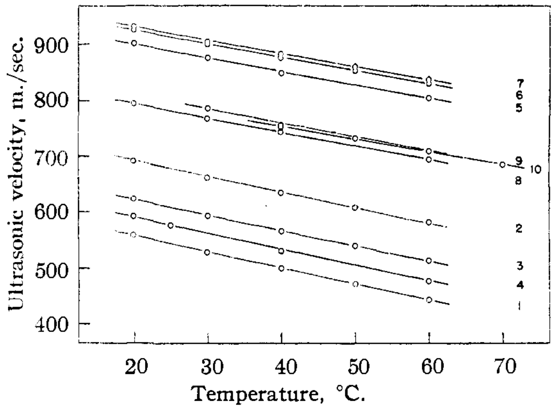

Fig. 2.—Plot showing the variation of ultrasonic velocity with temperature.

1—Hexadecafluoroheptane
2—bis-(Trifluoromethyl)-chlorononofluorocyclohexane
3—bis-(Trifluoromethyl)-decafluorocyclohexane
4—(Trifluoromethyl)-undecafluorocyclohexane
5—Chlorotrifluoroethylene polymer (MW 713)
6—Chlorotrifluoroethylene polymer (MW 886)
7—Chlorotrifluoroethylene polymer (MW 911)
8—Fluorolube oil (MW 860)
9—Fluorolube oil (MW 1016)
10—Fluorolube oil (MW 1099)

seen in Fig. 2. There is some indication, however, that the curves are slightly convex toward the temperature axis. The temperature coefficient of ultrasonic velocity, defined here as $\Delta V/\Delta T$, is approximately the same for all compounds.

Some values of the molecular sound velocity, $MV^{1/3}/d$, where V is the ultrasonic velocity, are listed in the last column of Table I. Values of the molecular refraction could also be computed from the data supplied in the tables. The comprehensive data on the several physical properties of the compounds studied lends itself to an examination of the correlations existing, but this is left to another time.

Acknowledgment.—The authors wish to acknowledge with gratitude the assistance of Dr. Clifford Beck and Dr. J. L. Gabbard of the Carbide and Carbon Chemicals Corporation, who supplied not only the liquids studied, but also those physical properties, other than ultrasonic velocities, quoted herein. One of us (R. T. L.) also wishes to acknowledge a Grant-In-Aid from the Research Corporation.

Summary

It has been found that the substitution of fluorine for hydrogen in twenty organic liquids results in extremely low values of the ultrasonic velocity. In the completely fluorinated hexadecafluoroheptane the velocity was found to be only 444 m./sec. at 60°, while in the parent hydrocarbon, heptane, the velocity is 987 m./sec. at the same temperature. It was noted that the velocity is approximately a linear function of the temperature in each of the liquids studied.

EMORY UNIVERSITY, GA. RECEIVED APRIL 15, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF EMORY UNIVERSITY]

Ultrasonic Velocity in Some Organic Halides: Constitutive Effects

BY R. T. LAGEMANN, J. S. EVANS AND D. R. McMILLAN, JR.

It has been shown that the sound velocity constant ($MV^{1/3}/d$) discovered by Rao is additive,[1,2,3] and the contributions to this molecular constant have been evaluated for a number of atoms and bonds. The summation of the contributions has been undertaken from the standpoint both of atomic[1] increments and of bond[4] increments, either of which forms a suitable mode of treatment[5] of additive molecular constants.

It has been suggested that the constant is also constitutive, and indeed it is, but no publication has explicitly demonstrated this. Inspection of previously published data on the ultrasonic velocity in organic halides reveals that considerable variation in the value of the additive increment assignable to a halogen atom (or bond) is found, depending on the compound used in the calculation. But at the same time, there is such wide disagreement in the velocity values quoted by various observers that one wonders if the constitutive effects are as pronounced as cursory examination reveals. It was therefore thought desirable to purify a number of organic halides by fractionation in a good column and measure both the ultrasonic velocity and the density with high precision.

Experimental

The ultrasonic velocity in twenty-five organic halides was measured by use of a variable-path ultrasonic interferometer and a 500-kc. crystal-controlled oscillator previously described.[6] About 50 cc. of each liquid was used and was contained in a gold-lined cup. During the measurements the interferometer was submerged in a water bath held at 20 ± 0.05° as measured on a Bureau of Standards calibrated thermometer. The usual precautions were taken to avoid satellites and to permit temperature equilibrium to be realized. For the determination of

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[1] Rao, *J. Chem. Phys.*, **9**, 682 (1941).

[2] Weissler, Fitzgerald and Resnick, *J. Applied Phys.*, **18**, 434 (1947).

[3] Lagemann, McMillan and Woolsey, *J. Chem. Phys.*, **16**, 247 (1948).

[4] Lagemann and Corry, *ibid.*, **10**, 759 (1942).

[5] Samuel, *ibid.*, **12**, 179 (1944).

[6] McMillan and Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).

velocity, groups of ten half-wave length intervals were measured.

Densities were measured using a 5-ml. pycnometer of the type described by Lipkin, Davison, Harvey and Kurtz.[7] The precautions suggested by those writers were observed.

The compounds used were Eastman Kodak Co. White Label, refractionated with a column packed with glass helices, which was equipped with a standard Penn State head and was equivalent to about twelve theoretical plates.

Discussion of Results

The measured values of the ultrasonic velocity at 20° are listed in Table I, along with values of the density. The estimated probable error of the velocity values is ±0.1%, while that of the densities is thought to be about ±0.05%. Velocities of some of the compounds have been measured by earlier workers, but the values are discordant and are not listed here.

TABLE I

MEASURED VALUES OF THE ULTRASONIC VELOCITY IN SOME ORGANIC HALIDES AT 20°

Compound	Density, g./cc.	Ultrasonic velocity, m./sec.	Adiabatic compressibility[a] (atm.$^{-1}$) ($\times 10^6$)
Fluorobenzene	1.0249	1189	69.93
Chlorobenzene	1.1042	1289	55.23
Bromobenzene	1.4953	1170	49.50
Iodobenzene[b]	1.8280	1114	44.66
n-Butyl chloride	0.8851	1140	88.09
n-Butyl bromide	1.2741	1019	76.59
n-Butyl iodide	1.6144	971.5	66.50
Methylene chloride	1.336[c]	1093	63.49
Methylene bromide	2.4843	963.2	43.96
Methylene iodide[b]	3.325[c]	973.3	32.17
Ethylene chloride	1.2524	1216	54.72
Ethylene bromide	2.1777	1009	45.70
Propylene chloride	1.1554	1162	64.95
Propylene bromide	1.9405	994.9	52.75
Chloroform	1.4870	1001	68.01
Bromoform[b]	2.8904	931.2	40.44
Ethyl bromide[b]	1.4606	900	85.65
Ethyl iodide	1.9357	876	68.21
o-Chlorotoluene	1.0826	1319	53.80
o-Bromotoluene	1.4237	1205	49.02
s-Tetrachloroethane	1.5947	1170	46.42
s-Tetrabromoethane	2.9666	1041	31.52
p-Chlorotoluene	1.0697	1308	55.37
p-Bromotoluene	1.3934[d]	1164[d]	53.67[d]
Carbon tetrachloride	1.5942	937.8	72.27

[a] The values of adiabatic compressibility were computed from the densities and ultrasonic velocities given. [b] Eastman White Label, not refractionated. [c] Lange, "Handbook of Chemistry," Handbook Publishers Inc., Sandusky, Ohio. [d] 30°.

The effect of halogen substitution on velocity at 20° can be observed in Table I. Without exception, the substitution of bromine for chlorine results in a lowered velocity. Considering all the halogens, one may write

$$H > Cl > F > Br > I$$

where the symbols represent sound velocities at 20° in halogen derivatives, each containing the same number of the indicated halogens and having the same structure. Methylene iodide is an exception to the rule. At other temperatures the order of velocities may not be that given above, since the temperature coefficients are not the same in the various halogenated compounds. It is often said that the adiabatic compressibility is a more useful and fundamental property than is ultrasonic velocity. From Table I it may be seen that the adiabatic compressibility decreases in the order F, Cl, Br, I, as halogens are successively substituted, to which rule no exception is found for the compounds studied.

If a given halogen is progressively substituted for hydrogen in a hydrocarbon, the velocity is generally lowered as, for example, in the series methylene chloride, chloroform and carbon tetrachloride. This finding is supported by velocity measurements on some fluorocarbons.[8] However, there are exceptions, as may be seen in the series monobromoethane, dibromoethane, and tetrabromoethane, and it is better to apply the rule to adiabatic compressibilities.

Enough information is available for each compound to permit calculation of the molecular sound velocity, $MV^{1/3}/d$, where M is the molecular weight and V is the ultrasonic velocity measured at the same temperature as the density, d. The values of the constant for some of the compounds studied are listed in Table II. Values at 20° are given but measurements (not given here) show that $MV^{1/3}/d$ for each compound remains constant over a range of temperature. It will be seen that the constant, although essentially an additive function, possesses certain anomalies due to constitutive influences.

First, let us consider the CH_2 increments found from homologous series. Rao[1] found the CH_2 increments of the molecular sound velocity to vary from 174 to 203 units in several hydrocarbon series and gives an average value of 195. Lagemann, McMillan and Woolsey[3] found it to range from 183 to 194 in a series of 1-olefins with an average value of 190. It may be concluded from the above and from some unpublished data that the CH_2 increment is not necessarily constant as we go from one series to another, nor even as we progress through any one series. Some of the variation is no doubt due to experimental error and some to impurity of compounds, although some is undoubtedly real. Considering the available data, there appears to be somewhat more variation in the molecular sound CH_2 increments than in the parachor CH_2 increments. This fact, of course, will influence the results of computations of other molecular sound increments, since it is customary to use carbon and hydrogen increments to obtain other atomic (or bond) increments.

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(7) Lipkin, Davison, Harvey and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

(8) Lagemann, Wolf, Evans and Underwood, THIS JOURNAL, **70**, 2994 (1948).

TABLE II

COMPARISON OF THE MOLECULAR SOUND VELOCITIES OF COMPOUNDS CONTAINING EQUAL NUMBERS OF CHLORINE AND BROMINE ATOMS

Number of halogen atoms	Compound	Velocity, m./sec.	Molecular velocity, $MV^{1/3}/d$	Per cent. difference
1	Chlorobenzene	1289	1110	+0.3
	Bromobenzene	1170	1107	
	n-Butyl chloride	1140	1093	+1.0
	n-Butyl bromide	1019	1082	
	o-Chlorotoluene	1319	1282	+0.3
	o-Bromotoluene	1205	1278	
	p-Chlorotoluene	1308	1294	+0.2
	p-Bromotoluene	1164	1291	
	n-Propyl chloride	1158[a]	907.4	+0.3
	n-Propyl bromide	1033[a]	904.4	
2	Methylene chloride	1093	654.9	−5.6
	Methylene bromide	963.2	691.4	
	Ethylene chloride	1216	843.7	−2.6
	Ethylene bromide	1009	865.3	
	Propylene chloride	1162	1028	−1.1
	Propylene bromide	994.9	1039	
3	Chloroform	1001	803.2	−6.3
	Bromoform	931.2	854.2	
4	*s*-Tetrachloroethane	1170	1109	−6.5
	s-Tetrabromoethane	1041	1181	

[a] Measured at 2° by Pellam and Galt, *J. Chem. Phys.*, **14**, 608 (1946).

The constitutive aspect of the molecular sound velocity is dramatically brought out by those compounds differing only in the replacement of chlorine by bromine. For pairs of compounds possessing but one chlorine or one bromine atom and otherwise alike, the constant is essentially the same, as may be seen in Table II. This means that if we use predetermined increments for the C and H atoms, then the chlorine increment must equal the bromine increment. This is indeed anomalous behavior if we think of the molecular sound velocity as being a measure of molecular volume at equal velocity of sound transmission. No similar effect is found for the halides in the case of the other molecular properties such as the parachor or molar refraction. The effect could scarcely be coincidental, since five cases have been found, covering both aliphatic and aromatic compounds. As we progressively substitute bromine and chlorine, however, the constant of the brominated compound is progressively larger than the constant of the chlorinated compound, though in no regular way. This increase is in accord with the idea that the molecular volume of bromine is greater than that of chlorine.

As a consequence of the listings in Table III, one will find almost as many incremental values for the halogens as one has compounds from which to calculate them, assuming the carbon and hydrogen contributions remain fixed. This is the case whether one uses atomic or bond increments. The atomic values of Table III are computed by use of the C and H increments given by Rao[1]; the bond values are based on the C–H and C–C increments of Lagemann and Corry.[4]

TABLE III

ATOMIC AND BOND INCREMENTS OF THE MOLECULAR SOUND VELOCITY AS CALCULATED FROM SEVERAL COMPOUNDS[a]

	Atomic increments			Bond increments		
Compound	Cl	Br	I	C–Cl	C–Br	C–I
Carbon tetrachloride	233.6			236.1		
Chloroform	233.6			236.0		
Chlorobenzene	259.5			236.2		
n-Butyl chloride	220.5			223.4		
s-Tetrachloroethane	226.0			228.6		
Ethylene chloride	226.8			229.4		
Methylene chloride	229.9			232.2		
Propylene chloride	221.4			224.2		
o-Chlorotoluene	234.5			211.6		
p-Chlorotoluene	246.5			223.6		
Bromoform		250.6			253.0	
Bromobenzene		254.5			231.2	
n-Butyl bromide		209.5			212.4	
s-Tetrabromoethane		244.0			246.6	
Ethylene bromide		237.6			240.1	
Methylene bromide		248.2			250.5	
Propylene bromide		227.0			229.6	
o-Bromotoluene		230.5			207.6	
p-Bromotoluene		243.5			220.6	
Iodobenzene			303.5			280.2
n-Butyl iodide			256.5			259.5
Methylene iodide			301.8			304.0

[a] The atomic increments were calculated assuming C = 10, H = 92.5, and a double bond = 110 units. The bond increments were calculated assuming (C–H) = 95.2, (C–C) = 4.25, and (C═C) = 129.

It is apparent from Table III that prediction of the molecular sound velocity by the summing of atomic or bond increments as now formulated is not entirely satisfactory for the organic halides studied, as only a rough estimate can be obtained. Of course, this estimate is not without value, nor is the correlation between prediction and measurement in hydrocarbons invalidated. It does mean, however, that the extension of the additive properties of the molecular sound velocity to the organic halides, at least, should be undertaken with caution.

From the foregoing it may be seen that the molecular velocity of sound is a highly constitutive property. This is in agreement with current belief[9] that the use of a limited number of constant increments is only a first approximation method of computing molecular properties. We may assume that there are many constitutive effects not yet known. That such exist is seen in the values found for the *o*- and *p*-isomers, for example. However, the very fact that the property is particularly sensitive to constitutive effects will make it valuable.

Acknowledgments.—The authors take pleasure in acknowledging the generous assistance of the Research Corporation through a Frederick Gardner Cottrell Grant to one of us (R. T. L.).

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(9) Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, New York, N. Y., 1945. p. 679.

We also wish to acknowledge an illuminating discussion with Dr. O. R. Quayle.

Summary

The ultrasonic velocity has been measured in twenty-five organic halides at 20°. It is found that the molecular sound velocity is essentially the same for two compounds structurally alike but for the substitution of a bromine for a chlorine atom. The property is highly constitutive in nature and the summation of atomic or bond increments to obtain the molecular sound velocity of organic halides must be done with care.

EMORY UNIVERSITY, GA. RECEIVED APRIL 5, 1948

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

Polarographic Investigation of Hexamminecobaltic Chloride in Various Supporting Electrolytes[1]

BY H. A. LAITINEN, JOHN C. BAILAR, JR., HENRY F. HOLTZCLAW, JR.,[2] AND J. V. QUAGLIANO[3]

Preliminary work on the polarographic reduction of cobaltic coördination compounds was undertaken in this laboratory by Herda.[4] Using tenth molar potassium nitrate as the supporting electrolyte, 0.02% gelatin to suppress maxima and a minute droplet of octyl alcohol to prevent foaming of the gelatin solution, he measured half-wave potentials and diffusion currents for over thirty coördination compounds of cobalt.

Willis, Friend and Mellor[5] studied the polarographic behavior of a number of cobaltic compounds in *N* and 0.1 *N* potassium sulfate and 0.1 *N* sodium acetate without the use of maximum suppressing agents. The series of compounds formed by the progressive substitution of nitro groups for ammonia molecules in the hexamminecobaltic ion were studied both by Herda and by Willis, *et al.* While the general trend of the half-wave potentials was in agreement, the absolute values differed considerably.

It was therefore of interest to determine the effects of various capillary active substances and supporting electrolytes upon the half-wave potential and the diffusion current for the reduction of the hexamminecobaltic ion. It was found that both gelatin and octyl alcohol have a pronounced effect upon the half-wave potential. Supporting electrolytes of good coördinating ability, including sulfate as used by Willis, Friend and Mellor, have a significant effect both on the half-wave potential and the diffusion current.

Experimental

Polarograms were obtained in the early parts of the investigation with a manual apparatus essentially like that described by Lingane and Kolthoff,[6] but using a Fisher Elecdropode to measure the current instead of the shunted galvanometer and resistance box. A Sargent Model XX Polarograph was used in the more recent stages of the investigation. The potentials of the dropping electrode, during electrolysis, were measured against an external saturated calomel electrode. A cell of the type described by Lingane and Kolthoff[6] was used. Purified nitrogen or hydrogen was passed through the cell before each run. Values of *m* and *t* for the dropping mercury electrodes used were checked from time to time. The temperature in the cell was maintained at 25.0 ± 0.1° by means of a water thermostat. The hexamminecobaltic chloride was prepared and recrystallized according to the methods of Bjerrum and McReynolds.[7,8]

Results and Discussion

The effects of gelatin, octyl alcohol and methyl red upon the half wave potential, the slope of the current–voltage curve, and the diffusion current for the first reduction wave, Co(III) to Co(II), in 0.1 *N* potassium chloride are shown in Table I.

TABLE I

EFFECT OF CAPILLARY ACTIVE SUBSTANCES ON FIRST REDUCTION WAVE

0.001 *M* Hexamminecobaltic chloride: *m* equals 2.1 mg./sec.; *t* equals 3.4 sec./drop in 0.1 *M* KCl, open circuit

Supporting electrolyte	Half-wave potential $-E_{1/2}$ (*vs.* S. C. E.)	Slope	Diffusion current, microamperes (−0.8 v.)
0.1 *M* KCl	0.215 v	0.120	4.04
0.1 *M* KCl; 0.02% gelatin	0.320	0.100	3.81
0.1 *M* KCl; 0.02% gelatin; droplet octyl alcohol	.530	.080	3.91
0.1 *M* KCl; 0.0008% sodium methyl red	.240	.129	4.07
0.1 *M* KCl; 0.002% sodium methyl red	.271	.075	3.84

In each case, the half wave potential was shifted to a more negative value, the slope of the curve approached more nearly the reversible value, and the apparent diffusion current decreased in the presence of maximum suppressing agents. The smallest effects on the half-wave potential were

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[1] Abstracted from the doctoral theses of James V. Quagliano, 1946, and Henry F. Holtzclaw, Jr., 1947.

[2] Present address: Department of Chemistry and Chemical Engineering, University of Nebraska, Lincoln, Nebraska.

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[4] M. G. Herda, M.S. Thesis, University of Illinois, 1943.

[5] J. B. Willis, J. A. Friend and D. P. Mellor, THIS JOURNAL, **67**, 1680 (1945).

[6] J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 825 (1939).

[7] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 241.

[8] J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 216.