[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

An Electron Diffraction Investigation of the Monomers and Dimers of Formic, Acetic and Trifluoroacetic Acids and the Dimer of Deuterium Acetate[1]

BY J. KARLE[2] AND L. O. BROCKWAY

Introduction.—Recent spectroscopic studies[3,4] of the monomers and dimers of formic and acetic acids have indicated that the carbon to oxygen distances in the carboxyl group are not equal. Since an early electron diffraction study[5] on formic acid indicated equal carbon to oxygen distances, a repetition of the original study was suggested. In addition to this problem there arises the question concerning what changes, if any, occur in the monomers of the acids on association.

Robertson and Ubbelohde[6] studied the structure of deuterated oxalic acid dihydrate and observed an increase in length of the crystallographic unit cell in the direction of the hydrogen bridge. If the increase is located only in the bridge portion of the molecule, it would correspond to an expansion of the hydrogen bond of 0.044 Å. on substituting deuterium for hydrogen. Since an isotope effect in the dimer of acetic acid of 0.04 Å. might be detected by an electron diffraction investigation, the structure of the dimer of deuterium acetate was investigated.

Trifluoroacetic acid is a very strong acid whereas acetic acid is moderately weak. It was considered interesting therefore to attempt to observe a change in the acetic acid structure introduced by a trifluoromethyl group.

Experimental.—The method of obtaining electron diffraction photographs and a description of the apparatus have been given.[7]

Theoretical intensity curves were calculated using the formula

$$I(s) = \sum_{i}\sum_{j} Z_i Z_j (\sin sr_{ij})/sr_{ij}$$

where $s = 4\pi\sin(\theta/2)/\lambda$. The structural parameters determined were compared to those obtained from radial distribution curves calculated by the Walter and Beach[8] formula assuming a_k, the approximate half width of the maxima and minima, to be 0.7 s unit.

In order to study the monomers of the acids, an apparatus was required for photographing the equilibrium vapor at approximately 150°. This was accomplished by means of a 500-ml. glass container and a nozzle which could be heated independently to the desired temperature. In the nozzle, the copper tube through which the vapor flows was heated by a spiral winding of resistance wire insulated by a Pyrex tube with beads fused on for spacing the turns of wire. The large glass container was heated by means of an electric oven.

An interesting feature of this apparatus is the type of vacuum seal used. The glass to metal tapered joint, which is employed for room temperature studies, was not used because of the danger of breakage and leakage at the higher temperatures. Instead, the seal was produced by attaching the upper end of the container which consisted of a flat, well ground ring of glass, whose inner and outer radii differed by about 5 mm., to a flat metal surface on the bottom of the nozzle. Between the glass and metal surfaces a very useful high temperature vacuum grease was employed. This grease, made from aluminum stearate and SAE 50 motor oil, is described by Puddington.[9] It also was used to lubricate the stopcock on the container of vapor and a vacuum was conveniently maintained at 160°. No attempt was made to reach higher temperatures.

The degree of dissociation of the dimer at the elevated temperature was calculated from T_1 (the observed room temperature), p_1 (the total pressure at T_1), K_1 (the equilibrium constant at T_1), ΔH (the heat of dissociation assumed constant over the temperature range) and T_2 (the temperature of the diffraction measurements). The equilibrium constants and heats of dissociation for formic and acetic acids were taken from the work of Coolidge[10] and MacDougall[11]; the equilibrium constant for trifluoroacetic acid was determined from the vapor density measurements described below and its heat of dissociation was assumed to be the same as that for acetic acid. Table I gives the dissociation data for the three acids.

TABLE I

F = Formic, A = acetic and T = trifluoroacetic acids.

Acid	T_1, °K.	P_1, mm.	K_1, mm.	ΔH, kcal.	T_2, °K.	P_2, mm.	K_2 $\times 10^{-3}$, mm.	α
F	303	22.5	3.6	14	403	48	1.13	0.93
A	303	21.0	0.7	16	416	50	0.95	0.91
T	305	22.5	5.0	16	390	46	1.56	0.95

These calculations are necessarily approximate in character due to the assumptions involved in employing the formulas. However, the small contribution to the electron scattering of the long distances occurring in the dimer are negligible for the amounts of the dimers indicated above. Also, the degree of dissociation which appears in Table I is the one for the first exposure and the dissociation for successive photographs must continuously increase since the total pressure in the system is decreasing. An average of fifteen exposures were taken from a single sample in the container. Since no detectable difference was observed between the first and last photographs of any of the monomers, it is therefore concluded that the dimer makes a negligible contribution to the scattering in these high temperature experiments.

No dissociation data for the vapor of trifluoroacetic acid could be found in the literature. Experiments were therefore performed to obtain a value corresponding to the conditions of the diffraction study. Since the intensity curves are not sensitive to differences in dissociation of one or two per cent., no attempt was made to make very precise measurements. The apparatus used was a two-liter bulb which could be filled to a measured pressure with vapor from a weighing bottle. The temperature was room temperature and α, the degree of dissociation, was calcu-

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(1) This paper is based upon the thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Faculty of the Graduate School of the University of Michigan by J. Karle. For supplementary tables order Document 1807 from American Documentation Institute, 1719 N St., N. W., Washington, D. C., remitting 50¢ for microfilm or 60¢ for photoprints.

(2) Present address: University of Chicago, Chicago, Illinois.

(3) L. G. Bonner and R. Hofstadter, *J. Chem. Phys.*, **6**, 531 (1938).

(4) M. M. Davies and G. B. Sutherland, *ibid.*, **6**, 755 (1938).

(5) Pauling and Brockway, *Proc. Natl. Acad. Sci.*, **20**, 336 (1934).

(6) J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc.* (London), **A170**, 222 (1939).

(7) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(8) J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940).

(9) I. E. Puddington, THIS JOURNAL, **65**, 990 (1943).

(10) A. S. Coolidge, *ibid.*, **50**, 2166 (1928); **52**, 1874 (1930).

(11) F. H. MacDougall, *ibid.*, **58**, 2585 (1936).

lated using the perfect gas law. The uncertainty is estimated to be within 20% of the average of the values obtained in Table II.

TABLE II

Expt.	P, mm.	V, ml.	T, °K.	w, g.	α
1	97.35	2128	300.5	2.3013	0.10
2	89.15	2128	299.0	2.1181	.10
3	100.40	2129	302.5	2.3215	.11
4	103.20	2128	302.5	2.3896	.11

The first two experiments were performed after a single vacuum distillation and the last two were performed on samples which were also pumped through phosphorus pentoxide.

Formic Acid Monomer.—The formic acid was prepared by passing hydrogen sulfide over the lead salt. It was further purified by the fractional vaporization method of Coolidge.[10] With regard to the question of possible decomposiion at the temperature of the experiment for the monomer, a set of photographs were taken and then the container was allowed to cool. About four hours later another series of photographs were taken at the high temperature. No change in patterns was observed indicating no significant decomposition.

A total of nineteen models were studied in which the longer carbon to oxygen distance (C—O) varied from 1.29 to 1.45 Å., the shorter carbon to oxygen distance (C=O) varied from 1.22 to 1.29 Å. and the enclosed angle (O—C=O) varied from 115 to 130°. Figure 1 represents a plot of C—O/C=O ratios *versus* the O—C=O angle, the range of uncertainty being enclosed within the dotted lines and the scale is fixed by setting C=O equal to 1.22 Å. in model K, equal to 1.24 Å. in models A, B, C, D, E, J, L and M, equal to 1.25 Å. in models I, N, O, Q and R, equal to 1.27 Å. in models P and S and equal to 1.29 Å. in models F, G and H. Figure 2 shows some of the corresponding intensity curves. All the curves except those marked with an *h* neglect the scattering due to the hydrogen distances in the molecule. In curves Ah and Bh, the C-H distance was assumed to be 1.09 Å. and the O-H distance to be 0.95 Å.

Curves A and B compare quite favorably with the observed features of the photographs. They contain an O—C=O angle of 117° and C—O/C=O ratios of 1.40/1.24 and 1.43/1.24, respectively. It is observed by comparison with curves Ah and Bh that the introduction of scattering terms due to the hydrogen distances does not alter the positions of the maxima and minima although there is a small effect on the qualitative features which must be taken into consideration.

Model I, which is unsatisfactory, is interesting since it occurs as the structural unit of the dimer possessing an O—C=O angle of 121° and a C—O/C=O ratio of 1.36/1.25.

Two significant peaks were obtained in the radial distribution curve in Fig. 3, one at 1.33 Å. composed of the unresolved C—O and C=O distances and the second at 2.27 Å. representing the distance between the oxygen atoms.

TABLE III

OBSERVED AND CALCULATED MAXIMA AND MINIMA OF FORMIC ACID MONOMER

Max.	Min.	I_k	S_0	S_A/S_0	S_B/S_0
2		15	6.23	0.979	0.970
	3	− 9	8.00	0.994	0.975
3		8	9.25	1.038	1.016
4		10	11.29	1.019	1.010
	5	− 6	13.10	1.008	1.008
5		4	14.46	1.024	1.007
	6		16.06	1.009	0.990
6		2	17.32	1.003	.993
	7		18.92	0.995	.990
7		3	20.38		
			Average	1.008	0.995
			Average deviation	±0.013	.013

On the basis of the quantitative agreement indicated in Table III, the following model is chosen for the monomer of formic acid: C—O = 1.42 ± 0.03 Å., C=O = 1.24 ± 0.03 Å., and ∠ O—C=O = 117 ± 2°. The average of the carbon to oxygen distances chosen is 1.33 Å. and the oxygen to oxygen distance is 2.27 Å.

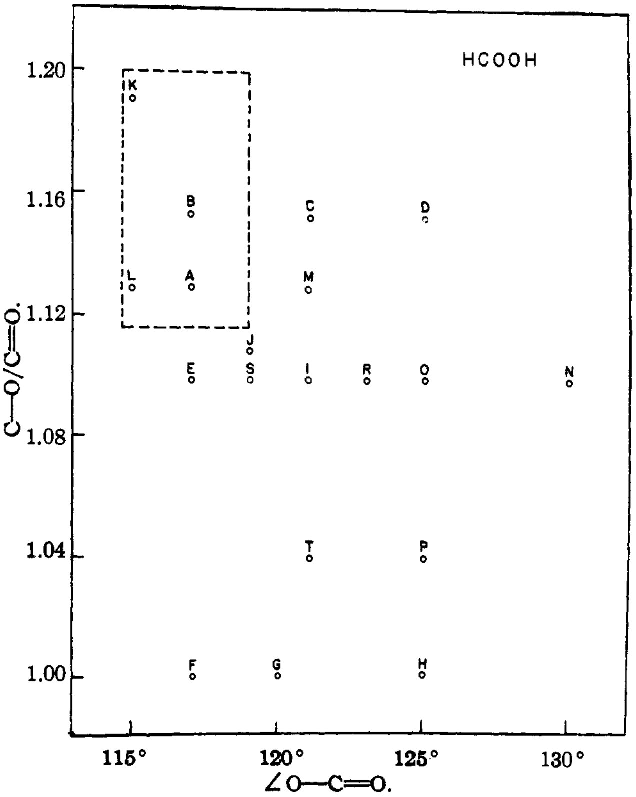


Fig. 1.—Models calculated for HCOOH. Dotted line encloses the models giving best agreement with the photographs.

Formic Acid Dimer.—In studying the dimer of formic acid, it was assumed from vapor density

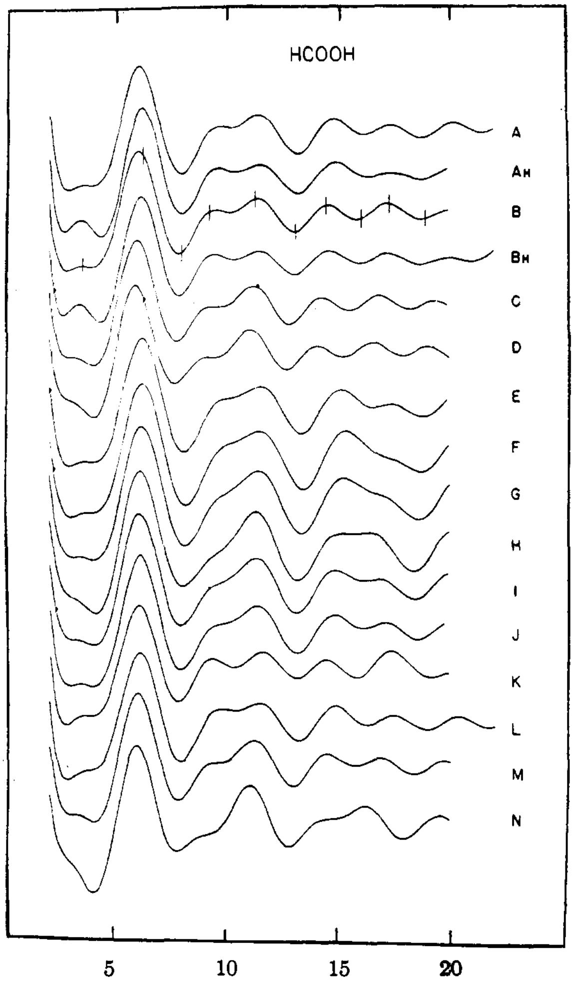
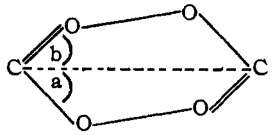


Fig. 2.—Calculated electron scattering curves for HCOOH.

data that the vapor striking the beam was 15% dissociated. Also, from dipole moment measurements,[12] it is indicated that the dimer has a center of symmetry. The molecule was assumed planar and to possess the following type of bridge



A total of twenty-four models were studied in which the C—O distance varied from 1.29 to 1.43 Å., the C═O distance varied from 1.24 to 1.29 Å., the OH—O distance varied from 2.65 to 2.80 Å., the O—C═O angle varied from 117 to 130° and angle *b* varied from 54 to 62.5°. Some of the intensity curves are reproduced in Fig. 4. The great complexity of a five parameter problem makes a complete survey prohibitive. It is believed however that the models considered lead to reasonable conclusions and limits of uncertainty.

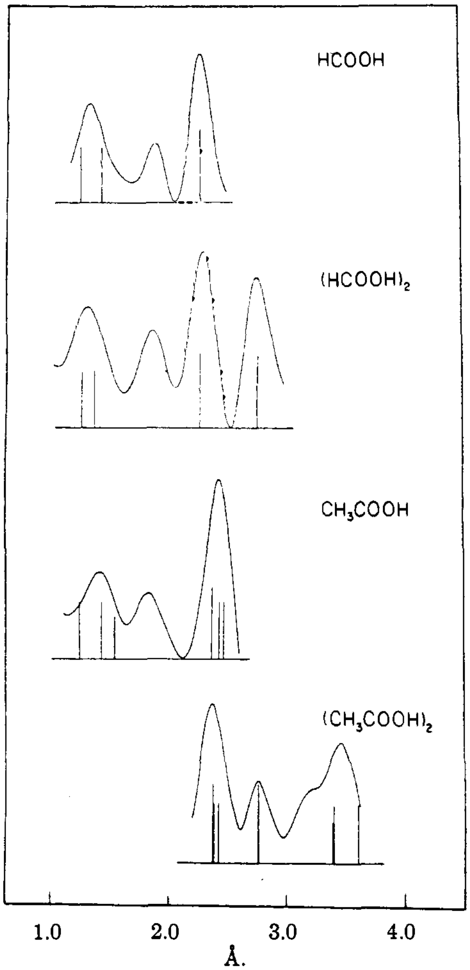


Fig. 3.—Radial distribution curves. The relative scattering powers associated with the interatomic distances are indicated by the heights of the vertical lines.

Models F and G which possess a C—O/C═O ratio of 1.36/1.25, angle O—C═O equal to 121° and angle *b* equal to 58°, are chosen as the best ones. Model F possesses an OH–O distance equal to 2.70 Å. whereas that of G is 2.76 Å. Models having equal carbon to oxygen distances, A, B and C, are unsatisfactory. Also unacceptable are models I and J which possess a C—O/C═O ratio comparable to that of the chosen monomer, 1.43/1.24.

Model B compares with the best model of Pauling and Brockway in which, however, they suggested 2.67 Å. instead of 2.65 Å. for the OH–O distance across the bridge. Better photographs and a study of a wider range of models account for a choice of structure different from that of model B.

The effect of a change of the OH–O distance to 2.65 Å., without changing the other parameters from their values in models F, is shown in curve

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[12] I. E. Coop, N. R. Davidson and L. E. Sutton, *J. Chem. Phys.*, 6, 905 (1938).

E. Curves D and K show the effect of making angle O—C═O 119° and 123°, respectively, the only change. A decrease of five per cent. from the value of the C—O/C═O ratio used in model F produces an almost negligible change in curve H although the latter model contains an oxygen to oxygen separation differing a little more from the radial distribution peak than that of model F.

The shape of the intensity curves is very sensitive to changes in angles *a* and *b*. Model L differs from G by a 2° change in these angles and the difference in appearance is striking. In model M these angle changes are accompanied by a change in the C—O/C═O ratio to 1.40/1.24 and in the OH-O distance to 2.74 Å.

Attempts to obtain a suitable model of the dimer from a structural unit based on the chosen monomer were unsuccessful.

Model N is interesting since it is based on the most suitable model for the dimer of acetic acid which has an O—C═O angle of 130°. A comparison of curves N and Nh shows the negligible effect of including the scattering due to hydrogen distances in the theoretical intensity curves.

The significant maxima in the radial distribution curve in Fig. 3 occur at 1.30 Å. composed of the unresolved C—O and C═O distances, at 2.30 Å. representing the O-O distance and at 2.75 Å. representing the OH-O distance.

On the basis of the quantitative results in Table IV, the following model is chosen for the dimer of formic acid C—O = 1.36 ± 0.04 Å.; C═O = 1.25 ± 0.03 Å.; ∠ O—C═O = 121 ± 2°; O—H—O = 2.73 ± 0.05 Å.: ∠ b = 58 ± 1°. In the previous investigation[5] the two C-O distances were reported equal at 1.29 Å.

TABLE IV

OBSERVED AND CALCULATED MAXIMA AND MINIMA OF FORMIC ACID DIMER

Max.	Min.	I_k	S_0	S_F/S_0	S_G/S_0
	2	−15	4.84		
2		15	5.87	0.993	0.983
	3		(6.62)		
3			(7.22)		
	4	− 8	8.42	0.994	0.988
4		8	9.61	1.000	0.987
	5	− 4	10.29	1.005	0.997
5		9	11.32	1.000	0.996
	6	−10	13.12	1.021	1.016
6		4	14.56	1.013	1.000
	7	− 3	15.64	1.007	0.991
7		3	16.71	0.998	0.981
	8		18.39	0.998	0.995
			Average	1.003	0.993
			Average deviation	±0.006	.007

Acetic Acid Monomer.—The acetic acid was made by the General Chemical Company and assayed at 99.5%. A melting point determination verified this figure and so no further purification was attempted.

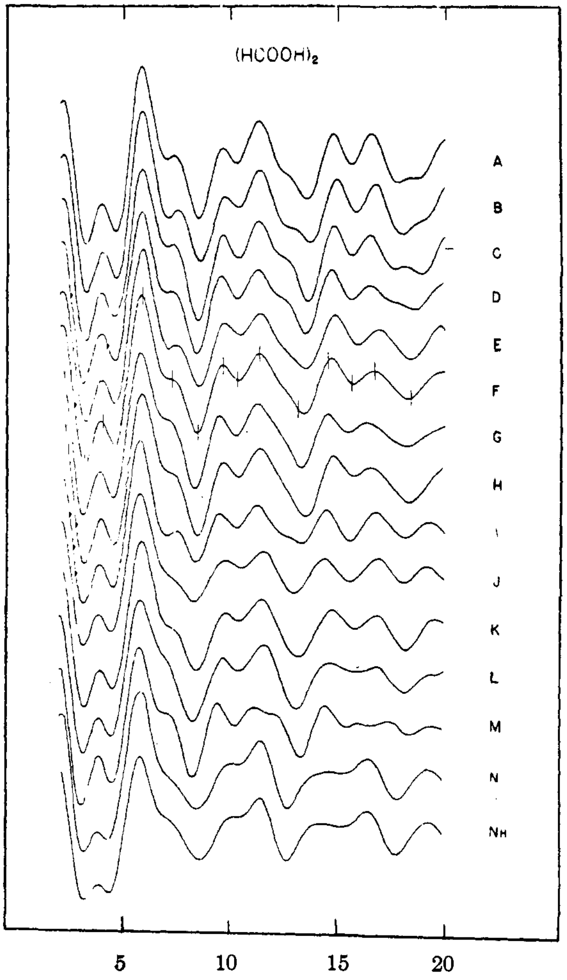

Fig. 4.—Calculated scattering curves for (HCOOH)₂.

In studying the structure of the monomer of acetic acid, the carbon and oxygen atoms were assumed to be coplanar. In the twenty models calculated the parameter ranges considered were: C—C, 1.48 to 1.54 Å.; C—O, 1.29 to 1.43 Å.; C═O, 1.22 to 1.29 Å.; O—C═O, 120° to 140°; C—C═O, 110° to 130°. Figure 5 reproduces some of the intensity curves.

Curves H, L, I and N are qualitatively acceptable intensity curves and possess the following respective values of the O—C═O and C—C═O angles: H (125°, 125°); L (127°, 123°); I (130°, 120°); N (135°, 115°). In each the C—O/C═O ratio is 1.43/1.24 and the C—C distance is 1.54 Å. A little less satisfactory are J (125°, 120°) and K (130°, 115°) with the bonded distances unchanged. and M (125°, 125°) with C—O/C═O equal to 1.40/1.24. No satisfactory intensity curve could be obtained with an O—C═O angle as low as 120°, illustrated by models A, B, P and Q. Curve R, the only one calculated with an O—C═O of 140°, is also unacceptable. Models C, D, E, F and O show the reversed intensities

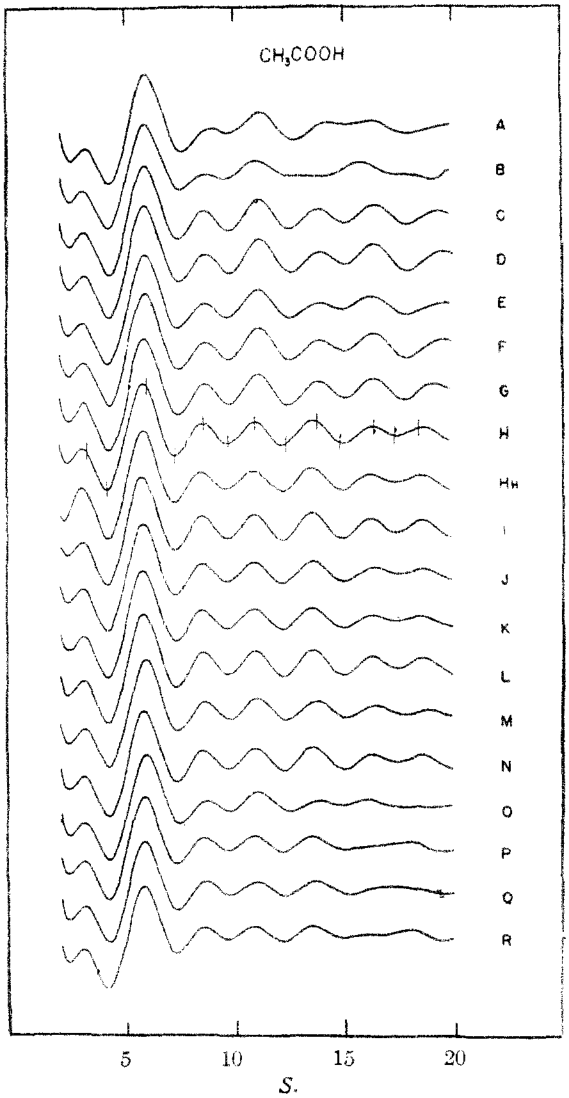

Fig. 5.—Calculated scattering curves for CH_3COOH.

produced by C—O/C═O ratios varying from 1.29/1.29 to 1.36/1.25 with the other parameters similar to those of the more acceptable curves. Model G, based on the structural unit of the dimer of acetic acid is also unsatisfactory because of the reversed relative intensities of some of the peaks.

A comparison of curves A and B shows the effect of changing the C—C distance from 1.48 to 1.54 Å. It is noted that the intensity curves are rather sensitive beyond the fourth maximum to changes in the C—C distance.

A comparison of curve H with Hh, which includes all of the hydrogen distances based on a structure with a tetrahedral arrangement of the CH_3 group, shows that the effect on the curves of neglecting the non-bonded hydrogen distances is negligible.

Since no sharp distinction is possible between the favorable curves, the values of the C—C═O and O—C═O angles must be considered very uncertain. In the acceptable range the monomer of acetic acid has its three longer distances arranged in an approximately equilateral triangle. Since, in calculating the intensity curves, two of the coefficients for the scattering terms are the same for these long distances and the third is only three halves larger, changes in the bond angles necessarily alter the resultant curves only very slightly.

The radial distribution curve for the monomer of acetic acid in Fig. 3 shows a rather broad peak at 1.41 Å. and thus the C—O, C═O and C—C distances are not resolved. Also unresolved are the longer carbon to oxygen distances and the oxygen to oxygen distance as shown by the largest peak which occurs at 2.43 Å. In this case the radial distribution curve is of no aid in fixing the structure of the molecule.

The following values are obtained for the structure of the monomer of acetic acid: C—O = 1.43 ± 0.03 Å.; C═O = 1.24 ± 0.03 Å.; ∠ O—C═O = 122–138°; C—C = 1.54 ± 0.04 Å.; ∠ C—C═O = 113–128°.

Table V shows that these values, based on the qualitatively acceptable curves, are in agreement with the quantitative results.

Table V

Observed and Calculated Maxima and Minima of Acetic Acid Monomer

Max	Min.	I_k	S_0	S_H/S_0	S_I/S_0
2		15	5.96	0.978	0.973
	3	−10	7.29	1.000	1.000
3		9	8.57	1.000	0.991
	4	− 5	9.74	0.996	0.996
4		9	10.91	1.003	1.003
	5	− 6	12.45	0.994	0.994
5		5	13.82	0.986	0.984
	6		14.89	1.007	1.007
6		3	16.40	0.997	0.994
	7		17.36	1.010	1.010
7		3	18.46	1.010	1.010
			Average	0.998	0.997
			Average deviation ±	.007	.009

Acetic Acid Dimer.—The association of acetic acid is assumed to involve the same type of coupling of single molecules as occurs in formic acid. It was also assumed that all four carbon atoms were on the same axis, since in a test an angular displacement of the methyl group through 7° made only a small change in the calculated intensity curves (M and N). The vapor striking the beam was considered to be 9% dissociated.

In the seventeen models calculated the parameter ranges considered were: C—C, 1.48 to 1.54 Å.; C—O, 1.29 to 1.43 Å.; C═O, 1.22 to 1.29 Å.; OH—O, 2.67 to 2.82 Å.; O—C═O, 120° to 130°; *b*, 55 to 65°. Some of the intensity curves appear in Fig. 6.

Model H is chosen as the best one possessing an O—C═O angle of 130°, an angle *b* of 60°, an

OH-O distance of 2.76 Å., a C-C distance of 1.54 Å. and a C—O/C═O ratio of 1.36/1.25. Models J and K with a ratio of 1.43/1.24 are unsatisfactory as are models A, B, C and D with equal carbon to oxygen distances and O—C═O angles ranging from 120 to 130°. Model G differs from H in possessing an OH-O distance 0.06 Å. smaller and model I possesses an OH-O distance 0.06 Å. larger. A comparison of curves F and G wherein the ratios are 1.32/1.27 and 1.36/1.25, respectively, shows only slight sensitivity to changes of the carbon to oxygen distances over this range.

Model E differs from F and model L differs from J in possessing an O—C═O angle of 125° instead of 130°. The difference in intensity curves produced is striking.

Model N is based on the most suitable model for the dimer of formic acid and is observed to produce a very unsatisfactory intensity curve.

The calculated models contain the bonded hydrogen distances whose lengths were assumed to be the same as applied to the monomer of formic acid. Curve Hh contains all the distances due to the hydrogen atoms and may be compared with curve H. A negligible difference is observed.

The radial distribution curve for the dimer of acetic acid in Fig. 3 contains only one useful peak. It is the relatively small one at 2.76 Å. corresponding to the OH—O separation across the bridge.

The structure chosen for the dimer of acetic acid in agreement with the quantitative results in Table VI is as follows: C—O = 1.36 ± 0.04 Å.; C═O 1.25 ± 0.03 Å.; ∠ O—C═O = 130 ± 3°; O—H—O = 2.76 ± 0.06 Å.; ∠ *b* = 60 ± 2°; C—C = 1.54 ± 0.04 Å.

TABLE VI

OBSERVED AND CALCULATED MAXIMA AND MINIMA OF THE DIMERS OF ACETIC ACID AND DEUTERIUM ACETATE

Max.	Min.	I_k	$S_0(\mathrm{HAc})_2$	S_H/S_0	$S_0(\mathrm{DAc})_2$
3		20	5.83	0.978	5.83
	4	− 7	7.05	1.010	7.05
4		7	8.26	1.017	8.23
5			9.30	0.997	9.25
	5	− 3	10.10	0.990	10.10
6		5	11.40	1.000	11.37
	6	− 5	12.56	1.000	12.60
7		4	13.93	0.995	13.89
	7	− 4	15.14	0.997	15.11
8		4	16.61	0.998	16.67
	8		17.85	1.000	
9			18.94	1.005	
			Average	0.999	
			Average deviation ±	.006	

Deuterium Acetate Dimer.—No difference was observed in the qualitative appearance of the photographs of the dimer of deuterium acetate and those of acetic acid. Table VI shows that the molecules also cannot be distinguished quantitatively. It must be concluded then that any difference in structure that exists between the dimer of deuterium acetate and that of acetic acid is within the uncertainty of the determination of the structure of the latter compound.

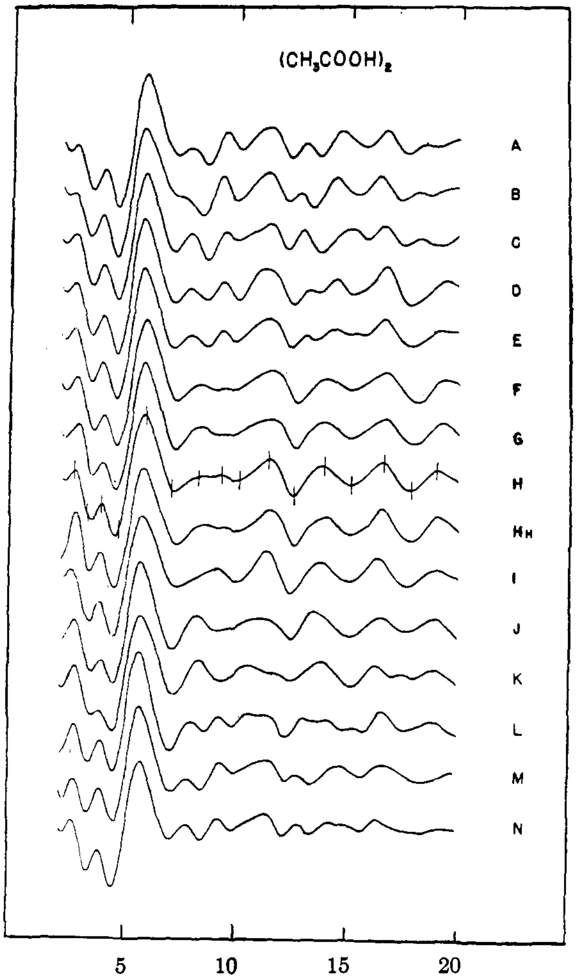

Fig. 6.—Calculated scattering curves for $(CH_3COOH)_2$.

The deuterium acetate used in these experiments was kindly supplied by Dr. Paul Gross of Duke University.

Trifluoroacetic Acid Monomer.—The trifluoroacetic acid used in the diffraction study and the vapor density study reported previously was kindly supplied by Dr. A. L. Henne of The Ohio State University.

In calculating the intensity curves, the CF_3 group was considered to be trigonally symmetric about the carbon to carbon axis, and the carbon and oxygen atoms were assumed to be coplanar. In the twenty-four models studied the parameter ranges considered were: C—C, 1.42 to 1.54 Å.; C—F, 1.33 to 1.36 Å.; C—O, 1.26 to 1.36 Å.; C═O, 1.25 to 1.36 Å.; F—C—F, 107.5° to 112°; O—C═O, 102° to 130°; C—C═O, 115° to 129°; orientation of the CF_3 group, fixed positions to a study of free rotation. Figure 7 shows some of

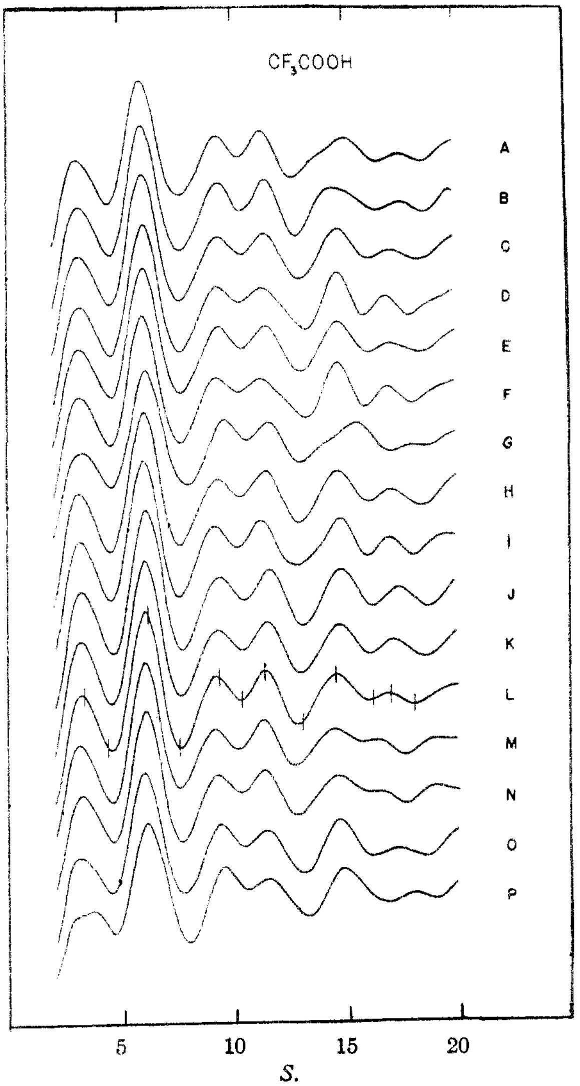

Fig. 7.—Calculated scattering curves for CF_3COOH.

the intensity curves. Although eight parameters present an exceedingly complex structure problem, a study of less than eight effective parameters was anticipated due to the possibility of a marked lack of sensitivity of the intensity curves to changes in some of the structural features.

A 15° orientation of a C—F bond out of the plane of the carboxyl group produces an intensity curve indistinguishable from one closely resembling a curve for free rotation within the range of variation of the shape of the carboxyl group considered in this paper. This is shown by a comparison of curve C possessing a 15° orientation with curve E composed of an average of twenty-four positions and is further substantiated by the similarity of curves D and F possessing C—O/C═O ratios of 1.29/1.29 and 1.36/1.25, respectively, and of models C and L wherein there occurs a change of 10° in the O—C═O angle in addition to a change in the C—O/C═O ratio. The models studied in which a C—F bond was placed in the plane of the carboxyl group were unsatisfactory as illustrated by curves B, A and G.

The relative intensities of the two maxima following the largest one in curves O and P do not agree with the visual interpretation of the photographs. These models possess O—C═O angles of 110° and 102°, respectively, and the qualitative effect may be ascribed to an increase in the oxygen to fluorine distances in the molecule.

It is possible to select eight more or less satisfactory intensity curves, curves D, F, C and H which have an O—C═O angle of about 120° and curves I, J, K and L with an O—C═O angle of 130°. All these curves possess a C–F distance of 1.36 Å. and a C–C distance of 1.48 Å. except J which has a C–C distance equal to 1.44 Å. However, it is noted that curve J is shifted with respect to the s_0 values, indicating some unusually small distances in the molecule. The orientation of the CF_3 group in these models is 15 and 30° with respect to the carboxyl group measured from the C—O side and the remaining parameters almost cover the maximum range of variation discussed above.

It is possible to draw definite conclusions only with regard to the structure of the CF_3 group in the monomer of trifluoroacetic acid: C—F = 1.36 ± 0.05 Å.; ∠ FCF = 110 ± 4°. As far as the orientation of the CF_3 group is concerned, there may be a preferred position excluding the one in which there is a C—F bond in the plane of the carboxyl group, there may be vibrations of rather large amplitude or there may be free rotation. No significant conclusions can be drawn about the C—O/C═O ratio and the C—C═O and O—C═O angles and it is not possible to fix with certainty the C—C distance since a change in the distance of 0.06 Å. is fairly well compensated for by a change in the F—C—F angle of 2°, as indicated by a comparison of curves M and N.

A radial distribution curve was not calculated because resolution of the many intramolecular

Table VII

Observed and Calculated Maxima and Minima of Trifluoroacetic Acid Monomer

Max.	Min.	S_0	S_L/S_0
2		6.15	0.984
	3	7.49	1.012
3		9.28	0.998
	4	10.30	1.000
4		11.34	1.005
	5	12.98	0.994
5		14.49	1.008
	6	16.15	0.994
6		16.96	1.000
	7	18.01	1.004
7		19.94	0.997
		Average	1.000
		Average deviation	±0.006

distances was not expected from the number of maxima and minima available for the calculation.

Trifluoroacetic Acid Dimer.—In addition to the assumptions which applied to the study of the monomer, a center of symmetry is believed to exist for the carbon and oxygen atoms and the same type of bridge was assumed as occurs in the dimers of formic and acetic acids. The four carbon atoms were assumed to be on a straight line and on the basis of the experiments reported above the vapor striking the electron beam was considered to be 11% dissociated. Thus there is one parameter in the dimer in addition to the eight required to fix the structure of the monomer, the distance across the hydrogen bridge. Unlike the monomer, the number of parameters which have a negligible effect on the resultant intensity is too small to lead to a structure determination whose degree of uncertainty may be readily estimated. However, the large number of qualitative features in the patterns are advantageous in limiting the range of variation.

A total of fifteen models were studied in which the C—F was equal to 1.36 Å., the C=O distance varied from 1.25 to 1.33 Å., the OH—O distance varied from 2.67 to 2.76 Å., the O—C=O angle varied from 110 to 130° and the C—C=O angle[13] varied from 115 to 125°. The remaining parameters covered the same range as in the study of the monomer. Figure 8 contains some of the intensity curves.

Model B is the most acceptable model and is based on the structure for the dimer of acetic acid except that the C—C distance is shortened from 1.54 to 1.48 Å. It possesses in addition a tetrahedral CF$_3$ group in which the C–F distance is equal to 1.36 Å. and a 15° orientation of a C–F bond with respect to the plane of the carboxyl group. Models A and C are similar but possess orientations of 0 and 30°, respectively.

As pointed out above, a marked sensitivity to changes in several of the parameters can be observed. A comparison of models N and B shows the effect of changing the C–C distance to 1.54 Å. Model E produces a very poor intensity curve and it differs from B in possessing equal C—C=O and C—C—O angles and equal C—O and C=O distances whose average is about 0.04 Å. less than that of model B. Model F has the same structure in the carboxyl group as does E with a C–C distance smaller by 0.04 Å. and an OH–O separation smaller by 0.06 Å. A comparison of curve G with curve H shows the relatively small change arising from a difference of 0.08 Å. in the OH–O distance.

The series of models K, L and M have the same orientation relation as models A, B and C. This is also true for models H, I and J. Models K, L and M have a CF$_3$ group similar to that of A, B and C but the structure of the carboxyl group is modeled after the one which occurs in formic acid dimer. Models H, I and J differ slightly in possessing an O—C=O angle of 120°, equal carbon to oxygen distances of 1.29 Å. and equal C—C=O and C—C—O angles.

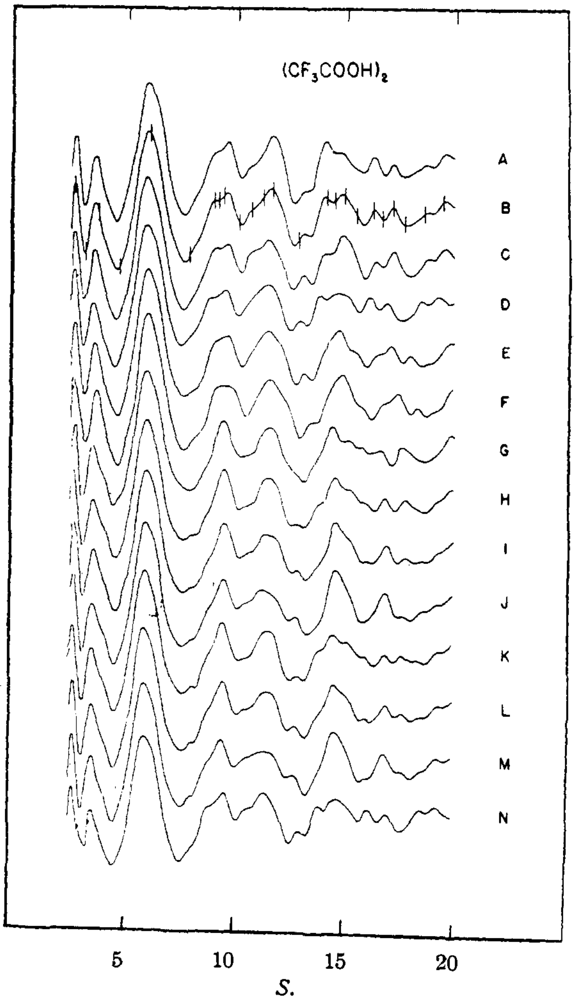

Fig. 8.—Calculated scattering curves for (CF$_3$COOH)$_2$.

From reasoning similar to that applied to the study of the monomer and the observation that the portion of the intensity curve of the dimer due to the scattering of the distances across the monomeric units is insensitive to changes in the orientation of the CF$_3$ group, a 15° orientation of a C—F bond out of the plane of the carboxyl group may be interpreted as producing an intensity curve which closely represents a curve of free rotation.

The following values are obtained for the parameters in the dimer of trifluoroacetic acid: C—F = 1.36 ± 0.03 Å.; ∠ FCF = 109 ± 2°; C—C = 1.48 ± 0.03 Å.; O—H—O = 2.76 ± 0.06 Å.; ∠ O—C=O = 130 ± 3°: ∠ b = 60 ± 3°. The CF$_3$ group probably rotates freely or vibrates in arcs of large amplitude. Nothing definite can be said about the relative length of

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(13) On the assumption that all four carbon atoms are on a straight line, ∠C—C=O is the supplement of angle *b* used to fix the structures of the dimers previously discussed.

the C—O and C=O distances but their average is about 1.30 Å.

As in the case of the monomer, no attempt was made to calculate a radial distribution curve since the large number of intramolecular distances could not be resolved from the available data. Table VIII shows that model B agrees well with the measurements on the diffraction photographs.

It should be noted that the structural unit of B is the monomer L which produces a very satisfactory intensity curve. However, this may be due to a lack of sensitivity in the intensity curves to changes accompanying dissociation of the same order of magnitude as those which occurred in formic acid. Thus, the important questions concerning precise values for the O—C=O and C—C=O angles in the monomer and the relative length of the C—O and C=O distances in the associated and dissociated forms remain unsolved.

TABLE VIII

OBSERVED AND CALCULATED MAXIMA AND MINIMA OF TRIFLUOROACETIC ACID DIMER

Max.	Min.	S_0	S_B/S_0
3		6.05	0.980
	4	7.84	0.974
4		8.99	1.000
	5	9.19	1.000
5		9.43	1.014
	6	10.11	1.014
6		10.69	1.001
	7	11.23	0.980
7		11.66	0.991
	8	12.81	1.015
8		14.14	0.994
	9	14.51	0.994
9		14.95	0.993
	10	15.49	1.020
10		16.26	1.004
	11	16.68	1.006
11		17.17	1.000
	12	17.70	1.006
12		18.59	1.008
13		19.49	1.006
		Average	1.000
		Average deviation	±0.009

Discussion

Several interesting structural features of the carboxyl group are shown by the foregoing results on formic and acetic acids. The two C–O distances in the unassociated carboxyl are distinctly different; indeed, the longer distance is the same as that observed in ether linkages while the shorter corresponds to the C—O linkage in ketones. It may be concluded from these results that the hydrogen atom is much closer to one oxygen than to the other. The attachment of the hydrogen to one of the two oxygens makes their attachments to the carbon as distinct from each other as an ordinary single and double bond. It is still expected that in the free carboxylate ion the two C–O links would be equivalent.

When the dimer is formed the longer C—O bond becomes about 0.06 Å. shorter than it was in both formic and acetic monomers, while the shorter C—O bond is unchanged. The difference between the two C—O bonds in the carboxyl is thereby reduced to about 0.1 Å. It appears, then, that although both of the carboxyl oxygens have an adjacent hydrogen in the dimer and are therefore more nearly alike than they were in the monomer, a considerable difference persists in the behavior of the two oxygens. The observed non-equivalence of the two C—O bonds requires a non-equivalence of the two O—H linkages; or in other words the diffraction results lead to the conclusion that the two hydrogen atoms in the carboxyl dimer are not located in the center positions in the respective OH—O bonds.

A further difference between the monomer and dimer is noted in formic acid in the O—C=O angle, which is 4° larger in the dimer. Since the O—O distance across the carboxyl is the same in both forms, it seems probable that the repulsion between the oxygen atoms prevents the decrease in their separation, which would have accompanied the shortening of the C—O distance if the O—C=O angle had remained unchanged.

The only significant difference between the results on formic and acetic acids is in the O—C=O angles. In the formic acid dimer this angle is 121° while in acetic acid dimer it is 130°. This angle happens to be indeterminate over a wide range (122–138°) in acetic acid monomer so that the monomer comparison cannot be made. The OH–O distance in the dimers is substantially the same, 2.73 and 2.76 Å.

Spectroscopic results on carboxylic acids are in general agreement with the above conclusions. Hofstadter[14] working on heavy formic acid and Herman and Hofstadter[15] on light and heavy acetic acids found an increase in the O-H and O-D distances from about 0.97 Å. in the monomers to about 1.07 Å. in the dimers. This increase would have to be up to 1.35 Å. if the hydrogen (or deuterium) atom were in the center of the OH—O dimer bond. Sutherland and Davies[4] report a somewhat smaller change in the O-H distance in the dimerization of acetic acid. They also report a difference of about 0.1 Å. between C—O and C=O although each distance is somewhat shorter than the diffraction values given in this paper.

Force constants of 5.4 × 10^5 dynes/cm. for the C—O and 11.8 × 10^5 dynes/cm. for the C=O in the formic acid monomer are reported by Hofstadter and Bonner.[3] The first value is close to that for an alcoholic C—O (4.5 × 10^5 dynes/cm.) while the second is essentially that for a carbonyl group. This comparison is consistent with the conclusions based on the diffraction results.

(14) R. Hofstadter, *J. Chem. Phys.*, **6**, 541 (1938).

(15) R. C. Herman and R. Hofstadter, *ibid.*, **6**, 534 (1938)

TABLE IX

DIFFRACTION RESULTS ON FORMIC, ACETIC AND TRIFLUOROACETIC ACIDS

Parameter	Formic Monomer	Formic Dimer	Acetic Monomer	Acetic Dimer
C—O	1.42 ± 0.03 Å.	1.36 ± 0.04 Å.	1.43 ± 0.03 Å.	1.36 ± 0.04 Å.
C═O	1.24 ± 0.03	1.25 ± 0.03	1.24 ± 0.03	1.25 ± 0.03
O—C═O	117 ± 2°	121 ± 2°	122 − 138°	130 ± 3°
OH—O		2.73 ± 0.05		2.76 ± 0.06
C—C			1.54 ± 0.04	1.54 ± 0.04
b		58 ± 1°		60 ± 2°
C—C═O			113-128°.	

Parameter	Trifluoroacetic Monomer	Trifluoroacetic Dimer
C—F	1.36 ± 0.05 Å.	1.36 ± 0.03 Å.
F—C—F	110 ± 4°	109 ± 2°
C—C		1.47 ± 0.03
OH—O		2.76 ± 0.06
Av. of C—O & C═O		1.30 ± 0.03
O—C═O		130 ± 3°
b		60 ± 3°
$-CF_3$	Free rotation or vibration in arcs of large amplitude.	

The isotope effect (increase in distance between associated carboxyl groups on substitution of D for H) found by Robertson and Ubbelohde in oxalic acid dihydrate was also studied by them in phthalic acid, α-resorcinol, β-resorcinol, sodium bicarbonate and in succinic and benzoic acids. No such effect was detected in phthalic acid or β-resorcinol while the other substances all show effects smaller than in oxalic acid. Our hope of checking on this effect in acetic acid vapor was not realized since the uncertainty of the determination of the OH–O distance is as large as the magnitude of the effect observed in oxalic acid dihydrate. The similarity of the electron diffraction photographs of light and heavy acetic acids does not exclude the possibility of an isotope effect as large as that occurring in some of the above-mentioned compounds.

In trifluoroacetic acid the structure of the carboxyl group could not be determined as completely as in the other acids because of the relatively high scattering power of the CF_3 group. In the dimer the average value of the C—O and C═O distances is 1.30 Å. as in the other acid dimers, but the individual values are indeterminate. The CF_3 group in both the monomer and dimer has about the same structure found in other compounds containing this group, *i. e.*, the C–F distance is 1.36 Å., and the F—C—F angle is near the regular tetrahedral value. The group is free to rotate or at least to oscilllate with large amplitude about the C—C axis.

In the dimer with a CF_3 group at each end some additional distances were determined. The C–C distance is only 1.48 Å., or 0.06 Å. shorter than in acetic acid. The effect of shortening the bond to the attached atom when fluorine is substituted for the hydrogen in a methyl group occurs in many other compounds as well, but here the fluorine substitution has the further interesting effect of loosening the acid hydrogen as shown by the high acid strength of aqueous solutions of trifluoroacetic acid. It might be supposed that because of the change in acidity the tendency toward dimerization would be affected; but while the degree of dissociation of the dimer is more than twice as great in trifluoroacetic acid as in acetic at 300°K. and the same total pressure, almost as large a difference in dissociation exists between formic and acetic acids where both are "weak" acids. The structure of the bridge in the dimer of acetic acid is not changed in any large degree by the substitution of fluorine since the OH–O distance is 2.76 ± 0.06 Å. in both acids.

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Summary

The structures of the monomeric and dimeric forms of formic, acetic and trifluoroacetic acids in the vapor state have been investigated by the electron diffraction method with the results summarized in Table IX. The two C—O bonds in the carboxyl group differ in both the monomer and the dimer. The OH–O distance across the bridge is substantially the same in all three dimers, while in the acetic acid the C—C bond is 0.06 Å. longer than in the fluorine substituted acid.

Acetic acid and the deuterated acid, $(CH_3COOD)_2$, show no detectable difference in their diffraction photographs.

Measurements were made on the vapor density and the dissociation constants of the dimeric trifluoroacetic acid.

A high temperature nozzle for introducing samples into the gas diffraction camera over the range from room temperature up to 160° is described.

ANN ARBOR, MICHIGAN RECEIVED JANUARY 14, 1944

[A CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

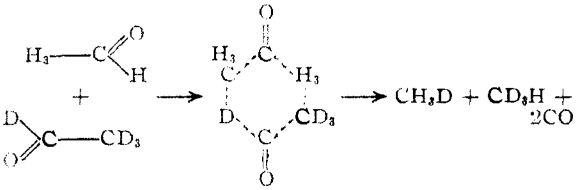
The Thermal Decomposition of Acetaldehyde

BY J. CARRELL MORRIS

Recent studies on the mechanism of the thermal decomposition of acetaldehyde into carbon monoxide and methane have indicated that the reaction proceeds, at least in part, by means of a reaction chain involving free radicals. Thus Burton, Ricci and Davis[1] were able to demonstrate that radio-lead was transported in a Paneth-type experiment in which acetaldehyde was decomposed under normal conditions. This undoubtedly showed the presence of free radicals in their experiments. Rice and Polly[2] and later, in a more extensive fashion, Smith and Hinshelwood[3] found that the normal thermal decomposition was inhibited by the addition of propylene to the gaseous acetaldehyde in the reaction vessel. These studies on inhibition, generally considered a very reliable test for the detection of radical chain reactions, led to an estimate that a minimum of about $^2/_3$ of the reaction occurred by means of free-radical chains.

In an attempt to confirm this conclusion and perhaps to check on more detailed phases of the mechanism of the reaction a somewhat different approach to the problem was devised. Mixtures of ordinary acetaldehyde and acetaldehyde-d_4 were allowed to decompose together and the resulting products were analyzed as to the isotopic composition of the methanes formed.

Such a determination might be expected to give a rather intimate knowledge of actual processes occurring in the reaction. For, if the decomposition were an intramolecular one, then the CH_3CHO could give just CH_4 and CO, while CD_3CDO would yield only CD_4 and CO. Consequently, if this mechanism were operative, the analysis should show none of the partially deuterated methanes. If the decomposition were a bimolecular one, then reactions of the type



should occur, yielding CD_3H and CH_3D as well as CH_4 and CD_4. One would not anticipate finding CH_2D_2, however. In the third plausible case, if the reaction took place by a chain mechanism, processes of the type

$$CH_3 + CD_3CDO = CH_3D + CD_3 + CO$$
$$CD_3 + CH_3CHO = CD_3H + CH_3 + CO$$

would be expected to produce CD_3H and CH_3D and perhaps also CH_2D_2, if the reactions were more complicated than those illustrated.

So, while it might not be possible by this method to distinguish between the latter two possibilities, such an analysis should certainly provide evidence differentiating the first possibility from the other two.

Benedict, Morikawa, Barnes and Taylor[4] have shown that such mixtures of the isotopic methanes may be analyzed readily by means of their infrared spectra. In particular, the absorption in the range 1000–1500 cm.$^{-1}$ is very characteristic of the particular isotopic methanes present in a mixture and their relative proportions. In the present study this method of analysis was followed by measuring the infrared absorption over the range 1000–1500 cm.$^{-1}$ of the samples of gas obtained from the decomposition of the mixtures of acetaldehyde and acetaldehyde-d_4. The results obtained led to the conclusion that the thermal decomposition of such mixtures produced CH_4 and CD_4 almost exclusively.[5] This is definite evidence that, contrary to the findings of previous authors,[1,2,3] the decomposition of acetaldehyde proceeds mainly by a unimolecular mechanism.

Confirmation for this point of view was obtained by an analysis of data on the absolute rate of the thermal decomposition of acetaldehyde. During the course of the present research it was noted that the rate of decomposition of "pure" acetaldehyde was materially decreased if the aldehyde were treated with hydroquinone and freshly distilled from it before use. The rates found after such treatment were considerably lower than the "normal" rates of Smith[6] or of Smith and Hinshelwood[3] and approached the "inhibited" rates found by the latter authors. A reasonable conclusion is that the positive indications of a chain reaction found in this decomposition were caused by a superimposed induced process initiated by an impurity.

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[1] M. Burton, J. E. Ricci and T. W. Davis, THIS JOURNAL, **62**, 265 (1940).

[2] F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

[3] J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **A180**, 237 (1942).

[4] W. S. Benedict, K. Morikawa, R. B. Barnes and H. S. Taylor *J. Chem. Phys.*, **5**, 1 (1937).

[5] J. C. Morris, THIS JOURNAL, **63**, 2535 (1941).

[6] R. E. Smith, *Trans. Faraday Soc.*, **35**, 1328 (1939).