[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Ultrasonic Investigation of Liquids. VI. Acetylene Derivatives[1]

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In recent years, the velocity of sound in liquids has acquired increased importance as a physical property useful for the investigation of molecular structure.[2] Several homologous series of organic and inorganic liquids have been investigated, among them the normal paraffins[3] and the 1-olefins.[4]

The present work consists of a similar study of the 1-alkynes and certain additional acetylene derivatives. By means of comparisons within this group, and also with members of the closely related paraffin and olefin series, the dependence of sound velocity on molecular structure is illustrated.

Experimental

The acetylene derivatives were procured from Farchan Laboratories. A few alkanes and alkenes (which had been omitted from the earlier work)[3,4] were obtained from the Connecticut Hard Rubber Co. and Phillips Petroleum Co. Each liquid was purified shortly before use by fractional distillation; the fraction retained had a boiling range of 0.5° or less.

The three-megacycle ultrasonic interferometer already described[5] was used for the measurement of sound velocity, with an estimated accuracy of ±0.05%. Density was determined with a 25-ml. pycnometer. Both properties were measured at 20° and at 30°.

Results and Discussion

Velocities and densities of the acetylene derivatives are listed in Table I. As the chain length increases from 1-pentyne to 1-dodecyne, the sound velocity at 20° increases from 1109 to 1319 meters/second. Somewhat higher values are possessed by 1,8-nonadiyne, phenylacetylene, and 3-butyn-1-ol. At 30° all the velocities are lower; the temperature coefficients are about −4 meters/second/degree, which is a common value.

Figure 1 is a graphical representation of the smooth increase of velocity with molecular weight, which shows that the slope decreases gradually. Curves similar to these have also been found in the cases of the 1-olefins[4] and the polydimethylsiloxanes.[6]

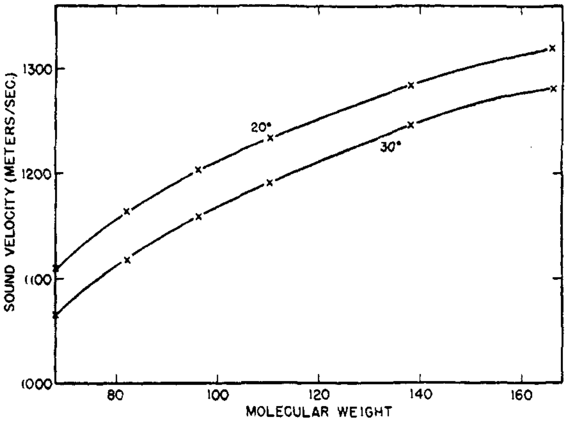

Fig. 1.—Sound velocity in 1-alkynes.

TABLE I

PROPERTIES OF ACETYLENE DERIVATIVES

Compound	Sound velocity, meters/sec. 20°	30°	Density, g./ml. 20°	30°	Adiabatic compressibility, 10^{-12} sq. cm./dyne 20°	30°	Molar sound velocity 20°	20°	M. S. V. increment for C≡C bond
1-Pentyne	1109.4	1066.2	0.6948	0.6823	116.94	128.93	1015	1020	246
1-Hexyne	1164.3	1117.0	.7188	.7079	102.63	113.22	1202	1204	235
1-Heptyne	1204.0	1160.0	.7353	.7244	93.82	102.59	1391	1395	231
1-Octyne	1233.9	1191.3	.7473	.7387	87.89	95.39	1582	1581	223
4-Octyne	1204.8	1162.8	.7506	.7422	91.79	99.65	1562	1561	203
1-Decyne	1285.6	1247.3	.7681	.7590	78.77	84.69	1957	1954	207
5-Decyne	1300.2	1259.1	.7700	.7613	76.82	82.86	1960	1961	213
1-Dodecyne	1318.8	1280.7	.7819	.7747	73.53	78.70	2332	2331	194
1,8-Nonadiyne	1374.9	1330.9	.8177	.8082	64.69	69.85	1635	1635	253
Phenylacetylene	1389.3	1344.3	.9275	.9183	55.86	60.26	1229	1228	236
3-Butyn-1-ol	1433.8	1395.5	.9268	.9171	52.49	55.99	853	854	234

Compressibility.—From the sound velocity v and density d, one can readily calculate the adiabatic compressibility $K_{ad} = (v^2d)^{-1}$. This quantity, which is defined in terms of the fractional change in volume per unit of applied pressure, often yields simpler correlations with molecular structure than the sound velocity itself.

(1) The opinions contained herein are the private ones of the writers and are not to be construed as official or reflecting the views of the Navy Department or the Navy service at large. Article not copyrighted.

(2) Weissler, THIS JOURNAL, **71**, 1272 (1949), and references contained therein.

(3) Parthasarathy, *Proc. Indian Acad. Sci*, **2A**, 497 (1935); Freyer, Hubbard and Andrews, THIS JOURNAL, **51**, 759 (1929); Schaafs, *Z. physik. Chem.*, **A194**, 28 (1944).

(4) Lagemann, McMillan and Woolsey, *J. Chem. Phys.*, **16**, 247 (1948).

(5) Weissler, THIS JOURNAL, **71**, 419 (1949).

(6) Weissler, *ibid.*, **71**, 93 (1949).

It is apparent from Table I that the compressibilities decrease with chain length, and that the values at 20° are somewhat less than 10% smaller than at 30°. These trends are found in many other homologous series.

In addition to the 1-alkynes, there were included two isomers which have the triple bond in the middle of the chain. The table shows that 4-octyne has a greater adiabatic compressibility than 1-octyne, but 5-decyne has a smaller compressibility than 1-decyne. This is additional evidence that it is the space between molecules which undergoes compression, rather than the chemical bonds themselves. If it were the bonds, 1-octyne and 4-octyne should have the same compressibility, because they have the same total number of bonds of each type. The observed difference is due to the different spatial configurations of the isomers, which causes their molecules to pack together in different ways.

It was considered of interest to compare the compressibilities of the alkynes, olefins, and paraffins. Where necessary to supplement data in the literature,[3,4] the velocity and density for members of the latter two series were determined as part of the present work. This new information is given in Table II. (Measurements could not be made at 30° for 1-pentene, because the liquid boils at this temperature.) As shown in Fig. 2, each alkyne possesses a smaller compressibility than either the alkane or the alkene with the same number of carbon atoms in the molecule. In the case of 5, 6 and 7 carbon molecules, it is the olefins which have the greatest compressibility. Inasmuch as the force constants of the single, double, and triple bonds increase regularly in that order, this again points out that it is not the chemical bonds which undergo compression.

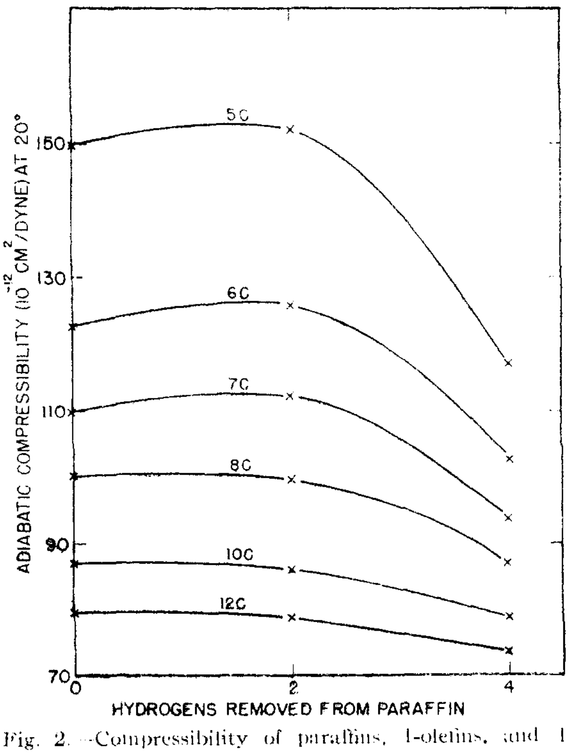

Fig. 2.—Compressibility of paraffins, 1-olefins, and 1-alkynes.

TABLE II

PROPERTIES OF SOME RELATED HYDROCARBONS

Compound	Sound velocity, meters/sec. 20°	30°	Density, g./ml. 20°	30°	Adiabatic compressibility, 10^{-12} sq. cm./dyne 20°	30°
n-Pentane	1032.3	982.2	0.6260	0.6160	149.90	168.27
n-Decane	1253.4	1215.5	.7314	.7239	87.03	93.50
n-Dodecane	1296.6	1260.9	.7497	.7428	79.34	84.68
1-Pentene	1014.0		.6404		151.87	
1-Hexene	1086.4	1044.5	.6736	.6642	125.78	138.00

Molar Sound Velocity.—Because it is approximately an additive function of the bonds in the molecule, the molar sound velocity[7] (defined as the molar volume times the cube root of sound velocity) has also been found useful for the correlation of sound velocity with molecular structure in liquids.

The molar sound velocities of these eleven acetylene derivatives are listed in the eighth and ninth columns of Table I. As expected, the values at 20° are almost the same as those at 30°. It is notable that the isomers 1-octyne and 4-octyne have similar values, as do also the isomeric pair of decynes.

There has been no previous evaluation of the molar sound velocity increment for the C≡C bond. This increment was calculated for each of the liquids, by subtracting the summation of increments for all other bonds in the molecule from the value listed in column 9. (For this purpose, the C–C increment was taken as 4.25, and the C–H as 95.2.) The results obtained, shown in the last column of Table I, vary over a considerable range: from 194 in dodecyne to 253 in 1,8-nonadiyne, with 225 as the average. Such a variation confirms Lagemann's recent conclusion, from his work on the organic halides, that molar sound velocity is not a purely additive property but has instead a highly constitutive nature.[8]

Summary

The velocity of sound in eleven liquid derivatives of acetylene has been measured at 20° and at 30°.

In every case, the adiabatic compressibility of a 1-alkyne is smaller than that of the *n*-paraffin or 1-alkene having the same number of carbon atoms.

For the C≡C bond, the molar sound velocity increment varies from 194 to 253 in these eleven compounds; the average value is 225.

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(7) Rao, *J. Chem. Phys.*, **9**, 682 (1941).

(8) Lagemann, Evans and McMillan, THIS JOURNAL, **70**, 2996 (1948).