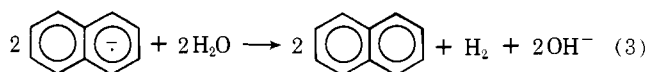


plete reduction of the naphthalene. When the sodium reduction of the naphthalene is not complete, it is readily sublimed from the solid mixture at room temperature.

All of the above mentioned data indicate that the solid salt of the naphthalene anion radical reacts with water to yield ~40% of the theoretical amount of hydrogen gas expected from eq 3. This production of H₂ compared with the lack of it from



the other polyacene systems is probably associated with its lower electron affinity (larger energy difference between the neutral molecule and the anion radical). It seems reasonable that the reaction proceeds through an intermediate that consists of a hydrogen bond between the water and the charged π cloud of the anion radical.⁷ The extra electron could then be pulled out of the antibonding MO and into the hydrogen 1s orbital with simultaneous breaking of the H-O bond in water.

This H₂ evolution via anion radical cleavage of water is in sharp contrast to the fact that only protonation has been observed previously. The possibility of photogeneration of anion radicals to be used for water cleavage and H₂ production with recovery of the neutral substrate should not be overlooked.

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References and Notes

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- (3) (a) G. R. Stevenson, I. Ocasio, and A. Bonilla, *J. Am. Chem. Soc.*, **98**, 5469 (1976); (b) unpublished results.
- (4) The technique is identical with that described in G. R. Stevenson and I. Ocasio, *J. Phys. Chem.*, **79**, 1387 (1975).
- (5) G. Stevenson and L. Echegoyen, *J. Am. Chem. Soc.*, **96**, 3381 (1974).
- (6) The noncondensable gas evolved from the reaction was shown to be hydrogen by first passing it through a liquid nitrogen trap and then into a CuO oven. The gas reduced the CuO to Cu and formed water.
- (7) The existence of hydrogen bonds to charged π clouds has been demonstrated for the anions of cyclooctatetraene; see G. R. Stevenson and A. Vassos, *J. Phys. Chem.*, **81**, 1526 (1977).

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A Self-Consistency Criterion for Two-Structure Theories

Sir:

Two-structure theories have been proposed for systems where the properties are thought to be intermediate between those of the individual structures. Thus water¹ has been described as a mixture of regions of ice-like material and regions of more closely packed molecules (or normal liquid). Aqueous electrolytes have been described^{2,3} as mixtures of ionic lattice-like regions with "Debye-Hückel" ("D-H") regions of random structure modified by electrostatic forces. It is not my

purpose at this time to discuss the over-all merits of any of these theories, but there is a self-consistency criterion which should be imposed upon any two-structure theory. The relative proportion of material in each structure should be given by the appropriate expression for equilibrium between the two structures. Thus the total Gibbs energy must be at its minimum with respect to distribution of material between the two structures. Also the activity or chemical potential for a component of the system must be the same for one structure as for the other structure.

Many recent theories⁴ conform either exactly or approximately to this equilibrium criterion. However, certain two-structure theories for strong electrolytes grossly violate this principle. Both the theory of Singh² and the earlier theory of Lietzke, Stoughton, and Fuoss³ use arbitrary transfer functions to shift the proportion of "D-H" solute to that of "lattice" solute with increasing concentration. For the first example of Singh, namely HCl, and with his equations and parameters, the chemical potential of the "D-H" solute is lower at all substantial concentrations than that of the "lattice" solute. This difference in chemical potential in favor of the "D-H" structure increases with concentration. Thus, at equilibrium there would be no shift to the "lattice" structure and the expected properties of the two-structure model, treated consistently, would be just those of the "D-H" structure.

References and Notes

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Nitroxide Radical as a Nuclear Spin Decoupling Reagent. Application to Carbon-13 Nuclear Magnetic Resonance Studies of Organothallium Compounds¹

Sir:

We wish to report here a novel use of a stable nitroxide radical as a nuclear spin decoupling reagent in the ¹³C NMR spectra of organothallium compounds which are very complicated owing to large ¹³C-Tl nuclear spin couplings. We have currently been interested in the use of stable free radicals as NMR spin probes (paramagnetic shift and relaxation reagents) for studying the intermolecular interaction associated with hydrogen bonding,² charge transfer interaction,³ and π -stacking interaction.⁴ Here we are concerned with the Lewis acid-base interaction⁵ between thallium in organothallium compounds and nitroxide radical which manifests itself as decoupling effect of long range ¹³C-²⁰⁵Tl coupling and simplifies the spectra enough to be assigned very easily.

It is well established that thallium in organothallium compounds serves as a Lewis acid toward electron-donating Lewis bases such as pyridine and triphenylphosphine oxide.⁶ This suggests that nitroxide radical may also form a weak complex with organothallium compounds at the central metal atom, resulting in effective relaxation of thallium nuclei. This nitroxide-thallium interaction may lead to Tl-¹³C nuclear spin decoupling.