NUCLEAR MAGNETIC RESONANCE INVESTIGATION ON THE SOLVENT SEPARATION OF AN ION PAIR

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NMR evidence has been presented for the existence of intimate and solvent-separated ion pairs in solutions for triphenylarsine-iodine complex. A method has been developed to determine K and n from the relative amounts of the two distinct species coexisting in equilibrium :

$$tpa.\ I^+,\ I_3^- + n\ \text{THF} \overset{K}{\rightleftharpoons} tpa.\ I^+ \| I_3^- \ .$$

It has been found that a single THF solvent molecule has managed to intercalate itself between the cation and the anion. A good inverse correlation between $E^+(I_3^-)$ values and Gutmann's donocity number of dipolar aprotic solvents has also been observed which supports that the better the solvent as a donor, the less the I_3^- ground state is capable of stabilization from its counter—ion.

INTRODUCTION

In polar solvents, the charge-transfer complex between triphenylarsine ((tpa) and iodine ionizes into the inner complex (Mulliken & Person 1969) tpa. I^+, I^-, which subsequently adds another I_2 molecule in a fast reaction to form the complex formulated as tpa. I^+, I_3^-. Abundant evidence from spectroscopy (Augdahl *et. al.*, 1965; and Bhat & Rao 1966), conductimetry and dipole moment measurement has been garnered in support for this scheme. The tpa. I^+, I_3^- complex could conceivably exist as the intimate, the solvent separated or the dissociated ion pair (Szwarc 1972). We have used proton magnetic resonance to monitor solvent-separation of this ion pair in binary mixtures of dioxane and tetrahydrofuran (THF).

EXPERIMENTAL

All of the solvents employed in the present investigation were commercially acquired and were spectro grade. Before use, they were dried over molecular sieve and redistilled. Triphenylarsine from E. Merck was purified by fractional crystallisation from ethanol, m. p. 60°C. Reagent grade iodine was resublimed before use.

NMR spectra were recorded on T-60 spectrometer operating at 60 MHz. Probe temperature was 30°C. TMS was used as internal reference. Chemical shift measurements were made employing the external-lock frequency sweep mode. For this purpose solvent signal (Dioxane or THF) was used. In each case, the frequency of TMS and tpa signals were measured with a Hewlett —Packard Model

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5302-A universal counter and then the chemical shift of the desired signals were calculated from these measurements.

Results and Discussion

When triphenylarsine (0.05 M) is dissolved in dioxane, it gives rise to a singlet resonance at $\delta = 7.35$, the *ortho, meta* and *para* protons being accidentally isochronous. Upon addition of iodine (0.2 M), complexation occurs and the proton resonance shifts downfield to $\delta = 7.70$. Such low-field shifts are diagnostic of partial donation of the lone pair to an acceptor, by analogy to the observations on amine-iodine complexes (Fratiello 1964; and Dratler 1971). Since no characteristic absorption of the I_3^- are found in the infrared (Ginn & Wood 1966; Klaboe 1967; and Yarwood & Person 1968) oi in the electronic (Katzin 1955) spectrum, it is concluded that the triphenylarsine-iodine complex is unionized in pure dioxane, as in carbon tetrachloride or cyclohexane.

However, as soon as the mole fraction of THF in the dioxane-THF mixture reaches 0.1, the phenyl resonance splits into well-separated singlets, of very unequal intensities, at $\delta = 7.75$ and $\delta = 7.90$ (Fig. 1). Their widths at half-height being equal, the intensity ratio R of these two peaks is conveniently measured from their heights. We have thus determined the relative amounts of the two distinct species coexisting in equilibrium. The I_3^- ion is shown to be present, at THF mole fractions greater than 0.2, by its characteristic absorption at 365 and 295 nm (Augdahl *et al.* 1965; Bhat & Rao 1966; and Katzin 1955). We identify the

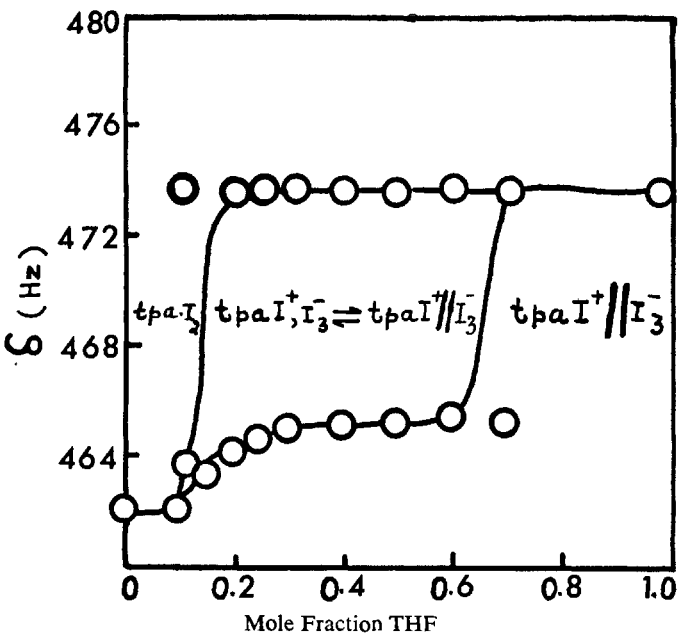


Fig. 1. Chemical shift due to intimate and solvent—separated ion pair formation of triphenylarsine—Iodine complex as a function of [THF] in mixtures of dioxane—THF.

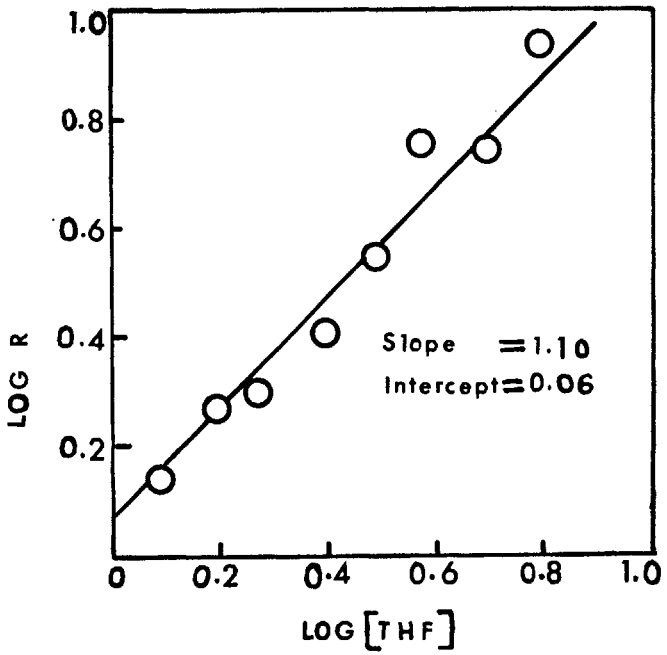


FIG. 2. Solvent separated ion pair formation of tpa. I^+, I_3^- as a function of [THF] in mixtures of dioxane—THF.

low-field proton resonance at $\delta = 7.90$ with the solvent-separated tpa. $I^+ \| I_3^-$ ion pair, and the high-field proton resonance at $\delta = 7.75$ with the intimate tpa. I^+, I_3^- ion pair. The increased charge separation implies a greater delocalization of positive charge unto the phenyl rings, which manifests itself in the increased value of the chemical shifts (Taylor & Kuntz Jr. 1969, 1970).

Consider the equilibrium :

$$\text{tpa. } I^+, I_3^- + n \text{ THF} \underset{\rightleftharpoons}{K} \text{tpa. } I^+ \| I_3^- \tag{1}$$

$$\text{with } K = \frac{[\text{tpa. } I^+ \| I_3^-]}{[\text{tpa. } I^+, I_3^-][\text{THF}]^n} \cdot \frac{\gamma\text{tpa. } I^+ \| I_3^-}{\gamma\text{tpa. } I^+, I_3^- . \gamma^n\text{THF}} \tag{2}$$

where n represents the number of solvent molecules involved in the solvation equilibrium reaction and γ is the Raoult activity coefficient.

Assuming constant activity coefficients Υ throughout the concentration range of Figure 1, and with $R = [\text{tpa. } I^+ \| I_3^-]/[\text{tpa. } I^+, I_3^-]$ determined from the NMR intensities, Equation (2) can be simplified into :

$$K. [\text{THF}]^n = R \tag{3}$$

or in logarithmic form :

$$\log R = n \log [\text{THF}] + \log K \tag{4}$$

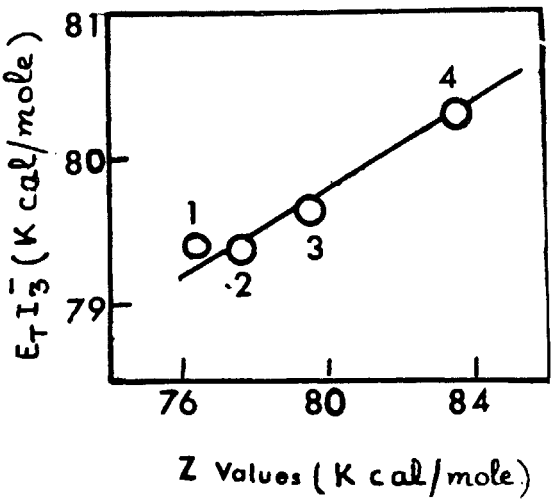


FIG. 3. Correlation between the transition energy of triiodide ion, E_T I_3^- (*ca.* 365 nm) and Kosower's Z value for protic solvents. 1. 2-propanol, 2. 1-butanol, 3. ethanol, 4. methanol.

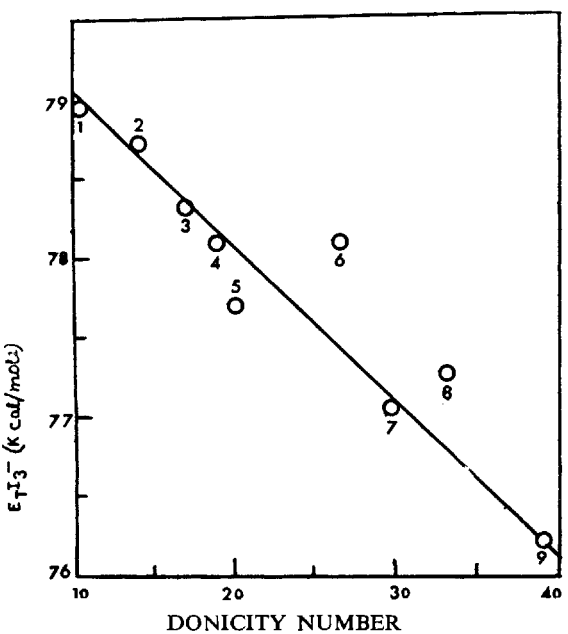


FIG. 4. Inverse correlation between E_T I_3^- (*ca.* 365 nm) and Gutmann's donicity number for dipolar aprotic solvents. 1. Aceticanhydride, 2. Acetonitrile, 3. Acetone, 4. Diethylether, 5. THF, 6. DMF, 7. DMSO, 8. Pyridine, 9. Hexamethylphosphoramide.

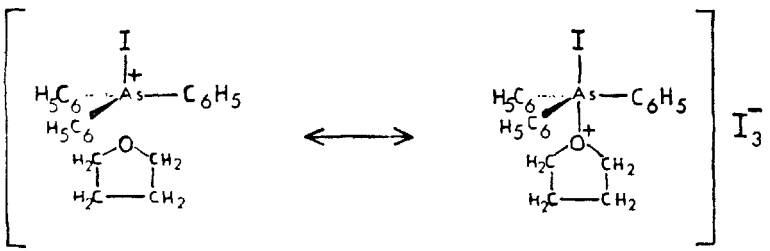
A graph of log R against log [THF] is indeed linear (Chan & Smid 1968), (Fig. 2). From the slope and intercept, the following values are derived :

$n = 1.1 \pm 0.08$

$K = 0.40 \pm 0.10$ 1. mol^{-1}.

Thus a single THF molecule has managed to intercalate itself between the anion and the cation. This result is reminiscent of the solvation number 1 also found for CH_3CN binding to $SbCl_5$, in which separate NMR signals were recorded for solvent molecules in the first coordination sphere and in the bulk of the solution (Ahmad & Schmulbach 1972; Hinton & Emiss 1967; and Hinton & Lincon 1971).

Our finding of distinct absorptions for the tight tpa. I^+, I_3^- species and for the loose tpa. $I^+ \parallel I_3^-$ species implies their separation by an energy barrier of at least 16 *Kcal.* mole^{-1} based upon the chemical shift difference. The pronounced stability of both species may be due in part to the large induction and disperssion forces for such highly polarizable anion and cation. Also, partial *As*—0 bond formation (Pauling 1970) as in :



would serve to offset the entropy loss of *ca.* 25 e.u. (Szwarc 1972) attdndant upon formation of the THF-containing ion pair.

As judged from chemical shifts other solvents are also effective in producing the tpa. $I^+ \parallel I_3^-$ species. We find that protic solvents stabilize the I_3^- ground state, presumably through hydrogen-bonding; the transition energy E_T for the $n \rightarrow \sigma^*$ absorption at *ca.* 365 nm is raised in proportion to the *Z*-value as given in Kosower (1958) of the solvent (Fig. 3). In marked contrast, there is a decrease of E_T in dipolar aprotic solvents and there is a good inverse correlation between the E_T values and the donicity number of the solvent Gutmann (1966, 1967) (Fig. 4). It confirms the analysis made above, with its emphasis on specific solvation : the better the solvent as a donor, the less the I_3^- ground state is capable of stabilization from its counter-ion.

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