tains (HD) = 9.2×10^7 (H) at end of 4 min. Even with the low value of (H) obtained by Patat and Sachsse,[18] 10^{-11} mole/liter, the formation of HD by this mechanism is rapid enough to account for the observed concentration at the end of 4 min., (HD) = 2×10^{-4}.

Appendix 2

Mixing of Hydrogens by Molecular Back Reactions.— Consider reactions (7), (8) and (9), and let the over-all rate constant for any ethane decomposition be k_1, and for any combination of ethylene and hydrogen be k_2. In the early stages of reaction $d(C_2H_4D_2)/dt = k_2(D_2)(C_2H_4)$. A maximum rate of formation of the mixed ethane over the time interval can be estimated by setting $(D_2) = (C_2H_4)$ equal to its final value (b), e.g., at the end of 4 min. at $610°$. Then $(C_2H_4D_2) = k_2b^2t$. Since $d(HD)/dt = k_1(C_2H_4D_2)$, (HD) = $\frac{1}{2}k_1k_2b^2t^2$. This value of (HD) would be the maximum obtainable through a sequence of forward and reverse reactions. From the work of Steacie and Shane[4] and the calculated equilibrium constant, $k_1 = 7.4 \times 10^{-4} \text{sec.}^{-1}$, and $k_2 = 1.4 \text{ lit.}^{-1} \text{sec.}^{-1}$ mole, at $610°$. At the end of 4 min. there is 4% H_2 or 4.3×10^{-4} mole/liter, and hence (HD) = 1.1×10^{-5}, or 2.6% of the isotopic hydrogens. Experimentally one finds 44% HD under these conditions. It may be noted that back-mixing becomes even less likely at lower temperatures (for comparable extents of reaction). For example, at $537°$ and a time of 30 min. the calculated % HD would be only 0.2%, whereas the observed is 45%.

Appendix 3

The Relative Rates of Dissociation of C_2H_6 and C_2D_6 into Methyl Radicals.—The equation of Gorin for the rate of combination of two methyl radicals is

$$k_b = 8\kappa\Gamma(\text{2/3})(kT)^{1/6}(3\alpha^2g/2)^{1/3}(\pi/m)^{1/2}\sigma^{-1}$$

Here α is the polarizability, κ the transmission coefficient, g the ionization potential, σ the symmetry number, and m

(18) F. Patat and H. Sachsse, Z. Elektrochem., **41**, 493 (1935).

the mass of the radicals. In comparing CH_3 and CD_3 radicals only the masses are significantly different, so that the rate ratio is $(18/15)^{1/2} = 1.09$.

The equilibrium constant for the dissociation is $K = f^2_{CH_3}/f_{C_2H_6}$. If vibrational terms are ignored,

$$K = \frac{\left[\frac{8\pi^2(8\pi^3I_2^2I_x)^{1/2}}{\sigma h^3} \cdot \frac{(2\pi mkT)^{3/2}}{h^3}\right]^2_{CH_3}}{\left[\frac{8\pi^2(8\pi^3I_2^2I_x^{1/2})}{\sigma h^3} \cdot \frac{(2\pi mkT)^{3/2}}{h^3}\right]_{C_2H_6}}$$

Then

$$K_{C_2H_6}/K_{C_2D_6} = \frac{m^3_{CH_3}m^{1/2}_{C_2D_6}}{m^3_{CD_3}m^{1/2}_{C_2H_6}} \cdot \frac{I^3_{CH_3}}{I^3_{CD_3}} \cdot \frac{(I^2_zI_x)^{1/2}_{C_2D_6}}{(I^2_zI_x)^{1/2}_{C_2H_6}}$$

$$= (0.760)(0.125)(1.414)I_{zC_2D_6}/I_{zC_2H_6}$$

The ratio of I_z for the ethanes is 1.35. Although vibrations have been neglected, it would be a good approximation at these temperatures to add a factor of $2^{1/2}$ to take into account the isotope effect on the internal rotations of the methyl groups. One, therefore, obtains $K_{C_2H_6}/K_{C_2D_6} = 0.254$. The ratio of the forward rates is then 3.6.

Another factor that may influence the isotopic composition of the methanes from the pyrolysis of $C_2H_6 + C_2D_6$ is the relative rate of the hydrogen-abstraction reaction with light and heavy methyl radicals. Trotman-Dickenson and Steacie[19] have studied the reaction of CD_3 radicals, from the photolysis of acetone-d_6, with neopentane. If the reaction $2CH_3 = C_2H_6$ is taken to be 9% faster than $2CD_3 = C_2D_6$ (from the equation of Gorin), the abstraction of a hydrogen atom by CD_3 would be about 7% slower than that by CH_3. This effect would tend to raise the stationary-state concentration of CD_3 compared to CH_3, but only by a small factor.

(19) A. F. Trotman-Dickenson and E. W. R. Steacie, "The Reactions of Methyl Radicals," American Chemical Society Symposium on Anomalies in Reaction Kinetics, Minneapolis, Minn., June, 1950.

The Solubility of Tetraethylammonium Chloride in Benzene–Ethylene Dichloride Mixtures

BY ARTHUR A. VERNON, GERSHON M. GOLDBERG[1a] AND JOHN H. LAROCHELLE[1b]

The solubility of tetraethylammonium chloride was determined for benzene–ethylene dichloride mixtures in the range of dielectric constant from 10.36 to 4.25. In this range the log S–log D plot is a straight line with a slope of about 7.

Introduction

Vernon and Sheard[2] reported the solubility of tetraethylammonium iodide in benzene–ethylene dichloride mixtures and found that a plot of logarithm of solubility against logarithm of dielectric constant gave a straight line with a slope of about five. In order to test this relationship for another solute, studies were made with tetraethylammonium chloride.

Experimental

Materials.—C.P. thiophene-free benzene was stored over anhydrous calcium chloride for several days and was then distilled over phosphorus pentoxide in a fractionating column, discarding the first and last fifths. The refractive index at $25.2°$ was 1.4978 compared with the "International Critical Tables" value of 1.49779.

Ethylene dichloride was stored over anhydrous calcium chloride and distilled from fresh anhydrous calcium chloride, discarding the first and last fifths. The index of refraction at $25.2°$ was 1.4422 compared to the "International Critical Tables" value of 1.44225.

(1) (a) Dougherty Refinery, Petrolia, Pa.; (b) University of Michigan, Ann Arbor, Mich.

(2) Vernon and Sheard, THIS JOURNAL, **70**, 20, 35 (1948).

Tetraethylammonium chloride was prepared by two methods. In the first method triethylamine was allowed to react with one hundred per cent. excess of ethyl chloride in 95% alcohol for three weeks. During this time the reaction flask was connected to a condenser through which ice water was circulated in order to keep the ethyl chloride loss to a minimum. After the completion of the reaction the solvent was evaporated and the solid was dried in a vacuum oven at $120°$ for 48 hours. The product analyzed 21.37 per cent. of chlorine by Volhard titration as compared to the theoretical 21.41 per cent.

A second method was developed which was shorter and more economical. Fifty per cent. excess of solid mercurous chloride was added to a 40 per cent. water solution of tetraethylammonium iodide and the mixture was kept at $60°$ for one week while stirring. The solid was removed by filtration and the filtrate was evaporated to one-half its volume with an additional 25 per cent. of mercurous chloride in order to insure completion of the reaction. The presence of unreacted iodide would be shown by a color change from the white of Hg_2Cl_2 to the greenish-brown of Hg_2I_2. After filtration, the solution was evaporated to dryness and the product dissolved in a small amount of 95 per cent. ethyl alcohol to precipitate any unreacted tetraethylammonium iodide. The solution was again filtered, evaporated to dryness, and the solid was dissolved in warm ethylene dichloride in the proportion of 20 cc. of solvent per gram of solid. The final purified product was crystallized in an ice-bath

dried in a vacuum oven at 120° for 48 hours. The chlorine analysis was 21.39 per cent.

Procedure.—The method of saturation and removal of solution was the same as reported by Vernon and Sheard.[2] The solute was extracted with water and, after evaporation to a volume of 50 cc., was analyzed by the modified Volhard procedure described by Swift, Arcand, Lutwack and Meier.[3] Ferric ammonium sulfate was used as an indicator.

Results

The solubility results given in Table I are the averages of two to four determinations.

TABLE I

SOLUBILITY OF TETRAETHYLAMMONIUM CHLORIDE IN ETHYLENE DICHLORIDE–BENZENE MIXTURES AT 25°

Volume, %, ethylene dichloride	Dielectric constant	Moles per liter of chloride × 10³
100.0	10.36	243.1 ± 3.2
93.5	9.02	159.8 ± 0.60
80.0	7.26	33.13 ± 0.22
69.0	6.09	7.27 ± 0.06
59.5	5.32	2.62 ± 0.01
43.0	4.25	0.576 ± 0.0025

The average deviation is no greater than 1.4% for any solvent mixture. Figure 1 shows a plot of the log of solubility against the log of dielectric constant. The values of dielectric constant were interpolated from the data reported by Vernon, Wyman and Avery.[4]

Discussion

As pointed out by Vernon and Sheard,[2] it is quite likely that at least triple ion formation exists in the solutions here studied and that straight line extrapolation to pure benzene might be justified

(3) Swift, Arcand, Lutwack and Meier, *Analytical Chemistry*, **22**, 306 (1950).

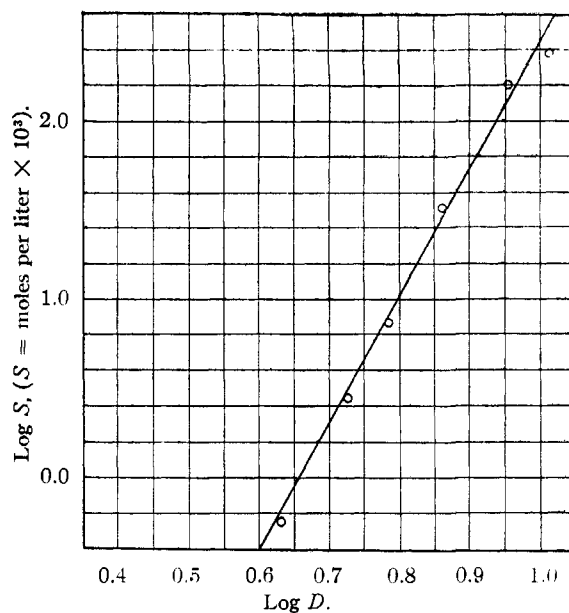(4) Vernon, Wyman and Avery, THIS JOURNAL, **67**, 1422 (1945).

Fig. 1.

if such conditions exist in pure benzene. Such an extrapolation gives a value of 4.0×10^{-11} mole per liter. Since this value is below that at which triple ions might be expected to exist, its value is doubtful.

The slope of the log S–log D plot is about 7 as compared to a slope of about 5 for tetraethylammonium iodide reported by Vernon and Sheard.[2]

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[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES OF NORTHEASTERN UNIVERSITY]

The Solubility of Quaternary Ammonium Salts in Methanol–Benzene Mixtures. The Anomalous Behavior of Tetraethylammonium Iodide

BY GERSHON M. GOLDBERG[1] AND ARTHUR A. VERNON

Solubilities of tetramethylammonium bromide, tetraethylammonium bromide and iodide and tetrabutylammonium iodide were determined in methanol–benzene mixtures. Tetraethylammonium iodide shows a maximum in the solubility—mole fraction plot which may be due to solvent interaction.

Introduction.—In continuation of work in progress in these laboratories on the general problem of solubility in low dielectric constant solvents, the methanol–benzene system was studied. Dielectric constant data for these mixtures were reported by Vernon and LaRochelle.[2]

Experimental

Materials.—C.P. thiophene-free benzene was stored over anhydrous calcium chloride for several days and distilled from phosphorus pentoxide in a fractionating column, discarding the first and last fifths. The refractive index was 1.4978 at 25.2° compared to the "International Critical Tables" value of 1.49779.

C.P. absolute methanol was dried over activated alumina and distilled from fresh activated alumina in the same way as benzene. The refractive index at 25° was 1.3269 com-

(1) Dougherty Refinery, Petrolia, Pa.

(2) Vernon and LaRochelle, THIS JOURNAL, **72**, 3293 (1950).

pared with the "International Critical Tables" value of 1.32773.

Tetraethylammonium iodide, prepared by the method of Vernon and Sheard[3] analyzed 49.3% of iodine compared to the theoretical value of 49.4%.

The other salts were obtained from the Eastman Kodak Company. Tetrabutylammonium iodide was dissolved in ethanol, cooled and ether was added to cause crystallization. After drying the % of iodine was 34.3 compared to the theoretical 34.4%. Tetraethyl- and tetramethylammonium bromides were crystallized from ethanol. The former had a bromide content of 38.0% compared to the theoretical 38.1%; the latter salt analyzed 51.8% compared to a theoretical value of 51.9%.

Procedure.—The thermostat consisted of a glass jar 12″ deep and 12″ in diameter placed in an insulated container. A water motor with a 6″ Alnico bar magnet mounted on the shaft was fixed in the bottom of the container while flat bottom flasks containing solute, solvent and a bar magnet stirrer were supported in the bath. When the motor was

(3) Vernon and Sheard, *ibid.*, **70**, 2035 (1948).