*The Molecular Structure of the Monomer and the Dimer of Acrylic Acid**

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Acrylic acid is known as an important source of some highly polymeric products, however its molecular structure has been left unsolved.

Recent electron diffraction study[1] of the monomer of formic and acetic acids has indicated that the two distances between the carbon atom and oxygen atoms in carboxyl group are not the same. This result essentially agreed with the structure of the monomer of formic acid of the electron diffraction sector-photometer method proposed by Karle and Karle[2]. Furthermore, various data[3] on the conjugated system show that the C–C single bond distance between two double bonds is shorter than its normal distance of 1.54 Å.

The present investigation was undertaken for the purpose of clarifying the stereochemical structure of acrylic acid, and also to elucidate the question as to what changes may occur on association of the monomer of the acid.

Experimental

Acrylic acid was prepared by hydrolysis of commercial grade methyl acrylate. On careful distillation of the acid, a fraction boiling at 50∼51°C/20 mmHg was collected.

Electron diffraction photographs were taken according to the usual manner using a camera reported in the previous paper[4] (camera distance, ca. 9 cm., electron wavelength, 0.056∼0.063 Å, determined by gold foil). The diffraction pattern were visually measured to the extent of ca. 70 of q-values.

Interpretation of Diffraction Patterns and Results

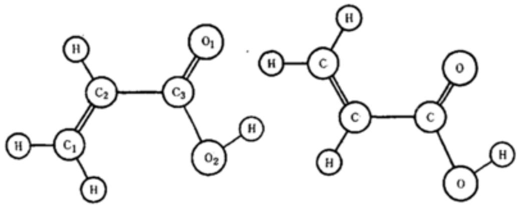
The well known formula for the calculation of the theoretical intensity curves are as follows:

$$I_{(q)}=\sum_i\sum_j \frac{Z_iZ_j}{r_{ij}} \exp(-a_{ij}q^2) \sin \frac{\pi}{10}qr_{ij}$$

$$q=(40/\lambda)\sin(\theta/2),\quad a_{ij}\fallingdotseq(\pi^2/200)\ <\Delta r_{ij}^2>$$

where r_{ij} is the distance between the i-th and j-th atom, λ the electron wavelength, θ the scattering angle, Z_i the atomic number of i-th atom, and $<\Delta r_{ij}>$ the mean square amplitude of r_{ij}. The exponential term is omitted as a first approximation, i. e., $\exp(-a_{ij}q^2)=0$.

Monomer of Acrylic Acid. — To obtain the monomer of the acid, a fine nozzle through which its vapor flowed out was heated at 170∼200°C by a spiral nichrome wire. No available data concerning the thermal equilibrium between the dimer and monomer of the vapor of this acid have appeared in literature. Also the temperature of the nozzle was controlled to obtain diffraction patterns different from those of the dimer. Some photographs were taken and these were then carefully compared with that of the dimer of the acid. In the regions of 20∼30 of q-values, a remarkable change was observed in these patterns. Eight satisfactory photographs were obtained.



trans — form *cis* — form

Fig. 1. Schematic model showing the *trans*- and *cis*-forms of acrylic acid.

It is assumed that all the atoms in this molecule are coplanar, and that the C–H distance and ∠CCH are 1.08 Å and 120°, respectively. The hydrogen atom in OH group was neglected, because its contribution to the total theoretical intensity curve was small. The parameters $C_1=C_2$, C_2–C_3, $C_3=O_1$ and C_3–O_2 used in the calculation of theoretical intensity curves, were varied from 1.32 to 1.45 Å, from 1.40 to 1.54 Å, from 1.18 to 1.24 Å and from 1.32 to 1.50 Å in steps of 0.02 or 0.03 Å, respectively, while the angles of $C_1C_2C_3$, $C_2C_3O_1$ and $O_1C_3O_2$ were varied from 110 to 130°, from 110 to 130° and from 110 to 135° in steps of 2 or 3°, respectively. In Fig. 2, the solid lines are the theoretical intensity curves of *trans*-form, and the chain lines are of *cis*-form.

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[1] J. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 574 (1944).

[2] I. Karle and J. Karle, *J. Chem. Phys.*, **22**, 43 (1954).

[3] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[4] T. Yuzawa and M. Yamaha, This Bulletin, **26**, 414 (1953).

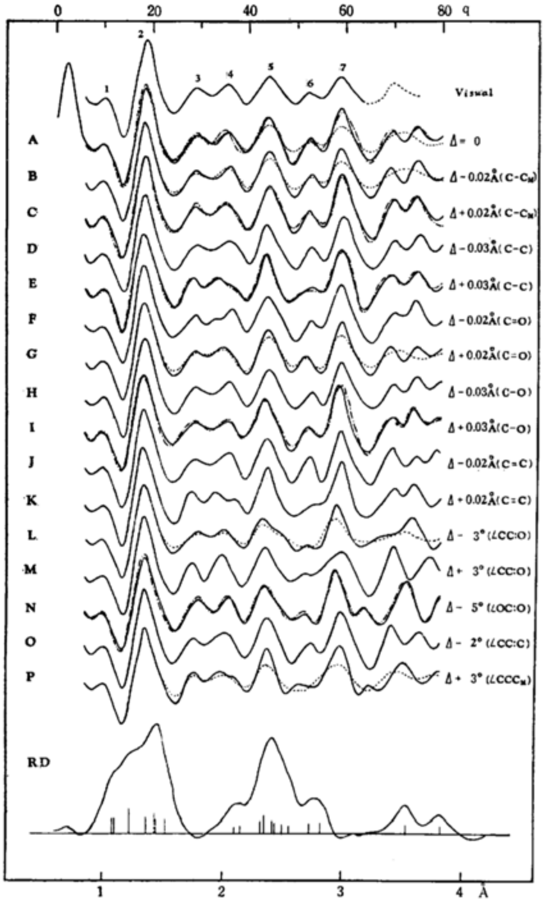

Fig. 2. Visual, theoretical intensity curves and radial distribution curve for acrylic acid. The notations on the right hand side of this figure show that the models deviate from the most probable model, for example, $\varDelta=0$ is the most probable model which has the parameter as follows: C–H, 1.08; C=C, 1.36; C–C, 1.44; C=O, 1.22; C–O, 1.43 Å; $\angle$C : CH=$\angle$C : CC=$\angle$CC : O, 120° and $\angle$OC : O, 125°.

The effect of thermal vibration on the theoretical curves was examined, the vibration factors a's listed in Table I being used, and the curves including these effects were shown in the dotted lines in the same figure.

A careful comparison was made between the visual and theoretical intensity curves. Curve A is in the best agreement with the visual one. The curves of several other models resemble the visual one, but they differ from it in some features. The 4th, 5th and 6th maxima of curve B shift outward, while in curve C the 3rd and 4th maxima shift inward. Curves D and E are taken for the purpose of ascertaining the limit of acceptability for C=O distance, both curves being in good agreement with the visual one in all respects, except for the small displacement of the positions of the 3rd, 4th and 6th maxima. Likewise curves F and G are used to show the limit for C–O distance. These curves are also rejected because of the disagreement with the visual curve in the range $q>45$. In curve H, the 4th and 6th maxima shift outward, while in curve I the 3rd and 5th maxima shift outward, while in curve I the 3rd and 5th maxima shift inward. Curves J and K are taken as typical ones for models which have values accepted as borderline: the features of these curves in the range $q>50$ disagree with the visual curve. In curve L, the 4th minimum and the 7th maxima both shift inward, while the 4th and 5th maximum shift outward. Curves M and N are shown as the acceptable limit for the angle $C_1C_2C_3$. In curve M, the 6th and 7th maxima shift outward greatly, on the other hand, in curve N the positions of the 5th maximum and minimum shift inward.

As shown in Fig. 2, the theoretical curves of the *trans*- and *cis*-forms remain almost unchanged in all features. Therefore, we could not distinguish the difference between the *trans*- and *cis*-configurations of this molecule.

From the above considerations, model A is regarded as the most acceptable one, while the others are all accepted as borderline fits. Seven models are selected from them, and their q_C/q_O values are summarized in Table II.

TABLE I. APPROXIMATE VIBRATION FACTORS a_{ij} USED IN CALCULATION FOR THE MONOMER AND DIMER OF ACRYLIC ACID

a_{ij}	Atom pairs	
	Monomer	Dimer
0	$C_1=C_2$, C_2-C_3, $C_3=O_1$, C_3-O_2	$C_1=C_2$, C_2-C_3, $C_3=O_1$, C_3-O_2
0.00010	$O_1'\cdots C_2$, $O_2'\cdots C_2$	$O_1'\cdots C_2$, $O_2'\cdots C_2$
0.00015	C–H, $O_1'\cdots O_2$, $C_1'\cdots C_3$	C–H, $O_1'\cdots O_2$, $C_1'\cdots C_3$
0.00020	$C'\cdots H$, $O_2''\cdots C_1$	$C'\cdots H$, $O_2''\cdots C_1$
0.00035	$O_1''\cdots C_1$	$O_1''\cdots C_1$
0.00040		$OH\cdots O'$
0.00060		$O_1\cdots O_1'$, $O_2\cdots O_2'$, $O_1\cdots C_3'$, $O_2\cdots C_3'$, $C_3\cdots C_3'$
0.00080		$O_1\cdots C_2'$, $O_2\cdots C_2'$, $C_3\cdots C_2'$, $C_2\cdots C_2'$, $O_1\cdots C_1'$, $O_2\cdots C_1'$
0.00100		$C_3\cdots C_1'$, $C_2\cdots C_1'$, $C_1\cdots C_1'$

TABLE II. q_C/q_O VALUES FOR ACRYLIC ACID

Feature		q_O	q_C/q_O Model							Wt.
Max.	Min.		A	C	D	F	G	I	M	
1		10.37	0.984	0.964	0.945	0.984	0.964	0.984	0.984	1
	1	14.25	0.983	0.983	0.983	0.969	0.982	0.976	0.982	1
2		19.06	0.995	0.971	0.984	0.979	0.997	0.976	0.984	2
	2	24.34	0.998	1.017	1.018	0.998	0.998	0.994	1.007	2
3		29.53	0.999	0.958	0.992	0.999	0.974	0.974	0.999	4
	3	32.48	0.998	0.939	0.970	0.964	0.959	0.985	0.978	2
4		35.57	1.001	0.984	1.012	1.006	0.990	0.984	0.998	4
	4	40.57	0.993	0.998	0.986	0.990	0.974	0.992	0.986	2
5		45.35	1.000	0.979	0.995	1.006	1.003	0.985	0.999	4
	5	49.08	1.006	0.993	1.007	1.011	1.009	1.007	1.006	1
6		52.38	1.004	1.008	1.012	0.998	1.009	1.016	1.016	2
	6	56.15	0.996	1.002	0.996	0.988	0.997	1.011	1.000	1
7		60.04	1.003	1.004	0.999	0.983	1.020	1.002	1.016	1
Wt. mean			0.998	0.981	0.995	0.994	0.989	0.988	0.996	
Wt. mean dev.			0.004	0.023	0.014	0.010	0.015	0.016	0.008	

The radial distribution curve for this molecule (RD curve in Fig. 2) was calculated using the following equation:

$$rD_{(r)}=\sum_{q=1}^{q_{\max}} I_{(q)O}\exp(-bq^2)\sin\frac{\pi}{10}qr$$

where $I_{(q)O}$ is the intensity read from the visual curve. The value of b was determined by setting the $\exp(-bq^2)=0.1$ at $q=70$. The curve shows that the first peak corresponds to the C-H, $C_1=C_2$, C_2-C_3, $C_3=O_1$ and C_3-O_2 distances, the second to the $C'\cdots H$, $C_1'\cdots C_3$, $O_1'\cdots O_2$, $O_1'\cdots C_2$ and $O_2'\cdots C_2$ distances, the third to the $O_2''\cdots C_1$ and fourth to the $O_1''\cdots C_1$ distance, respectively. Owing to the complex nature of the peaks, no attempt was made to resolve them. It is found, however, that the positions determined from the most probable model agree fairly well with the peaks observed in this radial distribution curve.

The following values are obtained for the structure of the monomer of acrylic acid:
$C_1=C_2=1.36\pm0.02$ Å; $C_2-C_3=1.44\pm0.03$ Å; $C_3=O_1=1.22\pm0.02$ Å; $C_3-O_2=1.43\pm0.03$ Å; $\angle C_1C_2C_3=120\pm2°$; $\angle C_2C_3O_1=120\pm3°$; $\angle O_1C_3O_2=125\pm5°$.

Dimer of Acrylic Acid. — It was assumed that the association of acrylic acid was the hydrogen bond coupling of two single molecules of the same type as in the case of formic and acetic acids, that the two planar acrylic acid molecules were coplanar, and also that the C_2, C_3, C_2' and C_3' atoms were laid on the same axis (as shown in Fig. 3). Many parameters were involved, so that the complete analysis on the molecular structure of the dimer of this acid would be very laborious. Therefore, some of the parameters of the most probable model obtained from the above-mentioned analysis of monomer of this acid were assumed to be as follows: C-H, $C_1=C_2$, $\angle C_2C_1H$ and $\angle C_1C_2C_3$ are assumed to be 1.08, 1.36 Å, 120 and 120°, respectively. Then the other parameters determining the structure C_2-C_3, $C_3=O_1$ and C_3-O_2 distances were varied from 1.40 to 1.50 Å, from 1.18 to 1.24 Å and from 1.30 to 1.43 Å in steps of 0.02 or 0.03 Å and O-H···O separation was varied from 2.65 to 2.80 Å with the same increment, while the angles of $\angle C_2C_3O_1$ and $\angle O_1C_3O_2$ were varied from 110 to 130° and from 120 to 135° in steps of 2 or 3°, respectively.

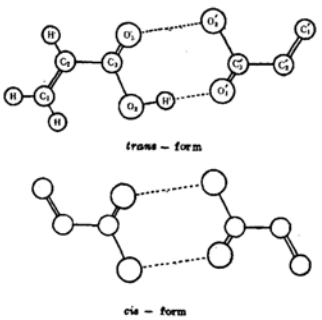

Fig. 3. Schematic model showing the skeletons and the numbering of atoms of the dimer of acrylic acid.

Some of the intensity curves are shown in Fig. 4. In this figure, the solid lines are the theoretical intensity curves of the *trans*-form, and the chain lines are of the *cis*-form. The effect of thermal vibration factors listed in Table I being used, the curves including these effects are shown in a dotted line in the same figure.

Curve E is in the best agreement with the visual one. In curve A, the 3rd and 4th maxima shift inward, while in curve B these maxima shift outward. A comparison of curves C and D, which possess 0.02 Å longer and shorter parameters, respectively, for $C_3=O_1$ distance, show that there are remarkable changes of the features

TABLE III. q_C/q_O VALUES FOR THE DIMER OF ACRYLIC ACID

Feature		q_O	q_C/q_O Model				Wt.
Max.	Min.		E	B	G	K	
1		12.28	1.005	0.915	0.968	0.982	1
	1	14.30	1.008	1.015	1.028	0.969	1
2		18.45	1.001	0.995	1.011	0.995	2
4		35.53	0.998	0.991	0.986	0.949	3
	4	40.24	1.005	0.989	1.025	1.016	2
5		45.18	1.000	1.022	1.014	0.999	3
	5	49.32	0.997	1.015	0.983	0.997	1
6		51.86	1.005	1.022	1.016	0.995	2
	6	55.45	0.989	0.996	0.997	0.983	1
7		60.48	1.009	1.011	1.011	1.007	1
Wt. mean			1.001	1.002	1.005	0.988	
Wt. mean dev.			0.005	0.017	0.016	0.017	

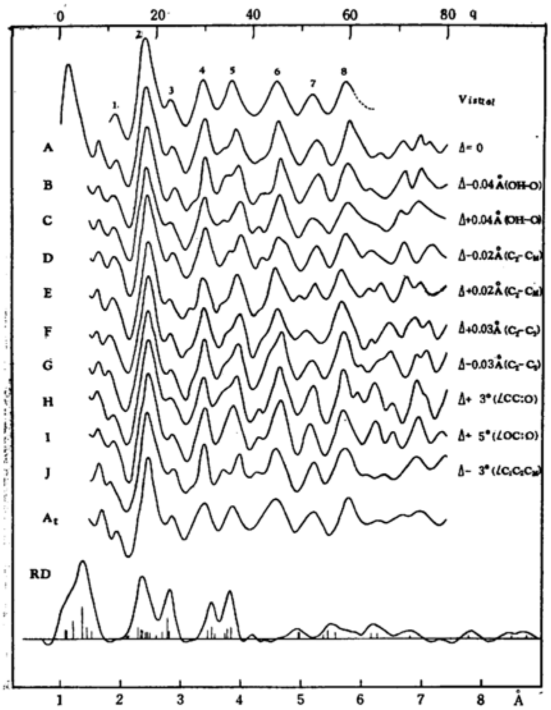

Fig. 4. Visual, theoretical intensity curves and radial distribution curve for the dimer of acrylic acid.
The notations on the right hand side of this figure show that the models deviate from the most probable model, for example, $\varDelta=0$ is the most probable model which has the parameter as follows; C-H, 1.08; C=C, 1.36; C-C, 1.44; C=O, 1.22; C-O, 1.36 Å; ∠C:CH=∠C:CC=∠CC:O, 120°; ∠OC:O, 1.25° and OH⋯O distance, 2.76 Å.

in the region of 20 to 30 q-values. Curve F differs from E, the former possessing a parameter of an OH⋯O distance which is 0.04 Å longer than in the latter; and curve G differs from E, the former possessing the same distance by 0.04 Å shorter. These curves disagree with the visual one in the positions of the 3rd and 4th maxima. In curves H and I, remarkable differences from the visual one are found in features between 20 and 30 of q-values and in positions of 3rd and 4th maxima. Curves J and K were examined for the purpose of ascertaining the limit of acceptability for C_2-C_3 distance, both curves being in good agreement with the visual one in all respects, except the 3rd and 6th maxima.

The radial distribution curve for the dimer of acrylic acid is shown in Fig. 2 (RD curve). The positions determined from the most acceptable model (shown in vertical lines in this curve) fairly well agree with the peaks observed in this radial distribution curve. A relatively small peaks is found at 2.76 Å corresponding to the separation across the bridge O-H⋯O.

The structure determined for the dimer of acrylic acid, which is in agreement with the quantitative results (q_C/q_O values in Table III), is as follows: C_1=C_2=1.36 Å (assumed); C_2-C_3=1.44±0.03 Å; C_3=O_1=1.22±0.02 Å; C_3-O_2=1.36±0.03 Å; $\angle C_1C_2C_3=120°$ (assumed); $\angle C_2C_3O_1=120\pm3°$; $\angle O_1C_3O_2=125\pm5°$; O-H⋯O=2.76±0.04 Å.

Discussion

The C=O and C-O distances in acrylic acid are the same as those observed in several interesting structural studies of the carboxyl group on formic and acetic acids. Therefore, no differences between a saturated and an unsaturated substituent attached to the carboxyl group could be found in this work.

Moreover, the C=C, C-C and C=O distances and the valence angles in this molecule generally agree with the corresponding bond lengths and valence angles of acrolein[5] and acrylyl chloride[6] which are obtained by electron diffraction studies. Bond shortening and bond elongation of C–C and C=C bonds in conjugated molecules were plausibly explained by the delocalization of π-electron. As a matter of fact, it may be considered that the order of conjugation in this molecule is the same as that calculated on acrolein by C. A. Coulson[7].

In the dimer, the C–O bond becomes 0.07 Å shorter than that in the monomer, while the C=O bond remains unchanged. Within the limits of accuracy of this work, the circumstances are the same as in the case of association of formic and acetic acids. Several investigations show that the heat of dimerization of some carboxylic acids is of the order of 13∼18 kcal./mol. The C–O bond shortening may be attributed for considerable part to the formation of a ring by two carboxyl groups across the hydrogen bridges.

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[5] H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951).

[6] T. Ukaji, This Bulletin, **30**, 737 (1957).

[7] C. A. Coulson, *Trans. Faraday Soc.*, **42**, 106 (1946).

[8] O. Z. Foz and J. Marcills, *Chem. Abstr.*, **44**, 8716*b* (1950); J. J. Fox and A. E. Martin, *Trans. Faraday Soc.*, **36**, 397 (1940); F. H. MacDougall, *J. Am. Chem. Soc.*, **63**, 3420 (1941).