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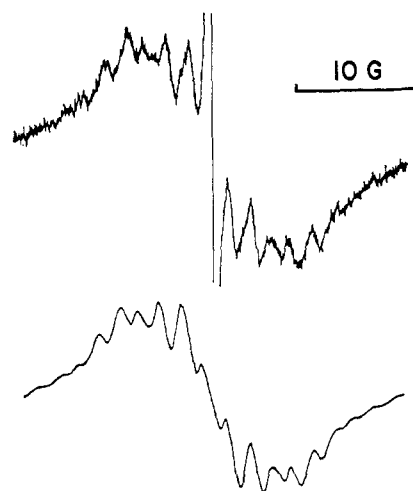*Received December 18, 1970*

Figure 1. Upper trace: experimental esr spectrum of sodium naphthalenide in tetrahydrofuran at 25°. The concentration of the neutral naphthalene is 0.98 *M*. The center peak is due to the potassium naphthalenide ion pair or the free ion (see ref 12 and 13). Lower trace: computer-simulated spectrum assuming a second-order rate constant of $2.1 \times 10^7 \, M^{-1} \, sec^{-1}$.

On the Structure of the Activated Complex in Atom-Transfer Reactions

Sir:

When aromatic compounds are reduced with alkali metals to form radical ions, their electron spin resonance (esr) spectra often exhibit splittings which are attributable to interactions of the unpaired electron with the metal nucleus.[1] The "ion-pair"splittings depend on the nature of the metal ions, temperature, and solvents. Several models have been proposed to explain the variation of these splittings with temperature,[1–3] and more recently, some detailed calculations have been reported which study the spin density at the alkali metal nucleus as a function of the metal–hydrocarbon distance.[4–7] To date, however, there has been a notable lack of experimental data on the actual metal–hydrocarbon distances. We present here preliminary results on the sodium naphthalenide system in which we have obtained a measure of the sodium–naphthalene distance in the transition state.

In order to perform this measurement, we have exploited the variation of the rate constant of the atom-transfer reaction with changing dielectric constant

$$Na^+C_{10}H_8^- + C_{10}H_8 \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} C_{10}H_8 + Na^+C_{10}H_8^- \qquad (1)$$

of the reaction medium. $C_{10}H_8$ and $C_{10}H_8^-$ represent the neutral molecule and the anion radical of naphthalene. We believe that this is the first report of such a measurement involving hydrocarbons, and it supports the suggestion that variations of the rate constant with concentration reported previously are due to changes in the dielectric constant of the solvent.[8]

In 1957 Marcus derived an expression which relates the rate constant of an electron-transfer reaction to the optical and static dielectric constants of the reacting medium.[9] Recently, this equation has been applied with some success to atom-transfer reactions.[10] For our system his equation assumes the form

$$\ln k = - \frac{R}{8aRT}\left[\frac{1}{D_{op}} - \frac{1}{D_s}\right] + \ln Z \qquad (2)$$

where k is the second-order rate constant, R is the gas constant, T is the temperature, Z is the collision frequency, and D_{op} and D_s are the optical and static dielectric constants. In (2) a is the distance of closest approach of the reacting species in the transition state, *i.e.*, the radius of the activated complex. Clearly, it would be desirable to have a knowledge of a both in the discussion of the structure of the ion pairs and in elucidating the mechanism of atom transfer.

Rates were measured in the intermediate-exchange region.[11] This region was chosen because it allowed us to monitor the ion-pair species involved in the reaction by simulating the exchange-broadened but uncollapsed spectrum. We wanted to be sure that indeed we were measuring the rate of exchange of a sodium naphthalenide ion pair with a given splitting[12,13] and that we were not changing the structure of the ion pair by varying the dielectric constant of the solution. Since the exchange spectra of ion pairs with different splittings differ markedly, such an effect would be easily observable. Figure 1 is a graphic illustration of the point, the top trace being the experimental spectrum and the lower trace the computer simulation. Altering the sodium splitting by as little as 0.1 G produces a perceptibly different spectrum than that shown in Figure 1.

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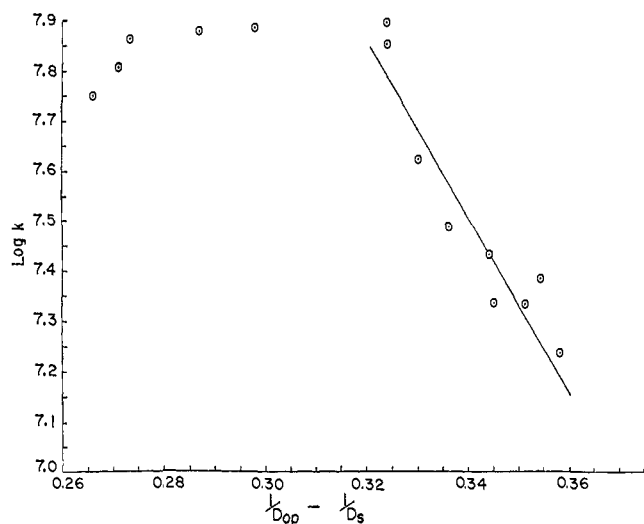
Figure 2. Log k vs. $(1/D_{op} - 1/D_s)$ for the sodium naphthalenide system at 25°.

Figure 2 is a plot of ln k vs. $(1/D_{op} - 1/D_s)$ for the sodium naphthalenide system at 25°. The static and optical dielectric constants were measured in the course of this work.[14] In the region of low naphthalene concentration [high values of $(1/D_{op} - 1/D_s)$] Marcus' relation is indeed obeyed. However, at high concentrations the curve deviates significantly from linearity. The reason(s) for this behavior is not certain, but we believe that it may be due to a combination of factors. The most appealing explanation is that we have altered the dielectric constant enough to change the nature of the ion pair. One might argue that at high $C_{10}H_8$ concentrations (lower dielectric constants) a tighter binding of metal to the hydrocarbon is favored, which results in a reduction of the rate constant. In addition, we note that at these high concentrations the esr spectra are collapsed into a single line so that we are no longer certain of the exchanging species involved in the reaction. Over the linear region a value of (1.8 ± 0.3) Å is calculated for a.

One might expect that the mechanism of an atom-transfer reaction such as (1) would involve the formation of a sandwich-type complex consisting of a sodium atom between the two naphthalene rings.[15] Assuming the crystallographic radius for the sodium ion (*ca.* 1 Å), we obtain a value of ~1 Å for the "thickness" of a naphthalene ring. This is some 1–1.5 Å less than previous estimates of the thickness of aromatic hydrocarbon ions.[3] Similarly, theoretical calculations[4–6] also predict that the metal–hydrocarbon distance should be in the neighborhood of 3 Å for the splitting (*ca.* 1 G) with which we are dealing. Thus, the size of the activated complex seems to be about 1–1.5 Å less than one would estimate from the data on static ion pairs. However, since we are dealing with an activated complex, it is not unreasonable that it would be somewhat smaller than an unreacting species. Initial measurements on the potassium naphthalenide system indicate

that a is larger than that for the sodium system. Further experiments are in progress and will be reported at a later date.

Although such an experiment as we have reported here does not measure directly the metal–hydrocarbon distance in an ion pair, it could provide information about the change in the radius of the activated complex with solvent and temperature and thus yield indirect information on the changes in metal–hydrocarbon distances that occur when the metal splitting changes. In view of the lack of experimental data so far, such experiments would clearly be of value. In addition, the experiments are relatively easy to perform and have the advantage that they should be applicable to a large number of systems.

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Extraction of a Phenyl Group from the Tetraphenylboron Anion by Some π-Cyclopentadienyl Derivatives of Ruthenium. A Ruthenium Complex Containing the Tetraphenylboron Anion Directly Bonded to the Metal[1]

Sir:

A previous study of the halogenation of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ revealed that the bridged halogeno cationic species $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2X]^+$ (X = Cl, Br, and I) are initially formed in these reactions and that nucleophilic attack of halide ions on the latter gives $(\pi\text{-}C_5H_5)Fe(CO)_2X$.[2] It has now been established that the reaction of $\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2$ with iodine in toluene at room temperature in the presence of NaB$(C_6H_5)_4$ and a little methanol parallels the corresponding reaction involving $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ and yields the stable bridged iodo derivative $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2I]B(C_6H_5)_4$. Similarly, the analogous bromination and chlorination reactions afford $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]B(C_6H_5)_4$ (X = Br and Cl). These latter products decompose rapidly in solution, however, and the cations $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]^+$ (X = Br and Cl) were best isolated and characterized as the yellow hexafluorophosphate salts. If the reactions of $\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2$ with bromine and chlorine in toluene in the presence of NH_4PF_6 and methanol are performed at $-80°$, green products are observed to separate from

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