

that the pyridine in the fourth solution was  $0 \pm 5\%$  in the form of complex at  $80^\circ$ .

These observations are in accord with the first paper in this series, where there were indications that pyridine complexes partially with phenol and fairly completely with *p*-nitrophenol at  $25^\circ$ ; also with the present work there is no indication of complexing with these reagents at  $100^\circ$ .

### Summary

Methyl halides, as well as triphenylmethyl halides, undergo concerted, termolecular displacements in benzene solution, requiring in the rate-determining step both pull on the leaving group and attack on carbon. The reaction of methyl bromide with pyridine in benzene solution is accelerated several fold by adding 0.05 *M* concentrations of *p*-nitrophenol or mercuric bromide which are more effective than the solvent benzene at solvating bromine. The effect is too large to be due to a general medium change. The kinetics are third order.

There is no apparent reason why these mechanisms should be less concerted in alcohol or water solution. A survey of the literature reveals that concerted, termolecular mechanisms are remarkably common. It is probable that nucleophilic displacements of anions from saturated carbon atoms are generally of this type, although they may often be cleverly camouflaged because the solvent functions as one (or two) of the three participating molecules.

A displacement proceeding by the carbonium ion mechanism can be kinetically first, second, or third order depending only on the degree of participation of the solvent. A displacement currently considered to proceed by the direct mechanism can also have any of these kinetic orders. The kinetic order or even the total number or type of reacting molecules involved can no longer be considered a criterion of mechanism.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF EMORY UNIVERSITY]

## Ultrasonic Velocity in Some Liquid Fluorocarbons<sup>1</sup>

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A rather thorough search of the literature reveals that no ultrasonic velocities have been reported for any liquid compound containing fluorine. A similar scarcity of information on ultrasonic velocity exists for liquid polymers—only two studies<sup>3,4</sup> having been made. It was therefore thought to be of interest to measure the velocity of sound in some fluorocarbons, including a series of fluorocarbon liquid polymers. The study was made under a contract from the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee, and we are indebted to them for the use of the compounds and for a compilation of certain physical properties. In addition to thirteen chlorotrifluoroethylene polymers, there were available four samples of fluorolube oil, three heavily fluorinated cyclohexane derivatives, and hexadecafluoroheptane. Values of density, index of refraction, molecular weight and viscosity were also furnished and are tabulated.

### Experimental

The ultrasonic velocities in the above-mentioned compounds were measured over the temperature range 20 to  $70^\circ$ , using an ultrasonic interferometer<sup>5</sup> described earlier. It is of the conventional moving-reflector type, and satel-

ites were removed by adjustment of the plane of the reflector. The ultrasonic frequency is obtained by applying the output of two separate high frequency oscillators to the grids of a mixer tube to produce a beat frequency of 500 kc./sec. in the tuned plate circuit of the mixer stage which drives the power amplifier. The plate circuit of the power amplifier is coupled to a resonant tank circuit by means of a variable link coupling.

The quartz crystal used to produce the ultrasonic wave in the liquid is X-cut and about 3.2 cm. in diameter. It is energized by the final tank circuit. As the interferometer reflector passes through successive half wave-length nodes, minima are indicated by the galvanometer in a vacuum tube voltmeter circuit.

The temperature of the liquids studied was controlled to  $\pm 0.03^\circ$  by means of a water-bath in which the interferometer could be submerged. It was noted that the galvanometer dips were less sharp in the case of the compounds of high viscosity. In the case of Fluorolube oil of molecular weight 1233 (viscosity = 448.5 cs. at  $60^\circ$ ) no nodes could be discerned and hence no velocities could be measured. The measured values of the ultrasonic velocity are listed in Tables I and II.

### Results and Discussion

**Low Velocity of Sound.**—From Tables I and II and Fig. 1 it may be seen that the velocity at any one temperature increases with increase in the molecular weight of the compound for each of the series. A similar change has been observed for liquid silicone polymers.<sup>4</sup> On the other hand, Weissler, Fitzgerald and Resnick<sup>3</sup> noted a general decrease of velocity with increase in molecular weight for the ethylene glycol polymers.

Perhaps the most striking feature of the results is that, in very case, the substitution of fluorine for hydrogen in the molecule has resulted in a compound yielding an extraordinarily low value

(1) This work was done under contract with Carbide and Carbon Chemicals Corporation.

(2) Now at Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

(3) Weissler, Fitzgerald and Resnick, *J. Applied Phys.*, **18**, 434 (1947).

(4) Weissler, New York meeting of the American Chemical Society, Sept. 16, 1947, reported on ultrasonic velocity in liquid silicone polymers.

(5) McMillan and Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).

TABLE I  
 CERTAIN PHYSICAL PROPERTIES OF SOME FLUOROCARBONS

Compound	Molecular weight	$n_D^{60}$ <sup>a</sup>	Viscosity <sup>a</sup> (c. s.) (60°)	Density <sup>a</sup> (60°/4°)	Ultrasonic velocity in meters per second					Molecular sound velocity (60°)
					20°	30°	40°	50°	60°	
Hexadecafluoroheptane	388		0.329(cp)	1.62027	557.8	528.8	500.0	471.8	444.0	1827
bis-(Trifluoromethyl)-chlorononofluorocyclohexane	416	1.3021	0.768	1.79126	691.8	663.1	635.5	608.6	582.3	1940
bis-(Trifluoromethyl)-decafluorocyclohexane	400		0.560	1.74636	623.6	593.4	566.8	539.9	513.1	1834
(Trifluoromethyl)-undecafluorocyclohexane	350 <sup>c</sup>		1.59 <sup>d</sup> (cp)	1.78751 <sup>d</sup>	592.6 <sup>e</sup>		531.3		477.8	1631
Chlorotrifluoroethylene <sup>b</sup>	713	1.38113	16.44	1.88543	900.6	876.7	851.9		804.0	3516
Chlorotrifluoroethylene <sup>b</sup>	886	1.38706	80.62	1.91385	926.3	900.4	877.6	853.7	830.8	4352
Chlorotrifluoroethylene <sup>b</sup>	911	1.38843	117.5	1.91934	934.7	906.0	881.6	858.5	836.4	4473
Fluorolube oil	860		15.70	1.95467	795.8	769.4	743.7		695.4	3897
Fluorolube oil	1016		70.01	1.96990		787.4	757.4		710.4	4602
Fluorolube oil	1099	1.32928	107.5	1.97817			753.6	732.8	709.4 <sup>f</sup>	4955

<sup>a</sup> These data were kindly supplied by Dr. J. L. Gabbard, Carbide and Carbon Chemicals Corp., Oak Ridge, Tenn.  
<sup>b</sup> Polymer. <sup>c</sup> Calculated. <sup>d</sup> 25°. <sup>e</sup> Velocity at 25° = 577.6 m./sec. <sup>f</sup> Velocity at 70° = 686.6 m./sec.

TABLE II

 ULTRASONIC VELOCITY IN A SERIES OF CHLOROTRIFLUOROETHYLENE POLYMERS AT 60°<sup>a</sup>

Molecular weight	Density, g./cc. (60°/4°)	Viscosity c. s. (60°)	Refractive index (60°)	Ultrasonic velocity, m./sec.
525	1.81492	1.98		731.0
563	1.83068	2.83	1.36468	746.9
577	1.83828	3.14	1.36578	752.5
664	1.86892	8.05	1.37559	785.0
686	1.87745	11.43	1.37755	793.8
713	1.88543	16.44	1.38113	804.0
727	1.88683	18.66	1.37976	803.2
789	1.90090	36.17	1.38238	813.6
846	1.90861	56.49	1.38395	823.2
886	1.91385	80.62	1.38706	830.8
894	1.91976	111.87	1.38632	830.4
911	1.91934	117.5	1.38843	836.4
948	1.92552	169.02	1.38763	838.7

<sup>a</sup> Except for the ultrasonic velocities, all values found in this table were kindly furnished by Dr. J. L. Gabbard, Carbide and Carbon Chemicals Corporation, Oak Ridge, Tenn.

of the ultrasonic velocity. Bergmann's<sup>6</sup> compilation of ultrasonic velocities in nearly two hundred organic liquids gives only one (ethyl bromide, velocity = 892 m./sec. at room temperature) having a velocity below 900 m./sec. at room temperature, the average being close to 1200 m./sec. All the fluorinated compounds listed in Tables I and II, however, possess velocities below 935 m./sec. with hexadecafluoroheptane yielding a velocity of only 444 m./sec. at 60°. This value lies in the region in which gas velocities are found and is the lowest velocity ever measured in a liquid at ordinary temperatures. The only lower value reported is for liquid helium.<sup>7</sup>

(6) L. Bergmann, "Ultrasonics," G. Bell and Sons, London, 1938.

(7) Findley, Pitt, Smith and Wilhelm, *Phys. Rev.*, **54**, 506 (1938), found liquid He I at 4.22° K. to have a velocity of 179.8 m./sec. Liepmann, *Helv. Phys. Acta.*, **125**, 421 (1939), found liquid nitrogen at -197°C. to have a velocity of 868 m./sec. Liepmann, *ibid.*, **9**,

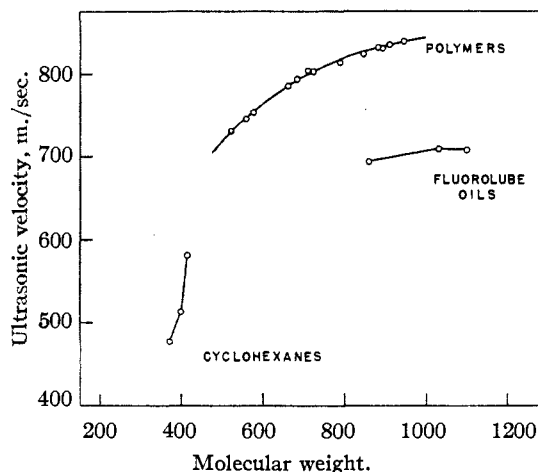


Fig. 1.—Plot of ultrasonic velocity at 60° versus molecular weight.

Such a decrease in velocity upon substitution of fluorine for hydrogen in the molecule could not be readily predicted since no previous velocities for compounds containing fluorine have been reported to the authors' knowledge. However, some work from this Laboratory, as yet unpublished, shows that fluorobenzene has a lower velocity than benzene.

Heptane, the parent hydrocarbon of hexadecafluoroheptane, has a velocity of 1154 m./sec.<sup>8</sup> at 20° and 987 m./sec.<sup>9</sup> at 60° in comparison with the 444 m./sec. found at 60° for the fluorocarbon.

**Variation of Velocity with Temperature.**—It is well known that the change of velocity with temperature is linear for most liquids. The compounds studied closely follow this rule as may be

507 (1936), gives 903 m./sec. for the velocity in liquid oxygen at -183.6°C.

(8) Freyer, Hubbard and Andrews, *THIS JOURNAL*, **51**, 759 (1929).

(9) By extrapolation from data of ref. 8.

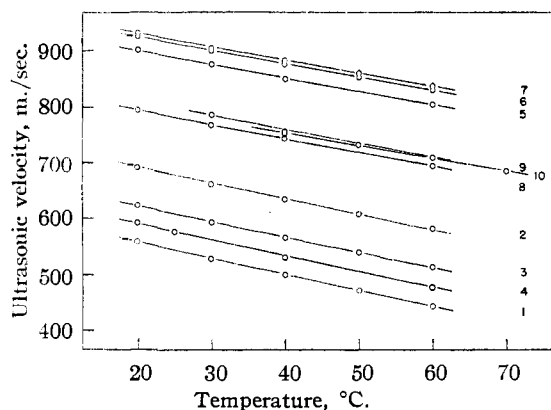


Fig. 2.—Plot showing the variation of ultrasonic velocity with temperature.

- 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.

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## Ultrasonic Velocity in Some Organic Halides: Constitutive Effects

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It has been shown that the sound velocity constant ( $MV^{1/3}/d$ ) discovered by Rao is additive,<sup>1,2,3</sup> 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<sup>1</sup> increments and of bond<sup>4</sup> increments, either of which forms a suitable mode of treatment<sup>5</sup> 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 as-

signable 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.<sup>6</sup> 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  $20 \pm 0.05^\circ$  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

- (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).