

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

## Hydrogen Bonds Involving the C-H Link. VIII.<sup>1</sup> The Solubilities of Completely Halogenated Methanes in Organic Solvents

BY M. J. COPLEY, G. F. ZELHOFER AND C. S. MARVEL

A study<sup>2</sup> of the solubility of halogenated methanes in various organic solvents has shown that compounds of the type  $\text{CHX}_3$  and  $\text{CH}_2\text{X}_2$  (where X is either a chlorine or a fluorine atom) are more soluble in donor solvents which do not contain active hydrogen atoms than would be predicted from Raoult's law. To account for this increase in solubility over the calculated value, it has been postulated that  $\text{C-H} \leftarrow \text{O}$  and  $\text{C-H} \leftarrow \text{N}$  bonds are formed by the hydrogen of the halogenated methane and the oxygen and nitrogen atoms of the solvent molecules. If this explanation is the correct one, it is obvious that completely halogenated methanes ( $\text{CX}_4$ ) would not show this enhanced solubility in donor solvents. The present paper contains solubility data on  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in a wide range of solvents. The solubilities are almost always lower than would be calculated, thus showing that compound formation between solvent and solute does not occur.

### Solubility Data

The procedure followed in making the solubility measurements was described in a preceding publication.<sup>2a</sup> The solvents were carefully purified by distillation and their boiling or melting points were checked. The solubilities were measured at  $32.2^\circ$  over a limited pressure range. With few exceptions the vapor pressures of the solvents were negligible when compared with the solute pressures at which measurements were made. Where the vapor pressure of a solvent was appreciable, a correction was applied in obtaining the solubility. The experimental values of the solubility were reproducible to within 1%. The variation of solubility with change in pressure obeyed Henry's law to within the limits of experimental error in practically all cases.

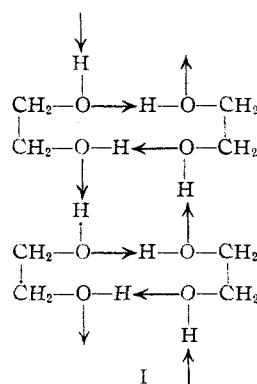
The observed gram per gram and mole fraction solubilities of  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$  at pressures equal to their vapor pressure at  $4.5^\circ$  are given in Table I. Corresponding data for  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_2\text{F}$ ,

taken from previous papers<sup>2b,c</sup> by the authors, are given wherever available. The statement in the table that the solubility is *very low* in acetamide and in phenol is based on the observation that when these solvents, which are solids at  $32.2^\circ$ , were melted, insufficient solute dissolved in the working pressure range to lower the melting point noticeably. The "ideal" or theoretical mole fractions stated at the top of Table I were calculated using Raoult's law and are the ratios of the vapor pressures<sup>2b</sup> at  $4.5^\circ$  to those<sup>2b</sup> at  $32.2^\circ$ .

### Discussion

In practically every solvent examined the solubility of the  $\text{CX}_4$  type is less than that calculated from Raoult's law. The very marked difference in the solubility of the  $\text{CX}_4$  types in ethers from that of the  $\text{CHX}_3$  and  $\text{CH}_2\text{X}_2$  types in the same solvents emphasizes the role of hydrogen bonding in the solubility process. In solvents which are not characterized by the presence of donor atoms, the solubilities of the hydrogen containing halogenated methanes do not differ widely from the completely halogenated derivatives. In alcohols which are associated through  $\text{O-H} \leftarrow \text{O}$  bonds the  $\text{CX}_4$  type has a very low solubility as compared with  $\text{CHCl}_2\text{F}$  and  $\text{CH}_2\text{Cl}_2$ . This suggests that although  $\text{OH} \leftarrow \text{O}$  bonds are stronger than  $\text{CH} \leftarrow \text{O}$  bonds, at equilibrium an appreciable number of  $\text{CH} \leftarrow \text{O}$  bonds are present in a solution of a hydrogen containing halogenated methane in alcohol.

Both types of halogenated methanes have ex-



(1) For the seventh communication of this series see *THIS JOURNAL*, **61**, 3161 (1939).

(2) (a) Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937); (b) Zellhoefer, Copley and Marvel, *THIS JOURNAL*, **60**, 1337 (1938); (c) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666, 2714 (1938).

TABLE I  
 SOLUBILITY OF HALOGENATED METHANES IN ORGANIC SOLVENTS

Solvents	CCl <sub>2</sub> F <sub>2</sub>		CCl <sub>2</sub> F		CHCl <sub>2</sub> F		CH <sub>2</sub> Cl <sub>2</sub>	
	G./g.	Mole fr.	G./g.	Mole fr.	G./g.	Mole fr.	G./g.	Mole fr.
Theoretical		0.453		0.356		0.381		0.311
Alcohols and Ethers								
<i>n</i> -Hexyl alcohol, C <sub>6</sub> H <sub>13</sub> OH	0.291	0.197	0.287	0.176	0.425	0.296		
Cyclohexanol, C <sub>6</sub> H <sub>11</sub> OH	.170	.123	.229	.143	.388	.274		
Phenol, C <sub>6</sub> H <sub>5</sub> OH	Very low		Very low		.269	.197	0.210	0.130
Ethylene glycol, HOCH <sub>2</sub> CH <sub>2</sub> OH	.0118	.00602	.0150	.00677	.100	.055		
Trimethylene glycol, HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	.0223	.0138	.0309	.0168	.106	.073		
Cyclohexyl methyl ether, C <sub>6</sub> H <sub>11</sub> OCH <sub>3</sub>	.648	.380	.637	.346	.900	.498		
Anisole, C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	.318	.220	.415	.244	.673	.415	.385	.328
Tetraethylene glycol dimethyl ether, CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>4</sub> CH <sub>3</sub>	.223	.290	.312	.336	1.110	.706	.580	.602
Acids and Esters								
Acetic acid, CH <sub>3</sub> COOH	.310	.133	.251	.0986	.688	.286	.280	.174
Propionic acid, C <sub>2</sub> H <sub>5</sub> COOH	.467	.223	.420	.185	.665	.330	.320	.218
Ethyl laurate, C <sub>11</sub> H <sub>23</sub> COOC <sub>2</sub> H <sub>5</sub>	.399	.430	.420	.412	.561	.556		
Ethyl caprylate, C <sub>7</sub> H <sub>15</sub> COOC <sub>2</sub> H <sub>5</sub>	.480	.406	.474	.373	.754	.557		
Aldehydes and Ketones								
Heptaldehyde, C <sub>6</sub> H <sub>13</sub> CHO	.525	.327	.534	.304	.979	.519	.473	.388
Cyclohexanone, C <sub>6</sub> H <sub>10</sub> O	.381	.236	.486	.257	1.278	.548	.630	.421
Acetylacetone, CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	.386	.242	.400	.226	1.023	.499	.455	.394
Acetylacetone, CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub>	.185	.147	.247	.170	1.163	.563	.572	.434
Nitrogen Compounds								
Cyclohexylamine, C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	.581	.322			1.070	.506	.520	.377
Aniline, C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	.0604	.0442	.113	.0706	.385	.258		
Dimethylcyclohexylamine, C <sub>6</sub> H <sub>11</sub> N(CH <sub>3</sub> ) <sub>2</sub>	.576	.377	.640	.372	.807	.500		
Dimethylaniline, C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	.262	.208	.382	.252	.695	.425		
Quinoline, C <sub>9</sub> H <sub>7</sub> N	.119	.113	.229	.177	.633	.443		
Acetamide, CH <sub>3</sub> CONH <sub>2</sub>	Very low		Very low		Very low		Very low	
<i>N</i> -Methylacetamide, CH <sub>3</sub> CONHCH <sub>3</sub>	.181	.0984	.256	.120	.955	.403	.427	.269
<i>N,N</i> -Dimethylacetamide, CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub>	.305	.180	.326	.171	1.870	.614	1.808	.452
Valeronitrile, C <sub>4</sub> H <sub>9</sub> CN	.470	.245			1.280	.550	0.630	.351
Benzonitrile, C <sub>6</sub> H <sub>5</sub> CN					.783	.438		
Nitrobutane, C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>			.356	.210	.780	.438		
Nitrobenzene, C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>					.471	.360		
Ethylmethylketoxime, C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> )C=NOH	.327	.190	.352	.182	.650	.338	.315	.244
Hydrocarbons and Bromides								
<i>n</i> -Decane, C <sub>10</sub> H <sub>22</sub>	.602	.415	.537	.357	.324	.309		
Mesitylene, C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub>	.532	.346	.568	.332	.668	.437	.328	.317
Bromobenzene, C <sub>6</sub> H <sub>5</sub> Br	.210	.214	.299	.255	.335	.338		
<i>n</i> -Hexyl bromide, C <sub>6</sub> H <sub>13</sub> Br	.367	.333	.396	.322	.398	.390		

tremely low solubility in glycols. This indicates that association in the glycols is more complex than in simple alcohols. The association in glycols may be such as that shown in I in which dimer units are fused together by cross linkages into complex molecules very similar to the type previously suggested for simple amides.<sup>2c</sup>

The solubilities of the completely halogenated methanes in ethyl laurate and ethyl caprylate are higher than had been expected. In fact trichloromonofluoromethane has a solubility in excess of

that calculated from Raoult's law in both of the esters. It is possible that this exception is due to the fact that the solubility calculated from the ratio of vapor pressures is lower than the value which would be obtained if fugacities were used.

The data on acetylacetone and acetylacetone show that chelation in the former increases the solubility of the CX<sub>4</sub> type, whereas it decreases solubility of hydrogen containing halogenated methanes. Chelation undoubtedly renders acetylacetone less polar than the unchelated diketone

and the  $CX_4$  type is consistently more soluble in the less polar solvents.

The extremely low solubilities of  $CCl_2F_2$  and  $CCl_3F$  in aniline as compared to their solubilities in dimethylaniline and aliphatic amines support the suggestion made in an earlier paper that there is considerable association in primary aromatic amines.<sup>2b</sup>

The solubilities of  $CHCl_2F$  in nitro compounds and nitriles show that these groups act as donor centers although when they are attached to a phenyl group<sup>2b</sup> they are much less effective donors than when attached to an alkyl group. A rather surprising case of solubility above the calculated

amount was found in the case of  $CHCl_2F$  in mesitylene.

### Summary

The solubilities of  $CCl_2F_2$  and of  $CCl_3F$  have been measured over a range of pressures in a wide variety of organic solvents. In practically every case the solubility was lower than that calculated from Raoult's law. These observations support the earlier postulation that intermolecular association through hydrogen bonding is an important factor in producing solubility of hydrogen containing halogenated methanes.

URBANA, ILLINOIS

RECEIVED OCTOBER 6, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

## The Action of Elementary Fluorine on Organic Compounds. VI. The Vapor Phase Reaction between Ethane and Fluorine in Progressively Varying Proportions

BY JOHN D. CALFEE,<sup>1</sup> NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

In a preceding communication (IV),<sup>2</sup> we have described preliminary experiments dealing with the vapor phase fluorination of ethane over a copper gauze catalyst, and the subsequent isolation of hexafluoroethane and other products. The present report describes a further study of this important reaction in which ethane and fluorine reacted in progressively varying proportions, and the more important products subsequently were separated and rectified. In each case, a perfectly quiet continuous change took place, which could be duplicated readily in every essential respect.

**The Apparatus.**—The fluorination chamber consisted of a section of brass pipe filled with small squares of 20-mesh copper gauze, essentially the same as that described before.<sup>2</sup> However, two tubes filled with sodium fluoride were used instead of one to absorb hydrogen fluoride, and special precautions were taken to make certain that no air whatever was drawn into the apparatus when the condensing trap was cooled with liquid air. Also, the quantities of the reacting gases were measured carefully; the ethane by means of a calibrated flowmeter, and the fluorine through the known electrical efficiency of the generator, recently measured by Lewis<sup>3</sup> and shown to be nearly constant at about 80% during most of the life of the charge. Furthermore, the products were not passed through potassium hydroxide solution, but were distilled directly, since

in general the ethane was in excess; thus no free fluorine was present.

The complete Booth-Podbielniak low-temperature rectification unit which was used to separate the products was constructed according to the principles described by Booth and Bozarth.<sup>4</sup> A diagram of the apparatus as adapted to our work, to be described in this and subsequent papers, is illustrated in Fig. 1. The unit consisted of three main parts, first, the boiler OO, the Podbielniak low-temperature column M, and the control manometer S with its contacts 1 and 2, together with the liquid air supply O and other accessories. Beyond the control valve K were the collecting system UU, VV, T, with manometers, and the melting point apparatus W. Finally came the gas density balance FF, with its thermostat, and an absolute manometer AA to measure accurately the pressures in the balance, as well as in any part of the receiving system. The temperature at the head of the column was measured by means of a thermocouple F, in connection with a recording potentiometer; and the boiler as well as the melting point apparatus was provided with a magnetic stirrer. The operating technique for this type of unit, together with the theoretical considerations involved, have been described before.<sup>4</sup>

**Results and Discussion.**—Four separate fluorinations of ethane were made in the manner already described, and the products condensed and rectified. There were isolated carbon tetrafluoride (b. p.  $-128^\circ$ ), two azeotropic mixtures, A and B, with constant boiling points, constant molecular weights, but wide melting ranges, ethane (b. p.  $-88^\circ$ ), hexafluoroethane (b. p.  $-78^\circ$ ), and some higher boiling material.

When azeotrope B (b. p.  $-96^\circ$ , mol. wt. 64) was passed repeatedly through a 10% sodium hydroxide solution,

(1) This paper, and also III and IV of this series, have been constructed wholly or in part, from Mr. Calfee's Doctorate Thesis, presented to the Graduate School of Duke University in May, 1938.

(2) Calfee and Bigelow, *THIS JOURNAL*, **59**, 2072 (1937).

(3) Hubert M. Lewis, unpublished work.

(4) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 476 (1937).