A small aliquot of aqueous xenon trioxide–hydrofluoric acid solution containing not more than 20 mg of solid xenon trioxide was placed in a Teflon microbeaker and evaporated under vacuum leaving solid xenon trioxide powder. The beaker containing the xenon trioxide was placed behind an explosion shield and approximately 4 ml of pure *t*-butyl alcohol was poured into the microbeaker rapidly. After 1 min the solution was carefully stirred by alternately drawing in and discharging from a dropper. It was necessary to stir without touching the solid xenon trioxide to avoid exploding the sample. Most of the supernatant was transferred to a volumetric flask using the medicine dropper technique, and new portions of *t*-butyl alcohol were added until all xenon trioxide dissolved. Trace impurities of transition metal ions, peroxides, or the deformations of the Teflon beaker due to previous decomposition of xenon trioxide caused the sample to explode. Traces of HF had no apparent effect.

The amount of xenon trioxide in *t*-butyl alcohol was determined iodometrically. The stability of the pure xenon trioxide solutions was followed for over a period of 6 weeks showing no loss in oxidizing power, but in the presence of trace amounts of impurities the concentration of xenon trioxide diminished on standing. Since the xenon trioxide was prepared from the xenon hexafluoride hydrolysate, the fluoride ion impurity was determined using the Orion fluoride activity electrode. The amount of fluoride found in *t*-butyl alcohol–xenon trioxide solutions did not exceed 1% of the xenon trioxide concentration. This fact eliminates the possibility of the presence of a significant amount of the $HF \cdot XeO_3$ species. The alkali salt of $HF \cdot XeO_3$, as $CsFXeO_3$, was reported by Selig[4] and Spittler, *et al.*[5]

The acid character of xenon trioxide and that of glacial acetic acid in *t*-butyl alcohol was determined by titrating aliquots with the standard potassium or rubidium *t*-butoxide in *t*-butyl alcohol using a pH meter and glass–calomel electrodes. The titration curves for both xenon trioxide and glacial acetic acid are shown in Figure 1. In both titrations the end point occurred at a 1:1 molar ratio of the substance titrated to the butoxide added. During the titration of xenon trioxide, an insoluble precipitate was formed which slowly decomposed on standing. The decomposition of this precipitate was followed not only by the "hi-low" titration method, but also by time-of-flight mass spectrometry. The wet analysis of the salt on standing indicated a gradual loss of the titer. Mass spectrometric measurements initially showed a substantial loss of *t*-butyl alcohol and small amounts of xenon and oxygen; then on gentle heating, the sample yielded more *t*-butyl alcohol and some acetone, xenon, oxygen, and carbon dioxide. The precipitate did not explode and showed no shock sensitivity, which is quite contrary to the alkali xenates.

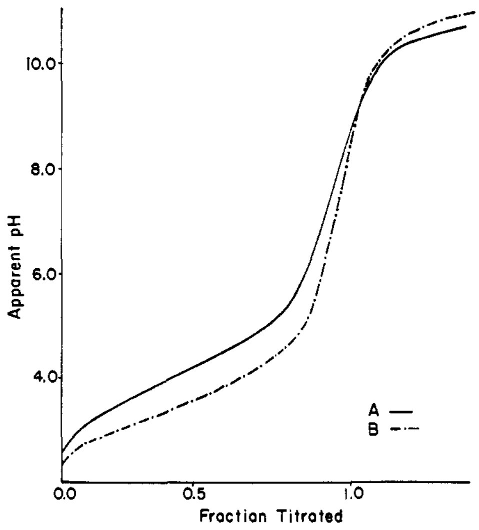

Figure 1. Apparent pH *vs.* fraction titrated. Curve A represents xenon trioxide and curve B glacial acetic acid.

The precipitate was isolated by centrifugation and was washed with ethyl ether. After drying for approximately 3 min the samples were analyzed immediately for the oxidation equivalent and for potassium or rubidium. The average values of the oxidation equivalents for potassium and rubidium salts were 61.3 ± 2 and 69 ± 2, respectively, corresponding to the calculated formula weights of 367 ± 12 for potassium salt and 413 ± 12 for the rubidium salt. These values compare well with the empirical formulas of $t\text{-BuO–XeO}_2\text{–OK} \cdot t\text{-BuOH}$ (363) and $t\text{-BuO–XeO}_2\text{–ORb} \cdot t\text{-BuOH}$ (410). However, it should be pointed out that these analyses cannot exclude the possibilities that the resulting salts may be $KHXeO_4 \cdot 2\ t\text{-BuOH}$, $(t\text{-BuO})_2XeO(OH)OK$, or $(\text{t-BuO})_2XeO_2 \cdot K^+OH^-$.

Attempts to isolate a proposed xenon trioxide–t-butyl alcohol ester failed. In fact, the loss of xenon trioxide during the concentration of dilute xenon trioxide solutions was observed when the xenon trioxide concentration reached approximately 0.4 *M*. It appears that the hypothetical ester-like species decompose in the vapor phase.

The nmr spectrum of approximately 0.3 *M* xenon trioxide in the *t*-butyl alcohol–D_2O system showed no bands for the methyl protons. However, it indicated a marked catalytic effect on the hydroxyl proton exchange.

The kinetic data, titrimetric studies, and analysis of the corresponding unstable salts suggest that the behavior of xenon trioxide in *t*-butyl alcohol may be best explained by the following reactions.

$$XeO_3 + t\text{-BuOH} = t\text{-BuOXeO}_3\text{H (solvated)}$$

$$t\text{-BuOXeO}_3\text{H} + t\text{-BuOK} = t\text{-BuOXeO}_3\text{K} \cdot t\text{-BuOH}$$

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Bruno Jaselskis, J. P. Warriner
Department of Chemistry, Loyola University
Chicago, Illinois 60626

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[4] H. Selig, *Inorg. Chem.*, **5**, 183 (1966).

[5] T. M. Spittler, B. Jaselskis, and J. L. Huston, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

Non-Coulomb Variation of Ionic Association in Polar Solvents

Sir:

The association constant K_A of rigid charged spheres of diameter a in a continuum of dielectric constant D is given by the equation[1]

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[1] R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

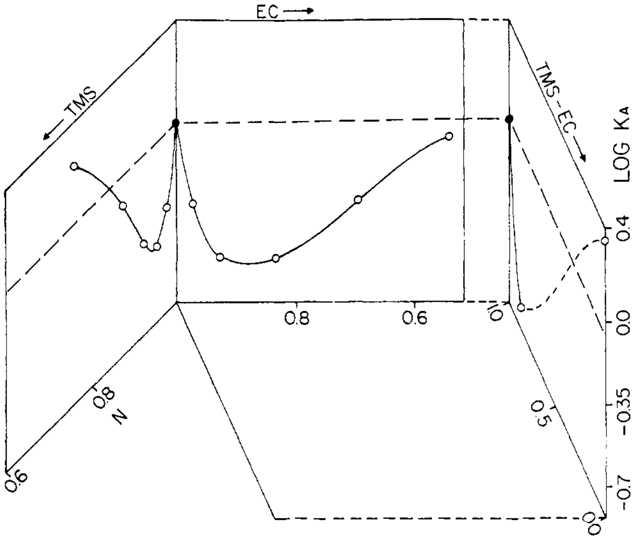

Figure 1. Association of potassium iodide in water and in mixed solvents at 25°.

$$K_A = K^0 \exp(e^2/aDkT) \qquad (1)$$

where e is unit charge and K^0 is a geometrical factor which measures excluded volume; according to (1), a plot of log K_A is linear in reciprocal dielectric constant, with K_A increasing as D decreases. The alkali halides in water–dioxane mixtures with D less than about 30 conform to the above model.[2] Until recently, it was impossible to determine association constants with any precision in solvents of higher dielectric constant; integration of the Fuoss–Onsager conductance equation[3] through terms of order $c^{3/2}$ now permits analysis of conductance data at higher concentrations (*e.g.*, to 0.1 N for 1:1 salts in water). It was found[3] that the log K_A–$(1/D)$ plots for a variety of 1:1 salts in water–dioxane mixtures was concave down in the range $78.5 \geq D > 30$, becoming linear in the range below 30. Alternatively described, extrapolation of the linear portion of the curve into the region of high dielectric constants gave values for K_A which were too high, as if the first additions of dioxane to water had two effects: the expected increase in K_A due to decreased dielectric constant, and another as yet unexplained one. The latter presumably correlates with the destruction of the water structure as dioxane is added. With dioxane, the dielectric effect dominates, because the dielectric constant of dioxane (2.2) is so low; a relatively small amount of dioxane makes a large change in D. Mixtures of water with several other aprotic solvents of higher dielectric constant (ethylene carbonate (EC) and tetramethylene sulfone (TMS)) were therefore studied, in order to enhance the nonelectrostatic effects. A completely new type of dependence of association on solvent composition was found, as shown in Figure 1, where log K_A for potassium iodide (vertical axis) is plotted against solvent composition (N = mole fraction of water). This surface shows that association in water is decreased by the addition of other solvents which may increase, decrease, or leave unchanged the dielectric constant.

The association constant in water ($K_A = 0.92$) is shown as the solid black point. As TMS is added, D decreases but initially, K_A *also* decreases; the minimum in the log K_A–TMS plane comes at $D \approx 71$ where $K_A = 0.33$. On further addition, K_A then rises, reaching the value 1.6 at $D = 59.4$ ($N = 0.76$, at 68 wt % TMS). Exactly the same pattern is observed when EC is added to water; here K_A again decreases on initial addition of aprotic solvent as D increases, but then on further addition of EC (with accompanying further *increase* of D), K_A *increases.* The minimum in the log K_A–EC plane is at $K_A = 0.24$, at $D \approx 81.5$ and $N \approx 0.87$ (40 wt % EC). Finally, in an anhydrous mixture ($D = 78.64$) of 25.6% TMS–74.4% EC, isodielectric with water, the association constant is 2.25, over twice the water value. Addition of water to this mixture (shown in the projected plane to the right in Figure 1) sharply decreases association, although the dielectric constant is changed but little; at $N = 0.876$, $D = 77.2$, and $K_A = 0.19$. Thus by varying solvent composition at essentially fixed dielectric constant, K_A can be varied up and down by an order of magnitude.

Alessandro D'Aprano, Raymond M. Fuoss
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut 06520

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[2] R. M. Fuoss, *Rev. Pure Appl. Sci.*, **18**, 125 (1968).

[3] R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U. S.*, **57**, 1550; **58**, 1818 (1967).

The 3,7-Transannular C–H Insertion Reaction in the Pyrolysis of the Sodium Salt of Pseudopelletierine Tosylhydrazone. A Simple and Novel Synthesis of N-Methylnorazaadamantane[1]

Sir:

Proximity effects in the transannular reactions of medium-sized rings have been well documented. Postulated intermediates include carbonium ions, carbanions, radicals, and carbenes.[2] Extreme cases of proximity would be expected in transannular reactions between C-3 and C-7 positions in bicyclo[3.3.1]nonane ring systems and their heterocyclic analogs, where a twin-chair conformation has been postulated.[3] Studies on the transannular reactions in such ring systems seem to be limited to solvolytic reactions to nonheterocyclic analogs.[5] We wish now to report a facile 3,7-transannular C–H insertion reaction in a 9-methyl-9-azabicyclo[3.3.1]nonane ring system using base-promoted decompositions of the tosylhydrazone (Ib) of pseudopelletierine (Ia), which has been postulated to prefer a double-chair conformation in the ground state.[4]

The dry sodium salt (Ic) of Ib, obtained readily by treatment of Ib-hydrochloride (mp 236–238° dec) with

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[1] The Synthesis of Adamantane Derivatives. VI. For the previous paper in this series, see T. Sasaki, S. Eguchi and T. Toru, *Tetrahedron Lett.*, 4135 (1968).

[2] (a) For an excellent review on transannular reactions in medium-sized rings, see A. C. Cope, M. M. Martin, and M. A. Mckervey, *Quart. Rev.* (London), **20**, 119 (1966); (b) for recent papers on transannular carbene reactions, see A. C. Cope and S. S. Hecht, *J. Amer. Chem. Soc.*, **89**, 6920 (1967); S. Oida and E. Ohki, *Chem. Pharm. Bull.* (*Tokyo*), **15**, 545 (1967).

[3] For example, see (a) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968), and references cited therein; (b) see also references quoted in ref 4.

[4] For conformational studies of Ia and its derivatives, see C.-Y. Chen and R. J. W. Le Fèvre, *J. Chem. Soc.*, *B*, 539 (1966), and references cited therein; H. S. Aaron, C. P. Ferguson, and C. P. Rader, *J. Amer. Chem. Soc.*, **89**, 1431 (1967); W. D. K. Macrosson, J. Martin, and W. Parker, *Tetrahedron Lett.*, 2589 (1965).

[5] For example, see M. A. Eakin, J. Martin, W. Parker, S. C. Egan, and S. H. Graham, *Chem. Commun.*, 337 (1968), and references cited therein.