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REACTION OF $O(^1D_2)$ WITH ETHANE IN LIQUID AND HIGH-PRESSURE SF_6

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Sulfur hexafluoride has been found to be completely inert toward $O(^1D_2)$ even in the liquid state, thus being quite suitable as a solvent for reactions of the $O(^1D_2)$ atom. The reaction between $O(^1D_2)$ and C_2H_6 was studied in high-pressure as well as liquid SF_6. The limiting quantum yield of C_2H_5OH was found to be 0.67 in the high pressure limit and as large as 0.88 in the liquid state.

The reactions of the excited oxygen atom, $O(^1D_2)$, with saturated hydrocarbons have received much attention because of their importance in atmospheric chemistry as well as in basic reaction kinetics. Although the reactions for propane$^{1)}$ and its higher homologs$^{2-6)}$ have been investigated extensively in the gas phase, few studies have been reported on such reactions in dense gaseous media$^{7)}$ or in solution.$^{8,9)}$ This has been due to the absence of appropriate solvent or gas which does not quench $O(^1D_2)$ at all.

We report here that sulfur hexafluoride, SF_6, is quite suitable as a solvent to be used for reactions of $O(^1D_2)$; SF_6 can be liquefied under pressure at room temperature and is entirely inert toward $O(^1D_2)$. Furthermore, it has proven to be useful as a pressurizing "gas" when the reaction system is kept above 46°C. We have adopted this solvent for the study of the reaction between $O(^1D_2)$ and C_2H_6. It has been found that SF_6 quenches the intermediate hot alcohol very effectively. The limiting quantum yield of C_2H_5OH in the gas phase was found to be significantly different from that in the solution phase.

The excited oxygen atom was generated by the direct photolysis of N_2O at 184.9 nm or of O_3 in 240 – 280 nm region. The reaction cell is made of stainless steel. Its design is similar to the one used previously.$^{10)}$ After the photolysis, the reaction mixtures were trapped at -196°C. Volatile components were collected by a Toepler pump and analyzed by a gas-chromatograph with a 2-m Molecular Sieve 5A column. SF_6 was removed at -131°C and the residue was directly subjected to gas-chromatographic analysis. A 1-m Porapak P column equipped with an FID detector was used.

Although DeMore and Jacobsen$^{11)}$ once used SF_6 as a solvent for the reaction of $O(^1D_2)$ with CO_2 at -45°C, no quantitative study has been made on the deactivation efficiency of high-pressure or liquid SF_6 toward $O(^1D_2)$. For this purpose, we have measured the quantum yield of N_2 in the photolysis of $N_2O-O_3-O_2-SF_6$ mixtures in 240 – 280 nm region at 25°C. The system is expected to involve the following sequence of reactions;

$$O_3 \xrightarrow{h\nu} O^*(^1D_2) + O_2(^1\Delta_g)$$

$$O^* + N_2O \longrightarrow N_2 + O_2 \qquad (1)$$
$$ \longrightarrow 2NO \qquad (2)$$

$$O^* + O_3 \longrightarrow 2O_2 \qquad (3)$$
$$ \longrightarrow O_2 + 2O \qquad (4)$$

$$O^* + O_2 \longrightarrow O + O_2 \qquad (5)$$

$$O^* + SF_6 \longrightarrow O + SF_6 \qquad (6)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (7)$$

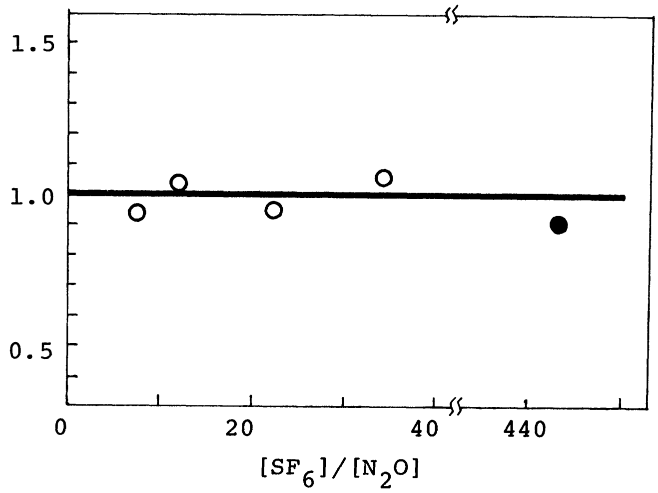

Fig. 1. Dependence of $\Phi_0(N_2)/\Phi(N_2)$ on the ratio $[SF_6]/[N_2O]$. (○), gas phase; (●), liquid phase.

where M stands for any chemical species in the system.

Under the conditions that $[N_2O] >> [O_3] >> [O_2]$, the ratio between the quantum yields of N_2 with and without SF_6 can be expressed as

$$\frac{\Phi_0(N_2)}{\Phi(N_2)} \simeq 1 + \frac{k_6[SF_6]}{(k_1+k_2)[N_2O]}$$

The observed ratios of the quantum yields, Φ_0/Φ, are plotted against $[SF_6]/[N_2O]$, in Fig. 1, where it can be seen that Φ_0/Φ is constant at unity, irrespective of $[SF_6]/[N_2O]$. The results indicate $k_6 = 0$, i.e., a complete inertness of SF_6 toward $O(^1D_2)$.

The earlier studies[1-6] on the reactions of $O(^1D_2)$ with propane and its higher homologs in the gas phase suggest the occurrence of three primary processes in the present system;

$$O^* + C_2H_6 \longrightarrow (C_2H_5OH)^* \qquad \text{insertion} \qquad (8)$$
$$ \longrightarrow C_2H_5 + OH \qquad \text{abstraction} \qquad (9)$$
$$ \longrightarrow CH_3CHO + H_2 \qquad \text{molecular elimination} \qquad (10)$$

followed by

$$(C_2H_5OH)^* \longrightarrow C_2H_5 + OH \qquad (11)$$
$$ \longrightarrow CH_3 + CH_2OH \qquad (12)$$

fragmentation

$$(C_2H_5OH)^* + M \longrightarrow C_2H_5OH + M \qquad \text{stabilization} \qquad (13)$$

$$CH_2OH + C_2H_6 \longrightarrow CH_3OH + C_2H_5 \qquad (14)$$

Recently, Lin and DeMore[7] studied the reaction between $O(^1D_2)$ and C_2H_6 in gaseous He pressurized up to 100 atm. Although the quantum yield of the stabilized product, C_2H_5OH, was found to increase with pressure, it did not level off even at the highest pressure used. They estimated the limiting quantum yield to be 0.4. This value is too low as compared with 0.6 – 0.7 found for higher paraffins.[2,3]

DeMore[8] investigated the same reaction also in liquid Ar. He claimed that no radical species is formed in the liquid-phase reaction. This suggests the absence of hydrogen abstraction by $O(^1D_2)$ in liquid Ar, in striking contrast to the results obtained in the gas phase.

In our investigation, SF_6 in the supercritical region was used as a pressurizing gas. Small amounts of CH_3OH and H_2 were found to be formed in addition to C_2H_5OH. Their quantum yields are listed in Table 1, together with the conditions employed for the photolysis. Apparently, C_2H_5OH is increased as the gas density increases, until it levels off at the SF_6 concentration of about 4000 μmol/cm^3.

In conformity to the above reaction scheme, (8) – (14), the reciprocal of $\Phi(C_2H_5OH)$ can be expressed as

$$\frac{1}{\Phi(C_2H_5OH)} = \left(\frac{k_8 + k_9 + k_{10}}{k_8}\right)\left(1 + \frac{k_{11} + k_{12}}{k_{13}[M]}\right)$$

Thus, if plots of $1/\Phi(C_2H_5OH)$ against $1/[M]$ is linear, the intercept should give the inverse of the branching ratio $k_8/(k_8 + k_9 + k_{10})$ and the slope divided by the intercept should equal the ratio of the rate constants between decomposition $(k_{11} + k_{12})$ and stabilization (k_{13}) of hot alcohol.

The expected linearity has been substantiated as is shown in Fig. 2. The branching ratio thus obtained was about 0.67 and the lifetime $(= 1/(k_{11} + k_{12}))$ of $C_2H_5OH^*$ came out to be 8.2×10^{-12} sec on the condition that $C_2H_5OH^*$ is stabilized at every collision with SF_6. The ratio 0.67 as a limiting quantum yield of C_2H_5OH seems to be more reasonable than the value estimated earlier by Lin and DeMore.$^{7)}$

The bottom two rows of Table 1 show the results in liquid SF_6 at 25°C. The quantum yield of C_2H_5OH formation amounts to 0.8 – 0.9, which is significantly higher than the limiting value in the gas phase (0.67). Even though there may be some uncertainties in these values due to possible experimental errors, the higher

Table 1. Data for the reaction of $O(^1D_2)$ with C_2H_6 in SF_6 at 52°C

$[N_2O]$ torr	$[C_2H_6]$ torr	$[SF_6]$ μmol/cm^3	$[N_2]$ μmol	Φ^a C_2H_5OH	Φ^a H_2	Φ^a CH_3OH
10.0	101	0	0.839	0.10	0.07	0.06
10.3	100	192	0.716	0.21	0.01	0.08
10.2	100	826	0.767	0.39	0.02	0.04
10.5	100	1610	0.960	0.51	0.06	0.06
10.3	101	2560	0.768	0.54	0.01	0.02
10.6	100	4990^b	0.800	0.59	0.01	0.02
10.3	100	8970^c	1.081	0.88		
10.0	100	8970^c	1.59	0.84		

a) Φ's were calculated on the basis of the $[N_2]$ corrected for the excess N_2 which is formed by the reaction $O^* + N_2O \longrightarrow N_2 + O_2$.

b) The density would correspond to 133 atm. at 52°C, if the ideal gas law could be applied.

c) In the liquid state. The photolysis was carried out at 25°C.

yield in the liquid phase seems to be real.

The apparent difference in Φ between gas- and liquid-phase experiments may be interpreted as follows. In the gas phase, the abstraction products OH and C_2H_5 could quickly fly apart after the reactive collision, while in the liquid phase the reaction between $O(^1D_2)$ and C_2H_6 would occur in a cage where both radicals would remain trapped sufficiently long to collide with each other to recombine into C_2H_5OH. The cage effect should in effect enhance the net quantum yield of C_2H_5OH beyond the actual branching ratio. The concept of cage effect can also reconcile the results of gas-phase studies with DeMore's conclusion[9] that in liquid Ar the reaction of C_2H_6 with $O(^1D_2)$ produced no radical species.

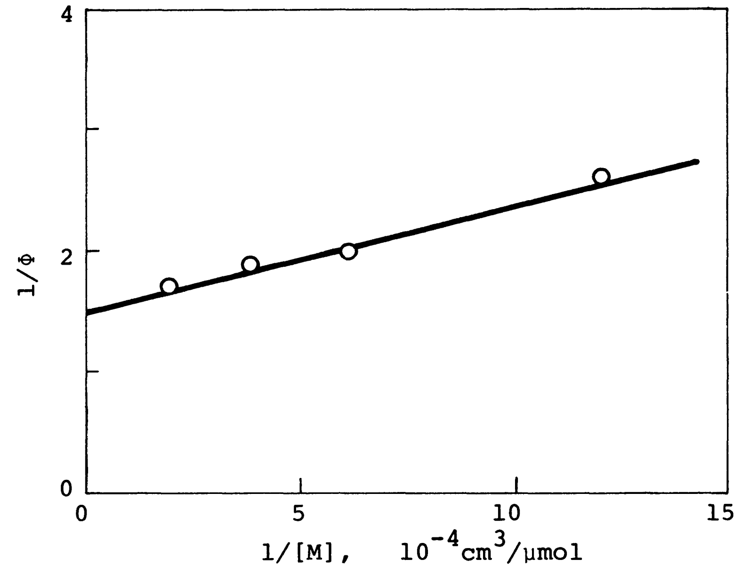

Fig. 2. Linear relationship between $1/\Phi(C_2H_5OH)$ and 1/[M].

The quantum yield of CH_3OH formation amounts to about 0.05. Methanol may have been originated from the reaction (14). The $\Phi(H_2)$'s listed in Table 1 are the data corrected for the H_2 formed by the photolysis of impurity ethylene in C_2H_6. Although $\Phi(H_2)$ amounts to 0.07 in the absence of SF_6, it is suppressed markedly with the increase in total density, reaching a limiting value of about 0.02. This value is very much in line with the results reported for higher paraffins.[2-7]

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References

1) H. Yamazaki and R. J. Cvetanović, J. Chem. Phys., 41, 3703 (1964). 2) G. Paraskevopoulos and R. J. Cvetanović, ibid., 50, 590 (1969). 3) G. Paraskevopoulos and R. J. Cvetanović, ibid., 52, 5821 (1970). 4) P. Michaud and R. J. Cvetanović, J. Phys. Chem., 76, 1375 (1972). 5) P. Michaud, G. Paraskevopoulos, and R. J. Cvetanović, ibid., 78, 1458 (1974). 6) A. J. Colussi and R. J. Cvetanović, ibid., 79, 1891 (1975). 7) C.-L. Lin and W. B. DeMore, ibid., 77, 863 (1973). 8) W. B. DeMore and O. F. Raper, J. Chem. Phys., 46, 2500 (1967). 9) W. B. DeMore, J. Phys. Chem., 73, 391 (1969). 10) O. Kajimoto and R. J. Cvetanović, J. Chem. Phys., 64, 1005 (1976). 11) W. B. DeMore and C. W. Jacobsen, J. Phys. Chem., 73, 2935 (1969).

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