

polar solvents. Further studies of these spectra are in progress.

The experiments were carried out with a Varian A-60 nmr spectrometer, equipped with a Varian Associates V-6031B variable low-temperature probe.

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### Contact and Solvent-Separated Ion Pairs of Carbanions.

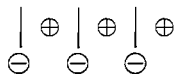
#### III. Reactivities in Proton-Abstraction Reactions

Sir:

It was recently shown<sup>1</sup> that changes in the absorption spectra of solutions of carbanions and radical ions upon varying the solvent composition and temperature could be interpreted in terms of two kinds of ion pairs, *i.e.*, contact and solvent-separated ion pairs. We have now studied the reactivity behavior of these species in proton-abstraction reactions and have made a number of interesting observations.

Alkali salts of the fluorenyl carbanion were allowed to react with 1,2- or 3,4-benzofluorene in dioxane, tetrahydrofuran, or 1,2-dimethoxyethane as solvent. The progress of the reaction was followed spectrophotometrically, and the rate constants were calculated from the initial slopes of the recorder tracings. In a number of instances a flow system was used, but even then some of the reactions were too rapid to obtain accurately the initial slopes. In these cases calculation of the rate constants was based on the half-life of the reaction. Although this will somewhat affect the accuracy of the data, the differences between the observed second-order rate constants for the various systems are large enough to justify a comparison. The results are reported in Table I.

The data for fluorenyllithium show a strong dependence of the rate constants on the carbanion concentration in all three solvents. The same is true of fluorenylsodium in dioxane. This suggests the presence of unreactive aggregates,  $[F^-, M^+]_n$ , in these solutions, and the kinetic measurements lead to an average aggregation number of 5 or even higher. This strong association, even in solvents like THF and DME, is surprising since no such association was observed for the less charge delocalized polystyryl salts in either THF or dioxane.<sup>2</sup> It is likely that the association of the fluorenyl salts is favored by the planar structure of the carbanion. This may lead to a sandwich-type aggregate in which many ion pairs are stacked up



An additional attractive force, particularly important for the lithium salts, may result from a tendency of the counterion to complex with the highly polarizable  $\pi$  cloud of the fluorenyl ring.

(1) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965); **88**, 307 (1966).

(2) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

**Table I.** Observed Rate Constants for the Reaction Fluorenyl<sup>-</sup>,M<sup>+</sup> + 1,2- or 3,4-Benzofluorene at 25°

[F <sup>-</sup> ,M <sup>+</sup> ]		[F <sup>-</sup> ,M <sup>+</sup> ]			
Solvent	$\frac{\times}{10^{-5}}, M$	$k_{obsd}, M^{-1} sec^{-1}$	Solvent	$\frac{\times}{10^{-5}}, M$	$k_{obsd}, M^{-1} sec^{-1}$
F <sup>-</sup> ,Li <sup>+</sup> + 3,4-Benzofluorene			F <sup>-</sup> ,Li <sup>+</sup> + 1,2-Benzofluorene		
THF	370	2.86	THF	40	1.6
	140	3.16		4.7	12.3
	61	5.0		4.2	19.9
	26.8	9.2		0.67	51.6
	10.8	29.0	DME	15.0	6.8
	3.3	60.0		4.5	14.4
	1.36	158.0		0.9	103
F <sup>-</sup> ,Na <sup>+</sup> + 1,2-Benzofluorene			F <sup>-</sup> ,N <sup>+</sup> Bu <sub>4</sub> + 1,2-Benzofluorene		
Dioxane	42	183	THF	32	3800
	20	294		1.5	3960
	8.1	660		1.3	3500
	2.8	1660	DME	24	~80,000
	1.2	4200		22	~80,000
			0.92	~50,000	
F <sup>-</sup> ,Cs <sup>+</sup> + 1,2-Benzofluorene			F <sup>-</sup> ,N <sup>+</sup> Bu <sub>4</sub> + 1,2-Benzofluorene		
Dioxane	46	860	THF	43	800
	11	1300		46	700
	2.8	1560	DME	35	810
THF	42	960		35	930
	43	1080	F <sup>-</sup> ,Na <sup>+</sup> + 1,2-Benzofluorene		
	1.9	1570	in		
		THF + CH <sub>2</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>4</sub> CH <sub>3</sub>			
			40	650	
			40	575	

Aggregation persists, at least for the lithium salts, even in THF and DME, where the ion pairs are solvent separated. This suggests that in the solvent-separated ion pair of fluorenyllithium the counterion is not fully surrounded by solvent molecules, since aggregation would then be sterically unfavorable and expected to be less than for the poorly solvated fluorenylcesium. Apparently, the lithium ion assumes a new average position in the solvent-separated ion pair; away from the carbanion but yet still close to the  $\pi$ -electron cloud of the ring system (see Figure 1). Such a position, made possible because of increased association with solvent molecules, would also lead to the observed red shift in the spectrum as compared to the contact ion pair and would at the same time energetically be favorable because of  $\pi$  complexing. Rate measurements with dioxane solutions of fluorenyllithium containing varying quantities of dimethyl sulfoxide again point to strong association of both contact and solvent-separated ion pairs in these systems. This type of association may well be responsible for the large discrepancies observed in the values for proton-transfer rate constants in solutions of fluorenyllithium in dimethyl sulfoxide,<sup>3</sup> in which different techniques and different carbanion concentrations were used.

Another interesting observation concerns the role of the counterion in proton-abstraction reactions. At low concentrations (*i.e.*, under conditions where aggregation vanishes), fluorenylsodium is as reactive or even more so in dioxane than in THF, while a strong increase in the rate constant is observed in DME. In the first two solvents the sodium salt is a contact ion pair, while in DME it is essentially solvent separated. Hence, less energy is needed in the latter case to transfer

(3) J. I. Brauman, D. F. McMillen, and Y. Kanazawa, *J. Am. Chem. Soc.*, **89**, 1728 (1967); C. D. Ritchie and R. E. Ushold, *ibid.*, **89**, 1730 (1967).

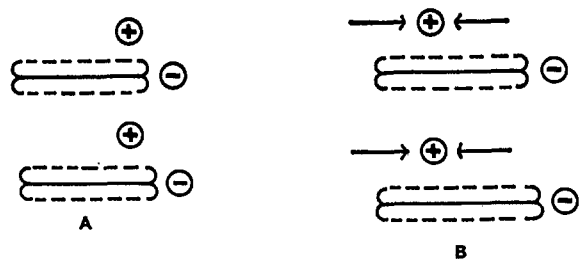


Figure 1. A represents an aggregate of contact ion pairs  $(F^-, M^+)_n$  and B that of solvent-separated ion pairs. The arrow denotes solvating molecules inducing a shift of the counterion to a new average position away from the center of negative charge.

the counterion to the new carbanion. For the tetrabutylammonium salt, the reactivity is found to be the same in THF as in DME. No solvent-separated ion pairs are observed for this salt in either solvent! However, the Coulomb interaction between carbanion and counterion is not the only rate-determining factor, since fluorenylcesium would then be expected to have a higher reactivity than fluorenylsodium in both dioxane and THF. The reverse is true, which suggests that the counterion activates the benzofluorene molecule and facilitates the proton-abstraction process (see Figure 2). Such an activation has been suggested in other reactions involving organometallic reagents.<sup>4</sup> The effect will rapidly decrease with increasing size of the counterion and may be essentially absent for cesium and tetrabutylammonium (the association of the lithium salts prevented us from obtaining the rate constant for the lithium ion pair).

It is significant that addition of the strongly dissociable  $\text{NaB}(\text{C}_6\text{H}_5)_4$  does not decrease the rate of the reaction but seems to even increase the rate slightly. Apparently, the free carbanion is not more, and presumably even less, reactive than the contact ion pair. This would also explain the concentration independence of the rate constants for the sodium and cesium salts in THF in spite of the increased free ion formation at low concentration.<sup>5</sup> These results are in agreement with the catalyzing role assigned to the counterion.

The solvent-separated ion pair, where Coulomb interaction has greatly weakened, would be highly reactive as long as the counterion can effectively activate the benzofluorene molecules. This appears to be the case in 1,2-dimethoxyethane. However, when the solvating entity prevents a close approach between the benzofluorene molecule and the counterion, the solvent-separated ion pair reactivity is expected to be less than that of the contact ion pair and may approach that of the free ion. Such appears to be the case in the system fluorenylsodium-tetrahydrofuran to which small quantities of tetraethylene glycol dimethyl ether were added. In the presence of this powerful solvating agent<sup>6</sup> the spectrum shows complete solvent-separated ion pair formation, yet the rate of proton abstraction is slower than in the absence of this reagent. Its high solvating power arises from the fact that probably all five oxygens are utilized in the solvation of the sodium ion and therefore effectively shield this ion from interaction with the benzofluorene molecule.

(4) A. A. Morton, "Solid Organoalkalimetal Reagents," Gordon and Breach Science Publishers Inc., New York, N. Y., 1964.

(5) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 318 (1966).

(6) L. L. Chan and J. Smid, to be published.

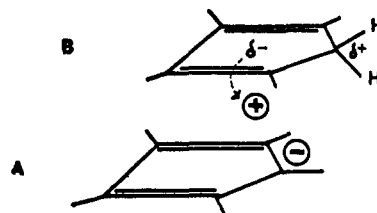


Figure 2. Activating role of the positive ion in proton-abstraction reactions. A and B represent the fluorenyl carbanion and the benzofluorene molecule, respectively.

The behavior of these carbanion salts in proton-abstraction reactions is the more interesting when the results are compared with those of addition reactions involving carbanions. In the anionic polymerization of styrene in THF<sup>2</sup> the free polystyryl ion was found to be about 800 times more reactive than the sodium contact ion pair, while the solvent-separated ion pair reactivity approaches that of the free ion.<sup>7</sup> In dioxane the ion pair reactivity increases substantially in the order  $\text{Li} < \text{Na} < \text{Cs}$ .<sup>8</sup> Both results indicate that in these reactions the Coulombic interaction between the carbanion and the counterion is of far greater importance than any possible interaction between the counterion and the reacting monomer, at least in ethereal solvents. Other types of carbanions and substrates will be investigated in order to establish whether the behavior of fluorene and its derivatives in proton abstraction reactions is unique in this respect.

**Acknowledgment.** The support of this research through a grant from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(7) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 796 (1967).

(8) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).

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### Indirect $^{15}\text{N}$ - $^1\text{H}$ Spin-Spin Couplings in Quinoline- $^{15}\text{N}$ , Its Ethiodide, and Its N-Oxide. Relative Signs and Solvent Dependence

Sir:

Previous observations,<sup>1,2</sup> of some interest, on the spin couplings between a nitrogen-15 nucleus in an aromatic ring and ring protons have prompted us to report here the correlation of indirect  $^{15}\text{N}$ - $^1\text{H}$  couplings with the electronic nature of the  $^{15}\text{N}$  atom as studied by using quinoline- $^{15}\text{N}$  (I), its ethiodide (II), and its N-oxide (III).<sup>3</sup> Coupling constants,  $J$ , in these compounds were obtained by comparing the pmr spectra of the  $^{15}\text{N}$  compounds with those of the corresponding  $^{14}\text{N}$  compounds in a variety of solvents (see Table I).<sup>4</sup> A pair of the pmr spectra of quinoline- $^{14}\text{N}$  and  $^{15}\text{N}$  in acetone- $d_6$  is shown in Figure 1 as an example.

(1) Y. Kawazoe, M. Ohnishi, and N. Kataoka, *Chem. Pharm. Bull. (Tokyo)*, **13**, 396 (1965).

(2) B. W. Roberts, J. B. Lambert, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5439 (1965).

(3) For the synthesis of III (97 atom %), see ref. 1. I and II were successively prepared from III in the usual way.

(4) Pmr spectra were taken with a Varian HA-100 spectrometer operating at 100 MHz in the frequency-swept and TMS-locked mode,