

water at 25 °C before each series of measurements. Further details of the experiments will be presented in a full paper.<sup>8,9</sup>

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### References and Notes

- (1) On pure water and dilute acid solutions the amide appeared to be aggregated as microcrystals rather than to spread as a monolayer.
- (2) See G. L. Gaines, Jr., "Insoluble Monolayers at Liquid-Gas Interfaces", Interscience, New York, N.Y., 1966, p 228 ff, for an example of film expansion as a result of protonation of an amino head group. Amides are weak Brønsted bases and so require strongly acid media for protonation. See M. Liller, *Adv. Phys. Org. Chem.*, **11**, 267 (1975), for discussion of this matter.
- (3) S. Stallberg-Stenhagen and E. Stenhagen, *Ark. Kemi, Mineral. Geol.*, **18A**, 2 (1945).
- (4) T. Tachibana and K. Hori, *J. Colloid Interface Sci.*, **61**, 398 (1977).
- (5) M. Lundquist has reported very careful studies of enantiomeric-racemic interactions: (a) *n*-eicosanol-2 and *n*-tetracosanol-2 and their acetates, *Ark. Kemi*, **17**, 183 (1961); (b) 2-methylhexacosanoic acid, *ibid.*, **21**, 395 (1965); (c) quasi-racemic monolayers of methyl 2-methylhexacosanoate and 2-acetoxytetracosane. Lundquist examined the monolayer behavior of these systems as a function of temperature and composition and found that their two-dimensional phase changes were sharply dependent on both.
- (6) T. Isemura and K. Hamaguchi, *Bull. Chem. Soc. Jpn.*, **27**, 125 (1954), noted different force-area curves for poly( $\gamma$ -benzyl L-glutamate) and the racemic polypeptides.
- (7) The original example of chiral monolayer behavior of *d*-eicosanol-2 vs. the synthetic material reported by the Stenhagens<sup>9</sup> could have been subject to error from this source since it was shown subsequently that the original racemic sample was impure (see K. Serck-Hanssen, S. Stallberg-Stenhagen, and E. Stenhagen, *Ark. Kemi*, **5**, 203 (1953)).
- (8) The following publications provide authoritative background to the study of monolayers at the air-water interface: (a) G. L. Gaines, Jr., in ref 2; (b) E. D. Goddard, Ed., *Adv. Chem. Ser.*, No. **144** (1975); (c) A. W. Adamson, "Physical Chemistry of Surfaces", 3rd ed, Wiley, New York, N.Y., 1976; (d) J. T. Davies and E. K. Rideal, "Interfacial Phenomena", Academic Press, New York, N.Y., 1963; (e) N. K. Adam, "The Physics and Chemistry of Surfaces", 3rd ed, Oxford University Press, London, 1941.
- (9) Evidence that the amide was behaving as a monolayer is taken from (a) the close correspondence between the film behavior portrayed in Figures 1 and 2; (b) the fact that force-area curves were reproducible and reversible; (c) the fact that film pressures held constant during stepwise compression up to intermediate pressures; (d) similarity of behavior of our films to those of Lundquist's. Film balance performance was checked from time to time against monolayers of pure stearic acid.

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### Noncoulomb Variation of Ion Pairing in Polar Solvents

Sir:

For the primitive model (rigid charged spheres of diameter  $a$  in a continuum), it is easy to show<sup>1</sup> that the association constant  $K$  for contact pairs is given by

$$K = (4\pi N a^3 / 3000) \exp(e^2 / a D k T) \quad (1)$$

( $N$  = Avogadro's number,  $e$  = unit charge,  $D$  = dielectric constant,  $k$  = Boltzmann's constant, and  $T$  = absolute temperature). Constants for systems in which the ions are large compared with solvent molecules (e.g., tetraalkylammonium tetraphenylborides in acefontrile-carbon tetrachloride mixtures<sup>2</sup>) conform to eq 1, but, for systems in which the ions are smaller than or comparable in size with solvent molecules, eq 1 fails completely to describe the change of  $K$  on changing the solvent.<sup>3</sup> Figure 1 displays the pairing constants for potassium iodide<sup>4</sup> in various mixtures of water, ethylene carbonate (EC), tetramethylene sulfone (TMSu), dimethyl sulfoxide (Me<sub>2</sub>SO), and tetrahydrofuran (THF). A 75:25 wt % mixture of EC and TMSu is isodielectric with water: addition of this mixture to water initially decreases and subsequently increases  $K$ . Ad-

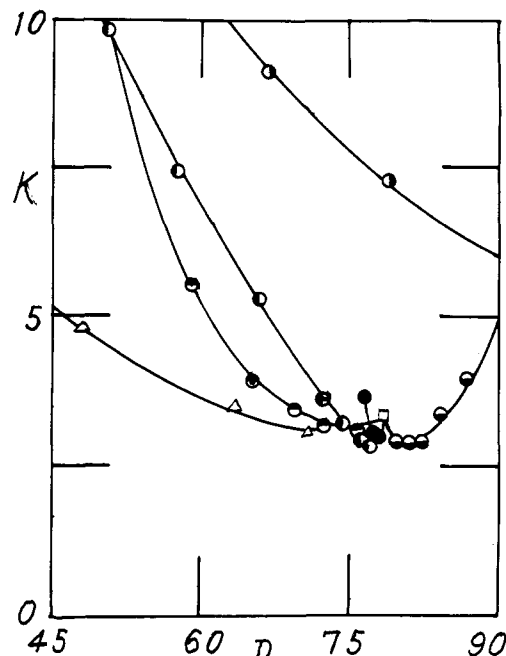
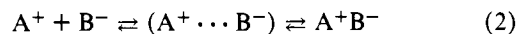


Figure 1. Pairing constants for potassium iodide in different solvents: □, H<sub>2</sub>O; ●, H<sub>2</sub>O-EC; ○, H<sub>2</sub>O-TMSu; ●, H<sub>2</sub>O-EC-TMSu (see text); ○, EC-TMSu; ●, H<sub>2</sub>O-Me<sub>2</sub>SO; Δ, H<sub>2</sub>O-THF.

dition of TMSu to water decreases both  $K$  and  $D$ , while addition of EC to water decreases  $K$  but increases  $D$ . Different  $K$ 's are seen in Figure 1 at the same values of  $D$ , while equal values of  $K$  are observed for different values of  $D$ . A smooth curve can be drawn through the points for a given solvent pair, but obviously no function  $K = F_0(aD)$  exists which describes the systems shown in Figure 1.

The qualitative explanation of the situation is simple: any theory based on the primitive model (which assumes only Coulomb interaction between ions) ignores completely all short range ion-ion and ion-solvent interactions. The latter are system specific and control the final steps in the formation of contact pairs in real solutions. Therefore the primitive model must be replaced by one which will permit inclusion of short-range effects in addition to those due to the long-range Coulomb force.

Consider the coupled equilibria



where the symbol  $(A^+ \cdots B^-)$  represents a solvent separated pair, and  $A^+ B^-$  a contact pair. Unpaired ions (concentration  $c\gamma$ ) are ions which find no other ion in a sphere of diameter  $R$  centered on those ions;  $R$  is the diameter of the Gurney cosphere. Paired ions are ions which find one ion of opposite charge in the range  $a \leq r \leq R$  where  $r$  is the center-to-center distance of the pair. Contact pairs are ions which find one ion of opposite charge in the shell of nearest neighbors; all other nearest and next-nearest neighbors are solvent molecules; if  $\alpha$  is the fraction of paired ions which are in contact, the concentration of contact pairs is  $\alpha c(1 - \gamma)$ . The first step of (1) is diffusion controlled; it can be shown<sup>5</sup> that

$$K_R = (1 - \alpha)(1 - \gamma) / c\gamma^2 f^2 \\ = (4\pi N R^3 / 3000) \exp(\beta / R) \quad (3)$$

where  $\beta = e^2 / D k T$ . For  $r > R$ , continuum theory may be used because by definition the solvent has bulk properties outside the cospheres. Consider a cation which finds an anion at the distance  $R$ : the anion may diffuse to distances  $r > R$  (become unpaired) or, by site interchanges with solvent molecules, eventually form a contact pair. The constant for the second step of (1) is

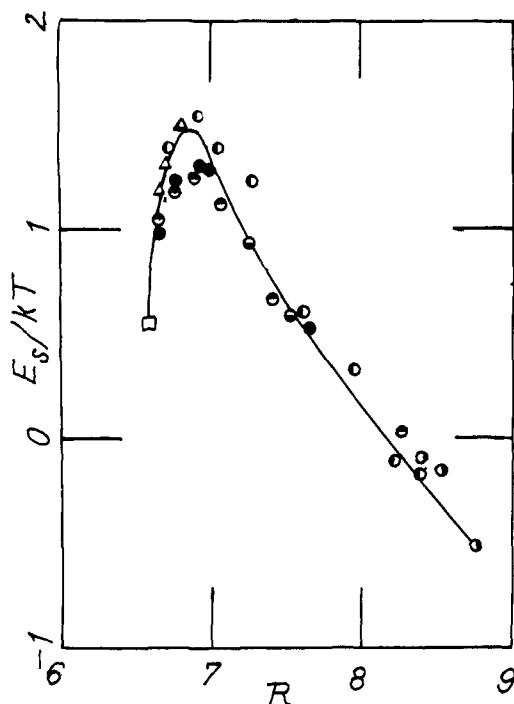


Figure 2. Correlation between pair energy and cosphere diameter. Same code as Figure 1.

$$K_s = \alpha / (1 - \alpha) = \exp(-E_s/kT) \quad (4)$$

where  $E_s$  is the energy difference between a pair in the states  $r = a$  and  $r = R$ . Combining (3) and (4) gives for the overall pairing constant  $K = (1 - \gamma) / c\gamma^2 f^2$

$$K = K_R(1 + K_s) = K_R \exp(-E_s/kT) \quad (5)$$

showing that  $K$  depends not only on  $D$  but also on the system-specific parameters  $R$  and  $E_s$ :  $K = F(D, R, E_s)$ .

Define  $G(R, E_s)$ , a surface in the  $(G, R, E_s)$  3-space, by dividing out the term in  $K$  which depends on long-range Coulomb forces:

$$G = K \exp(-\beta/R) = (4\pi NR^3/3000) \exp(-E_s/kT) \quad (6)$$

The steps in the formation of contact pairs from  $r = R$  pairs involve ion-solvent site interchanges; therefore  $E_s$  depends both on short-range ion-solvent interactions as well as on cation-anion interaction at  $r = a$ . The cosphere diameter  $R$  depends on dipole moment, polarizability, size and shape of solvent molecules, and ionic charge and size. For a given electrolyte, a plot of  $E_s/kT$  against  $R$  is the trace on the  $G(R, E_s)$  surface of the part of  $K$  which depends on short range parameters characteristic of the solvent. Figure 2 is the  $E_s/kT - R$  plot for potassium iodide in the various solvents listed in the caption of Figure 1. In contrast to Figure 1, where the  $K-D$  points are scattered over the plane, the points in Figure 2 cluster around a single curve. This correlation between the parameters  $E_s$  and  $R$  for such a variety of solvents suggests that (2) presents a realistic model for electrolytic solutions.

## References and Notes

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- (2) D. S. Berns and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 5585 (1960).
- (3) A. D'Aprano and R. M. Fuoss, *J. Am. Chem. Soc.*, **91**, 911 (1969).
- (4) A. D'Aprano, J. Komiyama, and R. M. Fuoss, *J. Solution Chem.*, **5**, 279 (1976).
- (5) R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 16 (1978).

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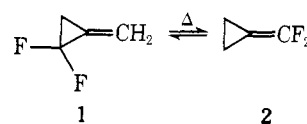
## Thermal Isomerization of 2,2-Difluoromethylenecyclopropane

Sir:

The effect of a fluorine substituent on the thermodynamic stability of a cyclopropane ring is not quantitatively well understood at present. Our earlier study of the geometrical isomerization of 1,1-difluoro-2,3-dimethylcyclopropane indicated that *gem*-difluoro substituents weaken cyclopropane to cleavage by  $\sim 9$  kcal/mol.<sup>1</sup> However, the only previous work which shed light on the *overall* thermodynamic effect of fluorine on a cyclopropane ring was that of Oth and Merényi, who examined the NMR spectra of monosubstituted bullvalenes. They found that *all* substituents including fluorine prefer *not* to be cyclopropane bound in the bullvalene equilibrium.<sup>2,3</sup> Benson and O'Neal expressed their interpretation of the available thermochemical data in 1968 by suggesting that each fluorine substituent increases the strain of cyclopropane by  $\sim 5$  kcal/mol.<sup>4</sup> This estimate is certainly consistent with our above-mentioned isomerization studies.

Hoffmann has examined the problem theoretically and predicted that all cyclopropane ring bonds would be weakened by fluorine substitution.<sup>5</sup> This prediction was brought into question by microwave spectral studies of 1,1-difluorocyclopropane which indicated that, while the  $C_2-C_3$  bond was indeed substantially lengthened with respect to cyclopropane itself, the  $C_1-C_2$  bonds were shortened and thus expected to be stronger.<sup>6</sup>

We would now like to present preliminary experimental kinetic and thermodynamic results on the thermal unimolecular isomerization of 2,2-difluoromethylenecyclopropane (1) to difluoromethylenecyclopropane (2). These results provide



the first experimental support for Hoffmann's prediction that not only the bond opposite to the fluorine-substituted carbon, but also those adjacent to the substituted carbon itself, in this case the  $C_2-C_3$  bond of **1**, are weakened. This study also provides the first quantitative evaluation of the relative thermodynamic stability of cyclopropane-bound fluorine vs. vinylic fluorine.

2,2-Difluoromethylenecyclopropane (**1**) was synthesized by the thermal decomposition of hexafluoropropylene oxide in the presence of an excess of allene.<sup>7</sup> It was characterized by an  $^1H$  NMR spectrum (100 MHz,  $DCCl_3$ ) ( $\delta$  1.84–2.06 (m, 2 H), 5.58–5.78 (m, 1 H), and 5.92–6.1 (m, 1 H)) and an  $^{19}F$  NMR spectrum (100 MHz,  $DCCl_3$ ) ( $\delta$  53.0 (m) (relative to TFA)). **1** was found to rearrange smoothly thermally to difluoromethylenecyclopropane (**2**) which was characterized by an  $^1H$  NMR absorption of  $\delta$  1.28–1.52 (t,  $J = 2$  Hz) and by a  $^{19}F$  NMR absorption at  $\delta$  9.13 (p,  $J = 4$  Hz). The reaction was found to follow good, reversible first-order kinetics. Equilibrium constants were obtained at six temperatures (see Table I), and a plot of  $\ln K$  vs.  $1/T$  yielded a  $\Delta H$  for the isomerization of  $-1.9 \pm 0.1$  kcal/mol. Rate constants were also obtained at six temperatures (see Table II), and an Arrhenius plot of this data gave a good straight line with the frequency factor and energy of activation being calculated by the method of least squares.

$$\log A = 13.25 \pm 0.2 \quad E_a = 38.3 \pm 0.4 \text{ kcal/mol}$$

2-Methylmethylenecyclopropane (**3**) has been shown to rearrange to ethylenecyclopropane with  $\log A = 14.26$  and  $E_a = 40.4$  kcal/mol,<sup>9</sup> 2,2-dimethylmethylenecyclopropane (**4**)