molecular elimination of HI, because the heat of the reaction of the HI elimination is higher than the energy of the C–I bond fission by 38 kcal mol^{-1}.[12] Thus, the sequence of the reaction in the CH_3I decomposition is assumed to be as follows:

$$(1)\quad CH_3I + M \rightleftarrows CH_3 + I + M$$

$$(2)\quad CH_3I + I \rightleftarrows CH_3 + I_2$$

TABLE 1. ELEMENTARY REACTIONS

Reaction	ΔH°_{298} / kcal mol^{-1}	ΔG°_T / kcal mol^{-1}	Rate constant / cm^3 mol^{-1} s^{-1}	Reference of rate constant
1	56.2	$-0.0357T+57.0095$	$k_1=10^{15.4}\exp(-42.6/RT)$	This work
2	20.1	$-0.00524T+20.2926$	$k_2=10^{14.0}\exp(-19.8/RT)$	a)
3	−0.2	$0.00166T-1.23$	$k_3=10^{11.8}\exp(-12.1/RT)$	Estimated
4	88.2	$-0.0393T+89.0048$	$k_4=10^{17.11}\exp(-89.6/RT)$	b)
5	36.1	$-0.02562T+37.2121$	$k_5=10^{13.99}\exp(-30.4/RT)$	a)
6	−94.1		$k_6=10^{13.5}$	Estimated
7	−54.5	$0.03067T-53.9849$	$k_{-7}=10^{16.0}\exp(-45.0/RT)$	Estimated
8	−18.4	$5.3541\times10^{-3}T-17.2616$	$k_8=10^{13.3}$	c)
9	−91.4		$k_9=10^{13.5}$	Estimated

a) T. Fueno, "Chemical Reaction Theory," Asakura Shoten (1975). b) J. Troe, "Fifteenth Symp. (Int.) on Combustion," The Combustion Institute, Pittsburgh (1975), p. 667. c) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(3) $CH_3I + CH_3 \rightleftharpoons CH_4 + CH_2I$
(4) $C_2H_6(+M) \rightleftharpoons 2CH_3(+M)$
(5) $I_2 + M \rightleftharpoons 2I + M$
(6) $2CH_2I(+M) \longrightarrow C_2H_4I_2(+M)$
(7) $CH_2I + I(+M) \rightleftharpoons CH_2I_2(+M)$
(8) $CH_2I + I_2 \rightleftharpoons CH_2I_2 + I$
(9) $CH_3 + CH_2I(+M) \longrightarrow C_2H_5I(+M)$.

This is based on the mechanism proposed for the photochemical reaction of CH_3I.[13] Table 1 lists the values of ΔH°_{298}, ΔG°_T, and the rate constants for the above reactions. Since there are no data for Reactions 3, 6, 7, and 9, the rate constants were estimated as follows. The value of k_3 was calculated by means of the BEBO method combined with the transition-state theory.[14] The values of k_6 and k_9 were assumed from the data of the recombination of CH_3 radicals. k_{-7} was estimated from the data of the present experiment. Computer simulations (Gear Program) were performed with the values in Table 1 by using the observed k_{2nd} value as the value of Reaction 1. As an example, Fig. 5 shows CH_3I profiles computed under the same conditions as those of the run shown in Fig. 1. It is found that there is no discrepancy between the profiles computed with Reaction 1 (solid line) and with the full reactions (dotted line) until 100 μs after the shock front (corresponding to about a 30% consumption of CH_3I). Therefore, the apparent second-order rate constant, k_{2nd}, which was measured at the early stage of the reaction, can be regarded as the low-pressure unimolecular rate constant of Reaction 1. The corresponding experimental profile is also shown in Fig. 5 by open circles. This is the one shown in Fig. 2 (open circles) connected by considering the effect of the products.[15]

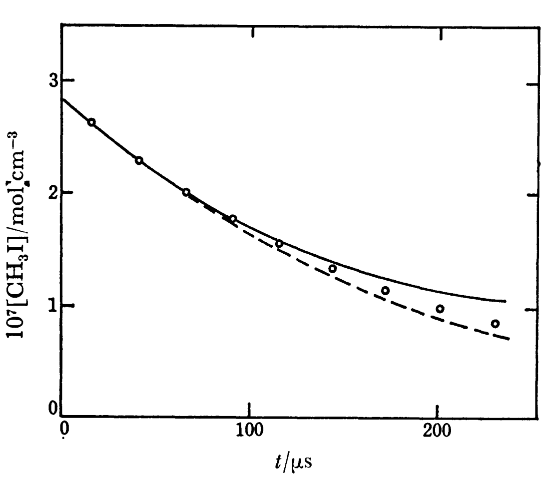

Fig. 5. Concentration profiles of CH_3I.
Conditions are the same as those in Fig. 1. ○: Experimental profile, ——: calculated by Reaction 1 alone, ----: calculated by using full reactions considered.

A rough estimation of the fall-off pressure, $P_{1/2}$, for Reaction 1 leads to $P_{1/2}\simeq 50$ atm at 1300 K (1 atm=101325 Pa).[16] Therefore, the pressure region in this work (0.4—3.2 atm) is considerably below the fall-off pressure. This is consistent with the experimental result that the rate constant of Reaction 1 was given as second-order. The activation energy of k_{2nd} (*i.e.*, k_1 at the low-pressure limit) is lower than the heat of reaction by about 13 kcal mol^{-1}. This may be explained by the low-pressure-limit unimolecular reaction theory. That is, a large part of the discrepancy could be compensated for by the participation of the internal energy in the decomposition. On the other hand, a small part of the discrepancy may be ascribed to the temperature dependence of the collision efficiency. The energy-transfer efficiency in collisions between the reactant and diluent molecules becomes small as the temperature rises. Moreover, at high temperatures available in shock waves, the collisional energy transfer becomes much less than the average thermal energy. From the experimental data of the low-pressure-limit rate constant, it is possible to estimate the collision efficiency and, in turn, the average energy $\langle \Delta E \rangle$ transferred per collision, on the basis of the strong collision rate constant. The value of $\langle \Delta E \rangle$ for a particular collision partner in one reaction is considered to be nearly constant, regardless of the temperature.[17] It is, therefore interesting to ascertain the $\langle \Delta E \rangle$ values for various collision pairs in one reaction.

It is possible to calculate an approximate value of the strong collision rate constant if it is not available from the experiments. An appropriate RRKM strong collision formulation is given as:[17]

$$k_0^{SC} = Z_{LJ}Q_{vib}^{-1}kT\rho_{vib}(E_0)F_EF_{rot}F_{anh}\exp(-E_0/RT),$$

where Z_{LJ} is the Lennard-Jones collision frequency; $\rho_{vib}(E_0)$, the vibrational energy level density at E_0; Q_{vib}, the vibrational partition function; E_0, the threshold energy; F_E, the energy dependence of the density of the states; F_{rot}, the centrifugal correction factor, and F_{anh}, the anharmonicity factor. Table 2 lists the calculated values of k_0^{sc} for several temperatures. The collision efficiency factor is defined as: $\beta_c \equiv k_0^{obs}/k_0^{sc}$, where k_0^{obs} is the low-pressure-limit rate constant obtained experimentally in a given heat bath. As is shown in Table 2, β_c is about 0.02 in the CH_3I–Ar system at the temperatures studied; this is comparable with the data for the simple bond fission of similar molecules (*e.g.*, $\beta_c=0.016$—0.020 for CH_4–Ar at 2000 K,[18,19] and $\beta_c=0.020$ for CH_3Cl–Ar at 2000 K[6]). The values of $-\langle\Delta E\rangle/kT$ are also listed in Table 2; they were evaluated by using this approximate relation:[17]

$$\beta_c/(1-\sqrt{\beta_c}) \simeq -\langle\Delta E\rangle/F_EkT.$$

The temperature dependence of β_c can be expressed as: $\beta_c \propto T^{-2.0}$. This agrees with the prediction of Tardy and Rabonovitch[20] rather than with the relation, $\beta_c \propto T^{-1}$, predicted by Luther and Troe.[21] The value of $-\langle\Delta E\rangle \simeq 70$ cal mol^{-1} obtained here for the CH_3I–Ar system is not unreasonable compared with the recent data for triatomic molecules diluted in Ar.[22]

It is found from the present results that, as a heat bath, Ar is inefficient in supplying the energy by means of both T-T and T-V energy-transfer processes.[23] Although uncertainties in the details of β_c and $\langle\Delta E\rangle$ remain, the data obtained in the present work make it quite clear that weak collision efficiencies are of importance for high-temperature reactions. Further investigations are needed for the CH_3I pyrolysis in various diluents including polyatomic molecules.

Table 2. Calculated results of k_0^{sc} a)

T / K	k_0^{sc} / cm^3 mol^{-1} s^{-1}	F_E	β_c	$-\langle\Delta E\rangle/kT$
1100	3.13×10^8	1.28	0.028	0.043
1200	2.11×10^9	1.31	0.021	0.033
1300	1.00×10^{10}	1.35	0.018	0.027
1400	3.79×10^{10}	1.38	0.015	0.024
1500	1.13×10^{11}	1.42	0.014	0.023

a) Input data for the calculation of k_0^{sc}: threshold energy, $E_0=56.0$ kcal mol^{-1}; Lennard-Jones collision diameters, $\sigma(CH_3I)=4.23$ Å[b)], $\sigma(Ar)=3.54$ Å[c)]; Lennard-Jones well depths, $\varepsilon(CH_3I)/k=519$ K[b)], $\varepsilon(Ar)/k=93.3$ K[c)]; vibrational frequencies of CH_3I, $\nu=2969.8$, 3060.1 (2), 1251.5, 1435.5 (2), 532.8, 882.4 (2) cm^{-1}.[d)] b) G. A. Millor and R. B. Bernstein, *J. Phys. Chem.*, **63**, 710 (1959). c) R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, "The Properties of Gases and Liquids," 3rd ed, McGraw-Hill, N. Y. (1977). d) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," Vol. I, NSRDS-NBS 39 (1972).

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6) In the case of the CH_3Cl pyrolysis, the initiation reaction was found to be the C–Cl bond fission (O. Kondo, K. Saito, and I. Murakami, to be published).

7) Exceptionally, in the pyrolysis of CHF_3 (Ref. 2), second-order rate constants were measured at total pressures up to 18 atm.

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10) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Princeton, N. J. (1967), Vol. 3.

11) The data reductions of all the experimental runs were performed without any corrections for the absorption of products.

12) In the decomposition of halomethanes, the following two channels are possible: (1) $CH_3X \rightarrow CH_3 + X$ and (2) $CH_3X \rightarrow CH_2 + HX$. The differences in the heats of reaction, $\Delta H_r^\circ(1) - \Delta H_r^\circ(2)$, are 27, −6, −22, and −38 kcal mol^{-1} for X=F, Cl, Br, and I respectively. In our preliminary experiments on the CH_3Cl and CH_3Br pyrolysis, it was found that these molecules decomposed *via* the C–X bond fission. From these facts, it can be expected that CH_3I also decomposes *via* the C–I bond fission.

13) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Co., N. Y. (1960), Chap. 8.

14) H. S. Johnston, "Gas Phase Reaction Rate Theory," The Ronald Press Co., N. Y. (1966).

15) Computer simulations showed that, during the pyrolysis of CH_3I, such products as CH_2I_2, C_2H_5I, and $C_2H_4I_2$ increase as the reaction proceeds. Among these products, which are considered to have an absorption at the UV region, the concentration of C_2H_5I increases up to the order of 10^{-10} mol cm^{-3}. On the other hand, the other two products are less than that of C_2H_5I by two orders; thus, they are negligible. In additional experiments, the absorption coefficient of C_2H_5I at 275 nm was measured to be about 4×10^6 cm^2 mol^{-1} in the temperature range of 1000—1300 K. Therefore, the absorption profile obtained for the CH_3I–Ar system was corrected by subtracting the absorption of C_2H_5I.

16) The value of the fall-off pressure was calculated by this relation:

$$P_{1/2} \simeq \nu(\lambda Z)^{-1}\{1+D_0/(n+1)RT\}^{-n}RT,$$

where ν is the mean frequency of the vibrations; D_0, the bond-dissociation energy; λ, the steric factor, and n, the effective number of the internal degrees of freedom for the

reaction. The values of λ and n were determined to be 0.016 and 5.75 respectively by using a classical collision theory.

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23) It is considered that the effective T-T process occurs when the masses of colliding molecules are nearly equal to each other, and that the effective T-V process occurs when the diluent molecule is so small as to have a high translational velocity.