A Critical Study of the Medium Activity Coefficient of Ions between Water and Methanol Based upon the $\gamma_{\mathrm{BPh_4^-}} = \gamma_{\mathrm{AsPh_4^+}}$ and Ferrocene (Strehlow) Assumptions

Sir:

In recent years Parker[1] and Popovych[2] have written excellent reviews on the present status of the problem of the medium effect or medium activity coefficient (γi) or transfer coefficient (Γ, French school) of ions. Thermodynamically it is impossible to ever determine exactly the medium effect; values of γi can be found only on the basis of extrathermodynamic assumptions. Values of γi for a given ion found on the basis of different assumptions may differ considerably from one another.[2,3] In recent years, one or both of the two most popular assumptions adopted by several workers have been (1) that the medium effects on the cation and anion of the salts tetraphenylphosphonium tetraphenylborate,[4] triisoamyl-*n*-butylammonium tetraphenylborate[5] (TABBPh$_4$), and tetraphenylarsonium tetraphenylborate[6] (AsPh$_4$BPh$_4$) are the same and (2) that the potential of the ferrocene–ferricinium couple is not affected by the solvent.[7] Objections to the former assumption have been raised by Coetzee.[8] In a recent paper, Parker and his coworkers[9] have compared $\gamma_{\mathrm{Ag^+}}$ values among a host of organic solvents based on the above two assumptions, in addition to the assumptions that $\gamma_{\mathrm{BPh_4^-}} = \gamma_{\mathrm{CPh_4}}$ and that there is a negligible liquid junction potential between two half-cells in different organic solvents (under conditions that cations and anions in a given solvent have the same mobility). They found a fair agreement among values based on the various assumptions. Water was excluded as a reference solvent because of the difficulty of finding a reliable value of the solubility product $K^{\mathrm{sp}}_{\mathrm{AgBPh_4}}$ in water. We have determined[10] the value in water by a chemical-exchange method, shaking silver tetraphenylborate with potassium iodide and silver iodide with sodium tetraphenylborate until equilibrium was attained.

Popovych[2,11] derived by an indirect way (*vide infra*) $K^{\mathrm{sp}}_{\mathrm{TABBPh_4}}$ in water, and in his review paper (see ref 2, p 109) lists values of ${}^{\mathrm{W}}\gamma^{\mathrm{M}}$ for several cations and anions. For both log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{TAB^+}}$ and log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{BPh_4^-}}$, a value of -4.20 (expressed on the molar scale) is given. We have calculated log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{BPh_4^-}}$ = log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{AsPh_4^+}}$, applying the equation

$$\log {}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{AsPh_4BPh_4}} = \log {}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{AsPh_4A}} + \log {}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{CBPh_4}} - \log {}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{CA}}$$

in which C represents K$^+$ or Ag$^+$ and A is picrate (Pi$^-$), ClO$_4^-$, or I$^-$. The following values of pK^{sp} at ionic strength of zero have been used in water and methanol: AsPh$_4$Pi, 8.8[9] and 3.9;[9] KBPh$_4$, 7.53[5b] and 5.23;[5b] KPi, 3.36[5b] and 4.41;[5b] AsPh$_4$ClO$_4$, 8.4[12] and 5.4;[13] KClO$_4$, 1.94[14] and 4.7;[15] AgBPh$_4$, 17.2[10] and 14.4;[10] AsPh$_4$AsI, 5.1[9] and 2.3;[9] AgI, 16.0[16] and 18.4.[16] We find for $-$log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{BPh_4^-}}$ with C = K$^+$ and A = Pi$^-$, 4.1; with C = K$^+$ and A = ClO$_4^-$, 4.05; with C = Ag$^+$ and A = Pi$^-$, 4.15; and with C = Ag$^+$ and A = I$^-$, 4.0. The good agreement between these values and those of Popovych[11] attests to the reliability of the values of pK^{sp} and also to the fact that the various solids are not solvated in water and methanol. We then find that log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{K^+}} = 5.23 - 7.53 + 4.1 = 1.8$ and log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{Ag^+}} = 14.4 - 17.2 + 4.1 = +1.3$. From the values of the standard potentials of potassium and silver in water[17] of -2.925 and $+0.799$ V and in methanol[18] of -2.921 and $+0.764$ V, respectively, we find log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{Ag^+}} = 1.1$, taking the above value of log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{K^+}} = 1.8$ as the more reliable one. Considering the uncertainty in the values of p$K^{\mathrm{sp}}_{\mathrm{AgBPh_4}}$, the agreement with the above value of 1.3 is gratifying.

Now we consider the ferrocene (Strehlow) assumption for the evaluation of log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{Ag^+}}$. Using voltammetry with a platinum disk electrode (Pt) in the cell

$$\mathrm{Ag}\left|\begin{array}{l}0.01\ M\ \mathrm{AgClO_4}\\ 0.01\ M\ \mathrm{Et_4NClO_4}\end{array}\right\|\ 0.1\ M\ \mathrm{Et_4NPi}\left|\begin{array}{l}\text{ferrocene } 0.0002\ M\\ 0.02\ M\ \mathrm{Et_4NClO_4}\end{array}\right|\mathrm{Pt}$$

Parker, *et al.*,[9] obtained a value of log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{Ag^+}} = -2.1$. Their emf values in water and in methanol appear to be of the right order of magnitude. Values of $E_{\mathrm{Fc}}{}^0 - E_{\mathrm{Ag}}{}^0$ in water agree within 10 mV with those found by ordinary voltammetry at the rotated platinum wire electrode in this laboratory[19] and by cyclic voltammetry by French workers.[20] Chiang[21] found in methanol the oxidation of ferrocene at a rotated platinum disk electrode to be reversible. He used an aqueous sce as reference half cell. From potentiometric measurements with appropriate cells, combined with Chiang's data, we find a value of $E_{\mathrm{Fc}}{}^0 - E_{\mathrm{Ag}}{}^0$ in methanol which agrees within 20 mV with that of Parker, *et al.*[9] Hence, their value of log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{Ag^+}} = -2.1$ appears to be of the right order of magnitude. The difference between log ${}^{\mathrm{W}}\gamma^{\mathrm{M}}_{\mathrm{Ag^+}}$ obtained by the tetraphenylborate and ferrocene assumptions therefore amounts to some three units.

In a subsequent paper will be reported values of ${}^{\mathrm{W}}\gamma^{\mathrm{S}}$i of several cations and anions among water, methanol, and three aprotic solvents. The main object of the present communication is to sound a warning not to accept a value of an ion medium activity coefficient, obtained on the basis of any of the two and other assumptions with water as a reference solvent, as the true value.

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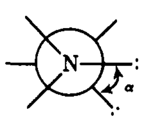
Geometry of Hydrazine Cation Radicals

Sir:

The simplest example of a molecule containing a vicinal lone pair–lone pair interaction is hydrazine, the geometry of which has received a fair amount of study, both experimentally and theoretically.[1] Because interaction of the lone-pair orbitals is destabilizing, hydrazines which are free to rotate adopt a gauche conformation, **1**, α approaching 60–90°, to minimize overlap, although steric constraints can force α to assume almost any value.[2] A consequence of the destabilizing electronic interaction is that hydrazines are particularly easily oxidized. Although hydrazinium cation radicals which have N–H bonds are so unstable that flow systems are required for detection by esr,[3] tetraalkylhydrazinium cation radicals are conveniently stable for esr study.[4] We have been interested in the geometry of hydrazinium radicals, since it should be quite different from that of the hydrazine. When an electron is removed, considerable flattening at the nitrogens should occur. Esr studies of hydrazinium radicals have been interpreted as showing the proper nitrogen splitting for sp^2 hybridization at nitrogen[3] (odd electron in pure p orbitals), but the present state of knowledge about nitrogen splittings does not allow very much accuracy in prediction of a(N) values.



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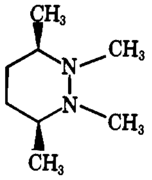

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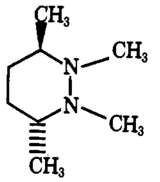

3

The esr splitting for a hydrogen on the carbon α to a hydrazinium nitrogen (a "β" splitting in the usual esr nomenclature) should be given by the relationship $a(\mathrm{H}) = (A + B\cos^2\theta)\rho_\alpha$, where A is small, B is large (about 50 G for a p orbital on carbon and apparently[4] about the same size for the spin-bearing orbital at a hydrazinium nitrogen), θ is the dihedral angle between the C–H bond and the spin-bearing orbital axis, and ρ_α is the spin density at the hydrazinium nitrogen. In a six-ring hydrazinium radical cation, for any one conformation the splitting for the two hydrogens of an α-methylene group would be different, since different θ values would be involved, but ring flipping and nitrogen inversion are expected to be fast on the esr time scale at accessible temperatures. The observed splitting will therefore reflect a weighted average value of θ over all the conformations which are populated.

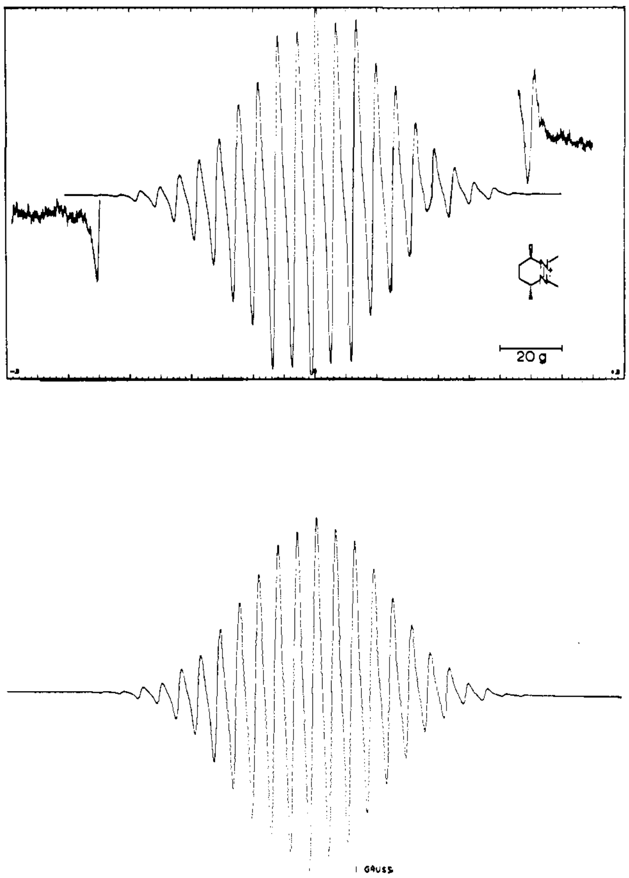

Figure 1. Esr spectrum of $3^{\cdot+}$ compared with a simulation using the splittings quoted in the text.

We wish to report esr results for *cis*- and *trans*-1,2,3,6-tetramethylhexahydropyridizine[5] (**2** and **3**, respectively) which demonstrate that even in a relatively unstrained six-membered ring, the hydrazinium group is not planar. Electrolytic oxidation of the hydrazines in acetonitrile (0.05 M in sodium perchlorate) gave the hydrazinium radical cations, and the esr spectra were recorded. The spectrum of $\mathbf{2}^{\cdot+}$ consisted of 13 groups of lines, and analyzed for $a(6\mathrm{H}) = 12.4$ G, $a(2\mathrm{N}) \approx a(2\mathrm{H}) = 13.1$ G. In contrast, the spectrum of $\mathbf{3}^{\cdot+}$ consisted of 21 lines with a separation of about half that observed for the cis compound, and analyzed for $a(6\mathrm{H}) \approx a(2\mathrm{N}) \approx 12.4$, $a(2\mathrm{H}) \approx 6.2$ (Figure 1). It is clear that averaged values are being observed for the methine hydrogen splittings, and that these C–H bonds are, on the average, better aligned for overlap with the hydrazinium spin-bearing orbitals in $\mathbf{2}^{\cdot+}$ than in $\mathbf{3}^{\cdot+}$.

Assuming that the hydrazinium group was flat, $\mathbf{2}^{\cdot+}$ would exist in the equilibrating half-chair conformations **2a** $\rightleftharpoons$ **2b**, and the methine hydrogen splitting observed would be the average of that for a pseudoaxial and a pseudoequatorial hydrogen, since **2a** and **2b** are of equal energy. The corresponding conformations for the trans compound, **3a** and **3b**, are not of equal energy, because of the 1,3-dipseudoaxial $\mathrm{CH_3}$–H interactions of **3b**. Because the ratio of **3a**/**3b** would be considerably

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(5) Anderson[2] has prepared **3** previously; final purification was by preparative vpc. The low-temperature nmr spectra are consistent with the structures.