The Applicability of the Theory of R. A. Marcus to the Electron-Transfer Reactions between Polycyclic Aromatic Hydrocarbons and Their Anion Radicals

Kosaku Suga and Shigeru Aoyagui
Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received July 13, 1972)

The rates of electron-transfer from the anthracene-anion radical to anthracene, 1,2-benzanthracene, and pyrene are measured by the electron spin resonance method, with a line-broadening procedure, under experimental conditions in which anion radicals are in a state of free ions or of loose ion pairs. The dependence of the observed rate constants on the standard free energy of reaction, the dielectric constant of the solvent, and the temperature are discussed on the basis of the theory of R. A. Marcus. The free energy of nuclear reorganization, as estimated from the ΔG°-dependence of the rate constants, is much smaller than that predicted theoretically. The observed rate constants are almost independent of the dielectric constants of the solvents; consequently, the reorganization free energy of the solvent must be smaller than the theoretical value. The entropy term contributes to the activation energy to almost the same extent in the solvents with different dielectric constants; this is inconsistent with the theoretical prediction and requires a smaller value for the free energy of solvent reorganization than its theoretical value.

A number of rate constants for electron-transfer reactions between polycyclic aromatic hydrocarbons and their anion radicals have been measured by the electron spin resonance (ESR) method since the pioneering work of Ward and Weissman.[1] It has been revealed that these anion radicals form ion pairs with alkali ions and that the formation of such ion pairs affects the electron-transfer rates.[2] According to Hirota,[3] there can be two kinds of ion pairs, the tight ion pairs whose ESR spectra exhibit hyperfine splittings due to alkaki ions, and the loose ion pairs which yield ESR spectra without such hyperfine splittings. The rate constants of about 10^7 and $10^9 \mathrm{M}^{-1}\mathrm{sec}^{-1}$ were attributed to the tight and the loose ion pairs respectively. On the other hand, there is no difference between the rate constants of loose ion pairs and free ions;[3b] thus, it is not necessary to distinguish the loose ion pairs from free ions in the following discussion. They will be designated "free ions" in this paper for the sake of simplicity.

The electron-transfer reactions of hydrocarbon free anions can be pure electron-transfer reactions without the formation and/or rupture of chemical bonds; they resemble those of metal-complex ions with an outer-sphere mechanism. Thus, the theory of Marcus[4] is expected to be applicable to the former reactions, which have been scarcely discussed on the basis of the molecular theory. A test applying Marcus' theory to these reactions may be an approach to elucidating their microscopic mechanism. Moreover, such a test will serve to improve and refine the theory itself.

In this paper we will examine the applicabliity of the Marcus' theory to the electron-transfer reactions between hydrocarbon molecules and their radical anions when the latter reactants are in a free-ion state. The following aspects should be emphasized at the outset: first, the theoretical equation for the rate constant contains several parameters which can be specified experimentally; the standard free energy of reaction, the dielectric constant of the solvent, the temperature, and the molecular radii of the reactants; thus, the dependence of the rate constant on these parameters must be examined as a whole, not individually. Secondly, it is preferable that the measurements be made with at least two measuring techniques based on different principles. Such a comparative study as this is not only necessary for an examination of the reliability of the measuring technique itself, but it may inform us of the influence on the observed rate constants of the experimental conditions, which may be inevitably different from method to method.

This paper will deal with the ΔG°, D_s, and T parameters.[5] A comparison between the ESR and the pulse-radiolysis methods will be made with regard to D_s. The ΔG°-dependence obtained by the methods of pulse radiolysis, the quenching of the fluorescence, and ESR has already been discussed comparatively elsewhere.[7]

Experimental

Procedures. The electron-transfer rates were determined from the increase in the linewidth of the central hyperfine line in the ESR spectra of anthracene anion radicals after the addition of a known amount of neutral molecules. The rates of cross-electron-transfer reactions were evaluated with the procedure described in the preceding paper.[8] The con-

---

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

[2] P. J. Zandstra and S. I. Weissman, *ibid.*, **84**, 4408 (1962).

[3] a) N. Hirota, *ibid.*, **90**, 3606 (1968). b) N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968).

[4] a) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956). b) R. A. Marcus, *ibid.*, **43**, 679 (1965).

[5] Spherical molecular shape of the reactants is assumed in the theory of Marcus,[4] but all the reactants in this investigation are planar. Thus the molecular radii of the reactants, *a's*, appearing in his theoretical expression for the rate constant cannot be well-defined quantities even when the molecular geometry is given. In fact we could not prove the *a*-dependence of the rate constant predicted theoretically.[6]

[6] K. Suga, S. Ishikawa, and S. Aoyagui, This Bulletin, **46**, 808 (1973).

[7] K. Suga, H. Mizota, Y. Kanzaki, and S. Aoyagui, "Current Topics of Kinetic Parameters of Electron-transfer Reactions," ed. by N. Tanaka, Tohoku University, (1972), p. 71; *J. Electroanal. Chem.*, in press.

[8] K. Suga and S. Aoyagui, This Bulletin, **45**, 1375 (1972).

centration of the anthracene anion radicals was determined spectroscopically using the value for the extinction coefficient reported by Balk *et al.*[9]

Materials. All the aromatic hydrocarbons as well as the solvents used were commercially obtained. The anthracene (A), 1,2-benzanthracene (B), and pyrene (P) were recrystallized from benzene and ethanol. The solvents were purified to remove all traces of acidic materials, water and oxygene. The tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were purified in a way described previously.[8] The *N,N*-dimethylformamide (DMF) was refluxed over calcium hydride, distilled, and then allowed to stand over calcium hydride in a vacuum for about two weeks; it was degassed after the evolution of hydrogen gas had ceased and then distilled into a glass ampoule containing solid sodium anthracenide in order to remove the residual water and oxygen.

Preparation of Radical Solutions. Only the anthracene radical anion was required in this experiment. A DME solution of its sodium salt was prepared by dissolving solid sodium anthracenide into DMF because of the reactivity of this solvent with sodium metals. The sodium anthracenide was prepared by the soidum reduction of anthracene in THF and was then made free from the solvent by distillation. The solutions in the DME–DMF mixed solvent were prepared by mixing the DME solution with DMF.

Measuring Devices. The ESR measurements were carried out on a JEOL Model JES-3BSX spectrometer operated at about 9.5 kMHz, with 100 kHz field modulation. The modulation amplitude was 0.03—0.08 Gauss. The temperature was maintained and controlled with a JEOL Model JES-UCT-2AX variable-temperature adaptor on the ESR cavity. All the measurements were made at 25°C unless otherwise stated.

Results and Discussion

According to the theory of Marcus,[4] the rate constant of the electron-transfer reaction, $R_1^- + R_2 = R_1 + R_2^-$, when the non-coulobmic interaction between reactants and between products can be neglected, is given by the following equation:

$$k = Z \exp(-\Delta G^*/RT), \tag{1}$$

with;

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

$$\lambda = \lambda_0 + \lambda_i, \tag{3}$$

$$\lambda_0 = e^2(1/2a_1 + 1/2a_2 - 1/r)(1/D_{op} - 1/D_s). \tag{4}$$

In these equations, Z is the bimolecular collission number of the hypothetical uncharged species in solution when they have a unit concentration; ΔG^* and ΔG° are the activation free energy and the standard free energy of the reaction respectively; λ is the free energy needed to reorganize both the solvent molecules and the reactants in forming the activated complex; λ_0 and λ_i are the contributions to λ from the reorganization of the solvent and of the bonds in the reactants respectively; e is the electronic charge; a_1 and a_2 are the radii of the reactants; D_s and D_{op} are the static and optical dielectric constants respectively, and r is the distance between the centers of the reactants in the activated complex.

Equation (1) can be rewritten in the form:

$$k = k_0 \exp(-\Delta G^\circ/2RT) \exp[-(\Delta G^\circ)^2/4RT], \tag{5}$$

with

$$k_0 = Z \exp(-\lambda/4RT), \tag{6}$$

where k_0 is the rate constant of the electron-exchange reaction with $\Delta G^\circ = 0$. In deriving Eq. (5), it is assumed that the values for λ of the cross-electron-transfer reaction and of the electron-exchange reactions, $R_1^- + R_1$ and $R_2^- + R_2$, are the same. The validity of this assumption will be discussed below.

Table 1. Observed rate constants, corrected forward rate constants and corrected backward rate constants for the electron transfer reactions $A^- + A, A^- + B$, and $A^- + P$ in DME at 25°C

Reactions	ΔG° (eV)	k_{obs} (M^{-1} sec^{-1})	$\overrightarrow{k}_a$ (M^{-1} sec^{-1})	$\overleftarrow{k}_a$ (M^{-1} sec^{-1})
$A^- + A = A + A^-$	0	$(1.8 \pm 0.2) \times 10^9$	2.4×10^9	2.4×10^9
$A^- + B = A + B^-$	0.052	$(5.4 \pm 1.0) \times 10^8$	5.9×10^8	4.5×10^9
$A^- + P = A + P^-$	0.113	$(9.6 \pm 1.5) \times 10^7$	9.7×10^7	7.8×10^9

ΔG°-Dependence of the Electron-transfer Rates. When the ΔG°-dependence of the electron-transfer rates are examined, the reaction rates between different mloecular species must be measured. Measurements were made on the A^-/B and A^-/P couples in the DME solvent. Plots of the increase in the linewidth *vs.* the concentration of added neutral molecules are illustrated in Fig. 1. The linearity of each plot is satisfactory. The rate constants of the cross-electron-transfer reactions calculated from the slopes of the straight lines in Fig. 1 are listed in Table 1, together with the rate constant of electron exchange between A^- and A.

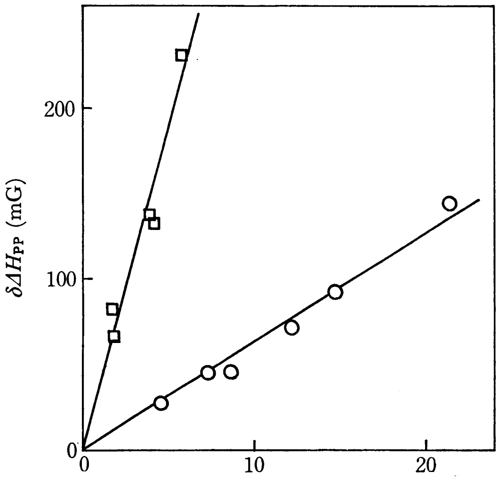

Fig. 1. Linewidth broadening ($\delta\Delta H_{PP}$) *vs.* concentration of neutral molecules in the cross electron transfer reactions in DME: □, $A^- + B = A + B^-$; ○, $A^- + P = A + P^-$.

Equation (2) shows that the rate constants of cross-electron-transfer reactions are dependent only on ΔG° when λ is a constant. According to the theory of Marcus, on the one hand, the λ value of the cross-electron-transfer reaction between A^- and B is approximately equal to the mean value of the λ's for two exchanging couples, A^-/A and B^-/B. On the other

---

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

hand, the rate constants of the electron-exchange reactions between polycyclic aromatic hydrocarbons and their anion radicals generated by sodium reduction in DME are nearly equal: *e.g.*, $2.0\times10^9\mathrm{M^{-1}sec^{-1}}$ for $\mathrm{P^-/P}$⁶⁾ and $1.8\times10^9\mathrm{M^{-1}sec^{-1}}$ for $\mathrm{A^-/A}$. Although the electron-exchange rate of $\mathrm{P^-/P}$ has never been measured, it is quite probable that its rate constant is almost identical with those for $\mathrm{A^-/A}$ and $\mathrm{P^-/P}$. Consequently, it is reasonable to assume that both cross-electron-transfer reactions treated in this paper have an λ value identical with that of the $\mathrm{A^-/A}$ couple. The λ value for an exchange reaction is obtainable experimentally with Eq. (6) and the observed k value when Z is given. In the following discussion, Z is taken to be 10^{11} and $10^{10}\mathrm{M^{-1}sec^{-1}}$.

The observed k value must be corrected for diffusion. In the case of an activation-diffusion mixed control, the corrected or activation-controlled rate constant, k_a, is given by the equation:

$$1/k_a = 1/k - 1/k_d, \qquad (7)$$

where k and k_d are the observed and the diffusion-controlled rate constants respectively. k_d can be estimated with the equation $k_d=4RT/3\eta$.¹⁰⁾ The observed k value for $\mathrm{A^-/A}$, $1.8\times10^9\mathrm{M^{-1}sec^{-1}}$, is of the same order of k_d, $7.2\times10^9\mathrm{M^{-1}sec^{-1}}$, in DME at 25°C; this is a rate constant controlled by both the activation and the diffusion processes.

The rate constants for cross-electron-transfer reactions with negative ΔG° values are not obtainable in the present procedure. They are estimated with the ΔG° value of the reaction, the corrected forward rate constant, k_a, and the following equation:

$$\overleftarrow{k}_a = \overrightarrow{k}_a \exp(-\Delta G^\circ/RT) \qquad (8)$$

Table 1 compiles the values for $\overleftarrow{k}_a$ and $\overrightarrow{k}_a$ thus obtained.

The λ value for the electron exchange reaction of anthracene, as calculated with the k_a in Table 1, is 8.8 kcal mol⁻¹ when Z is assumed to be $10^{11}\mathrm{M^{-1}sec^{-1}}$. The rate constants of electron-transfer reactions calculated with this λ value and Eq. (5) are drawn by dotted lines in Fig. 2. An identical plot with $Z=10^{10}\mathrm{M^{-1}sec^{-1}}$ and, consequently, with $\lambda=3.4$ kcal mol⁻¹ is shown by a dot-dash line. The solid straight line in the same figure shows the relation between k and ΔG° when the third term on the right-hand side of Eq. (2) is neglected; this line embodies the so-called "Linear Free Energy Relationship".³⁾

The corrected observed rate constants are plotted with closed circles in Fig. 2. They fit best with the dot-dash line. However, it is rather unlikely that the collision number in solution is $10^{10}\mathrm{M^{-1}sec^{-1}}$; according to recent reasoning, this is considered to be two or three times as large as the collision number in the gas phase, which is about $10^{11}\mathrm{M^{-1}sec^{-1}}$.

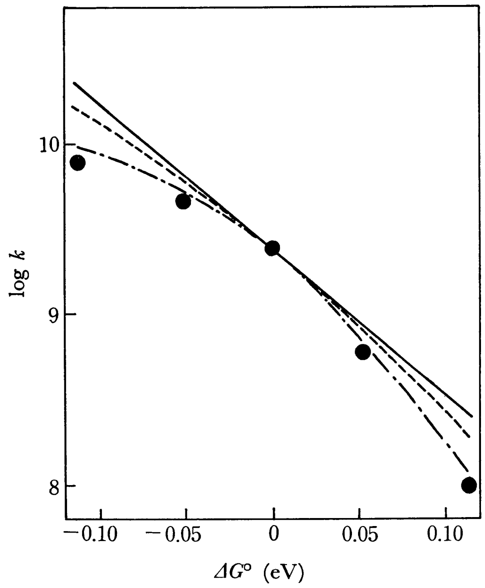

Fig. 2. ΔG°-dependence of electron transfer rates: ●, corrected observed values for rate constants in DME; ——, k *vs.* ΔG° plotted according to Eq. (5), the quadratic term in ΔG° neglected; ------ and -·-·-, k *vs.* ΔG° plotted according to Eq. (5) with λ of 8.8 and 3.4 kcal mol⁻¹ respectively.

Dependence of the Electron-transfer Rates on the Dielectric Constant of Solvents. The ESR measurements of the electron-transfer rates of aromatic hydrocarbon anion radicals have been made almost exclusively in solvents with low dielectric constants, *e.g.*, in DME ($D_s=7.2$ at 25°C), even when free anion radicals were studied. There is one exception: a measurement in DMF ($D_s=36.7$ at 25°C) with electrolytically-generated radical anions.¹¹⁾ Because of the large amount of supporting electrolytes indispensably present in the solution, however, it may be meaningless to compare the results with those obtained in solutions which do not contain such electrolytes.

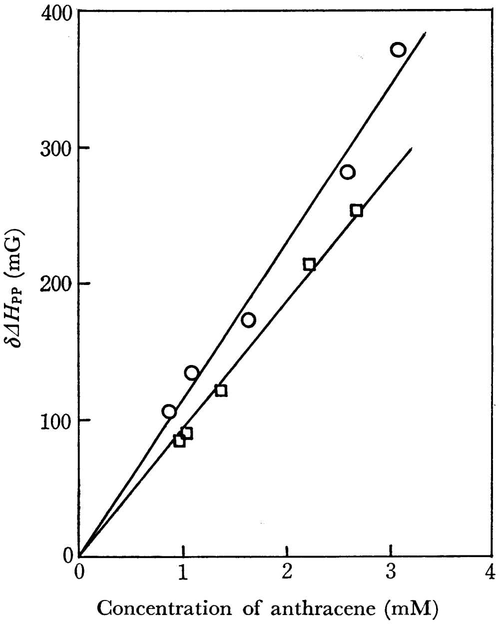

Fig. 3. Linewidth broadening *vs.* concentration of A in the electron exchange reaction between A⁻ and A: ○, in DME; □, in DMF.

---

10) M. P. Eastmen, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.*, **51**, 2690 (1969).

11) P. A. Malachesky, T. A. Miller, T. Layloff, and R. N. Adams, "Exchange Reactions," Proceeding of International Symposium on Exchange Reactions held at Upton, 1966, p. 157.

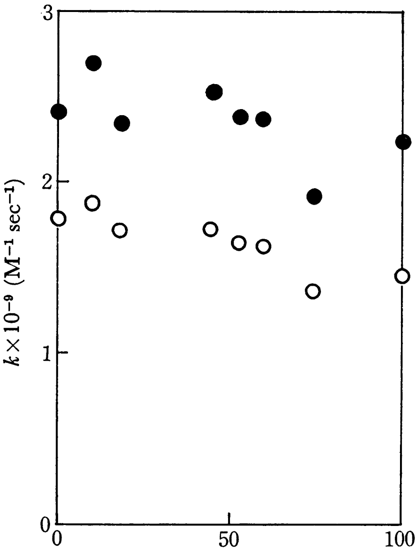

Fig. 4. Rate constants of electron exchange between A⁻ and A *vs.* weight percent of DMF in the mixture of DME and DMF: ○, observed values; ●, diffusion-corrected values.

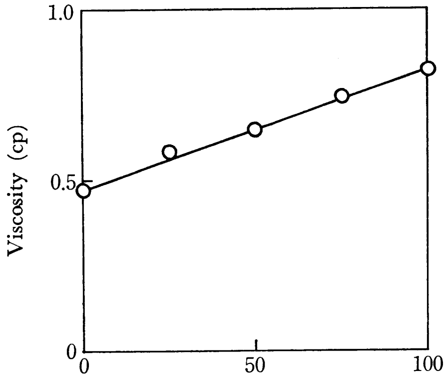

Fig. 5. Viscosities of DME–DMF mixtures.

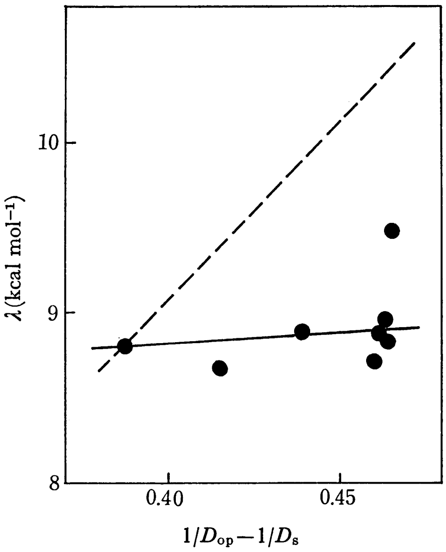

Fig. 6. Dependence of λ on the dielectric constants of solvents: ●, λ values calculated from Eq. (6) with corrected observed values for rate constants; ------, λ *vs.* $1/D_{op}-1/D_s$ plotted according to Eq. (4), the terms in the first parentheses estimated semi-empirically from λ values in DME.

The electron-exchange rates between anthracene and its anion radical were measured in several mixtures of DME and DMF. The correction of the linewidth for the decrease in the radical concentration was made in the same way as in the measurements of the cross-electron-transfer rates. Figure 3 illustrates the relations between the linewidth increase and the concentration of anthracene added in DMF and in DME respectively. The rate constants thus obtained are plotted in Fig. 4 with open circles against the weight percent of DMF in the mixed solvent. The corrected rate constants are shown with closed circles. The data for the viscosity of the DME–DMF mixture required in the correction are shown in Fig. 5; it is found that they depend almost linearly on the ratio of the composites.

Figure 4 shows that the corrected rate constants are nearly constant within the limits of experimental error. According to Eq. (4), the rate constant depends on D_s through the dependence of λ_0 on D_s. In the electron transfer of aromatic hydrocarbon-anion radicals, the contribution of λ_i to λ can be neglected; λ_0 is then approximately proportional to $(1/D_{op}-1/D_s)$. Since the D_{op} of each solvent is almost fixed, the value for λ, and consequently that for the rate constant also, are both substantially dependent only on D_s. The dotted line in Fig. 6 shows a theoretical plot of λ against $(1/D_{op}-1/D_s)$ drawn semi-empirically with the λ value and the slope calculated from the rate constant obtained in DME. The corrected observed λ values are plotted with closed circles in the same figure. The data for D_s in a DME–DMF mixture were not available. They were estimated from the D_s values of both solvents on the assumption that the D_s for the mixture depends linearly on the mixing ratio. The latter assumption was based on the fact that the viscosity of the mixture behaves in this manner without any molecular association at any specific mixing ratio, as is shown in Fig. 5. Figure 6 shows that λ depends on D_s to a much smaller extent than was predicted theoretically. This might be due to the neglect of the dielectric saturation in estimating the contribution to the activation free energy from solvent reorganization. This point will be discussed further later.

There has been an investigation examining the dependence of the rate constant on the dielectric constant of solvents with the pulse-radiolysis method.[12] Measurements were made on the electron-transfer from the pyrene anion to 9,10-dimethylanthracene; it was found that the results supported the theory of Marcus. However, it must be noticed that, on the one hand, the observed value for k is close to the diffusion-controlled one in this experiment. Consequently, errors in both the k_d and k values would seriously affect the accuracy of the corrected k_a values. On the other hand, the value for k_d was taken as that of the rate constant for

---

[12] a) S. Arai, D. Grev, and L. M. Dorfman, *J. Chem. Phys.*, **46**. 2572 (1967). b) J. R. Brandon and L. M. Dorfman, *ibid.*, **53**, 3849 (1970).

reactions with sufficiently large negative ΔG° values, *e.g.* $6.7\times10^9 M^{-1} sec^{-1}$ in isopropanol. This is about four times the value calculated from $k_d=4RT/3\eta$; the validity of this relation has recently been reexamined in the ESR investigation of the Heisenberg spin-exchange process between tetracyanoethylene mononegative ions.[10] Moreover, the rate constants reported of the reactions with positive ΔG° values, *e.g.*, A^-/P, are as small as about one-tenth of that obtained by the ESR method. It is rather close to the value for an electron transfer from the anthracene$^-$-tetrabuthylammonium$^+$ ion pair to pyrene.[8] This suggests the ion pair (not loose ion pair) formation of the anthracene anion with some organic cationic species generated by electron-beam irradiation.

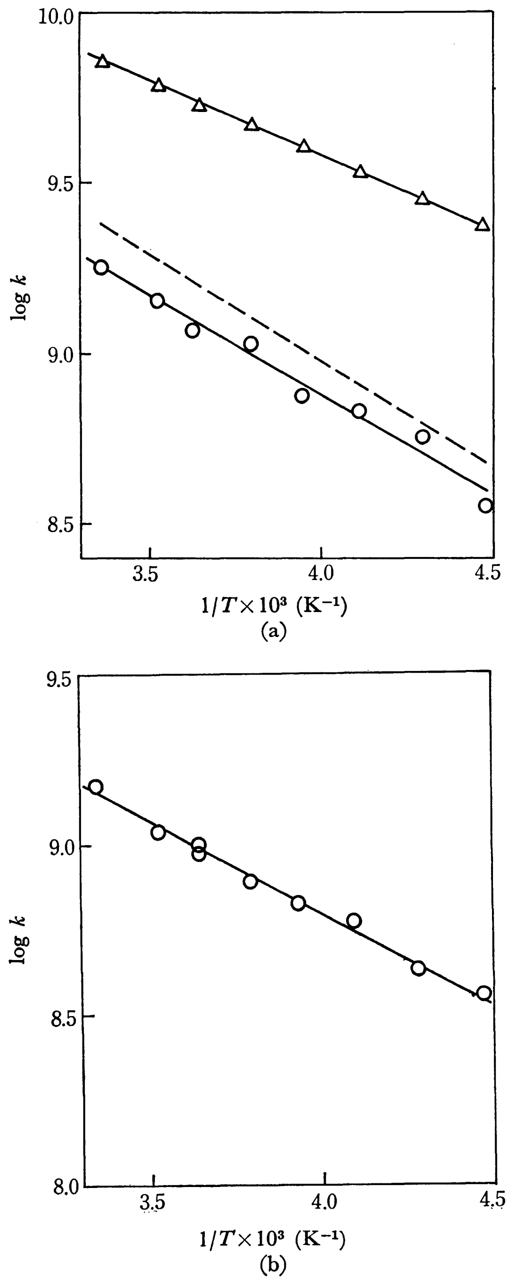

Fig. 7. Temperature dependence of rate constants of electron exchange between A^- and A in (a) DME and (b) DMF: ○, observed values; △, calculated values for k_d; ------, diffusion-corrected rate constants.

Temperature Depencence of the Electron-transfer Rates. Figures 7a and 7b show the temperature dependence of the rate constants of the electron-exchange reactions between anthracene and its anion radical in DME and DMF respectively. The observed rate constants are shown by open circles. The calculated k_d values and the corrected rate constants are shown in Fig. 7a by triangles and a dotted line respectively. The activation energies obtained from Fig. 7 are listed in Table 2.

TABLE 2. SEMI-EMPIRICAL ESTIMATE OF ACTIVATION ENTHALPY AND OBSERVED ACTIVATION ENERGY OF THE REACTION A^-+A IN DME AND DMF (energies in kcal mol^{-1})

Solvents	$Z=10^{11}$ M^{-1} sec^{-1}		$Z=10^{10}$ M^{-1} sec^{-1}		E_a
	ΔH^*	ΔG^*	ΔH^*	ΔG^*	
DME	3.34	2.21	1.28	0.84	2.7±0.3
DMF	2.45	2.24	0.94	0.85	2.6±0.2

The corrected activation energy is nearly equal to the apparent one. The activation energy obtained from the calculated diffusion controlled rate constants in DME is 2.25 kcal mol^{-1}. The results in DMF could not be corrected, because the data for the viscosity of DMF at low temperatures were not available. The apparent activation energy in this solvent was assumed to be equal to the corrected one.

The activation energies in DME and in DMF are nearly equal; they are rather smaller than the activation energy obtained by Hirota in DME, 3 kcal mol^{-1}.[13]

TABLE 3. NON-EMPIRICAL ESTIMATE OF λ_0 (λ's IN kcal mol^{-1})

Solvents	$(\lambda_0)_{calc}$		λ_{obs}
	$a=5.15$ Å $r=10.3$ Å	$a=2.85$ Å $r=5.70$ Å	
DME	12.5	22.5	8.81
DMF	14.9	26.8	8.84

The activation enthalpy of the electron-transfer reactions can be expressed in terms of the activation free energy in the sense of Marcus' theory, ΔG^*, as follows:

$$\Delta H^* = \Delta G^* - T(\partial \Delta G^*/\partial T).$$

It is ΔH^* that should be compared with the experimental activation energy, E_a. When λ_i is assumed to be negligible, ΔH^* is expressed as follows:

$$\Delta H^* = (1/4)[\lambda_0 - T(\partial\lambda_0/\partial T)].$$

In view of the fact that only D_s depends on the temperature in Eq. (4), the above equation can be rewritten in the following form:

$$\Delta H^* = (1/4)\left[\lambda_0 + T\frac{\lambda_0}{1/D_{op}-1/D_s}\frac{\partial}{\partial T}\left(\frac{1}{D_s}\right)\right]. \qquad (9)$$

The temperature dependence of the dielectric constant of solvents is expressed by the empirical equations:

---

[13] a) N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967). b) N. Hirota, "Radical Ions," ed. by E. T. Kaiser and L. Kevan, Interscience Publishers, New York (1968), p. 35.

$D_s(\text{DME})=-2.83+2950/T$[14] and $D_s(\text{DMF})=-24.8+18300/T$.[15] The λ_0 values are obtainable from the observed rate constants using an appropriate value for Z. Table 2 shows the values for ΔH^* calculated from Eq. (9) with Z values of 10^{11} and $10^{10}\text{M}^{-1}\text{sec}^{-1}$. The values for ΔG^* and E_a are also included in the table.

It may be seen from Table 2 that ΔH^* agrees with E_a fairly well when Z is $10^{11}\text{M}^{-1}\text{sec}^{-1}$. Moreover, it may be noticed that the experimental activation energies in the two solvents are nearly equal; this differs from the theoretical prediction that the extent of the contribution to ΔH^* from the entropy term would be different in DME and DMF solutions.

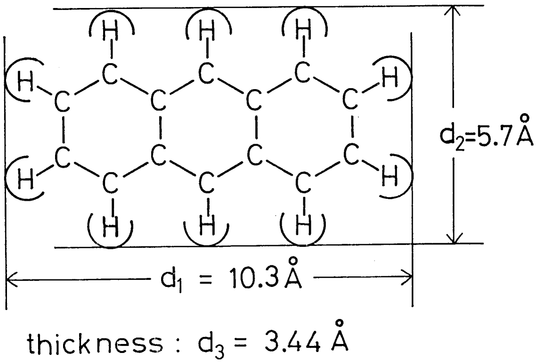

Fig. 8. Molecular geometry and dimensions of anthracene.

Non-empirical Estimate of λ_0. In the above discussion, the λ values were determined semi-empirically from the observed rate constants with an appropriate value for Z. According to Marcus' theory, λ_0 can be estimated non-empirically using Eq. (4) when λ_i is negligible. In deriving Eq. (4) Marcus assumed the reactants to be spherical. The reactants in the present discussion, *i.e.*, anthracene and its anion, however, have planar structures; the molecular radii must be estimated in an arbitrary way from the molecular geometry. Figure 8 shows the molecular geometry and dimensions of anthracene. In estimating d_1 and d_2 in Fig. 8, the van der Waals radii were taken into account besides the bond distances. The thickness, d_3, is rather indefinite. Because of the possible closest approach of reactants which may put the anthracene molecular planes face to face, it is assumed that the thickness is equal to the distance between the molecular layers in graphite, 3.44 Å. The value for λ_0 was calculated on the assumption that $a=a_1=a_2=r/2$. The value of a was tentatively taken as $d_1/2$ and $d_2/2$. Table 3 shows that even with the largest a value possible, *i.e.*, 5.16 Å, the calculated λ_0 values do not agree with the observed values. The agreement will be even less satisfactory for smaller a values.

Concluding Discussion. The following aspects were pointed out in the above examination of experimental results made on the basis of the Marcus' theory. First, the observed rate constants depend on ΔG° in such a way as is predicted theoretically when λ takes the value of 3.4 kcal mol^{-1}; this λ value is much smaller than that predicted by Eq. (4) with $Z=10^{11}\text{M}^{-1}\text{sec}^{-1}$, 8.8 kcal mol^{-1}. Secondly, the rate constant is almost independent of D_s against the theoretical prediction. Thirdly, there is no difference between the experimental activation energies in DME and in DMF; thi might be a result of the difference in D_s; in other words, the activation entropy contributes to E_a to almost the same extent in solvents with different D_s values. The second and the third points require that the contribution of λ_0 to the activation free energy be smaller than that predicted theoretically. The inclusion of λ_i into λ cannot provide any successful elucidation: the situation that λ_0 is small, while $\lambda=\lambda_0+\lambda_i$ is large, is not probable in view of the first point.

The inconsistency between the theoretical predictions and the experimental results might be removed by reasoning as follows: when the non-coulombic interactions between reactants as well as products, which were neglected in deriving Eq. (2), are taken into consideration, the activation free energy can be expressed by:[4b]

$$\Delta G^* = (w^r+w^p)/2 + \lambda/4 + \Delta G^\circ/2 + (\Delta G^\circ+w^p-w^r)^2/4\lambda, \tag{10}$$

where w^r and w^p are the reversible work to bring two reactants together and two products together respectively, from the bulk of solution to the positions they would occupy in the activated complex. Generally, w's can be coulombic and/or non-coulombic. Here, one of the reactants as well as the products being neutral, they are non-coulombic. If $w^r=w^p=w$ is assumed for the sake of simplicity, Eq. (10) becomes:

$$\Delta G^\circ = w + \lambda/4 + \Delta G^\circ/2 + (\Delta G^\circ)^2/4\lambda. \tag{11}$$

Let $w=1.4$ kcal mol^{-1} and $\lambda=3.4$ kcal mol^{-1}, in view of the following facts: the observed ΔG^* for the A$^-$/A couple is 2.2 kcal mol^{-1} when Z is $10^{11}\text{M}^{-1}\text{sec}^{-1}$, and the ΔG°-dependence of the observed rate constants can be elucidated by taking λ as 3.4 kcal mol^{-1}. Then, λ_0 can be quite small; this is consistent with the requirements of the second and third points.

Such a small λ value, however, cannot agree with that estimated non-empirically from Eq. (4), 12 kcal mol^{-1}. The agreement might be expected if the value of $1/D_{op}-1/D_s$ is one-fourth to one-third smaller than that calculated with the macroscopic D_s value or, consequently, if D_s is as small as 2 or 3. However, it is hardly probable that such a strong dielectric saturation occurs in the vicinity of hydrocarbon anions, which have an extensively-spread charge distribution.

In conclusion, the observed rate constants for the electron-transfer reactions between aromatic hydrocarbons and their anions depend on the parameters, *i.e.*, the standard free energy of reaction, the dielectric constant of the solvent, and the temperature, as a whole in some different way from that predicted by the theory of Marcus. This is inconsistent with the results of the previous investigations, which treated the parameters individually.[12b,16]

---

[14] C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Amer Chem. Soc.*, **87**, 5548 (1965).

[15] J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, New York (1970), p. 446.

[16] D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).

There is some possibility that the most fundamental assumption in the Marcus' theory, *i.e.*, the small overlap of the wave functions of reactants, might not be completely fulfilled in the reactions in which the aromatic hydrocarbons participate.