Effect of Ion-Clustering and Dianion Formation on the Rate of Protonation of Anthracenide by Alcohols and Water in Two Ethereal Solvents

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Abstract: Anthracenide radical anions were formed by the reaction of anthracene with potassium or sodium in tetrahydrofuran (THF) and in dimethoxyethane (DME). The rate of reaction of the radical anion with a series of alcohols and with water was followed spectrophotometrically by using a scanning stopped-flow apparatus. The reactions of $K^+An\cdot^-$ in both solvents and of $Na^+An\cdot^-$ in THF were essentially second order in $(M^+An\cdot^-)$ and of variable (0–1) order in the proton donor. The reactions of $Na^+An\cdot^-$ with ethanol and with water in DME were first order in $(Na^+An\cdot^-)$. The protonation rates in DME were substantially lower than in THF. The second-order protonation was eliminated when a cation-complexing agent (dicyclohexyl-18-crown-6) was added to prevent contact-pair formation. The reaction of $K^+An\cdot^-$ with ethanol in THF was studied in detail over a wide range of ethanol and anthracene concentrations. At low concentrations of ethanol (<0.01 *M*) the rate depended upon the ratio (EtOH)/(An), consistent with the formation and subsequent protonation of the anthracene dianion. The pseudo-second-order rate constant increased with (EtOH) but became essentially independent of (An) at higher concentrations of ethanol. Above (EtOH) ≈ 0.1 *M*, a first-order contribution to the decay became apparent. All of the results are consistent with protonation of a number of species in which the protonation rate follows the order $An\cdot^-||M^+ < An\cdot^-,M^+ \ll An^{2-},2M^+$. The symbols $An\cdot^-||M^+$ and $An\cdot^-,M^+$ represent solvent-separated and contact ion pairs, respectively, while $An^{2-},2M^+$ represents the dianion species (probably contact-paired with two cations). At high concentrations of the proton donor the results suggest the protonation of an intermediate quadrupole ion-cluster (or complex between An and $An^{2-},2M^+$) either directly or *via* the species $K^+\cdot ROH$ which is present in the cluster.

Aromatic radical anions are protonated according to the stoichiometry

$$2Ar\cdot^- + 2ROH \longrightarrow ArH_2 + Ar + 2RO^- \quad (1)$$

in which ArH_2 is the dihydro product of the parent hydrocarbon. On the basis of this stoichiometry, Paul, Lipkin, and Weissman[1] proposed the mechanism

$$Ar\cdot^- + ROH \longrightarrow ArH\cdot + RO^- \quad (2)$$

$$ArH\cdot + Ar\cdot^- \longrightarrow ArH^- + Ar \quad (3)$$

$$ArH^- + ROH \longrightarrow ArH_2 + RO^- \quad (4)$$

If reaction 2 is rate limiting the predicted rate law becomes

$$-d[Ar\cdot^-]/dt = k[Ar\cdot^-][ROH] \quad (5)$$

Pulse-radiolysis studies of a series of aromatic compounds in pure alcohols[2] and in mixtures of ethanol and other solvents[3,4] and esr,[5,6] electrochemical,[5,6] and stopped-flow[7] studies of electrolytically produced aromatic anions in *N,N*-dimethylformamide (DMF)–water mixtures indicate that, in these polar solvents, the decay of the anion is first order. These studies also show that the reaction rate is markedly influenced by the solvent composition, but they do not permit one to separate the order in proton donor from general solvent effects. For example, although Fujihira, Suzuki, and Hayano[7] presumed the reaction in DMF–water mixtures to be first order in water, the rate constant increased exponentially with water content, an observation which was attributed to stabilization of the transition state by hydrogen bonding.[8]

In stopped-flow studies of the protonation of sodium naphthalenide and anthracenide with water in THF, DME, and mixtures of these solvents, Bank and Bockrath[9] found the reaction to be first order in both Na^+-$Ar\cdot^-$ and ROH in agreement with the generally accepted mechanism.[1] The effect of solvent and of added glyme suggested that ion pairing plays an important role in the mechanism. In a recent study of the protonation of perylenide anion by alcohols in THF, Levin, Sutphen, and Szwarc[10,11] demonstrated convincingly that the major protonation pathway is *via* the dianion and that the formation of contact pairs is essential to the reaction scheme. The rate-limiting protonation of the dianion is preceded by the disproportionation equilibrium

$$2Ar\cdot^-,M^+ \rightleftharpoons Ar^{2-},2M^+ + Ar \quad (6)$$

In agreement with this mechanism, the reaction was found to be second order in $(M^+Ar\cdot^-)$, first order in ROH, and inverse first order in Ar. The designation $(M^+Ar\cdot^-)$ refers to the total solute in all of its forms while $(Ar\cdot^-, M^+)$, $(Ar\cdot^-||M^+)$, etc., refer to particular species.

In a preliminary report of the present study[12] we showed that the reaction of anthracenide radical anion $(An\cdot^-)$ with a series of alcohols in THF was second

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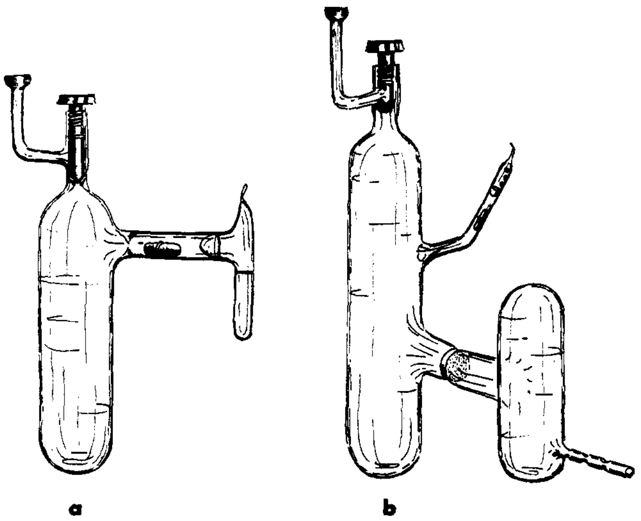

Figure 1. Preparation vessels: (a) for ROH solutions; (b) for $M^+An\cdot^-$ solutions.

order in $An\cdot^-$ and of low order in the proton donor. The data were consistent with a mechanism which involved protonation of a quadruple ion-cluster, but the effect of added anthracene was not studied over a wide enough concentration range to rule out the dianion mechanism. The present paper considers an overview of the reactions of the anthracenide radical anion with a number of alcohols and with water in THF and in DME. After a preliminary survey had shown that the reactions were complex, several alternate mechanisms were tested by studying the rate of reaction of $K^+An\cdot^-$ with ethanol in THF over a wide range of ethanol and anthracene concentrations. Under these conditions, the reactions were slow enough to be followed spectrophotometrically in a stopped-flow apparatus which permitted scanning of the spectra.[13] These results and those of other workers suggest that the protonation rate depends upon the degree of charge localization. According to this viewpoint, the free anion represents the limit of slow protonation and the ion-paired dianion the opposite extreme of nearly diffusion-controlled protonation.

Experimental Section

Because of the instability of aromatic anions in contact with air, all materials were handled *in vacuo* or under a helium atmosphere. Teflon needle-valve stopcocks and Fischer-Porter Teflon joints were used in the vacuum system due to the incompatibility of most stopcock greases with THF. In addition, specially designed Teflon plungers were used in the syringes in the stopped-flow system.[14] The syringes and plungers were constructed so that the region behind the primary liquid seal could be evacuated. Failure to do this resulted in some decomposition of the radical anion solutions in the syringes. Although aromatic anions react with Teflon, the reaction was so slow after preliminary rinsing that it had no detectable effect upon the absorbance of the radical anion.

Zone-refined anthracene was obtained from James Hinton Co., Valparaiso, Fla. Weighed quantities were introduced into the solutions by using evacuated break-seal tubes. Dicyclohexyl-18-crown-6, obtained from E. I. du Pont de Nemours Co., was used without further purification. Alkali metals were introduced into evacuated vessels by distillation through a series of constrictions on a side-arm tube. Distilled water was passed through an ion-exchange column and then redistilled. After the water had been degassed, weighed amounts were stored in evacuated break-seal vessels. Alcohols were purified on a Nester–Faust annular Teflon spinning band distillation column. The alcohols so treated were anhydrous methanol, ACS analyzed reagent grade from Matheson Coleman and Bell; spectral grade absolute ethanol; Fisher Certified reagent grade 2-propanol and *tert*-butyl alcohol. The alcohols were also degassed and stored in evacuated break-seal vessels.

The solvents (THF from Burdick and Jackson, DME from Matheson Coleman and Bell) were dried successively with calcium hydride and with benzophenone ketyl. The latter was formed by the reaction of benzophenone with an excess of sodium–potassium alloy. Solvents were vacuum distilled from solutions of the ketyl before use.

Potassium hydroxide and potassium ethoxide were prepared by vacuum distillation of water (or ethanol) onto weighed quantities of potassium which had been sealed in fragile bulbs by the method of Watt and Sowards.[15] The resultant K^+OR^- samples were stored in evacuated break-seal vessels.

Solutions of the aromatic anions, of ROH, and of K^+OR^- were prepared in the vessels of the type shown in Figure 1. After the proper sample tubes had been attached, the main vessel was weighed and evacuated to about 1×10^{-6} Torr. When aromatic anion solutions were to be prepared, an alkali metal was distilled into a side arm which was separated from the main vessel by a glass frit. Solvent was distilled into the vessel, the whole vessel was reweighed, and the various break-seals were opened. Anthracene radical anion was formed by allowing a portion of the anthracene solution to contact the metal surface. In order to exclude the dianion, a known excess of anthracene was always present. After the solutions had been prepared, the vessels were attached to the stopped-flow apparatus. In the later studies with ethanol in THF all vessels and the flow system were prerinsed with $K^+An\cdot^-$ solutions.

The stopped-flow system was designed so that it could be evacuated to about 3×10^{-6} Torr. The solutions came into contact with only quartz, glass, and Teflon. The ROH and $Ar\cdot^-$ solutions were rapidly mixed in a four-jet quartz mixing cell. The cell was constructed from 0.1-cm i.d. quartz tubing, which also served as the optical cell (path length 0.1 cm). Inlet holes to the mixing chamber (0.05-cm diameter) were drilled by using an Airbrasive unit (S. S. White Co.). The course of the reaction was followed spectrophotometrically by using a Perkin-Elmer Model 108 rapid scan monochromator, RCA 6199 and 7102 multiplier phototubes, and related electronics.[13] The use of double-beam techniques and digital smoothing of the data permitted amplification of low absorbance signals so that initial absorbances as low as 0.2 could be used with satisfactory signal-to-noise ratios. The data were stored in analog form on magnetic tape by using an Ampex SP-300 FM direct recorder–reproducer, and were converted to digital form with a Varian C-1024 computer of average transients. A nonlinear least-squares curve-fitting program[16] was used to analyze these data. This program could be used with either integrated or differential rate expressions.

Results and Discussion

The radical anions of anthracene, formed by reaction with potassium and with sodium in THF and in DME, were characterized by their optical spectra.[17] Reactions of these anions with proton donors were studied by following the decay of the anthracenide peaks at 370 and 720 nm. Previous studies of these reactions[18,9b] have shown that the product is 9,10-dihydroanthracene. Only when the decay was fast ($t_{1/2} \gtrsim 20$ msec) was the absorbance followed at fixed wavelength. Otherwise the spectrum was repeatedly scanned at either 60 or 120 scans/sec during reaction. Limitations on the range of the photomultipliers prevented simultaneous observation of both the 370- and 720-nm regions. In order to avoid interference from the parent hydrocarbon the longer wavelength region was usually examined. Representative traces of the 720-nm region during reaction

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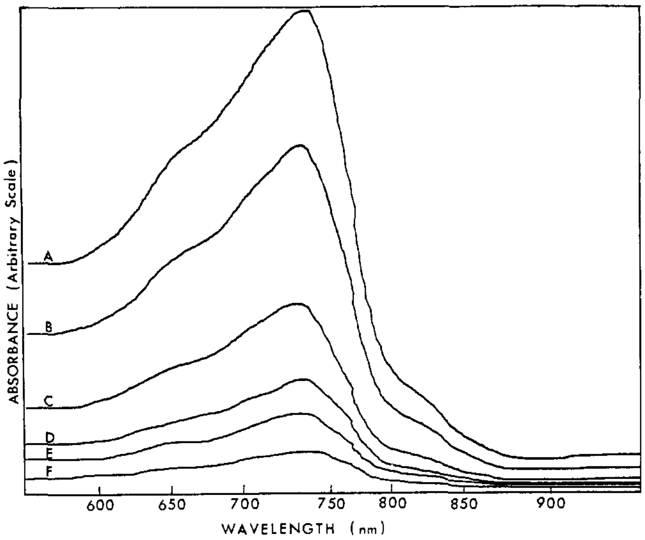

Figure 2. Decay of spectrum of $K^+An\cdot^-$ during reaction with EtOH in THF.

with ethanol in THF are shown in Figure 2. No absorptions other than those of An and $An\cdot^-$ were observed in any experiment although the region from 350 to 1000 nm was carefully examined (however, only when ROH was present in excess). When solutions of the anion were mixed with solvent, the diluted anion solution had an absorbance half that of the stock solution and was usually stable for many minutes in the mixing chamber.

The disappearance of $K^+An\cdot^-$ was found to be second order in its absorbance (Figure 3). The fit of a pseudo-second-order rate law over three to four half-lives was observed for the $K^+An\cdot^-$ protonation whenever the concentration of ROH was high enough to permit the pseudo-order treatment. (The onset of first-order protonation at high ethanol concentrations will be considered later.) An indication of the dependence of the pseudo-second-order rate constant upon the ROH concentration for various proton donors is shown by Figure 4. In order to include the values for ethanol, the rate constants are plotted *vs.* (ROH)/(An) rather than (ROH). However, only for the ethanol case was (An) varied over a wide range. Since at high values of (EtOH) the rate was independent of (An) (see later), data at high (An) and (EtOH) are not included in Figure 4. The data obtained in the early rate studies are given in Table I. Only limited ranges of the ROH concentration and usually only a single concentration of An were studied. (The case of EtOH in THF will be considered in detail later.) The data for methanol, 2-propanol, and *tert*-butyl alcohol in THF and for water and ethanol in DME were obtained in single runs and have not been independently verified. In view of the complexity of the protonation reactions and the likely sensitivity to air, moisture, and other impurities, we must treat the results of single experiments with caution.

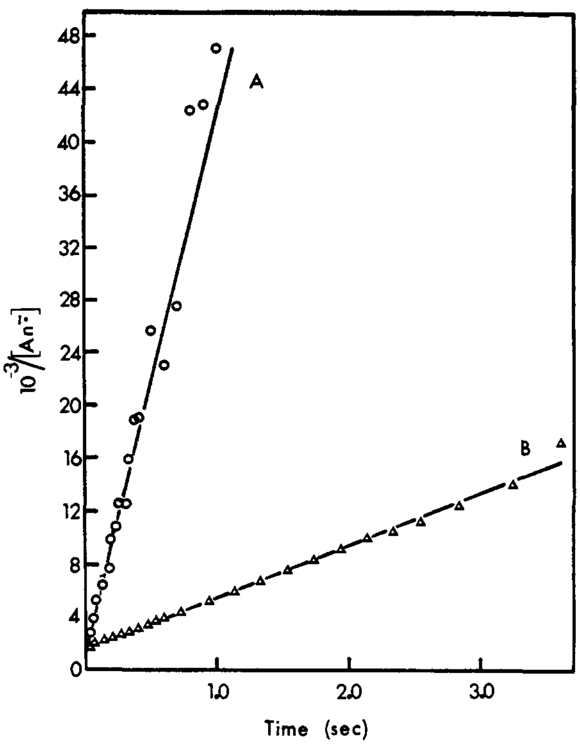

Figure 3. Pseudo-second-order plots of the reactions of $K^+An\cdot^-$ with (A) 0.047 *M* water in THF and with (B) 0.012 *M* water in DME.

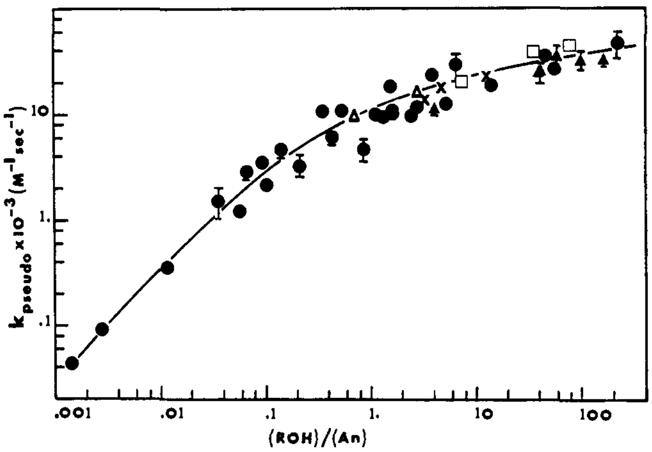

Figure 4. Log–log plot of k_{ps} (second order) *vs.* (ROH)/(An) for the reactions of $K^+An\cdot^-$ with: (□) *i*-PrOH, (▲) H_2O, (×) *t*-BuOH, (Δ) MeOH, (●) EtOH in THF.

Even with the reservations noted above, several conclusions seem justified. (1) In THF, at least at high values of (ROH)/(An), the second-order protonation rate seems to be essentially independent of the nature of the proton donor. (2) In THF, the order in (ROH) decreases from approximately unity to about one-third as the concentration of proton donor increases. (3) For both water and ethanol in DME, the pseudo-second-order rate constant shows a low order in the proton donor and is considerably smaller than for comparable concentrations in THF.

The existence of a reversible protonation of the anion prior to the rate-determining step, according to

$$An\cdot^- + ROH \rightleftarrows AnH\cdot + RO^- \qquad (7)$$

or of catalysis by RO^- seems to be ruled out by the fact that the reaction did not deviate from second-order behavior during the build-up of RO^-. This was checked by experiments in which $[RO^-]$ was varied, at constant [ROH], for the reactions of $K^+An\cdot^-$ with water and with ethanol in THF. No significant variation in the rate constants were observed over the range of $[RO^-]$ used (up to $\sim 6 \times 10^{-3}$ *M*).

Table I. Pseudo-Second-Order Rate Constants[a] for the Reaction $2K^+An\cdot^- + 2ROH \rightarrow AnH_2 + 2K^+OR^- + An$

THF	$10^2(ROH)_0$, M	$10^4(K^+An\cdot^-)_0$, M	$10^3(An)_0$, M	No. of pushes	$10^{-4}\langle k\rangle$, M^{-1} sec^{-1}	$10^{-4}\sigma$, M^{-1} sec^{-1} [b]
EtOH	0.212	2.9	0.58	4	2.33	0.11
	0.230	5.8	0.98	7	0.95	0.12
	0.411	2.4	0.60	4	2.86	0.82
	0.495	5.9	0.97	4	1.23	0.16
H_2O	0.41	5.2	1.03	9	1.13	0.18
	3.78	2.6	0.66	4	3.50	0.91
	4.71	5.0	1.17	5	2.49	0.57
	8.60	5.3	2.30	5	2.37	0.23
	11.10	2.4	0.68	4	3.26	0.51
	22.30	4.9	2.30	5	3.22	0.67
i-PrOH	1.20	4.2	1.69	3	2.00	0.11
	5.50	6.9	1.59	6	3.91	0.32
	11.40	3.9	1.56	7	4.45	0.32
t-BuOH	0.54	4.7	1.69	6	1.37	0.15
	0.80	5.3	1.70	5	1.71	0.20
	2.03	5.8	1.59	8	2.22	0.14
MeOH	0.099	6.4	1.41	6	0.98[c]	0.02
	0.361	7.8	1.29	8	1.62[d]	0.16
DME						
H_2O	1.18	5.0	1.44	4	0.364	0.061
	1.19	3.7	1.57	2	0.316	0.002
	3.57	4.9	1.45	3	0.400	0.035
EtOH	0.07	5.4	1.40	3	0.131[d]	0.008
	0.13	5.8	1.36	4	0.110[d]	0.001
	0.26	5.8	1.36	2	0.187[d]	0.005

[a] Based upon $d(An\cdot^-)/dt = -k(An\cdot^-)^2$. An extinction coefficient of 9.6×10^3 at 720 nm was used. [b] $\sigma = [1/(n-1)\Sigma^n_{i=1}(k_i - \langle k_i\rangle)^2]^{1/2}$. This gives a measure of the reproducibility from push to push. The estimated standard deviation of k_i obtained by fitting individual decay curves is generally smaller by a factor of 3. [c] Initial rate constant from empirical fit of data. [d] Good pseudo-second-order fit even though pseudo-order kinetics may not be valid.

Since no absorbing intermediates were observed and since the kinetics of decay of the 370- and 720-nm peaks of $An\cdot^-$ were not wavelength dependent, application of the steady-state treatment to postulated intermediates was presumed valid.

Pronounced effects of contact ion-pair formation on reaction rates have been observed in a number of systems.[9,11,19,20] To test the effect of contact ion-pair formation on the kinetics of protonation of $K^+An\cdot^-$ the rates of reaction with water and with ethanol in DME were measured. Although the dielectric constants of DME and THF are nearly the same (7.15 and 7.39 at 25°), the ability of DME to solvate cations is greater.[21,22] Consequently, the formation of contact ion pairs is less favored in DME than in THF.

The reaction of $K^+An\cdot^-$ with H_2O and with EtOH in DME remained essentially second order in the absorbance. However, the rates were about an order of magnitude slower than in THF (Table I). As indicated above, these data have not been independently verified. In contrast to most of the data obtained with THF as the solvent, the reactions in DME were slow enough that background decay and instrumental problems might make the results only qualitatively useful.

These results show that a major mechanism for the protonation of $K^+An\cdot^-$ in THF and in DME involves reaction steps prior to the protonation step. These first reaction steps appear to be hindered by increased solvation of the cation. The zero-order dependence on water in DME suggests that, in this case, the formation of the intermediate is much slower than the protonation step. The effect on the reaction rate of a change in the solvent was even more striking when $K^+An\cdot^-$ in ethylenediamine was mixed with 0.19 M water in ethylenediamine. In this instance, no reaction was observed, even over a period of 5 to 10 min. This result is consistent with the very low rate constant (2×10^{-4} M^{-1} sec^{-1}) reported by Hayano and Fujihira[8] for the protonation of $An\cdot^-$ by H_2O in dilute solutions in DMF.

In a further attempt to check the importance of ion pairing, a few experiments were done in which the reactions of water and of ethanol with sodium anthracenide ($Na^+An\cdot^-$) in THF and in DME were studied. Sodium was chosen as the cation on the basis of conductance data which indicate that $Na^+An\cdot^-$ is less strongly ion paired than is $K^+An\cdot^-$ in THF at 25°.[23]

The reaction of $Na^+An\cdot^-$ with ethanol in THF was second order in $[Na^+An\cdot^-]$ and appeared to be of low order in [EtOH]. The rate was similar to that observed for the reaction of $K^+An\cdot^-$ with ethanol in THF and indicates no pronounced difference between the reactions of $Na^+An\cdot^-$ and $K^+An\cdot^-$ in this case. Two attempts were made to study the rate of reaction of $Na^+An\cdot^-$ with water in THF. In one case, pseudo-second-order decay was observed. However, in the other case (the first attempt), a large first-order component was also observed. Although there were no obvious problems with stability, this inconsistency forced us to eliminate this reaction from quantitative consideration. It is possible that the true rate constant for the pseudo-first-order reaction of $Na^+An\cdot^-$ with water in THF is considerably smaller than that reported by Bank and Bockrath[9b] for this system at 20°. For example, their rate constant ($2k = 1328$ M^{-1} sec^{-1}) would predict a maximum half-life of 32 msec for $[H_2O] = 0.0163$ M. For

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a typical push at this water concentration, however, we find successive half-lives of 180, 450, and 700 msec beginning at an anthracenide concentration of 1.2 × 10^{-4} M. By contrast, however, our run which showed a large pseudo-first-order contribution but was presumably carried out under similar conditions gave successive half-lives of 26, 34, and 26 msec for $[H_2O]$ = 0.047 M compared with the value of 11 msec predicted from the published rate constant.[9b] Although we presumed that our lack of reproducibility in this case was caused by the reaction of $Na^+An\cdot^-$ with impurities, it is possible that the pseudo-first-order reaction with water is either catalyzed or inhibited by impurities. In any case, it will require further work to clarify the nature of the pseudo-first-order process.

Striking differences were encountered when the reaction of $Na^+An\cdot^-$ with ethanol or with water in DME was studied. First, the rate of decay of $Na^+An\cdot^-$ in DME was much slower than in THF. Second, the decay could be well described by a rate law which was first order in the absorbance. The difference between the reaction of $K^+An\cdot^-$ and of $Na^+An\cdot^-$ with water in DME is shown in Figure 5. The dependence of the first-order rate upon the concentration of proton donor was not extensively studied because of the slowness of the reaction and the problems with competing decay processes in this run. Recently, Szwarc and coworkers[24] have made an extensive study of this system which includes the variation of the first-order rate constant with concentration and nature of the proton donor.

Although the rates of protonation of $Na^+An\cdot^-$ have not been studied as extensively by us as those of K^+-$An\cdot^-$, certain conclusions can be drawn about the effect of cation and solvent. The reactions of both $K^+An\cdot^-$ and $Na^+An\cdot^-$ are slower in DME than in THF. Furthermore, in DME the reactions proceed more slowly when sodium rather than potassium is used. Finally, there is clearly a difference in the rate law which describes the disappearance of $K^+An\cdot^-$ compared with $Na^+An\cdot^-$ in DME (Figure 5).

The results are consistent with a mechanism in which contact ion-pair formation facilitates the protonation through pathways which lead to both pseudo-first-order and pseudo-second-order disappearance of the radical anion. Under most of the conditions used in this study, the second-order mode of reaction predominates over the slower first-order reaction. When conditions are less favorable to the formation of contact ion pairs, the second-order protonation reaction slows down and it appears that the first-order process also becomes slower. However, the pseudo-first-order reaction was not studied in enough detail to permit reliable evaluation of the order in ROH or the rate constant.

While the value of the rate constant[24] for the first-order reaction of $Na^+An\cdot^-$ with EtOH in DME (6.5 M^{-1} sec^{-1}) is much smaller than that obtained by pulse radiolysis in pure ethanol[2] (2.3 × 10^4 M^{-1} sec^{-1}), a recent study indicates that this difference is probably due at least in part to solvent effects. It was shown[4] that the pulse radiolysis of biphenyl in ethanol–amine mixtures gave rates which decreased upon addition of the amine. The marked increase in the rate of protonation of $An\cdot^-$ by water in DMF as the concentration of water is increased[7] also illustrates the importance of the solvent effect. The recent study of Bank and Bockrath[9a] indicates that sodium naphthalenide in THF undergoes a rapid protonation which is first-order in each reactant. Preliminary studies in this laboratory of the reaction of potassium terphenylide with ethanol in THF showed that this reaction may also be fast ($k \approx$ 1 × 10^5 M^{-1} sec^{-1}) and first order in both the radical anion and in ethanol. However, in this case, the anion solution showed visual and spectrophotometric indications of some decomposition in the syringe. Therefore, in view of possible effects of decomposition products on the kinetics of protonation, the fast first-order decay might be an artifact.

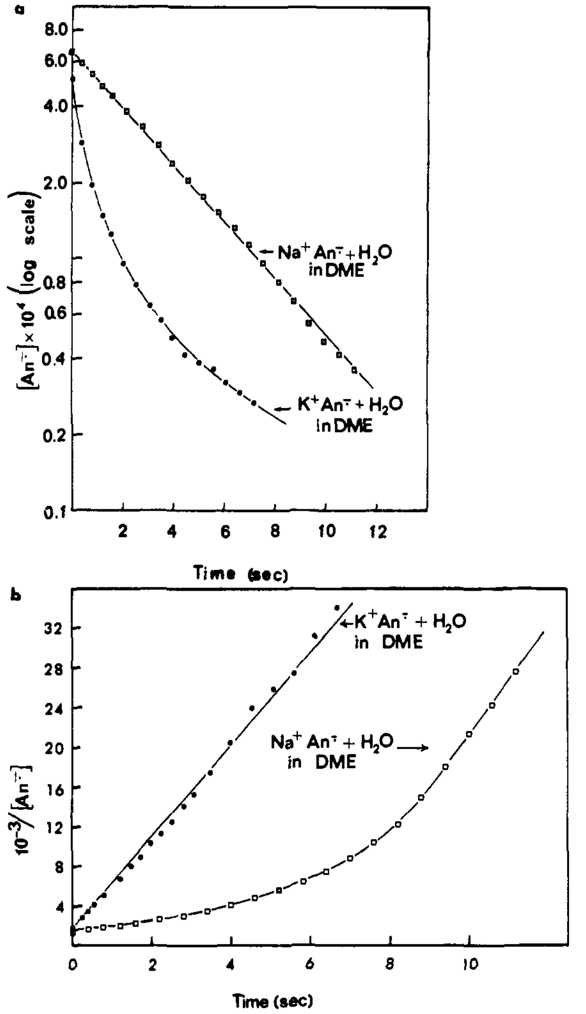

Figure 5. Pseudo- (a) first- and (b) second-order plots of the reactions of (●) $K^+An\cdot^-$ with 0.0357 M water in DME and of (□) $Na^+An\cdot^-$ with 0.0124 M water in DME.

Recently, Levin, Sutphen, and Szwarc[10] completed a comprehensive study of the protonation kinetics of sodium perylenide in THF. The reaction was shown to be second order in $Na^+Pe\cdot^-$, first order in ROH, and inverse first order in Pe. Their work is in complete agreement with a mechanism which involves formation and subsequent protonation of the ion pair of the dianion, Pe^{2-}, $2Na^+$, according to

$$2Pe\cdot^-,Na^+ \overset{K}{\rightleftharpoons} Pe^{2-},2Na^+ + Pe \qquad (8)$$

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Table II. Observed and Calculated Pseudo-Second-Order Rate Constants for the Reaction of $K^+An\cdot^-$ with EtOH in THF and Pseudo-First-Order Contribution at High Ethanol Concentrations

$10^3(EtOH)_0$, M	$10^3(An\cdot^-)_0$, M	$10^2(An)_0$, M	No. of pushes	Pseudo-second-order rate constants, M^{-1} sec^{-1} $\times 10^{-4}$			Pseudo-first-order rate constants, sec^{-1}	
				$\bar{f}_{\text{calcd}}$ (eq 31)	$\bar{f}_{\text{obsd}}$	σ^a	$\bar{k}_1$	σ^a
0.06	0.83	4.43	1	0.00605	0.00421^b			
0.12	0.73	4.42	1	0.0121	0.00868^b			
0.51	1.12	4.40	4	0.0505	0.0367^b	0.086		
0.60	0.76	1.06	2	0.177	0.121^b	0.015		
0.78	0.24	0.237	2	0.563	1.08^b	0.05		
1.06	1.23	1.04	2	0.286	0.210^b	0.026		
1.13	0.58	0.220	2	0.688	1.14^b	0.08		
1.33	1.92	0.153	3	0.815	0.460^e	0.116		
1.51	2.12	4.35	4	0.143	0.151^c	0.051		
1.65	0.56	2.55	3	0.224	0.286^b	0.049		
2.07	2.24	0.989	3	0.476	0.336^c	0.084		
2.22	1.09	2.53	3	0.287	0.345^b	0.037		
2.43	1.86	0.155	4	0.948	1.06^c	0.22		
3.14	0.25	0.236	5	0.940	0.927^b	0.018		
3.50	0.60	0.219	5	0.978	1.08^b	0.29		
3.53	2.41	2.46	3	0.421	0.462^c	0.075		
4.23	2.05	0.998	6	0.716	0.604^c	0.11		
4.55	1.66	0.166	6	1.07	1.18^c	0.18		
8.70	0.19	0.062	6	1.26	1.85^d	0.26		
8.73	0.14	0.833	3	1.04	0.995^d	0.11		
37.66	1.97	2.46	4	1.83	1.83^d	0.08	0.55	0.16
85.74	1.28	4.39	4	3.06	3.52^d	0.09	3.73	1.48
86.38	1.74	0.160	5	3.22	2.54^d	0.12	1.42	0.83
88.95	0.97	0.199	4	3.28	3.56^d	0.20	3.62	0.28
131.4	0.20	0.062	3	4.35	4.70^d	1.37	6.74	0.33
446.5	0.90	4.42	6	12.2	9.48^d	1.44	53.1	8.2
449.5	0.37	0.238	3	12.3	18.4^d	5.5	53.1	12.7

[a] See footnote *b* from Table I. [b] Rate constants after various extents of reaction from fit of eq 14. [c] Initial rate constants from fit of eq 14. [d] From fit of data to parallel first- and second-order decay. [e] Initial rate constant from empirical fit of data.

$$Pe^{2-},2Na^+ + ROH \xrightarrow{k} Na^+PeH^- + Na^+OR^- \quad (9)$$

$$Na^+PeH^- + ROH \xrightarrow{\text{fast}} PeH_2 + Na^+OR^- \quad (10)$$

Although our preliminary results[12] were not in complete agreement with a similar mechanism for the protonation of $K^+An\cdot^-$ in THF, we had not investigated the reaction over a wide enough range of concentrations of ROH and An to rule out the "dianion mechanism."

$$2An\cdot^-,K^+ \underset{k_-}{\overset{k_+}{\rightleftharpoons}} An^{2-},2K^+ + An \quad (11)$$

$$An^{2-},2K^+ + ROH \xrightarrow{k_1} K^+AnH^- + K^+OR^- \quad (12)$$

$$K^+AnH^- + ROH \xrightarrow{\text{fast}} AnH_2 + K^+OR^- \quad (13)$$

This mechanism yields the rate law

$$\frac{-d(K^+An\cdot^-)}{dt} = \frac{2k_+(K^+An\cdot^-)^2}{1 + \{k_-(An)/k_1(ROH)\}} \quad (14)$$

which at low values of the ratio (An)/(ROH) reduces to

$$-d(K^+An\cdot^-)/dt = 2k_+(K^+An\cdot^-)^2 \quad (15)$$

while at high values of the ratio it becomes

$$\frac{-d(K^+An\cdot^-)}{dt} = \frac{2k_+k_1(K^+An\cdot^-)^2(ROH)}{k_-(An)} \quad (16)$$

An alternative mechanism, the "ion-cluster mechanism,"[12] was in reasonable accord with the original data. This mechanism involves the protonation of an ion-cluster according to

$$2An\cdot^-,K^+ \underset{k_-'}{\overset{k_+'}{\rightleftharpoons}} (An\cdot^-,K^+)_2 \quad (17)$$

$$(An\cdot^-,K^+)_2 + ROH \xrightarrow{k_1'} K^+AnH^- + K^+OR^- + An \quad (18)$$

followed by reaction 13. This gives the rate law

$$\frac{-d(K^+An\cdot^-)}{dt} = \frac{2k_+'(K^+An\cdot^-)^2}{1 + \{k_-'/k_1'(ROH)\}} \quad (19)$$

It should be noted that the formation of triple and quadruple ion-clusters is expected[25,26] in solvents such as THF. However, this process would be too fast to explain the low value of k_+'. Therefore, in considering this mechanism, we presumed that partial or complete electron transfer from one radical anion to the other occurred prior to the protonation step.

In order to distinguish between these possible mechanisms an extensive study of the effect of the concentration of ROH and of free An was undertaken. For this purpose the reaction of $K^+An\cdot^-$ with ethanol in THF was chosen. The concentration of EtOH was varied from a value less than that of $K^+An\cdot^-$ to such a high concentration (~0.5 M) that the pseudo-first-order reaction became appreciable. The lower limit of (An) was restricted by the necessity to prevent formation of An^{2-} and the upper limit (0.04 M) was high enough to give a 40-fold range of concentration of An.

Only at concentrations of both An and EtOH appreciably greater than that of $K^+An\cdot^-$ is pseudo-order kinetics valid. Otherwise, the increase in (An) and decrease in (EtOH) during reaction must be considered. At high concentrations of EtOH especially after the first one or two half-lives, the first-order decay became important. In these cases, the decay of absorbance was fitted (by using a nonlinear least-squares program[16]) by mixed first- and second-order expressions. The data

(25) R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **57**, 1 (1935).
(26) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

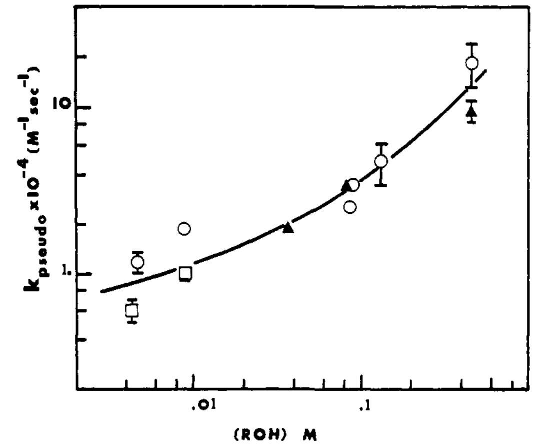

Figure 6. Log–log plot of k_{ps} (second order) *vs.* (EtOH) for the reaction of $\mathrm{K^+An\cdot^-}$ with EtOH in THF: (○) low initial free An concentration; (□) medium initial (An); (▲) high initial (An).

in this region are given in Table II. Below about 0.05 *M* in EtOH the first-order contribution was negligible.

Both the "dianion mechanism" and the "ion-cluster mechanism" predict that the second-order decay will become independent of (EtOH) at high ethanol concentrations because of the limit set by k_+ or k_+'. However, as seen in Figure 6, this did not occur. Also, the rate did not depend significantly upon (An) at high concentrations of ethanol as required by the dianion mechanism. Clearly, *neither* of these reaction mechanisms fits the data at high ethanol concentrations. On the other hand, the data for (ROH) $\lesssim$ 0.01 *M* are reasonably consistent with the dianion mechanism. Figure 7 shows the influence of the ratio (ROH)/(An) on the rate compared with that of (ROH) alone.

The effect of solvent on the protonation rate found in this work and by others[9,24] indicates the important role played by contact ion pairing. To provide a further test of this role, we added "crown," dicyclohexyl-18-crown-6,[27] to the solution of $\mathrm{K^+An\cdot^-}$ prior to protonation. The "crown" forms a complex with the cation and breaks up the contact ion pair.[28,29] The effect on the protonation rate was very dramatic as shown in Figure 8. The second-order component vanished completely when "crown" was present in excess, and the first-order component decreased by a factor of about 100. When less than the stoichiometric amount of "crown" was used, the fast initial decay was followed by a much slower, first-order decay. These results show that even the first-order protonation rate is much faster for the contact ion pair than for the solvent-separated ion pair.

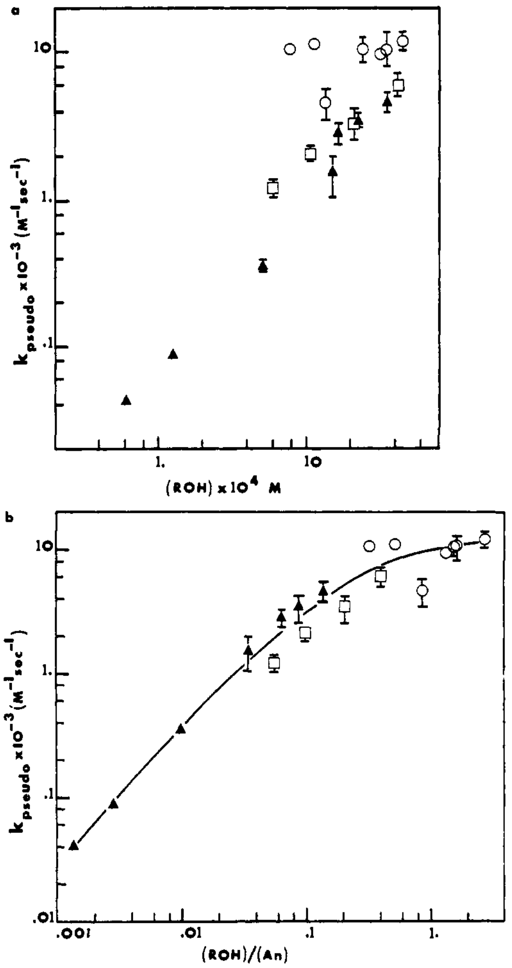

Figure 7. Log-log plot of k_{ps} (second order) *vs.* (a) (EtOH) and (b) (EtOH)/(An), for the reaction of $\mathrm{K^+An\cdot^-}$ with EtOH in THF: (○) low $(\mathrm{An})_0$; (□) medium $(\mathrm{An})_0$; (▲) high $(\mathrm{An})_0$.

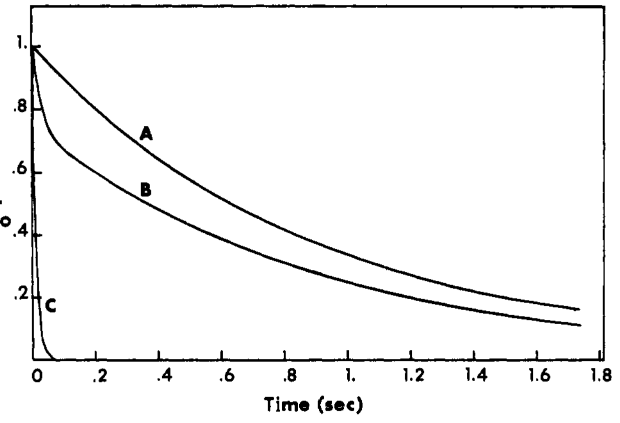

Figure 8. C/C_0 *vs.* time for the reaction $2\mathrm{K^+An\cdot^-} + 2\mathrm{EtOH} \rightarrow \mathrm{AnH_2} + \mathrm{An} + 2\mathrm{K^+EtO^-}$ (THF): (A) (crown) > $(\mathrm{K^+An\cdot^-})$, (B) (crown) < $(\mathrm{K^+An\cdot^-})$, (C) no crown. $(\mathrm{EtOH})_0$ = 0.45 *M* for all cases.

The protonation rate seems to depend upon the degree of charge localization, with the free radical anion at one extreme and the ion-paired dianion at the other. The contact pair, $\mathrm{An\cdot^-,M^+}$, protonates at an intermediate rate. Presumably, the quadruple ion-cluster $(\mathrm{An\cdot^-,M^+})_2$, would protonate at a rate intermediate between that of the contact ion pair and the dianion. We have considered a large number of possible mechanisms in attempts to fit the data over the entire range of concentrations of EtOH, An, and $\mathrm{An\cdot^-}$. Two types of mechanisms adequately describe the ethanol data and will be considered separately. The order of presentation does not indicate a preference for one mechanism over the other (both fit the data equally well). However, the effect of the nature of the proton donor makes the second mechanism somewhat more plausible in our view.

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(27) C. J. Pedersen, *J. Amer. Chem. Soc.*, 89, 7017 (1967).

(28) J. L. Dye, M. T. Lok, F. J. Tehan, R. B. Coolen, N. Papadakis, J. M. Ceraso, and M. DeBacker, *Ber. Bunsenges. Phys. Chem.*, 75, 659 (1971).

(29) K. H. Wong, G. Konizer, and J. Smid, *J. Amer. Chem. Soc.*, 92, 666 (1970).

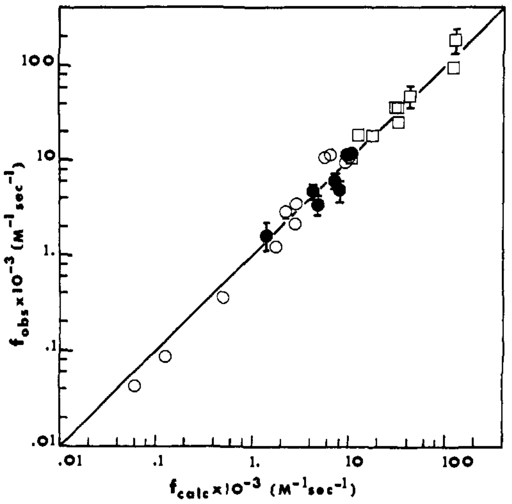

Figure 9. Log-log plot of f_{obsd} *vs.* f_{calcd}: (○) f_{obsd} at various extents of reaction; (●) f_{obsd} from initial rates; (□) f_{obsd} from parallel first- and second-order fit of entire decay curve.

Dianion and Ion-Cluster Mechanism. An estimate of the equilibrium constant for the reaction

$$2\mathrm{An}\cdot^-,\mathrm{M}^+ \rightleftharpoons (\mathrm{An}\cdot^-,\mathrm{M}^+)_2 \tag{20}$$

can be made by using the Fuoss expression[25,26]

$$K_Q = \frac{N_{Av}}{2000}\left(\frac{\pi}{3}\right)^{3/2} \frac{\mu^2}{DkT}\frac{e^y}{y^{7/2}}\left(\frac{1}{2\lambda^2} - 1\right)^{-1/2} \tag{21}$$

in which μ is the dipole moment of the ion pair considered as an ellipsoid of major axis a and minor axis λa, and

$$y = \mu^2/[(\lambda a)^3 DkT] \tag{22}$$

A value of a = 5.7 Å was estimated by fitting the observed ion-pair association constant of $\mathrm{Na^+An\cdot^-}$[20] by the Fuoss equation[26]

$$K_a = (4\pi a^3 N_{Av}/3000)e^b \tag{23}$$

with

$$b = e^2/aDkT \tag{24}$$

The value of K_Q obtained in this way is 48 M^{-1}. An alternate approach which uses the Fuoss-Kraus expression[30] for the triple-ion formation constant and assumes that the equilibrium constant for the reaction

$$\mathrm{An}\cdot^-,\mathrm{K}^+,\mathrm{An}\cdot^- + \mathrm{K}^+ \rightleftharpoons (\mathrm{An}\cdot^-,\mathrm{K}^+)_2 \tag{25}$$

is the same as the ion-pair association constant, yields $K_Q = 67\ M^{-1}$.

Incorporation of the ion-cluster species as an intermediate which can be protonated gives the overall reaction scheme

$$2\mathrm{An}\cdot^-,\mathrm{K}^+ \overset{K_Q}{\rightleftharpoons} (\mathrm{An}\cdot^-,\mathrm{K}^+)_2 \underset{k_-''}{\overset{k_+''}{\rightleftharpoons}} \mathrm{An}^{2-},2\mathrm{K}^+ + \mathrm{An} \tag{26}$$

$$\mathrm{An}^{2-},2\mathrm{K}^+ + \mathrm{ROH} \xrightarrow{k_1} \mathrm{K^+AnH^-} + \mathrm{K^+OR^-} \tag{27}$$

$$(\mathrm{K^+An}\cdot^-)_2 + \mathrm{ROH} \xrightarrow{k_2} \mathrm{K^+AnH^-} + \mathrm{K^+OR^-} + \mathrm{An} \tag{28}$$

followed by reaction 13. This yields the rate law

$$\frac{-d(\mathrm{K^+An}\cdot^-)}{dt} = \frac{2k_+''K_Q(\mathrm{K^+An}\cdot^-)^2}{1 + \{k_-''(\mathrm{An})/k_1(\mathrm{ROH})\}} + 2K_Qk_2(\mathrm{K^+An}\cdot^-)^2(\mathrm{ROH}) \tag{29}$$

At high values of (ROH), this rate law refers to the pseudo-second-order decay, after correction for the first-order process. Of course, the ion-cluster cannot be kinetically distinguished from the "caged-complex" of $\mathrm{An^{2-},2M^+}$ with An as suggested by Rainis, Tung, and Szwarc.[24]

Because the rate expression (eq 29) has three adjustable parameters, $k_+''K_Q$, k_-''/k_1, and K_Qk_2 whose separation depends upon the variation of (An) and (ROH), it is difficult to fit to the data directly. Therefore, an indirect approach was used. The rate expression was written as

$$-d(\mathrm{K^+An}\cdot^-)/dt = f(\mathrm{An,ROH})(\mathrm{K^+An}\cdot^-)^2 \tag{30}$$

in which

$$f(\mathrm{An,ROH}) = \frac{2k_+''K_Q}{1 + \{k_-''(\mathrm{An})/k_1(\mathrm{ROH})\}} + 2K_Qk_2(\mathrm{ROH}) \tag{31}$$

depends upon the three parameters and the concentrations of An and ROH. From their initial concentrations and material balance, these concentrations are known at any point in the reaction. At high concentrations of ROH and of An, f(An,ROH) is just the pseudo-second-order rate constant. At low concentrations of (ROH) the entire progress curve could be fitted by eq 14 of the "dianion mechanism" so that f(An,ROH) could be calculated at both the initial concentrations and at various extents of reaction. To adjust the parameters in this case it was necessary to use a least-squares differential equation fitting routine.[16] Finally, eq 31 was fitted by least squares to the data over the entire range of concentrations of An and ROH. The data are given in Table II and are shown graphically in Figure 9. It can be seen that this equation agrees (within one or two standard deviations of repeated pushes) with the data over nearly a 10^3 variation of the function f(An,ROH). The values of the constants in eq 31 are given in Table IIIa.

Table III

	Calculated constants from eq 31 (a) With EtOH	(b) With all proton donors
$k_+''K_Q$, M^{-1} sec^{-1}	$(5.33 \pm 0.32) \times 10^3$	$(6.09 \pm 0.71) \times 10^3$
k_-''/k_1	0.316 ± 0.063	0.35 ± 0.14
k_2K_Q, M^{-2} sec^{-1}	$(1.25 \pm 0.07) \times 10^5$	$(1.33 \pm 0.08) \times 10^5$

In order to check the validity of this procedure, all of the decay curves were computed *via* eq 30 by using the least-squares values of the three parameters obtained from all of the data. Only the initial absorbance was adjusted. The agreement was, in general, excellent over the entire progress curve. Figure 10 shows the calculated and observed concentrations of $\mathrm{K^+An\cdot^-}$ *vs.* time for widely varying initial conditions. The curves shown in this figure were chosen on the basis that they showed deviations between calculated and observed

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(30) R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 55, 2387 (1933).

concentrations about equal to the average deviation of all of the rate data.

Cation-Solvation Mechanism. A second interpretation is suggested by the pronounced effect of water concentration on the rate of protonation of $An\cdot^-$ in DMF–water mixtures.[7] This effect (which is formally equivalent to a reaction order of nearly five in water above (H_2O) = $3M$) was attributed to the stabilization of charge localization in the transition state by hydrogen bonding.[8,31] A similar effect could be operative in the present study, so that the rate of formation of the dianion, and/or the rate of protonation of the ion-cluster, would be increased by the presence of ROH in the vicinity of the anion. An easy way to bring ROH into close proximity is *via* cation solvation. A similar scheme has been proposed for proton or deuteron exchange on carbanions.[32] According to this mechanism, potassium ion is solvated by ROH

$$K^+ + ROH \overset{K_s}{\rightleftarrows} K^+\cdot ROH \qquad (32a)$$

or

$$An\cdot^-,K^+ + ROH \overset{K_s}{\rightleftarrows} An\cdot^-,K^+\cdot ROH \qquad (32b)$$

Substitution of $K^+\cdot ROH$ for the THF-solvated cation in the contact ion pair with $An\cdot^-$ could increase the charge localization on the radical anion in the vicinity of the cation. Whether this leads to an increased rate of formation of the dianion or to a concerted protonation of the quadruple ion-cluster is difficult to assess. The former gives the expression 33 (assuming the same

$$f(An,ROH) = \frac{2k_+ + 2K_sk_a(ROH)}{[1 + \{k_-(An)/k_1(ROH)\}][1 + K_s(ROH)]^2} \qquad (33)$$

dianion species to be formed) with k_a the accelerated dianion formation rate constant. The concerted protonation of the quadruple ion-cluster leads to eq 34.

$$f(An,ROH) = [1 + K_s(ROH)]^{-2} \times \left[\frac{2k_+''K_Q}{1 + \{k_-''(An)/k_1(ROH)\}} + 2K_QK_sk_2'(ROH)\right] \qquad (34)$$

Equations 31, 33, and 34 all fit the data about equally well because: (1) K_s(ROH) is generally small compared to 1 so that the term $[1 + K_s(ROH)]^2$ is about unity (this was tested by fitting the data with eq 33), (2) at concentrations of EtOH high enough for the first-order term in (ROH) to be important, the value of the term containing (An)/(ROH) is small compared to unity.

The paucity of data for the other proton donors and the lack of verification by replicate runs make it somewhat hazardous to use these data to distinguish between the alternatives. However, the apparent insensitivity to the nature of the proton donor (Figure 4) suggests that a cation-solvation mechanism may be responsible for the breakdown of the dianion mechanism at high concentrations of the proton donor. To reactions 11, 12, and 32b we add reactions which effectively yield the reaction

$$An\cdot^-,K^+ + An\cdot^-,K^+\cdot ROH \xrightarrow{k_d} K^+AnH^- + K^+OR^- + An \qquad (35)$$

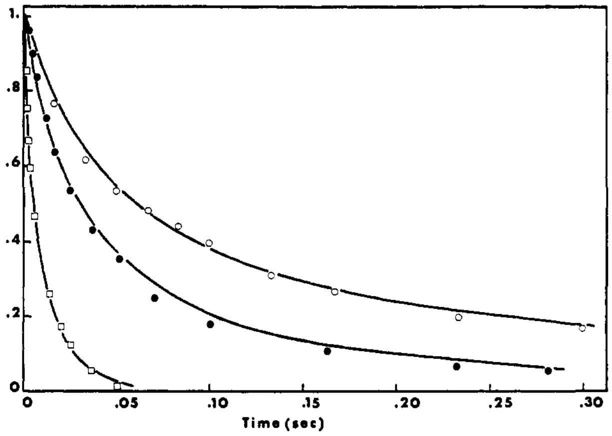

Figure 10. C/C_0 *vs.* time for the reaction of $K^+An\cdot^-$ with EtOH in THF at three different values of $(EtOH)_0$. Solid lines (——) represent calculated curves. The constants of eq 31 used for this calculation are given in Table IIIa.

The reaction described by eq 35 might go through the dianion with subsequent protonation by the ROH which is complexed to the cation. This protonation could be so rapid that the reverse reaction could not compete. Alternatively, the proton transfer and the electron transfer might be concurrent. In order to explain the insensitivity to the acidity of the proton donor, it must be presumed that reaction 12 is nearly diffusion controlled. The rate law derived from this mechanism is

$$f(An,ROH) = [1 + K_s(ROH)]^{-2} \times \left[\frac{2k_+}{1 + \{k_-(An)/k_1(ROH)\}} + 2k_dK_s(ROH)\right] \qquad (36)$$

This equation has the same form as eq 34. If, as expected from the fit of the data, $K_s(ROH) << 1$, eq 36 has the same dependence upon (An) and (ROH) as does eq 31. A fit of eq 31 to the data for all proton donors in THF given in Tables I and II yields the constants given in Table IIIb. A measure of the "goodness of fit" is given by the standard deviation of f_{calcd}/f_{obsd}. This is 0.27 for the ethanol data given in Table II and the constants of Table IIIa and increases to 0.36 when the data from Table I are included and the constants of Table IIIb are used. Therefore, any systematic effects caused by changing the proton donor are small. However, it should be noted that except for the case of ethanol, (An)/(ROH) was low enough that eq 36 might be insensitive to this ratio.

Summary and Conclusions

These results and those of other workers[7,9,10,11,24] show that the protonation rate of aromatic radical anions in solution depends not only upon the acidity of the proton donor but also very strongly upon the state of aggregation of the ions in solution. For the case of $K^+An\cdot^-$ in THF, direct protonation by ROH appears to be slow compared with fast second-order processes. At low concentrations of ROH the major protonation pathway is *via* the dianion species, An^{2-},$2K^+$ which apparently has a protonation rate near the diffusion-controlled limit. At higher concentrations of the proton donor, the rate becomes independent of the anthracene concentration while remaining largely second order in $K^+An\cdot^-$. This suggests the protona-

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[31] S. Hayano and M. Fujihira, *Bull. Chem. Soc. Jap.*, **44**, 2051 (1971).

[32] S. M. Wong, H. P. Fisher, and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 2235 (1971).

tion of an ion-cluster $(An\cdot^-,K^+)_2$, in which electron transfer to yield $An^{2-},2K^+,An$ may occur prior to the rapid protonation step. An attractive alternative is rapid protonation of one of these species by an ROH molecule which is coordinated to K^+ within the complex.

The effect of solvent and of "crown" upon the protonation rate clearly shows that the pseudo-second-order pathway requires formation of contact ion pairs. Even the pseudo-first-order component is markedly decreased when contact pair formation is prevented.

Although specific solvent effects may alter the protonation rates significantly, the results to date on a variety of systems (excluding those in the pure alcohols[2-4]) are consistent with an overall scheme in which the dominant factor is the degree of charge localization in the aromatic system. We expect localization of charge to decrease in the order

$$\underset{(1)}{(An^{2-},2M^+)} > \underset{(2)}{(An\cdot^-,M^+)_2} > \underset{(3)}{(An\cdot^-,M^+)} > \underset{(4)}{(An\cdot^-\|M^+)} > \underset{(5)}{(An\cdot^-)}$$

The rate constants for protonation of these species by ethanol will be designated as k_1 through k_5, respectively. According to the results obtained in DMF as solvent,[8] $k_5 \approx 2 \times 10^{-4}\ M^{-1}\ sec^{-1}$. If we presume that $Na^+An\cdot^-$ exists in DME largely as the solvent-separated ion pair then the data of Rainis, Tung, and Szwarc[24] permit the estimate, $k_4 \approx 6\ M^{-1}\ sec^{-1}$. We have for $K^+An\cdot^-$ in THF, $k_4 \overset{\sim}{<} 2\ M^{-1}\ sec^{-1}$ (with crown), $k_3 \approx 200\ M^{-1}\ sec^{-1}$, but we cannot be certain that these reactions are bimolecular; indeed, in such solvents as DMF the rate constants for the reaction with water depend very strongly upon the concentration.[7]

The value chosen for k_2 depends upon the nature of the protonated species and hence upon the mechanism used. If the protonated species is a complex such as $An^{2-},2K^+,An$, then we expect k_2 to be near the diffusion-controlled limit ($k_d \approx 1.7 \times 10^{10}\ M^{-1}\ sec^{-1}$). If the proton donor is already present in the complex as $K^+\cdot ROH$, then the protonation step is not bimolecular but it is presumably rapid. The interaction of the alcohol with K^+ and with the negative charge on the aromatic system could make the alcohol more acidic so that a facile proton transfer could occur. At the other extreme, we would expect protonation of the ion-cluster $(An\cdot^-,K^+)_2$ to be slower than that of the dianion, but faster than that of the ion pair $(An\cdot^-,K^+)$. From our value $K_Qk_2 = 1.25 \times 10^5\ M^{-2}\ sec^{-1}$ and the estimate $K_Q = 50\ M^{-1}$ we obtain $k_2 \approx 2.5 \times 10^3\ M^{-1}\ sec^{-1}$. With such a low rate constant, we would expect the rate of protonation of the ion cluster to change with the acidity of the proton donor. Since all of the proton donors which were tested showed about the same behavior, the alternate reaction mechanism, in which intracomplex protonation by $K^+\cdot ROH$ occurs, seems preferable.

Potentiometric data[33] yield an overall disproportionation equilibrium constant for the reaction in THF

$$2An\cdot^-,K^+ \underset{k_-}{\overset{k_+}{\rightleftarrows}} An^{2-},2K^+ + An \qquad (11)$$

of about 1×10^{-5}. From the contribution of the dianion mechanism (Table III), we find k_+ (or $k_+''K_Q$) $\cong 5 \times 10^3\ M^{-1}\ sec^{-1}$, which gives k_- (or k_-'') $\approx 5 \times 10^8\ M^{-1}\ sec^{-1}$. The value $k_-/k_1 \cong 0.3$ (Table III) yields $k_1 \cong 1.5 \times 10^9\ M^{-1}\ sec^{-1}$.

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