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Some Remarks on the Fragmentation of Excited Ions in the Radiolysis of Hydrocarbons

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The fragmentation of excited ions in the liquid-phase radiolysis of hydrocarbons is explained by a new mechanism, which involves the fragmentation of a highly excited ion (M^{+**}). The M^{+**} ion is considered here to be the electronic excited states and to decompose by the following mechanism. The electronic excitation energy can spread over all C–C bonds in a molecule before its fragmentation and, when the mean excitation energy per C–C bond exceeds its bond energy, the excited ion decomposes instantaneously in one vibration. Further, the mass spectra of isobutane and isooctane are calculated by a simplified quasi-equilibrium theory by introducing the highly excited ion and are compared with experimental mass spectra and with the calculated values without introducing the highly excited ion.

The mechanism of fragmentation of excited ions in gases at low pressure has usually been studied by an analysis of mass spectra. Quasi-equilibrium theory originally proposed by Rosenstock *et al.*[1] has been developed by several investigators[2] and successfully applied to an interpretation of mass spectra of polyatomic molecules. The theory is based on the fundamental assumption that the

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[1] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

[2] The development of this theory is reviewed by H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," Academic Press, New York, (1963).

TABLE 1. FRAGMENTATION OF EXCITED SATURATED HYDROCARBON IONS IN THE LIQUID PHASE

	C CC–C$^+$	C CC–C$^+$ C	C CC–CC$^+$	C C CC–CC$^+$	C C CC–CCC$^+$ C
Bond energy of ion (eV)[a]	0.61	0.35	0.82	0.74	0.56
$G(M^{+*}) + G(M^{+**})$	2.3[c]	1.76[c]	0.83—1.6[d]	1.2—1.8[d]	1.6—1.7[d]
$G(M^{+**})$	1.15	1.0	0.23	0.50	0.36
f[b]	0.50	0.57	0.28—0.14	0.42—0.28	0.22—0.21

a) J. L. Franklin and F. W. Lampe, *Trans. Faraday Soc.*, **57**, 1449 (1961).

b) $f = G(M^{+*})/\{G(M^{+*}) + G(M^{+**})\}$

c) $G(M^{+*}) + G(M^{+**})$ was obtained in the radiolysis of isobutane[6] and neopentane[7] in the gas phase at low pressure.

d) $G(M^{+*}) + G(M^{+**})$ was calculated from the mass spectrum by assuming $W = 25$ eV. The uncertainty in the values is due to the secondary decomposition of fragment ions in the mass spectrometer.

randomization of excitation energy among oscillators occurs before dissociation of the excited ion.

Molecular orbital theory developed by Hirota *et al.*[3] has been successfully applied to the mass spectra of organic compounds.

Recently, the present authors studied the radiolysis of hydrocarbons such as neopentane,[4] isooctane,[4] isobutane,[5] isopentane[5] and 2,3-dimethylbutane[5] in the liquid phase, and found that the fragmentation of excited ions is important. Since collisions between neighboring molecules in a liquid take place roughly in 10^{-13} sec, some of the excited ions must decompose in the period of one vibration ($\lesssim 10^{-13}$ sec) before collisional deactivation. Therefore, the mechanism of such a fast decomposition should be explained by some new theory other than the quasi-equilibrium theory which assumes the randomization of vibrational excitation energy among oscillators.

In the present work, we attempt to explain the fragmentation of excited ions in the liquid phase by a new simple mechanism.

Mechanism of Fragmentation of Excited Ions

It was found by a previous study[6] on the effect of density in the radiolysis of butanes that excited ions are divided into two types. Thus, the ionic fragmentation of a hydrocarbon molecule can be depicted as

$$\begin{aligned} M &\longrightarrow M^{+*} + e & (1)\\ &\longrightarrow M^{+**} + e & (2)\\ M^{+*} &\longrightarrow F^{+} + R & (3)\\ M^{+*} + M &\longrightarrow M^{+} + M & (4)\\ M^{+**} &\longrightarrow F^{+} + R & (5) \end{aligned}$$

where M is the hydrocarbon molecule, for example, C_4H_{10}, M^{+*} is the excited ion which decomposes slowly and consequently is more efficiently deactivated with increasing density. M^{+**} is another type of ion which is highly excited and decomposes in the period of one vibration, not being susceptible to collisional deactivation even at high densities above 0.1 g cc^{-1}. F^+ is a fragment ion, for example $C_3H_7{}^+$, and R is a fragment radical, for example CH_3. In order to obtain further information on the fragmentation of highly excited ions, the ionic fragmentation of several hydrocarbons in the liquid phase was studied using ion scavengers. Results reported previously[4,5] are summarized in Table 1. $G(M^{+**})$ represents the yields of ionic fragmentation in the liquid phase, obtained from the yields of carbonium ion (F^+). $G(M^{+*})+G(M^{+**})$ represents the yields of ionic C–C bond rupture from the total excited ions and can be obtained from radiolysis in the gas phase or from the mass spectrum assuming $W=25$ eV. The yields of ionic C–C bond rupture from the M^{+**} ion relative to those from total excited ions are represented by $f=G(^{+**})/\{(G(M^{+*})+G(M^{+**})\}$. Though the bond energy of isobutane is approximately the same as that of isooctane, the f-value of isobutane is much greater than that of isooctane. This indicates that the fragmentation of M^{+**} ion depends upon the number of carbon atoms in the ion. On the other hand, though the number of carbon atoms in neopentane is the same as that of isopentane, the f-value of neopentane is much greater than that of isopentane. This shows that the fragmentation of M^{+**} ion also depends upon the bond energy of ions. The selective C–C bond rupture of M^{+**} ion suggests intramolecular energy transfer within the period of one vibration. It is difficult to attribute the energy transfer in a short time ($\lesssim 10^{-13}$ sec) to the transfer of vibrational energy. Therefore, it is attributed to the transfer of electronic excitation energy. The rate of intramolecular

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3) K. Hirota and Y. Niwa, *J. Phys. Chem.*, **72**, 5 (1968). The related papers are cited therein.

4) K. Tanno, T. Miyazaki, K. Shinsaka and S. Shida, *J. Phys. Chem.*, **71**, 4290 (1967).

5) K. Tanno, S. Shida and T. Miyazaki, *ibid.*, **72**, 3496 (1968).

6) T. Miyazaki, *ibid.*, **71**, 4282 (1967).

7) T. Miyazaki and S. Shida, This Bulletin, **39**, 2344 (1966).

transfer of electronic excitation energy is given by the following equation,[8]

$$\Delta n = 2.22\times10^{15}\,|\beta|\,t \qquad \text{(I)}$$

where β is the resonance integral between neighboring carbon atoms in a molecule and Δn the numbers of carbon atoms over which the excitation energy can migrate in t sec. Since β of saturated hydrocarbons amounts to 1—2 eV, we get $\Delta n = 100-200$ at 5×10^{-14} sec. That is, the excitation energy can spread in a time of 5×10^{-14} sec over a large number of atoms, C_{100}–C_{200}. If the highly excited ion (M^{+**}) decomposes from the electronically excited states, it may be reasonable to assume the following mechanism: First, the electronic excitation energy can spread over all C–C bonds in a molecule prior to its fragmentation, even in a highly exicted ion. Second, the excited ion decomposes instantaneously in one vibration, when the mean excitation energy per C–C bond exceeds its bond energy. If the potential energy surfaces for the excited states are repulsive, the second assumption may be valid. In the present study, the distribution function of excitation energy for saturated hydrocarbons is taken from that for *n*-butane, which was obtained experimentally by Chupka and Kaminsky.[9] Since the number of C–C bonds in the isobutane ion is three and the bond energies are 0.61 eV, ions with an excitation energy exceeding 1.83 eV behave as a $C_4H_{10}^{+**}$ ion and ions with an exictation energy of 0.61 eV to 1.83 eV behave as an $C_4H_{10}^{+*}$ ion. The amounts of $C_4H_{10}^{+**}$ and $C_4H_{10}^{+*}$ ions present are obtained from the distribution function of excitation energy. The calculated f is compared with the observed one in Fig. 1. Allowing for the simplicity of the present treatment and some errors in the experimental values, we may say that the fragmentation of excited ions in the liquid phase is explained by this mechanism. The calculated values of f are slightly higher than the experimental ones. This result suggests that part of excitation energy spreads over C–H bonds, and that about 15% of the total excitation energy may spread over C–H bonds in the short time of rapid decomposition. The distribution of excitation energy in an ion may be related to the initial energy absorption of atoms in the ion. If the initial energy absorption is assumed proportional to the electron density of atoms in the ion, about 70% of the total energy will be absorbed in the carbon atoms in a saturated hydrocarbon ion. It is nescessary in the future to investigate the competing fragmentation reaction with the intramolecular energy transfer from a theoretical as well as an experimental aspect.

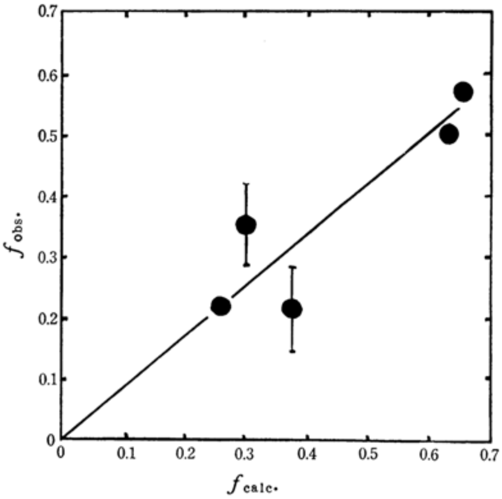

Fig. 1. Comparison of calculated f-values with obseved f-values.

Interpretation of Mass Spectra by the Introduction of a Highly Excited Ion (M^{+**})

The mass spectra of saturated hydrocarbons have hitherto been explained by quasi-equilibrium theory.[1] According to a simplified treatment[10] of this theory, the rate constant for dissociation

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[8] J. L. Magee, "Comparative Effects of Radiation," John Wiley and Sons, Inc., New York (1960), p. 130. The system consists of a chain of N molecules. When the system suffers particle impact, at the initial instant of time $t=0$, the excitation is located on a particular member of the chain, say the p_{th}. The excitation will migrate after a lapse of time. The probability that the excitation will be located on the q_{th} member of the chain at time t is expressed as

$$P(p,q,t) = \left[J_{p-q}\left(\frac{4\pi|\beta|t}{h}\right)\right]^2$$

where $J_{p-q}(4\pi|\beta|t/h)$ is the Bessel function of integral order $p-q$ of the argument $4\pi|\beta|t/h$. β is the resonance integral between neighboring molecules of the chain. If the excitation spreads over Δn units of the chain at time t,

$$(\Delta n)^2 = \overline{(q-p)^2} = \sum_{c=1}^{N}(q-p)^2 P(p,q,t)$$

If we limit our consideration to long chains, it follows that

$$(\Delta n)^2 = \overline{(q-p)^2} = 2\sum_{n=0}^{\infty} n^2 J_n^2\left(\frac{4\pi|\beta|t}{h}\right)$$

and it has been found by the use of tabulated Bessel functions that

$$\Delta n = 0.707 \times \frac{4\pi|\beta|t}{h} = 2.22\times10^{15}\,|\beta|\,t$$

It is necessary to refer to the original paper by J. L. Magee for more detailed arguments.

[9] W. A. Chupka and M. Kaminsky, *J. Chem. Phys.*, **35**, 1991 (1961).

[10] D. P. Stevenson, *Radiation Res.*, **10**, 610 (1959).

of a molecule ion with an excitation energy of ε is given by $k(\varepsilon)$:

$$k(\varepsilon) = A\left(1-\frac{\varepsilon_0}{\varepsilon}\right)^{S-1} \tag{II}$$

where S is the number of degrees of vibrational freedom of the ion and ε_0 the bond dissociation energy. A is the frequency factor and is taken as $10^{14}\ \text{sec}^{-1}$ for a simple bond dissociation process. It has been reported that if k is calculated from Eq. (II) using the experimental values of ε_0 and ε and the full number of degrees of vibrational freedom (S), the mass spectrum can not be understood. Several modifications2) have been undertaken in order to improve the rate constant for fragmentation. For example, it was assumed that the higher transition probability of the excited ion compared with the experimental value was taken in the region of high excitation energy and that the effective number of internal degrees of freedom was considerably less than the full number expected from the molecular structure of the ions.

As proposed in the previous section, the excited ions are divided into two species, M^{+*} and M^{+**}. Since the existence of M^{+**} ion has been hitherto ignored in the calculation of mass spectra by quasi-equilibrium theory, we therefore attempt here to calculate mass spectra introducing the highly excited ion (M^{+**}) in addition to the M^{+*} ion which decomposes according to quasi-equilibrium theory (Calculation A). We also calculate mass spectra by the quasi-equilibrium theory without introducing the M^{+**} ion (Calculation B). Calculations are carried out under the following assumptions.

Calculation A: The excited ion consists of two species M^{+*} and M^{+**}, and the formation of either M^{+*} or M^{+**} is determined by the following two conditions. First, when the mean excitation energy per C–C bond exceeds the bond energy, the excited ion belongs to the M^{+**} ion and decomposes in the period of one vibration.

$$k(\varepsilon) \geqq 10^{13}\ \text{sec}^{-1}, \quad \varepsilon_{\max} \geqq \varepsilon > n\varepsilon_0$$

where n is the number of C–C bonds in an ion. Second, when the mean excitation energy per C–C bond does not exceed the bond energy, the excited ion belongs to the M^{+*} ion and decomposes after the accumulation of excitation energy in a particular bond.

$$k(\varepsilon) = \text{Eq. (II)}, \quad n\varepsilon_0 \geqq \varepsilon > \varepsilon_0$$

Calculation B: Only the fragmentation of M^{+*} ion is considered and quasi-equilibrium theory is applied over the whole range of excitation energy.

$$k(\varepsilon) = \text{Eq. (II)}, \quad \varepsilon_{\max} \geqq \varepsilon > \varepsilon_0$$

The distribution function of excitation energy for isobutane and isooctane was taken as that of n-butane.9) For analytical convenience, $k(\varepsilon)$ was calculated from Eq. (II) summing over integrals for all internal energies of 0.5 eV. ε_0 used is given in Tables 2 and 3. The effective number of internal degrees of freedom (S) was determined using the condition $k(\varepsilon_{\max}) \leqq 5\times 10^{12}\ \text{sec}^{-1}$. Under this condition, the quasi-equilibrium of vibrational excitation energy among the oscillators may be satisfied. In the present calculation, only the primary decomposition was considered. Actually, the secondary decomposition of fragment ions (reaction (7) and (8)) follows after the primary decomposition (reaction (6)) in a msas spectrometer.

$$i\text{-}C_4H_{10}^+ \longrightarrow C_3H_7^+ + CH_3 \tag{6}$$

$$C_3H_7^+ \longrightarrow C_3H_5^+ + H_2 \tag{7}$$

$$C_3H_5^+ \longrightarrow C_3H_3^+ + H_2 \tag{8}$$

The amount of $C_3H_7^+$ produced in the primary decomposition of isobutane ion can be considered as the sum of $C_3H_7^+$, $C_3H_5^+$ and $C_3H_3^+$. In Tables 2 and 3, the calculated yields of major fragment ions from isobutane ion and isooctane ion are compared with experimental mass spectra. The mass spectra of isobutane are correctly interpreted qualitatively by assuming both M^{+*} and M^{+**} (Calculation A), while the treatment assuming only M^{+*} (Calculation B) fails in a proper interpretation. The mass spectra of isooctane can be understood through both methods of calculation. This is because the ratio of M^{+**} to the total excited ions of isooctane is at best about 25% and the introduction of M^{+**} does not appreciably affect the results, while the corresponding ratio of isobutane amounts to 60%.

TABLE 2. FRAGMENTATION OF i-$C_4H_{10}^+$

	ε_0	Mass spectra	Calculation Aa)	Calculation Bb)
$C_3H_7^+$	0.61 eV	1	1	1
$C_3H_6^+$	0.25 eV	0.23	0.50	1.49

a) Calculated by assuming M^{+**} and M^{+*}
b) Calculated by assuming only M^{+*}

TABLE 3. FRAGMENTATION OF i-$C_8H_{18}^+$

	ε_0	Mass spectra	Calculation Aa)	Calculation Bb)
$C_4H_9^+$	0.56 eV	1	1	1
$C_4H_8^+$	0.40 eV	0.31	0.22	0.25

a) Calculated by assuming M^{+**} and M^{+*}
b) Calculated by assuming only M^{+*}

It has been shown above that the highly excited ion (M^{+**}) is probably important in the radiolysis of hydrocarbons. However, the mechanism of its fragmentation proposed here is too simple and requires revision in the future from a theoretical as well as experimental aspect.

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