© 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 358—362 (1982) [Vol. 55, No. 2

The Electron Exchange Rates of Anthracene/Anthracene Radical Anion Ion-paired with Various Tetraalkylammonium Cations

Kosaku Suga* and Shigeru Aoyagui

Department of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152

(Received March 13, 1981)

The electron exchange reaction between anthracene and its radical anion formed by the sodium reduction of the parent molecule in 1,2-dimethoxyethane, tetrahydrofuran, and a tetrahydrofuran-1,4-dioxane mixture was studied by ESR spectroscopy in the preseuce of tetraalkylammonium cations of various kinds and amounts. Analytical equations were presented to evaluate the rate constants of two competitive electron exchange reactions between anthracene and its anion, which was ion-paired in part with a tetraalkylammonium cation and in part with a sodium cation. The experimental results obeyed the theoretical equations and, consequently, yielded the electron exchange rate constants for the ion pairs of the former type, which were unaffected by the coexistence of the ion pairs of the latter type. They were of the order of $10^8\ \mathrm{M^{-1}\,s^{-1}}$ ($1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$), a value which was one order of magnitude smaller than the rate constant for the solvent-separated ion pair of anthracene anion with sodium cation. They were smaller for tetraalkylammonium cations with longer carbon chains. These findings are discussed on the basis of the theory of Marcus.

It is a well-known fact that a solution of anthracene radical anion (A^-) formed by sodium reduction of anthracene (A) in tetrahydrofuran (THF) gives an ESR spectrum with hyperfine splittings due to ^{23}Na, besides those due to ^{1}H.[1,2] This specific splitting pattern is considered to be evidence for the tight ion-pairing between $\mathrm{Na^+}$ and A^-. In a previous paper[2] we reported a finding that the ^{23}Na-splittings disappeared on addition of tetrabutylammonium perchlorate ($\mathrm{Bu_4NClO_4}$) to this solution, and suggested that A^- formed a more stable ion pair with $\mathrm{Bu_4N^+}$ than with $\mathrm{Na^+}$. By using a solution of this composition, measurements were made on the electron exchange rate constants for a few redox systems of aromatic hydrocarbons and their radical anions ion-paired with $\mathrm{Bu_4N^+}$. No kinetic information had been available concerning the electron transfer reaction of ion pairs, except those of alkali metal cations.

In that work, however, no regard was paid on other kinds of ion pairs coexisting with those between $\mathrm{Bu_4N^+}$ and A^-. According to Hirota *et al.*[3] sodium dihydroanthrylide (NaA) in THF exists as the following chemical species: the free anion, A^-, the loose or solvent-separated ion pair, $\mathrm{Na^+}\!:A^-$, and the tight ion pair, $\mathrm{Na^+}\cdot A^-$. Conductometrically, A^- can be distinguished from the others and ESR-spectroscopically, $\mathrm{Na^+}\cdot A^-$ can be distinguished. Consequently, there is an unfortunate possibility that our previous rate constant for the A/A^- electron exchange in the presence of $\mathrm{Bu_4N^+}$ was an average of the rate constants for the reactions in which A^-, $\mathrm{Na^+}\!:A^-$, $\mathrm{Bu_4N^+}\!:A^-$, and $\mathrm{Bu_4N^+}\cdot A^-$ participated. $\mathrm{Na^+}\cdot A^-$ is excluded on the basis of the previous finding described above.

This paper presents an analytical procedure to obtain the rate constant for the electron exchange between an aromatic hydrocarbon and its anion ion-paired with a tetraalkylammonium cation in the presence of the ion pair with $\mathrm{Na^+}$. It is applied to the redox systems of A/A^- ion-paired with various kinds of tetraalkylammonium cations ($\mathrm{R_4N^+}$).

Experimental

Anthracene was recrystallized twice from benzene. The perchlorates of tetrabutylammonium, tetrapropylammonium ($\mathrm{Pr_4N^+}$), tetraethylammonium ($\mathrm{Et_4N^+}$), and tetramethylammonium ($\mathrm{Me_4N^+}$) were prepared from perchloric acid and the respective tetraalkylammonium iodides ($\mathrm{R_4NI}$). They were recrystallized from water and then from ethylacetate. $\mathrm{Bu_4NI}$ was synthesized by the usual methods from tributylamine and butyl iodide. Other iodides, including tetraamylammonium iodide ($\mathrm{Am_4NI}$), were commercially obtained.

The purification of the solvents used, THF, 1,2-dimethoxyethane (DME), and 1,4-dioxane (DO) and the preparation of the test solution were performed in the same way as described previously.[4] Sodium metal was used as the reducing agent.

The electron-transfer rates at 25±2°C were determined by the conventional method based on the line broadening of ESR spectra. A JEOL Model JES-3BSX spectrometer was used.

Analytical Procedure

The following ion pairs may exist in a solution containing NaA and a large excess of $\mathrm{R_4NClO_4}$: $\mathrm{Na^+}\!:A^-$, $\mathrm{R_4N^+}\cdot A^-$, $\mathrm{R_4N^+}\!:A^-$, $\mathrm{Na^+\cdot ClO_4^-}$, $\mathrm{Na^+\!:ClO_4^-}$, $\mathrm{R_4N^+\cdot ClO_4^-}$, and $\mathrm{R_4N^+\!:ClO_4^-}$. Since we cannot distinguish between $\mathrm{R_4N^+}\cdot A^-$ and $\mathrm{R_4N^+}\!:A^-$, $\mathrm{R_4N^+\cdot ClO_4^-}$ and $\mathrm{R_4N^+\!:ClO_4^-}$, and $\mathrm{Na^+\cdot ClO_4^-}$ and $\mathrm{Na^+\!:ClO_4^-}$, these couples of ion pairs are denoted by the common formulae $\mathrm{R_4N^+A^-}$, $\mathrm{R_4N^+ClO_4^-}$, and $\mathrm{Na^+ClO_4^-}$, respectively.

Among these ion pairs and the free ions the following equilibria are established:

$$\mathrm{Na^+ + A^- \overset{K_1}{\rightleftharpoons} Na^+\!:A^-}, \tag{1}$$

$$\mathrm{R_4N^+ + A^- \overset{K_2}{\rightleftharpoons} R_4N^+A^-}, \tag{2}$$

$$\mathrm{R_4N^+ + ClO_4^- \overset{K_3}{\rightleftharpoons} R_4N^+ClO_4^-}, \tag{3}$$

$$\mathrm{Na^+ + ClO_4^- \overset{K_4}{\rightleftharpoons} Na^+ClO_4^-}, \tag{4}$$

where the K's are the formation constants of the ion pairs.

When the concentration of A^- is much smaller than that of $\mathrm{Na^+\!: A^-}$, which is true of solutions of low dielectric constants, the anthracene molecules added to this solution undergo the following electron exchange reactions:

$$\mathrm{Na^+\!: A^-} + \mathrm{A} \overset{k_1}{\rightleftharpoons} \mathrm{A} + \mathrm{Na^+\!: A^-}, \tag{5}$$

$$\mathrm{R_4N^+A^-} + \mathrm{A} \overset{k_2}{\rightleftharpoons} \mathrm{A} + \mathrm{R_4N^+A^-}, \tag{6}$$

where k's are the electron-exchange rate constants. The values for the coupling constant and the line width of the ESR spectrum of a solution containing $\mathrm{Na^+\!: A^-}$ and $\mathrm{R_4N^+A^-}$ should be, respectively, the average values for the spectra of these ion pairs, if the following exchange reaction is sufficiently fast:

$$\mathrm{Na^+\!: A^-} + \mathrm{R_4N^+A^-} \rightleftharpoons \mathrm{R_4N^+A^-} + \mathrm{Na^+\!: A^-}. \tag{7}$$

This condition may be fulfilled, since the solution containing NaA and $\mathrm{R_4NClO_4}$ gave only a single ESR spectrum similar to that of free $\mathrm{A^-}$. Therefore, it is assumed after Stevenson *et al.*[5] that the observed increase in line width is equal to the weighted mean of the increases due to Reactions 5 and 6. Then the observed rate constant, k, can be expressed in terms of k_1 and k_2 as follows:

$$\begin{aligned} k &= (k_1[\mathrm{Na^+\!: A^-}] + k_2[\mathrm{R_4N^+A^-}])/([\mathrm{Na^+\!: A^-}] + [\mathrm{R_4N^+A^-}]) \\ &= (k_1 + k_2K_2[\mathrm{R_4N^+}]/K_1[\mathrm{Na^+}])/(1 + K_2[\mathrm{R_4N^+}]/K_1[\mathrm{Na^+}]), \end{aligned} \tag{8}$$

where the brackets mean the concentration in molarity.

When it is assumed that the K values are large enough for the existence of any free ions to be neglected, which may be true of solvents of low dielectric constant such as THF, DME, and DO, Eq. 8 can be rewritten as follows (see Appendix):

$$k = k_2 + (k_1-k_2)/(1 + K_2K_4[\mathrm{R_4NClO_4}]_0/K_1K_3[\mathrm{A^-}]_0), \tag{9}$$

where the subscript 0 denotes the analytical concentration of the substance indicated. Equation 9 can be linearized with respect to $[\mathrm{R_4NClO_4}]_0$ or its inverse in the following forms:

$$(k_1-k)^{-1} = K^{-1}(k_1-k_2)^{-1}[\mathrm{R_4NClO_4}]_0^{-1} + (k_1-k_2)^{-1}, \tag{10}$$

or

$$(k-k_2)^{-1} = K(k_1-k_2)^{-1}[\mathrm{R_4NClO_4}]_0 + (k_1-k_2)^{-1}, \tag{11}$$

with

$$K = K_2K_4/K_1K_3[\mathrm{A^-}]_0. \tag{12}$$

When the k_1 value is known, the k_2 value can be obtained from the intercept of a linear plot of $(k_1-k)^{-1}$ *vs.* $[\mathrm{R_4NClO_4}]_0^{-1}$ and the K value can be obtained from the intercept and the slope together. When k_1 is not known, measurements must be made by using a concentration $[\mathrm{R_4NClO_4}]_0$ high enough for the relation $K[\mathrm{R_4NClO_4}]_0 \gg 1$ to be satisfied. Then Eq. 9 can be adequately approximated by the following linear relation between k and $[\mathrm{R_4NClO_4}]_0^{-1}$:

$$k = k_2 + (k_1-k_2)/K[\mathrm{R_4NClO_4}]_0. \tag{13}$$

The k_2 value is obtained from the intercept of the linear plot drawn after Eq. 13. The k_1 value can then be obtained from the intercept and the slope together.

Results and Discussion

ESR Spectra of NaA in Solutions with and without R_4N^+. The ESR spectrum of NaA in THF exhibited hyperfine splittings due to ^{23}Na, whereas that in DME did not. The ^{23}Na hyperfine coupling constant was as large as 0.15 mT for a 1:1 THF–DO mixed solution whose dielectric constant was lower than that of THF. According to Hirota *et al.*[3] the ion-pairing reaction of $\mathrm{A^-}$ with $\mathrm{Na^+}$ and the conversion reaction between $\mathrm{Na^+\cdot A^-}$ and $\mathrm{Na^+\!: A^-}$ are both very rapid and, consequently, the ^{23}Na hyperfine coupling constant of the ion pair is the mean value of the coupling constants for $\mathrm{Na^+\cdot A^-}$ and $\mathrm{Na^+\!: A^-}$ or $\mathrm{A^-}$.

No ^{23}Na hyperfine structure was observed in the spectra for 0.1 mM NaA solutions in THF and THF–DO when they contained more than 0.5 mM $\mathrm{R_4NClO_4}$ (R=Me, Et, Pr, Bu, and Am). This result can be explained on the basis of the ion-pair concept of Hirota *et al.* in the following way: most anthracene anions in DME exist as $\mathrm{A^-}$ and $\mathrm{Na^+\!: A^-}$; in THF and THF–DO containing no $\mathrm{R_4N^+}$, a part of the anthracene anions exist as $\mathrm{Na^+\cdot A^-}$; in the presence of $\mathrm{R_4N^+}$, however, $\mathrm{Na^+\cdot A^-}$ may be converted into $\mathrm{R_4N^+\cdot A^-}$ and $\mathrm{R_4N^+\!: A^-}$. The analytical equations derived above are based on these premises.

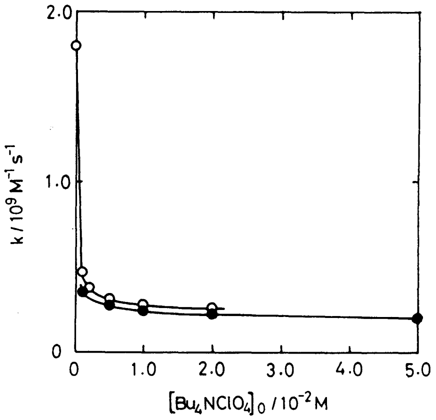

Fig. 1. Dependence of the electron-exchange rate constants for A/$\mathrm{A^-}$ in (○) DME and (●) THF on the concentration of added $\mathrm{Bu_4NClO_4}$, $[\mathrm{Bu_4NClO_4}]_0$.

Dependence of k on $[Bu_4NClO_4]_0$. Figure 1 shows the rate constants for the electron exchange reactions between anthracene and its radical anion in THF and DME at various $\mathrm{Bu_4NClO_4}$ concentrations. The k value in DME decreases very rapidly with increasing $[\mathrm{Bu_4NClO_4}]_0$ and then decreases gradually, approaching the value of *ca.* 2×10^8 $\mathrm{M^{-1}\,s^{-1}}$. The k *vs.* $[\mathrm{Bu_4NClO_4}]_0$ curve in THF also behaves in a similar way. The k value at $[\mathrm{Bu_4NClO_4}]_0=0$ in DME, 1.8×10^9 $\mathrm{M^{-1}}$ $\mathrm{s^{-1}}$, was taken from our previous paper.[4] This is regarded as the k_1 value. The same quantity in THF could not be obtained from ESR spectra, because ^{23}Na hyperfine lines due to $\mathrm{Na^+\cdot A^-}$ made them too complicated to be analyzed. The k *vs.* $[\mathrm{R_4NClO_4}]_0$ curves for $\mathrm{Pr_4NClO_4}$ and $\mathrm{Et_4NClO_4}$ in DME are shown in Fig. 2. Because of the low solubility of these salts, the available concentration ranges were much narrower than the range for $\mathrm{Bu_4NClO_4}$.

Evaluation of k_2. The $(k_1-k)^{-1}$ *vs.* $[\mathrm{R_4NClO_4}]_0^{-1}$ plot for $\mathrm{Bu_4NClO_4}$ in DME is shown in Fig. 3. The

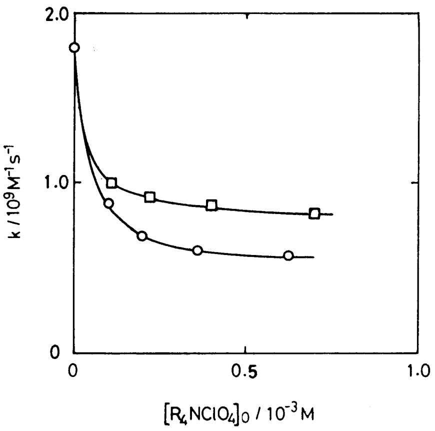

Fig. 2. Dependence of the electron-exchange rate constants for A/A$^-$ in DME on the concentrations of (□) Et_4NClO_4 and (○) Pr_4NClO_4.

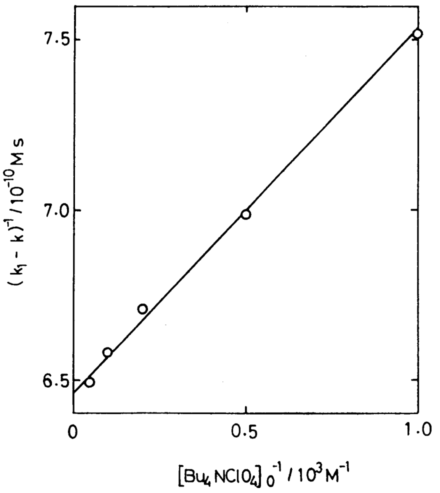

Fig. 3. $(k_1-k)^{-1}$ *vs.* $[Bu_4NClO_4]_0^{-1}$ in DME plotted after Eq. 10.

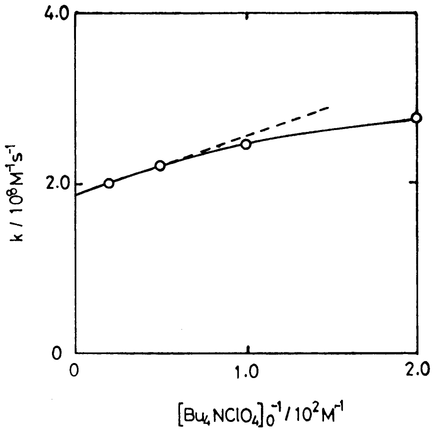

Fig: 4. k *vs.* $[Bu_4NClO_4]_0^{-1}$ in THF plotted after Eq. 13.

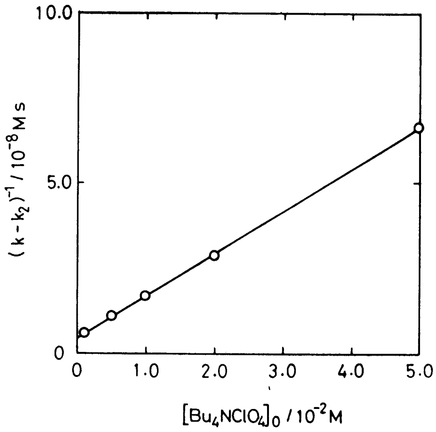

Fig. 5. $(k-k_2)^{-1}$ *vs.* $[Bu_4NClO_4]_0$ in THF plotted after Eq. 11.

experimental points lie on a straight line in accord with the theoretical requirement of Eq. 10. The values for k_2 and K were obtained, respectively, as 2.5×10^8 M^{-1} s^{-1} and 4.8×10^3 M^{-1}.

Since the k_1 value in THF is not known, the k_2 value in this solvent was determined to be 1.8×10^8 M^{-1} s^{-1} from the intercept of the k *vs.* $[Bu_4NClO_4]_0^{-1}$ plot at $[Bu_4NClO_4]_0\rightarrow\infty$ in Fig. 4. The linearity of the experimental plot of $(k-k_2)^{-1}$ *vs.* $[Bu_4NClO_4]_0$ was excellent, as is shown in Fig. 5. On the basis of Eq. 11 the k_1 and K values were obtained, respectively, as 5×10^8 M^{-1} s^{-1} and 2.5×10^2 M^{-1}. However, it should be noted that this k_1 value was obtained at the infinite dilution of Bu_4NClO_4 at which the tight ion pair $Na^+\cdot A^-$ exists. Thus, the physical meaning of k_1 in THF is less clear than that in DME. The difference between the k_1 values in THF and DME may be caused by these circumstances, rather than the difference between the solvent properties.

The literature values for K_1 and $K_3(Bu_4N^+ClO_4^-)$ in THF at 25 °C are 2.3×10^5 M^{-1} [6] and 1.6×10^6 M^{-1}, [7] respectively. The $[A^-]_0$ value was held constant at about 10^{-4} M. According to Eq. 12 and the K value just obtained, the product K_2K_4 would be of the order of 10^{10} M^{-2}. Although neither K_2 nor K_4 is known, this may be a reasonable value, because most of the association constants in THF at 25 °C fall in the range of 10^4—10^6 M^{-1}. [7-9]

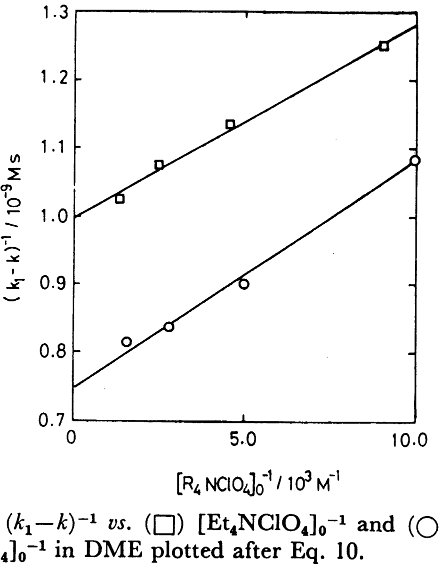

Fig. 6. $(k_1-k)^{-1}$ *vs.* (□) $[Et_4NClO_4]_0^{-1}$ and (○) $[Pr_4NClO_4]_0^{-1}$ in DME plotted after Eq. 10.

Equation 9 has been derived under the condition $[R_4NClO_4]_0 \gg [A^-]_0$. Though this condition was not fulfilled in the DME solutions of Pr_4NClO_4 and Et_4NClO_4, as seen in Fig. 2, the $(k_1-k)^{-1}$ *vs.* $[R_4NClO_4]_0$ plots in Fig. 6 exhibited the linearity required by Eq. 10 and yielded the following k_2 and K values: $k_2=4.6\times10^8$ (Pr_4NClO_4) and 8.1×10^8 (Et_4NClO_4) $M^{-1}s^{-1}$; $K=3.4\times10^4$ (Pr_4NClO_4) and 2.3×10^4 (Et_4NClO_4) M^{-1}.

These K values are compared with the value 4.8×10^3 M^{-1} for the Bu_4NClO_4 case. It may be safe to conclude that $K_2=KK_1K_3[A^-]_0/K_4$ is larger for smaller R_4N^+ ions, because K_3 may be larger for smaller ions and K_1, K_4, and $[A^-]_0$ are invariable.

TABLE 1. RATE CONSTANTS FOR ELECTRON-EXCHANGE REACTIONS BETWEEN $R_4N^+A^-$ AND A IN DIFFERENT SOLVENTS

R_4NClO_4	$k_2/10^8\ M^{-1}\ s^{-1}$		
	DME	THF	THF+DO (1 : 1)
Et_4NClO_4	8.1	(7.5)$^{b)}$	(6.6)$^{d)}$
Pr_4NClO_4	4.6	(4.9)$^{c)}$	(3.8)$^{d)}$
Bu_4NClO_4	2.5	1.8	(2.9)$^{e)}$
Am_4NClO_4	(1.5)$^{a)}$		

a) Obtained only with a 1 mM Am_4NI solution. b) Obtained only with a saturated solution of Et_4NClO_4 whose concentration is less than 5 mM. c) Obtained only with a 5 mM Pr_4NClO_4 solution. d) Obtained only with a saturated solution of R_4NClO_4. e) Obtained only with a 1 mM Bu_4NClO_4 solution.

The k_2 values thus obtained are summarized in Table 1. This also shows some approximate k_2 values in parentheses. Each of them was obtained at a fixed R_4NClO_4 concentration. Consequently, they should be averages of the real values for k_1 and k_2. However, the contribution of k_1 cannot be important, because k_1 and k_2 are of the same order and, furthermore, Figs. 1 and 2 suggest that anthracene anion should exist exclusively as $R_4N^+A^-$ under the given experimental conditions. In fact, the previously reported k value in THF containing 20 mM Bu_4NClO_4, 2.0×10^8 M^{-1} s^{-1},[2] is in good agreement with the k_2 value described above, 1.8×10^8 M^{-1} s^{-1}. This agreement points to the validity of the previous rate constant values obtained with no consideration of the competing reaction of Eq. 2. This may be due to the high Bu_4NClO_4 concentration which would make Na^+: A^- negligible.

Table 1 shows that $R_4N^+A^-$ undergoes a slower electron exchange than Na^+: A^-, whose k value in DME is 1.8×10^9 M^{-1} s^{-1}, and that the electron exchange rate decreases with increasing length of alkyl carbon chain. The former finding is in contrast with the finding of Campion *et al.*[10] that the rate of electron exchange between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ in aqueous solutions is enhanced in the presence of R_4N^+ cations, whereas the latter agrees with theirs. However, it is doubtful that such a comparison makes sense. One of the reactants is uncharged in our experiments, but in theirs both reactants are highly charged and, consequently, the electrostatic repulsion between the reactants can have a serious effect on the electron exchange rate. They suggested that the ion-pairing of the reactant anions with R_4N^+ cations might reduce the effective charge on the reactants and thus might cause the enhancement in electron exchange rate. However, our experimental results show that the electrostatic effect is not the only effect of ion-pairing on the electron exchange rate.

The theories of electron transfer reaction which have been proposed so far are applicable only to reactions with the outer-sphere mechanism.[11] It is evident that the electron-transfer reaction between A and $R_4N^+A^-$ do not belong to this category of reaction. However, it may be worthwhile to extend the basic concept of nuclear rearrangement in the Marcus theory[12] to the reactions of our present concern. The intervening of R_4N^+ between A and A^- elongates their separation; the elongation may be greater for R_4N^+ with longer carbon chains. According to the theory, such a longer distance can account for the higher outer-sphere reorganization energy and, in turn, for the lower reaction rate. Furthermore, the intervening of R_4N^+ may decrease the activation entropy and, consequently, the rate constant, because the effective collision number in the electron exchange between $R_4N^+A^-$ and A may be smaller than that between A^- and A. It is probable that these effects are reflected in the observed rate constants.

Appendix

Derivation of Eq. 9. In solvents of low dielectric constants such as those used in this work, the concentrations of free ions are all negligible compared with those of the associated species. Then the following stoichiometric relations can be written among the chemical species existing in a solution containing sodium dihydroanthrylide and tetraalkylammonium perchlorate:

$$[R_4N^+A^-] + [R_4N^+ClO_4^-] = [R_4NClO_4]_0, \qquad (A1)$$

$$[Na^+:A^-] + [R_4N^+A^-] = [A^-]_0, \qquad (A2)$$

and

$$[Na^+ClO_4^-] = [R_4N^+A^-]. \qquad (A3)$$

When $[R_4NClO_4]_0 \gg [A^-]_0$, the terms $[R_4N^+A^-]$ and $[Na^+:A^-]$ can be neglected in comparison with $[R_4N^+ClO_4^-]$ and $[R_4N^+A^-]$, respectively. Consequently the following relations are obtained:

$$[R_4NClO_4]_0 = [R_4N^+ClO_4^-] = K_3[R_4N^+][ClO_4^-], \qquad (A4)$$

and

$$[A^-]_0 = [Na^+ClO_4^-] = K_4[Na^+][ClO_4^-], \qquad (A5)$$

which lead to the relation

$$[R_4N^+]/[Na^+] = K_4[R_4NClO_4]_0/K_3[A^-]_0. \qquad (A6)$$

Equation 9 in the text can be obtained from Eqs. 8 and A6.

References

1) A. Crowley, N. Hirota, and R. Kreilick, *J. Chem. Phys.*, **46**, 4815 (1967).

2) K. Suga and S. Aoyagui, *Bull. Chem. Soc. Jpn.*, **45**, 1375 (1972).

3) N. Hirota, R. Carraway, and W. Schook, *J. Am.*

Chem. Soc., **90**, 3611 (1968).

4) K. Suga and S. Aoyagui, *Bull. Chem. Soc. Jpn.*, **46**, 755 (1973).

5) G. R. Stevenson, R. Concepcion, and I. Ocasio, *J. Phys. Chem.*, **80**, 861 (1976).

6) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966).

7) C. Treiner and J. C. Justice, *C. R. Acad. Sci.*, *Ser. C*, **269**, 1364 (1969).

8) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).

9) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

10) R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *Inorg. Chem.*, **6**, 672 (1967).

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

12) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).