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Second-order Rate Constants for the Decomposition of Methyl Iodide in Different Rare Gases

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Synopsis. The thermal gas-phase decompostion of methyl iodide was studied in He and Kr over the temperature range of 1025—1520 K and the total-density range of (0.96—2.3)×10^{-5} mol cm^{-3}. The results showed that, at high temperatures, these inert gases act as "weak colliders." From the low-pressure limit rate constants, the relative values of the collision efficiency, $\beta_c(M)$, were evaluted as;

$$\beta_c(\mathrm{He}):\beta_c(\mathrm{Ar}):\beta_c(\mathrm{Kr})=1.7:1.0:0.46$$

by connecting them with the previously reported data for an Ar mixture.

Studies of thermal decomposition in the low-pressure region provide important information of collisional intermolecular energy transfers. Although, at low temperatures, inert gas effects have been reported in many thermal systems,[1] at high temperatures (above 1000 K), only a few data are available from shock-tube studies, mostly in rare gases.[2]

In our previous study,[3] the thermal decomposition of methyl iodide in Ar was found to be controlled by the collisional activation step at temperatures above 1000K and at around atmospheric pressure. On the basis of the kinetic data, weak collision parameters were evaluated, and the energy-transfer behavior in collisions was discussed. In the present work, further investigations are made with regard to the thermal decomposition of CH_3I in Kr and Kr–He systems.

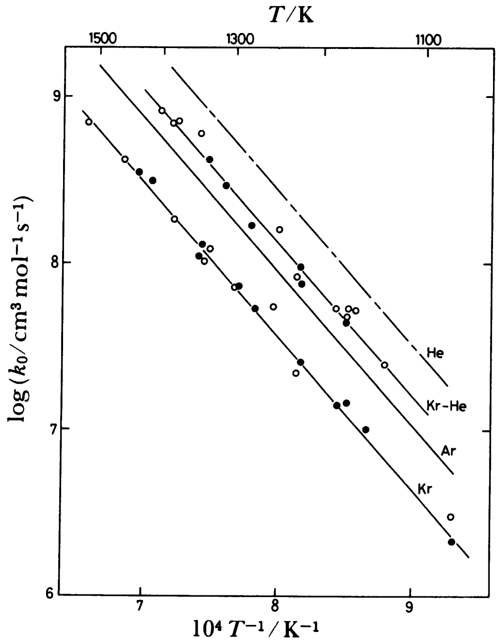

Fig. 1. Arrhenius plots of k_0 for different heat bath gases. Total density; ●: (1.0±0.1)×10^{-5} mol cm^{-3}, ○: (2.2± 0.1)×10^{-5} mol cm^{-3}. k_0(Ar) was cited from Ref. 3.

Experimental

The experiments were performed in a shock tube 9.4 cm in inner diameter. A detailed explanation of the equipment and the procedures has been given in the previous paper.[3] The decomposition rate of CH_3I was measured by monitoring the time dependent UV absorption at 275 nm.

Purified methyl iodide was diluted by the use of Kr (>99.95%) and He (>99.995%). As it was difficult to generate adequate shock conditions in He, a mixture of 50%Kr—50%He was used as the diluent to obtain the rate data in He. The temperature range behind the shock waves was from 1025 to 1520 K, while the total density range was 9.6×10^{-6}—2.3×10^{-5} mol cm^{-3}.

Results and Discussion

The absorption profiles of methyl iodide behind the shock waves in Kr and Kr–He were essentially the same as those of the experiment in Ar.[3] In the present experiment, Lambert-Beer's law was also ascertained to hold in the present concentration range. In Fig. 1, Arrhenius plots of the second-order rate constants, $k_0=k/[\mathrm{M}]$, are shown for the different systems, where $k=\ln([CH_3I]_0/[CH_3I]_t)/t$ and where [M] denotes the concentration of the diluent gas M. The data for the Ar mixture, which were measured in the previous work, are also included in Fig. 1. From the facts that, in the Ar system, the decomposition occurred in the low-pressure region and that the k_0 values in Kr and Kr–He are of the same order as those of the Ar system, the decomposition in the present systems may be regarded as being in the low-pressure region. In fact, the estimated high-pressure rate constant was higher than the k_0 value by more than two orders of magnitude.

In the Kr and Kr–He systems, the reaction scheme for the overall decomposition is considered to be the same as in the Ar system, for there is no reason to consider that some of the secondary reactions are greatly enhanced by the change in the diluent gas from Ar to Kr or He. Thus, we obtain the low-pressure rate constants for the initiation reaction in Kr and He in the same manner as in the Ar system. The decomposition rate at the early stage of the reaction is written for the Kr system as;

$$-\mathrm{d}[CH_3I]/\mathrm{d}t = k_0(\mathrm{Kr})[CH_3I][\mathrm{Kr}],$$

where

$$k_0(\mathrm{Kr}) = 10^{15.0}\exp(-178\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

On the other hand, for the Kr–He system the decomposition rate is expressed as;

$$-\mathrm{d}[\mathrm{CH_3I}]/\mathrm{d}t = k_0(\mathrm{Kr})[\mathrm{CH_3I}][\mathrm{Kr}] + k_0(\mathrm{He})[\mathrm{CH_3I}][\mathrm{He}],$$

provided that there are no additional interactions due to the mixing of the rare gases. Thus, the value of k_0(He) was evaluated from k_0(Kr) and k_0(Kr–He) as;

$$k_0(\mathrm{He}) = 10^{15.88} \exp(-178\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

These rate constants have error limits of 20% in the temperature range of 1100—1500 K. In Fig. 1, the k_0(He) value is shown by a dashed line.

The collision efficiency, β_c, and the average energy, $<\Delta E>$, transferred per activating and deactivating collision were evaluated by the procedure described in the previous paper.[3,4] In Table 1, the evaluated values for these parameters are listed at four temperatures; the data for the Ar system are included. From Table 1, the importance of the weak collision effects is clearly demonstrated in these systems by the fact that $\beta_c \ll 1$. The temperature dependence of β_c for these weak colliders is expressed as $\beta_c \propto T^{-2}$, as in the previous papers.[3,5] This temperature dependence is larger than the theoretical prediction ($\beta_c \propto T^{-1}$).[6] Accordingly, we have found the temperature dependence of $<\Delta E>$ to be proportional to T^{-1} for the present systems. Large temperature dependences of $<\Delta E>$ are not unusual in the case of low collision effciencies at high temperatures.[7]

In general, the relative ordering of the energy-transfer efficiency in different bath gases depends on several limitations on the effective collisions, such as the relative masses, the relative translational energy of the colliding molecules, and the direction of the colliding molecules or the local position to be attacked. In the present systems, the ordering is $\beta_c(\mathrm{He}) > \beta_c(\mathrm{Ar}) > \beta_c(\mathrm{Kr})$; this is the same as for the $-<\Delta E>$ values. That is, the average energy transferred per collision is larger for a lighter collision partner in the decomposition of CH_3I. This means that a fast collision is more effective in the enrgy transfer between translation and vibration modes. In this respect, it is of interest to compare the present results with such similar molecule-Ar systems as CH_3Cl-Ar[5] and CF_3I-Ar.[8] In the CH_3Cl-Ar system, $-<\Delta E>$ is as twice as large as that in the CH_3I-Ar system.[9] On the other hand, in the CF_3I-Ar system, $<\Delta E>$ is nearly the same as that in the CH_3I-Ar system. These facts also establish the effectiveness of fast collisions in T–V energy transfers at high temperatures in these systems. For different types of reactions, however, fast collisions are not necessarily dominant. For example, in the data for the decomposition of triatomic molecules, such as N_2O, NO_2, NOCl, and O_3, in different heat baths, Ar is less effective than Kr (except for N_2O).[2] This seems to suggest that some other factors are more important in these systems.

Table 1. Weak collision parameters

T/K	β_c			$-\langle\Delta E\rangle$/J mol^{-1}		
	He	Ar	Kr	He	Ar	Kr
1100	0.049	0.028	0.014	730	400	180
1200	0.037	0.022	0.010	600	330	150
1300	0.030	0.018	0.009	540	300	140
1400	0.027	0.016	0.008	510	290	130

References

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4) Input data for the calculations of the strong collision-rate constants: threshold energy, E_0=234 kJ mol^{-1}; Lennard-Jones collision parameters, $\sigma(\mathrm{CH_3I})$=4.23Å, σ(He)=2.551Å, σ(Ar)=3.542Å, σ(Kr)=3.665Å, $\varepsilon(\mathrm{CH_3I})/k$=519K, $\varepsilon(\mathrm{He})/k$=10.22K, $\varepsilon(\mathrm{Ar})/k$=93.3K, $\varepsilon(\mathrm{Kr})/k$=178.9K; vibrational frequencies of CH_3I=2969.8, 3060.1(2), 1251.5, 1435.5(2), 532.8, 882.4(2) cm^{-1}.

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9) The $<\Delta E>$ value for the CH_3Cl-Ar system at 1100K was estimated roughly by extrapolation using the relation $\beta_c \propto T^{-2}$, which was determined experimentally in the range of 1800—2100K.[5]