The writer is especially indebted to Mr. Donald L. Reed for making the isotope extractions with greensand.

BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.   RECEIVED MARCH 31, 1939

Hydrogen Bonding by Negatively Substituted CH Groups. VI. Acetylenic Compounds[1]

BY M. J. COPLEY AND C. E. HOLLEY, JR.

In a series of articles[2-5] the solubilities of several gaseous halogenated methanes (of the types CH_3X, CH_2X_2, CHX_3 and CX_4) in a number of donor solvents were reported. The extremely high solubilities (or large negative deviations from Raoult's law) observed for the halo-forms were accounted for on the basis that complexes are formed through the bonding of the hydrogen of the haloform to an exposed pair of electrons on an oxygen or nitrogen atom present in the solvent. New evidence for the existence of complexes of this type was observed recently by Buswell, Rodebush and Roy[6] while studying the infrared absorption spectra of solutions in carbon tetrachloride of chloroform with an ether, a ketone, or an amine.

Since the presence of the highly electronegative halogen atoms on the carbon atom of a haloform activates the hydrogen and makes it available for coördination, it is logical to suspect that other strongly negative groups attached to a CH radical will lead to the same behavior on the part of the hydrogen. Among the compounds in which such CH groups occur are the acetylenes (1-alkynes), the derivatives of formic acid, the triarylmethanes, molecules containing an active methylene group, etc.

In Table I the mole fraction solubilities of acetylene at a partial pressure of one atmosphere are compared with the theoretical mole fractions calculated from Raoult's law. The observed mole

(1) Original manuscript received July 11, 1938.
(2) G. F. Zellhoefer. *Ind. Eng. Chem.*, **29**, 584 (1937).
(3) Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).
(4) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666 (1938).
(5) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2714 (1938).
(6) Buswell, Rodebush and Roy, *ibid.*, **60**, 2528 (1938). See also Gordy, *ibid.*, **60**, 605 (1938).

fractions are calculated from data in the "International Critical Tables," Vol. III, p. 269, and in an article by James.[7] There exists a close parallelism between the observed order of solubilities and the order[3,4] observed for chloroform or monofluorodichloromethane in similar types of solvents. Solubilities are greatly in excess of those predicted by Raoult's law in the ethers, esters, and ketones; solubilities are much less than the theoretical in solvents containing an active hydrogen (ethyl alcohol and acetic acid) where the solvent molecules are already associated by means of the more stable O–H–O bonds; no enhancement of solubility is obtained in aromatic compounds when the donor atom is attached to the benzene
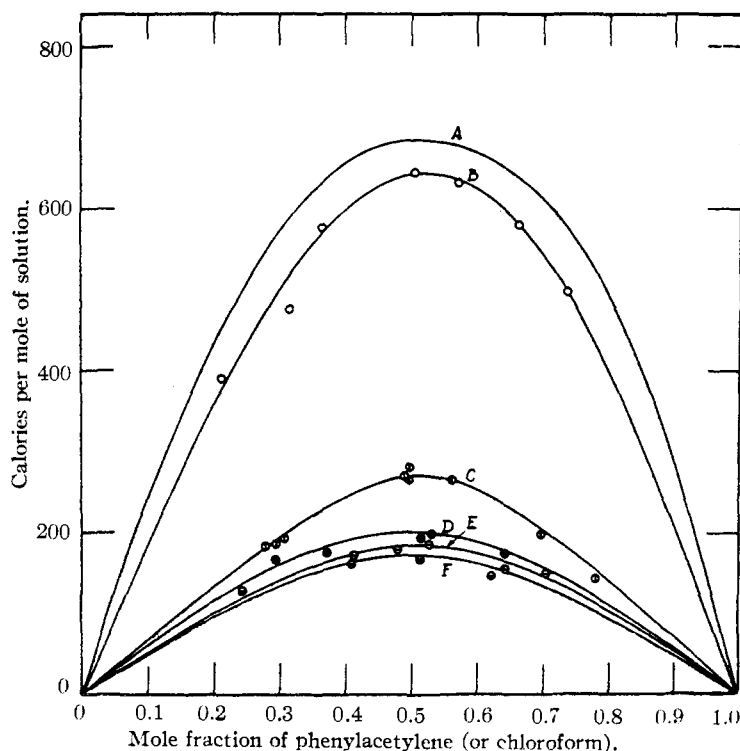

Fig. 1.—The heat evolved per mole of solution at 3° *versus* the mole fraction of phenylacetylene (or chloroform): A, chloroform and diethyl ether; B–F, phenylacetylene and, respectively, N,N-dimethylacetamide, diethyl ether, acetone, cyclohexylamine, methyl acetate.

ring; and normal or less than normal solubilities are found in compounds which do not contain a donor atom. The appreciably lower solubilities in formates than in acetates possibly are due to activity of the hydrogen of the acid residue of formates which leads to some intermolecular association. The solubilities[4] of monofluorodichloromethane are also appreciably lower in the N-disub-

(7) James, *Ind. Eng. Chem.*, **5**, 118 (1913).

TABLE I

SOLUBILITIES OF ACETYLENE AT A PARTIAL PRESSURE OF 1 ATMOSPHERE IN ORGANIC SOLVENTS

Compound	Temp., °C	Mole fraction Obsd.	Mole fraction Calcd.
Acetal, $CH_3CH(OC_2H_5)_2$	−10	0.200	0.04
Methylal, $CH_2(OCH_3)_2$	−10	.192	.04
Acetaldehyde, CH_3CHO	−10	.177	.04
Ethyl acetate, $CH_3COOC_2H_5$	−10	.168	.04
Ethyl formate, $HCOOC_2H_5$	−10	.144	.04
Methyl acetate, CH_3COOCH_3	−10	.163	.04
Methyl formate, $HCOOCH_3$	−10	.142	.04
Isoamyl acetate, $CH_3COOC_5H_{11}$	−10	.166	.04
Isoamyl formate, $HCOOC_5H_{11}$	−10	.095	.04
Acetic acid, CH_3COOH	18	.0150	.0245
Ethyl alcohol, C_2H_5OH	18	.0151	.0245
Benzene, C_6H_6	4	.0252	.0342
Aniline, $C_6H_5NH_2$	4.2	.0223	.034
Dimethylaniline, $C_6H_5N(CH_3)_2$	0.3	.037	.0382
Nitrobenzene, $C_6H_5NO_2$	3.8	.0223	.0345
Cyclohexane, C_6H_{12}	3	.0175	.0352
Acetone, CH_3COCH_3	0.0	.092	.038
Acetone, CH_3COCH_3	15	.074	.026
Acetone, CH_3COCH_3	15	.490	.312[a]
Acetone, CH_3COCH_3	25	.0402	.0206

[a] Pressure of acetylene 12 atmospheres.

stituted formamides than in N-disubstituted acetamides.

A further test of this idea is being made by means of vapor pressure–composition studies and by measuring the heats of mixing of a monosubstituted acetylene (phenylacetylene) with a number of donor solvents.

Figure 1 shows the heat evolved at 3° per mole of solution as a function of the mole fraction of phenylacetylene when it is mixed with, respectively, N,N-dimethylacetamide, diethyl ether, acetone, cyclohexylamine, and methyl acetate. The calorimeter and method of making the heat measurements were described previously by Zellhoefer and Copley.[8] The maxima of the curves in Fig. 1 occur very close to a mole fraction of 0.5 and indicate that in each case an equimolar complex is formed. Curve A is a plot of the heat of mixing data for chloroform and diethyl ether obtained by McLeod and Wilson.[9] Comparison of curves A and C shows that the hydrogen of chloroform is a better acceptor than the hydrogen of phenylacetylene, although the latter is more acidic, and thus emphasizes the influence of different groups on the carbon to which the active hydrogen is attached. Gordy[10] has observed that when CH_3OD is mixed with ethers, esters, or ke-

(8) Zellhoefer and Copley, THIS JOURNAL, 60, 1343 (1938).
(9) McLeod and Wilson, Trans. Faraday Soc., 31, 596 (1935).
(10) Gordy, J. Chem. Phys., 7, 93 (1939).

tones, the largest shift in the OD fundamental band is shown with ethers. The somewhat larger amount of heat obtained here with dimethyl ether than with methyl acetate or acetone also indicates that with phenylacetylene an ether oxygen is a better electron donor than an ester or ketone oxygen.

As would be expected from previous solubility measurements[4] on monofluorodichloromethane in ethers and N-disubstituted amides, considerably more heat is evolved on mixing phenylacetylene with N,N-dimethylacetamide than with diethyl ether. The nitrogen atom of N-disubstituted amides appears to be the best electron donor atom for forming hydrogen bonds.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS   RECEIVED MARCH 23, 1939

The Preparation and Melting Point of 1-Iodoanthraquinone

BY ALBERT E. GOLDSTEIN

In the course of an investigation involving halogenated anthraquinones,[1] it became necessary to prepare 1-iodoanthraquinone. Investigation of the literature revealed but one procedure for the purpose—the method of Laubé.[2] The recorded yield of crude product appears as 27 g. (90%). It was found that, if the reported procedure were carefully followed, the crude yield invariably amounted to 7–8 g. If the procedure of Laubé is modified in the light of an observation made by Scholl and Mansfeld,[3] then the results obtained are in agreement with those of Laubé.

The melting point of 1-iodoanthraquinone is given by Laubé as 177°. Brass and Eichler[4] give the melting point as 176°. Nowhere is any mention made of the color of the compound. The repeated preparation of 1-iodoanthraquinone by the author and by others in these Laboratories invariably has yielded a crude compound melting at 195–197°. Two recrystallizations of the crude material yielded a compound melting at 204–205° instead of 177° as given by Laubé. Nitrobenzene has been found to be a more satisfactory solvent for the recrystallization than glacial acetic acid. The color of the product varies from brownish-yellow to dark brown.

(1) A. E. Goldstein with J. H. Gardner, THIS JOURNAL, 56, 2130 (1934).
(2) Laubé, Ber., 40, 3566 (1907).
(3) Scholl and Mansfeld, ibid., 43, 1739 (1910).
(4) Brass and Eichler, ibid., 67B, 785 (1934).