[CONTRIBUTION FROM THE DEPARTMENTS OF PHYSICS AND CHEMISTRY OF EMORY UNIVERSITY]

Ultrasonic Velocity in a Series of Alkyl Phenyl Ketones and a Series of Alkyl *p*-Xylyl Ketones

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The variation of sound velocity with molecular weight has been studied in a series of 9 alkyl *p*-xylyl ketones and in a series of 9 alkyl phenyl ketones at temperatures ranging from 10 to 40°. It was found that the relationship is remarkably different from that observed for other homologous series. There occurs a minimum in the velocity of sound in each series in the region of the compounds which possess five, six or seven carbon atoms in the side chain. Values of density and adiabatic compressibility are given for 30°.

There is at present no detailed theory of the compressibility of liquids which leads to an accurate estimate of the velocity of sound from more fundamental considerations. The excellent, pioneering free volume theory of Kittel[1] leads to estimates of the correct order of magnitude only. Efforts[2] to calculate empirically the velocity of sound by summing "bond" or "atomic" increments to achieve a "molar sound velocity" for molecules in the liquid phase have been only partially successful. The usefulness of the latter method is hindered by the constitutive nature of the molecular property[3] chosen, which is particularly noticeable in the organic halides.[4] Furthermore, the approximate additivity of the molar property, $MV^{1/4}/d$, where V represents the velocity of sound, is essentially an expression of the approximate additivity of the molar volume, and any attempt to calculate V for a compound, after adding the appropriate increments of "molar sound velocity," often leads to values widely divergent from the measured value.

The work in this field has concerned itself mostly with the measurement of ultrasonic velocity in homologous series of organic compounds in the hope that as data were accumulated some information useful in the formulation of theory might be uncovered. The present report gives the results of measurements on the velocity of sound in two series of ketones. These results differ remarkably from those for series previously studied in that the velocity of sound is not a single-valued function of the molecular weight.

Experimental

The ultrasonic velocity in a series of alkyl *p*-xylyl ketones and in a series of alkyl phenyl ketones was measured by means of a variable-path ultrasonic interferometer energized by a 500 kc. crystal-controlled oscillator described earlier.[5] About 25 ml. of each liquid was sufficient for the measurements and was contained in a gold-lined brass cup. For the determinations, made at temperatures ranging from 20 to 40°, the interferometer containing the liquid studied was submerged in a constant temperature water-bath held to within ±0.05° of the desired temperature as indicated by a Bureau of Standards calibrated thermometer.

The compounds used had been recently distilled in a good column. Except for the last two members of each series, the preparation and purity of these compounds are described elsewhere.[6,7] The last two compounds of each series were prepared and purified in a manner similar to that used for the others.

Results

Table I lists the measured values of the ultrasonic velocity at various temperatures as well as the density and adiabatic compressibility at 30° of the eighteen ketones studied. The estimated probable error of the velocity values is ±0.15%. The densities were measured with a 3-ml. double-arm pycnometer of the type described by Lipkin, *et al.*[8] The adiabatic compressibility, K_{ad}, was calculated from the sound velocity, V, and the density, d, by means of the equation

$$K_{ad} = 1/V^2d \qquad (1)$$

Figure 1 shows the variation of ultrasonic velocity with molecular weight for each of the two series.

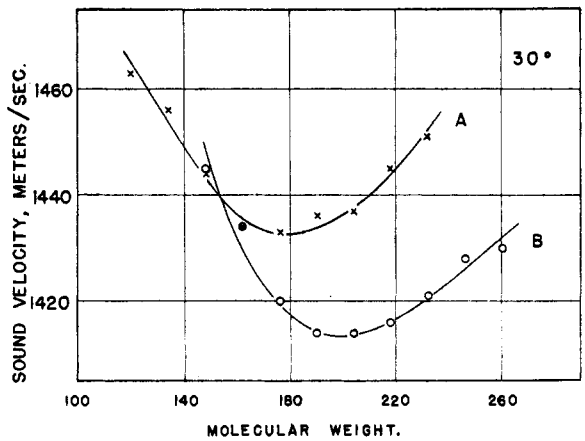

Fig. 1.—Sound velocity in two series of ketones: A, alkyl phenyl ketones; B, alkyl *p*-xylyl ketones.

Discussion of Results

It can be noted that the variation of ultrasonic velocity with molecular weight cannot be expressed as a single-valued functional relationship. This is a phenomenon which is highly unusual. It is unique to find two members of a series (except at very high molecular weights) to possess the same velocity of sound, as do, for example, propyl phenyl and octyl phenyl ketone. Heretofore, series have fallen into one of two classifications in this regard: (a) series in which velocity increases with increase in molecular weight, as in the 1-olefins[9] and monohydric alcohols,[10] or (b) series in which velocity decreases with

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TABLE I

SOME PHYSICAL PROPERTIES OF *p*-XYLYL ALKYL KETONES AND ALKYL PHENYL KETONES

Ketones	Ultrasonic velocity (meters/sec.) 10°	20°	25°	30°	35°	40°	d^{30}_{4},[a,b]	Adiabatic compressibility (atmos. $\times 10^5$ at 30°)
2,5-Dimethylphenyl methyl	1521	1481		1445			0.9870	49.15
2,5-Dimethylphenyl ethyl	1506	1472		1434			.9730	50.63
2,5-Dimethylphenyl propyl	1493	1454		1420			.9577	52.46
2,5-Dimethylphenyl butyl	1492	1452		1414			.9460	53.56
2,5-Dimethylphenyl amyl	1489	1453		1414			.9377	54.03
2,5-Dimethylphenyl hexyl	1490	1453		1416			.9308	54.28
2,5-Dimethylphenyl heptyl	1492	1456		1421			.9245	54.26
2,5-Dimethylphenyl octyl	1498	1460		1428			.9215	53.91
2,5-Dimethylphenyl nonyl	1500	1463		1430			.9150	54.14
Methyl phenyl	1537	1502		1463			1.0193	46.43
Ethyl phenyl		1493		1456			1.0014	47.72
Propyl phenyl		1477		1444			0.98014	49.57
Butyl phenyl	1505	1471		1434			.96481	51.06
Amyl phenyl			1448	1433	1414		.95347	51.74
Hexyl phenyl			1451	1436	1419		.94371	52.05
Heptyl phenyl			1452	1437	1422		.93604	52.41
Octyl phenyl			1460	1445	1425		.93021	52.15
Nonyl phenyl				1451[c]	1427	1403	.....	...

[a] C. T. Lester and E. C. Suratt, THIS JOURNAL, 71, 2262 (1949). [b] J. R. Proffit, Ph.D. Thesis, Emory University, 1950. [c] Extrapolated from the values at 35° and 40°.

increase in molecular weight, as in the esters of acetic acid.[11] Class (a) is larger than class (b). One possible exception is the case of the fatty acids,[12] where the second member, acetic acid, yields the lowest velocity. This abnormality may be explained as being due to the unusual characteristics of the first member of the series, formic acid. Omitting formic acid, the series falls into class (a) above. Whereas the minimum in the acids is accompanied by abrupt changes in density and in compressibility, the change in the ketone series is smooth for the ultrasonic velocity and has no minimum or maximum in the density or in the compressibility. Another possible exception may be found in the series of hydrocarbons beginning with benzene. In this series a velocity maximum occurs for xylene. However, only four members of this series have been studied. Parthasarathy[13] has made a summary of the relations between velocity of sound and chemical constitution in liquids.

The minimum value of the ultrasonic velocity occurs for both the series in the vicinity of those compounds which have five, six or seven carbon atoms in the side chain. For the existence of such a minimum, which has been pointed out as unique, we have no ready explanation. The increase in velocity which follows the velocity minimum can be explained by saying that the side chain, as it grows longer, becomes more and more predominant in its influence on the velocity of a compressional wave, and, as is generally true for straight chain hydrocarbons, velocity increases with increase in molecular weight.

It will be seen that two of the compounds in one series which are isomers of two in the other series possess almost identical velocities. The other isomer pairs do not. It will also be seen that over this range of temperature there is found a linear relationship between velocity and temperature for any one compound. The temperature coefficient of the velocity of sound for each of the compounds lies in the range minus 3 to minus 4 meters/second-degree, or within the range commonly found for organic liquids.

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