2046 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2046—2050 (1971) [Vol. 44, No. 8

The Protonation of Aromatic Hydrocarbon Radical Anions. II. Interpretations of the Rate Constants in Terms of HMO Calculations

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(Received December 14, 1970)

The rates of the protonation of aromatic hydrocarbon radical anions with water in dimethylformamide (DMF)-water mixtures were measured by means of the decay of the visible absorption maxima of radical anions with time. The rates were found to be greatly accelerated by the increasing water content in DMF-water mixtures. This behavior suggests that the negative charge is much more localized in the transition state than in the original radical anion. The rate constants in DMF could be obtained by extrapolation. The correlation of these rate constants to the molecular structure of radical anions was discussed on the basis of the results of HMO calculations. This correlation and the solvent effect could be interpreted by means of the charge-transfer mechanism.

In a previous paper[1] a study of the mechanism of the protonation of the aromatic hydrocarbon radical anions in DMF-water mixtures was reported; there the radical anions of biphenyl, naphthalene, phenanthrene, anthracene, 1,2-benzanthracene, and pyrene were found to decay by a first-order reaction:

$$\frac{d[R^{\bar{\cdot}}]}{dt} = -2k[H_2O][R^{\bar{\cdot}}] = -k_{app}[R^{\bar{\cdot}}] \qquad (1)$$

through the following sequence:

$$R^{\bar{\cdot}} + H_2O \xrightarrow{k} RH\cdot + OH^- \qquad (2)$$

$$RH\cdot + R^{\bar{\cdot}} \rightleftarrows RH^- + R \qquad (3)$$

$$RH^- + H_2O \xrightarrow{k'} RH_2 + OH^- \qquad (4)$$

The same results were obtained for anthracene by the use of the ESR technique by Umemoto.[2]

The present paper will deal with the rate of the protonation reaction of Eq. (2) in DMF-water mixtures obtained by measuring the change in the visible absorption maximum with the time,[1] with the effect of the solvent on the rate, and with the correlation of the observed rate constants with the molecular structures of the reagents.

Experimental

All the materials and apparatus were the same as in the previous paper.[1] As the supporting electrolyte, tetraethylammonium bromide (TEAB) was used. The measurements of the absorbance against the time were carried out at the λ_{max} of the radical anions: biphenyl, 407 mμ; naphthalene, 368 mμ; phenanthrene, 421 mμ; anthracene, 725 mμ; 1,2-benzanthracene, 415 or 758 mμ, and pyrene, 742 mμ. All the measurements were carried out at 20°C.

Results and Discussion

The Solvent Effects on the Rate of Protonation. The apparent rate constants, k_{app}, which are equal to $2k[H_2O]$ are given in Table 1, while the effect of the water content on the rate constant, $k(\text{M}^{-1}\text{sec}^{-1})$, as calculated from k_{app}, is shown in Fig. 1.

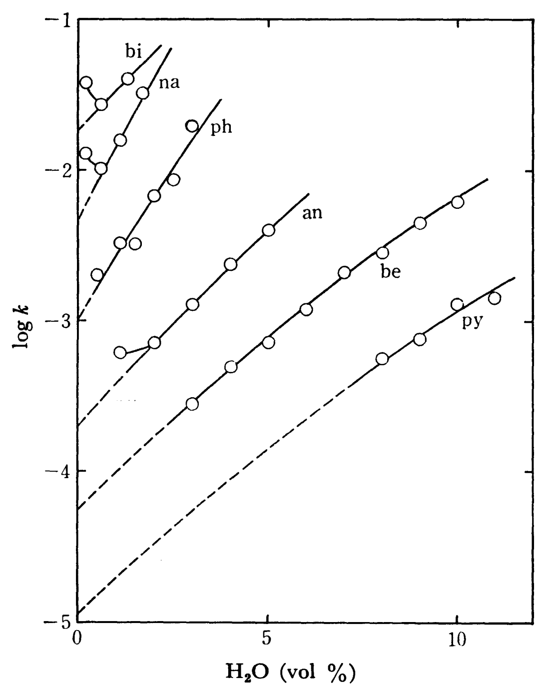
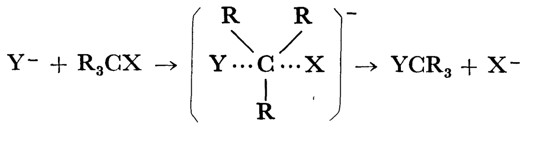


Fig. 1. The effect of water content on the rate constant k: bi, biphenylide; na, naphthalenide; ph, phenanthrenide; an, anthracenide; be, 1,2-benzanthracenide; py, pyrenide radical anion.

It is well known[3] that a bimolecular reaction such as that between anions and polar molecules shown in Eq. (5) is very much faster in dipolar aprotic solvents than in protic solvents:



$$Y^- + R_3CX \rightarrow \left(Y\cdots\overset{R\quad R}{\underset{R}{C}}\cdots X \right)^- \rightarrow YCR_3 + X^- \qquad (5)$$

where protic solvents, such as water, methanol, and formamide, are hydrogen-bond donors, while dipolar aprotic solvents, such as DMF, dimethylsulfoxide (DMSO), and acetonitrile, are not hydrogen-bond donors but are highly polar molecules. This behavior can be explained qualitatively as follows: a small anion, Y^-, in the original system where the negative

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[1] S. Hayano and M. Fujihira, This Bulletin, **44**, 1496 (1971).

[2] K. Umemoto, *ibid.*, **40**, 1058 (1967).

[3] A. J. Parker, "Advances in Physical Organic Chemistry," Vol. 5, ed. by V. Gold, Academic Press, New York, N. Y. (1967), p. 173.

TABLE 1. OBSERVED RATE CONSTANTS k_{app}

(a) Biphenyl

H_2O, %	k_{app}, sec^{-1}
0.2	8.6×10^{-3}
0.6	1.9×10^{-2}
1.3	5.9×10^{-2}

(b) Naphthalene

H_2O, %	k_{app}, sec^{-1}
0.2	2.9×10^{-3}
0.6	7.0×10^{-3}
1.1	2.0×10^{-2}
1.7	6.2×10^{-2}

(c) Phenanthrene

H_2O, %	k_{app}, sec^{-1}
0.5	1.1×10^{-3}
1.1	4.0×10^{-3}
1.5	5.3×10^{-3}
2.0	1.5×10^{-2}
2.5	2.4×10^{-2}
3.0	6.6×10^{-2}

(d) Anthracene

H_2O, %	k_{app}, sec^{-1}
1.1	7.6×10^{-4}
2.0	1.6×10^{-3}
3.0	4.4×10^{-3}
4.0	1.1×10^{-2}
5.0	2.2×10^{-2}

(e) 1,2-Benzanthracene

H_2O, %	k_{app}, sec^{-1}
3.0	9.4×10^{-4}
4.0	2.2×10^{-3}
5.0	4.0×10^{-3}
6.0	8.2×10^{-3}
7.0	1.6×10^{-2}
8.0	2.5×10^{-2}
9.0	4.5×10^{-2}
10.0	6.9×10^{-2}

(f) Pyrene

H_2O, %	k_{app}, sec^{-1}
8.0	5.1×10^{-3}
9.0	7.6×10^{-3}
10.0	1.4×10^{-2}
11.0	1.7×10^{-2}

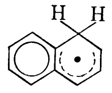
charge is concentrated is greatly stabilized by the hydrogen-bonding interaction with protic solvents as compared with the activated complex in the transition state, where the charge is more dispersed, while such a specific solvation does not occur in aprotic solvents. Consequently, the activation free energy of the reaction in Eq. (5) in aprotic solvents is smaller than that in protic solvents.

As is shown in Fig. 1, however, such is not the case for the protonation reaction of aromatic hydrocarbon radical anions with water, where the reaction is faster in more protic media. The reason for this behavior seems to be as follows: the negative charge is more localized on a certain atom in the activated complex than in the original radical anion, and, therefore, the activated complex is more stabilized than is the radical anion by changing the solvent from aprotic to protic.[4]

The effect of increasing of water content on the rate constants depends upon the molecular structures of the aromatic hydrocarbons. That the rate constants of naphthalenide and phenanthrenide are more influenced by the water content than is biphenylide radical anion predicts that the rate of the protonation of biphenylide will be slower than those of naphthalenide and phenanthrenide in the case of higher-water-content media. In fact, the rates of the protonation of aromatic hydrocarbon radical anions in 2-propanol were measured by Dorfman *et al.*[5,6] to be in this order: naphthalenide>phenanthrenide>biphenylide.

As has been described above, the rates of the reactions of anions with polar molecules are greatly influenced by the hydrogen-bonding interaction of the anions with protic solvents. Therefore, for the rate constants obtained in aprotic solvents, the effect of the molecular structure on the rate can be interpreted in terms of MO calculations, without taking the hydrogen-bonding effect into account. In the present system, the rate constants in DMF free from water can be obtained by extrapolation. Increases in k were found at low concentrations of water (Fig. 1). These may be due to additional decay through other reactions, *e.g.*, protonation with DMF[7,8] or with impurities. These reactions can be practically eliminated from competition with the protonation with water if enough water is added.

Interpretations of the Rate Constants of the Protonation in Terms of HMO Calculations. Because of the succeeding rapid electron-transfer reaction (Eq. (3)), no products of the protonation reaction (Eq. (2)) could be observed in the present system. However, the structures of the products may be similar to that of the so-called σ-complex[9] in the aromatic substitution reaction, as is shown below, where naphthalene is taken as an example:



(6)

These structures were ascertained experimentally for the analogous reactions in low-temperature alcohols.[10,11]

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[4] S. Hayano and M. Fujihira, This Bulletin, **44**, 2051 (1971).

[5] S. Arai, E. L. Tremba, J. R. Brandon, and L. M. Dorfman, *Can. J. Chem.*, **45**, 1119 (1967).

[6] L. M. Dorfman, *Accounts Chem. Res.*, **3**, 224 (1970).

[7] D. L. Maricle, *Anal. Chem.*, **35**, 683 (1963).

[8] S. Wawzonek, R. Berkey, E. W. Blaha, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

[9] G. W. Wheland, *J. Amer. Chem. Soc.*, **64**, 900 (1942).

[10] J. A. Leone and W. S. Koski, *ibid.*. **88**, 224 (1966); J. A. Leone and W. S. Koski, *ibid.*, **88**, 656 (1966).

[11] T. Shida and W. H. Hamill, *ibid.*, **88**, 3689 (1966).

In order to interpret the course of the reduction process, Hoijtink[12] assumed that the logarithm of the rate constant of protonation is linearly proportional to the charge density at a particular carbon atom. Then, the rate constant was expressed by:

$$k = \kappa \exp (C\rho_s/kT) = \kappa \exp (\gamma \rho_s) \quad (7)$$

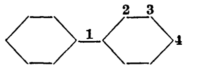
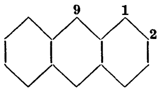
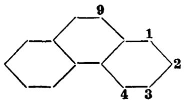
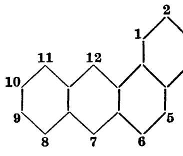
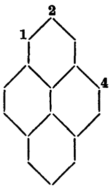
where κ, C, and γ are constants and where the charge (or spin) density, ρ_s, at a carbon atom, s, is given by the square of the coefficient in the HMO for the first antibonding level. By this equation, the position in the hydrocarbon molecule at which proton addition occurs was explained, but the relative rates among different species could not be explained.

The rate constants of analogous reactions in alcohol

$$R^{\overline{\cdot}} + ROH \xrightarrow{k_a} RH\cdot + RO^- \quad (8)$$

were obtained by the technique of pulse radiolysis by Dorfman *et al.* They found that the rate constants for Reaction (8) depend upon the properties of the alcohol[6,13] and the nature of the aromatic radical anions.[5,6] They showed a fairly good correlation between the values for k_a and the acidity of the alcohol. They attempted to interpret the dependence of k_a on the nature of the aromatic radical anions in terms

TABLE 2. SPIN DENSITIES, LOCALIZATION ENERGIES AND COEFFICIENTS OF THE ENERGY OF THE LOWEST VACANT MO CALCULATED WITH SOME AROMATIC HYDROCARBONS

Molecule	$-m_{m+1}$[b]	Position	ρ_s	L_s^-	L	$2m_{m+1}+L$	k, M^{-1} sec^{-1}
Benzene	1.000	—	0.167[b]	1.536	2.536[a]	0.536	
Naphthalene	0.618	α	0.181[b]	1.681	2.299[b]	1.063	4.6×10^{-3}
		β	0.069	1.862	2.480		
Biphenyl	0.705	1	0.123				1.8×10^{-2}
		2	0.090	1.695	2.400[b]	0.990	
		3	0.020	1.839	2.544		
		4	0.158	1.742	2.447	1.037	
Anthracene	0.414	1	0.096[b]	1.84	2.25[a,b]		2.0×10^{-4}
		2	0.047	1.99	2.40		
		9	0.192	1.599	2.013	1.185	
Phenanthrene	0.605	1	0.116	1.713	2.318		1.0×10^{-3}
		2	0.002	1.893	2.498		
		3	0.099	1.849	2.454		
		4	0.054	1.761	2.366		
		9	0.172	1.694	2.299	1.089	
1,2-Benzanthracene	0.452	1	0.000				5.5×10^{-5}
		2	0.041				
		3	0.009				
		4	0.026				
		5	0.083				
		6	0.089				
		7	0.198	1.597	2.049	1.145	
		8	0.105				
		9	0.038				
		10	0.056				
		11	0.090				
		12	0.155	1.648	2.100	1.196	
Pyrene	0.445	1	0.136[b]	1.745	2.190[b]	1.300	1.2×10^{-5}
		2	0.000	2.10	2.55		
		4	0.087	1.83	2.28		

a) Ref. 14. b) Ref. 15.

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[12] G. J. Hoijtink, *Rec. Trav. Chim.*, **76**, 885 (1957); G. J. Hoijtink, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 7, ed. by P. Delahay and C. W. Tobias, Interscience Publishers, New York, N. Y. (1970), p. 221.

[13] S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

of the delocalization energy, but did not succeed. This failure was partly because the k_a values obtained in protic solvents were used for comparison.

The spin density, ρ_s, and the localization energy, L_s^-, of radical anions, and the coefficient, m_{m+1}, of the energy of the lowest vacant MO of the aromatic hydrocarbons studied in the present work, are given in Table 2, in which some of the values have been calculated by the present authors and others cited from the literature.[14,15] For comparison, the values of benzene are also given. The localization energy, L_s^-, is given by:

$$L_s^- = M^- - M_s \tag{9}$$

where the π-energy of the radical anion is $(n+1)\alpha + M^-\beta$ and that of protonated radical is $(n-1)\alpha + M_s\beta$, where s denotes the position of the carbon atom, and n, the number of π-electrons of the parent molecule. It is reasonable to assume that the protonation will occur at the position at which the localization energy is the smallest. Therefore, Hoijtink's assumption may be superseded by this localization method as far as the problem is the position at which the protonation occurs predominantly. The predictions by Hoijtink accord with those by the localization method except in the case of biphenyl. The experimental results[15] in the reduction of hydrocarbons with alkali metals agree with these predictions. The spin density of the biphenylide radical anion is the highest at position 4, but the localization energy is the smallest at position 2, and the reduction products have been reported to be 2,5-dihydrobiphenyl[16] or 1,4-dihydrobiphenyl.[17] The following discussion will be based on the assumption that the protonation occurs at the position with the smallest localization energy except in the cases of biphenylide and 1,2-benzanthracenide. For biphenylide, position 4 is also considered. The reduction product of 1,2-benzanthracenide has been reported to be the 7,12-dihydro-derivative.[18] The positions 7 and 12 are taken into consideration, for the two positions are not equivalent to each other.

For the common proton donor, the standard free energy of the protonation reaction (2) should have a linear relation with the value of the smallest localization energy, L^-, if the σ-bond energy changes caused by proton addition and the free energy changes of solvation are practically constant for these hydrocarbons:

$$\Delta G^\circ = L^- + \text{const.} \tag{10}$$

From the linear free-energy relationship, the logarithms of the observed rate constants can be expected to be linear in relation to the localization energy.

The ionization potential, I, of the radical anion

$$R^{\bar{\cdot}} \rightarrow R + e \tag{11}$$

is equal to the electron affinity of the parent molecule and is correlated with m_{m+1} by the following equation:

$$I = -(\alpha + m_{m+1}\beta) \tag{12}$$

These ionization potentials are known to be linear in relation to the polarographic half-wave potentials (or the reduction potentials) in aprotic solvents,[19] and a correlation between the reduction potentials and the rates of the analogous reactions has been reported.[20]

In Table 2, the rates of the protonation of aromatic hydrocarbon radical anions with water in DMF are also given. Neither the highest spin density, ρ_s, the smallest localization energy, L^-, nor m_{m+1} (or ionization potential I) is, however, found to have a linear relation to the observed rate constants.

In the preceding discussion, the reactivity has been attributed to only either the electronic structures of the aromatic substrate or those of reagents, and these treatments cannot make the reaction completely clear. We undertook to interpret this reaction by means of the charge-transfer mechanism proposed by Nagakura.[21] By this concept, it would be possible not only to explain the orientation rule, but also to predict the electronic structures of the activated complexes. Furthermore, the dependence of the protonation rates on the acidity of proton donors will be explained more feasibly.

According to Nagakura's mechanism, the reaction can be interpreted as a transfer process between the no-bond and charge-transfer structures (abbreviated hereafter to CT structure) and the reaction process can be represented by the potential energy curve shown in Fig. 2, where the protonation of naphthalenide is taken as an example. Curves 1 and 2 are associated with the no-bond and CT structures respectively. Curve 1 shows a repulsive feature, while Curve 2 resembles the Morse curve. The reaction proceeds along the dotted line which is formed by the resonance between the no-bond and CT structures. Further

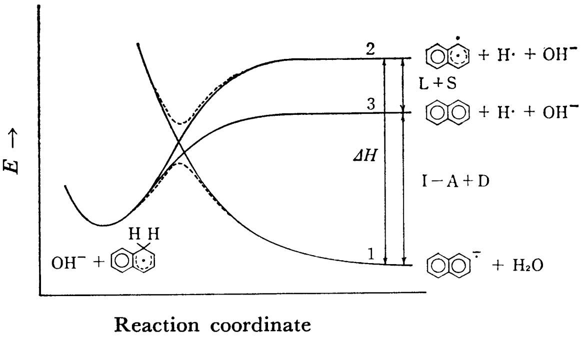

Fig. 2. Potential energy curve for the protonation of naphthalenide radical anion with water.

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[14] F. H. Burkitt, C. A. Coulson, and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

[15] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961), pp. 160, 178, 428.

[16] I. P. Egorov, E. P. Kâplan, Z. I. Letina, V. A. Shiapochnikov, and A. D. Petrov, *J. Gen. Chem. U. S. S. R.*, **28**, 3284 (1958).

[17] W. Hückel and R. Schwen, *Ber.*, **89**, 150 (1956).

[18] W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936).

[19] A. Maccoll, *Nature*, **163**, 178 (1949).

[20] M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *J. Amer. Chem. Soc.*, **91**, 6505 (1969).

[21] S. Nagakura, *Tetrahedron*, **19**, Suppl. 2, 361 (1963).

detailed discussion about the physical meaning of this diagram can be referred to Ref. 21. As is shown in Fig. 2, the energy difference, ΔH, between the no-bond and CT structures at an infinite distance is given as follows:

$$\Delta H = I - A + D + L + S \tag{13}$$

where I is the ionization potential of a radical anion, A is the electron affinity of the OH· radical, D is the dissociation energy of an O–H bond of the proton donor, L is the localization energy of aromatic hydrocarbon for the following process:

(14)

and S is the energy required for the change in the hybridization from the sp^2 to the sp^3 of the ring carbon atom attacked by the reagent.

Nagakura also assumed that the activation energy, ΔE^*, is approximately proportional to the energy difference, ΔH:

$$\Delta E^* = a\Delta H \tag{15}$$

where a may be regarded as a constant for at least a fixed combination of the aromatic substrate and a reagent. Hereafter, a will be assumed to be constant in the present systems. A, D, and S can be considered as constants for the series; consequently, the logarithms of the rate constants should show a linear relation to the sum of $I+L$. However, no such linear relation was found, as has been noted before, for L_s^- in Table 2 is equal to $L+m_{m+1}$, which has a linear relation to $L+I$. The position at which protonation occurs can, however, be explained in terms of the localization energy.

The reason why the relative reaction rates cannot be interpreted adequately by Eqs. (13) and (15), is as follows: the contribution of the $L+S$ terms to the activation energy probably does not parallel that of the $I-A+D$ terms, since any localization of electrons and hybridization from sp^2 to sp^3 occurs only in response to the approach of the reagent and at an infinite separation these terms are completely eliminated.[22] Therefore, the potential curve 2 of the CT structure in Fig. 2 should be written as Curve 3.

As a result, the contribution of $L+S$ to the activation energy is found to be less than that of $I-A+D$; the activation energy should be written as follows:

$$\Delta E^* = a(I-A+D) + b(L+S) \tag{16}$$

$$a > b \tag{17}$$

The position attacked by a proton is still interpreted by the L term.

For the present system, a plot of the logarithms of the observed rate constants against $2I+L$ (or $2m_{m+1}+L$) gives a linear correlation, as is shown in Fig. 3, where a is taken temporarily to be double b. For the present, the ratio of a to b is arbitrary to some extent. In Table 2, the values of $2m_{m+1}+L$ are given instead of $2I+L$. If much more data for the rate constants of the reactions were obtained for the series where only the ionization potentials are greatly different and the localization energies are almost constant, or for the series where only the localization energies are different, the values of a and b in Eq. (16) could be determined experimentally. The benzene radical anion is known to be protonated much more rapidly than the biphenyl radical anion.[11] This is reflected by the small value of $2m_{m+1}+L$ shown in Table 2.

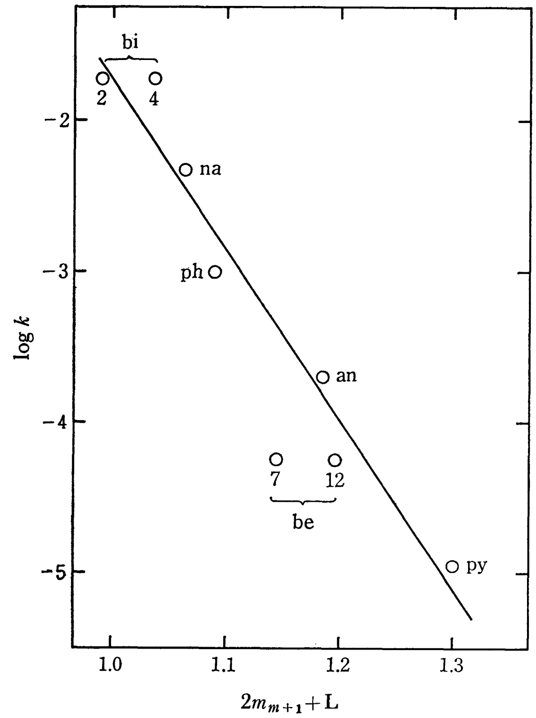

Fig. 3. Correlation of log k for protonation *versus* $2m_{m+1}+L$. For biphenylide and 1,2-benzanthracenide, the values for the positions 2,4 and 7,12, respectively, are shown. The abbreviations are the same as in Fig. 1.

In Eq. (14), the $-A$ and D terms represent the properties of the reagents, and the dependence of the rate constants on the properties of such proton donors as alcohols, water, and phenols can be interpreted by these terms. The activation energies are found from Eq. (16) to be smaller, as the reagents are more acidic, *i.e.*, as the dissociation energy, D, of the O–H bond is smaller and the electron affinity, A, of OH· or OR· is larger.

In addition, the solvent effect on the rate of protonation can be interpreted by this mechanism. The activated complex is a charge-transfer complex in which the no-bond and CT structures contribute to the resonance in almost equal proportions.[21] Therefore, the magnitude of the electron transfer between the radical anion and water is very close to 50% at the transition point: *i.e.*, about half a negative charge is localized on the oxygen atom of water in the activated complex. The solvent effect on the rates described above must be due to such a localized negative charge in the activated complex.[4]

The authors wish to thank Dr. M. Senō and Dr. M. Sukigara for their helpful discussions.

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[22] See comment by R. D. Brown in Ref. 21, p. 376.