be noted, however, that each indicator exhibits the same color intensity for two different *p*H values.

Summary

1. The dissociation curves and acid and basic dissociation constants of 8-hydroxyquinoline-5-sulfonic acid and its 7-iodo, 7-bromo, 7-chloro- and 6-methyl derivatives were determined.

2. Of the compounds investigated, 7-chloro-8-hydroxyquinoline-5-sulfonic acid was found to be the most practical for use as an indicator.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Hydrogen Bonds Involving the C-H Link. XI.[1] Effect of Structure on Bonding of Donor and Acceptor Molecules

BY C. S. MARVEL, M. J. COPLEY AND EMANUEL GINSBERG

Heat of mixing data have been used by several investigators to study the formation of compounds of halogenated hydrocarbons, such as chloroform, bromoform, pentachloroethane and trichloroethylene with solvents such as ethers, esters and amines.[2] The more recent experimenters in this field have concluded that this is a satisfactory

TABLE I

HEAT OF MIXING DATA FOR MIXTURES OF DONOR AND ACCEPTOR LIQUIDS

Acceptor	Donor	Mole fraction of acceptor	Heat of mixing per mole of solution at 3°, cal.
$CHCl_3$	n-$C_4H_9NH_2$	0.500	700^{a}
$CHCl_3$	$C_6H_{11}NH_2$	.500	800^{a}
$CHCl_3$	$C_6H_{11}N(CH_3)_2$	.565	1166
$CHCl_3$	$C_6H_5N(CH_3)_2$	.600	280^{b}
$CHCl_3$	$CH_3CON(CH_3)_2$	.500	920^{c}
$CHCl_3$	$C_6H_5CON(C_2H_5)_2$	.453	1090
$CHCl_3$	n-C_4H_9CN	.477	390
$CHCl_3$	C_6H_5CN	.505	297
$CHCl_3$	$CN(CH_2)_3CN$	.507	233
$CHCl_3$	$CN(CH_2)_3CN$	.666	253
$CHCl_3$	$CN(CH_2)_3CN$	.680	261
$CHCl_3$	$C_6H_5NO_2$	.444	118
$CHCl_3$	$C_2H_5ONO_2$	.448	113
$CHCl_3$	CH_3NO_2	.500	None
$CHCl_3$	$C_6H_5OCH_3$	.509	175
$CHCl_3$	$C_6H_{11}OCH_3$	.471	665
$CHCl_3$	$(C_2H_5)_2O$	.5	700^{d}
$CHCl_3$	CH_3COCH_3	.458	495
$CHCl_3$	$CH_3CO_2C_2H_5$	.513	544
$CHCl_3$	$C_6H_5SO_3C_2H_5$	.540	249
$CHCl_3$	$C_6H_5SO_3C_2H_5$	.614	285
$CHCl_3$	$C_6H_5SO_3C_2H_5$	.663	270
$CHCl_3$	$(C_2H_5O)_2SO_2$	.577	257
$CHBr_3$	C_6H_5N	.486	498^{e}
$CHBr_3$	$CH_3CON(CH_3)_2$	.468	918^{e}
$CHBr_3$	$CH_3CON(CH_3)_2$	.515	901^{e}
$CHBr_3$	$(C_2H_5)_2O$	.483	515^{e}
$CHBr_3$	CH_3COCH_3	.592	342^{e}
CH_2Cl_2	$CH_3CON(CH_3)_2$	.520	527
CH_2Cl_2	$(C_2H_5)_2O$	.382	245
CH_2Br_2	$CH_3CON(CH_3)_2$	.483	400
CH_2Br_2	$(C_2H_5)_2O$	.461	200
CH_2I_2	$CH_3CON(CH_3)_2$	.506	100^{f}
CH_2I_2	$(C_2H_5)_2O$	.50	None^{f}
$C_6H_5CHCl_2$	$CH_3CON(CH_3)_2$	.376	426
$C_6H_5CHCl_2$	$CH_3CON(CH_3)_2$	.600	500
$C_6H_5CHCl_2$	$(C_2H_5)_2O$	.484	232
$C_6H_5CHCl_2$	CH_3COCH_3	.451	200
$(C_6H_5)_2CHCl$	$CH_3CON(CH_3)_2$	.495	208^{g}
$(C_6H_5)_2CHCl$	$(C_2H_5)_2O$	.500	Very sl.^{g}
$HCCl_2CCl_2H$	C_5H_5N	.482	589
$HCCl_2CCl_2H$	C_6H_5N	.545	605
$HCCl_2CCl_2H$	C_6H_5CN	.505	362
$HCCl_2CCl_2H$	$C_6H_5NO_2$	.5	140^{h}
$HCCl_2CCl_2H$	C_6H_6	.5	125^{h}
$HCCl_2CCl_2H$	CH_3COCH_3	.481	610
$HCCl_2CCl_2H$	CH_3COCH_3	.587	610
$HCCl_2CCl_2H$	$CH_3CO_2C_2H_5$	.496	608
$HCCl_2CCl_2H$	$CH_3CO_2C_2H_5$	.520	572
$CCl_2{=}CHCl$	$CH_3CON(CH_3)_2$	.720	212
$CCl_2{=}CHCl$	$C_6H_5NO_2$	.5	None^{h}
$CCl_2{=}CHCl$	C_6H_6	.5	None^{h}
$CCl_2{=}CHCl$	$(C_2H_5)_2O$	.541	278
$CCl_2{=}CCl_2$	$CH_3CON(CH_3)_2$	.5	None
$CCl_2{=}CCl_2$	$(C_2H_5)_2O$	.5	None
$C_6H_5CCl_3$	$CH_3CON(CH_3)_2$	.298	249
$C_6H_5CCl_3$	$CH_3CON(CH_3)_2$	.494	305
$C_6H_5CF_3$	$CH_3CON(CH_3)_2$	.535	120
CH_3NO_2	$CH_3CON(CH_3)_2$	.535	118
$HC(OC_2H_5)_3$	$CH_3CON(CH_3)_2$	.483	Sl. cooling
$HC(OC_2H_5)_3$	n-C_6H_{14}	.469	Cooling
$CH_2(OC_2H_5)_2$	$CH_3CON(CH_3)_2$	.482	Sl. cooling
$CH_2(OC_2H_5)_2$	n-C_6H_{14}	.504	Cooling

[a] R. W. Spence, private communication. [b] Ref. 2b. [c] C. E. Holley, private communication. [d] Ref. 2d. [e] Measured at 10° instead of 3°. [f] Measured at 7° instead of 3°. [g] Measured at 14° instead of 3°. [h] Measured at 5° instead of 3°.

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(1) For the tenth communication in this series see Marvel, Dietz and Copley, THIS JOURNAL, **62**, 2273 (1940).

(2) (a) Guthrie. *Phil. Mag.*, (5) **18**, 495 (1884); (b) Weissenberger and others, *Monatsh.*, **45**, 425 (1924); **46**, 47, 57, 281, 295, 301 (1925); (c) Trew, *Trans. Faraday Soc.*, **28**, 509 (1932); Trew and Watkins, *ibid.*, **29**, 1310 (1933); (d) McLeod and Wilson, *ibid.*, **31**, 576 (1935); (e) Zellhoefer and Copley, THIS JOURNAL, **60**, 1343 (1938); (f) Copley and Holley, *ibid.*, **61**, 1599 (1939).

means of studying the degree of hydrogen bonding involved in these mixtures. The present work was carried out in order to make some comparisons of the donor ability of various solvents and to discover other types of C–H compounds which will undergo bonding with donor solvents.

Experimental

The method was that previously described.^{2e,f} When the heat of mixing is 700 to 1000 calories, the measurement is accurate to ±1.5–2%. When the heat of mixing is 200 to 300 calories the accuracy of the method is much less and the values may be ±5% in error. The compounds studied were commercial products of reagent quality which were redistilled to constant boiling point and the purity of each was checked by refractive index. The samples were carefully dried. The heats of mixing were measured at 3° except in cases where one constituent was solid at this temperature. Determinations were usually made at compositions having equal mole fraction of donor and acceptor molecule. Where there was a multiplicity of either donor atoms or acceptor atoms concerned, more complete heat of mixing curves were determined (see Figs. 1 to 4).

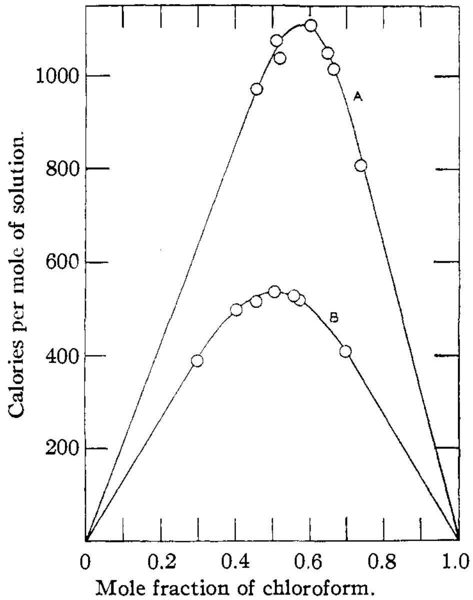


Fig. 1.—The heat evolved per mole of solution at 3° *versus* the mole fraction of chloroform: A, ethyl phosphate; B, pyridine.

The data are collected in Table I and Figs. 1 to 4. Bonding is indicated by a heat of mixing and the amount of heat is probably an approximate indication of the measurable strength of the bond.

Discussion of Results

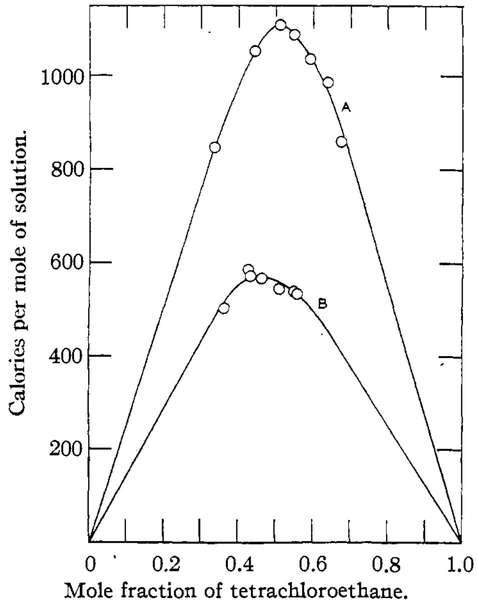


Fig. 2.—The heat evolved per mole of solution at 3° *versus* the mole fraction of tetrachloroethane: A, N,N-dimethylacetamide; B, ethyl ether.

The most complete comparison of the donor solvents can be made by a study of the heat of mixing data for chloroform. The highest heat of mixing of chloroform was obtained with dimethylcyclohexylamine, an aliphatic tertiary amine. It is interesting to note that the aliphatic primary amines and the more or less aromatic pyridine and the truly aromatic dimethylaniline give distinctly lower heats of mixing with chloroform. The low values for primary aliphatic amines may be due to N–H—N association in the compounds. On the other hand, tertiary amides are almost as effective donor molecules as are the tertiary amines. Nitro groups either attached to oxygen

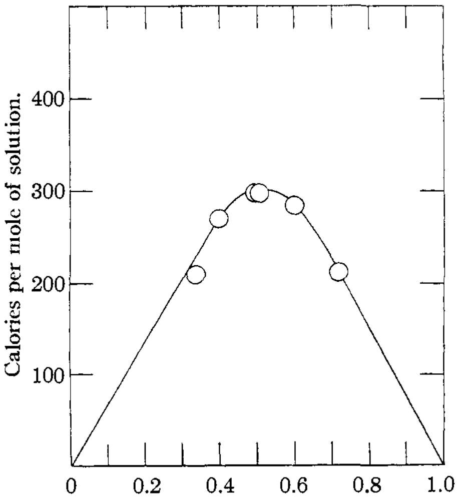
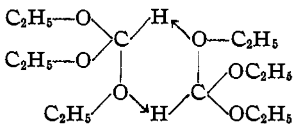


Fig. 3.—The heat evolved per mole of solution at 3° *versus* the mole fraction of trichloroethylene on mixing with N,N-dimethylacetamide.

or carbon are relatively ineffective as donor groups. Nitrile groups are quite effective donor centers.

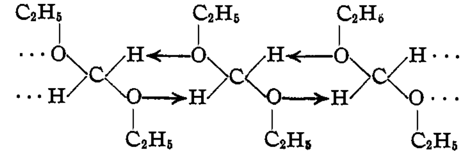
An oxygen in ethers, esters, and ketones is effective as a donor atom. A negative group such as phenyl directly attached to an oxygen atom greatly decreases the strength of the bond formed with an active C–H as is shown clearly by the results on anisole (175 cal.) and methyl cyclohexyl ether (665 cal.). Ethers in general are more effective donors than ketones or esters. The esters of the acids of sulfur are ineffective donor solvents whereas the alkyl phosphates are as effective as the tertiary amines.

The results obtained with ethylal and ethyl orthoformate are especially interesting. The maximum heat of mixing for chloroform and ethylal comes at 0.67 mole of chloroform (see Curve B, Fig. 4) and the peak in the ethyl orthoformate curve (Curve A, Fig. 4) comes at the same mole fraction. When orthoformic ester or ethylal is diluted with any inert solvent cooling occurs. These results suggest association of the acetal and ortho ester. Calculations of the boiling points of these two compounds by Kinney's method[3] also indicate the same thing. Thus ethylal boils at 89° whereas the calculated boiling point is 57.5° and ethyl orthoformate boils at 146° and its calculated boiling point is 114°. Ethyl orthoformate might readily yield a dimer (I) which would still have two ethoxy groups for each monomeric molecule available as donor groups. This agrees well with the heat of mixing results. Ethylal



I

may associate in a more complex manner (for example II) but apparently the bonds are less strong.



II

These results are significant in connection with the physical behavior of paraformaldehyde which shows many properties of a cross-linked polymer.

Comparisons between chloroform and bromoform show that the heat of mixing with a given donor solvent is always slightly less with bromoform than with chloroform. The same is true for methylene bromide as compared to methylene chloride. The hydrogen atoms in methylene iodide show very little tendency for bonding even with such a strong donor solvent as dimethylacetamide.

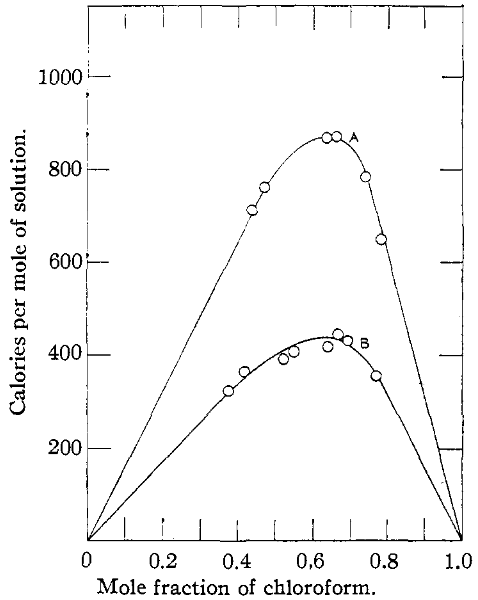


Fig. 4.—The heat evolved per mole of solution at 3° *versus* the mole fraction of chloroform: A, orthoformic ester; B, ethylal.

Comparisons between the heats of mixing of chloroform, benzal chloride and diphenylchloromethane and various donor solvents show that the phenyl group has less activating effect than chlorine in promoting bonding by a neighboring hydrogen atom.

Benzotrichloride gives some heat when mixed with donor solvents thus showing that the hydrogen atoms of the ring are activated to some extent as would be expected from consideration of the principle of vinylogy.[4] Benzotrifluoride, however, is only very slightly effective as an acceptor molecule.

sym-Tetrachlorethane has two hydrogens which may be capable of bonding. However, inspection of the heat of mixing curves (Fig. 2) shows that the maximum heat comes at the ratio of 1 mole of the tetrachloroethane and 1 mole of the donor solvent. This result is similar to findings of Zellhoefer and Copley[2e] that only one oxygen atom in the dimethyl ether of ethylene glycol is effective as a donor atom toward chloroform. Although the

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[3] Kinney, This Journal, **60**, 3032 (1938); **61**, 3236 (1939).

[4] Fuson, *Chem. Rev.*, **16**, 1 (1935).

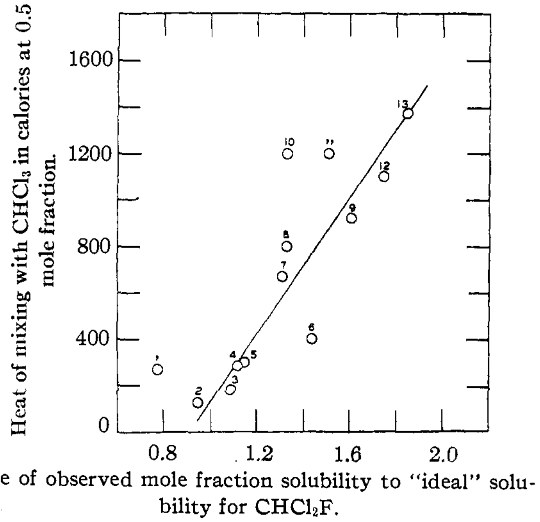

Fig. 5.—Heats of mixing *versus* solubilities of $CHCl_2F$ in various solvents:

1. Glutaronitrile[a]
2. Nitrobenzene
3. Anisole
4. N,N-Dimethylaniline
5. Benzonitrile
6. Valeronitrile
7. Cyclohexyl methyl ether
8. Cyclohexylamine
9. N,N-Dimethylacetamide
10. N,N-Dimethylcyclohexylamine
11. Ethylene glycol dimethyl ether[b]
12. Ethyl phosphate
13. Tetraethylene glycol dimethyl ether[b]

[a] Measured at 0.67 mole fraction instead of 0.5 mole fraction.
[b] See reference 2e.

hydrogen atoms are activated by only two chlorine atoms in *sym*-tetrachloroethane, the hydrogen will, therefore, appear to be as strong as those of chloroform.

The hydrogen atom in trichloroethylene has a very weak acceptor activity. This result checks with the results of solubility studies.[1] Weissenberger, Schuster and Parner[2b] have found that the hydrogen atom in pentachloroethane is about equal to that in chloroform as an acceptor.

Nitromethane which is undoubtedly associated gives only slight heat when mixed with dimethyl acetamide. The fact that some heat was liberated indicates that the bonds formed in the new combination must be stronger than those broken down in the dissociation of the nitromethane.

In Fig. 5 are plotted the heats of mixing of certain solvents with chloroform against the ratio of observed mole fraction solubility to ideal solubility for $CHCl_2F$ in these solvents.[5] This graph shows that a very good correlation exists between heats of mixing for one haloform and solubilities of another haloform in donor solvents. In every case where one of these properties indicates strong hydrogen bonding, the other shows it as well. Likewise where one property indicates weak hydrogen bonds the other also shows it.

Summary

Heats of mixing data on chloroform and various solvents have given some indication of their effectiveness as donor molecules. Comparisons of the heat obtained when mixing a given solvent with chloroform and bromoform or the methylene halides have shown that bromine is slightly less effective than chlorine in promoting acceptor activity by neighboring hydrogen atoms. Iodine is not effective to an appreciable extent. *sym*-Tetrachloroethane is a very effective acceptor molecule and trichloroethylene is slightly effective in this capacity. Evidence for the association of acetals and ortho esters has been obtained.

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[5] Zellhoefer, *Ind. Eng. Chem.*, **29**, 548 (1937); Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337, 2660, 2714 (1938); **61**, 3550 (1939); **62**, 222 (1940).