[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. V. Acetylenic Halides and Alcohols

BY J. A. TOUSSAINT AND H. H. WENZKE

Previous investigations by Pflaum and Wenzke[1] and Wilson and Wenzke[2] have shown that there is a considerable reduction in the carbon to halogen moment when the halogen is directly attached to an acetylenic carbon atom. The latter investigators have shown that this reduction of moment is sufficiently great in the aryliodoacetylenes to cause a reversal of direction of moment in the carbon to iodine linkage. In the alkyl iodides the negative end of the dipole is of course toward the iodine atom but in the aryliodoacetylenes the iodine is positive. In an effort to determine further the inductive influence of the triple bond on the carbon to halogen moment, certain alkynyl halides were investigated. At the same time information was obtained on the influence of the triple bond on the resultant moment of the C–O–H group.

Preparation of Compounds

1-Hydroxyheptane, b. p. 172–176°, was purchased from the Eastman Kodak Co. and refluxed for ten hours over anhydrous calcium oxide. The dehydrated alcohol was fractionated three times under reduced pressure. A final cut, boiling from 88.4–88.6° at 24 mm., was used in the measurements.

1-Hydroxy-3-octyne[3] was prepared by the formation of the acetylenic Grignard reagent, subsequent condensation with ethylene oxide and hydrolysis. The compound was dried over anhydrous potassium carbonate and sodium sulfate. The product was fractionated three times under reduced pressure. The portion used boiled at 97° at a pressure of 15 mm.

1-Hydroxy-3-nonyne was prepared and purified in a similar manner and a portion of the alcohol boiling at 106° at 15 mm. was obtained.

1-Hydroxy-2-heptyne[4] was prepared through the formation of the acetylenic Grignard reagent, but with condensation with formaldehyde and subsequent hydrolysis. The authors removed the excess dissolved formaldehyde and paraformaldehyde by treating the ether extracts with a 10% solution of sodium bisulfite. The product was dried over anhydrous potassium carbonate and sodium sulfate, fractionated three times and a sample of the alcohol boiling at 95° under a pressure of 23 mm. was used. 1-Hydroxy-2-octyne was prepared by the method analogous to that used for 1-hydroxy-2-heptyne. A cut taken from 110.3 to 110.8° at 24 mm. was selected.

1-Bromo-2-octyne was prepared from 1-hydroxy-2-octyne by the method of M. Tchao Yin Lai,[5] through the action of phosphorus tribromide on the alcohol. The product was dried over calcium chloride, fractionated three times and a portion boiling from 86.8–87.3° at 11 mm. was employed in the determinations. 1-Bromo-2-heptyne, 1-chloro-2-heptyne, 1-chloro-2-octyne were similarly obtained. The boiling points of the compounds used in this work were: 1-bromo-2-heptyne, 84° at 20 mm.; 1-chloro-2-heptyne 70.8–71.3° at 24 mm.; and 1 chloro-2-octyne, 80.5–81° at 15 mm.

1-Iodo-2-heptyne and 1-iodo-2-octyne were prepared by the method of Hans Finkelstein[6] from the corresponding bromides and chlorides through the action of potassium iodide in acetone. Since the hydroxyalkynes and their iodo derivatives boil at almost the same temperature, special care had to be exercised to prevent contamination

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF ACETYLENIC ALCOHOLS

Solvent, dioxane; temp., 25°

c_2	ϵ	d
	1-Hydroxy-2-octyne	
0.00000	2.2440	1.02782
.02641	2.3746	1.02119
.02961	2.3890	1.02042
.03443	2.4146	1.01932
	1-Hydroxy-3-nonyne	
0.00000	2.2440	1.02782
.02431	2.3478	1.02057
.05275	2.4692	1.01247
.08256	2.6059	1.00453
	1-Hydroxy-2-heptyne	
0.00000	2.2440	1.02782
.02517	2.3702	1.02225
.03014	2.3931	1.02130
.03475	2.4192	1.02042
	1-Hydroxy-3-octyne	
0.00000	2.2440	1.02782
.02682	2.3615	1.02115
.04760	2.4508	1.01596
.04967	2.4619	1.01550
.05086	2.4655	1.01517
.06973	2.5520	1.01070
	1-Hydroxyheptane	
0.00000	2.2440	1.02782
.03618	2.3620	1.01609
.03732	2.3865	1.01371
.04819	2.4261	1.01007

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(1) Pflaum and Wenzke, THIS JOURNAL, **56**, 1106 (1934).

(2) Wilson and Wenzke, *ibid.*, **56**, 2025 (1934).

(3) Danehy, The Synthesis of Some Primary Acetylenic Alcohols, Thesis, University of Notre Dame, 1934.

(4) M. Tchao Yin Lai, *Bull. soc. chim.*, **53**, 682 (1933).

(5) M. Tchao Yin Lai, *ibid.*, **53**, 1533 (1933).

(6) Hans Finkelstein, *Ber.*, **43**, 1528 (1910).

of the latter by the former. Consequently, before treatment with potassium iodide, the bromides and chlorides were very carefully fractionated so as to remove all alcohol present. The compounds were dried over calcium chloride and fractionated three times. 1-Iodo-2-heptyne boiled at 86.3–86.8° at 10 mm. and 1-iodo-2-octyne boiled at 98.2–99.2° at 9 mm.

With the exception of 1-hydroxy-3-octyne, 1-hydroxy-3-nonyne, 1-hydroxy-2-octyne and 1-bromo-2-octyne the acetylenic compounds reported in this article have not been previously recorded in the literature.

The equipment and method used in the determination of dielectric constants has been described previously.[7] Refractive indices were determined with a Pulfrich refractometer. The refractometer was kept at a constant temperature of 25° by siphoning water from a constant temperature water-bath through the instrument.

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF ACETYLENIC HALIDES

Solvent, benzene; temp., 25°

c_2	ϵ	d
	1-Chloro-2-heptyne	
0.00000	2.2760	0.87253
.03101	2.4319	.87524
.04091	2.4838	.87599
.05046	2.5289	.87698
	1-Bromo-2-heptyne	
0.00000	2.2760	0.87253
.03933	2.4728	.89385
.04148	2.4805	.89481
.05038	2.5230	.89971
.05605	2.5484	.90267
	1-Iodo-2-heptyne	
0.00000	2.2760	0.87253
.03628	2.4122	.90861
.04521	2.4455	.91716
.04812	2.4558	.92006
	1-Chloro-2-octyne	
0.00000	2.2760	0.87253
.02722	2.4145	.87468
.03525	2.4581	.87524
.04097	2.4819	.87597
.05027	2.5377	.87677
	1-Bromo-2-octyne	
0.00000	2.2760	0.87253
.03604	2.4524	.89116
.04032	2.4754	.89358
.05267	2.5532	.90202
	1-Iodo-2-octyne	
0.00000	2.2760	0.87253
.03496	2.4006	.90682
.04450	2.4351	.91599
.05694	2.4803	.92758

TABLE III

POLARIZATIONS AND MOMENTS OF ACETYLENIC HALIDES AND ALCOHOLS

Compound	P_∞	MR_D	$\mu \times 10^{18}$
1-Hydroxyheptane	96.06	36.19	1.70
1-Hydroxy-3-octyne	104.89	38.69	1.79
1-Hydroxy-3-nonyne	108.54	43.29	1.78
1-Hydroxy-2-heptyne	108.64	34.28	1.89
1-Hydroxy-2-octyne	112.42	38.77	1.89
1-Chloro-2-heptyne	116.59	37.93	1.95
1-Chloro-2-octyne	121.96	42.57	1.96
1-Bromo-2-heptyne	115.39	41.21	1.89
1-Bromo-2-octyne	120.89	46.03	1.90
1-Iodo-2-heptyne	100.85	46.96	1.61
1-Iodo-2-octyne	104.36	51.65	1.60

TABLE IV

Compound	$\mu \times 10^{18}$	Compound	$\mu \times 10^{18}$
1-Hydroxyheptane[8]	1.71	1-Bromopropane[10]	1.94
1-Hydroxyoctane[9]	1.68	1-Bromobutane[11]	2.05
		1-Bromobutane[12]	1.97
1-Chloropropane[10]	1.94	1-Iodopropane[10]	1.85
1-Chlorobutane[11]	2.05	1-Iodobutane[11]	1.89
1-Chlorobutone[12]	1.97	1-Iodobutane[12]	1.88

Discussion of Results

The data on the alkyl halides reported in the literature are none too concordant. Table IV lists the moments of some alkyl halides and alcohols taken from sources considered reliable. It is evident by comparing the data of Table III with those of Table IV that the moments of the alkyl chlorides are only slightly larger than those of 1-chloro-2-heptyne and 1-chloro-2-octyne. The influence of the triple bond on the carbon to chlorine moment in the latter compounds is very small. A similar comparison with the bromo derivatives shows that the influence of the triple bond is somewhat greater. The moments of the acetylenic bromides are about 0.06 unit less than those of the alkyl bromides. The pronounced influence of the triple bond on the carbon to iodine moments for the cases where the iodine is directly attached to the acetylenic carbon atom is still shown although to a lesser degree in the acetylenic iodides. The alkyl iodides have moments around 0.27 unit higher than the acetylenic iodides. The triple bond affects quite materially the moments of the alcohol groups. 1-Hydroxy-2-heptyne and 1-hydroxy-2-octyne have moments almost 0.2 unit higher than the moments of

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[7] Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **5**, 187 (1934).

[8] Sherrill, THIS JOURNAL, **50**, 1982 (1928).

[9] Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

[10] Parts, *Z. physik. Chem.*, **B12**, 312 (1931).

[11] Smyth and Rogers, THIS JOURNAL, **52**, 2227 (1930).

[12] Parts, *Z. physik. Chem.*, **B7**, 327 (1930).

heptyl and octyl alcohols. The interposition of another CH$_2$ group between the alcohol group and the triple bond reduces the inductive effect of the latter although its influence is still felt. 1-Hydroxy-3-octyne and 1-hydroxy-3-nonyne have moments about 0.09 unit higher than the aliphatic alcohols. Dioxane was used as the solvent for the determination of the moments of the alcohols. Hydrocarbons promote the association of hydroxyl compounds and for this reason are not as suitable as dioxane. As the moments of the alcohols reported in the literature were determined in benzene as a solvent it was felt advisable to determine the moment of heptyl alcohol in dioxane. The moment of 1.70 found in dioxane checks well with the value 1.71 found in benzene.

Summary

1. The moments of the acetylenic halides have been shown to be influenced by the position of the triple bond. The influence is least with the chloro compounds and the greatest with the iodo compounds.

2. The moments of the acetylenic alcohols are higher than those of the normal aliphatic alcohols. The inductive effect is felt although there are two carbon atoms between the acetylenic carbon and the hydroxyl group.

3. The moments of 1-hydroxy-3-octyne, 1-hydroxy-3-nonyne, 1-hydroxy-2-heptyne, 1-hydroxy-2-octyne, 1-chloro-2-heptyne, 1-chloro-2-octyne, 1-bromo-2-heptyne, 1-bromo-2-octyne, 1-iodo-2-heptyne, 1-iodo-2-octyne and 1-hydroxyheptane have been determined and reported.

NOTRE DAME, IND. RECEIVED FEBRUARY 7, 1935

[CONTRIBUTION FROM THE WALKER LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

The Binary System Lead Iodide–Lead Oxide[1]

BY HENRY S. VAN KLOOSTER AND ROBERT M. OWENS

Lead iodide, when heated in air, decomposes with the liberation of iodine and the formation of oxy-iodides.[2] None of the oxy-iodides which have been reported in the literature[3] have been examined from the standpoint of the phase rule. The authors decided therefore to determine the phase diagram of the binary system lead iodide–lead oxide by means of heating and cooling curves. The melting point of lead iodide has been previously found to be 412°.[4] The melting point of lead oxide has been recorded in the literature as high as 906°[5] and as low as 835°.[6] Quite recently Addink[7] determined the melting point of pure lead oxide in a platinum crucible and found the value 884 ± 1°, which has been used by the authors in this investigation.

Apparatus and Materials.—The apparatus was substantially the same as that used previously[4] to prevent the decomposition of the lead iodide. For the low-melting mixtures ordinary glass tubes were satisfactory, for those with more than 45% lead oxide Pyrex tubes were used. The 87 and 90% PbO mixtures were fused in stainless steel and in nickel tubes in which the bare thermocouple was inserted. The wires had to be rewelded after each experiment when used unprotected since they became badly corroded by the fused mixtures. The lead iodide and lead oxide were Baker C. P. products which were used without further purification. Undercooling on solidification was small in melts containing not over 50% of lead oxide and did not exceed more than 5 to 10°. In melts rich in lead oxide the undercooling and the resulting discrepancies in the values found on heating and on cooling were quite considerable as can be seen from the table. The data obtained from heating curves, therefore, were used exclusively for the construction of the diagram on the PbO side. This procedure, which has been recommended in cases where crystallization is slow and undercooling large,[8] was followed for another reason also, *viz.*, the attack on the glass wall and the porcelain thermocouple-tube by the molten mixtures rich in lead oxide. Since the heat ab-

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[1] A thesis presented by Robert M. Owens in partial fulfilment of the requirements for the degree of Chemical Engineer at Rensselaer Polytechnic Institute.

[2] R. Brandes, *J. pharm. Chim.*, [2] **41**, 33 (1829).

[3] Mellor, "Treatise," Vol. VII, p. 766.

[4] Henry S. van Klooster and Edwin I. Stearns, THIS JOURNAL, **55**, 4121 (1933).

[5] Doeltz and Mostowitsch, *Metallurgie*, **4**, 289 (1907).

[6] R. Ruer, *Z. anorg. allgem. Chem.*, **49**, 365 (1906).

[7] N. W. H. Addink, *Proefschrift*, Utrecht, 57 (1933).

[8] Findlay, "The Phase Rule," 1927, p. 107.