profile of Fig. 4, is characteristic of the hydrolysis of the uncharged psicofuranine. The line may be extrapolated with a slope of unity to the pH equal to the pK_w at that temperature. This appropriate pK_w as derived from the literature[11] (Table IV) may be inserted into equation 17 so that the log k at this pH serves as an estimate of log k_3.

Similarly, the k_4 value may be estimated by extrapolation of the straight line above the pH of the plotted inflection on the alkaline branch of the log k *vs.* pH profile of Fig. 4. Such log k_3 and log k_4 values are listed in Table IV and their Arrhenius plots are given in Fig. 8. Also, Table IV lists the pK_a values as estimated from the points of maximum inflection in the alkaline branch of the profiles of Fig. 4.

The slopes of the Arrhenius plots in Fig. 8 are 5,110 so that by equation 4 the heat of activation is 23.4 kcal./mole. The respective intercepts, log C, of these plots are: for k_3', 10.92; k_3, 11.08; k_4, 11.55.

Discussion

The hydrolysis of a nucleoside such as psicofuranine is subject to both specific acid and base catalysis. The rates of hydrolysis are about 2.5 times faster when the catalytic species attacks the neutral nucleoside than when it reacts with the similarly charged species. The variation in the apparent bimolecular rate constant, k_{H^+}, for the acid hydrolysis is to be expected with respect to the degree of protonation of the adenine moiety of psicofuranine. The variation in the apparent bimolecular rate constant, k_{OH^-}, for the basic hydrolysis confirms the previously published evidence[13] presented for the acidity of the sugar portion of nucleosides of pK_a *ca.* 12.

The kinetic procedures presented herein permit a valid estimation of the apparent hydrogen ion dissociation constant of a nucleoside. Such derived values are presented in Table IV.

The possible products of alkaline degradation could be adenine and psicose as in the acid hydrolysis with the sugar subjected to further reaction under the influence of alkali. However, it must be realized that the method of assay used could not differentiate between non-hydrolyzed nucleoside or some possible degradation intermediate(s). Such an intermediate must survive borohydride reduction so that on the subsequent acid hydrolysis the necessary functionality to react with diphenylamine must be retained or generated.

The asymptotic value of the color assay approached with time on alkaline degradation is significant and indicative of alkali undegraded material and/or the presence of protected carbonyl. One of several possible explanations is that di- or polysaccharides are produced by the action of alkali.

It is of interest to note that the apparent first-order rate constants in HCl solution for this ketonucleoside do not agree, even in magnitude, with the findings of Levene and Sobotka[14] for aldonucleoside hydrolysis. Their value is $k = 7 \times 10^{-4}$ in 0.1 N HCl at 100°. It is assumed that the units are min.$^{-1}$. At 60° and in 0.1 N HCl, the value of k determined by extrapolation of the 60° data in Fig. 3 is much greater; $k = 7.25 \times 10^{-3}$ sec.$^{-1}$ or 0.435 min.$^{-1}$. This indicates that the ketonucleoside is more susceptible to acid hydrolysis than the aldonucleoside. Confirmation of this point may be obtained from the comparison of the hydrolysis rates of simple glucosides. The half-life, $t_{1/2}$, of methyl β-glucopyranoside in 0.05 N HCl at 60° is 1.04×10^5 min., but that of methyl β-fructopyranoside is 12.8 min.[15]

Acknowledgment.—The author is greatly indebted to Mrs. Lillian G. Snyder for excellent technical assistance.

[13] P. A. Levene and L. W. Bass, "Nucleic Acids," Chem. Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1931, pp. 162–172, and references therein.

[14] P. A. Levene and H. Sobotka, *J. Biol. Chem.*, **65**, 463 (1925).

[15] W. W. Pigman and R. M. Goepp, Jr., "Chemistry of the Carbohydrates," Academic Press, Inc., New York, N. Y., 1948, p. 203.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO.]

Hexane Isomer Equilibrium Studies

BY ALAN SCHRIESHEIM AND SARGIS H. KHOOBIAR

RECEIVED JUNE 12, 1959

The equilibrium hexane isomer distribution has been obtained over the temperature range 26.6–40.6°, using infrared spectrometry. There is substantial disagreement between the experimentally determined values and those calculated from entropies and enthalpies of combustion. The experimentally observed concentration of 2,2-dimethylbutane is lower than the calculated value, while that of 2-methylpentane is higher than the calculated value. The reason for these discrepancies is not known, but it does indicate that thermodynamic hydrocarbon properties should be used with caution.

Introduction

Several relatively recent papers have appeared on a direct experimental determination of the equilibrium concentration of hexane isomers in the liquid phase.[1-4]

van Eijk measured this equilibrium at one temperature, 80°.[2] He did not differentiate between the two dimethylbutane isomers and their sum was

[1] B. L. Evering and E. L. d'Ouville, THIS JOURNAL, **71**, 440 (1949).

[2] J. J. B. van Eijk van Voorthuijsen, *Rec. trav. chim. Pays-Bas*, **66**, 323 (1947).

[3] H. Koch and H. Richter, *Angew. Chem.*, **A59**, 31 (1947).

[4] J. A. Ridgway, Jr., and W. Schoen, Abstracts of Papers, Division of Petroleum Chemistry, A.C.S. Meeting, Boston, Mass., April, 1959. This work appeared after the present paper had been written. In Dr. Ridgway's paper, the equilibrium determinations were carried out at higher temperatures than those reported here. The conclusions reached are similar to those of the present authors.

TABLE I

HEXANE ISOMER EQUILIBRIUM VALUES

	Experimental						Calculated[5]	
Temp., °C.	26.6		32.2		40.6		25.0	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
n-C_6	5.0	3.1	5.3	3.2	5.9	3.9	3.0	1.6
3-MP	10.0	7.1	10.6	7.7	11.4	8.7	5.0	3.3
2-MP	20.4	16.2	21.8	17.8	22.2	18.6	14.4	10.7
2,3-DMB	9.6	8.3	10.3	9.1	10.0	9.0	8.9	7.4
2,2-DMB	55.0	65.3	52.8	62.2	50.5	59.8	68.7	77.0

far from the values calculated from thermodynamic properties.[5]

Koch investigated the equilibrium at a lower temperature, 25°, and obtained an equilibrium isomer concentration that varied considerably from that calculated from thermodynamic data.[5]

The most comprehensive study in this area was undertaken by Evering and d'Ouville.[1] They measured the hexane isomer equilibrium at several temperatures ranging from 21 to 204°. Evering and d'Ouville found that their experimentally determined equilibrium concentrations differed considerably from those calculated from the entropies and heats of combustion. However, these experiments were conducted on a fraction of petroleum naphtha containing C_5- and C_6-cyclic and acyclic hydrocarbons, aromatics and olefins. In addition, equilibrium was assumed to exist because the Motor octane numbers of the products remained constant—a method which is relatively insensitive to small changes in product composition. Analyses were preformed by refractive index methods—a technique which is admittedly difficult to apply to the hexane isomers, since their molar refractions are so similar. In the work reported here, infrared spectrometry and gas liquid partition chromatography were used.

Experimental Methods

A batch type apparatus consisting of a 500-cc. three-neck flask was employed throughout the course of this investigation. This flask was fitted with a constant voltage stirrer which entered the flask through a ground glass joint. A reflux condenser, cooled by tap water, was attached to the flask, and the reflux outlet was connected to a gas collecting device to measure any decomposition products. The third neck was fitted with a self-sealing neoprene diaphragm. The flask was placed in a constant temperature bath which was controlled to ±0.1°. Samples were obtained periodically by puncturing the diaphragm with a hypodermic syringe and withdrawing a small amount of material.

An experiment was made as follows. The catalyst (activated aluminum halide) was placed into the reactor in the constant temperature bath. The hexane isomer in question was also placed in the bath in a glass-stoppered bottle. When bath temperature had been reached, the isomer was added to the reactor containing the catalyst. Stirring action was initiated and samples periodically withdrawn by means of a hypodermic syringe. These samples were ice-water washed and analyzed by infrared spectrometry.

The infrared spectrometric procedure used the baseline scanning technique. This technique has been described elsewhere.[6-8] A Perkin-Elmer model 21 recording infrared spectrophotometer was used throughout the course of this work. This instrument was equipped with NaCl optics, and the measurements were performed with a 0.1 mm. sealed, quantitative NaCl cell.

The hexane isomers used in the equilibrium studies were Phillips Petroleum 99 mole % minimum purity grade. Each isomer was subjected to gas-liquid partition chromatography and bromine number analysis. The bromine numbers showed no olefins. In no instance did the gas-liquid chromatogram show more than 1% impurity, and the impurity was, in every instance, another hexane isomer. Five vol. % methylcyclopenthane was added to each isomer in order to eliminate cracking side reactions. Experimental results are shown with the methylcyclopentane backed out of the calculations.

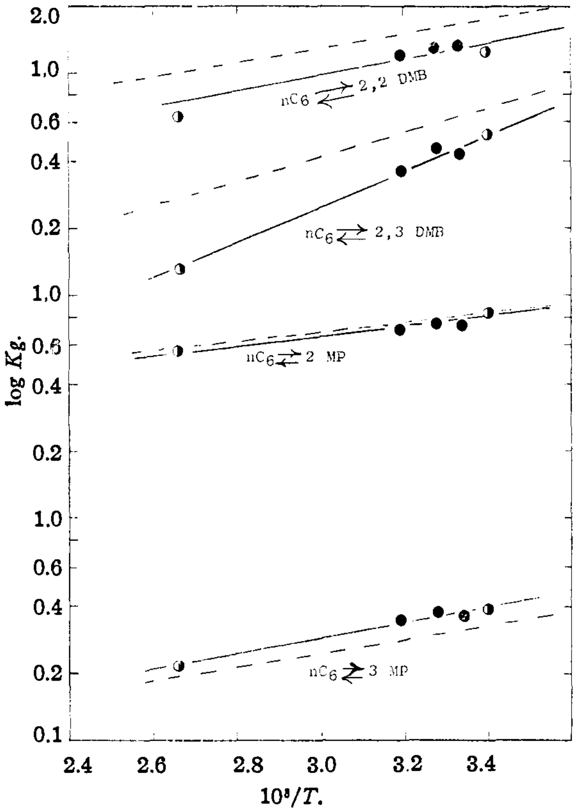

Fig. 1.—Comparison of the hexane isomer equilibrium concentration: as a function of temperature for this work, ●; Evering and d'Ouville's work, ◑; and the calculated values, – – – –.

Hexane Equilibrium.—Table I shows the results of experiments at 26.6, 32.2 and 40.6° in which equilibrium was reached. The values in the liquid phase were experimentally determined. The vapor equilibrium values were calculated from these data from a knowledge of the fugacities of each component.[1]

These experimental values are compared with those calculated from thermodynamic data at 25° The data on which the latter values are based—heats and entropies of isomerization—predict

---

(5) E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **34**, 403 (1945).

(6) H. H. Willard, L. L. Merritt, Sr., and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand and Co., Inc., Princeton, N. J., 1958, p. 177.

(7) Frey, *J. Applied Phys.*, **17**, 150 (1946).

(8) Mortimer, Symposium on Molecular Structure and Spectrometry, Ohio State Univ., June, 1946.

TABLE II

ENTROPIES AND ENTHALPIES OF HEXANE ISOMERIZATION

Conv. of hexane to	ΔH, cal./mole				ΔS, e.u.			
	This work	Evering[1]	Condon[9]	Calcd.[5]	This work	Evering[4]	Condon[1]	Calcd.[5]
n-C_6	0	0	0	0	0	0	0	0
2-MP	1100	1310	1740	1710	0.70	0.78	1.82	1.86
3-MP	850	820	1090	1020	1.4	1.12	2.00	1.59
2,3-DMB	2500	2500	2500	2500	6.5	6.07	5.48	5.13
2,2-DMB	4100	4620	4950	4390	8.4	8.93	6.89	6.74

substantially more 2,2-dimethylbutane and less 2-methylpentane than is actually found. Condon[9] indicates that this discrepancy is largely the result of differences in the heat content and entropy of 2,2-dimethylbutane and the entropy of 2,3-dimethylbutane.

Vapor phase equilibrium constants for the isomerization of n-hexane to each of its four isomers are plotted in Fig. 1 and compared with those calculated from thermodynamic data. Also shown in this figure are the experimental values of Evering and d'Ouville at 21–100°. The values repeated here are in good agreement with Evering and d'Ouville's indicating that the multitude of components in the virgin naphtha, used during the course of their work, did not affect equilibrium.[1]

The experimental entropies and enthalpies of isomerization are compared with the calculated values in Table II. Also shown are the experimental values of Evering[1] and the values calculated by Condon[9] from a best fit of the experimental data of several investigators. The values reported in the present work were obtained over a relatively narrow temperature range but agree well with those of Evering. They differ from the values calculated by Condon mainly in the entropy of 2-methylpentane. This might be due to the narrow temperature range investigated with a consequent decrease in the reliability of the isomerization heats.

Further work will be needed before definite conclusions can be reached. However, the work reported here, on pure hexane isomers, offers conclusive proof that thermodynamic values previously reported for hydrocarbons must be used with a degree of caution.

The data above hexane are very sparse, but limited heptane isomerization results indicate some disagreement between experimental and calculated equilibrium values.[9] The reason for these particular differences seems to be in the heat of combustion of 2,3-dimethylbutane. A re-evaluation of thermodynamic hydrocarbon values, and conditions under which they can be used with confidence, appears to be in order.

Acknowledgment.—The authors would like to acknowledge the help obtained in the Process Research Division of Esso Research & Engineering Co., and also to Esso Research & Engineering Co. for permission to publish this work. We would particularly like to acknowledge the analytical help provided by Messrs. W. A. Dietz and H. Pobiner, and the advice and encouragement of Messrs. D. L. Baeder and J. P. Longwell.

LINDEN, N. J.

---

[9] F. E. Condon in "Catalysis," Vol. 6, Edited by P. H. Emmett, Reinhold Publ. Corp., New York, N. Y., 1958.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Thermal Decomposition of Thiolsulfonates[1]

BY JOHN L. KICE, FRED M. PARHAM AND ROBERT M. SIMONS

RECEIVED JUNE 3, 1959

The thiolsulfonates $RSO_2SCH_2C_6H_5$, where R = $(C_6H_5)_2CH$– or $C_6H_5CH_2$–, undergo thermal decomposition in inert solvents in the temperature range 130–200° with essentially quantitative evolution of sulfur dioxide and the formation of varying amounts of $RSCH_2C_6H_5$, RH, stilbene, dibenzyl disulfide and R–R. Investigation of the kinetics of the decomposition indicates that for both thiolsulfonates the reaction is a simple first-order process. Under comparable conditions the rate of decomposition of the benzhydryl compound is about 150 times greater than that of the α-toluenethiolsulfonate, providing evidence that the C–SO_2 bond is broken in the rate-determining step. For both thiolsulfonates the rate of decomposition is noticeably dependent on solvent, being considerably faster in relatively polar solvents (nitrobenzene, benzonitrile) than in non-polar solvents (1-chloronaphthalene, 2-methylnaphthalene, etc.). This fact, together with the complete failure of the diphenylmethanethiolsulfonate to initiate the polymerization of styrene, seems most consistent with a mechanism for the thiolsulfonate decomposition involving a rate-determining heterolytic fission of the C–SO_2 bond followed by recombination of the fragments with loss of sulfur dioxide. This recombination is believed to occur in two ways, one yielding $RSCH_2C_6H_5$, the other RH and $C_6H_5CH{=}S$. This last product then decomposes to yield the stilbene observed. The other minor products apparently result from subsequent reactions of some of the compounds initially formed.

Thiolsulfonates (RSO_2SR') represent a relatively little investigated class of organic sulfur compounds. Most studies of their chemistry have been concerned with their displacement reactions (eq. 1), which appear to involve nucleophilic attack on the sulfur–sulfur bond.

$$RSO_2SR' + A^- \longrightarrow RSO_2^- + R'S\text{–}A \qquad (1)$$

We, however, were more intrigued by an early report[2] that benzyl α-toluenethiolsulfonate ($C_6H_5CH_2SO_2SCH_2C_6H_5$) underwent thermal decomposition to afford at

---

[1] Presented in part at the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

[2] J. A. Smythe, *J. Chem. Soc.*, **121**, 1400 (1922).