The Thermal Decomposition of CF_3I in Ar

Ko Saito,* Yuji Yoneda, Hiroyuki Tahara,
Sadao Kidoguchi, and Ichiro Murakami
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka-ku, Hiroshima 730

(Received February 24, 1984)

Synopsis. The thermal decomposition of CF_3I behind reflected shock waves was studied by means of the UV absorption over the temperature range of 935—1235 K and in the density range of 6.3×10^{-6}—3.8×10^{-5} mol cm^{-3}. The decomposition rate was in the fall-off region, and the main process was the C-I bond fission. The rate constants corresponding to the limiting high- and low-pressure regions were determined to be;

$$k_\infty = 10^{14.67}\exp(-27200/T)\ \mathrm{s^{-1}}$$

and;

$$k_0/[\mathrm{Ar}] = 10^{14.71}\exp(-15000/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

In connection with the other halogenated methanes, the thermal unimolecular rate constant of the CF_3I decomposition is interesting from such points of view as the contribution of the internal vibrational modes to the bond rupture and the energy transfer in collisions between the reactant and the heat bath. In the past, the high-pressure rate constant for the primary process, $CF_3I \rightarrow CF_3 + I$, was determined by Danidov *et al.*[1] in the temperature range between 608—723 K. Skorobogatov[2] evaluated an Arrhenius expression for the rate constant over the temperature range between 400—1400 K on the basis of the equilibrium constant and the rate data for the reverse reaction. In their study of the kinetics of the CF_3 radical, Modica and Sillers[3] used a low-pressure rate constant evaluated from the classical collision theory, not from experiments.

The main purpose of the present study is to determine the high- and low-pressure rate constants for the primary reaction in order to ascertain the unimolecular behavior in Ar.

Experimental

A 9.4-cm-i.d. shock tube was used for this experiment. The optical system to follow the UV absorption was essentially the same as in previous works;[4,5] that is, a deuterium lamp, a 25-cm monochromator, a photomultiplier, and a digital memory were the basic line-up of the time-resolved absorption system. The disappearance rate of the shock-heated CF_3I was measured by observing the absorption at 290 nm with FWHM=1.65 nm. The absorption coefficient (base e) was determined to be $(1.8\pm0.5)\times10^5$ cm^2 mol^{-1} over the temperature range of 900—1250 K.

CF_3I (PCR Research Chemicals) was used after trap-to-trap distillations. Mixtures (0.67—2.0 mol% CF_3I in Ar) were prepared in 25-l cylindrical glass reservoirs and then allowed to stand for more than 12h before use.

Results and Discussion

Figure 1 shows some typical absorption records at different temperatures. The apparent first-order rate constant, k_a, was determined by means of this definition: $k_a = -d(\ln[CF_3I])/dt$. The k_a's observed varied with the total density, suggesting that the decomposition was in the fall-off region. Table 1 lists the Arrhenius parameters for k_a determined at three different total densities.

In order to evaluate the high- and low-pressure rate constants, k_∞ and $k_0/[\mathrm{Ar}]$, the fall-off data were extrapolated to high and low pressures along with the fall-off curves, which were themselves calculated by the reduced form of the Kassel theory.[6] This was performed in the usual manner described in a previous paper.[7] By fitting the fall-off curves to the data points, the two Arrehnius expressions for the limiting pressures were evaluated as;

$$k_\infty = 10^{14.67}\exp(-27200/T)\ \mathrm{s^{-1}}$$

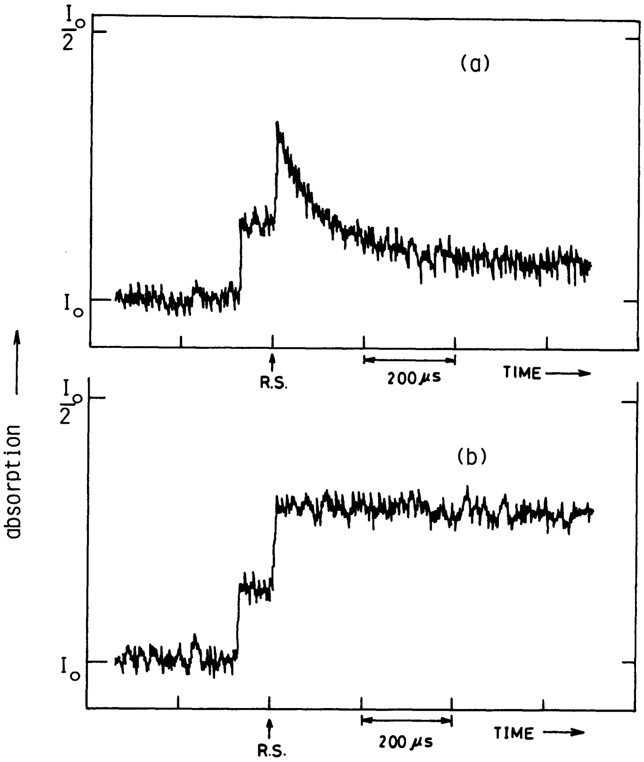

Fig. 1. Typical absorption records at 290 nm. a: [M] $=2.20\times10^{-5}$ mol cm^{-3}, Temp=1200 K, 1.0 mol% CF_3I in Ar; b: [M]$=2.05\times10^{-5}$ mol cm^{-3}, Temp= 930 K, 1.0 mol% CF_3I in Ar.

Table 1. Arrhenius parameters for k_a

Total density	A	E_a
mol cm^{-3}	cm^3 mol^{-1} s^{-1}	kJ mol^{-1}
6.3×10^{-6}	5.8×10^{8}	130
1.0×10^{-5}	1.6×10^{9}	134
$(3.5\pm0.3)\times10^{-5}$	9.6×10^{9}	146

and;

$$k_0/[\mathrm{Ar}] = 10^{14.71}\exp(-15000/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}},$$

with an error limit of about 50% in the temperature range of 950—1235 K.

The initial decay of CF_3I diluted in Ar is considered to proceed *via* the following reactions;

$$(1)\quad CF_3I\ (+Ar) \longrightarrow CF_3 + I\ (+Ar),$$

$$(2)\quad CF_3I + I \longrightarrow CF_3 + I_2,$$

$$(3)\quad CF_3I + CF_3 \longrightarrow CF_2I + CF_4,$$

$$(4)\quad CF_3I + CF_3 \longrightarrow C_2F_6 + I.$$

The effects of Reactions (2)—(4) on the decay rate were examined by using a series of reactions with appropriate rate constants. As a result, the participation of these secondary reactions was found to be negligibly small at the early stage, where the decay rates were measured. Thus, it was ascertained that the evaluated values for k_∞ and $k_0/[\mathrm{Ar}]$ corresponded to Reaction (1).

The Arrhenius parameters for k_∞ obtained in the present work are comparable to the values estimated by Skorobogatov,[2] $k_\infty = 10^{14}\exp(-26500/T)\ \mathrm{s^{-1}}$. The present rate constant exceeds this by a factor of 2.6 at 1000 K; it is thus in good agreement. However, the value obtained by Danidov *et al*,[1] $k_\infty = 10^{15.40}\exp(-23750/T)\ \mathrm{s^{-1}}$, exceeds the present value by about two orders at 1000 K. For the low-pressure-rate constant, on the other hand, there are no experimental data to be compared. An estimation by Modica and Sillers[3] using the classical collision theory is too low (less than two orders) compared with the present results. The cause of this large discrepancy is perhaps the high bond-dissociation energy (240.1 kJ mol^{-1}) used in their calculation.

The weak collision parameters were calculated by the use of a relation between observed and strong collision rate constants,[8] as has been performed for some similar molecules.[5,7] Table 2 lists the calculated results for the collision efficiency, β_c, and the average energy transferred per collision, $\langle \Delta E \rangle$, together with the data for CH_3I.[5]

It is of interest to compare the rate data between CF_3I and CH_3I in the same temperature range, because the molecular constants of these molecules differ substantially from each other, although the dissociation energies of the C-I bonds are very close. We can see from Table 2 there is no serious difference in the weak collision parameters between the two systems. However, the dissociation of CH_3I in Ar was in the low-pressure region; this was in contrast to that of CF_3I under the same conditions.[5] The fall-off pressures at 1100 K were estimated to be 130 and 2270 atm for CF_3I and CH_3I respectively.[9] This apparently low fall-off pressure of the CF_3I decomposition seems to show that this molecule acts as if its internal degrees of freedom were larger than that of CH_3I. In fact, the effective numbers of the internal freedom, S_{eff}, are 5.76 and 3.06 for CF_3I and CH_3I respectively, where $S_{\mathrm{eff}} = -T^{-1}$-$[\mathrm{d}\ln Q_{\mathrm{vib}}/\mathrm{d}(1/T)]$.[6] The fall-off pressure of the CF_3I decomposition is rather close to that of the CF_3CN decomposition in Ar at the same temperature.[10]

TABLE 2. COMPARISON OF WEAK COLLISION PARAMETERS BETWEEN CF_3I AND CH_3I

System	T/K	β_c	$-\langle \Delta E \rangle$/J mol^{-1}
CF_3I-Ar[a]	1100	0.032	490
	1200	0.021	347
CH_3I-Ar[d]	1100	0.028	393
	1200	0.021	326

a) Input data for the calculation of the strong collision-rate constants: threshold energy, $E_0 = 223$ kJ mol^{-1}; Lennard-Jones collision diameters,[b] $\sigma(CF_3I) = 5.05$ Å, $\sigma(\mathrm{Ar}) = 3.54$ Å; Lennard-Jones well depths,[b] $\varepsilon(CF_3I)/k = 300$ K, $\varepsilon(\mathrm{Ar})/k = 119$ K; vibrational frequencies of CF_3I,[c] 1074, 1185(2), 742, 539(2), 284, 260(2) cm^{-1}. b) R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, "The Properties of Gases and Liquids," 3rd ed., McGraw-Hill, N. Y. (1977). c) JANAF Thermochemical Tables, 2nd ed., Natl. Bur. Stand. (1971). d) Ref. 5.

References

1) O. B. Danidov, V. V. Edagin, V. Yu. Zadesskii, and I. L. Yanev, *Kinet. Katal.*, **16**, 302 (1975).

2) G. A. Skorobogatov, *Kinet. Katal.*, **23**, 18 (1982).

3) A. P. Modica and S. J. Sillers, *J. Chem. Phys.*, **48**, 3283 (1968).

4) K. Saito, T. Yokubo, T. Fuse, H. Tahara, O. Kondo, T. Higashihara, and I. Murakami, *Bull. Chem. Soc. Jpn.*, **52**, 3507 (1979).

5) K. Saito, H. Tahara, O. Kondo, T. Yokubo, T. Higashihara, and I. Murakami, *Bull. Chem. Soc. Jpn.*, **53**, 1335 (1980).

6) J. Troe and H. G. Wagner, *Ber. Bunsenges. Phys. Chem.*, **71**, 937 (1967). The Kassel parameters for the reaction considered are: S_k=6.52, 6.76, and 6.98, and B_k=21, 20, and 18 at 1000, 1100, and 1200 K respectively.

7) O. Kondo, K. Saito, and I. Murakami, *Bull. Chem. Soc. Jpn.*, **53**, 2133 (1980).

8) J. Troe, *J. Chem. Phys.*, **66**, 4745, 4758 (1977).

9) This value was evaluated from the fall-off curves calculated for the decomposition of CH_3I.

10) The data are cited K. Okada, O. Kajimoto, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **51**, 4434 (1978).