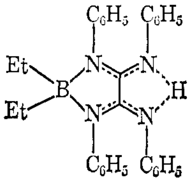
and the BEt_2 multiplet centered at 9.1 in the correct 4:3:10 ratio.

Diethylboryl methanesulfonate was obtained similarly as a distillable pyrophoric liquid, bp 70–73° (2.5 mm). Its nmr spectrum consists of the methyl singlet at τ 7.05 and BEt_2 multiplet at 9.1 in a 3:10 ratio.

Both compounds were stored as relatively air-stable 1 *M* toluene solutions and were used as such for borylation reactions. For instance, the difficultly available N-diethylboryl-*sym*-tetraphenyloxamidine (I), mp 184–185°, was obtained in 74% yield by the reaction of $MeSO_3BEt_2$ with the monosodium salt of *sym*-tetraphenyloxamidine. *Anal.* Calcd for $C_{30}H_{31}BN_4$: C, 78.6; H, 6.77; N, 12.2. Found: C, 78.6; H, 6.57; N, 12.4. The infrared spectrum has an NH band at 3250 cm^{-1} and the nmr spectrum is likewise confirmatory with τ 0.83 s (NH), aromatic multiplet at $\sim$3.1, and BEt_2 at $\sim$9.3 in a 1:20:10 ratio.

Dialkylboryl sulfonates were also useful in preparing 4,4-dialkylpyrazaboles, not available by the direct route. Thus 4,4-dibutylpyrazabole (II), bp 142–144 (1.7 mm), was synthesized in 62% yield by the reaction of $MeSO_3BBu_2$, prepared *in situ*, with $KH_2B(1\text{-pyrazolyl})_2$. *Anal.* Calcd for $C_{14}H_{26}B_2N_4$: C, 61.8; H, 9.57; N, 20.6. Found: C, 61.8; H, 9.86; N, 20.6. The nmr spectrum had two overlapping doublets (J = 2.4, 0.9 Hz) centered at τ 2.52, a triplet (J = 2.4 Hz) at 3.83, and the BBu_2 multiplet around 9, with sharp peaks at 9.17 and 9.25 in the correct 2:1:9 ratio. The BH_2 hydrogens were discernible by integration.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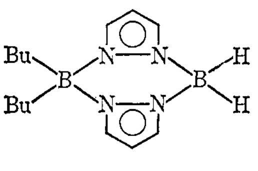
II

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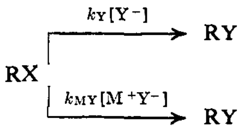
The Nonnucleophilicity of Inorganic Ion Pairs[1,2]

Sir:

For 53 years the phenomenon of decreasing second-order rate constants with increasing nucleophile concentration for bimolecular nucleophilic substitution at a saturated carbon atom has been ascribed to incomplete dissociation of the nucleophilic salt, resulting in competitive intervention with anionic nucleophile of ion-paired nucleophile. This interpretation of published data, dignified as the Acree hypothesis,[3] has been widely accepted,[4] and in fact the kinetic trend of published data *can* in general be accommodated arith-



metically by a kinetic equation derived from the equilibrium and the scheme given above. That this is not

$$M^+X^- \overset{K_D}{\rightleftarrows} M^+ + X^-$$

the explanation for the lowered rate constant with increasing salt concentration ($k_2 = 7.50 \times 10^{-4}$ l. M^{-1} sec^{-1} at 5.0×10^{-6} *M* and $k_2 = 2.34 \times 10^{-4}$ l. M^{-1} sec^{-1} at 1.24×10^{-2} *M* lithium chloride) observed in the replacement of chloride ion in methyl chloride in 95% aqueous acetone by lithium radiochloride[36] is the subject of the present communication.

The system under discussion lends itself admirably to a study of the question at hand since concentrations of inorganic chloride as low as 10^{-6} *M* (complete dissociation) can be employed. Under conditions where $[MeCl] \gg [LiCl]_s$ (stoichiometric concentration of inorganic chloride) the kinetic expression for the reaction becomes $kt = (2.303/a) \log (C/X)$, where a = [MeCl] and C and X are counts of inorganic radioactivity initially and at time t, respectively; thus pseudo-first-order kinetics are expected, independent of $[Cl^-]$ and thus of $[Li^+Cl^-]$.

As indicated above it is observed experimentally that second-order rate "constants" do in fact decrease with increasing chloride ion concentration by a factor of 3.22 as lithium chloride concentration (stoichiometric) increases by a factor of 2500 ($[LiCl]_s \leq 0.1$ [MeCl]). Since the rate expression for radiochloride incorporation is independent of chloride concentration this result must have its cause in something other than ion-pair association.

Substantiating this conclusion is the observation that other nonnucleophilic salts, including the perchlorates of lithium, sodium, potassium, and rubidium as well as lithium salicylate, when combined with low ($\leq 8 \times 10^{-5}$ *M*) stoichiometric concentrations of lithium chloride, accomplish similar rate depressions for the displacement of chloride ion by radiochloride, whose magnitudes can be predicted quite accurately from a knowledge of their ion-pair dissociation constants, K_D, and Debye–Hückel theory. Under these conditions a plot of log k *vs.* $(C\Theta)^{1/2}$ (C = stoichiometric concentration of salt and Θ is the degree of dissociation, determined experimentally from conductivity studies) is, according to theory, predicted to be a straight line with slope = −7.33, the deviation from constancy being ascribed to a simple medium effect. In Table I are listed the observed slopes of plots for the investigated salts.

It is of special interest and importance that lithium chloride is not exceptional, its slope being similar in magnitude to those of the other investigated salts.

An alternate way of appraising the data is to compare predicted (from Debye–Hückel theory and dissociation constants) and experimental rate constants. This is done at two levels of concentration of salt (*ca.* 0.001 and 0.005 *M*) in Table II. The agreement will be seen to be good if not excellent.

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[1] Part VIII of the series "Nucleophilic Substitution at a Saturated Carbon Atom."

[2] Supported in part by the National Science Foundation.

[3] H. C. Robertson and S. F. Acree, *J. Am. Chem. Soc.*, 39, 1902 (1915).

[4] Representative papers include W. Bruce, M. Kahn, and J. A. Leary, *ibid.*, 87, 2800 (1965); L. J. LeRoux and S. Sugden, *J. Chem. Soc.*, 1279 (1939); Y. Pocker and A. J. Parker, *J. Org. Chem.*, 31, 1526 (1966); N. N. Lichtin and K. N. Rao, *J. Am. Chem. Soc.*, 83, 2417 (1961).

Table I. Observed Slopes[a] of a Plot of Log k *vs.* $(C\Theta)^{1/2}$ for Various Salts in the Reaction of Radiochloride Ion with Methyl Chloride

Salt	Observed slope
LiCl	−8.5
Lithium salicylate	−10.0
$LiClO_4$	−9.1
$NaClO_4$	−7.1
$KClO_4$	−6.3

[a] Theoretical slope = −7.3.

Table II. Calculated[a] and Experimental Rate Constants with Added Salts in the Reaction of Radiochloride Ion and Methyl Chloride in 95% Aqueous Acetone at 60°

	[Salt] = 0.001 *M*	$k \times 10^4$ l. mol^{-1} sec^{-1}		[Salt] = 0.005 *M*	$k \times 10^4$ l. mol^{-1} sec^{-1}	
Salt	Θ	Exptl	Calcd	Θ	Exptl	Calcd
LiCl	0.494	4.00	4.71	0.325	3.11	3.79
$LiC_7H_5O_3$	0.306	5.10	5.59	0.162	3.94	4.60
$LiClO_4$	0.789	4.03	4.59	0.611	3.63	2.96
$NaClO_4$	0.937	4.55	4.54	0.832	2.65	2.52
$KClO_4$	0.872	4.48	4.49	0.743	3.00	2.67
$RbClO_4$	0.909	3.76	4.41			

[a] Calculated from the equation $\log (k/k_0) = -7.3(C\Theta)^{1/2}$.

It will be apparent that the phenomenon of a decreased rate constant with increased salt concentration is general and independent of the nature of the salt, whether nucleophilic or nonnucleophilic. It therefore cannot generally be ascribed to the intervention of ion pairs as nucleophiles. Since nucleophilic lithium chloride is in no way unique in its behavior, the phenomenon is most reasonably assumed to reflect the operation of a simple medium effect, consistent with Debye–Hückel theory.

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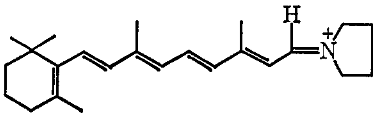
Effect of Solvent Polarizability on the Absorption Spectrum of *all-trans*-Retinylpyrrolidiniminium Perchlorate

Sir:

The origin of the anomalous spectroscopic properties of the visual pigments and their photoproducts is one of the intriguing problems confronting research on the physiochemical mechanism of vision. The several models[1–5] to explain the 500- and 478-nm absorption bands of cattle rhodopsin and metarhodopsin I(MRH_{478}), respectively, propose that retinal (11-*cis* and all-*trans* in the case of rhodopsin and MRH_{478}, respectively) bound to opsin as a protonated imine[6–9] is the chromophore responsible for the visible absorption band. Protonated imines of retinal, however, possess absorption maxima in water and alcohol at ~440 nm;[10] to explain the longer wavelength absorption bands of rhodopsin and MRH_{478}, existing theory postulates that the chromophore interacts electrostatically with opsin side-chain groups.[1,11] In this communication we report that the absorption maximum of all-*trans*-retinylpyrrolidiniminium perchlorate[12,13] **1**, which we have chosen for our immediate purposes as a convenient model for the rhodopsin chromophore, shifts from 454 (±4) nm in polar but nonpolarizable solvents to as much as 508 nm in polarizable solvents. We further provide a spectroscopic model which qualitatively explains the unusual phenomenon in both solution and the visual pigments.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The remarkable effect of solvent on the absorption maximum of **1** is illustrated in Table I.[14] The table is divided into two sections, one containing solvents that are polar, but *not significantly polarizable*, the other solvents mostly also polar, *but all of them polarizable.* Those solvents described as polarizable are capable of substantial *induced* dipole interactions. As seen in the "nonpolarizable" section, the absorption maximum of **1** (454 ± 4 nm) is not appreciably shifted by either large changes in solvent polarity or the ability of the solvent to hydrogen bond. These data force us to conclude that hydrogen-bond forces and dipole–dipole interactions do not perturb the electronic structure of the iminium salt **1** in a way which significantly alters the λ_{max} of the chromophore.

As seen in the polarizable solvent section of the table, aromatic solvents such as benzene and pyridine moderately red shift the λ_{max} to 464 and 471 nm, respectively. The effect of organic halides on the absorption maximum is in the expected order: I > Br > Cl, although we wish to emphasize at the outset that we are *not* dealing with intermolecular charge-transfer transitions.[14] Another important factor is the bulk geom-

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(1) For reviews of the spectral properties of the visual pigments, their photoproducts, and some physical models proposed to explain them, see: (a) R. Hubbard, D. Bownds, and T. Yoshizawa, *Cold Spring Harbor Symp. Quant. Biol.*, **30**, 301 (1965); (b) C. D. B. Bridges, "Photobiology, Ionizing Radiations; Comprehensive Biochemistry," Vol. 27, Elsevier Publishing Co., New York, N. Y., 1967, p 31; (c) E. W. Abrahamson and S. E. Ostroy, *Progr. Biophys.*, **17**, 181 (1967).

(2) G. A. J. Pitt, *Exptl. Eye Res.*, **3**, 316 (1964).

(3) C. S. Irving and P. A. Leermakers, *Photochem. Photobiol.*, **7**, 665 (1968).

(4) I. G. Galindo, *Bull. Math. Biophys.*, **29**, 677 (1967).

(5) J. Heller, *Biochemistry*, **7**, 2906 (1968).

(6) D. Bownds and G. Wald, *Nature*, **205**, 254 (1965).

(7) M. Akhtar, P. T. Blosse, and P. B. Dewhurst, *Life Sci.*, **4**, 1221 (1965).

(8) M. Akhtar, P. T. Blosse, and P. B. Dewhurst, *Chem. Commun.*, 631 (1967).

(9) R. C. Poincelot, P. G. Millar, R. L. Kimbel, Jr., and E. W. Abrahamson, *Nature*, **221**, 256 (1969).

(10) G. A. J. Pitt, F. D. Collins, R. A. Morton, and P. Stok, *Biochem. J.*, **59**, 122 (1955).

(11) R. Hubbard, *Nature*, **221**, 432 (1969).

(12) Prepared by the method of N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963).

(13) The difference between the respective spectral properties of *cis*- and *trans*-retinal isomers is relatively insignificant with respect to the magnitude of the anomolous red shifts observed for both isomers in the opsin environment.

(14) We should note, as do Bayliss and McRae,[15] that the most easily measured and recorded spectral data are the absorption maxima, rather than the more theoretically relevant O–O bands. Such are extremely difficult to determine energetically in structureless spectra, thus the usual reliance on values of λ_{max}. Since the long-wavelength band changes neither in shape nor approximate oscillator strength with solvent variation for the chromophore of interest (**1**), use of values of λ_{max} is physically reasonable for our purposes; also on this same basis *the spectra cannot result from intermolecular charge transfer transitions.*

(15) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954), and related references therein.