

Table I. Experimental and Spectral Data for Methyl Dihalonicotinate

| cmpd | yield, ^a % | mp, ^a °C | method used ^b | IR ν , ^c cm ⁻¹ | proton NMR, ^d ppm | | |
|------|-----------------------|---------------------|--------------------------|---|------------------------------|----------------|-----------------|
| | | | | | H ₄ | H ₆ | CH ₃ |
| I | 86 | 76-77 | (A) B | 1718, 1418, 1362, 1300, 1274, 1205, 1020, 844, 758, 649 | 8.53 d | 8.95 d | 4.00 s |
| II | 80 | 87-88 | A | 1727, 1592, 1418, 1309, 1282, 1183, 1093, 760, 590 | 8.03 dd | 8.83 d | 3.98 s |
| III | 49 | 48-49 | A (B) | 1709, 1427, 1403, 1294, 1266, 1111, 1047, 769, 645 | 8.30 d | 8.60 d | 3.99 s |
| IV | 42 | 42-43 | (A) B | 1704, 1425, 1401, 1292, 1258, 1111, 1042, 766, 649, 587 | 8.15 d | 8.47 d | 4.01 s |
| V | 73 | 68-69 | B | 1715, 1572, 1412, 1355, 1299, 1266, 1183, 1099, 1015, 755 | 8.33 m | 8.93 m | 4.00 bs |
| VI | 89 | 90-91 | B | 1718, 1412, 1355, 1299, 1258, 1183, 1099, 1005, 755 | 8.50 m | 8.93 m | 4.03 s |
| VII | 89 | 48-49 | B | 1712, 1437, 1403, 1383, 1292, 1258, 1105, 1026, 763, 641 | 8.30 m | 8.65 m | 4.07 s |
| VIII | 83 | 75-76 | B | 1705, 1439, 1399, 1282, 1235, 1183, 1105, 1036, 769, 645 | 8.50 m | 8.78 m | 4.10 bs |

^a After recrystallization from aqueous ethanol. ^b A indicates the acid chloride method; B indicates the diazomethane method. Where both methods are indicated, the one in parentheses gave the reported (and highest) yield. ^c Only the most intense absorption bands are reported. ^d Signals were observed in the correct area ratio. s = singlet, d = doublet, m = ill-defined multiplet, bs = broad singlet, dd = doublet of doublets.

crude methyl ester as a yellow-white solid. The crude ester was stirred with a 15% sodium carbonate solution (20 mL) at room temperature for 15 min, filtered, and recrystallized from aqueous ethanol to yield 1.09 g of pure methyl 5-bromo-6-chloronicotinate (I) as white fluffy needles.

Diazomethane Method. Typical Procedure. A freshly prepared solution of diazomethane in ether was slowly added at room temperature to a solution of 2,5-dibromonicotinic acid (1) (1.0 g, 0.00356 mol) in anhydrous ether (45 mL) until the yellow color of diazomethane persisted and nitrogen evolution ceased. The ether was allowed to evaporate slowly in the hood draft overnight, affording the crude methyl ester as a white solid. The solid was stirred with a 15% sodium carbonate solution (30 mL) for 15 min, filtered, and recrystallized from aqueous ethanol to yield 0.93 g of pure methyl 2,5-dibromonicotinate (VII) as white fluffy needles.

Acknowledgment

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Supplementary Material Available: Elemental analyses (C, H, N) for the methyl dihalonicotinates (1 page). Ordering information is given on any current masthead page.

Solubility of Organic Substances in Liquid Xenon

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The solubility of various organic substances in liquid xenon at 60-95-atm pressure and temperatures of 0-40 °C is described. Large organic neutral species dissolve readily; attempts to dissolve ion pairs or free ions failed.

The importance of solvation on proton transfers continues to be a matter of lively interest (1). A low-dielectric solvent that does not selectively solvate either anions or cations and is transparent at visible and infrared wavelengths would lend itself to spectrophotometric comparisons with other nonaqueous solvents, such as acetonitrile, dimethyl sulfoxide, and methanol,

frequently used by kineticists. There is a considerable literature describing the use of liquid xenon as a solvent (2), particularly for simple substances such as CO₂ and CH₃OH dissolved in liquid xenon at low pressures and cryogenic temperatures. Liquid xenon is an attractive solvent to work with because it is either a liquid or a supercritical fluid at easily accessible pressures (60-95 atm) and temperatures (0-40 °C) and because the method of preparing solutions by pressurizing pure gas in a sealed system makes it easy to prepare very pure solutions.

Experimental Methods

Xenon gas with 1 ppm impurity levels was obtained from Cryogenic Rare Gas Laboratories, Inc., Newark, NJ. The materials to be studied were placed in the observation cell, a stainless-steel vessel with three sapphire windows that was constructed from designs reported in the literature (3). Valves

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Table I. Solubility of Substances in Liquid Xenon at 60-95-atm Pressure and 0-40 °C Temperatures

| substance | soluble | insoluble | estimated amount dissolved, g mL ⁻¹ |
|--|---------|-----------|--|
| picric acid | × | | 5 × 10 ⁻³ |
| picrate ion (both DABH ⁺ and H ⁺ as counterions) | | × | |
| <i>p</i> -nitrophenol | × | | 3 × 10 ⁻³ |
| <i>p</i> -nitrophenolate ion (protonated triethylamine counterion) | | × | |
| <i>p</i> -nitrophenolate-protonated triethylamine (ion pair) | | × | |
| <i>p</i> -nitrophenol-triethylamine (neutral complex) | × | | 4 × 10 ⁻³ |
| (dimethylamino)azobenzene (DAB) | × | | 1.6 × 10 ⁻⁵ |
| DABH ⁺ (picrate counterion) | | × | |
| tetrabutylammonium picrate (ion pair) | | × | |
| fluorenyl anion-dibenzo-30-crown-10/K ⁺ complex | | × | |
| crystal violet (chloride salt) | | × | |
| crystal violet (perchlorate salt) | | × | |

and fittings from High Pressure Equipment Co., Erie, PA, were used to connect the cell to the pressurizing apparatus. The xenon was pressurized by condensing into a cylinder from the supply cylinder using liquid nitrogen, closing off the supply, and then allowing the cylinder to warm back up to room temperature. Final pressurization was achieved with a volume reducing hand crank pressure generator. The cell was thermostated by circulating fluid through the inside of the top of the cell. Solubility observations were made spectrophotometrically with a Cary 14 spectrophotometer.

Discussion and Results

Solutes were selected for study on the basis of their promise for producing weak electrolyte equilibria involving ion pairs that would be susceptible to rate studies by the spectrophotometric electric field jump relaxation technique (4). It was hoped that a spreading of electrical charge over larger ions would enhance their solubility in xenon.

The solubility observations are summarized in Table I. Problems were experienced with the materials coating the bottom of the cell and the cell windows, so the reported quantitative solubilities are not intended to represent the maximum molar solubility of the materials. The values are intended only as a rough guide. All observations of actual dissolution were confirmed by at least one repetition of the experiment.

Solubility in all cases was observed to improve drastically when the pressure was increased from 60 to 80 atm, and then more slowly from 80 to 95 atm. From these solubility data it appears that xenon in the pressure regimes studied here will not be a useful solvent for kinetic investigations of weak electrolyte equilibria.

Acknowledgment

The possible use of xenon as a solvent in E-jump kinetic studies was drawn to our attention by Peter Rentzepis of Bell Labs. Jiri Jonas, University of Illinois, made helpful suggestions regarding the construction of high-pressure sample cells.

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Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 1. Binary Mixtures of 1,3-Dioxolane with 1,2-*trans*-Dichloroethylene, Trichloroethylene, and Tetrachloroethylene

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The vapor-liquid equilibrium data of the binary mixtures of 1,3-dioxolane with 1,2-*trans*-dichloroethylene, trichloroethylene, and tetrachloroethylene were obtained with a Stage-Müller apparatus at isobaric subatmospheric pressures. The values of the activity coefficients were correlated by means of the Wilson expression, whose parameters show a marked dependence on the temperature.

In two previous papers (1, 2) the system 1,3-dioxolane-water was studied with the aim of finding satisfactory correlations both of the vapor-liquid data and of the liquid-phase enthalpy of mixing ΔH_m . We chose this system on account of the strong nonideality in the liquid phase and of the anomalous ΔH_m curve showing an inversion of sign as a function of the

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