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On the Electron-transfer Reaction Rate between Different Molecular Species of Aromatic Hydrocarbons as Measured by ESR

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The rate constants of electron-transfer reactions between the anthracene anion radical and pyrene, and those between the former radical and 1,2-benzanthracene, were measured by the ESR method in tetrahydrofuran containing 20 mM of tetra-*n*-butylammonium perchlorate. In the analysis of the experimental results, correction of the ESR line width was made for the change in the radical concentration caused by the addition of neutral molecules. The rate constants thus obtained were $(2.0\pm0.4)\times10^7\text{M}^{-1}\text{sec}^{-1}$ and $(8.1\pm1.0)\times10^7\text{M}^{-1}\text{sec}^{-1}$ respectively at 25°C. Under the same experimental conditions, the rate constants of the electron exchange of anthracene and pyrene with their respective anions were about one-tenth of the rate constants of free anions. This fact led us to the supposition that the anion radicals had been combined with tetra-*n*-butylammonium ions into stable ion-pairs in our experiment. A semi-empirical method was proposed for the theoretical calculation of the rate constant according to the theory of R. A. Marcus. The agreement of the observed and the calculated rate constants was satisfactory. Further discussion of the dependence of the rate constant on the standard free energy of reaction was made in connection with the so-called "Linear Free Energy Relationship."

Kinetic studies of electron-transfer reactions in liquid solutions have been reported mainly on metal-complex ions. They have been summarized in several review articles.[1-3] The theoretical treatments have also been made by many investigators, and several excellent theoretical works have been presented, especially on the rate of electron-transfer reactions with outer-sphere mechanisms.[4-8]

However, there have been only a few experimental investigations of the kinetics of the electron-transfer reactions of organic compounds. Probably this is due to the difficulty in the measuring technique, which can be attributed to their large reaction rate and to the instability of the anion radicals. As to theoretical treatments of them, very few investigations have been done. The kinetic study of the electron-transfer reaction of organic compounds began with an electron spin resonance measurement of the rate of the electron exchange between naphthalene and its anion radical by Ward and Weissman;[9] this was followed by measurements of several kinds of anion radicals under various conditions. However, there has been no systematic experimental work which can be the basis for theoretical work. The difficulty is thought to be due to the formation of ion-pairs between anion radicals and cations.

It is known that the radical anions prepared by the reduction of aromatic hydrocarbons with alkali metals form ion-pairs with alkali metal ions in ethereal solvents with low dielectric constants, such as tetrahydrofuran (THF) and methyltetrahydrofuran. Further, the ion-pairs are in several different states, which are dependent on the nature of both the solvent and the cation.[10] These circumstances have troublesome influences on the analysis of the electron-transfer rate.

We have been engaged in experimental work to investigate the dependence of the rate of the electron transfer upon some of the physico-chemical parameters of the reaction, such as the standard free energy of the reaction (ΔG°), the dielectric constant of the solvent, the molecular radius of the reactants, and the temperature. The free anion radicals were expected to be generated by

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1) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

2) N. Sutin, *Ann. Rev. Nuclear Sci.*, **12**, 285 (1962).

3) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

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6) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

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8) N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1961).

9) R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957).

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the electrolytic reduction of hydrocarbons, in which tetraalkylammonium salt was used as a supporting electrolyte. However, it was found that, when tetra-*n*-alkylammonium perchlorate was added to the solution, the ESR spectrum of the solution of the radicals produced by the reduction with alkali metals did not have any hyperfine splittings due to alkali ions. This result suggested that the anion radicals could form stabler ion-pairs with tetraalkylammonium ions than those with alkali metal ions; this idea has been supported by other experiments.[11,12] Therefore, the investigation of the electron-transfer reaction of the free anion radical cannot be made in the presence of tetraalkylammonium ions. However, in this case, some new information may be obtained on the electron-transfer reaction of the stable ion-pairs themselves. The electron-transfer reaction of the ion-pairs of the hydrocarbon anion radicals with cations besides metal ions have never been investigated.

This paper will treat the electron-transfer rate from the ion-pairs of anthracene anions with tetra-*n*-butylammonium ions to hydrocarbons other than anthracene in order to examine its dependency on $\Delta G°$. Until now the measurements of the electron-transfer rate by the ESR method have been carried out exclusively of the electron-transfer between the same species of molecules, *e.g.*, between naphthalene and its anion radical.[9] Measurements must be made for a couple of different molecular species for the dependence of the electron-transfer rate upon $\Delta G°$ to be investigated. Measurements on such a couple can, in principle, be made with the ESR method. In the following reaction of an anion radical, R_1^-, with a neutral molecule, R_2,

$$R_1^- + R_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R_1 + R_2^-$$

the rate constant, k_1, can be determined by the line-broadening of the spectrum of R_1^- after adding R_2, if the coexistence of R_2^- in the solution does not disturb the observation of the ESR spectrum of R_1^-. In practice, however, the measurement is possible only when $\Delta G°$ is positive, *i.e.*, when the position of the equilibrium of the reaction is located on the left-hand side of the equation. Moreover, there is another restriction on the value of $\Delta G°$. When the $\Delta G°$ of the reaction is large, the equilibrium is located on far left-hand side of the reaction; consequently, the reaction rate is too slow to be measurable with this method. Hence, the $\Delta G°$ values of reactions the rates of which are measurable range within about 0—0.3 eV. The electron-transfer reactions dealt with in this paper are those between anthracene anion radicals and 1,2-benzanthracene, and those between anthracene anion radicals and pyrene, the $\Delta G°$ values of which are 0.052 eV and 0.113 eV respectively.[13]

Experimental

The aromatic hydrocarbons used, anthracene, pyrene, and 1,2-benzanthracene, were obtained by the recrystallization of the commercial reagents from benzene or ethyl alcohol.

Tetra-*n*-butylammonium perchlorate was prepared by adding an excess of perchloric acid to an aqueous solution of tetra-*n*-butylammonium iodide and then by filtering the precipitate. It was recrystallized from water first, and then from ethyl acetate. Tetra-*n*-butylammonium iodide was synthesized by the usual method from tri-*n*-butylamine and *n*-butyl iodide.

Tetrahydrofuran was used as a solvent throughout this investigation. It was refluxed over sodium metal, distilled, and then allowed to stand over sodium metal in a vaccum for a week. After the evolution of hydrogen gas had ceased, the solvent was distilled and stored in an ampoule containing anthracene and sodium metal in a vacuum in order to remove the trace of both oxygen and water. The stored solution was deep blue because of the presence of anthracene anion radicals. The solution of mono-negative ion radicals of hydrocarbons was prepared by the usual method, using a solvent redistilled from the stored solution.

The measurements of the ESR spectra were made with a JEOL JES-3BS spectrometer operated at about 9.7 kMHz, with 100 kHz field modulation and with a modulation amplitude of 0.03—0.08 gauss.

The rates of the electron-transfer reactions were determined from the increase in the linewidth of the ESR spectra of the radical anions after the addition of a known amount of neutral molecules. The measurements were carried out at 25°C.

The concentrations of the anion radicals were determined with a Shimadzu MPS-50L multipurpose autorecording spectrophotometer.

Results

The anthracene anion radicals prepared by the reduction of anthracene with sodium metal in THF yielded a rather unresolved ESR spectrum, as is shown in Fig. 1a. This spectrum evidently exhibited the hyperfine splittings due to a sodium nucleus, the coupling constant of which was about 0.5 gauss. On the other hand, no sign of hyperfine splittings due to sodium were seen in the spectrum of the solution of the anth-

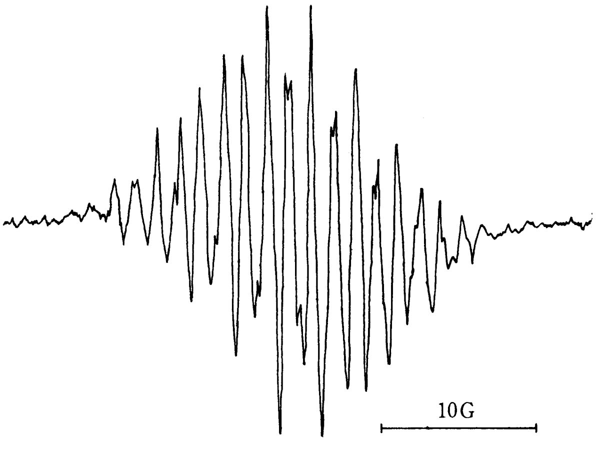

Fig. 1a. ESR spectrum of anthracene anion radical prepared by sodium reduction in THF. Radical concentration: 0.3 mM.

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[11] J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).

[12] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

[13] J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Phys. Chem.*, **71**, 3063 (1967).

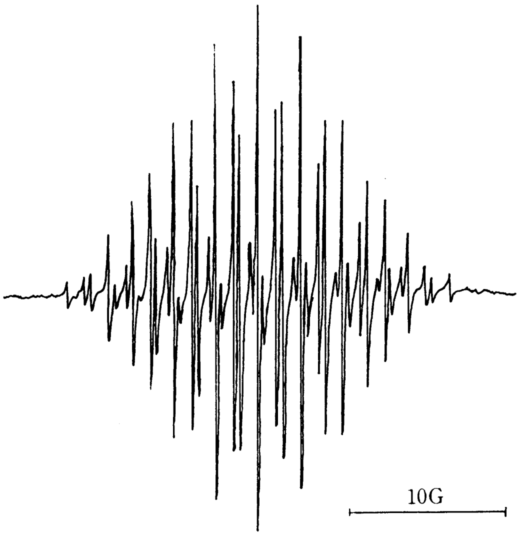

Fig. 1b. ESR spectrum of anthracene anion radical prepared by sodium reduction in THF and added by 20 mM of tetra-*n*-butylammonium perchlorate.

racene anion containing 20 mM of tetrabutylammonium perchlorate, though it was prepared in the way described above. The latter spectrum was a normal one with hyperfine splittings due to just three kinds of protons, as is shown in Fig. 1b. These results suggest that the sodium ion in the ion-pair had been replaced by the tetrabutylammonium ion.

The rates of electron-transfer reactions can be determined by measuring the increase in the linewidth after the addition of neutral molecules. However, this is the case only when the concentration of anion radicals is kept unchanged before and after the addition of neutral molecules. This is because a part of the linewidth of the ESR spectrum of anion radicals is caused by the spin-exchange interaction, the rate of which is dependent on the concentration of anion radicals. In the electron-transfer reactions between different molecular species, the initial concentration of the anion radical is decreased both by the following equilibrating reaction:

$$R_1^- + R_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R_1 + R_2^- \qquad (1)$$

and by the decomposition of the anion radicals, accompanied by the addition of neutral molecules. Accordingly, the linewidth should be corrected for the change in the concentration of anion radicals in this experiment.

It is necessary to examine the dependence of the linewidth upon the concentration of anion radicals in order to make a linewidth correction. Figure 2 shows this relation obtained experimentally. The concentration of anion radicals was determined by the use of the electronic spectra, the extinction coefficient by Balk *et al.* being used.[14] Figure 3 shows a typical spectrum of the anthracene anion radical; it is almost identical with that obtained by Balk *et al.* The plot of the observed linewidth against the radical concentration was linear, as is shown in Fig. 2. Such a dependence of the linewidth on the radical concentration is thought to be due to the spin-exchange interaction. The second-order rate constant of the spin-exchange process in solution can be calculated by the analysis of the relation in Fig. 2. It is 4.8×10^9M^{-1}sec^{-1}, a nearly diffusion-controlled value. The theoretical value of the diffusion-controlled rate constant in THF at 25°C[15] is 7.1×10^9M^{-1}sec^{-1}.

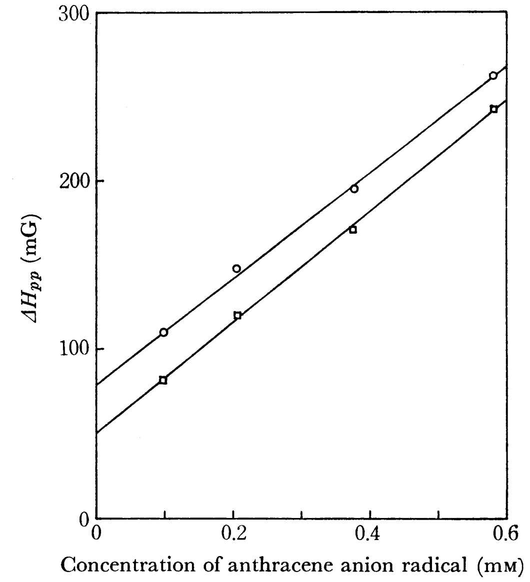

Fig. 2. Plots of linewidth against concentration of anthracene anion radical.
○: observed linewidth for the solution containing both anthracene and its anion radical ($A^- + A = 1$ mM), □: linewidth subtracted by the contribution of electron exchange between anthracene and its anion radical. ΔH_{pp}: peak-to-peak linewidth.

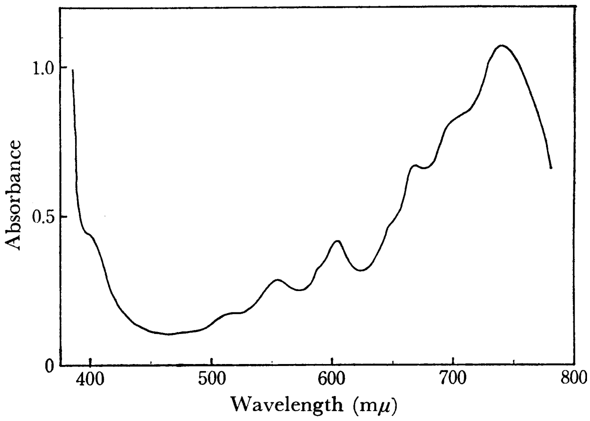

Fig. 3. Electronic spectrum of anthracene anion radical in THF containing 20 mM of tetra-*n*-butylammonium perchlorate.

In our measurements of the rates by the ESR method, the concentration of anion radicals before the addition of the neutral molecules was determined by means of the relation shown in Fig. 2, and their concentration after addition, by means of the relative intensity of the central hyperfine lines. The intensity is defined here as the product of the derivative half amplitude (I) and the square of the peak-to-peak linewidth (ΔH_{pp}), on the

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[14] P. Balk, G. J. Hoijtink, and J. W. H. Schreurs, *Rec. Trav. Chim. Pays-Bas*, **76**, 813 (1957).

[15] M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.*, **51**, 2690 (1969).

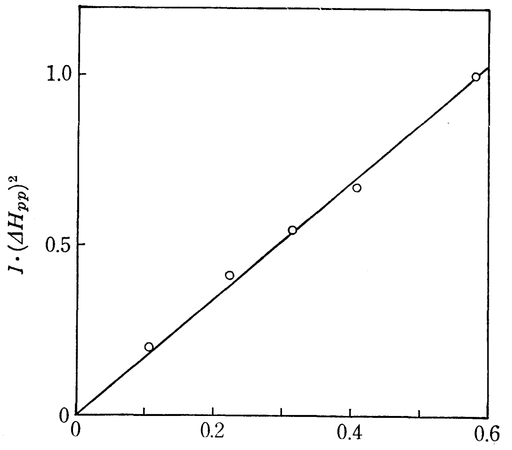
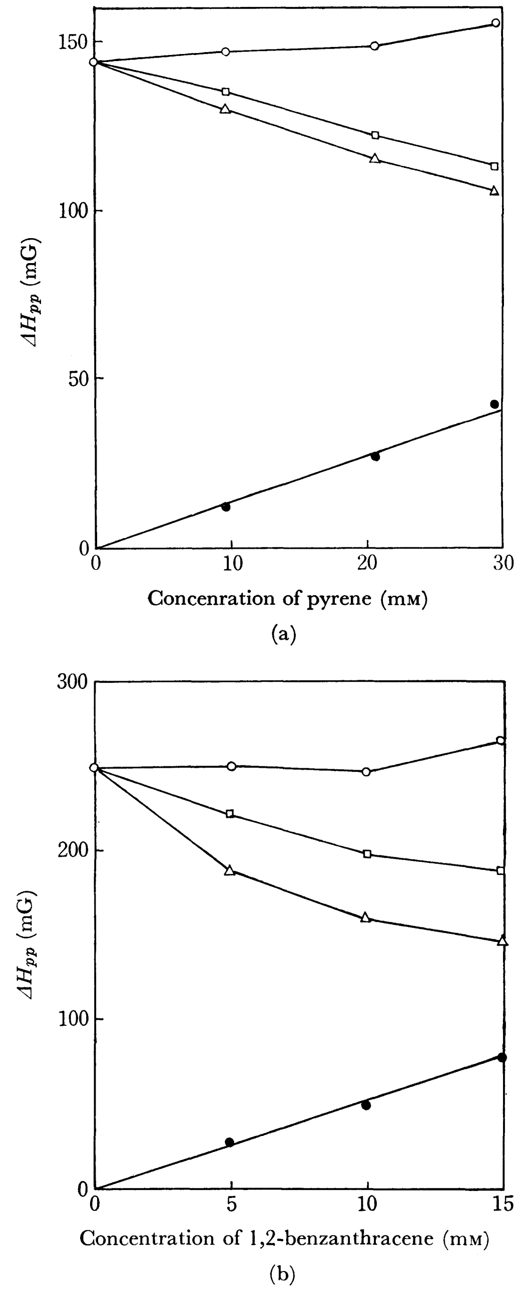


Fig. 4. Correlation between the relative intensity of ESR spectrum and the concentration of anthracene anion.



(a)

(b)

Fig. 5. Linewidth of ESR spectrum of anthracene anion radical plotted against the concentration of added neutral molecule of different kind from anthracene. ○: observed linewidth, □: the calculated contribution of first four terms in the right hand side of Eq. (2), △: the calculated contribution of first three terms of Eq. (2), ●: the difference between two upper plots, *i.e.*, the contribution of electron transfer reaction between different molecular species.
a) electron transfer reaction between A^- and P.
b) electron transfer reaction between A^- and B.

assumption that the Lorentzian line shape is unchanged after the addition of neutral molecules. It may be confirmed from Fig. 4 that the concentration obtained by the above method is in agreement with that determined spectroscopically.

When the equilibrium of the reaction (1) is attained, the linewidth, $\Delta H_{pp}(R_1^-)$, of the ESR spectrum of the anion radical, R_1^-, is given by the following equation:

$$\Delta H_{pp}(R_1^-) = c_1 + c_2[R_1^-] + c_3[R_1] + c_4[R_2^-] + c_5[R_2] \quad (2)$$

where $[R_1^-]$, $[R_1]$, $[R_2^-]$, and $[R_2]$ are the concentrations of the individual species. The five terms on the right-hand side of the equation are as follows: the first term is the linewidth intrinsic to the anion radical R_1^-; the second term is the linewidth due to the spin-exchange interaction between R_1^- ions; the third term is due to the electron transfer between R_1^- and R_1; the fourth term is due to the spin exchange interaction between R_1^- and R_2^-; the fifth term is due to the electron transfer between R_1^- and R_2. The c_1 and c_2 constants are obtainable from Fig. 2. The c_3 constant is estimated by means of the rate constant of the electron-transfer reaction between R_1^- and R_1. The fourth term in Eq. (2) is the linewidth due to the spin-exchange interaction between R_1^- and R_2^-, which may be diffusion-controlled, as is the interaction between R_1^- ions. Consequently, c_4 can be taken to be equal to c_2. It is c_5 that must be determined here. Its determination is feasible if $[R_1^-]$, $[R_2^-]$, $[R_1]$, and $[R_2]$ were known. Since $[R_1^-]$, $[R_1]$, and the added quantity of R_2 are already known, $[R_2^-]$ and $[R_2]$ can be evaluated by means of the mass action law, in which the equilibrium constant, K, is calculated from the difference in the standard reduction potential, $\Delta E°$, between R_1 and R_2 by the use of the equation $K = \exp(\Delta E° \boldsymbol{F}/\boldsymbol{RT})$.

The contributions of each term in Eq. (2) to the linewidth are illustrated in Fig. 5. The symbolic notations A, P, and B means anthracene, pyrene, and 1,2-benzanthracene resectively. The uppermost plot in Fig. 5 is the plot of the observed linewidth against the concentration of added neutral molecules. The next lower plot indicates the linewidth due to the first four terms on the right-hand side of Eq. (2), each of them being evaluated by the above method. The third plot from the top shows the contribution of the first three terms of Eq. (2) to the linewidth. Accordingly, the difference between two upper plots is the linewidth attributed to the electron transfer between the different molecular species in question. This is shown as the lowermost plot in the figures. It was because of the cancelling effect of the decrease in the radical concentration of the linewidth that an increase in the measured

Table 1. Observed rate constants of electron transfer reactions in THF containing 20 mm of Bu_4NClO_4

Reaction	ΔG° (eV)	$k_1(\text{M}^{-1}\text{sec}^{-1})$
$A^- + A = A + A^-$	0	$(2.0 \pm 0.1) \times 10^8$
$P^- + P = P + P^-$	0	$(2.3 \pm 0.2) \times 10^8$
$A^- + B = A + B^-$	0.052	$(8.1 \pm 1.0) \times 10^7$
$A^- + P = A + P^-$	0.113	$(2.0 \pm 0.4) \times 10^7$

value of the linewidth was not observed when neutral molecules were added. The rate constants thus obtained are shown in Table 1, together with the ΔG° values of these reactions.

Figure 6 shows the similar plots for the couple of anthracene and its anion.

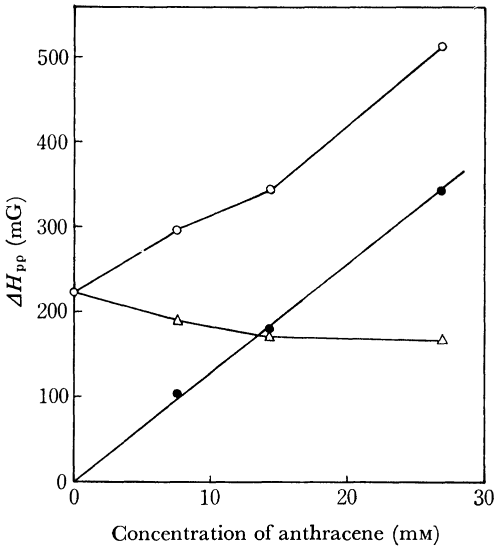


Fig. 6. Linewidth of ESR spectrum of anthracene anion radical plotted against the concentration of added parent molecule. ○: observed linewidth, △: the calculated linewidth with the exclusion of the contribution of electron transfer reaction, ●: the difference between two former plots, *i.e.*, the contribution of electron transfer reaction to the linewidth.

Discussion

The observed rate constants of the electron transfer between the same molecular species in Table 1 are seen to be about one-tenth of the rate constants for the free anions or their solvent-separated ion-pairs which were obtained with sodium metal in 1,2-dimethoxyethane (DME).[16] This suggests that A^- forms an ion-pair with the tetra-*n*-butylammonium ion (Bu_4N^+) in THF, although the ESR spectrum of A^- after the addition of tetrabutylammonium perchlorate does not have hyperfine splittings due to any of alkali ion, nitrogen atom, or protons in Bu_4N^+. The details of the effect of the ion-pairing of anion radicals with Bu_4N^+ ions on the electron-transfer rate will be reported later.

The rate constants of the electron-transfer reactions between different kinds of molecules are smaller for larger ΔG° values, as is shown in Table 1. The rate constant of the reaction between A^- and P was about one-tenth of that reported by Lyons *et al.*,[17] who worked with potassium and DME. The latter was $1.9 \times 10^8 \text{M}^{-1}\text{sec}^{-1}$. Although the extent of ion-pair formation between A^- and K^+ is not clear in their experiment, it is considered that the large rate constant is attributable to the large concentration of free ions or solvent-separated ion-pairs.[18]

The theories on the electron-transfer process which have been proposed should be examined in order to make a quantitative discussion of the ΔG° dependence of the electron-transfer rate. There have been several theoretical investigations of the electron-transfer processes of metal complex ions.[2-8] Marcus' work on those reactions which proceed with an outer-sphere mechanism and which are not accompanied by the formation or the rupture of the chemical bonds is thought to be the most outstanding.[4-7] The activation free energy of the electron-transfer reactions is obtained in this theory by calculating the energy of the reorientation of the solvent molecules in the vicinity of the discharging complex ions to form the activated complex, on the assumptions that the metal complex ions are the spheres of the conductor and that the solvent is a dielectrically unsaturated continuum. Moreover, the energy of the expansion and shrinkage of the inner coordination shell for the formation of the activated complex was also taken into consideration in the calculation of the activation free energy.[5-7]

According to the theory, the rate constant of the electron-transfer reaction, in which one of the reactants is neutral and the number of the transferring electron is one, is given by the following equation:[4-7]

$$k_1 = Z \exp(-\Delta G^*/RT) \tag{4}$$

where ΔG^* satisfies the equations:

$$\Delta G^* = (1/4)(1 + \Delta G^\circ/\lambda)^2 \lambda \tag{5}$$

$$\lambda = \lambda_0 + \lambda_i \tag{6}$$

$$\lambda_0 = e^2(1/2a_1 + 1/2a_2 - 1/r)(1/D_{op} - 1/D_s) \tag{7}$$

In these equations, Z is the bimolecular collision number of the hypothetical uncharged species in solution; e is the electric charge of the electron; λ_o and λ_i, the contributions to λ from the solvent and the inner coordination shell respectively; a_1 and a_2, the respective radii of the reactants; r, the distance between the centers of the reactants in the activated complex, and D_s and D_{op}, the static and the optical dielectric constants respectively.

In the present electron-transfer reaction of the organic ion radical, the model of Marcus is not consistent with the features of this reaction in two respects: the reactants are planar, and the anion radicals form ion-pairs. However, if λ is treated as a parameter which can be determined experimentally, no non-empirical estimation of those factors appearing in Eqs. (5) to (7)

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[16] N. Hirota, "Radical Ions," ed. by E. T. Kaiser, and L. Kevan, Interscience Publishers, New York, N. Y. (1968).

[17] L. E. Lyons, J. E. Moore, and G. C. Morris, *Aust. J. Chem.*, **21**, 2789 (1968).

[18] This value is inconsistent with our own unpublished data, $0.97 \times 10^8 \text{M}^{-1}\text{sec}^{-1}$, which was obtained with sodium metal and DME.

will be necessary. Accordingly, the examination of the dependence of the rate constants on ΔG° can be made by comparing the experimental value of the rate constant with that calculated by the above-mentioned method. In the electron-transfer reactions between the same species of molecules as those between anthracene and its anion radical, the ΔG° of the reaction is equal to zero and, accordingly, $\Delta G^* = \lambda/4$; therefore, the value of λ can be determined from the experimental value of the rate constant, if Z is given.

Generally, the value of λ is different for each reaction. As is shown in Table 1, however, the rate constants of the electron-transfer reactions between the ion-pair of the anion radical with the tetrabutylammonium ion and its parent molecule were nearly equal, *e.g.*, those of the reactions between $A^-Bu_4N^+$ and A, and between $P^-Bu_4N^+$ and P, were 2.0×10^8 and $2.3 \times 10^8 M^{-1}sec^{-1}$ respectively. If it is assumed that Z is 10^{11}, λ for $A^-Bu_4N^+$ and $P^-Bu_4N^+$ are of nearly equal values, *i.e.*, 14.7 and 14.4 kcal·mol^{-1} respectively. Because the λ of the cross electron-transfer reaction is thought to be equal to the mean value of the λ of the original reactions,[6] the λ values for the reactions $A^- + P = A + P^-$ and $A^- + B = A + B^-$ may be equal to that of $A^- + A = A + A^-$. Although there is some uncertainty in the value of Z, the value of 10^{11} proposed by Marcus[6] was taken here. ΔG° was calculated with the use of the data of the reduction potential of hydrocarbons by Chaudhuri *et al.*,[13] which were obtained in THF by means of potentiometric titration. The observed and the calculated values are both listed in Table 2; they are in agreement with one other. Although there is some difficulty in the non-empirical application of Marcus' theory to the electron-transfer reactions of organic ion radicals, the above results show that the ΔG°-dependence of the rate constants of those reactions can be calculated with this theory when λ is considered as a parameter.

TABLE 2. COMPARISON OF THE OBSERVED AND THE CALCULATED VALUES OF RATE CONSTANT OF ELECTRON TRANSFER REACTIONS BETWEEN DIFFERENT MOLECULAR SPECIES

Reaction	ΔG°(eV)	$k_1^{obs}(M^{-1}sec^{-1})$	$k_1^{theor}(M^{-1}sec^{-})^1$
$A^- + B = A + B^-$	0.052	8.1×10^7	7.0×10^7
$A^- + P = A + P^-$	0.113	2.0×10^7	1.9×10^7

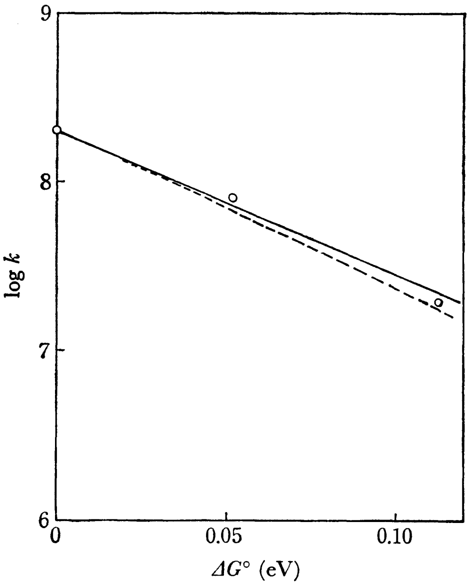

Fig. 7. Dependence of the rate constant of electron transfer reaction upon standard free energy of reaction (ΔG°). ○, observed value; ------, calculated value; ——, calculated value with the second order term in ΔG° being neglected.

It is known that there is a so-called "Linear Free Energy Relationship" between the rate constant of the chemical reaction and the standard free energy of the reaction; that is, there is a linear relation between ln k and ΔG°:

$$\ln k = A - \alpha \Delta G^\circ / RT \qquad (8)$$

where A and α are constants. The theory of Marcus shows that the quadratic term in ΔG° must also be included in the relation. If the quadratic term in the expansion of Eq. (4) is neglected, the value of 0.5 will correspond to the value of α in Eq. (8).[6] The plots of log k_1^{obs} and log k_1^{theor} against ΔG° are shown in Fig. 7, where a straight line drawn between log k and ΔG° by neglecting the quadratic term in Eq. (5) is also shown. On the basis of these results only it is difficult to decide whether or not the quadratic term in ΔG° contributes to the activation free energy. However, it is clear that the coefficient of the linear term is nearly equal to 0.5.