Kinetics of Protonation of Sodium Anthracenide by Alcohols and Water in Dimethoxyethane. The Nature of Protonating and Protonated Species

A. Rainis, R. Tung, and M. Szwarc*

Contribution from the Department of Chemistry,
State University of New York, College of Environmental Science and Forestry,
Syracuse, New York 13210. *Received August 16, 1972*

Abstract: Kinetics of protonation of sodium anthracenide $(A\cdot^-,Na^+)$ in DME by alcohols and water was investigated by the stop-flow technique. Protonation by MeOH, EtOH, *i*-PrOH, and H_2O is first order in $A\cdot^-,Na^+$ but mixed first and second order in ROH; *i.e.*, the monomeric ROH and the dimeric $(ROH)_2$ seem to be the protonating agents. The rate of protonation by the latter (k_{p2}) is much faster than by the former (k_{p1}), namely, k_{p1} = 10.5, 6.5, 2.4, 0.57, and 2.2 M^{-1} sec^{-1}, while $k_{p2}K_d$ = 875, 310, 31, 0, and 62 M^{-2} sec^{-1} for MeOH, EtOH, *i*-PrOH, *t*-BuOH, and H_2O, respectively. K_d denotes the dimerization constant, $2ROH \rightleftarrows (ROH)_2$. Participation of dianions of anthracene $(A^{2-},2Na^+)$ is observed in the protonation by *t*-BuOH, although not in the reaction of other reagents. Owing to slow disproportionation, $2(A\cdot^-,Na^+) \rightleftarrows (A\cdot^-,Na^+)_2 \rightleftarrows (A^{2-},2Na^+;A) \rightleftarrows A^{2-},2Na^+ + A$, the stationary concentration of the "solvent caged" complex $(A^{2-},2Na^+;A)$ seems to be *higher* than that of the "diffused out of cage" $(A^{2-},2Na^+)$. Consequently, the pseudo-rate constant describing the reaction which is second order in $(A\cdot^-,Na^+)$ is only slightly affected by the variation of [A] although it increases with [ROH].

Kinetics of protonation of radical anions by alcohols or water has been studied recently by several research groups.[1-4] Protonation of sodium naphthalenide $(N\cdot^-,Na^+)$ by water in tetrahydrofuran (THF) was investigated by Bank and Bockrath[1] who found the reaction to be first order in both reagents pointing to the rate-determining character of the first proton addition (eq 1). This reaction is followed

$$N\cdot^-,Na^+ + H_2O \xrightarrow{k_1} NH\cdot + Na^+OH^- \qquad (1)$$

then by rapid steps 2 and 3 yielding dihydronaphtha-

$$NH\cdot + N\cdot^-,Na^+ \xrightarrow{\text{fast}} NH^-,Na^+ + N \qquad (2)$$

$$NH^-,Na^+ + H_2O \xrightarrow{\text{fast}} NH_2 + Na^+OH^- \qquad (3)$$

lene (NH_2). A search for transients, such as $NH\cdot$ or NH^-,Na^+, led to negative results, thus providing conformation for the above mechanism originally suggested by Paul, Lipkin, and Weissman.[5]

Protonation of various free-radical anions $(Ar\cdot^-)$, derived from aromatic hydrocarbons by means of pulse radiolysis, was investigated by Dorfman and his associates.[2] Pure alcohols or their mixtures with other solvents were the reaction media. The observed pseudo-first-order kinetics was accounted for by reaction 4. However, the resulting $ArH\cdot$

$$Ar\cdot^- + ROH \xrightarrow{k_4} ArH\cdot + RO^- \qquad (4)$$

radical probably was not converted into ArH^- because the concentration of $Ar\cdot^-$ in pulse radiolysis is exceedingly low. The large variation of k_4 observed in mixed solvents[2b] was attributed to the complexing of ROH with the other component of the solution and not to changes in the character of the solvation shell surrounding the $Ar\cdot^-$ ion.

Studies of the protonation of sodium perylenide $(Pe\cdot^-,Na^+)$ in THF by a variety of alcohols revealed the importance of dianions as the protonated species.[3] The disappearance of $Pe\cdot^-,Na^+$ followed second-order kinetics and the protonation was retarded by the parent hydrocarbon (Pe). Hence, in spite of its low concentration $Pe^{2-},2Na^+$ is the protonated reagent and the rate of its protonation exceeds by far the rate of protonation of $Pe\cdot^-,Na^+$. Nevertheless, the disproportionation, $2Pe\cdot^-,Na^+ \rightleftarrows Pe^{2-},2Na^+ + Pe$, is still capable of maintaining the equilibrium concentration of $Pe^{2-},2Na^+$ in the reaction and this accounts for its kinetics.

In their studies of protonation of sodium and potassium anthracenides $(A\cdot^-,Na^+$ and $A\cdot^-,K^+)$ by alcohols and water, Dye and his associates[4] focused their attention on the nature of the protonated species.[6] Their work indicated that the nature of ion pairs profoundly affects their reactivity, the protonation being by an order of magnitude faster in THF, where the salts presumably form tight (or tighter) ion pairs, than in dimethoxyethane (DME) where only loose ion pairs seem to be present. Moreover, extensive studies of protonation of $A\cdot^-,K^+$ in THF by ethanol demonstrated that dianions, $A^{2-},2K^+$ as well as dimeric radical ions, $(A\cdot^-,K^+)_2$ are the important protonated agents participating in the reaction. However, their presence was not revealed by a direct spectroscopic search.

Ours studies, described in this paper, overlap to some extent with Dye's investigation.[4] We followed the kinetics of protonation of $A\cdot^-,Na^+$ in DME by MeOH, EtOH, *i*-PrOH, *t*-BuOH, and H_2O, concentrating our attention on the nature of the protonating agents, since in our systems (*t*-BuOH being an exception) only the ion pairs $A\cdot^-,Na^+$ seemed to be the protonated species. We agree with Dye in finding

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(1) S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971).

(2) (a) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964); (b) J. R. Brandon and L. M. Dorfman, *ibid.*, **53**, 3849 (1970); (c) L. M. Dorfman, *Accounts Chem. Res.*, **3**, 224 (1970).

(3) G. Levin, C. Sutphen, and M. Szwarc, *J. Amer. Chem. Soc.*, **94**, 2652 (1972).

(4) E. R. Minnich, L. D. Long, J. M. Ceraso, and J. L. Dye, *ibid.*, in press.

(5) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

(6) We are indebted to Professor Dye for providing us with his manuscript prior to its publication.

the protonation of this salt by EtOH and H_2O in DME to be first order in radical anion; however, since the relevant rate constants of Dye were only approximate[4] the numerical comparison is not justified.

Experimental Section

The present investigation was limited to the study of the kinetics of protonation of $A\cdot^-,Na^+$ in DME by MeOH, EtOH, *i*-PrOH, *t*-BuOH, and H_2O. The solvent (Eastman) and the alcohols were commercially acquired, chemically pure reagents. DME was first dried with lithium aluminum hydride and then vacuum distilled into a storage bulb containing benzophenone ketyl and liquid sodium-potassium alloy. When needed, the solvent was withdrawn by vacuum distillation.

The alcohols were dried by distilling them from their solution of the appropriate sodium alcoholate. They were transferred on a high vacuum line into calibrated capillaries and then to glass ampoules equipped with break-seals, where dilution with the desired amount of solvent was accomplished. Such ampoules were eventually sealed off *in vacuo* and, when needed, attached to a manifold to be described later.

Solutions of $A\cdot^-,Na^+$ in DME were prepared by reducing anthracene (fluorescent grade) with metallic sodium. Such preparations are now standard and well known (see, *e.g.*, ref 7a and 7b) and also were performed on a high-vacuum line. The resulting solutions contained an excess of anthracene and a fourfold excess of rigorously dried Na^+,BPh_4^-, the latter being added to suppress the dissociation of $A\cdot^-,Na^+$ into free ions. The concentrations of A were calculated from the weight of the introduced hydrocarbon and $[A\cdot^-,Na^+]$ was determined spectrophotometrically (λ_{max} of $A\cdot^-,Na^+$ in DME is 730 nm, ϵ 1.0×10^4). The final solutions were stored in evacuated glass ampoules, each equipped with a break-seal.

The kinetics was studied by a stopped-flow technique, using a Durrum stopped-flow spectrophotometer with a 2-mm cuvette for faster reactions, and a more primitive, all glass device described elsewhere[7c] for slower kinetics. The progress of protonation was followed by recording the optical density of $A\cdot^-,Na^+$ at 730 nm (ϵ 1.0×10^4) as a function of time.

The ampoules containing the desired reagents were sealed to a glass manifold attached to a sample-handling unit. This unit involved a vacuum line and a connection through a scrubber containing a concentrated solution of sodium biphenylide in DME to a cylinder of purified, oxygen-free nitrogen. This unit was attached to the valve block of the Durrum instrument when it was used in the study. By opening the desired stopcocks the sample-handling unit could be evacuated (it was found to be vacuum tight). It was then filled with the purified N_2 and the reagents introduced into the unit by crushing the appropriate break-seals. By further manipulation of the appropriate stopcocks the driving syringes could be filled with the reagents. The driving syringes, the valve block, and other parts of the Durrum instrument were flushed several times with the reagents prior to the actual kinetic runs, and then 4–5 determinations were made at each concentration. The arrangement used in our studies permitted also dilution of the alcohol solutions by a required factor.

The kinetic results were displayed on a storage oscilloscope and photographed, when the Durrum instrument was used, or recorded on a chart of a Cary-14 spectrophotometer when the more primitive device was utilized (see ref 7c). The kinetic data obtained in repetitive runs agreed within 5%.

Results and Discussion

Protonation of $A\cdot^-,Na^+$ in DME by MeOH, EtOH, *i*-PrOH, *t*-BuOH, and H_2O was investigated at a constant temperature of 25 ± 1°. To ascertain the absence of free $A\cdot^-$ ions, an excess of sodium tetraphenylboride ($[Na^+,BPh_4^-] \sim 4 \times 10^{-3}$ *M*) was added to the investigated solutions. The initial concentration of $A\cdot^-,Na^+$ was approximately constant in most of the runs, being about 1×10^{-3} *M*, while the concentration of the protonating reagents was varied from the lowest value of about 5×10^{-3} *M* up to about 1×10^{-1} *M*. Hence, in all our experiments $[ROH] \gg [A\cdot^-,Na^+]_0$, a feature which simplifies the kinetics of the reaction.

The product of protonation is 9,10-dihydroanthracene. It has been shown[4] that the intermediate products, *i.e.*, $AH\cdot$ and AH^-, do not accumulate in the reacting systems, and hence the reaction

$$A\cdot^-,Na^+ + ROH \longrightarrow AH\cdot + RO^-,Na^+$$

is the rate-determining step, although $2A\cdot^-,Na^+$ are consumed for each $A\cdot^-,Na^+$ reacting in the above step.

Kinetics of the protonation by all the protonating reagents but *t*-BuOH showed the reaction to be first order in $A\cdot^-,Na^+$. Plots of log (optical density) *vs.* time show no deviations from linearity in the whole period of observation (about 5 half-life times). The pseudo-first-order rate constants are approximately proportional to [ROH] in power *higher* than one; in fact the plots of log $k_{pseudo\ I}$ *vs.* log [ROH] deviate slightly from linearity.

The dependence of the pseudo-first-order constants, $k_{pseudo\ I}$, on the concentration of the protonating reagents needs closer examination. One may always seek refuge in a thermodynamic approach and invoke a concentration dependence of activity coefficients of the protonating reagents in order to account for the deviations of $k_{pseudo\ I}$ from simple proportionality with [ROH]. We prefer, however, to take a more molecular-minded approach and to account for our findings in terms of specific protonating species. We assume that the alcohols and water exist in DME mainly in two forms: as monomeric alcohols hydrogen bonded to DME and as dimers. Both are capable of protonating $A\cdot^-,Na^+$, although the respective rate constants are different, the dimers being much more reactive than the monomers. Let us assume also that the mole fraction of the dimers is small in the concentration range studied in our work and then the concentration of the monomer would be virtually identical with the total concentration of alcohol (or water), *i.e.*, [ROH]. Thus

$$k_{pseudo\ I} = 2k_{p1}[ROH] + 2k_{p2}K_d[ROH]^2$$

where k_{p1} and k_{p2} denote the "true" bimolecular rate constants of protonation by ROH and $(ROH)_2$, respectively, and K_d is the equilibrium constant of the dimerization.

$$2ROH \overset{K_d}{\rightleftarrows} (ROH)_2$$

A rearrangement of the above equation leads to the linear relation

$$k_{pseudo\ I}/[ROH] = 2k_{p1} + 2k_{p2}K_d[ROH]$$

between $k_{pseudo\ I}/[ROH]$ and [ROH]. Such linear plots are shown in Figures 1 and 2 for MeOH, EtOH, *i*-PrOH, and H_2O, respectively. The relevant values of k_{p1} and $k_{p2}K_d$ can then be calculated from the intercepts and slopes, and these are listed in Table I.

Linearity of the plots shown in Figures 1 and 2 supports our estimate of $[(ROH)_2]$ to be less than 10% of [ROH]. Hence, the equilibrium constants of these dimerizations should be smaller than 1 *M*, and therefore k_{p2}'s have to be substantially greater than the corresponding k_{p1}'s. Is this justified? Protonation

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(7) (a) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Wiley-Interscience, New York, N. Y., 1968; (b) R. V. Slates and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965); (c) J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168 (1962).

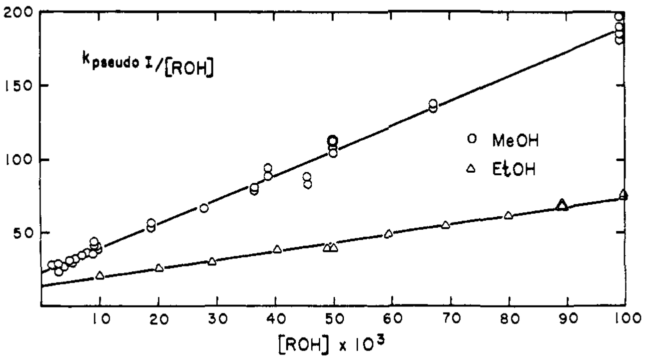
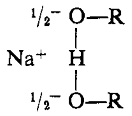


Figure 1. Plot of $k_{\text{pseudo I}}$/[ROH] *vs.* [ROH] for the protonation of $\mathrm{A}\cdot^-,\mathrm{Na}^+$ in DME by MeOH and EtOH.

Table I. Rate Constants of Protonation of $\mathrm{A}\cdot^-,\mathrm{Na}^+$ in DME by Monomeric (k_{p1}) and Dimeric ($k_{\mathrm{p2}}K_{\mathrm{d}}$) Alcohols (or Water)

Protonating reagent	k_{p1}, M^{-1} sec^{-1}	$k_{\mathrm{p2}}K_{\mathrm{d}}$, M^{-2} sec^{-1}
MeOH	10.5	875
EtOH	6.5	310
i-PrOH	2.4	31
t-BuOH	0.57	0
H_2O	2.2	69

by the monomeric ROH yields $\mathrm{RO}^-,\mathrm{Na}^+$ while protonation by $(\mathrm{ROH})_2$ produces a species stabilized by hydrogen bond, namely



$$\begin{array}{l} {}^{1}\!/_{2}^{-}\ \mathrm{O{-}R} \\ \mathrm{Na}^+\ \ \mathrm{H} \\ {}^{1}\!/_{2}^{-}\ \mathrm{O{-}R} \end{array}$$

This may account for the much greater acidity of $(\mathrm{ROH})_2$ than of the monomeric ROH hydrogen bonded to DME.

It is interesting to compare the decrease of k_{p1}'s along the series MeOH, EtOH, *i*-PrOH, and *t*-BuOH with the corresponding decrease of $k_{\mathrm{p2}}K_{\mathrm{d}}$'s. The latter decrease more rapidly than the former, and it is plausible to conclude that this result is due to the substantial decrease of the equilibrium constant of the dimerization which apparently is hindered by the increased bulkiness of R. The case of *t*-BuOH[8] is particularly illuminating. Apparently the hindrance caused by the bulky *t*-Bu group is sufficiently large to prevent any significant dimerization of this alcohol under our experimental conditions.

The kinetics of the protonation by *t*-BuOH indicates simultaneous participation of two reactions in the overall process, one first order and the other second order in $\mathrm{A}\cdot^-,\mathrm{Na}^+$, *i.e.*

$$-\mathrm{d}[\mathrm{A}\cdot^-,\mathrm{Na}^+]/\mathrm{d}t = k_{\mathrm{I}}[\mathrm{A}\cdot^-,\mathrm{Na}^+] + k_{\mathrm{II}}[\mathrm{A}\cdot^-,\mathrm{Na}^+]^2$$

Solution of this differential equation gives

$$\{\ln (X_0/X)\}\Big/\int_0^t X\,\mathrm{d}t = k_{\mathrm{II}} + k_{\mathrm{I}}t\Big/\int_0^t X\,\mathrm{d}t$$

where X denotes $[\mathrm{A}\cdot^-,\mathrm{Na}^+]$. Hence, plots of $\{\ln (X_0/X)\}/\int_0^t X\,\mathrm{d}t$ *vs.* $t/\int_0^t X\,\mathrm{d}t$ should be linear, their slopes giving k_{I} and their intercepts k_{II}. A typical plot of this kind is shown in Figure 3 in which optical densities were used instead of concentrations. For the sake of comparison, we included in this figure the usual first-order plot. Inspection of this figure clearly shows the linearity of the former plot and the initial deviation from the linearity of the latter.

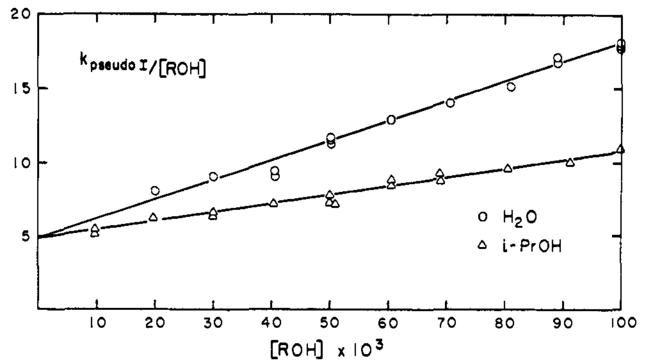


Figure 2. Plot of $k_{\text{pseudo I}}$/[ROH] *vs.* [ROH] for the protonation of $\mathrm{A}\cdot^-,\mathrm{Na}^+$ in DME by *i*-PrOH and H_2O.

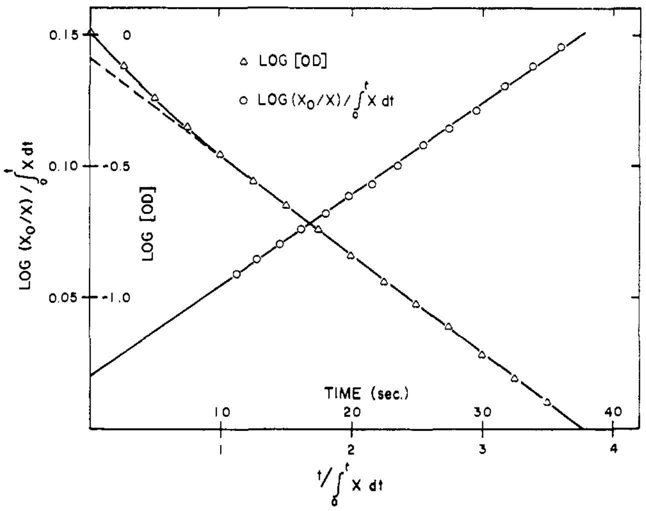


Figure 3. Plot of $\log (X_0/X)/\int_0^t X\,\mathrm{d}t$ *vs.* $t/\int_0^t X\,\mathrm{d}t$ for protonation of $\mathrm{A}\cdot^-,\mathrm{Na}^+$ in DME by *t*-BuOH. X denotes the optical density of $\mathrm{A}\cdot^-,\mathrm{Na}^+$ at time t. For the sake of comparison the Δ give the conventional plot of log (optical density of $\mathrm{A}\cdot^-,\mathrm{Na}^+$) *vs.* time. Note its slight curvature in the early stages of the reaction.

Using the above method we obtained the values of k_{I} and k_{II} listed in Table II. A plot of log k_{I} *vs.* log [*t*-BuOH] is shown in Figure 4; it is linear with a slope of unity. Hence, for *t*-BuOH, $k_{\mathrm{I}} = k_{\mathrm{p1}}\cdot$[*t*-BuOH] and $k_{\mathrm{p2}} = 0$, the value of k_{p1} being listed in Table I. The data in Table II show also that k_{I} is independent of anthracene concentration, as expected on the basis of the proposed mechanism.

The values of the second-order rate constants, k_{II}, are less accurate than those of k_{I}, and a considerable scatter is seen in the data listed in Table II. They show that k_{II} increases with increasing [*t*-BuOH] but only slightly decreases as [A] increases.

Two mechanisms predict a second-order dependence of the rate of protonation on $[\mathrm{A}\cdot^-,\mathrm{Na}^+]$; namely, the protonation of dianions,[3] $\mathrm{A}^{2-},2\mathrm{Na}^+$, and the protonation of dimers,[4] $(\mathrm{A}\cdot^-,\mathrm{Na}^+)_2$. The former mechanism predicts a substantial decrease of the observed rate constants with increasing [A], since the dianion is formed by the disproportionation

$$2\mathrm{A}\cdot^-,\mathrm{Na}^+ \rightleftharpoons \mathrm{A}^{2-},2\mathrm{Na}^+ + \mathrm{A}$$

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[8] The determination of k_{p1} and k_{p2} for *t*-BuOH is discussed in the following paragraphs.

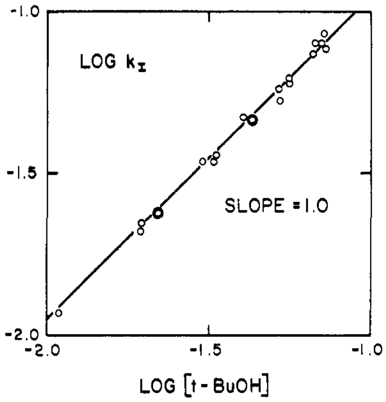

Figure 4. Plot of log k_I *vs.* log [*t*-BuOH] for the protonation of $A\cdot^-,Na^+$ in DME by *t*-BuOH, slope = 1.

Table II. Pseudo-First- and Second-Order Rate Constants (k_I and k_{II}) of Protonation of $A\cdot^-,Na^+$ by *t*-BuOH in DME at 25°

10^2[*t*-BuOH], *M*	10^2[A], *M*	k_I, M^{-1} sec^{-1}	k_{II}, M^{-2} sec^{-1}
	At Constant [A]		
7.18	1.13	0.0850	78.2
7.20	1.13	0.0800	97.4
7.30	1.12	0.0764	105.8
6.60	1.13	0.0743	105.8
6.78	1.10	0.0805	92.0
5.56	1.11	0.0628	82.8
5.52	1.12	0.0598	82.8
5.30	1.01	0.0529	128.8
5.20	1.03	0.0575	82.8
4.25	1.12	0.0460	69.0
4.30	1.11	0.0460	69.0
4.03	1.01	0.0471	69.0
3.32	1.11	0.0356	59.8
3.28	1.13	0.0345	55.2
3.02	1.01	0.0345	52.8
2.19	1.11	0.0237	40.0
2.17	1.12	0.0239	37.8
1.95	1.01	0.0221	38.6
1.95	1.01	0.0209	40.0
1.08	0.99	0.0117	23.4
	At Variable [A]		
5.13	3.75	0.0633	69.0
5.30	3.81	0.0633	59.8
5.43	3.32	0.0575	96.6
5.30	3.29	0.0621	62.2
5.25	2.83	0.0645	64.4
5.30	2.31	0.0621	59.8
5.27	1.81	0.0621	76.0
5.25	1.81	0.0575	69.0
5.30	1.01	0.0598	97.4
4.90	0.11	0.0442	125.0
4.97	0.10	0.0425	129.0

while no dependence on [A] is expected in the latter case

$$2A\cdot^-,Na^+ \rightleftarrows (A\cdot^-,Na^+)_2$$

In spite of the scatter, the data collected in Table II under the heading "At variable [A]" show k_{II} to increase only by a factor of 2 as [A] decreases by a factor of 30. This implies that the mechanism involving dimers contributes more to the observed process than that postulating the protonation of the dianions.

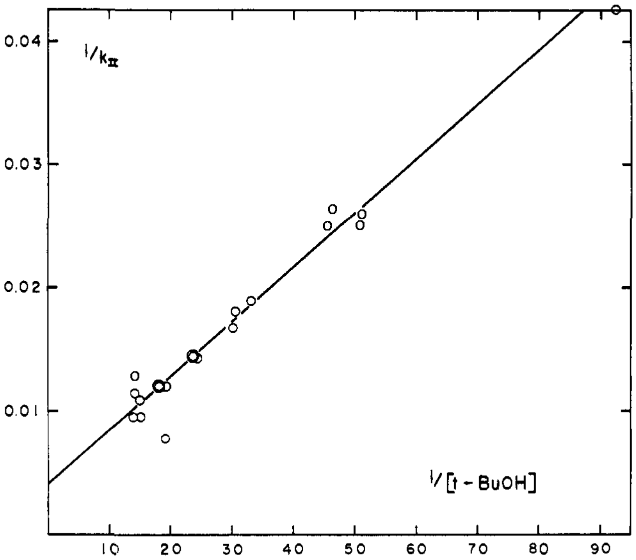

Figure 5. Plot $1/k_{II}$ *vs.* 1/[*t*-BuOH].

The dimerization of *t*-BuOH is shown to be negligible in DME and therefore in this system the monomeric butanol is the only protonating reagent. The same is expected in the protonation of the dimer $(A\cdot^-,Na^+)_2$. Thus its stationary state should be determined by the following scheme

$$2A\cdot^-,Na^+ \underset{k_b}{\overset{k_f}{\rightleftarrows}} (A\cdot^-,Na^+)_2$$

$$(A\cdot^-,Na^+)_2 + ROH \xrightarrow{k_{IIp}} AH^-,Na^+ + A + RO^-,Na^+$$

leading to the relation

$$k_{II} = 2k_f k_{IIp}[ROH]/(k_b + k_{IIp}[ROH])$$

or

$$1/k_{II} = 1/2k_f + k_b/2k_f k_{IIp}[ROH]$$

A plot of $1/k_{II}$ should be therefore linear with 1/[ROH] as shown in Figure 5. This linear relation seems to be fairly well obeyed, in spite of some scatter of the experimental points, yielding $k_f = 1.3 \times 10^2\ M^{-1}$ sec^{-1} and $k_{IIp}k_f/k_b = 1.1 \times 10^3\ M^{-2}$ sec^{-1}. The derived value of k_f is, however, much too low, because the dimerization of two ion pairs is essentially a diffusion-controlled reaction. This invalidates the otherwise plausible mechanism. The way out of that dilemma was suggested by Dye.[4] Apparently the dimer $(A\cdot^-,Na^+)_2$ is relatively unreactive, as stressed earlier by one of us,[3] and it negligibly contributes to the protonation. The conversion of $(A\cdot^-,Na^+)_2$ into a "solvent caged" complex $(A^{2-},2Na^+;A)$ produces a very strong base which is rapidly protonated. Thus, the modified mechanism is represented by the steps

$$2A\cdot^-,Na^+ \underset{k_b}{\overset{k_f}{\rightleftarrows}} (A\cdot^-,Na^+)_2 \underset{k'_b}{\overset{k'_f}{\rightleftarrows}} (A^{2-},2Na^+;A)$$

$$(A^{2-},2Na^+;A) + ROH \xrightarrow{k'_{IIp}} AH^-,Na^+ + A + RO^-,Na^+$$

and the assumption of stationary state leads to

$$k_{II} = 2k_f k'_f k'_{IIp}[ROH]/\{k_b k'_b + (k_b + k'_f)k'_{IIp}[ROH]\}$$

Obviously $k_b \gg k'_f$, and hence

$$1/k_{II} = k_b/2k_f k'_f + k_b k'_b/2k_f k'_f k'_{IIp}[ROH]$$

or

$$1/k_{\text{II}} = 1/2Kk'_{\text{f}} + 1/2KK'k'_{\text{IIp}}[\text{ROH}]$$

where $K = k_{\text{f}}/k_{\text{b}}$ and $K' = k'_{\text{f}}/k'_{\text{b}}$. Hence, the linear relation between $1/k_{\text{II}}$ and $1/[\text{ROH}]$ is retained but the meaning of the intercept and slope is changed; *viz.*, the intercept gives $1/2Kk'_{\text{f}}$ and the slope $1/2K \cdot K'k'_{\text{IIp}}$. According to this mechanism $Kk'_{\text{f}} = 1.3 \times 10^2\ M^{-1}\ \text{sec}^{-1}$ and $KK'k'_{\text{IIp}} = 1.1 \times 10^3\ M^{-2}\ \text{sec}^{-1}$. An argument similar to that developed by Dye[4] results in an estimate that $K \approx 100\ M^{-1}$ (the dipole of $\text{A}\cdot^-,\text{Na}^+$ is greater in DME than in THF) and hence $k'_{\text{f}} \sim 1.3\ \text{sec}^{-1}$ and $K'k'_{\text{IIp}} \approx 11\ M^{-1}\ \text{sec}^{-1}$, both values being now acceptable.

The self-consistency of the above scheme should be examined. The basicity of $\text{A}^{2-},2\text{Na}^+$ in DME is probably even higher than that of perylene^{2-},2Na^+ in THF. Hence, the protonation constant of the former dianion, k'_{IIp}, may be larger than that of perylene^{2-},2Na^+ ($\sim 1 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, see ref 3), and a reasonable value of $10^8\ M^{-1}\ \text{sec}^{-1}$ for k'_{IIp} may be proposed. This leads to a plausible value of $K' \sim 10^{-7}$, since $K'k'_{\text{IIp}} = 11\ M^{-1}\ \text{sec}^{-1}$, and to a reasonable estimate of $k'_{\text{b}} \sim 10^7\ \text{sec}^{-1}$. The necessity of solvation of two Na^+ may account for the relatively low value of k'_{b}.

The proposed scheme leads to the conclusion that the protonation of the "free" $\text{A}^{2-},2\text{Na}^+$, which diffused out from the cage, does not contribute much to the reaction, particularly when [A] is not smaller than $10^{-2}\ M$. This implies the inequality of stationary concentrations, $[\text{A}^{2-},2\text{Na}^+] < [(\text{A}^{2-},2\text{Na}^+;\text{A})]$. We have determined the disproportionation constant of $\text{A}\cdot^-,\text{Na}^+$ in DME

$$2\text{A}\cdot^-,\text{Na}^+ \rightleftarrows \text{A}^{2-},2\text{Na}^+ + \text{A} \qquad K_{\text{dispr}}$$

by the potentiometric titration technique, described elsewhere.[9] The results[10] led to $\epsilon_1 = 0.723$ V, $\epsilon_2 = 0.280$ V, and therefore $K_{\text{dispr}} = 4 \times 10^{-8}$. The disproportionation may be described by the sequence of reactions

$$2\text{A}\cdot^-,\text{Na}^+ \overset{K}{\rightleftarrows} (\text{A}\cdot^-,\text{Na}^+)_2 \overset{K'}{\rightleftarrows}$$
$$(\text{A}^{2-},2\text{Na}^+;\text{A}) \overset{K''}{\rightleftarrows} \text{A}^{2-},2\text{Na}^+ + \text{A}$$

and therefore $K_{\text{dispr}} = K, K', K'' = 4 \times 10^{-8}$. Accepting the values $K \sim 100\ M^{-1}$ and $K' \sim 10^{-7}$, we conclude that $K'' \sim 4 \times 10^{-3}\ M$. This is again reasonable since the polarizability of anthracene and its high electron affinity may account for a strong attraction between A and $\text{A}^{2-},2\text{Na}^+$.

For the concentration of anthracene $[\text{A}] \sim 10^{-2}\ M$, maintained in most of our experiments, the ratio $[\text{A}^{2-},2\text{Na}^+]/[(\text{A}^{2-},2\text{Na}^+;\text{A})] \sim 0.4$. Hence, our plausible choice of k'_{IIp} value leads to the required condition $[\text{A}^{2-},2\text{Na}^+] < [(\text{A}^{2-},2\text{Na}^+;\text{A})]$ confirming the self-consistency of the proposed mechanism (see also the General Remarks at the conclusion of this paper).

The question arises as to why the second-order reaction does not contribute to the protonation by MeOH, EtOH, *i*-PrOH, and H_2O. In all these systems the first-order reaction is much faster than in the *t*-BuOH case. Inspection of the data shows that the combined effect of the monomeric and dimeric *i*-PrOH makes even this relatively slow protonation 8 times faster than the direct protonation of $\text{A}\cdot^-,\text{Na}^+$ by *t*-BuOH. The rate of protonation of the dianion complex $(\text{A}^{2-},2\text{Na}^+;\text{A})$ is probably much less affected by the nature of the alcohol due to the high basicity of the dianion. Thus, the contribution of the second-order reaction to the protonation by *i*-PrOH would be relatively small, and even smaller when EtOH or MeOH are the protonating reagents. Consequently, this reaction becomes imperceptible in the kinetic studies of these systems.

Effect of Sodium Tetraphenylboride. Our experiments were performed in solutions containing $\text{Na}^+\text{BPh}_4^-$ in order to repress the presence of the free $\text{A}\cdot^-$ ions. Could this addition have any other effect upon the kinetics of the studied process? To answer this question, the protonation by H_2O (0.1 *M*) was studied in the absence and presence of $\text{Na}^+\text{BPh}_4^-$, other conditions being the same. In the absence of $\text{Na}^+\text{BPh}_4^-$ the first-order plot is slightly curved (concave), the pseudo-first-order rate constants calculated from the initial slope being 2.1, 2.0, 2.1, and again 2.0 sec^{-1}. Similar experiments performed in the presence of $\text{Na}^+\text{BPh}_4^-$ led to pseudo-first-order rate constants of 1.8, 1.8, and again 1.8 sec^{-1}. Hence, specific effects, if any, are small. The slightly concave shape of the plot log (optical density) *vs.* time obtained in the absence of the boride may result from the increasing proportion of the free $\text{A}\cdot^-$ ions which seem to be less reactive than $\text{A}\cdot^-,\text{Na}^+$.

The effect of $\text{Na}^+\text{BPh}_4^-$ was more thoroughly investigated in the protonation by *t*-BuOH. The results, summarized in Table III, show that the presence of $\text{Na}^+\text{BPh}_4^-$ has a negligible effect upon k_{I} which seems to pass through a maximum, although the observed variations are within narrow limits of 25%. Provided these small variations are significant, they may indicate the operation of two effects, one enhancing the other retarding the protonation. Association of Na^+ cation with alcohol may enhance its

Table III. Effect of $\text{Na}^+,\text{BPh}_4^-$ on the Rate of Protonation of $\text{A}\cdot^-,\text{Na}^+$ in DME by *t*-BuOH

$10^2[\text{Na}^+, \text{BPh}_4^-]$, *M*	10^2[A], *M*	10^3[*t*-BuOH], *M*	k_{I}, sec^{-1}	k_{II}, $M^{-1}\ \text{sec}^{-1}$
0	1.1	4.9	0.039	101
0	1.0	5.0	0.040	90
0	1.1	4.8	0.040	92
2.2	1.1	4.9	0.051	64
2.15	1.0	5.1	0.051	70
2.0	1.1	4.9	0.048	64
4.4	1.1	4.9	0.045	58
4.3	1.0	5.0	0.044	60
4.3	1.0	5.1	0.044	64
10.7	1.1	5.0	0.036	45
10.6	1.1	5.1	0.038	37
10.7	1.1	5.0	0.038	41
10.5	1.0	5.1	0.039	40

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(9) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628(1965).

(10) Our potentiometric studies in DME will be reported shortly. We found all the studied disproportionation constants much lower in DME than in THF, indicating the importance of solvation in this process; see also ref 11. Previous studies of Hoijtink, *et al.*,[12] led to a value even lower than ours, *viz.*, $\epsilon_1 - \epsilon_2 = 0.58$ V.

(11) J. F. Garst and R. S. Cole, *J. Amer. Chem. Soc.*, **84**, 4352 (1962).

(12) G. J. Hoijtink, E. De Boer, P. H. Van der Maij, and W. P. Weijland, *Recl. Trav. Chim. Pays-Bas*, **75**, 487 (1956).

acidity, while the formation of triple ions, $Na^+,A\cdot^-,Na^+$, or complexes $(A\cdot^-,Na^+,BPh_4^-Na^+)$ may reduce the basicity of $A\cdot^-$.

A definite trend is observed in the values of k_{II} which decrease with increasing $[Na^+,BPh_4^-]$. The effect of triple ions, $Na^+,A\cdot^-,Na^+$ or complexes $(A\cdot^-,Na^+,BPh_4^-,Na^+)$, upon the equilibrium of dimerization and disproportionation provides the most plausible explanation of our findings. The formation of either species decreases the dimerization and disproportionation constants and therefore retards the second-order reaction. Although this effect slightly complicates the behavior of the system it does not affect our main conclusions.

General Remarks

Any direct bimolecular solution reaction, $A + B \rightleftarrows C + D$, involves at least two intermediates, the solvent caged complex of the reagents, (A,B), and of the products, (C,D). A more detailed description of the process is therefore

$$A + B \overset{K'}{\rightleftarrows} (A,B) \overset{K''}{\rightleftarrows} (C,D) \overset{K'''}{\rightleftarrows} C + D$$

where the overall equilibrium constant $K = K'K''K'''$.

In most systems the concentrations of complexes (A,B) and (C,D) are small compared to those of the reagents and products. However, it appears that in our system and under conditions maintained in this work the concentration of such a complex $(A^{2-},2Na^+;A)$ is relatively large when compared to that of $A^{2-},2Na^+$. The *equilibrium* concentration of $A^{2-},2Na^+$ is extremely low, *viz.*, 4×10^{-12} *M;* however, this is not the reason for the inequality $[A^{2-},2Na^+;A] > [A^{2-},2Na^+]$, because the ratio $[A^{2-},2Na^+;A]/[A^{2-},2Na^+]$ depends only on [A] and not on $[A^{2-},2Na^+]$. It may be that the diamagnetic dimers[13-16] such as $(TCNQ\cdot^-,Na^+)_2$, $(\text{phenanthroquinone}\cdot^-\ \text{salt})_2$, $(TCNE\cdot^-,Na^+)_2$, $(\text{thianthrene}\cdot^+,ClO_4^-)_2$, etc., exemplify systems having a high proportion of (C,D)-type complexes.

The question arises why a situation similar to that found in this work was not observed in the protonation of sodium perylenide $(Pe\cdot^-,Na^+)$ in THF.[3] The disproportionation constant in that system is about 1000 times higher than in the anthracene–DME system, but this would not account for the difference in their behavior. There is no obvious reason to expect the respective K'' to be much different for the perylene and anthracene complexes. We can offer only one explanation which accounts for the results; namely, the reactivity of the $(Pe^{2-},2Na^+;Pe)$ complex is much lower than that of $Pe^{2-},2Na^+$, while $(A^{2-},2Na^+;A)$ and $A^{2-},2Na^+$ are approximately equally reactive. The Na^+ cations could be imbedded in the $(Pe^{2-},2Na^+;Pe)$ sandwich and therefore not easily accessible, but they are still accessible in the $(A^{2-},2Na^+;A)$ complex. We intend to investigate this problem further. It should be stressed that studies of protonation of $Pe\cdot^-,N_a^+$ were repeated and the inverse dependence on [Pe] was fully confirmed.

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Appendix

The observations reported in our paper could be interpreted in alternative ways. For example, Fujihira, *et al.*,[17] proposed the following scheme.

$$A\cdot^-,Na^+ + ROH \longrightarrow AH\cdot + Na^+OH^- \qquad (a)$$

$$A\cdot^-,Na^+ + ROH \rightleftarrows A\cdot^-(Na^+,ROH) \qquad (b)$$

$$A\cdot^-(Na^+,ROH) + ROH \longrightarrow AH\cdot + (Na^+,ROH)OR^- \qquad (c)$$

Such a scheme leads to the same kinetics as ours and therefore formally is verified by experiments. However, this mechanism does not appear plausible since it demands two types of encounters of $A\cdot^-,Na^+$ with ROH—one leading to protonation while the other forms a stable complex (ROH in the solvation shell of Na^+ ion) which is protonated only in the subsequent encounter with a second molecule of ROH. On the other hand, the existence of the dimers $(ROH)_2$ is well understood and confirmed by numerous observations.

The low value of $k_f = 1.3 \times 10^{-2}$ *M* could also be interpreted in an alternative way; for example, assume that $A\cdot^-,Na^+$ exists in THF in two forms—abundant loose pairs and infrequent tight pairs, both species being in equilibrium with each other. Assume further that only the tight pairs are capable of forming dimers. Then k_f is given by a product $k_f'''K_{is}$, where k_f''' is the rate constant of formation of the dimer from *tight* pairs and K_{is} the equilibrium constant of conversion of loose pairs into tight pairs. Although this mechanism accounts for the low value of k_f it leaves us still with the unsatisfactory situation demanding the dimer to be more reactive than the monomeric $A\cdot^-,Na^+$. This difficulty is removed in our proposal.[18]

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(13) T. L. Staples and M. Szwarc, *J. Amer. Chem., Soc.*, **92**, 5022 (1970).

(14) R. Cheng, *J. Phys. Chem.*, 74, 2029 (1970).

(15) M. de Sorgo, B. Wasserman, and M. Szwarc, *ibid.*, 76, 3468 (1972).

(16) R. M. Boyd and W. D. Philips, *J. Chem. Phys.*, **53**, 2927 (1965).

(17) S. Mayano and L. M. Fujihira, *Bull. Chem. Soc. Jap.*, **44**, 2046 (1971).

(18) NOTE ADDED IN PROOF. A recent paper by S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **94**, 6076 (1972), reports the kinetics of protonation of sodium anthracenide by water. Three solvents were used, THF, THF + DME, and DME. We agree with the authors that the reaction in DME (and maybe even in DME + THF) is first order in anthracenide and independent of the concentration of anthracene. However, we question their findings indicating the first-order dependence on water concentration in the range 0.01–4.5 *M*. Their reported rate constant of 17 M^{-1} sec^{-1} for the protonation in DME compares with our value of 18 M^{-1} sec^{-1} for $[H_2O] = 0.1$ *M*, but this constant decreases to 6 M^{-1} sec^{-1} at $[H_2O]$ of 0.01 *M*.