[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

The Vapor Phase Association of Trifluoroacetic Acid

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The vapor phase dimerization of trifluoroacetic acid has been evaluated on the basis of vapor density measurements at pressures from 150 to 560 mm. and temperatures from 80 to 130°. The presently available data for the dimer dissociation constants of a number of aliphatic acids, when reduced to a single temperature, indicate a small but significant correlation of the magnitude of the dissociation constant with the nature of the carboxyl substituent. It is suggested that this correlation is an entropy, rather than an enthalpy, effect.

A series of investigations[1,2] of the vapor phase association of carboxylic acids has been concluded with an examination of trifluoroacetic acid. The experimental techniques and methods of calculation employed were those described in the previously reported work.

Anhydrous trifluoroacetic acid, obtained from the Columbia Organic Chemicals Co., was subjected to repeated fractional distillation in a vacuum system. The purity of the product of this treatment was attested by a very sharp melting point at −15.4°.[3] The data obtained in measurements of the vapor density of this material are given in Table I. The apparent molecular weight, M, was calculated as dRT/P; and K_2', the apparent dimerization constant, as $m(M - m)/P(2m - M)^2$—where m represents the formula weight of the monomeric acid.

The only previously reported vapor density data for this acid appear to be a few isolated trials made at room temperature by Karle and Brockway.[4] These authors worked with densities approximating 1 g./l., with which the minimum density covered in the present research corresponds quite closely. The extrapolation, over some 50°, of the least squares line representing our lowest isometric of $-\log K_2'$ against $(1/T)$ yields a value of $-\log K_2'$ that may be compared with the average value of the apparent equilibrium constant reported (as accurate to but ±20%) by Karle and Brockway. This comparison actually yielded agreement to 2%. The slope of the isometric involved gives for the apparent heat of dimerization a value of −14.5 kcal., considerably less negative than the conjectural figure of −16 kcal. cited by Karle and Brockway. The heat of formation of any aggregates higher than the dimer will, of course, contribute to this apparent heat of dimerization; and the true heat of dimerization, calculated below, is found to be 0.5 kcal. less negative than the apparent heat.

TABLE I

VAPOR PHASE DIMERIZATION OF TRIFLUOROACETIC ACID

t, °C.	P, mm.	d, g./l.	M	$-\log K_2'$
131.2	560.5	3.072	138.2	3.214
117.7	510.0	3.072	146.85	2.953
103.3	454.8	3.067	158.3	2.641
93.9	420.4	3.068	167.1	2.411
118.1	468.5	2.784	145.0	2.960
94.2	387.2	2.777	164.3	2.438
81.5	347.5	2.778	176.8	2.105
130.7	456.1	2.450	135.3	3.208
118.0	418.2	2.448	142.8	2.966
103.5	374.1	2.448	153.7	2.659
93.6	344.5	2.447	162.5	2.427
81.4	310.2	2.444	174.2	2.117
130.9	302.6	1.554	129.4	3.224
118.8	280.4	1.555	135.6	2.988
103.0	249.6	1.556	146.2	2.658
94.7	233.3	1.556	153.0	2.470
81.2	207.5	1.555	165.6	2.138
119.2	198.6	1.058	130.4	3.006
102.7	177.3	1.058	139.9	2.669
94.4	165.8	1.0585	146.4	2.476
81.0	147.5	1.059	158.6	2.146

The values of $-\log K_2'$ listed in Table I were reduced to a series of "standard" temperatures and, applying the method of least squares, isothermal plots of $-\log K_2'$ as a function of density were prepared. The pronounced slope of these isotherms indicates the presence in the acid vapor of aggregates higher than the dimer. The extent of the genuine dimerization is, however, easily estimated without making any assumption about the (trimeric, tetrameric and/or collision complex) character of these aggregates. It is necessary only to extrapolate the isotherms to zero density. There are then obtained limiting values of $-\log K_2'$ that can be equated with the corresponding values of $-\log K_2$, where K_2 is the true thermodynamic dimerization constant. The extrapolation procedure is particularly powerful when, as here, it is conducted over a limited range and along apparently linear and well-defined isotherms. The points representing a plot against $(1/T)$ of the extrapolated values for $-\log K_2$ all fall quite exactly on the line, fitted to them by the method of least squares, with equation

$$-\log K_2 = 10.800 - 3053/T$$

This expression for the vapor phase dimerization of trifluoroacetic acid is very nearly the same as that by which Coolidge has described[5] the vapor phase dimerization of formic acid. The heat of dimerization of trifluoroacetic acid is calculated from the above equation as −14.0 kcal.

The Dimerization of the Paraffin Acids.—From their studies of the dimerization of the paraffin acids in benzene solutions, Maryott, Hobbs and Gross arrived[6] at the generalization: "In going through the aliphatic series from formic acid to stearic acid there is a progressive . . . increase in the tendency to associate." A complete comparison of the re-

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(1) E. W. Johnson and L. K. Nash, THIS JOURNAL, **72**, 547 (1950).

(2) R. E. Lundin, F. E. Harris and L. K. Nash, *ibid.*, **74**, 743 (1952).

(3) F. Swarts, *Bull. sci. roy. acad. Belg.*, **8**, 343 (1922).

(4) J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).

(5) A. S. Coolidge, *ibid.*, **50**, 2166 (1928).

(6) A. A. Maryott, M. E. Hobbs and P. M. Gross, *ibid.*, **71**, 1671 (1949).

sults obtained in the solution and in the vapor phase is unfortunately impossible, owing to the unavailability of the necessary Henry's law coefficients. However, even a partial comparison of these results is illuminating. For each acid studied in the vapor phase the equation expressing $-\log K_2$ as a function of $(1/T)$ can be solved for the equilibrium constant at 160°, a temperature close to or within the working ranges in all the vapor studies. The 30° values for the equilibrium constants in solution and the 160° values for the equilibrium constants in the vapor phase, expressed in fundamentally different units, are listed in Table II. The parallelism of the trends in the two sets of constants is conspicuous. This suggests that Maryott, Hobbs and Gross' generalization may be applicable to the vapor phase as well as to the solution phase dimerization of aliphatic acids. This possibility may also imply an appreciable similarity in the behavior of these acids as vapors and as solutes in non-polar liquids.

TABLE II

DIMER DISSOCIATION OF ALIPHATIC ACIDS

Acid	Benzene solution[6] Dissociation constant at 30° in mole fraction units	Vapor State[1,2,5] Dissociation constant at 160°, in atmospheres	Heat of dissociation, in kcal. per mole dimer
Trifluoroacetic		7.4	14.0
Chloroacetic	8.8		
Formic	7.1	5.5	14.1
Acetic	2.4	1.8	13.8
Propionic	2.3		
Butyric	2.1	1.6	13.9
Heptanoic		1.65	13.3
Stearic	1.7		
Trimethylacetic	1.3	1.1	14.0

In interpreting the trend of the dissociation constants listed in the first column of figures in Table II, Maryott, Hobbs and Gross have remarked that the more electronegative the substituent attached to the carboxyl group the less is the acid's tendency to dimerize. They suggest that this substituent effect involves a trend in the strengths of the dimer bonds with which the trend in the equilibrium constants is coördinated: "Other things being equal, any substituent which . . . tends to draw electrons away from the carboxyl group and thereby makes the effective charge on the oxygens less negative should weaken the hydrogen bonds." In view of the current belief[7] that the hydrogen bonds in the acid dimers are to a considerable extent ionic in character, Maryott, Hobbs and Gross' hypothesis does not at first seem implausible. But it is obviously utterly incompatible with the data on the heats of vapor phase dimerization of the aliphatic acids. These data are listed in the last column of Table II. If anything, the bonds maintaining the more extensively dissociated dimers appear to be very slightly the stronger. It is notable that the heats of vapor phase dimerization for five aliphatic acids all fall within 1.5% of −14.0 kcal. The figure for the sixth (heptanoic) acid does, indeed, fall outside this very narrow range—but it does so by no more than the comparatively large experimental error possible in this one instance. Thus despite the differences in the electronegativities of the carboxyl substituents in these acids, and despite the differences in the various acids' tendencies toward dimerization, the heats of dimerization appear to be invariant.

It is not difficult to discover the origin of the discrepancy between the data obtained in the experimental study of gas phase dimerization and the prediction of Maryott, Hobbs and Gross. The observed trend in the equilibrium constants signifies only a trend in the free energies of dimerization. In the absence of data indicating constancy of the entropy of dimerization, the trend in the equilibrium constants cannot be taken (as Maryott, Hobbs and Gross have taken it) to be a secure indication of a coördinated trend in the strengths of the dimer bonds and, hence, in the enthalpies of dimerization. Furthermore, the structural argument offered in support of the postulated trend in the strength of dimer bonding is also open to question. *Both* of the oxygen atoms on the carboxyl group are subject to the inductive effect of strongly electronegative substituents. The reduction of the negative charge on the carbonyl oxygen does, to be sure, tend to reduce the strength of a hydrogen bond in which this oxygen acts as the electron donor. But the reduction of the effective negative charge on the hydroxyl oxygen is well known[7] to increase the polarity of the hydroxyl group, with an increase in the effective positive charge of its hydrogen atom. (This enhanced polarity is manifest in the increase of ionization constant produced in carboxylic acids by the introduction of strongly electronegative groups, *e.g.*, as in passing from acetic acid through the chloroacetic acids to trichloroacetic acid, a strong acid.) In the symmetrical hydrogen bonds stabilizing the dimeric acids the weakening effect of a diminished effective negative charge on the electron donor oxygen, produced by the inductive effect of electronegative substituents, must then be largely compensated by a coördinated increase in the polarity of the hydroxyl group with which it interacts. This prediction of effective constancy in the strength of the hydrogen bonds in dimeric acids is plainly in complete accord with the data on the heats of vapor phase dimerization listed in the last column of Table II; it is equally concordant with electron diffraction data indicating[4] constancy of the O–H—O bond distance in the dimers of acids as different as acetic acid and trifluoroacetic acid; and it is manifestly the antithesis of the conclusion drawn by Maryott, Hobbs and Gross.

An explanation of the observed trend in the dimer dissociation constants of the aliphatic acids in terms of the conjectural existence of a corresponding trend in the strengths of the hydrogen bonds maintaining the dimer molecules seems inadmissible. The trend of the dimer dissociation constants must, therefore, arise in a coördinated trend of the entropies of dimerization. We have made a preliminary examination of the possibility that this entropy effect arises simply from the variation of the masses and moments of inertia of the various

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(7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944.

carboxyl substituents. A calculation has been made of the variation in the apparent entropy of dimerization produced by variations in the translational and rotational entropy of dimerization for the several lower aliphatic acids—ignoring the contribution of the dimer ring vibrations, comprehensive data on which are unavailable. This calculation does not afford a satisfactory explanation of the variation in the observed entropies of dimerization. It seems improbable that the correlation of dimer dissociation constant with electronegativity of the carboxyl substituent is entirely fortuitous. Vapor phase data are available for relatively few acids, but solution phase studies have been carried out on a large number of substances; and Maryott, Hobbs and Gross' hypothesis that there is a correlation of dimer dissociation constant in a non-polar solvent with acid ionization constant in a polar solvent draws strength from the recently reported work of Barton and Kraus.[8] How the variation in electronegativity of the carboxyl substituents is effective in producing a coördinated variation in the entropy (and free energy) of dimerization is a question that can be resolved only by further study.

(8) B. C. Barton and C. A. Kraus, THIS JOURNAL, **73**, 4561 (1951).

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3-Thiapentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions[1]

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The following thermodynamic properties of 3-thiapentane were determined experimentally: heat capacity of the solid and liquid between 15 and 320°K., triple point (169.21°K.), heat of fusion (2845 cal. mole^{-1}), vapor pressure [$\log_{10} p = 6.92836 - 1257.833/(t + 218.662)$ (p in mm. and t in °C.)], heat of vaporization (8185, 7906 and 7591 cal. mole^{-1} at 324.70, 344.16 and 365.26°K., respectively, heat capacity of the vapor [$C^\circ_p = 2.76 + 9.4965 \times 10^{-2}\,T - 3.794 \times 10^{-5}\,T^2$ cal. deg.$^{-1}$ mole^{-1} (350 to 490°K.)], second virial coefficient of the vapor [$B = V - RT/P = -385 - 26.76 \exp(1250/T)$ cc. mole^{-1}], entropy of the liquid (64.36 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.), entropy of the vapor (90.43, 92.17 and 94.02 cal. deg.$^{-1}$ mole^{-1} at 324.70, 344.16 and 365.26°K., respectively) and the heat of formation [for the reaction: $4\text{C(graphite)} + 5\text{H}_2\text{(g)} + \text{S (rhombic)} = (\text{C}_2\text{H}_5)_2\text{S (liq)}$, $\Delta H^\circ_{298.16} = -28.5$ kcal. mole^{-1}]. The functions $-(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $H^\circ - H^\circ_0$, S° and C°_p were computed from spectroscopic and molecular structure data. Values of the height of the potential barriers hindering internal rotation, which were required for these calculations, were evaluated from the experimental entropy and heat capacity data. The heat, free energy and equilibrium constant of formation of 3-thiapentane were computed for selected temperatures up to 1000°K.

Because the alkane sulfides constitute one of the classes of organic sulfur compounds that occur in petroleum, selected members of that class have been included in the program of this Laboratory for studying the thermodynamic properties of sulfur compounds which occur in or are derivable from petroleum. Before this program was begun, the simplest alkane sulfide, 2-thiapropane (dimethyl sulfide), had been studied calorimetrically by Osborne, Doescher and Yost,[3] who obtained a value of the entropy of the vapor. Tables of the thermodynamic functions of 2-thiapropane were subsequently published by Barrow and Pitzer[4] and by Binder.[5] The first alkane sulfide studied in this Laboratory was the next higher homolog, 2-thiabutane (methyl ethyl sulfide). The results of that study, which included experimental values of the entropy and heat capacity of the vapor and calculated values of the thermodynamic functions, were the subject of a recent publication.[6] The present paper presents the results of a similar investigation of a third alkane sulfide, 3-thiapentane (diethyl sulfide). Successful development of a rotating-bomb calorimeter for determining the heats of combustion of organic sulfur compounds has made it possible to include in this paper an experimental value of the heat of formation of 3-thiapentane and tables of the heat, free energy and equilibrium constant of formation at selected temperatures.

Experimental

The experimental work described in the following sections consisted of calorimetric and vapor pressure studies of 3-thiapentane which yielded values of the heat capacity in the solid, liquid and vapor states, the heats of fusion and vaporization, the vapor pressure, the entropy of the liquid and vapor, and the heat of formation.

The Material.—The 3-thiapentane used for the experimental measurements consisted of a small sample of highly purified material and a larger sample of material of somewhat lower purity. These were purified at the Laramie Station of the Bureau of Mines as part of A.P.I. Research Project 48A. The sample of higher purity was used for low temperature studies and for measurements of the vapor pressure and heat of combustion. Its purity was determined during the low temperature studies by measuring the melting point as a function of the fraction melted. The

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(1) This investigation was performed as part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) Deceased.

(3) D. W. Osborne, R. N. Doescher and D. M. Yost, THIS JOURNAL, **64**, 169 (1942).

(4) G. M. Barrow and K. S. Pitzer, *Ind. Eng. Chem.*, **41**, 2737 (1949).

(5) J. L. Binder, *J. Chem. Phys.*, **18**, 77 (1950).

(6) D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **73**, 261 (1951).