platinum cannot be involved in the activation energies. Since all other factors remain constant, the differences in the apparent activation energies for the catalytic reactions must represent differences in the true activation energies for the hydrogenation of these compounds on platinum.

The heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, and benzene are $-28,600$, $-55,400$, and $-49,800$ cal. respectively.[2,7] The corresponding value for 1,4-cyclohexadiene may be estimated as twice that of cyclohexene, or $-57,200$. If one assumes that the hydrogenation of benzene proceeds by the path benzene $\rightarrow$ 1,3-cyclohexadiene $\rightarrow$ cyclohexene $\rightarrow$ cyclohexane, and that the first step is rate determining, it is necessary that the energy of activation for the hydrogenation of benzene, catalytically or otherwise, be at least 5600 calories. If, by any possibility, the hydrogenation of benzene should pass through the intermediate 1,4-cyclohexadiene, the energy of activation would have to be at least 7,400 calories. The actual energy of activation, 7,400 cal., is surprisingly close to either of these requirements.

The resonance stabilization of the benzene ring as calculated from the heats of hydrogenation

(7) Kistiakowsky. Ruhoff, Smith and Vaughan, *ibid.*, **58**, 137 (1936).

is 36,000 calories.[2] One would probably expect the activation energy for the hydrogenation of benzene to be at least equal to this value. If this reasoning is correct, it would appear that the benzene molecule must be adsorbed on the platinum catalyst in such a manner that its resonance is destroyed, and that the slow rate of hydrogenation of the benzene nucleus when compared to that of simple unsaturated compounds cannot be attributed to resonance.

It is also interesting to note that the conjugated 1,3-cyclohexadiene has a faster rate of hydrogenation than is found for the unconjugated 1,4-cyclohexadiene. The difference in the activation energies is probably within experimental error.

Summary

The catalytic hydrogenations of benzene, the cyclohexadienes, and cyclohexene on platinum have been studied from a kinetic viewpoint. Rate constants and activation energies have been determined for each of these reactions. The low value for the activation energy of the hydrogenation of benzene when compared with the resonance energy of the molecule indicates the probability that such resonance is destroyed when the benzene is adsorbed on the catalyst.

KNOXVILLE, TENNESSEE   RECEIVED AUGUST 20, 1948

Catalytic Hydrogenation of Furan and Substituted Furans on Platinum

BY HILTON A. SMITH AND JOHN F. FUZEK

Studies of the kinetics of catalytic hydrogenation of the benzene nucleus on Adams platinum catalyst have been previously reported.[1,2] This work has now been extended to include furan and several substituted furan compounds. The aim has been to determine in a quantitative manner the effect of structure on the rate of hydrogenation of the furan nucleus with Adams platinum catalyst in acetic acid solution. Particular attention has been given the effect of varying the type of the substituent group on the rate. The results obtained have been compared with those for corresponding benzene compounds. Where necessary for such comparisons, additional work was also done in the benzene series.

Experimental

Preparation of Materials.—Furan and 2-methylfuran (E. I. du Pont de Nemours and Company) were treated with Raney nickel catalyst, dried, and fractionated in a ten-foot Vigreux column.

Furoic acid (Eastman Kodak Company) was purified by recrystallization and subsequent conversion to the methyl ester. This was dried, treated with Raney nickel and activated charcoal, and fractionated. The product

(b. p. 181.8–182.0 (736 mm.), $n^{20}D$ 1.3880) was converted to the acid which was recrystallized and dried.

2,5-Dimethylfuran (Eastman Kodak Company) was azeotropically distilled with methanol (azeotrope b. p. 60.8° (743 mm.), 35–40% by volume 2,5-dimethylfuran), separated after addition of water, dried and fractionated.

Benzyl alcohol and **benzoic acid** were Eastman products. The alcohol was treated with Raney nickel and anhydrous magnesium sulfate, and fractionated. As in previous work, the benzoic acid was used without further purification.

Furfural and **furfuryl alcohol** (Quaker Oats Company) were treated with Raney nickel catalyst, anhydrous magnesium sulfate and activated charcoal for several hours. The solids were removed by filtration and the furan derivatives distilled through a fourteen-foot Vigreux column. The center fractions boiled within a 0.1° range.

Dibenzofuran (diphenylene oxide) (The Reilly Tar and Chemical Corporation) was treated with Raney nickel catalyst and activated charcoal in hot ethanol solution. The solution was filtered several times and the crystals recovered on cooling. They were then recrystallized from benzene. This cycle was repeated three times. The resulting crystals when dry melted within a range of 0.5°. Further purification failed to narrow this melting range.

The **Adams platinum catalyst** was prepared from 3.5-g. batches of platinum chloride in the usual manner.[3] Several of these finished batches of catalyst were mixed and then standard rates obtained as in previous work.[1] The acetic

(1) Smith, Alderman and Nadig. THIS JOURNAL, **67**, 272 (1945).
(2) Smith and Pennekamp. *ibid.*, **67**, 276 (1945).

(3) Adams, Voorhees and Shriner, "Organic Syntheses," **8**, 92 (1928).

acid used in the hydrogenations as a solvent was distilled through an eight-foot Vigreux column. The fraction boiling within the 0.1° range was retained. Tank hydrogen was used directly as in previous work.[1]

Hydrogenation Procedure.—The hydrogenations were carried out in a standard Parr low-pressure catalytic apparatus which was modified by substitution of a 0.790 liter hydrogen tank for the 4.02 liter tank supplied.[4] The runs were made as previously described,[1] except that due to the low boiling points of some of the materials used, the reaction bottle was not evacuated, but flushed several times with hydrogen prior to each run. It was also desirable to control the temperature of the reaction rather carefully. This was accomplished by the use of a brass jacket surrounding the reaction bottle. Water was circulated through this jacket at a rate of several gallons per minute from a constant-temperature-bath. A check of the temperature of the reaction mixture before and after the reaction indicated that the temperature of the circulating water leaving the jacket was within 0.1° of the crude temperature within the reaction bottle. The temperature during a run was maintained within ±0.2° in most cases.

Hydrogenation Products.—The products of hydrogenation were usually recovered from the acetic acid solution by neutralization of the acetic acid with sodium hydroxide solution with resulting separation of the layer of alcohol product. This product was dried over anhydrous magnesium sulfate and distilled through a four-foot Vigreux column or a twenty-inch Vigreux column depending on the quantity of material available. The fractions obtained were identified by their physical properties and the usual identification procedures. Difficulty was encountered in the isolation of the hydrogenation product of furfuryl alcohol since it was a dihydric alcohol and failed to separate from the neutralized acetic acid solution. Identification was affected by refluxing for several hours the filtered reaction mixture to which a small amount of concentrated sulfuric acid had been added. The diacetate thus formed proved to be easier to isolate. In the case of the product from the hydrogenation of furoic acid, the δ-hydroxyvaleric acid was converted partially to the lactone during the distillation; hence, the entire product was treated with a dehydrating agent and isolated as the lactone.

Properties of the reactants and products isolated are given in Table I.

TABLE I

PROPERTIES OF COMPOUNDS HYDROGENATED AND THEIR PRODUCTS

Compound	$n^{20}D$	Dist. temp., °C. B. p.	Mm.	M. p.
Furan	1.4209	30.4	740	
2-Methylfuran	1.4318	63.2	740	
2,5-Dimethylfuran	1.4402	92.5	740	
Furfuryl alcohol	1.4845	170.4	747	
Furoic acid				131.0
Dibenzofuran				82.0
Furfural	1.5243	161.2	744	
Benzyl alcohol	1.5391	203.0	740	
Benzoic acid				121.5
Products as isolated				
Butanol	1.3991	116.1	740	
2-Methyltetrahydrofuran	1.4059	80.1	743	
2-Pentanol	1.4054	118.8	743	
2-Hexanol	1.4125	137.6	736	
1,2-Pentanediol diacetate	1.4210	114.0	27	
Tetrahydrofuroic acid	1.4612	128	17	
δ-Hydroxyvaleric acid	1.4630	130	17	
δ-Valerolactone	1.4575	124	24	
Dicyclohexylene oxide	1.4990	162	45	

(4) Fuzek and Smith, THIS JOURNAL, **70**, 3743 (1948).

Experimental Calculations and Results

It has been established in previous work that the hydrogenation of the benzene nucleus is first order with respect to the hydrogen pressure, zero order with respect to the concentration of the hydrogen acceptor, and directly proportional to the amount of catalyst used.[1,2] Tables II, III and IV illustrate the fact that these conditions are true for the hydrogenation of the furan nucleus provided the shaking is adequate to maintain equilibrium. Table IV shows that for 2,5-dimethylfuran, the maximum amount of catalyst which can be used and still maintain shaking equilibrium is very low, namely, 0.03 g. This maximum amount of catalyst appears to be a function of the material undergoing hydrogenation.

TABLE II

EFFECT OF HYDROGEN PRESSURE ON THE RATE CONSTANT FOR THE HYDROGENATION OF THE FURAN NUCLEUS

Furan compound	Rate constant k, (liters/g. min.) Pressure (p. s. i. a.)					
	60	45	40	35	30	20
Furan	0.518			0.502		0.542
2-Methylfuran	.356		0.390			.384
2,5-Dimethylfuran	.576	0.560			0.574	.599
Furfuryl alcohol	.305		0.328			.319

TABLE III

EFFECT OF CONCENTRATION OF HYDROGEN ACCEPTOR ON THE RATE CONSTANT FOR THE HYDROGENATION OF THE FURAN NUCLEUS

Furan compound	Rate constant. k, (liters/g. min.) Concn. (moles/l.)				
	0.11	0.22	0.30	0.66	1.20
Furan			0.518	0.542	0.507
2-Methylfuran	0.328	0.356	.354		
2,5-Dimethylfuran		.576	.551	0.552	
Furfuryl alcohol	.312	.305	.316		

TABLE IV

EFFECT OF THE AMOUNT OF CATALYST ON THE RATE CONSTANT FOR THE HYDROGENATION OF THE FURAN NUCLEUS

Furan compound	Rate constant. k (liters/g. min.) g./catalyst					
	0.01	0.02	0.03	0.04	0.05	0.07
Furan		0.475	0.479		0.518	0.448
2-Methylfuran			.356		.366	
2,5-Dimethylfuran	0.571	.576	.566	0.503	.438	
Furfuryl alcohol			.305		.321	

Calculations for the rate constant have been made according to the modified first order equation for heterogeneous reactions.[4] A sample hydrogenation curve is given in Fig. 1. This shows that a plot of log p_0/p versus time results in a straight line. If the slope of this line is multiplied by 2.303 V, the value for the rate constant is obtained. Tabulation of such rate constants is given in Table V.

Since most of the reaction rate constants were determined at several temperatures, an apparent activation energy can be obtained from a plot of the Arrhenius equation. This equation may be represented as $k = Ae^{-E/RT}$ or $\log_e k = -E/RT + \log_e A$. Thus a plot of log k versus $1/T$ should
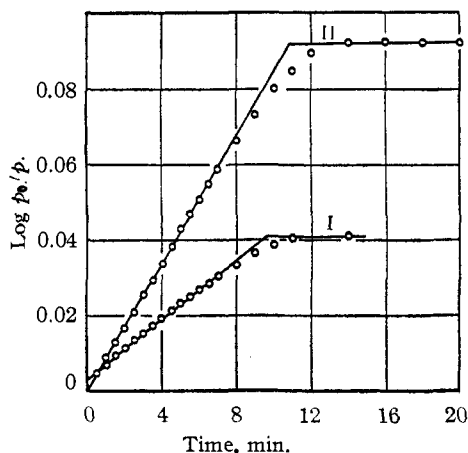
Fig. 1.—Sample hydrogenation curves: I, hydrogenation of 0.003 mole of dibenzofuran on 0.100 g. of platinum oxide in 50 ml. of acetic acid at 50°; II, hydrogenation of 0.015 mole of furan on 0.050 g. of platinum oxide in 50 ml. of acetic oxide at 26°.

TABLE V

RATE CONSTANTS FOR THE HYDROGENATION OF SOME
BENZENE AND FURAN COMPOUNDS

Derivative	k^a (liters/g. min.) Furan cpd.	Benzene cpd.	Ratio F/B
Parent compound	0.554	0.288	1.92
2-Methyl	.490	.178[a]	2.75
2,5-Dimethyl	.700	.186[b](p)	3.76
2-COOH	.148	.112[a]	1.32
2-CH$_2$OH	.384	.133	2.89
2-CHO	.269		
Dibenzofuran	.386		

[a] All rate constants are corrected to a catalyst activity of 0.112 for benzoic acid. This corresponds to the value of 0.0250 in a hydrogen volume of 4.43 liters as previously reported.[1]

result in a straight line whose slope when multiplied by 2.303 R is the apparent activation energy. Such plots are given in Fig. 2. A tabulation of activation energies and A factors for the furans studied is given in Table VI along with comparable values for corresponding benzene compounds.

TABLE VI

APPARENT ACTIVATION ENERGIES AND A-FACTORS FOR
SOME BENZENE AND FURAN DERIVATIVES

Derivative	Furan compound E.	A.	Benzene compound E.·	A.	Ratio
Parent compound	8000	2.28 × 10⁵	7400[a]		1.08
2-Methyl	8600	5.37 × 10⁵			
2,5-Dimethyl	10200	1.14 × 10⁷			
2-COOH	11400	1.75 × 10⁷	7400	1.75 × 10⁴	1.54
2-CH₂OH	9300	1.45 × 10⁶	6700	6.08 × 10³	1.40
2-CHO[b]	4400	3.21 × 10²			
Dibenzofuran	8800	2.03 × 10⁶			

[a] See ref. 6. [b] These values are for the hydrogenation of furfural to furfuryl alcohol only and do not involve hydrogenation of the ring.

(5) Smith and Pennekamp, THIS JOURNAL. **67**, 279 (1945).
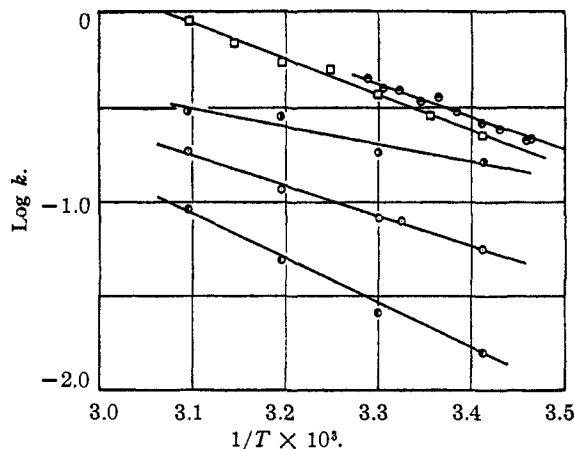(6) Smith and Meriwether. *ibid.*. **71**. 413 (1949).

Fig. 2.—Sample Arrhenius curves: ⊖, furan; □, 2-methylfuran; ◑, furfural; ⊙, benzoic acid; ◑, dibenzofuran.

Discussion

The products of hydrogenation in the case of the furan derivatives are interesting since not only are the two double bonds in the furan ring hydrogenated, but also the ring is usually broken. A single product results from cleavage of either furan or 2,5-dimethylfuran regardless of which of the two carbon–oxygen bonds is cleaved. The former results in butanol while the latter yields hexanol-2. In both instances, the yield is almost quantitative. However, for 2-methylfuran, furfuryl alcohol and furoic acid, there are two possible products in each case, depending on which carbon–oxygen bond is broken. Ring cleavage of furoic acid occurred at the carbon–oxygen bond nearest the carboxyl group. This was shown by the fact that the principal product isolated was δ-hydroxyvaleric acid which even under mild dehydrating conditions is unstable, losing water to give δ-valerolactone. This latter compound was easier to identify due to its stability. A trace of tetrahydrofuroic acid was also obtained; the quantity was estimated at less than 10% from both the amount isolated and the deficiency in the calculated hydrogen uptake during the hydrogenation process.

The hydrogenation of 2-methylfuran and furfuryl alcohol resulted in ring cleavage at the carbon–oxygen bond removed from the functional group. For the methyl derivative, about 80 to 90% of the product was s-amyl alcohol. The remainder was 2-methyltetrahydrofuran. This amount was accounted for also in the amount of hydrogen absorbed in the process of hydrogenation. The furfuryl alcohol was hydrogenated almost quantitatively to 1,2-pentanediol. This product was difficult to isolate in an acetic acid solution, hence was converted to the diacetate which was more readily recovered and identified.

The formation of the tetrahydro derivative in two cases arouses interest as to the possible mechanism of the hydrogenation reactions considered. Since in all hydrogenations of 2-methylfu-

ran and furoic acid some of the tetrahydro compound was obtained, it appears questionable that the tetrahydro derivative can be an intermediate in the reaction, as it failed to hydrogenate further even when a quantity of fresh catalyst was added to the reaction mixture. Further evidence was obtained by preparing pure tetrahydrofuran by the catalytic reduction of furan on Raney nickel catalyst in absolute ethanol. This compound was purified by distillation and then subjected to hydrogenation conditions using Adams platinum catalyst and acetic acid solvent. No observable reaction occurred even after three hours. Further support for the reaction mechanism not involving the tetrahydro derivative was obtained by Bradley,[7] who hydrogenated dihydrofuran on Adams platinum catalyst in dioxane and found that only one mole of hydrogen was absorbed per mole of acceptor while furan itself rapidly absorbed three moles. From the above-cited evidence, it appears that there are two modes of reaction which the hydrogenation can follow; first, to give the cleavage product, and second, to give the tetrahydro derivative. Apparently these are two competing reactions, with the former playing the more important role in the hydrogenation of furan compounds, but the second becoming detectable for 2-methylfuran and furoic acid. Further evidence that the tetrahydro compounds are not intermediates in the reaction was obtained by analysis of partially hydrogenated samples of the various furans under study. For the other reactions studied (excepting 2-methylfuran, furoic acid and dibenzofuran), the analysis showed only the initial product and the final cleavage product.

It thus appears that, in general, the furan compounds are completely hydrogenated to the cleaved product, i. e., reaction occurs with three moles of hydrogen per mole of compound before desorption from the catalytic surface.

The hydrogenation of dibenzofuran was most interesting as the reaction in this case left the furan ring intact, thus requiring six moles of hydrogen per mole of compound.[7] When a sample which had been allowed to react with only three moles of hydrogen per mole of compound was analyzed only the original dibenzofuran and the final product dicyclohexylene oxide could be isolated. Also no break in the rate curve appears when three moles of hydrogen are adsorbed (see Fig. 1). Apparently hydrogenation proceeds in such a manner that both rings are hydrogenated before the molecule is desorbed from the catalyst. Furthermore, the presence of the two benzene rings probably stabilizes the furan ring and thus prevents cleavage. This was the only furan compound studied which did not cleave to a major extent on hydrogenation.

The study of the hydrogenation of furfural was greatly hampered by the unstable nature of the compound. Even when the reactions were carried out immediately after distillation, poisoning of the catalyst was so pronounced that only the rate of hydrogenation of the aldehyde to the alcohol could be determined with the small amount of catalyst used.[8] This small amount of catalyst was necessary in order to maintain shaking equilibrium as previously discussed. Further purifications proved to be of no value. Hence the rate constant and activation energy reported are obviously subject to considerable inaccuracies. It is estimated that the probable maximum error would be about ±15%.

A comparison of the rate constants for the furan compounds and the corresponding benzene compounds is made in Table V. The values given for the benzene derivatives previously reported have been corrected for the volume of the hydrogen void according to an equation applicable to heterogeneous reactions.[4] The ratios of the rate constants for furan to benzene derivatives is given in the last column. This ratio varies from 1.32 to 3.76; the average value is 2.5. For every derivative, the furan compound gave a rate constant considerably higher than the corresponding benzene compound.

As Table VI shows, the activation energies, as well as the rate constants for the hydrogenation of furan compounds, are greater than for the corresponding benzene derivatives. The average ratio is about 1.34. Individual values are tabulated in Table VI. The higher activation energy for furan compounds may possibly be attributed to the greater energy requirement in ring cleavage. The frequency factor for the furan compounds is also much greater than for the corresponding benzene derivatives, being of the order of 10^3 larger. This factor may account for the slower rates for benzene derivatives. It is also possible that the frequency factor as determined includes other variables dependent upon solubility relations.

In conclusion it should be indicated that the activation energies as determined should be reasonably accurate in every case except for furfural as already discussed. In the other cases, maximum deviation from the least-squares value was less than 4% while the average deviation was 2.2%. In the case of furfural, the maximum deviation was 15% and the average was 9.4%.

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Summary

A study has been made of the kinetics of catalytic hydrogenation of some furan compounds and comparison made with corresponding benzene derivatives. The reactions were carried out at pressures up to five atmospheres absolute, in acetic acid solution, using Adams platinum catalyst. The rate constants, activation energies and frequency factors have been tabulated.

It has been shown that the rate constants,

(7) Bradley, Iowa State Coll. J. Sci., 12, 108 (1937).

(8) Kaufmann and Adams, THIS JOURNAL, 45, 3029 (1923).

activation energies, and the frequency factors are considerably higher for the furan compounds

than for corresponding benzene derivatives.

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Ultrasonic Investigation of Molecular Properties of Liquids. IV. Cyclic Compounds[1]

BY ALFRED WEISSLER

Recent interest in the chemical applications of ultrasonics has prompted several studies[2-6] of the relation between sound velocity and molecular structure of liquids, mainly in the aliphatic field. An emerging conclusion is that the velocity of sound is a useful and important physical property, comparable to density or refractive index.

The present work was undertaken in order to extend the correlation between sound velocity and chemical structure into the classes of aromatic, alicyclic, and heterocyclic compounds. In order to simplify the interpretations, molecules containing a substituent instead of hydrogen on a ring carbon were excluded. For a few of the twenty-two liquids chosen, the velocity had been measured previously at scattered temperatures; these were included here because of the necessity for self-consistent data at a standard temperature.

Experimental

The compounds were obtained from commercial sources, except for 1,4-thioxane, which was synthesized[7] from β,β'-dichlorodiethyl ether and alcoholic sodium sulfide. Each was purified before use by fractional distillation through a 40-cm. Widmer column. In order to free pyrrolidine from tenaciously-held water, it was let stand over sodium for a day, then distilled from sodium.

A three-megacycle ultrasonic interferometer, designed by Mr. Burton G. Hurdle, was used to measure sound velocities. This instrument is very similar to the one-megacycle interferometer previously described,[2] but it requires only 10 ml. of sample, because of the further scaling-down of physical dimensions permitted by the higher frequency.

If desirable, one could construct an ultrasonic interferometer which requires only a few drops of liquid sample, merely by going to a somewhat higher frequency. This illustrates the decisive advantage of ultrasonic frequencies in measuring the velocity of sound.

To minimize contamination by corrosion of the brass interferometer cell, all interior surfaces were gold plated. A 0.003-inch tantalum foil was used as the floor of the cell, directly beneath which lay the quartz crystal source of ultrasound.

Refractive indices for D light were determined with an Abbe refractometer, and densities with a 25-ml. pycnometer. Measurements of all three physical properties were made at 30°.

(1) The opinions contained herein are the private ones of the writer 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, **70**, 1634 (1948); **71**, 93 (1949).

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

(4) Lagemann. Woolf. Evans and Underwood. THIS JOURNAL, **70**, 2994 (1948).

(5) Burton, J. Acoust. Soc. Am., **20**, 186 (1948).

(6) Schaafs. Z. physik. Chem., **A194**, 28–50, 66–85, 170–178 (1944).

(7) Clarke. J. Chem. Soc., **101**, 1806 (1912).

Results and Discussion

The values of sound velocity, density and refractive index for the twenty-two compounds are listed in Table I. These velocities lie in the range 1100–1550 meters/second, just as is the case for the majority of unhalogenated liquids. The estimated accuracy for the velocities is about $\pm 0.03\%$.

It is apparent from the table that a compound with two rings in the molecule possesses a higher sound velocity than that associated with either of the constituent rings. Other generalizations are difficult to find, however. For example, it is not true that a five-membered ring always has a lower (or a higher) velocity than its six-membered homolog; cyclopentane's is lower than cyclohexane's, but tetrahydrofuran's is higher than tetrahydropyran's.

The present data vitiate a conclusion drawn by Schaafs,[8] to the effect that in a pair of unhalogenated liquids of practically the same molecular weight, the one with the higher density also has the higher sound velocity. Both thiophene and dihydropyran have a molecular weight of 84.1, yet thiophene has the higher density but the lower sound velocity. Similarly, cyclopentene has a lower density than furan, but a higher velocity, although both have a molecular weight of 68.1.

Thus it appears that any correlations would have to take into account the specific force-interactions between molecules due to the chemical structure. For this purpose, the adiabatic compressibility is more suitable than the raw sound velocity.

Adiabatic Compressibility.—From the sound velocity v and density d, the adiabatic compressibility K_{ad} of a medium may be calculated readily, using the relation

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

The values so obtained, presented in Table I, support the following generalizations. Increasing the saturation of a six-membered ring, as from benzene to cyclohexane, causes the adiabatic compressibility to increase also. Even if a nitrogen or oxygen atom is substituted for one of the six carbons, as in the pyridine or pyran systems, the rate of increase of compressibility with saturation remains about the same (Fig. 1). In the five-membered rings, however, no such uniformity exists: furan has a greater compressibility than tetrahydrofuran, yet pyrrole's is smaller than that of pyrrolidine.

(8) Schaafs, Ann. Physik, **40**, 401 (1941).