vacuo. A weighed sample was refluxed with CH_2Cl_2, H_2O, and HCl for 4 hr, and the aqueous phase treated with excess NH_4OH and dimethylglyoxine. *Anal.* Calcd for $NiC_{10}Cl_{10}$: Ni, 11.01%. Found: Ni, 11.22%.

Reaction of C_5Cl_5HgCl with $C_5H_5Fe(CO)_2I$. C_5Cl_5HgCl[1] (0.95 g, 2 mmol), $C_5H_5Fe(CO)_2I$[39] (0.61 g, 2 mmol), and $CHCl_3$ (30 ml) were stirred overnight under N_2. The solution was filtered, mixed with heptane, and reduced in volume. A noncrystallizable oil settled out. Chromatography on alumina decomposed the oil immediately giving a blue color. Decomposition products C_5Cl_5H and $C_5H_5Fe(CO)_2Cl$ were identified by ir.

Reaction of 1 with Tributylphosphinecopper(I) Iodide. Thallous ethoxide (2.71 g, 10.9 mequiv) was dissolved in 10 ml of ether and cooled to −78° under N_2. C_5Cl_5H (2.59 g, 10.9 mmol) in 25 ml of ether was added, followed by $(C_4H_9)_3PCuI$[40] (4.21 g, 11.0 mmol) in 25 ml of ether. A clear colorless solution and yellow precipitate resulted. On warming to less than 0° the solution became multicolored and then deposited copper metal.

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(39) G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, 7, 10 (1963).

(40) R. B. King and F. G. A. Stone, *ibid.*, 7, 110 (1963).

Reactions of Aromatic Radical Anions. VII.[1] Kinetic Study of the Reaction of Sodium Anthracene with Water[2a]

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Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12203. Received August 7, 1971

Abstract: The kinetics of the reaction of sodium anthracene with water has been studied. The rate law is $-d[\text{Anth}\cdot^-]/dt = 2k_1[\text{Anth}\cdot^-][H_2O]$, with a value of k_1 at 20° of 664 M^{-1} sec^{-1} in tetrahydrofuran. The dihydroanthracenyl anion intermediate is more reactive than the radical anion. Activation parameters, the deuterium kinetic isotope effect, and the effect of ion pairing are included in the study. The mechanisms of protonation of sodium anthracene and sodium naphthalene are directly analogous; however, contrary to molecular orbital localization energy calculations, sodium anthracene is considerably less reactive than sodium naphthalene. The state of ion pairing of the radical anion has a marked effect upon reactivity. Finally, water bound to solvent-separated or free sodium ion is postulated to be the kinetically active proton donor. The discussion includes comparison of this system with other related work.

Our previous kinetic study of the reaction of sodium naphthalene with water verified the Paul, Lipkin, and Weissman mechanism.[3] Since the reactivity of sodium naphthalene toward a proton source is significantly less than that of a structurally related anion, the dihydronaphthyl anion, the likely intermediate, could not be detected. Most unexpectedly, the reactivity of tight ion pairs was found to be greater than solvent-separated ion pairs. Similar findings in other systems have since been reported by others.[4,5] A comparable kinetic study of the reaction of sodium anthracene with water would help to answer two fundamental questions about the relationship between structure and reactivity: can the relative reactivities be accounted for on the basis of a simple molecular orbital treatment, and what is the complex role of solvent and aggregation state in these reactions?

Results and Discussion

In contrast to naphthalene, reduction of anthracene by sodium metal proceeds to the dianion metal adduct in the ethereal solvents used. Since what is sought is the kinetic behavior of the monometal adduct, this presents a possible ambiguity. The problem was solved by taking advantage of the fast electron transfer reaction of sodium naphthalene and of the equilibrium constant (calculated from the known reduction potentials[6a,b]) for the reaction

$$2\text{Anth}\cdot^- \rightleftharpoons \text{Anth}^{2-} + \text{Anth} \qquad (1)$$

Two stock solutions were prepared, one of sodium naphthalene and the other of anthracene (in excess based on sodium naphthalene) and water in the appropriate ether solvent. On mixing in the stopped-flow device, rapid electron transfer from sodium naphthalene provides solely the monometal adduct of sodium anthracene and the subsequent protonation is then followed.

The validity of this method rests on three assumptions. First, the electron transfer to anthracene is kinetically faster than the protonation of sodium naphthalene. Second, the concentration of sodium naphthalene in equilibrium with sodium anthracene is ki-

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(1) Previous paper in this series: S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, 93, 430 (1971).

(2) (a) Abstracted in part from the Ph.D. Thesis of B. Bockrath, State University of New York at Albany, Albany, N. Y., Aug 1971; (b) NDEA Title IV Fellow.

(3) D. E. Paul, P. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, 78, 116 (1956).

(4) E. S. Petrov, M. I. Terekhova, and A. I. Shatenshtein, *Dokl. Akad. Nauk SSSR*, 192, 422 (1970).

(5) (a) E. R. Minnich and J. L. Dye, Abstracts of Papers, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1971; (b) J. L. Dye, private communication; we are grateful to Professor Dye for supplying us with this information prior to publication.

(6) (a) E. deBoer, *Advan. Organometal. Chem.*, 2, 115 (1964), and references cited therein; (b) J. Jagur-Grodzinski, M. Feld, S. Yangand, and M. Szwarc, *J. Phys. Chem.*, 69, 628 (1965).

netically insignificant. Third, the equilibrium concentration of the sodium anthracene dianion is also kinetically insignificant.

Rapid electron transfer is assured by the known rate constants for reductions of this type.[7-9] For example, in pulse radiolysis studies, reduction of anthracene by the biphenyl radical anion in isopropyl alcohol has a bimolecular rate constant of 6.4 × 10^9 M^{-1} $\sec^{-1}$ at 25°.[7] In tetrahydrofuran the rate constant for electron exchange between sodium naphthalene and neutral naphthalene is found to be 2.7 × 10^7 M^{-1} $\sec^{-1}$ by esr techniques.[8] Since the rate constant for exchange is a function of the reduction potential difference,[9] a reasonable estimate for the reaction of sodium naphthalene and anthracene is $\sim 10^8$ M^{-1} $\sec^{-1}$. The half-life for the exchange is calculated from the known excess anthracene concentration of 10^{-2} M: $\tau = 0.693/([10^8][10^{-2}]) \cong 7 \times 10^{-7}$ sec = 0.7 μsec. The calculated half-life of 0.7 μsec indicates that complete reduction of anthracene occurs within a very small fraction of the instrument dead time of 15 msec.[10]

The following thermodynamic argument

$$\text{Nap}\cdot^- + \text{Anth} \rightleftharpoons \text{Anth}\cdot^- + \text{Nap} \qquad (2)$$

serves to rule out the possibility of kinetically significant concentrations of sodium naphthalene in equilibrium. We obtain a value for the equilibrium constant (K) from the reduction potentials measured against biphenyl in dimethoxyethane (DME)[6a] and tetrahydrofuran (THF).[6b] From these values, values of K are calculated to be in the range 0.7–5.0 × 10^{11}. Thus from the expression

$$K = \frac{[\text{Anth}\cdot^-][\text{Nap}]}{[\text{Nap}\cdot^-][\text{Anth}]} \qquad (3)$$

and the fact that

$$[\text{Nap}] \cong [\text{Anth}] \qquad (4)$$

a condition that is determined by the experimental method,[11] we can write using the average value for K

$$\frac{[\text{Nap}\cdot^-]}{[\text{Anth}\cdot^-]} \cong 3.5 \times 10^{-12} \qquad (5)$$

The effect of this equilibrium concentration of sodium naphthalene on the rate can be evaluated by writing the rate law as the sum of two reactions

$$\frac{-\text{d}[\text{Anth}\cdot^-]}{\text{d}t} = 2k_1[\text{H}_2\text{O}][\text{Anth}\cdot^-] + 2k_1'[\text{H}_2\text{O}][\text{Nap}\cdot^-] \qquad (6)$$

where k_1 and k_1' are the bimolecular rate constants for the protonation of sodium anthracene and naphthalene, respectively, and the rate law for sodium anthracene has for the present been assumed (*vide infra*) to be the same as that for sodium naphthalene.[1] The value of k_1' is 1.01 × 10^4 M^{-1} $\sec^{-1}$ in THF at 20°,[1] and substitution of this value into eq 6 after rearrangement leads to

$$\frac{-\text{d}[\text{Anth}\cdot^-]}{\text{d}t} = 2[\text{H}_2\text{O}][\text{Anth}\cdot^-](k_1 + 3.5 \times 10^{-8}) \qquad (7)$$

Therefore, protonation of sodium naphthalene would contribute to the overall rate to an extent greater than 1% only if $k_1 \leq 3.5 \times 10^{-6}$ M^{-1} $\sec^{-1}$. As the measured rate constants are at least six orders of magnitude greater than this value, protonation of equilibrium concentrations of sodium naphthalene is kinetically insignificant.

Protonation of significant concentrations of the anthracene dianion can be ruled out in an analogous fashion. From eq 1

$$K = \frac{[\text{Anth}^{2-}][\text{Anth}]}{[\text{Anth}\cdot^-]^2} \qquad (8)$$

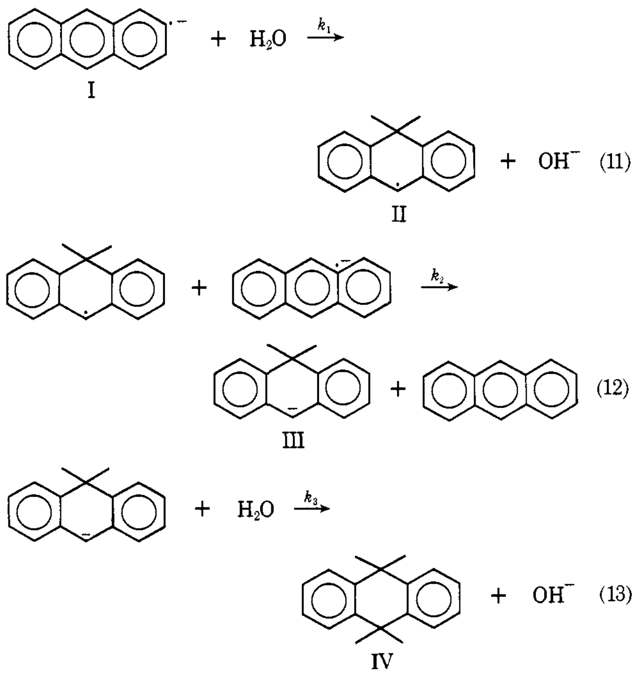
and K, obtained from the reduction potentials, is 10^{-10} [6a] and 10^{-5}.[6b] The larger value is used in the following calculations to ensure no ambiguity. During reaction the concentration of neutral anthracene is $\sim 10^3$ greater than that of sodium anthracene,[11] and

$$\frac{[\text{Anth}^{2-}]}{[\text{Anth}\cdot^-]} \leq 10^{-8} \qquad (9)$$

Again, expressing the overall rate law as the sum of two reactions, we obtain

$$\frac{-\text{d}[\text{Anth}\cdot^-]}{\text{d}t} = [\text{H}_2\text{O}][\text{Anth}\cdot^-](2k_1 + 10^{-8}k_2) \qquad (10)$$

where k_1 and k_2 are the rate constants for protonation of the mono- and diadducts, respectively. Therefore, if protonation of the equilibrium concentration of dianion is to contribute more than 10% to the overall rate, then $k_2 = 2 \times 10^{+7}k_1$. As the average measured value of k_1 is $\sim 1 \times 10^2$ M^{-1} $\sec^{-1}$, contributions of greater than 10% are expected only if $k_2 \geq 2 \times 10^9$ M^{-1} $\sec^{-1}$. A bimolecular rate constant for the protonation of the dianion that is equal to the limits of diffusion control is unlikely. Equally important, di-



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[7] S. Arai, D. A. Grev, and L. M. Dorfman, *J. Chem. Phys.*, **64**, 2572 (1967).

[8] N. Hirota, R. Carraway, and W. Schook, *J. Amer. Chem. Soc.*, **90**, 3611 (1968).

[9] L. Lyons, *Aust. J. Chem.*, **21**, 2789 (1968).

[10] B. Bockrath, Ph.D. Thesis, State University of New York at Albany, Albany, N. Y., 1971.

[11] The details of this are discussed in the Experimental Section.

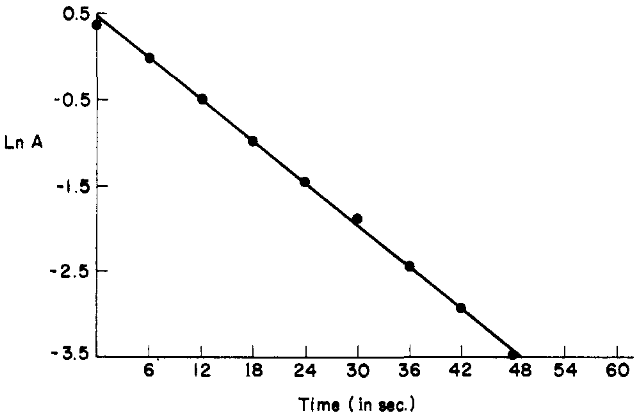

Figure 1. Pseudo-first-order plot for the disappearance of sodium anthracene in THF–DME with an excess of water at 20.0°.

anion participation predicts a non-first-order dependency on the anthracene radical anion and an inverse dependency on neutral anthracene. In the following section we will show that neither of these criteria obtain.

The Rate Law. Analogous to the sodium naphthalene study, the following mechanism and kinetic expression may be written for sodium anthracene (eq 11–14).

$$\frac{d[\text{Anth}\cdot^-]}{dt} = -2k_1[H_2O][\text{Anth}\cdot^-] \qquad (14)$$

The first-order dependency in both sodium anthracene and water is based on k_2 and $k_3 \gg$ than k_1.[1] That the reaction obeyed second-order kinetics was verified for both components. First, with an excess of water, the decay of sodium anthracene was clearly first order, as shown in Figure 1. In all of the kinetic runs, correlation coefficients for the least-squares determination of the pseudo-first-order constant are in the range 0.95–0.99. Control experiments indicate that such values indicate strict first-order behavior. These observations contrast with those of similar study at initial sodium anthracene concentration about two to three orders of magnitude higher than used in the present work.[5a,b] Dye reports second-order dependency for sodium anthracene and fractional-order dependency for the proton donor (alcohols).[5a,b] The second-order behavior for sodium anthracene is attributed to rapid protonation of dimers of sodium anthracene contact ion pairs. Accordingly, it appears that dimerization of sodium anthracene is not kinetically important in the concentration range $\sim 10^{-4}$ M but dominates at a concentration of 10^{-2} M. This suggests that exploration of interim concentrations would reveal the point of onset for second-order behavior which would link the two studies, and moreover valuable information about the rate of sodium anthracene dimerization could be derived. For our part, such a study must await construction of a new observation cell.

The first-order dependency of sodium anthracene is inconsistent with significant contributions from protonation of the dianion whose rate expression is second order in radical anion

$$\frac{-d[\text{Anth}\cdot^-]}{dt} = k_b[H_2O]\frac{[\text{Anth}\cdot^-]^2}{\text{Anth}} \qquad (15)$$

An additional consequence of the dianion path is the inverse dependency on neutral hydrocarbon. We have demonstrated that this dependency does not obtain in the sodium anthracene study by variation of the anthracene concentration at constant sodium anthracene and water concentration and by variation of the ratio of anthracene to sodium anthracene at constant water concentrations. Inspection of the data in Table I reveals that the rate constant is not a function of either of these variables, and hence the dianion route can be ruled out.

Table I. Second-Order Rate Constants at 20.0° for the Reaction of Sodium Anthracene and Water at Select Anthracene and Sodium Anthracene Concentrations

$[\text{Anth}]_0 \times 10^2$	$[\text{Anth}\cdot^-]_0 \times 10^5$	k,[a] M^{-1} sec^{-1}
1.32	5.57	11.5[b]
2.04	5.51	11.7[b]
1.99	2.64	11.8[c]
1.99	6.09	10.1[c]

[a] In THF-DME. [b] $[H_2O] = 1.27$ M. [c] $[H_2O] = 0.214$ M.

Our assumption that k_2 is very large and probably approaches diffusion control has adequate analogy.[12,13] That $k_3 > k_1$ was verified experimentally in a manner similar to the sodium naphthalene study.[1]

The reaction is monitored at the wavelength of maximum absorption for the dihydroanion III and the kinetics are compared to kinetics monitored at the radical anion I maximum. We reproduced the reported absorption spectrum of the dihydroanthracene anion,[14] which has a single maximum in the visible range at 455 nm with ϵ 2330 in DME. The anthracene radical anion I, on the other hand, has absorption maxima at 720 nm (ϵ 8600) and 365 nm ($\epsilon > 10^4$), but is at a minimum at 455 nm ($\epsilon \sim 800$).[3] Thus, the window in the radical anion spectrum at the anion maximum affords detection of anion concentrations equal to or greater than ~15% of the initial radical anion concentration. If the reactivity of the anion were equal to or less than the radical anion, *i.e.*, $k_3 \leq k_1$, the accumulation of III would be detected at 455 nm. Table II records the rate constants measured at the radical anion and anion maxima.

Table II. Second-Order Rate Constants at 20.0° for the Reaction of Sodium Anthracene and Water at Select Wavelengths

$\lambda_{\max}$, nm	$k_1 \times 10^{-2}$, M^{-1} sec^{-1}
720	6.64 ± 0.57[a]
455[b]	9.50 ± 0.82

[a] In THF with $[H_2O] = 0.0244$ M and $[\text{Anth}\cdot^-]_0 = 0.715\text{–}1.10 \times 10^{-4}$ M. [b] At this wavelength the initial absorbance is 0.16 and can be easily followed for three or more half-lives.

In actual fact the rate constant measured at the maximum for III is greater than that measured at the maximum I. While this deviation from equality is real and reproducible, it only slightly exceeds the experimental

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[12] J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4261 (1966).

[13] J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971), and references cited therein. We are grateful to Professor Garst for providing us with a preprint.

[14] N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, 87, 4529 (1965).

accuracy and does not lend itself to meaningful discussion about significance. More importantly we can confidently conclude that the rate constant measured at the maximum for III is definitely not significantly less than that measured at the maximum of I. Moreover, the kinetics are clearly pseudo-first-order at both wavelengths. Accordingly, there is no accumulation of III and therefore $k_3 > k_1$ in analogy with the sodium naphthalene study. The reactivity order, anion > radical anion, can be accounted for on the basis of charge densities at the reactive site. The charge density of 0.193 at the 9 position of the radical anion is available from esr studies,[15] and the charge density of the anion is calculated from HMO parameters[16] to be 0.400.

The Order with Respect to Water. A comparatively low value for the rate constant in THF-DME (*vide infra*) afforded an excellent opportunity to investigate the effect of an extended range of water concentration upon the kinetic expression. In previous work,[1] the range was restricted at high concentrations by prohibitively short half-lives and at low concentrations by the necessity of maintaining pseudo-first-order conditions. In the sodium anthracene case, however, a study of the water concentration range of nearly four powers of 10 (8.2×10^{-3}–4.5 *M*) was possible. Multiple determinations of the pseudo-first-order rate constant were made at eight different concentrations. The plot of log [k_{obsd}] *vs.* log [H_2O] is linear (see Figure 2). The slope obtained by the least-squares method is 0.94, with a correlation coefficient of 0.97. We consider the deviation from 1.0 to be insignificant and the reaction is first order in water. In alcohol protonation studies of the perylene radical anion, related plots of log k_b^* *vs.* log [ROH] with slopes 0.94–1.1 are all considered to be experimentally indistinguishable from unity.[17] Thus, although the state of aggregation of water is expected to undergo considerable change over this variation in concentration, the reaction remains first order in water.

Analogous behavior has been observed in the reactions of water with cesium in ethylenediamine,[18] and with sodium in dioxane.[19] In direct contrast, pulse radiolysis studies of the biphenyl radical anion with proton donors in various cosolvents yield an indeterminate order for the proton donor.[20] In pulse radiolysis work, hydrogen-bonded solvent structure is of critical importance in the rate of proton abstraction, whereas in the present work and the other two cited instances such does not appear to be the case.

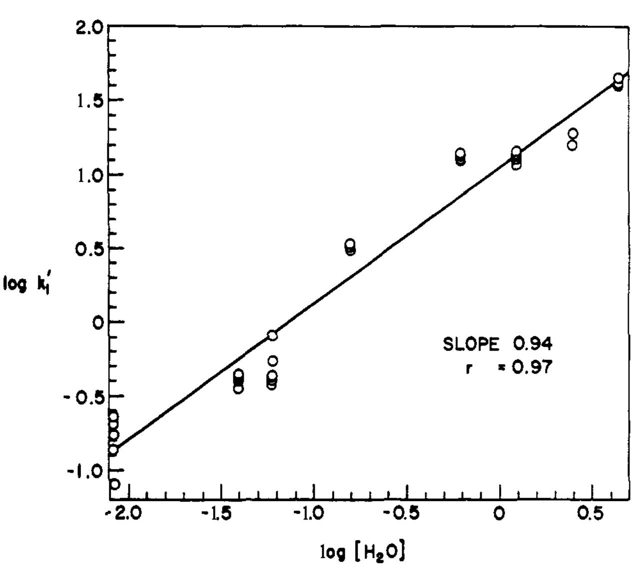

Figure 2. Log of the pseudo-first-order rate constant *vs.* log of the water concentration for the reaction of sodium anthracene and water in THF-DME at 20.0°.

A major difference between the stopped-flow and pulse radiolysis experiments is the nature and proximity of the counterion present by virtue of the alkali metal reduction. In stopped-flow studies the aromatic radical anion is not present as a free ion.[21] In pulse radiolysis, on the other hand, the reactive aromatic radical anion must be a free ion because reaction of the radical anion with the counterion, solvent cation (ROH_2^+), is faster than reaction with the neutral alcohol proton donor.[22,23] Therefore, an important distinction is the close presence of the sodium counterion in the stopped-flow work.

In order to relate this physical difference with the kinetic differences, we must ascribe a major role for sodium counterion coordination of water when it is present. If we consider that the sodium ion solvates a water molecule significantly better than the ether and/or water itself, then it follows that the water molecule so solvated is more "acidic" than either free or solvent solvated water. With this as the active proton-donating species in the stopped-flow work, the absence of significant solvent solvation and the simple first-order dependency are rationalized.[24] In the absence of the small, hard counterion, solvent solvation becomes dominant and this accounts for the disparate behavior of the pulse radiolysis studies.

Support for this hypothesis is derived from the observed increased rate upon addition of sodium ion at constant water concentration. Thus, addition of sodium tetraphenylboron (0.028 *M*) to the stock solution of sodium anthracene increased the observed rate constant by a factor of 22.4. Further addition (0.085 *M*), however, had only a modest effect in increasing the rate constant ($k_{\mathrm{rel}} = 24.7$). Clearly, sodium ion has a catalytic effect upon the protonation rate, but the amount of enhancement is not linearly related to the amount of added sodium salt.[25] Further work is required to de-

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(15) E. deBoer and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 4549 (1958).

(16) C. A. Coulson and A. Streitwieser, "Dictionary of π Electron Calculations," W. H. Freeman, San Francisco, Calif., 1965.

(17) G. Levin, C. Sutphen, and M. Szwarc, *J. Amer. Chem. Soc.*, **94**, 2652 (1972); we are grateful to Professor Szwarc for providing us with a preprint of this paper.

(18) R. R. Dewald, J. L. Dye, M. Eigen, and L. DeMaeyer, *J. Chem. Phys.*, **39**, 2388 (1963).

(19) T. A. Miskinova and L. G. Gindin, *Dokl. Akad. Nauk SSSR*, **117**, 1027 (1957); *Chem. Abstr.*, **52**, 13387 (1958).

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

(21) For leading references, see M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968.

(22) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

(23) L. M. Dorfman, *Accounts Chem. Res.*, **3**, 224 (1970).

(24) This implies that the ratio of kinetically active sodium ion coordinated with water to the total sodium ion concentration is small, and therefore requires the presence of substantial concentrations ot sodium ion in forms that are not kinetically active. This is valid in thaf the presence of sodium hydroxide has no effect upon the reaction rate in this reaction. Related results have been obtained by Dye and Dewald.[5a]

(25) An alternate explanation for the effect of added sodium tetraphenylboron considers that free anthracenides and their pairs are present in 5×10^{-5} *M* solution, the former being less reactive than the latter.

Table III. Rate Constants and Derived Data for the Reaction of Sodium Anthracene and Water in Various Solvent Systems

System	k,$^{20°a}$	$\Delta G^{\ddagger b}$	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$
THF	664 ± 57	13.4 ± 0.7	11.5 ± 7	−6.5 ± 2.3
THF-DME[d]	13.0 ± 7.4	15.6 ± 1.6	17.8 ± 1.6	7.3 ± 5.5
DME	17.1 ± 5.3	15.4 ± 1.8	16.5 ± 1.8	3.6 ± 6.1
THF-tetraglyme[e]	5.63 ± 0.58	16.2 ± 0.5	15.5 ± 0.5	−2.4 ± 1.7

[a] In M^{-1} sec^{-1}. [b] In kcal/mol, in the temperature range 10–40°. [c] In eu, in the temperature range 10–40°. [d] 50/50 by volume mixture. [e] 13 mole % tetraglyme.

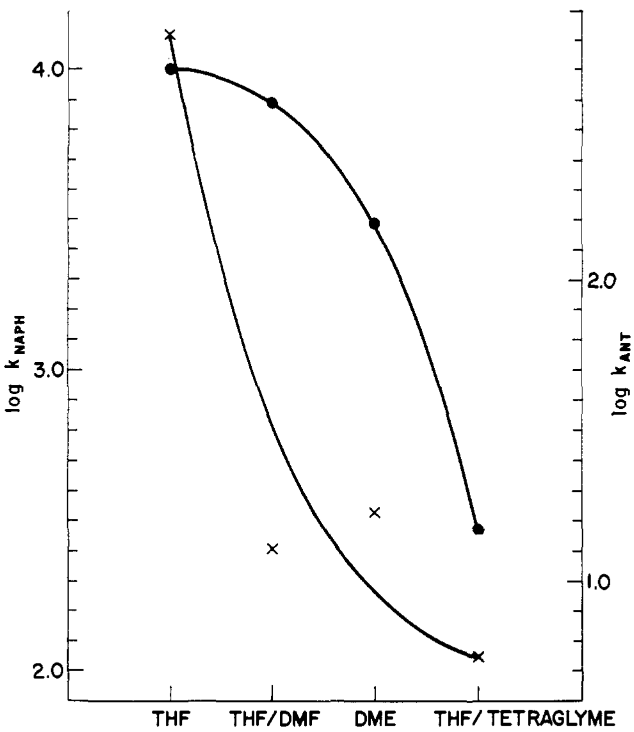

Figure 3. Log of the rate constants for reaction of sodium naphthalene and sodium anthracene with water in various solvent systems. (Values along the x axis are illustrative rather than quantitative.) ●, sodium naphthalene rate constants; ×, sodium anthracene rate constants.

fine the complex role of the sodium ion in the protonation reaction.

The State of Ion Pairing and Reactivity. In our previous study, four solvent systems were selected[1] to provide known aggregation states where the equilibrium constants favored one ionic form greatly over the others for sodium naphthalene.[26,27] A monotonic decrease in reactivity for proton abstraction was observed in going from tight ion pairs to glymated ion pairs.[1] For comparison, the reactivity of sodium anthracene toward water was studied in the same solvent systems. Table III and Figure 3 summarize the data.

Sodium anthracene in THF is more reactive than in any of the other solvent systems and the reactivity in the other solvent systems is essentially the same. In addition, Figure 3 contrasts the pattern of reactivity for sodium naphthalene. The two reactions are not linearly related on a free-energy basis and therefore probably involve different types of transition states. Moreover, the plot suggests that while the solution state and reactivity of sodium naphthalene change monotonically, for sodium anthracene there is essentially only one change in reactivity, *i.e.*, in going from THF to THF-DME.

Inspection of the literature indicates that although there has been a fair amount of work on the system,[28–31] a complete specification of the ion-pairing state of sodium anthracene in the several solvent systems is not available at this time. Previous understanding that sodium anthracene is completely dissociated in THF[29,30] has been proved erroneous by both esr[31] and conductimetry[28] work. It seems clear that sodium anthracene is not a free ion in THF, but it is not obvious what kind of an ion pair, contact or solvent-separated or mixture thereof, obtains at room temperature in pure THF. Hirota comments that it exists mostly as a loose ion pair;[31b] however, extrapolation of his data on mixed solvents reveals that although loose ions would predominate, the equilibrium constant is such that substantial amounts of the tight ion pair would be present also. Szwarc found a heat of dissociation for sodium anthracene in THF of 6.1 kcal/mol.[28] This value is intermediate between that of a contact ion pair (7.3–8.2 kcal/mol) and a solvent-separated ion pair (~1.5 kcal/mol).[28] On this basis we conclude that the most consistent description of the pure THF system is an equilibrium mixture of the two ion pairs.

The effect of solvent variation to THF–DME or DME itself poses more serious problems. While solvent variation was included in the conductance study,[28] sodium anthracene was not one of the reported salts. Nevertheless, by analogy with sodium triphenylene that was studied and the conclusions of the DME study that "all the investigated salts form virtually solvent-separated pairs in the latter solvent" (DME),[28] we may assume that sodium anthracene in DME is probably a solvent-separated ion pair. With the added reasonable though unsupported assumption that addition of DME or tetraglyme to THF shifts the equilibrium substantially to the solvent-separated ion pair, the kinetic data may be accounted for.

Similar to the sodium naphthalene study, tight (contact) ion pairs are more reactive for proton abstraction.[1] Thus in THF, where both kinds of ion pairs

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The addition of an excess (0.028 M) of sodium tetraphenylboron converts virtually all the free anthracenides into more reactive pairs and, hence, the observed k increases. Further addition would then be of no significance. We consider this explanation to be less likely since even if free ions were totally unreactive this requires that the solution without added sodium tetraphenylboron is largely dissociated (~95% free ions). Such extensive dissociation is not expected in view of the known value of 4.5 × 10^{-6} M for the dissociation constant of sodium anthracene in related systems (R. V. Slates and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965)).

(26) K. Hofelmann, J. Jagur-Grodzinki, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 4645 (1969), and references cited therein.

(27) N. Hirota, *ibid.*, **90**, 3603 (1968), and references cited therein.

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

(29) A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

(30) K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *ibid.*, **42**, 1993 (1965).

(31) (a) N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968); (b) A. H. Crowley, N. Hirota, and R. Kreilick, *J. Chem. Phys.*, **46**, 4815 (1967).

exist, the rate is greater than in the other solvent systems where only the less reactive solvent-separated ion pair is present. The reactivity difference of $\sim$45 is comparable to the reactivity variation of $\sim$50 found in the sodium naphthalene study where the ion pair variation is known to be from contact ion pairs to solvent-separated ion pairs.[1] The similarity of these values lends added support to the assumption that both states exist for sodium anthracene in THF.

Water in the Several Solvent Systems. One of the assumptions inherent in the above discussion is that the effect of solvent changes on the availability of hydrogen-bonded water protons does not vary significantly for the several solvents. That this was the case was shown by control experiments to determine the effect of solvent variations on the state of hydrogen bonding of dissolved water. Following the method of Fratiello and Luongo,[32] the influence of solvent on hydrogen bond formation was estimated from the vibrational spectra. The shift on the OH stretching band compared with pure water is used as a measure of the association. Table IV summarizes the relevant data.

Table IV. Stretching Frequencies of Water[a] in the Several Solvent Systems

Solvent system	ν free[b]	$\Delta\nu$[c]	ν bonded[d]
THF	3547	227	3241
THF-DME[e]	3550	230	3241
DME	3547	227	3241
THF-tetraglyme[e]	3550	230	3241

[a] 1% H_2O by volume. [b] Stretching frequencies obtained from spectra of first overtone in the region 1.4–1.6 μ, using a 1-cm silica cell and a Cary 14 spectrophotometer. [c] Shift differences relative to the pure water-OH bond at 3320 cm^{-1}. [d] A doublet is observed for the OH stretching frequency. This is attributed to complex formation with the ether resulting in two nonequivalent protons, one bound and one free. [e] 50/50 by volume.

The observed shifts are the same as that found for dioxane[32] and are the same for all the solvent systems. The association of water does not vary throughout the series, and therefore changes in reactivity of the aromatic radical anions with solvent cannot be attributed to a dependency of the availability of protons on the direct interaction of the ether solvents and water.

Comparison of Protonation Rates of Sodium Anthracene and Sodium Naphthalene. In view of the above discussion, meaningful comparison of the protonation rate constants for sodium anthracene and sodium naphthalene must be done at comparable solution states. For DME, where both are essentially solvent-separated ion pairs, $k[\text{Naph}]/k[\text{Anth}] \cong 182$. This value is surprising in view of the calculated charge densities of 0.193 and 0.181 at the reactive positions of anthracene and naphthalene, respectively.[16] One would have expected the anthracene radical anion to be as reactive or more than the naphthalene radical anion.[33] Obviously the use of molecular orbital calculations for estimating reactivity differences is far from satisfactory, in contrast to the very adequate correlation obtained for charge densities and prediction of protonated products.[34] The reason for this discrepancy is not clear. A similar lack of correlation of reactivities expected from molecular orbital calculations and the observed reactivity differences has been found in pulse radiolysis studies with anthracene and naphthalene.[35] Thus, the discrepancy is not peculiar to the solution state of the radical anion.

Kinetic Isotope Effect. The kinetic isotope effect had been determined for sodium naphthalene in THF,[1] where the radical anion exists largely as tight ion pairs. In this case, the isotope effect could be at a minimum by virtue of the most favorable counterion participation. If the tight ion pair represents one extreme of counterion availability, then the glymated ion pair of sodium anthracene in THF–tetraglyme represents the other extreme. It was of interest to determine if diminished participation by counterion led to an enhanced kinetic isotope effect. Therefore the deuterium isotope effect for sodium anthracene was measured in the THF–tetraglyme solvent system at 20°.

The value of the second-order rate constant using H_2O was determined as $5.63 \pm 0.58\ M^{-1}$ sec^{-1} from 11 experiments. The value of the second-order rate constant using D_2O was determined as $2.78 \pm 0.67\ M^{-1}$ sec^{-1} from eight experiments. This level of precision and accuracy for the rate constants (10–25%) is the same as that found for stopped-flow studies on the isotope effect of other similarly sensitive reactants.[36] Comparison of $k_H/k_D = 2.02 \pm 0.68$ for sodium anthracene with the kinetic isotope effect for the sodium naphthalene tight ion pair, $k_H/k_D = 1.37 \pm 0.44$,[1] reveals that only a small difference is observed in the two systems. The two values are not quite outside the experimental error, but if anything, discrimination between OH and OD seems slightly greater in the case of glymated sodium anthracene. This is consistent with the above argument and with a lessened ability of glymated sodium ion to coordinate incipient hydroxide ion relative to the tight ion pair in THF.

It is interesting to compare these isotope effects with those found for other systems. Shatenshtein and coworkers[4] report $k_H/k_D \approx 1$ for the proton abstraction by either potassium naphthalene or potassium biphenyl from triphenylmethane. Diethyl ether was used as solvent, which promotes the formation of tight ion pairs. The authors contrasted the small isotope effect with that found for the metallation of triphenylmethane by butyllithium, which has an isotope effect of $\simeq$10.[37] The large difference is taken as indicative of the difference between a protophilic reaction, where a C–H bond is broken at the transition state, and a metallation reaction, where electrophilic attack of the cation on a C–H bond is important. A small isotope effect is assumed to be associated with the latter mechanism. In comparison with the present work, it is significant that emphasis is placed on the importance of the counterion in the proton transfer to radical anion for both cases, even though triphenylmethane and water are very different acids. These two protonation reactions proceed at very different rates; nevertheless, they have the

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[32] A. Fratiello and J. P. Luongo, *J. Amer. Chem. Soc.*, **85**, 3073 (1963).

[33] This expectation includes the fact that there are four equivalent positions in naphthalene and only two in anthracene.

[34] (a) A. Streitwieser, AFOSR Report No. 547, March 1961; (b) U. S. Department Comm. Office Tech. AD 255, 313 (1961).

[35] S. Arai, E. L. Tremba, J. R. Brandon, and L. M. Dorfman, *Can. J. Chem.*, **45**, 1119 (1967).

[36] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **90**, 3415 (1968).

[37] E. A. Kourizhnykh, F. S. Yakushin, and A. I. Shatenshtein, *Kinet. Katal.*, **9**, 5 (1968).

common importance of the counterion at the transition state.

Because of the great difference in acidity of the proton donors, and a corresponding reactivity difference of about six orders of magnitude, the isotope effect is not expected to be the same for reaction of water and triphenylmethane. The use of the kinetic isotope effect as a measure of the position of the transition state involves the assumption that the isotope effect rises to a maximum for a symmetrical transition state and then diminishes as the transition state begins to resemble products.[38,39] However, a recent study by Bordwell and Boyle[40] on the correlation of ΔpK with the primary isotope effect disparages a simple reliable relationship between the two. The plot of k_H/k_D *vs.* ΔpK has a great deal of scatter and only a gentle slope on either side of $\Delta pK \sim -1$ to -2. Bordwell concludes, "the hope, which at one time seemed bright, for a simple general correlation of Brønsted coefficients, kinetic isotope effects, and solvent isotope effects with the extent of proton transfer in the transition state has proved vain."

In view of Bordwell and Boyles' work, it is not surprising that the isotope effect is nearly the same with either water or triphenylmethane as the proton donor. This fact may be related to the strong influence of the counterion that is found in both cases. Overall, the most consistent picture of the transition state remains as Streitwieser[35] first visualized—attack by proton donor with little bond reorganization of the aromatic radical anion.

Conclusion

The present study provides further evidence for the validity of the Paul, Lipkin, and Weissman[3] mechanism for the protonation of radical anions. Moreover, protonation of the intermediate anion, the dihydroanthracenyl anion, is considerably faster than protonation of the radical anion, which reinforces the postulate that radical anions are weaker bases than anions.

The present study suggests that sodium anthracene is a mixture of tight and loose ion pairs in THF and essentially loose ion pairs in THF–DME, DME, and THF–tetraglyme. Since the state of aggregation of the radical anion has a pronounced effect upon reactivity, the large spread of reactivities may afford an independent and useful means of determining the solution state of radical anions in various solvent systems. Further correlations are needed before much confidence can be placed on extrapolations; however, the method would offer considerable advantages and should be explored.

Water bound to solvent-separated or free sodium ion is postulated to be the kinetically active proton donor. This accounts for the unexpected first-order dependency in water up to high water concentrations and is supported by observed added sodium ion catalysis. The hypothesis can be tested in a variety of ways, including the addition of sodium ion to pulse radiolysis studies and the addition of other ions of predictable behavior to stopped-flow studies. More work is needed to define adequately the complex role of solvent and the metal cation.

The striking conclusion of this study is the low absolute magnitude for the rate constant of protonation of sodium anthracene. This kinetic basicity is surprisingly low for a conjugate carbon base, and has implications for both the study of reaction mechanisms of radical anions and for synthetic exploitation. Whereas in most radical anion reactions there is a competition between electron transfer and nucleophilic attack, our results suggest that choice of an aromatic moiety of lower reduction potential may alter the rate constants for both electron transfer and nucleophilic attack in the same direction. Therefore, lower reduction potentials are not certain to provide enhanced nucleophilic *vs.* reductive reactivity.

Synthetic utility may be derived from the very rapid electron transfer rates. The reduction of anthracene by sodium naphthalene occurs without complication in 4.5 *M* water. Under these conditions, the half-life for protonation of sodium naphthalene is 20 μsec, but the half-life of electron transfer must be substantially shorter. Considering that the half-life for protonation of sodium anthracene is 12 msec under the same conditions, even comparatively slow electron transfer reactions could proceed in the presence of molar quantities of water. The synthetic advantages for reductions of water-soluble substrates are under active investigation. Moreover, the control of competitive electron transfer and proton abstraction with a single substrate by solvent variation is discussed elsewhere.[41]

Experimental Section

Materials. Naphthalene was obtained from Eastman Organic Chemicals, No. 168, or Matheson Coleman and Bell, No. NX5, and used without further purification. Vapor phase chromatography did not reveal the presence of any impurity, and the ultraviolet spectra were identical with the published spectra of naphthalene.[42] Anthracene (Matheson Coleman and Bell, No. AX1590) was recrystallized from toluene before use. Sodium (Matheson Coleman and Bell) was stored under xylene and washed with pentane before use. 9,10-Dihydroanthracene was prepared by reduction of anthracene with sodium metal and isopropyl alcohol in tetrahydrofuran. The product was recrystallized from ethanol, mp 107–108° (lit.[43] mp 108°). The infrared spectrum was identical with the published spectrum.[44] Deuterium oxide (99.8% D) was obtained from Stohler Isotope Chemicals. THF, chromatoquality from Matheson Coleman and Bell, and DME, Puriss grade from Aldrich Chemical Co., were both distilled from sodium benzophenone ketyl immediately before use. Tetraglyme, from Eastman Organic Chemicals, or from Pfaltz and Bauer, Inc., was vacuum-distilled from Na–K alloy, and then redistilled from sodium benzophenone ketyl prior to use, bp 128° (7 mm). Sodium tetraphenylboron, >99.5%, from Fisher Scientific, was used without further purification. Karl–Fischer reagent was obtained from Fisher Scientific.

Apparatus. The stopped-flow apparatus has been described earlier.[1] Radical anion solutions were prepared and analyzed in a flask similar to the design of Waack and Doran.[45] A Cary 14 spectrophotometer was used to record the visible and uv spectra of the stock solutions. Water concentrations were determined by Karl–Fischer titrations with a Labindustries aquametry apparatus. Chromatography was performed using an F & M Model 5750 Research Gas Chromatograph equipped with a flame detector and helium as the carrier gas. A 4 ft × 0.25-in. column of 10% Carbo-

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[38] F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

[39] E. R. Thornton, *J. Org. Chem.*, **27**, 1943 (1962).

[40] F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 512 (1971).

[41] S. Bank and S. P. Thomas, manuscript in preparation.

[42] R. A. Friedel, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, N. Y., 1951, No. 195.

[43] "The Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p C-122.

[44] Sadtler Index No. 709 K.

[45] R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **85**, 1651 (1963).

wax at 160° was used for the naphthalene analyses and a 2-ft × 0.25-in. column of 10% Carbowax was used for the anthracene–dihydroanthracene analyses.

Kinetic Procedures. A typical kinetic experiment was carried out as follows. THF (89.9 g, 102 ml) was distilled from the sodium benzophenone ketyl under argon into the radical anion generating flask. The solvent was distilled directly onto a piece of freshly cut sodium (~0.5 g, 21.7 mg-atoms) and a glass-covered magnetic stirring bar. At the end of the distillation, the flask was removed from the still and naphthalene (81.3 mg, 0.635 mmol) was added. The flask was resealed and stirred for several hours. The concentration of this stock solution was determined to be 0.0176 M from the absorbance at 365 nm.

The water and anthracene stock solution was prepared from 0.1697 g (0.954 mmol) of anthracene, 30.0 μl of water, and 78 ml (68.6 g) of THF. The water concentration determined by Karl–Fischer titration was 0.0357 M.

The stopped-flow apparatus, which was thermostated at 20°, was prepared for kinetic runs by flushing the entire apparatus successively twice with pure THF and a relatively concentrated (~0.3–0.5 M) solution of sodium naphthalene in THF. Stock solutions were transferred to the stopped-flow apparatus by gas tight syringes. After several flushes with the stock solutions in the respective chambers, the oscilloscope traces of four kinetic runs at 365 nm were recorded. The reaction products were collected at the exit port in aqueous ammonium chloride. Gas chromatographic analysis revealed that the products were anthracene and 9,10-dihydroanthracene.

In addition to the kinetic trace on the oscilloscope, reference lines for ground and the maximum output of the phototube were recorded. The oscilloscope screen was photographed and the intensities at various times were determined. The remainder of the calculations was done by a computer program which converted the intensities to absorbance and plotted ln A_t *vs.* time to obtain the slope by the method of least squares.

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Measurement of the Kinetics and Activation Parameters for the Hydroboration of Tetramethylethylene and Measurement of Isotope Effects in the Hydroboration of Alkenes[1,2]

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Abstract: The kinetics of the hydroboration of tetramethylethylene (TME) with borane in tetrahydrofuran (THF) have been studied. The rate of formation of 2,3-dimethyl-2-butylborane is found to be first order in both borane and TME. The activation energy and entropy for the reaction are 9.2 ± 0.4 kcal/mol and −27 ± 1 eu. The hydrogen–deuterium kinetic isotope effect is found to be 1.18. The reaction is considered to involve the direct reaction between a molecule of the borane–THF complex and alkene in a very early transition state. The ^{1}H/^{3}H isotope effects in the hydroboration of various alkenes with borane and selected mono- and dialkylboranes have been measured. The $k_{^1\mathrm{H}}/k_{^3\mathrm{H}}$ decreases markedly as the degree of substitution on the double bond increases: monosubstituted alkenes, 10.0–11.3 (calculated on the basis of no hydrogen exchange between borane species); disubstituted alkenes, 8.7–9.0; trisubstituted alkenes, 4.2–4.3; and TME, ~3.3. Similarly, $k_{^1\mathrm{H}}/k_{^3\mathrm{H}}$ decreases as the degree of substitution on boron increases. The $k_{^{10}\mathrm{B}}/k_{^{11}\mathrm{B}}$ isotope effect in the hydroboration of various substituted alkenes with borane increases only slightly with increasing substitution on the double bond (1.03 to 1.05).

Despite the great synthetic utility and wide applicability of the hydroboration reaction, many of the intimate details of the mechanism of the reaction have not been investigated. The relatively slow reaction of diborane with simple alkenes in the gas phase to produce trialkylboranes was discovered by Hurd in 1948.[3] In a kinetic study of the gas phase reaction of diborane with ethylene, Whatley and Pease[4] observed that the rate of reaction followed the kinetic expression $-\mathrm{d}p/\mathrm{d}t = k[\mathrm{B_2H_6}]^{3/2}/(1 - 2.0[\mathrm{B_2H_6}]/[\mathrm{C_2H_4}])$, and proposed the following sequence of steps to account for the observed kinetics.

$$\mathrm{B_2H_6} \rightleftharpoons \mathrm{2BH_3}$$

$$\mathrm{BH_3} + \mathrm{B_2H_6} \rightleftharpoons \mathrm{B_3H_9}$$

$$\mathrm{B_3H_9} + \mathrm{C_2H_4} \longrightarrow \mathrm{B_2H_5C_2H_5} + \mathrm{BH_3}$$

More recently, Fehlner[5] has studied the gas phase reaction of borane, derived by the pyrolysis of borane–trifluorophosphine, with ethylene. The rate of reaction to form ethylborane (~2×10^9 l. mol^{-1} sec^{-1}) is approximately 10^3 faster than the reaction of diborane with ethylene, and is first order in both borane and ethylene,[6] the absolute rate constant being given by the expression

$$\text{rate} = 10^{10.2} \exp\{-2000/RT\} \text{ l. mol}^{-1} \text{ sec}^{-1}$$

The hydroboration of alkenes in diglyme solution was

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(1) Part XXIV of a series on Transfer Reactions Involving Boron; for part XXIII, see D. J. Pasto and P. W. Wojtkowski, *J. Organometal. Chem.*, **34**, 251 (1972).

(2) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (Grant No. 1225, A1,3), and to the National Institutes of Health for partial support (Grant No. CA-07194).

(3) D. T. Hurd, *J. Amer. Chem. Soc.*, **70**, 2053 (1948).

(4) A. T. Whatley and R. N. Pease, *ibid.*, **76**, 835 (1954).

(5) T. P. Fehlner, *ibid.*, **93**, 6366 (1971).

(6) This observation is not consistent with the observation and mechanistic scheme proposed by Whatley and Pease[4] in that borane, if present, would be expected to react faster with ethylene than the other borane species.