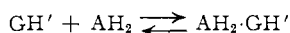


complexed chlorophyll, the mechanism leads to equation 1. In terms of this mechanism, K' of equation 1 is the dissociation equilibrium constant of the complex and K has the same significance as in mechanism A.

A mechanism essentially similar to C was suggested by Watson¹⁰ to explain certain observations on the quenching of the fluorescence of methanolic solutions of chlorophyll a or b by phenylhydrazine. The value of K' based upon the fluorescence quenching is 3×10^{-1} mole⁻¹, while that based upon the chlorophyll-sensitization of the methyl red oxidation of phenylhydrazine⁶ is 1×10^{-2} mole⁻¹. While there are obvious plausible interpretations of this difference, the data hardly warrant further speculation.

Qualitatively, all of the data are in agreement with the assumption that the sensitized molecules in their triplet, rather than their ground state, are in the equilibrium¹¹



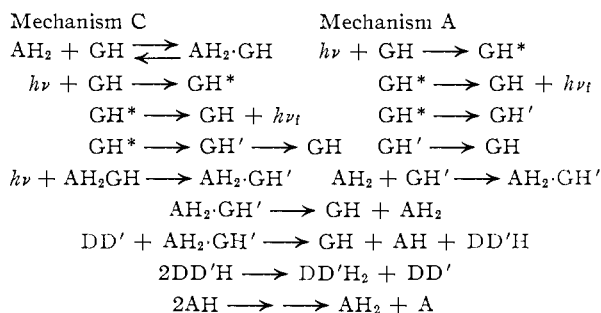
and that the reaction is due to collisions between this labile complex $\text{AH}_2 \cdot \text{GH}'$ and a dye molecule.

(10) W. F. Watson, *Trans. Faraday Soc.*, **48**, 526 (1952).

(11) Cf., Th. Foerster, *Z. Elektrochem.*, **54**, 42 (1950).

This mechanism leads to an equation consistent with the data obtained at higher, constant concentrations of the reducing agent. However, it does not fit the data of reference 6, particularly at low and variable phenylhydrazine concentrations, and for this reason probably should be rejected.

To summarize, the present more extensive data seem to be incompatible with the mechanism which Livingston and Pariser⁷ postulated for the chlorophyll a-methyl red-phenylhydrazine system. Of the remaining possibilities, either of the following alternative mechanisms appears to be equally consistent with the available data.



MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

The Vapor Phase Dissociation of Some Carboxylic Acids. III.¹ Trifluoroacetic Acid and Trifluoroacetic Acid-*d*^{2,3}

By MODDIE D. TAYLOR AND MALCOLM B. TEMPLEMAN⁴

RECEIVED FEBRUARY 15, 1956

The vapor phase dissociation of trifluoroacetic acid and trifluoroacetic acid-*d* has been studied in the pressure range below one-tenth atmosphere, and over the temperature range of 30 to 150°. The data are summarized by the equation: $\log_{10} K(\text{mm.}) = -3071/T + 10.869$ for trifluoroacetic acid, and $\log_{10} K(\text{mm.}) = -3042/T + 10.815$ for trifluoroacetic acid-*d*. The heats of dissociation for the two acids are 14,060 and 13,920 cal., respectively, and their equilibrium constants at 100° are 435 and 461. These data suggest that the hydrogen bond is somewhat stronger than the deuterium bond. In agreement with the observation of Professor Nash, trifluoroacetic acid is found to be dissociated to about the same extent as formic acid; but, contrary to his observations, the former is found to be dissociated to a much greater extent than acetic acid. The results of this study bring the data obtained by the vapor phase dissociation technique in agreement with that obtained from studies in solution.

In recent years, much interest has been exhibited in the association of molecules through the mechanism of hydrogen bonding. Many studies have been performed in both the vapor phase and in solution in an effort to establish the relationship between the strength of the hydrogen bond and the structure of the molecule. Though this relationship has been essentially established for the carboxylic acids, the question as to whether the order obtained by studies in solution is the same as that obtained by studies in the vapor phase is not settled. Nash,⁵ who made the most complete series of vapor

phase studies, finds that although his constants obtained by vapor phase dissociation studies are not inconsistent with the order of hydrogen bond strength predicted by studies in solution, the heats of dissociation obtained appear to be invariant for the different carboxylic acids.^{1,8} Heats of dissociation obtained by the present author, on the other hand, appear to give an order parallel to that indicated by studies in solution. One objective of this study was to determine whether the values for trifluoroacetic acid fall in line with the ones previously obtained in this series of studies for other acids.

Very few investigations have been performed to establish whether the hydrogen or deuterium bond is stronger. Studies made by Herman⁶ are probably insufficiently precise to permit a conclusive decision. They suggest that the deuterium bond is slightly stronger than the hydrogen bond. Studies

(1) Paper II, M. D. Taylor and J. Bruton, *THIS JOURNAL*, **74**, 4151 (1952).

(2) This investigation was supported by a grant from The American Academy of Arts and Sciences.

(3) Presented before the Division of Physical and Inorganic Chemistry, 129th National Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

(4) Taken from a dissertation submitted by Malcolm B. Templeman in partial fulfillment of the requirements for the M.S. degree in Harvard University.

(5) R. E. Lundin, F. E. Harris and L. K. Nash, *THIS JOURNAL*, **74**, 1651 (1952).

(6) R. C. Herman, *J. Chem. Phys.*, **8**, 256 (1940); R. C. Herman and R. Hofstadter, *ibid.*, **6**, 531, 534 (1938).

by Professor Hildebrand⁷ of hydrogen fluoride and of deuterium fluoride yielded a heat of association for DF which is 300 cal. higher than that for HF, assuming the association occurs according to the equation $6\text{HF} \rightleftharpoons (\text{HF})_6$. This suggests that the deuterium bond might be 50 cal. stronger than the hydrogen bond. Since the mechanism of dissociation proposed is merely the principal reaction occurring (the authors admit that other polymers than $(\text{HF})_6$ may be present), the certainty of these results cannot be regarded as completely established. A second purpose of this research was to determine whether any difference exists between the extent of dissociation of trifluoroacetic acid and tri fluoroacetic acid-*d*.

Experimental

Method and Apparatus.—The apparatus, method of analysis, procedure of measurement, and method of calculation have been discussed elsewhere.⁸ In these studies it was found that the precision of the analytical technique was insufficient to give the proper P_0 except in fortuitous cases. In most cases the proper P_0 was obtained by a method of approximations.⁹ The slope of improper lines is very sensitive to small changes in P_0 , but the slope of proper lines is affected very little by such changes.

Purification of Trifluoroacetic Acid.—Trifluoroacetic acid¹⁰ was distilled in a Todd fractionating column and boiled at 71.8° (cor.). Swarts¹¹ reports a boiling point of 72.4°. It was further purified by fractional freezing, according to the method of Ritter and Simons,¹² and finally purified by fractionation in the vacuum line. The purified acid exhibited a vapor pressure of 28.75 mm. at 0° and of 10.2 mm. at its triple point. It froze extremely sharply just below its melting point.

Preparation and Purification of Trifluoroacetic Acid-*d*.—One hundred grams of trifluoroacetic acid was treated with 100 g. of P_2O_5 and the mixture heated. The product was distilled directly through a Todd fractionating column and trifluoroacetic anhydride came over at 39.0° (cor.). Stacy¹³ reports a boiling point of 39.0°. The anhydride (65.6 g.) was obtained for a yield of 71%. A second preparation gave about the same yield. No attempt was made to obtain a high yield since a high purity was our main interest. Eighty grams of the anhydride was treated slowly with 5.1 g. of 99.8% pure D_2O . A very vigorous reaction took place immediately with the evolution of considerable heat. Excess anhydride was distilled away. The trifluoroacetic acid obtained was distilled through the column and boiled at 71.2° (cor.). The pure acid had a vapor pressure of 29.62 mm. at 0° and 9.83 mm. at its triple point.

TABLE I

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
-9.1	15.48	40.3	224.1
-4.7	21.24	50.4	353.0
-4.3	21.30	60.9	516.7
0.0	28.75	65.3	599.6
9.9	50.63	65.4	601.1
19.5	84.08	71.5	749.0
29.9	135.6		

Near b.p. $\log P_0(\text{mm.}) = -1737/T + 7.915$. Over most of middle range $\log_{10} P(\text{mm.}) = -1895/T + 8.389$. Near f.p. $\log P(\text{mm.}) = -1986/T + 8.723$.

(7) R. W. Long, J. H. Hildebrand and W. E. Morell, *THIS JOURNAL*, **65**, 182 (1943).

(8) M. D. Taylor, *ibid.*, **73**, 315 (1951).

(9) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

(10) Thanks are extended to the Minnesota Mining and Manufacturing Co., St. Paul 6, Minn., and to the Columbia Organic Chemicals Co., Inc., for supplying free of charge, the trifluoroacetic acid used in this investigation.

(11) F. Swarts, *Bull. classe sci. Acad. roy. Belg.*, **8**, 343 (1922).

(12) H. L. Ritter and J. H. Simons, *THIS JOURNAL*, **67**, 757 (1945).

(13) M. Stacy, *et al.*, *J. Chem. Soc.*, 2977 (1949).

Results and Discussion

Complete vapor pressure studies have been made for both acids. The data are summarized in Tables I and II. A summary of properties de-

TABLE II

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
-9.3	16.62	35.2	183.2
-6.3	20.17	40.8	225.6
-4.6	22.54	45.9	293.2
0.0	29.62	50.0	347.2
4.5	38.39	54.4	411.4
10.3	53.59	59.3	484.8
14.6	67.67	59.8	504.4
19.4	87.15	64.8	602.0
24.5	113.5	69.7	721.5
30.3	140.7	72.9	802.5

Near b.p. $\log_{10} P(\text{mm.}) = -1781/T + 8.056$. Over most of middle range $\log_{10} P(\text{mm.}) = -1843/T + 8.240$. Near f.p. $\log_{10} P(\text{mm.}) = -1937/T + 8.566$.

rived from this data and other significant ones are given in Table III. Attention is called to the close

TABLE III

Property	F_2CCOOH	F_3CCOOD
Purity, %	99.9	99.8
B.p., °C. (meas.)	71.8	71.2
(calcd.)	71.9	71.3
F.p., °C. (lit.)	-15.6	...
(calcd.)	-15.6	-17.4
V.p., 0°C.	28.75	29.62
V.p. (triple pt.)	10.2	9.83
Heat of vap., (b.p.)	7949	8150
(calcd. per G.F.W.)	4568	4788
Heat of vap., (av.)	8672	8435
(calcd. per G.F.W.)	4360	4239
Heat of vap., (f.p.)	9088	8864
(calcd. per G. F. W.)	4776	4454
Degree of dissoc., (b.p.)	0.1722	0.1750
Degree of dissoc., (35°)	.0511	.0535
Degree of dissoc., (f.p.)	.00544	.00523
Apparent mol. wt., g. (b.p.)	194.6	195.8
Apparent mol. wt., (35°)	217.0	218.4
Apparent mol. wt., g. (f.p.)	226.8	228.9
dT/dP , (b.p.), deg./mm.	0.039	0.038
B.p. of trifluoroacetic anhydride	39.0 (cor.)	

TABLE IV

t , °C.	P (mm.)	P_i (mm.)	α	K (mm.)
33.1	27.88	22.70	0.2282	6.126
40.5	30.02	23.25	.2912	11.12
49.5	32.73	23.92	.3683	20.56
60.0	36.37	24.70	.4725	41.80
69.9	39.96	25.43	.5714	77.49
80.0	43.59	26.18	.6650	138.3
91.0	47.38	26.99	.7555	251.9
100.3	50.33	27.68	.8183	408.0
110.7	53.29	28.45	.8731	683.6
120.2	55.68	29.16	.9095	1065
129.9	57.84	29.88	.9357	1628
140.2	59.97	30.64	.9573	2626
149.8	62.11	31.35	.9812	6412

TABLE V
 SUMMARY OF DISSOCIATION STUDY III, CF₃COOD

<i>t</i> , °C.	<i>P</i> (mm.)	<i>P</i> ₁ (mm.)	α	<i>K</i> (mm.)
30.4	26.78	21.89	0.2236	5.634
41.1	29.57	22.66	.3049	12.13
50.6	32.72	23.34	.4019	25.21
60.3	36.02	24.04	.4983	47.59
70.0	39.46	24.74	.5950	86.49
80.3	43.05	25.49	.6889	155.5
90.7	46.54	26.24	.7736	277.5
99.9	49.18	26.90	.8283	429.8
110.7	52.17	27.68	.8848	775.2
120.4	54.46	28.38	.9190	1183
130.1	56.48	29.11	.9402	1721
140.5	58.68	29.83	.9672	3399
149.7	60.71	30.48	.9918	14660

$P_0 = 19.70$, $\Delta H = 13,920$ cal. Equation of line
 $\log_{10} K = -3042/T + 10.803$.

for lines in these three regions are given in the tables containing vapor pressure data. The heats of vaporization as ascertained directly from the curves and as computed for a formula weight are listed in Table III. It is interesting that trifluoroacetic acid-*d* has a lower heat of vaporization at its freezing point, but a higher heat of vaporization at its boiling point than does the ordinary acid. The heat of vaporization data are estimated to be accurate to ± 100 cal. The values for the degree of dissociation and the apparent molecular weight are calculated on the assumption that the pressure is 760 mm.

A typical study for trifluoroacetic acid is shown in Table IV and one for trifluoroacetic acid-*d* is shown in Table V. Fourteen such studies were performed for the former and eight for the latter. Complete data for the other studies are listed else-

 TABLE VI
 SUMMARY OF DATA FOR TRIFLUOROACETIC ACID

Study	P_0^a (mm.)	$-A^b$	B^b	ΔH (cal.)	K_{75} (mm.)	K_{100} (mm.)	K_{150} (mm.)
I	19.47	3060	10.849	14,003	114.3	444.6	4140
II	24.76	3091	10.938	14,149	114.3	450.8	4286
III	25.00	3068	10.860	14,040	111.2	434.5	4065
IV	21.92	3086	10.912	14,122	111.5	438.5	4150
V	19.54	3003	10.651	13,741	105.7	400.9	3573
VI	18.64	3114	11.008	14,250	115.5	459.2	4446
VII	20.25*	3071	10.834	14,053	102.3	401.9	3767
VIII	20.63	3060	10.814	14,003	105.4	410.2	3820
IX	22.81	3092	10.952	14,149	117.2	462.4	4405
X	12.27*	3006	10.688	13,761	113.0	428.6	3846
XI	15.75*	3096	10.950	14,167	113.8	449.8	4325
XII	10.48	3080	10.901	14,099	113.0	442.6	4179
XIII	26.34	3059	10.839	13,999	112.2	436.5	4065
XIV	22.96	3114	10.975	14,250	106.9	425.6	4121
Av.		3071.4	10.869	14,056	111.2	434.7	4084.9
P.E. (mean)				25	0.8	4.0	46
%P.E. (mean)				0.18	0.72	0.91	1.12

Eq. which summarizes data $\log_{10} K(\text{mm.}) = -3071/T + 10.869$

^a Pressure of dimer at 0°; starred values were measured. ^b Constants in the equation $\log_{10} K = -A/T + B$.

 TABLE VII
 SUMMARY OF DATA FOR TRIFLUOROACETIC ACID-*d*

Study	P_0 (mm.)	$-A$	B	ΔH (cal.)	K_{75} (mm.)	K_{100} (mm.)	K_{150} (mm.)
I	19.46	3002	10.689	13,737	115.9	440.5	3909
II	18.14	2986	10.644	13,664	116.1	438.5	3846
III	19.70	3042	10.803	13,920	115.6	446.7	3998
IV	22.12	3040	10.806	13,911	118.0	456.0	4160
V	24.20	3093	10.994	14,154	128.2	507.0	4809
VI	19.60	2994	10.658	13,701	114.0	429.5	3820
VII	19.29	3085	10.954	14,117	125.0	484.2	4581
VIII	20.00	3092	10.970	14,163	122.2	482.0	4592
Av.		3041.8	10.8148	13,920.9	119.4	460.6	4214
P.E. (mean)				49	1.2	6.4	99
% P.E. (mean)				0.3544	1.024	1.397	2.336

Eq. which summarizes data $\log_{10} K(\text{mm.}) = -3042/T + 10.815$

correlation between the measured and calculated boiling points and freezing points of trifluoroacetic acid. Heats of vaporization, and other values not measured directly, were calculated from the plot of $\log P$ versus $1/T$ for the vapor pressure data. Such curves were essentially linear over most of the middle range but curved slightly downward near both the boiling and freezing points. Equations

where.¹⁴ Plots of $\log K$ versus $1/T$ yielded essentially straight lines, usually with some curvature at the top where the sample was nearly completely dissociated. The results of these studies are summarized in Tables VI and VII. In Table VIII, ΔH , K_{100} , ΔF_{100} and ΔS have been compiled. The data suggest that the deuterium bond is

(14) M. B. Templeman, Master's Thesis, Howard University, 1956.

weaker than the hydrogen bond by slightly more than 100 cal. in ΔH and of *ca.* 50 cal. in ΔF . This conclusion is supported by the higher vapor pressure and the higher heat of vaporization of trifluoroacetic acid-*d* at its boiling point. A possible explanation of the increased strength of the hydrogen bond over that of the deuterium bond lies in the larger volume of the latter, which would result in a much smaller charge density for it. Since the energy of the hydrogen bond is believed to be derived mainly from electrostatic attraction, the weaker deuterium bond is expected.

In Table VIII, the relative order of hydrogen bond strength of the carboxylic acids as measured

TABLE VIII

COMPARISON OF DISSOCIATION DATA OBTAINED FROM SOLUTION STUDIES, AND FROM VAPOR PHASE STUDIES BY TAYLOR

Acid	In benzene		In vapor phase	
	K_d at 30°	K_{100} (mm.)	ΔF_{100} (cal./mole)	ΔH (cal./mole)
F ₃ CCOOH	..	435	415	14,050
Cl ₃ CCOOH	8.8
Formic	7.1	301	686	14,110
Acetic	2.4	92.0	1570	15,270
Propionic	2.3	88.6	1594	15,175

in solution,¹⁵ and as measured in the vapor phase by this investigator are compared. This order is found to be identical with that obtained by Mayotte, Hobbs and Gross¹⁵ and supports their statement: "Other factors being equal, any substituent which, either by inductive or resonance effects, tends to draw electrons away from the carbonyl group and thereby make the effective charge on the oxygens less negative should weaken the hydrogen bond responsible for association." As has been observed before, it appears that the stronger the carboxylic acid the weaker is the hydrogen bond. One would expect that drawing electrons away from the carboxyl group could, in addition to

(15) A. Maryotte, M. E. Hobbs and P. M. Gross, *THIS JOURNAL*, **71**, 1673 (1949).

weakening the hydrogen bond (by making the charge on the oxygen less negative), also strengthen the bond (by increasing the positive charge on the OH hydrogen). Since this strengthening effect takes place to a very small extent, if at all, one must assume that the positive charge on any hydrogen in a carboxyl group is already close to its maximum value.

Data in Table IX show excellent agreement between the values for trifluoroacetic acid obtained

TABLE IX

A SUMMARY OF SIGNIFICANT THERMODYNAMIC PROPERTIES OF ACIDS STUDIED

	A	B	K_{100} ^o (mm.)	ΔF_{100} ^o cal./mole	ΔH , cal./mole	ΔS_{100} , cal. mole ⁻¹ deg. ⁻¹
F ₃ CCOOH	-3072	10.869	435	415	14,050	36.5
(by Nash)	-3053	10.800	414	449	13,971	36.2
F ₃ CCOOD	-3042	10.815	461	370	13,920	36.3

by Nash and those obtained in this investigation. Failure of such agreement in the case of acetic acid⁸ is difficult to understand, as is also the essential constancy of the values for the heat of dissociation for all the acids studied by Nash. Confidence in the results obtained in this series of studies is increased by the findings of Weltner¹⁶ that the thermodynamic constants that we obtained for acetic acid (measured under the same conditions and with the same apparatus used in this study) were essentially in agreement with those determined by him using a completely different procedure.

The precision of the data reported in this investigation is believed to be as follows. For trifluoroacetic acid: ± 100 cal. in the heat of dissociation with a probability of greater than 95%; ± 10 in K_{100} with a probability of greater than 90%. For trifluoroacetic acid-*d*: ± 100 cal. in the heat of dissociation with a probability of greater than 80%; ± 10 in K_{100} with a probability of greater than 70%.

(16) W. Weltner, *ibid.*, **77**, 3941 (1955).

WASHINGTON, D. C.

[CONTRIBUTION NO. 1337 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermoelectric Properties of Metal-Ammonia Solutions. II. The Thermoelectric Power of Sodium and Potassium Solutions at -78° and the Effect of Added Salt on the Thermoelectric Power of Sodium at -33°

BY GERARD LÉPOUTRE AND JACOB F. DEWALD¹

RECEIVED OCTOBER 7, 1955

Measurements of the thermoelectric power of sodium and potassium solutions in liquid ammonia at -78° and of mixed sodium-sodium chloride solutions at -33° are reported. The results in dilute solution show an anomalously large dependence of thermoelectric power on temperature and on concentration of salt, as well as a small but significant dependence on the nature of the metal ion.

Introduction

The first paper in this series² reported on the thermoelectric power of solutions of sodium and potassium in liquid ammonia at -33° . While the data at high concentration were in remarkably

good accord with present day ideas of the nature of these solutions, an anomalously large concentration dependence of thermoelectric power was observed in the concentration region below 0.1 molar. In this latter region the data for sodium were essentially indistinguishable from those for potassium solutions. The present paper reports our in-

(1) Bell Telephone Laboratories, Murray Hill, N. Y.

(2) J. F. Dewald and G. Lepoutre, *THIS JOURNAL*, **76**, 3369 (1954).