BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 808—812 (1973)

The Dependence of the Electron-transfer Rates of Aromatic Hydrocarbon Anion Radicals upon the Molecular Radii of the Reactants

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

(Received September 22, 1972)

The applicability of the theory of R. A. Marcus is tested, the behavior of the rate constant being examined as a function of the molecular radii of the reactants. The rate constants of the electron-transfer reactions from the anion radicals of pyrene, perylene, and tetracene to their respective parent molecules are measured under experimental conditions in which the anion radicals are in a free ion or loose ion-pair state. The rate constants thus obtained and subsequently corrected for diffusion are 2.8×10^9, 3.0×10^9, and 2.6×10^9 $M^{-1}sec^{-1}$ respectively, in 1,2-dimethoxyethane at 25°C. These rate constants, as well as others obtained elsewhere for naphthalene and anthracene, are compared with those predicted theoretically, assuming a spherical and an oblate spheroidal molecular shape. The consistence between the theoretical and experimental results is not satisfactory; the variation in the observed rate constants with the molecular radii of the reactants is much smaller than that expected theoretically. The spin-exchange rate constants for anion radicals of pyrene, perylene, and tetracene are also determined to be 7.0×10^9, 5.1×10^9, and 4.8×10^9 $M^{-1}sec^{-1}$ respectively, in the same solvent at 25°C.

The theoretical expression of R. A. Marcus for the rate constants of electron-transfer reactions contains the following parameters, adjustable experimentally: the standard free energy of reaction, the dielectric constant of the solvent, the temperature, and the molecular radii of the reactants.[1] In the preceding paper,[2] we have discussed the applicability of this theory to the electron transfer from polycyclic aromatic hydrocarbon anion radicals to their respective parent molecules by examining the dependence of the rate constants on the following three parameters: the standard free energy of reaction, the dielectric constant of the solvent, and the temperature. It has been revealed that the contribution to the activation free energy from the nuclear reorganization energy, especially from the reorganization energy of the solvent, is smaller than that predicted theoretically.

This paper will deal with the dependence of the rate constants of the last parameter mentioned above, *i.e.*, the molecular radii of the reactants, in the homogeneous electron-transfer reactions; the rate constants of elec-

---

[1] R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

[2] K. Suga and S. Aoyagui, This Bulletin, **46**, 755 (1973).

tron-transfer reactions from the pyrene, perylene, and tetracene anion radicals to their respective parent molecules are measured in 1,2-dimethoxyethane (DME) under experimental conditions in which the anion radicals are in a free ion or loose ion-pair state. A theoretical estimate of the rate constants is made on the assumption of spherical and non-spherical molecular shapes.

Experimental

The pyrene was purified in a way similar to that described previously.[2] G.R.-grade perylene and tetracene were obtained from the Tokyo Kasei Kogyo Co. and were used without further purification. The hydrocarbons were reduced with sodium metals in DME. The purification of the solvent and the preparation of radical solutions as well as the determination of their concentrations were performed in the same way as in the preceding paper.[2]

The rates of the electron-exchange reactions were determined ESR-spectroscopically by the conventional line-broadening method. Since the hyperfine lines in the ESR spectra of the anion radicals of perylene and tetracene were not perfectly resolved, their linewidth was determined by a computer-simulation method described elsewhere.[3] The linewidth parameter, l_2/l_1, was taken in this case in the way shown in Fig. 1. Figure 1(a) typically illustrates the central portion of the ESR spectra of the perylene anion radical, while (b) illustrates that with added perylene. In Fig. 2 the calculated l_2/l_1 values of the simulated spectra are plotted by triangles *versus* ΔH^{t}_{pp}, the given width of the hypothetical, unoverlapped hyperfine lines. The apparent linewidths of the overlapped hyperfine lines obtained from the simulated spectra are designated as ΔH^{a}_{pp} and are shown by circles in the same figure. The latter plot shows that the direct measurement of the linewidth is not practicable when the observed or apparent linewidth is larger than 0.15 Gauss in the case of perylene. Simulation was performed on a JEOL JRA-5 spectrum computer. As for the pyrene anion, on the other hand, its linewidth was determined according to a procedure described previously.[2]

All the measurements were carried out at 25°C.

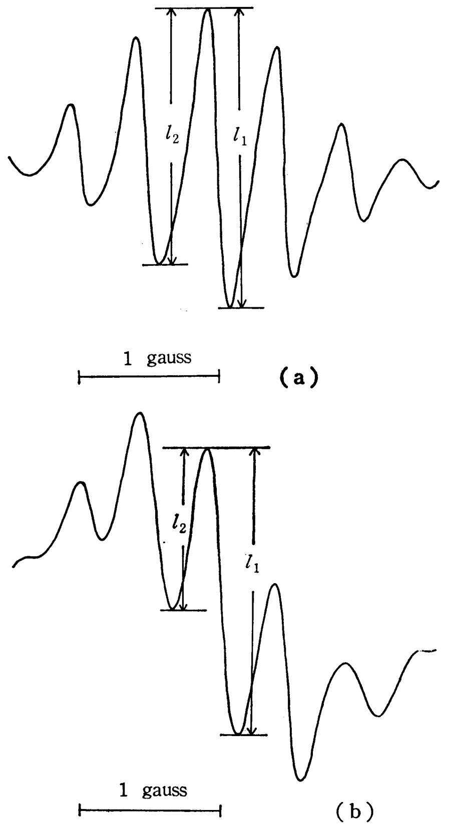

Fig. 1. Central portion of the ESR spectrum of the perylene anion radical: (a) without perylene added, (b) with perylene added.

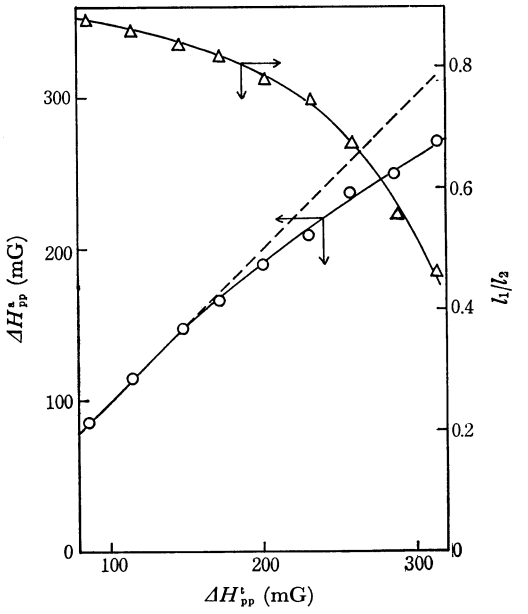

Fig. 2. Calculated l_2/l_1 values of the simulated spectra and the apparent linewidth (ΔH^{a}_{pp}) *vs.* the given linewidth of the hypothetical unoverlapped hyperfine lines (ΔH^{t}_{pp}).

Results

Figures 3, 4, and 5 illustrate the increase in linewidth due to electron exchange plotted against the concentrations of perylene, pyrene, and tetracene respec-

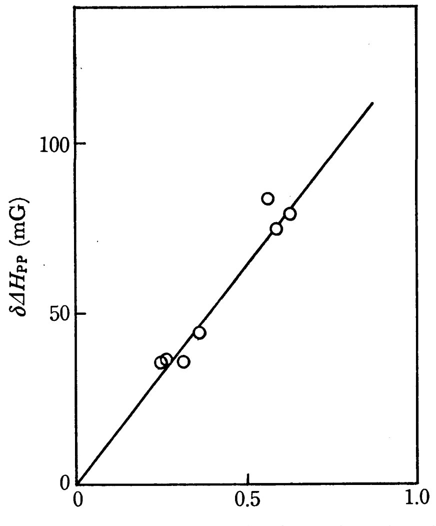

Fig. 3. Increase in the linewidth of the ESR spectrum of perylene anion due to electron exchange ($\delta\Delta H_{PP}$) *vs.* concentration of added perylene.

---

[3] T. Saji and S. Aoyagui, This Bulletin, in press.

TABLE 1. RATE CONSTANTS OF ELECTRON EXCHANGE REACTIONS BETWEEN AROMATIC HYDROCARBONS AND THEIR RESPECTIVE ANION RADICALS, AND MOLECULAR DIMENSIONS OF REACTANTS

Hydrocarbon	k_{obs}(M^{-1} sec^{-1})	k_a(M^{-1} sec^{-1})	d_1 (Å)	d_2 (Å)	d_3 (Å)
Naphthalene	1.6×10^{9}[a)]	2.1×10^{9}	7.85	5.7	3.44
Anthracene	1.8×10^{9}[b)]	2.4×10^{9}	10.3	5.7	3.44
Tetracene	1.9×10^{9}	2.6×10^{9}	12.75	5.7	3.44
Pyrene	2.0×10^{9}	2.8×10^{9}	9.87	7.85	3.44
Perylene	2.1×10^{9}	3.0×10^{9}	9.87	7.85	3.44

a) R. Change and C. S. Johnson, Jr., *J. Amer. Chem. Soc.*, **88**, 2338 (1966). b) Ref. 2.

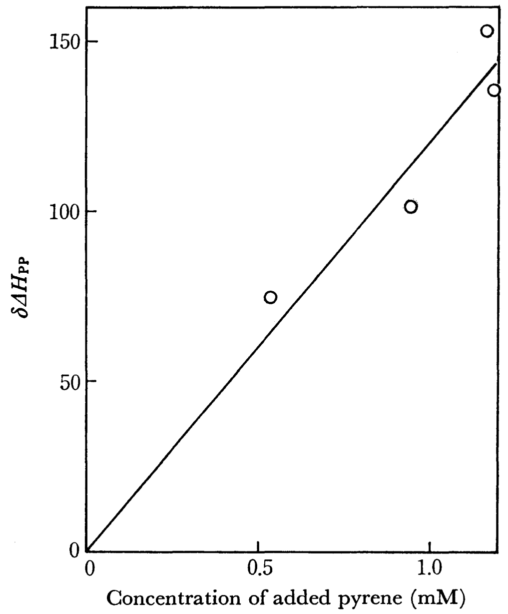

Fig. 4. Increase in the linewidth of the ESR spectrum of pyrene anion due to electron exchange ($\delta\Delta H_{PP}$) *vs.* concentration of added pyrene.

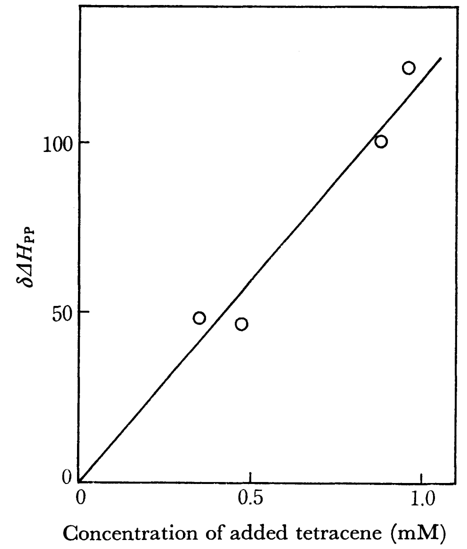

Fig. 5. Increase in the linewidth of the ESR spectrum of tetracene anion due to electron exchange ($\delta\Delta H_{PP}$) *vs.* concentration of added tetracene.

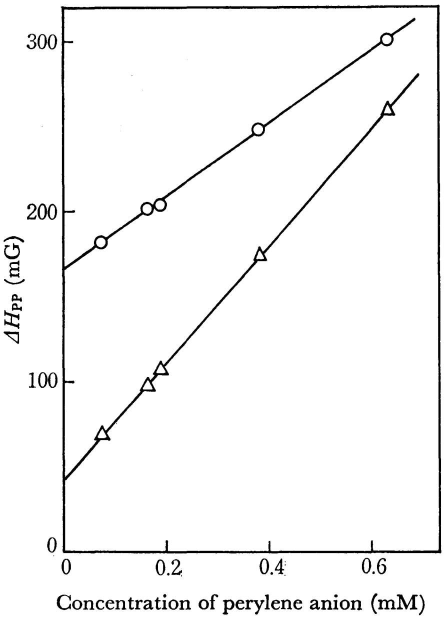

Fig. 6. Linewidth determined from the l_2/l_1 values of the observed spectra (ΔH_{PP}) *vs.* concentration of perylene anion radical. ○: observed linewidth for the solution containing both perylene and its anion radical ([Per$^-$]+[Per]= 0.95 mM), △: linewidth subtracted by the contribution due to electron exchange between perylene and its anion radical.

tively. The rate constants with and without correction for diffusion were determined from these figures according to the procedure described previously. They are presented in Table 1, designated as k_a and k_{obs} respectively. The values for the linewidth determined from the l_2/l_1 values of the observed spectra are typically plotted by circles *versus* the concentration of the perylene anion radicals in Fig. 6. The linearity of the plot was satisfactory; it supports this procedure in linewidth determination. The plot shown by triangles in the same figure is the linewidth from which the contribution due to electron exchange is eliminated; it corresponds to pure electron exchange. The second-order rate constant of a spin-exchange process between anion radicals can be determined from the slope of the latter plot.[4,5] The rate constants of the spin-exchange process thus determined are listed in Table 2. The diffusion-con-

TABLE 2. RATE CONSTANTS OF SPIN EXCHANGE PROCESS

Hydrocarbon anion radical	k (M^{-1} sec^{-1})
Pyrene$^-$	7.0×10^{9}
Perylene$^-$	5.1×10^{9}
Tetracene$^-$	4.8×10^{9}

---

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

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

trolled rate constant calculated theoretically is $7.2\times10^9 M^{-1}sec^{-1}$.[4,5] The agreement between the experimental and theoretical values was satisfactory. This may be another support of the present procedure of linewidth determination.

Discussion

According to the theory of Marcus,[1,6] the rate constant of an electron-exchange reaction, whose standard free energy is zero, is dependent on the molecular radii of the reactants. When the contribution to the activation free energy from the reorganization free energy of the inner-coordination shell can be neglected, the rate constant is expressed by the following equation:

$$k = Z\exp(-\Delta G^*/\boldsymbol{R}T) \qquad (1)$$

with:

$$\Delta G^* = (e^2/4)(1/2a_1+1/2a_2-1/r)(1/D_{op}-1/D_s) \qquad (2)$$

where Z is the bimolecular collision number of the hypothetical uncharged reactants in solution at a unit concentration (it is assumed to be $10^{11}M^{-1}sec^{-1}$ in this paper); ΔG^* is the activation free energy; a_1 and a_2 are the molecular radii of the reactants; r is the distance between the centers of the reactants within the activated complex, and D_{op} and D_s are the static and the optical dielectric constants of the solvent respectively.

In deriving the equations above, Marcus assumed the reactants to be spherical. However, in the electron-transfre reactions discussed here the reactants, *i.e.*, the aromatic hydrocarbons and their anion radicals, are not spherical but planar. Hence, we shall examine the dependence of the electron-transfer rates on the molecular radii of reactants using two models, the spherical and the non-spherical models. In each case, a knowledge of the geometry and dimensions of the reactant molecules is required. Table 1 shows the molecular dimensions of several polycyclic aromatic hydrocarbons. The d_1, d_2, and d_3 dimensions have been defined previously.[2]

Spherical Model. In this model, the reactants are assumed to be spherical. If $a_1=a_2=r/2=a$ is assumed as usual, the activation free energy is given by the following equation:

$$\Delta G^* = (1/8)(1/D_{op}-1/D_s)(e^2/a) \qquad (3)$$

Consequently, the activation free energy can be expected to be inversely proportional to a, the molecular radius of the reactants.

The values for the rate constant, k_{calc}, calculated from Eqs. (3) and (1) with $a=\sqrt{d_1d_2/2}$ and $Z=10^{11} M^{-1}sec^{-1}$ assumed, are shown in Table 3. They are considerably smaller than the corresponding values for the corrected observed rate constants. Furthermore, the variation in the calculated rate constants with the molecular radii of the reactants is larger than that in the observed values.

The behavior of the observed rate constants might agree with that of the calculated ones, when it is assumed that the solvent around the reactants is dielectrically saturated to have a dielectric constant of about 3. Such a strong saturation, however, probably cannot be realized in the present reactions, in which the reactants have a π-electron distribution spread extensively. The idea of a spherical model for a planar molecule must be discarded.

Non-spherical Model. In this model each reactant is assumed to be an oblate spheroid. In the theoretical estimate of ΔG^* according to Marcus, the free energy of the non-equilibrium polarization of a solvent must be calculated.[1] Such a calculation is quite difficult when the shape of reactants is not spherical. Hush[7] has derived an expression for ΔG^* almost identical with that of Marcus. His theory, however, is based on an assumption of an equilibrium polarization of the solvent. His reasoning is: the electron-transfer occurs through the activated complex, in which the probability of the electron being on one of the reactants is intermediate between the probabilities it has in the initial and final states; the solvent around the reactants stays in thermal equilibrium with the ionic charge. Consequently, if the non-spherical ions are in thermal equilibrium with the solvent and if their free energy of solvation can be calculated, the ΔG^* value for non-spherical reactants can be obtained.

According to Soma and Yamagishi,[8] the solvation free energy of an oblate spheroid, with a major axis of length of $2a$ and a minor axis of length of $2c$, is given by;

$$\Delta G_{solv} = -(q^2/2\sqrt{a^2-c^2})(1-1/D_s)\tan^{-1}\sqrt{(a^2-c^2)/c^2} \qquad (4)$$

where q is the charge of the spheroid. If an aromatic hydrocarbon is considered as an oblate spheroid with

TABLE 3. COMPARISON OF CORRECTED OBSERVED RATE CONSTANTS WITH CALCULATED RATE CONSTANTS BASED ON TWO MODELS

Hydrocarbon	$\sqrt{d_1d_2/2}$ (Å)	a^* (Å)	$k_{calc}(M^{-1}sec^{-1})$ Spherical model $a=\sqrt{d_1d_2/2}$	Non-spherical model $r=d_3$	Non-spherical model $r=2d_3$	k_a $(M^{-1}sec^{-1})$
Naphthalene	3.35	2.70	2.55×10^7	1.45×10^9	5.37×10^5	2.1×10^9
Anthracene	3.88	3.05	6.90×10^7	1.34×10^9	6.50×10^6	2.4×10^9
Tetracene	4.27	3.30	1.42×10^8	5.26×10^{10}	1.78×10^7	2.6×10^9
Pyrene	4.40	3.42	1.72×10^8	9.51×10^{10}	3.52×10^7	2.8×10^9
Perylene	4.40	3.42	$1.72\times10_8$	9.51×10^{10}	3.52×10^7	3.0×10^9

---

[6] R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).

[7] N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1967).

[8] M. Soma and H. Yamagishi, presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

$a=\sqrt{d_1d_2/2}$ and $c=d_3/2$, ΔG^* can be calculated from the following equation:

$$\Delta G^* = (e^2/4)(1/2a_1^*+1/2a_2^*-1/r)(1/D_{\text{op}}-1/D_{\text{s}}) \tag{5}$$

with:

$$1/a^* = (1/\sqrt{a^2-c^2})\tan^{-1}\sqrt{(a^2-c^2)/c^2} \tag{6}$$

The a^* values of each reactant have been calculated from the values of d_1, d_2, and d_3 in Table 1 and are listed in Table 3. Considering that r is fixed rather indefinetely in this case, this quatity is just an adjustable parameter even in the non-empirical calculations. The values for k_{calc} calculated from Eqs. (5), (6), and (1) with $r=d_3$ or $r=2d_3$ are tabulated in Table 3. When r is assumed to be d_3, on the other hand, the values for k_{calc} are much smaller than those for k_{a}. In either case, the variation in the calculated values with the molecular radii of the reactants is larger than that in the observed values. Consequently, even if r takes an appropriate value between d_3 and $2d_3$, k_{calc} does not agree with k_{a}.

Thus, the theory of Marcus, in both its original form (spherical model treatment) and its modified form (non-spherical model treatment), has failed to predict the experimental behavior of the rate constant as a function of the molecular radius. This suggests that the contribution to the activation free energy from the reorganization free energy of the solvent is again smaller than that predicted theoretically, as was seen in the previous paper concerning other parameters.