Protonation of Perylene Radical Anions by Alcohols and Water in Tetrahydrofuran

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Abstract: Kinetics of protonation of perylene radical anions ($Pe\cdot^-,Na^+$) by MeOH, EtOH, *i*-PrOH, *t*-BuOH, and water was investigated in THF at 25° by the stop-flow technique. The dianion, $Pe^{2-},2Na^+$, is the actual base that is protonated. This is evident from the rate of protonation which is second order in $Pe\cdot^-,Na^+$ and is inversely proportional to the concentration of the added perylene (Pe). Thus, the proposed mechanism is $2Pe\cdot^-,Na^+ \rightleftarrows Pe^{2-},2Na^+ + Pe\ (K_1)$; $Pe^{2-},2Na^+ + ROH \rightarrow$ protonated product (k_p). The rates of protonation are *first* order in ROH, the relative values of k_p being 100, 65, 44.5, and 9.25 for MeOH, EtOH, *i*-PrOH, and *t*-BuOH, respectively, and protonation by water is slightly slower than by *t*-BuOH. The Brønsted plot for MeOH, EtOH, and *t*-BuOH, using the p*K* values determined in DMSO, is perfectly linear with slope 0.42. Deuterated methanol was found to be seven times less reactive than CH_3OH, and D_2O about ten times less reactive than H_2O.

Previous studies in this laboratory demonstrated that some reactions of radical anions proceed through dianions.[1,2] For example, tetrahydrofuran (THF) does not protonate radical anions of diphenylacetylene ($DPA\cdot^-,Na^+$), while the respective dianions ($DPA^{2-},2Na^+$) are protonated even at −60°.[3] Consequently, a solution of $DPA\cdot^-,Na^+$ and sodium biphenylide ($B\cdot^-,Na^+$) in THF is protonated by the solvent as a result of the following sequence of reactions

$$DPA\cdot^-,Na^+ + B\cdot^-,Na^+ \rightleftarrows DPA^{2-},2Na^+ + B$$

$$DPA^{2-},2Na^+ + THF \longrightarrow$$
$$PhCH{=}\bar{C}Ph,Na^+ + \text{products of THF deprotonation}$$

Recently we investigated the protonation of perylene radical anions, $Pe\cdot^-,Na^+$, by *tert*-butyl alcohol (*t*-BuOH), isopropyl alcohol (*i*-PrOH), ethanol, methanol, and CH_3OD and by H_2O and D_2O. Our kinetic studies clearly demonstrate that the observed reactions are due to the protonation of the respective dianions, $Pe^{2-},2Na^+$, maintained at low equilibrium concentration by the disproportionation

$$2Pe\cdot^-,Na^+ \rightleftarrows Pe^{2-},2Na^+ + Pe \quad K_1$$

$$Pe^{2-},2Na^+ + ROH \xrightarrow{k_p} \text{products of protonation}$$

The evidence is provided by two observations: (1) for constant concentrations of perylene and the alcohol (both being in excess) the reaction is *second* order in $Pe\cdot^-,Na^+$, and (2) the protonation is retarded by the unreduced perylene, *i.e.*, at constant concentration of the alcohol

$$-d[Pe\cdot^-,Na^+]/dt = \text{constant}[Pe\cdot^-,Na^+]^2/[Pe]$$

This expression is predicted by the scheme proposed above and the constant is then interpreted as the product $2k_pK_1[ROH]$, the factor 2 arising from the loss of two $Pe\cdot^-,Na^+$ on the formation of one $Pe^{2-},2Na^+$. It is probable that the resulting carbanion PeH^- is also protonated; however, this reaction does not affect the kinetics of disappearance of $Pe\cdot^-,Na^+$. Note, however, that the electron affinity of the resulting dihydroperylene may be higher than that of Pe. This problem is now investigated. The high electron affinity of PeH_2 may require modification of the factor 2 into a factor of 4.

Experimental Section

The reaction was studied in THF solution at room temperature utilizing the stop-flow technique described elsewhere.[4] All the required solutions were prepared on the high-vacuum line and enclosed in sealed glass ampoules equipped with breakseals. The ampoules were fused to the stop-flow system and the reagents introduced, when needed, by crushing the seal with a magnetic hammer.

The methods of purification of the reagents and of the solvent are also described in ref 4. The initial concentrations of perylene (Pe) and of sodium perylenide ($Pe\cdot^-,Na^+$) were determined spectrophotometrically, and their concentrations in the reaction cell were calculated on the basis of the dilution factors. The absence of any detectable amounts of the $Pe^{2-},2Na^+$ dianions in the solution of $Pe\cdot^-,Na^+$ was also established spectrophotometrically.

The alcohols were distilled *in vacuo* from solutions of their alcoholate. This procedure assured the absence of moisture.

Sodium tetraphenyl boride in 2.5-fold excess was added to the solution of $Pe\cdot^-,Na^+$ to assure the absence of free $Pe\cdot^-$ ions. Thus, the investigated reactions have to be attributed to ion pairs.[5]

The progress of protonation was monitored by the absorbance at 577 nm (λ_{max} of $Pe\cdot^-,Na^+$). The mixed reagents reached the optical cell in about 0.1–0.2 sec and the progress of the reaction was followed after stopping the flow for 1–4 min.

Results

No detectable protonation occurred during the time of flow (0.1–0.2 sec). When the flow was stopped a second-order reaction ensued, provided Pe and alcohol were in excess. The second-order character of the reaction is evident from typical graphs shown in Figure 1. The slopes of the lines exemplified by Figure 1 give the *apparent* bimolecular rate constant k_b, and for the sake of comparison their values listed in the tables were standardized either for a constant [alcohol], when their dependence on [Pe] was investigated, or

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[1] G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, 67, 768 (1970).

[2] G. Levin and M. Szwarc, *Chem. Commun.*, 1029 (1971).

[3] G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, 92, 2268 (1970).

[4] M. Szwarc, "Carbanions, Living Polymers and Electron-Transfer Processes," Interscience, New York, N. Y., 1968, Chapter IV.

[5] Dissociation of sodium tetraphenyl boride is relatively high in THF [see, *e.g.*, C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, 87, 5548 (1965)]. Hence, this salt is often added to solutions of sodium salts of carbanions or radical anions in order to suppress their dissociation into free ions.

Table I. Protonation of Pe·⁻,Na⁺ by *t*-BuOH in THF. Dependence of k_b on $[Pe]_0$ for Constant $[t\text{-BuOH}]$[a]

$[t\text{-BuOH}]_0 \times 10^2$ M	$[Pe]_0 \times 10^3$ M	k_b, M^{-1} sec^{-1}	k_b[b] (standardized), M^{-1} sec^{-1}
7.7	17.0	12.1	8.45
6.1	17.7	9.6	8.45
5.9	17.8	8.85	8.05
5.0	14.4	10.1	10.9
5.1	14.5	10.1	10.6
5.9	14.6	10.9	9.9
5.3	10.6	13.5	13.5
5.4	10.7	15.4	15.1
5.2	6.5	21.4	21.8
5.8	6.5	22.8	22.8
5.3	4.9	27.0	27.0
5.3	4.9	27.2	27.2
5.3	4.9	27.9	27.9
5.3	3.0	43.0	43.0
5.3	3.0	44.5	44.5
5.3	3.0	44.5	44.5
5.3	2.0	58.5	58.5
5.3	2.0	62.5	62.5
5.3	2.0	58.5	58.5
5.3	1.45[c]	94.5	94.5
5.3	1.45[c]	92.0	92.0
4.8	1.45[c]	95.0	107
5.3	1.10[c]	121	121
5.3	1.10[c]	133	133
5.3	0.89[c]	140	140

[a] $[Pe\cdot^-,Na^+]_0 = 6.4 \times 10^{-4}$ *M*. [b] k_b(standardized) is calculated for $[t\text{-BuOH}] = 5.3 \times 10^{-2}$, *i.e.*, k_b (standardized) = k_b $(5.3/[t\text{-BuOH}]) \times 10^{-2}$. [c] In these experiments the amount of Pe formed in the reaction is significant when compared with $[Pe]_0$. Consequently, the formation of Pe was taken into account in the kinetic expression leading to k_b and the values $[Pe]_0$ represent the average concentration of Pe in the pertinent experiment.

Table II. Protonation of Pe·⁻,Na⁺ by *t*-BuOH in THF Dependence of k_b on $[t\text{-BuOH}]$ for Constant $[Pe]_0$[a]

$[Pe]_0 \times 10^2$ M	$[t\text{-BuOH}]_0 \times 10^3$ M	k_b, M^{-1} sec^{-1}	k_b[b] (standardized), M^{-1} sec^{-1}
1.14	2.4[c]	0.50[c]	0.52[c]
1.05	3.5	1.2	1.15
1.03	10.5	3.2	3.0
1.05	37.5	11.0	10.5
1.17	32.8	11.6	12.3
1.34	53	16.0	19.5
1.34	53	15.8	19.2
1.34	53	13.2	16.2

[a] $[Pe\cdot^-,Na^+]_0 = 6.5 \times 10^{-4}$ *M*. [b] k_b (standardized) = $k_b \cdot ([Pe]_0/1.10) \times 10^2$. [c] There is a significant decrease in $[t\text{-BuOH}]$ in this run. However, no correction accounting for this effect was introduced.

Table III. Protonation of Pe·⁻,Na⁺ by *i*-PrOH in THF[a]

$[Pe]_0 \times 10^2$ M	$[i\text{-PrOH}]_0 \times 10^2$ M	k_b, M^{-1} sec^{-1}	k_b[b] (standardized), M^{-1} sec^{-1}
1.02	3.9	43	40
1.17	3.3	33	35.3
1.22	0.87	9.35	10.3
1.22	0.87	8.5	9.4

[a] $[Pe\cdot^-,Na^+]_0 = 6.4 \times 10^{-4}$ *M*. [b] k_b(standardized) for a constant $[Pe]_0 = 1.10 \times 10^{-2}$ *M*.

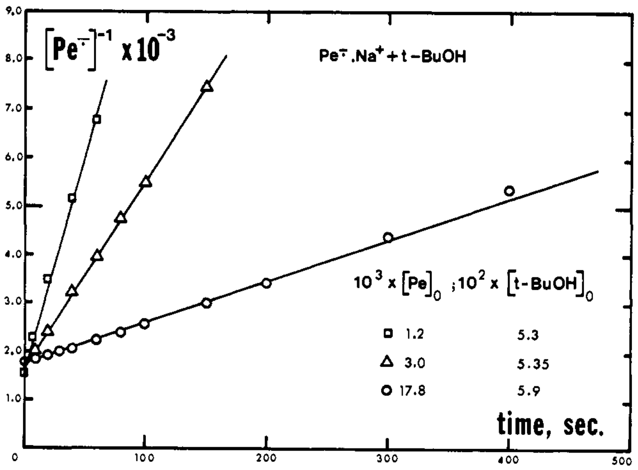

Figure 1. Plot of $1/[Pe\cdot^-,Na^+]$ *vs.* time for constant [Pe] and $[t\text{-BuOH}]$.

for a constant [Pe], when their dependence on [alcohol] was studied. These standardized k_b were denoted by k_b*.

The concentrations of the reagents in the reaction chamber are given in Tables I–V. The apparent second-order rate constants, standardized for a constant concentration of Pe while varying the concentration of the alcohol, are given in Tables II–V. Those stan-

Table IV. Protonation of Pe·⁻,Na⁺ by Ethanol in THF[a]

$[Pe]_0 \times 10^2$, M	$[EtOH] \times 10^2$ M	k_b, M^{-1} sec^{-1}	k_b[b] (standardized), M^{-1} sec^{-1}
0.99	1.62	41	37
0.74	2.0	55	37
0.87	3.3	72	57
0.87	3.3	83	65.5
0.56	4.2	139	70.5
0.98	9.1	184	164
0.87	10.1	187	148
0.76	11.2	216	149
0.76	11.2	254	175
0.98	20.3	394	350
0.95	20.9	393	338
0.88	22.5	420	336

[a] $[Pe\cdot^-,Na^+]_0 \approx 6 \times 10^{-4}$ *M*. [b] k_b (standardized) = $k_b[Pe]_0/1.10 \times 10^{-2}$.

Table V. Protonation of Pe·⁻,Na⁺ by CH_3OH and CH_3OD in THF

$[Pe]_0 \times 10^2$ M	[MeOH] × 10^2 M	k_b, M^{-1} sec^{-1}	k_b[a] (standardized), M^{-1} sec^{-1}
1.56	0.294	4.65	6.6
1.53	0.318	5.6	7.8
1.53	0.600	7.95	11.05
1.50	0.635	8.45	11.5
1.55	1.96	24.6	34.6
1.53	2.07	25.6	35.6
1.53	2.07	25.5	35.4
1.61	3.52	51.5	75.5
1.53	4.22	48.0	66.6
1.49	4.55	48.0	65.0
0.94	13.2	376	320
0.89	13.9	435	350
0.98	29.5	870	775
0.93	31.2	870	735
$[Pe]_0 \times 10^2$ M	$[MeOD] \times 10^2$ M	k_b, M^{-1} sec^{-1}	k_b[a] (standardized), M^{-1} sec^{-1}
1.49	0.345	0.84	1.14
1.53	1.45	2.41	3.36
1.53	1.45	2.56	3.56
1.45	4.00	6.85	9.05
1.53	4.22	6.80	9.40
1.53	4.22	6.80	9.40

[a] k_b (standardized) = $k_b[Pe]_0/1.10 \times 10^{-2}$.

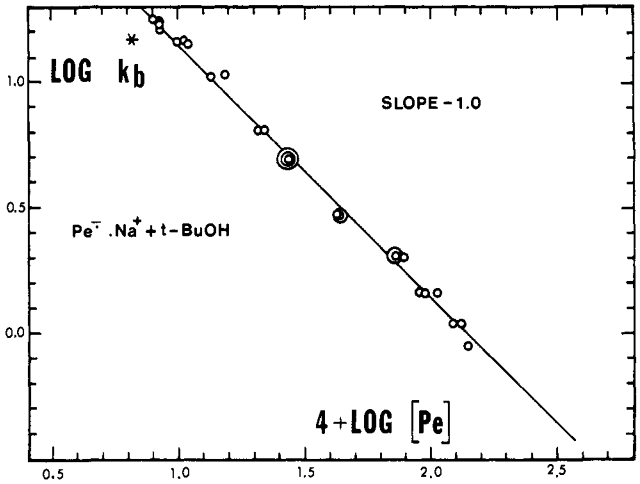

Figure 2. Log–log plot of k_b^* (standardized for a constant [t-BuOH]) *vs.* [Pe].

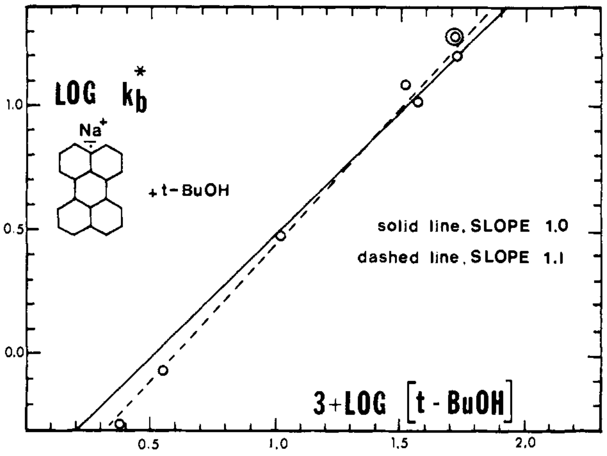

Figure 3. Log–log plot of k_b^* (standardized for a constant [Pe]) *vs.* [t-BuOH].

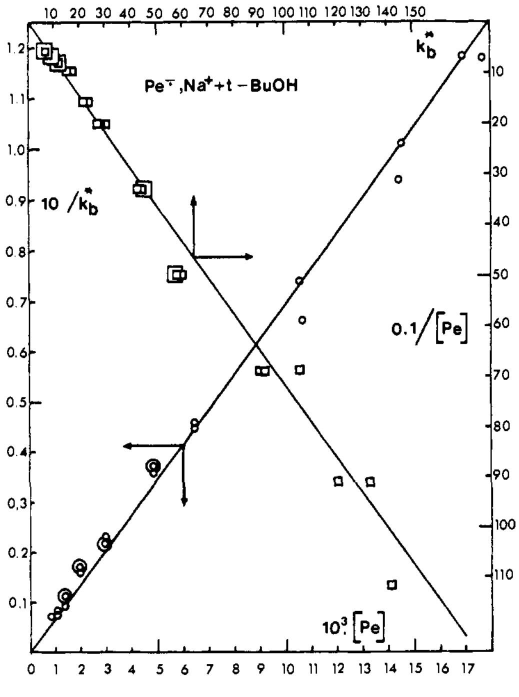

Figure 4. □, plot of $1/k_b^*$ (standardized for [t-BuOH] = 5.3×10^{-2} M) *vs.* [Pe] (left and down scale); ○, plot of k_b^* (standardized for [t-BuOH] = 5.3×10^{-2} M) *vs.* 1/[Pe] (up and right scale).

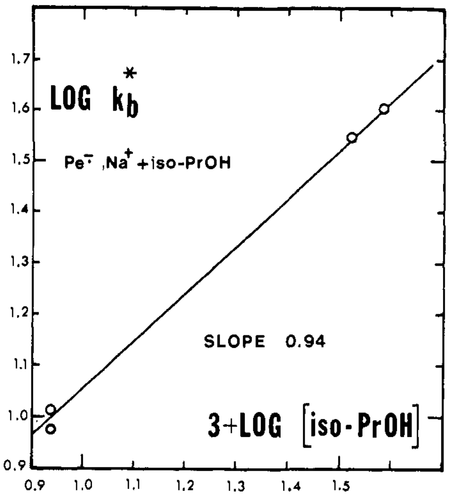

Figure 5. Log–log plot of k_b^* (standardized for a constant [Pe]) *vs.* [i-PrOH].

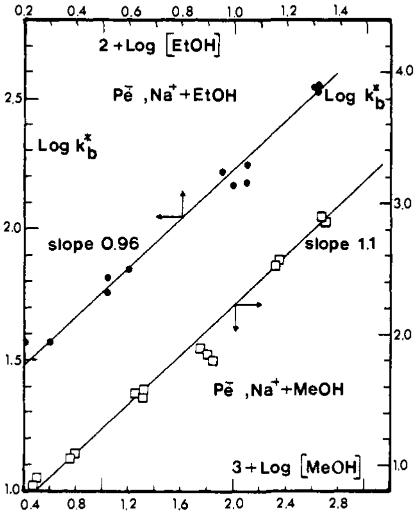

Figure 6. Log–log plot of k_b^* (standardized for a constant [Pe]) *vs.* [MeOH] (□) and [EtOH] (●). The arrows indicate the scales.

dardized for a constant concentration of alcohol, while varying the concentration of Pe, are given in Table I. The protonation by *tert*-butyl alcohol was most thoroughly investigated. The plot of log k_b^* *vs.* log [Pe], shown in Figure 2 for a constant [t-BuOH], is linear, the slope being -1. This proves the relation

$$\text{rate of protonation} \sim 1/[\text{Pe}]$$

Similarly, the plot of log k_b^* *vs.* log [t-BuOH] at a constant [Pe] is linear (see Figure 3). Although the "best" straight line has a slope 1.1, we feel that this deviation from 1.0 is insignificant and the reaction is first order in the alcohol.

The stationary state hypothesis for $Pe^{2-},2Na^+$ leads to the equation

$$1/k_b = (2k_pK_1)^{-1}\{[\text{Pe}]/[\text{ROH}] + \beta\} = (2k_pK_1)^{-1}([\text{Pe}]/[\text{ROH}]) + 1/2k_1$$

where $\beta = k_p/k_{-1}$. This equation is reduced to that used in our calculations, *viz.*

$$k_b = 2k_pK_1[\text{ROH}]/[\text{Pe}]$$

Table VI. Protonation of $Pe\cdot^-,Na^+$ by Water and D_2O in THF

Run	$10^2[H_2O]$, M	10^2[Pe], M	$10^3[Pe\cdot^-, Na^+]_0$, M	$2k_pK_1$, M^{-1} sec^{-1}
3c[a]	1.0	0.5	0.03	2.0
4c[a]	1.0	0.5	0.03	1.8
1c[b]	1.0	1.0	1.1	2.2
2c[b]	1.0	1.0	1.1	2.2
1d[c]	1.0	1.0	0.8	2.0
2d[c]	1.0	1.0	0.8	1.9
5b[c]	4.0	1.1	1.0	2.2
6b[c]	4.0	1.1	1.0	2.2
3d[c]	5.0	1.0	0.8	1.8
4d[c]	5.0	1.0	0.8	1.8
7b[c]	8.0	1.1	1.0	2.0
8b[c]	8.0	1.1	1.0	1.9
5d[c]	10	1.0	0.8	1.6
6d[c]	10	1.0	0.8	1.5
19a	10	0.9	0.5	1.95
16a	11	0.9	0.5	1.95
17a	13	0.6	0.4	1.65

Run	$10^2[D_2O]$, M	10^2[Pe], M	$10^3[Pe\cdot^-, Na^+]_0$, M	$2k_pK_1$, M^{-1} sec^{-1}
1	10.0	0.95	1.0	0.17
2	10.0	0.95	1.0	0.18

[a] Static system. In spite of the extremely low concentration of $Pe\cdot^-,Na^+$, which favors first-order reaction, the first-order contribution, if genuine, leads to a rate constant of protonation of radical anion by water of, at most, 0.02 M^{-1} sec^{-1}. [b] Freshly precipitated $NaBPh_4$. Perfect second-order reaction. [c] Unpurified $NaBPh_4$. Perfect second-order reaction up to 73–75% conversion. The slight deviation from the second-order behavior observed in the region 75–90% conversion could be due to small uncertainties in OD_∞ amounting to about 0.015 OD unit. However, if genuine it would indicate a contribution of the first-order reaction with $k_I \sim 0.1\text{–}0.7 \times 10^{-3}$ sec^{-1}; *i.e.*, the rate constant of protonation of the radical ion by water would be 0.01–0.007 M^{-1} sec^{-1}.

when $\beta \ll$ [Pe]/[ROH]. In order to obtain an upper limit for β, we plot in Figure 4 $1/k_b^*$ *vs.* [Pe]. The resulting straight line shows an intercept smaller than 0.5×10^{-3}, *i.e.*, $k_1 > 10^3$ M^{-1} sec^{-1}. From its slope we calculate $2k_pK_1 = 2.74$ M^{-1} sec^{-1}. The reliability of this value is checked by plotting k_b^* *vs.* 1/[Pe]. The resulting straight line is again shown in Figure 4. Although these two linear relations are mathematically equivalent (for $\beta \approx 0$), they differ from experimental point of view. The slope of the first line is strongly affected by the k_b^* values obtained at high concentration of perylene, while the values obtained at low concentration of perylene are those determining the slope of the second line. It is gratifying, therefore, to note the agreement, $2k_pK_1 = 2.60$ M^{-1} sec^{-1} if calculated by the alternative method. Combining our findings for $2k_pK_1$ and k_1, we find $\beta < 1.3 \times 10^{-3}$.

Protonation by other alcohols (*i*-PrOH, EtOH, MeOH, and CH_3OD) proceeds like the protonation by *t*-BuOH. The first-order dependence on the pertinent alcohol is demonstrated by Figures 5 and 6. The slopes of the lines log k_b^* *vs.* log [ROH] are 0.94 for *i*-PrOH, 0.96 for EtOH, and 1.1 for MeOH, all experimentally indistinguishable from unity.

The relative rate constants of protonation of Pe^{2-}, $2Na^+$ by the investigated alcohols are 100, 65, 44.6, and 9.25 for MeOH, EtOH, *i*-PrOH, and *t*-BuOH, respectively. The reactivity of MeOD is about seven times lower than that of MeOH; *i.e.*, the respective relative rate constant is 14.5, only slightly higher than for *t*-BuOH.

A series of experiments was performed with water, its concentration varying from 10^{-2} to 10^{-1} M. The reaction was found to be strictly second order when freshly precipitated and rigorously dried $NaBPh_4$ was used to suppress the dissociation of ion pairs. The results are summarized in Table VI and show that protonation of $Pe^{2-},2Na^+$ by water is slightly slower than by *tert*-butyl alcohol ($2k_pK_1 \sim 2$ M^{-1} sec^{-1} as compared with 2.7 M^{-1} sec^{-1}). It is doubtful whether the relatively insignificant first-order reaction, noted in some experiments, is a genuine indication of protonation of the radical ion. We believe it results from some impurities present in $NaPBh_4$. However, if this reaction represents indeed a direct protonation of $Pe\cdot^-$, Na^+ by water, the respective protonation rate constant is about 0.01 M^{-1} sec^{-1} or less.

Experiments performed with D_2O are included in Table VI. The respective rate constant is about ten times lower, indicating a large isotope effect in protonation of $Pe^{2-},2Na^+$ by water.

Discussion

The first-order dependence of the kinetics of protonation on ROH calls for a comment. In pure alcohol molecules of ROH are aggregated by hydrogen bonding and an equilibrium $n\text{ROH} \rightleftarrows (\text{ROH})_n$ is then established. If the monomeric ROH is the rapidly protonating agent, then the rate may show a fractional order on [ROH]. However, our results indicate that in THF and at low alcohol concentration ROH is monomeric, presumably because it is hydrogen bonded to the ether. It will be shown in a future publication from this laboratory that in the system, anthracene$\cdot^-$,Na^+ + CH_3OH in DME solvent, both monomeric and dimeric methanol protonated the radical anion (under the conditions of these experiments, contribution of dianions is negligible). The dimeric methanol was found to be a much stronger acid than the monomeric methanol and it protonates the radical–anion several hundred times faster than the monomeric CH_3OH.

The protonation studied by us is taking place in a constant aprotic medium, *viz.* THF, and therefore the observed relative rate constants, k_p, reflect the changes in the solution acidities of "monomeric" alcohols. This is evident from Figure 7 showing the Brønsted plot of log k_p *vs.* pK of the alcohol determined in dimethyl sulfoxide,[6] another aprotic medium. The points for MeOH, EtOH, and *t*-BuOH lie on a perfect straight line having a slope of 0.42. Unfortunately, the pK of isopropyl alcohol is not reported; our plot leads to its value of 27.8 whereas the value reported[6] for pK of *n*-propyl alcohol is 28.0. The value obtained in this investigation for the relative k_p of water, *i.e.*, ~7, suggests that the pK of water is ~29.5, in good agreement with Steiner's finding.[7] For the gas-phase reaction a higher acidity of alcohols than of water is indicated by recent studies of Brauman and Blair;[8] however, contrary to our findings, they find *t*-BuOH more reactive than MeOH. It seems that our work provides the first evidence for the substantially lower rate of protonation

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(6) C. D. Ritchie, "Solute-Solvent Interactions," Marcel Dekker, New York, N. Y., 1968, p 230.

(7) E. C. Steiner, ref 6, p 230.

(8) J. L. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

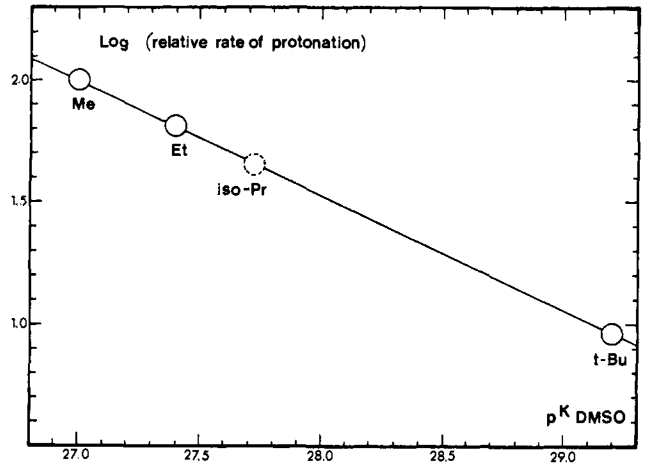

Figure 7. Brønsted plot of relative rate constants of protonation of $Pe^{2-},2Na^+$ in THF *vs.* pK of the alcohols in dimethyl sulfoxide. Unfortunately the pK values in THF are not available.

by water than by methanol provided that both reactions take place in the same aprotic medium.

Protonation of *free* ions of biphenylide and anthracenide by methanol, ethanol, and isopropyl alcohol in bulk was studied by Dorfman, *et al.*,[9] the respective bimolecular rate constants being 4 and 10 $\times$ 10^4 M^{-1} sec^{-1} for MeOH, 2.1 and 2.2 $\times$ 10^4 M^{-1} sec^{-1} for EtOH, and 0.85 and 0.40 $\times$ 10^4 sec^{-1} for *i*-PrOH.[10] The log–log plot of their constants *vs.* our relative k_p's yields steep lines. The steepness is justified by the large differences in pK of methanol in methanol[11] (18.3) and ethanol in ethanol[12] (20.4), while the differences of pK's of the same two alcohols in an aprotic and constant solvent, *viz.* THF in our studies, are probably similar to those found in DMSO, *viz.* 27.0 and 27.4, respectively.[6] The enormous effect of environment on the rate of protonation was demonstrated in a subsequent paper of Dorfman.[13]

The potentiometric titration of perylene by sodium biphenylide in THF[14] permits us to calculate K_1 = 1.2 $\times$ 10^{-6} and subsequently the absolute values of k_p. Thus, we obtain 1.2 $\times$ 10^6, 0.76 $\times$ 10^6, 0.52 $\times$ 10^6, and 0.11 $\times$ 10^6 M^{-1} sec^{-1}, for the bimolecular rate constants of protonation of $Pe^{2-},2Na^+$ in THF by MeOH, EtOH, *i*-PrOH, and *t*-BuOH, respectively. Comparison of our absolute values with those derived from Dorfman's data[9] ($\sim 10^3$–10^4 M^{-1} sec^{-1}) serves no purpose since the latter were determined in variable media (*i.e.*, protonation by CH_3OH in bulk methanol, by C_2H_5OH in bulk ethanol, etc.).

Having K_1 and the lower limit for k_1 we may calculate the lower limit of the rate constant for the exothermic electron-transfer reaction

$$Pe^{2-},2Na^+ + Pe \xrightarrow{k_{-1}} 2Pe\cdot^-,Na^+$$

Thus, $k_{-1} > 8.10^8$ M^{-1} sec^{-1} is in fair agreement with the rate constant of 7 $\times$ 10^6 M^{-1} sec^{-1} determined[15] for a similar electron-transfer process, sodium biphenylide + pyrene → biphenyl + sodium pyrenide.

Isotope Effect. Our results for CH_3OH and CH_3OD and for H_2O and D_2O show a large isotope effect implying a substantial degree of fission of the O–H bond in the transition state. Protonation of sodium naphthalenide by water in THF was studied by Bank and Bockrath.[16] They found the reaction to be first order in naphthalenide, a result which does not contradict our findings since the naphthalenide is greatly more reactive than $Pe\cdot^-,Na^+$. However, while our results indicate a large isotope effect ($\sim$10) for the protonation of $Pe^{2-},2Na^+$ by water, a very low isotope effect was reported by Banks. It is not yet clear why in this respect the two systems behave differently.

Role of Dianions in Some Protonation Reactions. We have seen that the protonation of some radical anions proceeds through dianions. The question arises why the final products are not formed directly, *e.g.*, through the sequence

$$Pe\cdot^-,Na^+ + ROH \xrightarrow{k_p'} PeH\cdot + RO\cdot^-,Na^+$$
$$PeH\cdot + Pe\cdot^-,Na^+ \longrightarrow PeH^-,Na^+ + Pe$$
$$PeH^-,Na^+ + ROH \longrightarrow PeH_2 + RO\cdot^-,Na^+$$

The protonation of a radical anion, a relatively weak base, by a *weak* acid seems to require a prohibitively high activation energy, while the protonation of a dianion, a powerful base, is relatively facile. Thus, in spite of their low concentration dianions provide an easier route to the products than radical anions, *i.e.*, under our experimental conditions $k_p'[Pe]/k_pK_1[Pe\cdot^-,Na^+] \ll 1$.

Protonation of anthracene radical anions by alcohols has been reported recently by Minnich and Dye[17] who found the reaction to be second order in radical anions. They concluded that dimers, *e.g.*, $(A\cdot^-,K^+)_2$, are protonated faster than the nonassociated radical anions, an unlikely event. It seems to us that the dianion, A^{2-}, $2Na^+$, is again the intermediate, and indeed studies performed in our laboratory confirm this conclusion (to be reported).

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(9) (a) S. Arai, E. L. Tremba, J. R. Brandom, and L. M. Dorfman, *Can. J. Chem.*, **45**, 1119 (1967); (b) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

(10) These data are calculated from Table I of ref 9a. Slightly different values are given in Table II and in ref 9b.

(11) C. D. Ritchie, G. A. Skinner, and V. D. Badding, *J. Amer. Chem. Soc.*, **89**, 2063 (1967).

(12) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(13) J. R. Brandom and L. M. Dorfman, *J. Chem. Phys.*, **53**, 3849 (1970).

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

(15) M. Fisher, G. Rämme, S. Claesson, and M. Szwarc, *Chem. Phys. Lett.*, **9**, 306 (1971).

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

(17) E. R. Minnich and J. L. Dye, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.