5.3×10^{-3} sec. under slightly different conditions.

3. The use of the lead guard-mirror technique has established that free hydrogen atoms certainly comprise less than 2% of the total number of mirror-active particles produced in the photolysis of propionaldehyde and are probably completely absent. The result supports the view that the free formyl radical is stable up to temperatures of 100°.

4. Propionaldehyde and acetone vapors have the same viscosity under the conditions of temperature and pressure used, and under similar conditions of illumination appear to produce approximately equal concentrations of alkyl radicals. The significance of this result in reference to the mechanism of the photolysis is discussed.

5. The possibility is also discussed that there may be competing free radical decompositions in the photolysis of propionaldehyde.

NEW YORK, N. Y. RECEIVED SEPTEMBER 23, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE WILLIAMS OIL-O-MATIC HEATING CORPORATION]

Hydrogen Bonding and the Solubility of Alcohols and Amines in Organic Solvents. XIII

BY M. J. COPLEY,[1] E. GINSBERG, G. F. ZELLHOEFER AND C. S. MARVEL

A study[2] of the solubilities of the volatile haloforms in donor solvents, free from hydroxyl or amide hydrogens, has shown that large negative deviations from Raoult's law are consistently observed. This behavior has been explained by the assumption that on mixing, intermolecular association of unlike molecules occurs through the mechanism of C—H←N or O bonds. Recent infrared absorption studies by Buswell, Roy, and Rodebush[3] and by Gordy[4] have confirmed this picture.

It is also desirable to make studies of the solubilities of volatile alcohols and amines in a variety of types of organic liquids containing donor atoms. Such studies would furnish further information on the influence of solute and solvent association on solubility. A comparison of the solubilities of an alcohol in a series of solvents containing different functional groups should give the relative strengths of the donor atoms. It is of interest to determine whether this relative order is the same as was observed for the haloforms in the same type of solvents. Gordy[5] has determined the shift of the OD fundamental frequency when CH_3OD is mixed with a series of different donor solvents. A relation should exist between his data and the relative solubilities of alcohols in similar solvents.

(1) Present address, Eastern Regional Research Laboratory, U. S. Department of Agriculture, Chestnut Hill Station, Philadelphia, Pennsylvania.

(2) (a) Zellhoefer, Copley, and Marvel, THIS JOURNAL, **60**, 1337 (1938); (b) Zellhoefer and Copley, *ibid.*, **60**, 1343 (1938); (c) Copley, Zellhoefer, and Marvel, *ibid.*, **60**, 2666 (1938); (d) Copley, Zellhoefer, and Marvel, *ibid.*, **61**, 3550 (1939).

(3) Buswell, Roy, and Rodebush, *ibid.*, **60**, 2528 (1938).

(4) (a) Gordy, *ibid.*, **60**, 605 (1938); (b) *J. Chem. Phys.*, **7**, 163 (1939).

(5) (a) Gordy, *ibid.*, **7**, 93 (1939); (b) Gordy and Stanford, *ibid.*, **8**, 170 (1940).

Experimental

The method used in making the solubility measurements is the same as that described in a previous paper[6] except that the lower vapor pressures involved made it advisable to substitute an oil or mercury manometer for the pressure gage. The materials used were all purified carefully by chemical means and fractional distillation where feasible. Solubility measurements were made over a range of pressures at a temperature of 32.2°. For comparative purposes, the solubilities at a partial pressure corresponding to the vapor pressure of the solute at 4.5° are used in Tables II and III and in the discussion. The vapor pressures of a number of the solutes at temperatures other than their boiling points which had not been previously reported in the literature were measured experimentally. Vapor pressures were determined at a number of different temperatures and a plot of logarithm of the pressure against $1/T$°K. was made. The vapor pressures tabulated in Table I were calculated from these plots.

TABLE I

VAPOR PRESSURES OF SOLUTES

	V. p. at 4.5°, mm.	V. p. at 32.2°, mm.
s-Butyl alcohol	5.5	31
i-Propylamine	223	743
n-Propylamine	106	397
Diethylamine	88	316
s-Butylamine	56.5	287.5
i-Butylamine	45.4	199
n-Butylamine	24	105

In Tables II and III the "ideal" or theoretical mole fraction solubility was calculated using Raoult's law, and is the ratio of the vapor pressure of the solute at 4.5° to its

(6) G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).

value at 32.2°. The ratio of observed to "ideal" mole fraction solubilities given in the last column of Tables II and III is used for comparison rather than absolute value of solubility, since the "ideal" mole fraction solubilities are different for the different solutes. The vapor pressures of the solvents are for the most part negligible, but where it was appreciable an approximate correction based on Henry's law was applied.

TABLE II

SOLUBILITY OF WATER AND ALCOHOLS IN ORGANIC SOLVENTS AT 4.5°

	Mole fraction "Ideal"	Mole fraction Observed	Ratio Observed/ "Ideal"
Triethylenetetramine			
H_2O	0.177	0.588	3.33
CH_3OH	.223	.605	2.71
C_2H_5OH	.200	.508	2.54
i-C_3H_7OH	.164	.357	2.17
n-C_3H_7OH	.148	.362	2.45
t-C_4H_9OH	.183	.376	2.05
s-C_4H_9OH	.178	.360	2.02
n-C_4H_9OH	.126	.345	2.74
Tetraethylene pentamine			
H_2O	.177	.622	3.51
Methylated triethylene tetramine I[a]			
H_2O	.177	.398	2.24
CH_3OH	.223	.588	2.63
C_2H_5OH	.200	.469	2.35
Methylated triethylene tetramine II[b]			
CH_3OH	.223	.523	2.35
C_2H_5OH	.200	.416	2.08
Triacetyl trimethyl triethylene tetramine[c]			
H_2O	.177	.610	3.45
CH_3OH	.223	.520	2.33
Hexamethylenediamine			
H_2O	.177	.382	2.08
CH_3OH	.223	.578	2.59
C_2H_5OH	.220	.445	2.02
i-C_3H_7OH	.164	.362	2.15
n-C_3H_7OH	.148	.370	2.50
t-C_4H_9OH	.183	.364	1.94
s-C_4H_9OH	.178	.385	2.15
n-C_4H_9OH	.126	.321	2.55
N,N-Dimethylacetamide			
H_2O	.177	.232	1.31
CH_3OH	.223	.369	1.65
C_2H_5OH	.200	.314	1.57
N-Methylacetamide			
CH_3OH	.223	.297	1.33
Adiponitrile			
CH_3OH	.223	.109	0.49
Sebaconitrile			
CH_3OH	.223	.114	0.51
Ethylene glycol			
H_2O	.177	.207	1.17
CH_3OH	.223	.188	0.84
C_2H_5OH	.200	.110	0.55
Glycerol			
H_2O	0.177	.239	1.35
Carbitol			
H_2O	.177	.126	0.71
Dimethyl ether of tetraethylene glycol			
H_2O	.177	.099	.56
Triethyl phosphate			
H_2O	.177	.104	.59
CH_3OH	.223	.390	1.75
C_2H_5OH	.200	.363	1.81
***n*-Tributyl borate**			
CH_3OH	.223	.186	0.83

[a] Prepared by methylation of triethylene tetramine with dimethyl sulfate. B. p. 97–107° (2–3 mm.). *Anal.* Calcd. for $C_9H_{24}N_4$ (trimethyl): C, 57.5; H, 12.8; N, 29.8. Found: C, 57.9; H, 12.6; N, 29.6. [b] Prepared by methylation of triethylene tetramine with formaldehyde and formic acid, b. p. 99–103° (2 mm.). *Anal.* Calcd. for $C_{10}H_{26}N_4$ (tetramethyl): N, 27.7. Calcd. for $C_{11}H_{28}N_4$ (pentamethyl): N, 25.9. Found: N, 26.3. Hence, the compound is a mixture containing an average of 4.7 methyl groups. [c] Prepared by acetylating methylated triethylenetetramine I with an excess acetic anhydride. The product is a viscous brown liquid with a green fluorescence, b. p. 200–225° (2–4 mm.). *Anal.* Calcd. for $C_{15}H_{20}O_3N_4$ (trimethyltriacetyltriethylenetetramine): N, 17.8. Found: N, 17.6.

TABLE III

SOLUBILITY OF AMINES IN ORGANIC SOLVENTS AT 4.5°

	Mole fraction "Ideal"	Mole fraction Observed	Ratio Observed/ "Ideal"
Water[a]			
CH_3NH_2	0.355	0.457	1.29
***n*-Octyl alcohol**			
n-$C_3H_7NH_2$	.267	.408	1.53
Ethylene glycol			
CH_3NH_2	.355	.662	1.86
i-$C_3H_7NH_2$	.300	.488	1.63
n-$C_3H_7NH_2$	.267	.465	1.74
$(C_2H_5)_2NH$	.279	.371	1.33
i-$C_4H_9NH_2$	.227	.381	1.68
n-$C_4H_9NH_2$	.229	.400	1.75
s-$C_4H_9NH_2$	.238	.397	1.67
1,3-Butylene glycol			
n-$C_3H_7NH_2$	.267	.460	1.72
Glycerol			
CH_3NH_2	.355	.652	1.84
$(CH_3)_2NH$	.344	.572	1.66
n-$C_3H_7NH_2$	.267	.497	1.86
Diethylene glycol			
CH_3NH_2	.355	.653	1.84
i-$C_3H_7NH_2$	.300	.517	1.73
n-$C_3H_7NH_2$	.267	.510	1.91
n-$C_4H_9NH_2$	.229	.384	1.68

TABLE III (*Concluded*)

	Mole fraction "Ideal"	Mole fraction Observed	Ratio Observed/"Ideal"
Triethylene glycol			
i-$C_3H_7NH_2$	0.300	.552	1.84
n-$C_3H_7NH_2$	.267	.519	1.94
n-$C_4H_9NH_2$	.229	.405	1.77
Tetraethylene glycol			
n-$C_4H_9NH_2$	.229	.410	1.79
Hexamethylenediamine			
n-$C_4H_9NH_2$	.229	.144	0.63
Triethylenetetramine			
n-$C_4H_9NH_2$	.229	.145	0.63

[a] Solubility values interpolated from curves given by Mehl, *Z. ges. Kälte Ind.*, **42**, 13 (1935).

Discussion

In Table II are given the solubilities of a number of alcohols in a few different polyethylene amines and their derivatives. For each alcohol the observed solubility was greatly in excess of the "ideal" solubility calculated by use of Raoult's law. The pure water and alcohols are strongly associated through O—H←O bonds. Some association may exist in the pure amines but previous work has shown that while the nitrogen atom of an amine is a good donor, the hydrogens are not sufficiently activated to act readily as acceptors. Reasoning from analogy with the behavior of haloforms,[2c] the simplest explanation of the extreme solubilities is obtained by assuming that O—H←N bonds are much stronger than O—H←O bonds. When equilibrium is reached after mixing, there are relatively few intermolecular complexes between like molecules but instead many between unlike molecules. Gordy[5b] observed that the shift of the fundamental frequency of OD was a maximum in mixtures of CH_3OD and aliphatic amines.

The solubilities of a series of eight alcohols were measured in triethylenetetramine. The extreme value (3.33) of the ratio of observed to ideal solubility obtained with water may result from partial ionization of the complex formed. It is noticeable that larger values of the ratio are obtained with the normal or straight chain alcohols than with secondary or tertiary alcohols where one might predict that steric hindrance may play a role due to branching of the chain.

Progressive methylation of triethylene tetramine leads to lower solubilities of water and alcohols. However, the solubility of water decreases more on methylation than that of the alcohols. On the other hand, when three of the methyl groups of the completely methylated triethylenetetramine are replaced by highly polar acetyl groups, the ratio (3.45) for water is greatly enhanced.

The high solubilities observed in the tertiary amides[2c] indicates that an amide nitrogen is as strong a donor as an amide nitrogen. Quantitatively this is best illustrated by comparing the ratios obtained using N,N-dimethylacetamide with that obtained for the reciprocal case, the solubility of *n*-propylamine in *n*-octyl alcohol, shown in Table III. However, all nitrogen atoms are not necessarily good donors as shown by the fact that less than theoretical solubilities were observed for methyl alcohol in adiponitrile and sebaconitrile. These results are similar to those[7] obtained previously with haloform in nitriles.

The solubilities of water, methyl alcohol, and ethyl alcohol were measured in some non-volatile polyhydric alcohols and esters. Some excess solubility for water in ethylene glycol and glycerol was observed whereas less than normal solubilities were observed for the two alcohols. The unexpectedly high solubilities of methyl and ethyl alcohols in triethyl phosphate may be connected with the presence of the semipolar oxygen.

In Table III the solubilities of a number of volatile amines are shown for several different solvents. These combinations are reciprocals of the ones shown in Table II. Hence, as one would expect, extremely high solubilities were observed for the amines in non-volatile polyhydric alcohols whereas they exhibited low solubilities in polyethyleneamines.

Summary

The solubilities of a number of volatile alcohols and amines are given for a variety of solvents including non-volatile polyhydric alcohols, polyethylene glycols, polyethylene amines, amides, esters, and ethers.

Extremely high solubilities were observed for alcohols in polyethylene amines and tertiary amides and for the amines in polyhydric alcohols and polyethylene glycols.

A plausible explanation of these results is obtained by applying to the data the hydrogen bond picture of solubility.

URBANA AND BLOOMINGTON, ILLINOIS
RECEIVED OCTOBER 25, 1940

(7) Copley, Zellhoefer and Marvel, THIS JOURNAL, **62** 227 (1940).