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# The Effects of the Exciting Energy on the Atomic and Molecular Detachments of Hydrogen in the Photolysis of Simple Molecules

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Photochemical studies of simple molecules have been mainly concerned with understanding the primary processes, together with their relative yields.[1]

In this note we wish to report on certain interesting features of the variation in the percentage of the molecular and atomic detachment processes of hydrogen in the photolyses of ethane, ethylene, water, and ammonia with the change in the excitation energy. The experimental data are qualitatively interpreted by a simple theoretical treatment of the RRKM theory.

The primary processes of ethane, ethylene, water, and ammonia are summarized in Table 1. The photolysis of ethylene at 1634 and 1849 Å was carried out using a bromine lamp and a low-pressure mercury lamp respectively. The results of our study of the photolysis of ethylene will be published elsewhere.[2] In these primary processes, we were most interested in the effect of the exciting energy on the hydrogen elimination primary processes. Figure 1 shows the percentage of the atomic detachment of hydrogen as a function of the excess photon energy, which is the energy difference between the photon energy and the heat of reaction for the atomic elimination. In the case of ethane, the total yield of Reactions (1) and (2) is taken as 100%.

It can clearly be seen in Fig. 1 that there are two kinds of energy dependency in these molecules; one increases its atomic percentage with an excess of energy, such as the cases of ethane and ethylene, while the other shows the oposite trend, such as the cases of water and ammonia. As is shown in Table 1, in the

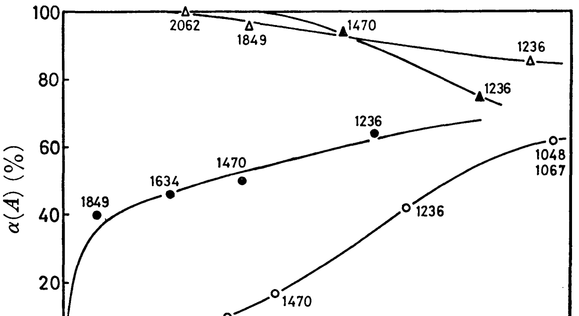

Fig. 1. Dependency of experimental percentage of atomic detachment on excess energy. The numbers in the figure show the wavelength (Å).

○: ethane, ●: ethylene, △: ammonia, ▲: water.

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[1] J. R. McNesby and H. Okabe, *Advan. Photochem.*, **3**, 157 (1964); J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y. (1966).

[2] H. Hara and I. Tanaka, to be published.

TABLE 1. PRIMARY PROCESSES IN THE PHOTOLYSES OF ETHANE, ETHYLENE, WATER AND AMMONIA

| | Primary process | $\Delta H$ (eV) | Relative yield (%) | | | |
|---|---|---|---|---|---|---|
| Ethane | | | 1048, 1067Å[a] | 1236Å[b] | 1470Å[b] | 1577Å[c] |
| (1) | $C_2H_6 + h\nu \longrightarrow C_2H_4 + H_2$ | 1.4 | 26 | 43 | 78 | $>90$ |
| (2) | $\longrightarrow C_2H_4 + 2H$ | 5.9 | 41 | 31 | 16 | $<10$ |
| (3) | $\longrightarrow CH_4 + CH_2$ | 3.8 | 16 | 26 | 6 | |
| (4) | $\longrightarrow CH_3 + CH_3$ | 3.8 | 15 | | | |
| Ethylene | | | 1236Å[d] | 1470Å[d] | 1634Å[e] | 1849Å[e] |
| (5) | $C_2H_4 + h\nu \longrightarrow C_2H_2 + H_2$ | 1.8 | 30 | 46 | 54 | 60 |
| (6) | $\longrightarrow C_2H_2 + 2H$ | 6.3 | 70 | 54 | 46 | 40 |
| Water | | | 1236Å[f] | 1270Å[g] | | |
| (7) | $H_2O + h\nu \longrightarrow H_2 + O$ | 5.1 | 25 | 6 | | |
| (8) | $\longrightarrow H + OH$ | 5.1 | 75 | 94 | | |
| Ammonia | | | 1236Å[f] | 1849Å[f] | 2062Å[h] | |
| (9) | $NH_3 + h\nu \longrightarrow NH + H_2$ | 4.1 | 14 | | | |
| (10) | $\longrightarrow NH_2 + H$ | 4.5 | 86 | $>96$ | $\sim 100$ | |

a ) S.G. Lias, G. J. Collin, R. E. Rebbert, and P. Ausloos, *J. Chem. Phys.*, **52**, 1841 (1970).
b ) H. Akimoto and I. Tanaka, *Ber. Bunsenges. Physik. Chem.*, **72**, 134 (1968).
c ) I. Tanaka znd H. Akimoto, 7th Informal Photochem. Conf., p. 42 (1966).
d ) H. Okabe and J. R. McNesby, *J. Chem. Phys.*, **36**, 601 (1962).
e ) See Ref. 2.
f ) J. R. McNesby, I. Tanaka, and H. Okabe, *J. Chem. Phys.*, **36**, 605 (1962).
g ) L. J. Stief, *ibid.*, **44**, 277 (1966).
h ) W. E. Groth, V. Schurath, and R. N. Schindler, *J. Phys. Chem.*, **72**, 3914 (1968).

case of the former the heat of reaction for molecular detachment is much smaller than that for atomic detachment, whereas in the case of the latter the difference between the heats of reaction between the two kinds of detachment is small.

The percentage of the atomic detachment was calculated from the relative rates of the molecular and atomic detachments, which were themselves estimated by the application of the simple RRKM theory to the excited state of the reactant. According to the RRKM theory, the unilmoecular rate constant is expressed as follows:[3]

$$k_E = A\frac{(E-E_a+a^+E_z{}^+)^{s-1}}{(E+aE_z)^{s-1}} \tag{1}$$

where $E$ is the excess energy of the electronic excited state ($E=E(h\nu)-E_0$, $E_0$ is the energy of the electronic excited state), $E_a$ is the activation energy, and $E_z$ and $E_z{}^+$ are the zero-point energies of the energized molecule and the activated complex respectively. The $a$ and $a^+$ quantities are empirical correction factors for the energized molecule and the activated complex respectively. The index, $s$, is the number of the vibrational mode, and $A$ is a constant evaluated from the properties of the species in question.

In this treatment the molecular and atomic detachments are assumed to be competitive processes from the excited state. Thus, the percentage of atomic detachment is given by $\alpha(A)=100\ k_E(A)/(k_E(A)+k_E(M))$, where $k_E(A)$ and $k_E(M)$ represent the rate constants for the atomic and molecular detachment process es respectively. Using Eq. (1), $\alpha(A)$ is expressed as follows:

$$\alpha(A) = \frac{100}{1+A'\left(1+\frac{\Delta E_a-\lambda}{E'-E_a(A)}\right)^{s-1}} \tag{2}$$

where $A'=A(M)/A(A)$, $E'=E+a^+(A)E_z{}^+(A)$, $\Delta E_a=E_a(A)-E_a(M)$, and $\lambda=a^+(A)E_z{}^+(A)-a^+(M)E_z{}^+(M)$.

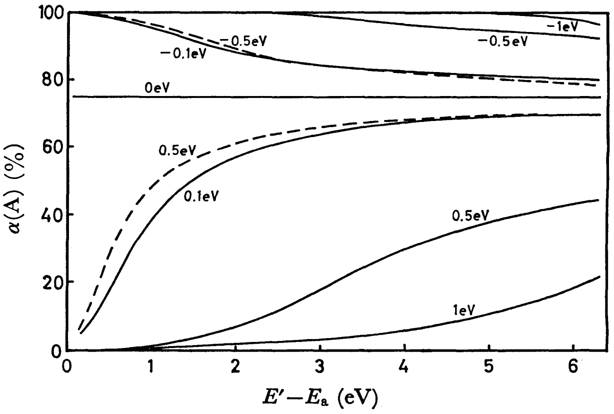

Fig. 2. Dependency of calculated percentage of atomic detachment on excess energy ($E'-E_a$) for various $\Delta E_a-\lambda$ values. ——: $s=18$, - - -: $s=3$.

Assuming $A'=1/3$, at which the percentage of atomic detachment is 75% for a large excess energy, the percentage of atomic detachment was calculated for several values of $\Delta E_a-\lambda$ and $s$ as a function of $E'-E_a$. The results are shown in Fig. 2 for the case of ethane ($s=18$) and also for water ($s=3$), but for the latter only the results for $\Delta E_a-\lambda=\pm 0.5$ eV are shown. As may be seen in Fig. 2, if $\Delta E_a-\lambda$ is positive, the molecular detachment percentage decreases, while if it is negative, it increases with an increase in $E'-E_a$, that is, the photon energy. Comparing these calculated results with the experimental one in Fig. 1, it can be predicted that ethane and ethylene have positive values of $\Delta E_a-\lambda$, while water and ammonia have negative values.

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3) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).