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

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It has been commonly recognized that the derivatives of acrylic acid which have a methyl group on the α-carbon atom are reactive than the one having no substituent. Theoretical and structural explanation of this chemical fact seems not yet to have been given. The present work is directed to clarifying the stereochemical structure of methacrylic acid, and also to elucidate the question concerning the changes which may occur on the introduction of the methyl group into the α-position of the acid and on the association of the monomeric acid.

Experimental

Methacrylic acid was prepared by hydrolysis of commercial grade methacrylate. On careful distillation of the acid, a fraction boiling at 75~76°C/20 mmHg was collected. It was stocked over hydroquinone.

The electron diffraction photographs were taken according to the usual manner using a camera reported in the previous paper[1] (camera distance, ca. 9 cm.; electron wavelength, 0.053~0.061 Å, determined by calibration with gold foil). The experimental technique concerning the photographs of the monomer of this acid was essentially the same in the case of the monomer of acrylic acid. The diffraction pattern was visually measured to an extent of ca. 70 of q-values.

Interpretations of Diffraction Patterns and Results

For the calculation of theoretical intensity curves, the authorized formula[3b] was used. The thermal vibration factor is omitted as a first approximation.

Monomer of Methacrylic Acid.—To examine if the temperature of the present experiment is sufficient for the thermal dissociation of the acid, some photographs were taken and these were carefully compared with that of the dimer of this acid. A remarkable change was observed

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

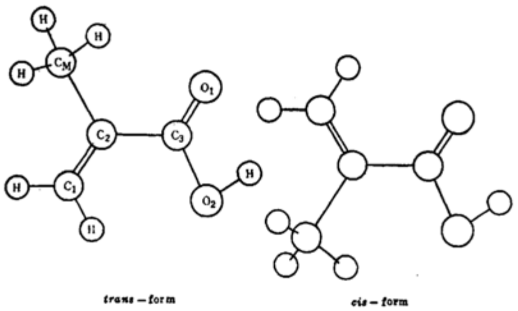

Fig. 1. Schematic model showing the *trans*- and *cis*-forms of methacrylic acid.

in the feature at about 23 of q-values in these patterns. Six satisfactory photographs were obtained.

On the basis of foregoing information[2,3], it is assumed that all the carbon and oxygen atoms in this molecule are coplanar, and that the C-H bond distance in the methyl group is 1.10 Å, in which each hydrogen atom forms tetrahedral configuration, and the C-H distance and ∠CCH in methylene group are 1.08 Å and 120°, respectively. The hydrogen atom in the hydroxyl group was neglected for the same reason as that described in the previous paper[3b]. The parameters C_1=C_2, C_2-C_3, C_3=O_1, C_3-C_2 and C_2-C_M (in methyl group), 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, from 1.32 to 1.50 Å and from 1.40 to 1.54 Å in steps of 0.02 or 0.03 Å, while the angles of $C_1C_2C_3$, $C_3C_2C_M$, $C_2C_3O_1$ 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 descriptive of the theoretical intensity curves of the *trans*-form, and the chain lines those of the *cis*-form. The effect of thermal vibration (the factors are listed in Table I) was then examined 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 quoted in this figure also resemble the observed intensity curve, but they differ from it in the features of some maxima and minima. Curves B and C agree with the visual one in all features, except for the position of the 4th maximum. While in curves D and E, the positions of the 3rd minimum and the 4th maximum and minimum, and the feature of the 6th peak differs from the visual curve. Curves F, G, H and I are taken for the purpose of ascertaining the limit of acceptability for C_3=O_1 and C_3-O_2 distances; these curves are in good agreement with the observed one in all features, except for the positions of the 4th and 6th maxima. In curves J and K, the positions of the 4th maximum and the intensity relations of the 6th peak are different from those of the visual one. Curves L and M are used to examine the limit of angle $C_2C_3O_1$. These curves are rejected because of the disagreement with the visual one in the range of $q>45$. Curves from N to P show the acceptable limit of the angles of $O_1C_3O_2$, $C_1C_2C_3$ and $C_2C_3C_M$, respectively. These curves have small differences in the positions and features of the 3rd minimum, the 4th and the 6th maximum.

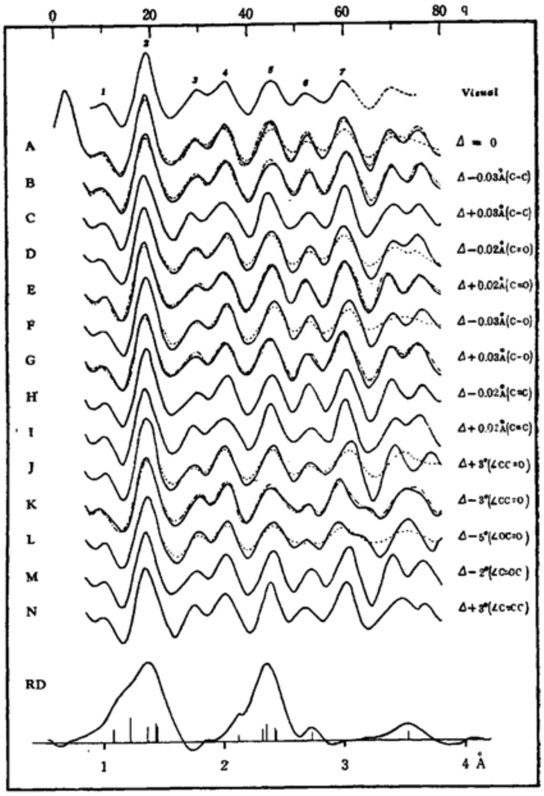

Fig. 2. Visual, theoretical intensity curves and radial distribution curve for methacrylic acid. The notations on the right hand side of this figure show that the models deviate from the most probable model, for example, $\Delta=0$ is the most probable model which has the following parameters; C-H=1.08, C_M-H (in methyl group)=1.10, C=C=1.36, C-C=1.44, C=C=1.22, C-O=1.43 Å, $\angle CC_MH=109.5°$, ∠C:CH=∠C:CC=∠CCC=∠CC:O=120° and ∠OC:O=125°.

The theoretical intensity curves of the *trans*- and the *cis*-forms remain almost unchanged throughout all the features. Therefore, we could not distinguish between the *trans*- and *cis*-configuration of this molecule.

From the above considerations, model A is regarded as the most acceptable one, while others are all accepted as on the borderline.

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[2] T. Ukaji, This Bulletin, **32**, 1266 (1959).

[3] (a) H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951). (b) T. Ukaji, This Bulletin, **30**, 737 (1957).

TABLE I. APPROXIMATE VIBRATION FACTORS USED IN CALCULATION FOR THE MONOMER AND DIMER OF METHACRYLIC ACID

Values of factor	Atom pairs: Monomer	Atom pairs: Dimer
0	$C_1=C_2$, C_2-C_3, C_3-C_M, $C_3=O_1$, C_3-O_2	$C_1=C_2$, C_2-C_3, C_2-C_M, $C_3=O_1$, C_3-O_2
0.00010	$O'_1\cdots C_2$, $O'_2\cdots C_2$, $C'_1\cdots C_M$, $C'_3\cdots C_M$, $C'_1\cdots C_3$	$O'_1\cdots C_2$, $O'_2\cdots C_2$, $C'_1\cdots C_M$, $C'_3\cdots C_M$, $C'_1\cdots C_3$
0.00015	C–H, C_M–H (in methyl group), $O'_1\cdots O_2$	C–H, C_M–H (in methyl group), $O'_1\cdots O_2$
0.00020	$C'_2\cdots H$, $C'_2\cdots H$ (in methyl group)	$C_2\cdots H$, $C'_2\cdots H$ (in methyl group)
0.00035	$O_2''\cdots C_1$, $O_1''\cdots C_M$	$O_2''\cdots C_1$, $O_1''\cdots C_M$
0.00040	$O_1''\cdots C_1$	$O_1''\cdots C_1$, $OH\cdots O'$
0.00060	$O_2''\cdots C_M$	$O_2\cdots C'_M$, $O_1\cdots O_1'$, $O_2\cdots O'_2$, $O_1\cdots C'_3$, $O_2\cdots C'_3$, $C_3\cdots C_3'$
0.00080		$O_1\cdots C'_2$, $O_2\cdots C'_2$, $C_3\cdots C'_3$, $O_1\cdots C'_1$, $O_2\cdots C'_1$, $C_3\cdots C'_M$, $O_1\cdots C'_M$, $O_2\cdots C_M$
0.00100		$C_3\cdots C'_1$, $C_2\cdots C'_1$ $C_1\cdots C'_1$, $C_1\cdots C'_M$, $C_2\cdots C'_M$
0.00120		$C_M\cdots C'_M$

TABLE II. q_C/q_O VALUES FOR METHACRYLIC ACID

Feature Max.	Feature Min.	q_O	q_C/q_O Model A	B	E	G	H	M	N	Wt.
1		10.44	0.982	0.986	0.982	0.977	0.987	0.982	0.977	1
	1	14.06	0.996	0.982	0.982	0.996	0.996	0.996	0.982	1
2		18.66	0.997	0.994	0.993	0.993	0.997	0.993	0.989	2
	2	24.27	1.001	1.009	1.009	1.009	1.009	1.001	1.003	2
3		29.02	1.004	1.004	0.982	0.999	1.004	1.009	1.020	4
	3	32.41	1.009	1.003	0.941	0.964	1.003	0.957	0.957	2
4		35.74	0.996	1.007	0.951	0.972	1.002	0.968	1.021	4
	4	39.21	1.002	1.005	1.000	1.005	1.014	0.992	1.002	2
5		44.00	1.000	1.007	0.995	1.005	1.006	0.994	0.989	3
	5	49.30	0.998	0.999	0.999	0.992	1.004	0.999	1.008	2
6		52.25	1.005	1.014	1.014	0.995	1.019	0.993	0.991	1
	6	55.02	0.999	1.009	1.004	0.999	1.007	0.967	0.985	1
7		58.96	1.001	1.001	1.005	1.006	0.997	1.009	0.986	1
Wt. mean			1.001	1.003	0.984	0.992	1.003	0.989	0.998	
Wt. mean dev.			0.004	0.007	0.020	0.012	0.006	0.014	0.016	

Seven models are selected from them, and their q_C/q_O values are summarized in Table II. The structural information deduced from the values of averages and the average deviations of q_C/q_O ratios is consistent with the above correlation analyses.

The RD curve in Fig. 2 is the radial distribution curve for this molecule. In this curve, the first peak corresponds to the C–H, C_M–H (in methyl group), $C_1=C_2$, C_2-C_3, C_2-C_M, $C_3=O_1$ and C_3-O_2 distances, the second, third and fourth to the $C'\cdots H$, $C'_2\cdots H$, $O'_1\cdots C_2$, $O'_2\cdots C_2$, $C'_1\cdots C_M$, $C'_3\cdots C_M$, $C'_1\cdots C_3$, $O''_2\cdots C_1$ and $O''_1\cdots C_M$, the fifth to the $O''_1\cdots C_1$ and the sixth to the $O''_2\cdots C_M$ distances, respectively. The interatomic distances determined from the most probable model (shown in vertical lines in this RD curve) are in good agreement with the peaks observed in this radial distribution curve.

The following values are obtained for the structure of the monomer of methacrylic acid: $C_1=1.36\pm0.02$ Å; $C_2-C_3=1.44\pm0.03$ Å; $C_2-C_M=1.52\pm0.02$ Å; $C_3=O_1=1.22\pm0.02$ Å; $C_3-O_2=1.43\pm0.03$ Å; $\angle C_1C_2C_3=120\pm2°$; $\angle C_3C_2C_M=120\pm3°$; $\angle C_2C_3O_1=120\pm3°$; $\angle O_1C_3O_2=125\pm5°$.

Dimer of Methacrylic Acid.—The circumstances of the association of methacrylic acid is assumed to be the same as in the case of the dimer of acrylic acid. The complete analysis on the molecular structure of the dimer of this acid may be very laborious because of the inclusion of so many parameters. Therefore, some parameters of the most probable model of the

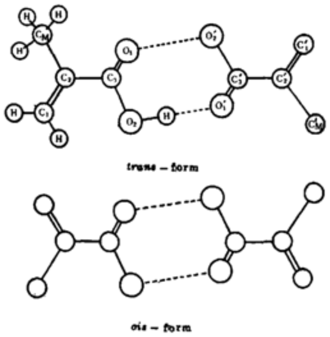


Fig. 3. Schematic model showing the skeletons and the numbering of atoms of the dimer of methacrylic acid.

monomer of this acid obtained from the above analysis were assumed to be as follows: C-H (in methyl group), C_M-H (in methyl group), C_1=C_2, C_3=O_1, $\angle C_2C_1H$, $\angle C_2C_MH$, $\angle C_1C_2C_3$, $\angle C_2C_3O_1$ and $\angle O_1C_3O_2$ were taken to be 1.08 Å, 1.10 Å, 1.36 Å, 1.22 Å, 120°, 109.5°, 120°, 120° and 125°, respectively. In the thirty models examined in this analysis, the parameters C_2-C_3, C_2-C_M and $C_1C_2C_M$ were varied from 1.40 to 1.50 Å, from 1.45 to 1.54 Å and from 110 to 130°, respectively.

Some of the theoretical intensity curves are shown in Fig. 4. These curves are representative of the theoretical intensity curves of the *trans*-form, and those of the *cis*-form are omitted in this figure for the reason that few differences are found between them. Curve A is in the best agreement with the visual one, and has parameters described in the notations of Fig. 4. In curves B and C, the 5th and 6th maxima have some different features from the visual curve; the position of the 7th maximum shifts outward in the former curve and the same maximum

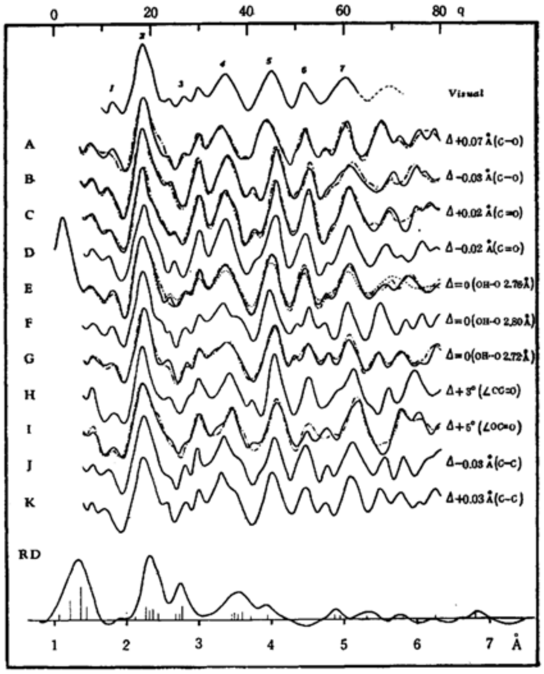


Fig. 4. Visual, theoretical intensity curves and radial distribution curve for the dimer of methacrylic acid. The notations on the right hand side of this figure show that the models deviate from the most probable model, for example, $\Delta=0$ is the most probable model which has the following parameters; C-H=1.08, C_M-H (in methyl group)=1.10, C=C=1.36, C-C=1.44, C=O=1.22, C-O=1.36 Å, ∠C : CH=∠C : CC=$\angle CCC_M$=∠CC : O=120°, $\angle CC_MH$=109.5°, ∠OC:O=125° and OH···O=2.75Å.

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

Feature		q_O	q_C/q_O Model					Wt.
Max.	Min.		A	C	E	G	J	
1		11.35	1.007	0.978	0.965	0.951	0.933	1
	1	14.21	1.002	0.993	0.999	0.968	0.968	1
2		17.86	1.003	0.994	1.011	1.025	1.008	1
	2	21.65	1.000	0.998	0.995	1.016	1.025	1
3		23.02	1.000	0.991	0.984	0.995	1.021	2
	3	26.41	0.983	0.985	0.962	1.003	0.996	2
4		29.63	1.006	1.012	0.996	1.012	1.006	4
	4	32.57	0.998	0.998	0.996	0.998	0.981	3
5		35.65	1.005	1.036	1.023	1.035	1.014	2
	5	40.23	0.998	0.989	0.997	0.994	0.982	1
6		44.77	1.002	1.014	0.994	1.026	0.999	2
	6	49.15	1.005	1.001	0.983	1.001	1.000	1
7		52.28	1.010	0.997	1.002	0.999	1.006	1
	7	55.51	1.006	0.999	0.999	0.991	0.993	1
8		59.05	1.005	1.004	0.986	0.999	1.001	1
Wt. mean			1.001	1.002	0.993	1.004	0.994	
Wt. mean dev.			0.005	0.011	0.012	0.015	0.014	

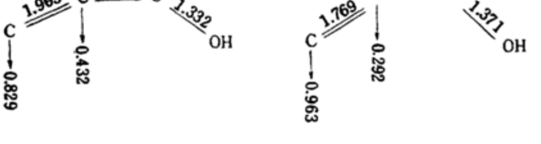
shifts inward in the latter. Curves D and F are taken for the purpose of ascertaining the limit of acceptability for C_2–C_M distance, both curves being in good agreement with the visual one in all the positions of maxima and minima; however, small peaks and shoulders appear among them. In curve F, the 3rd minimum and 7th and 8th maxima shift inward and the 5th maximum outward, while in curve G, the 5th and 6th maxima shift outward. In curves H and I, the 4th and 5th minima and 6th maximum have different positions, but in curve J small peaks appear between the 4th and 5th and 6th maxima. Curve A shows the effect of thermal vibration on curve A, using the vibration factors listed in Table I.

The radial distribution curve for the dimer of methacrylic acid is shown in Fig. 4 (RD curve). The curve shows that the positions and their relative height of peaks determined from the most probable model (as shown in vertical lines) agree fairly well in general with the peaks observed in this radial distribution curve.

The structure of the dimer of methacrylic acid, which is in agreement with the quantitative results in Table III, is determined as follows: C_2–C_M=1.52±0.02 Å, $\angle C_1C_2C_M$=120±3° and O_1–H···O_2 separation 2.75±0.04 Å; and all other parameters are the same as in the dimer of acrylic acid.

Discussion

The C_1=C_2, C_2–C_3, C_3=O_1 and C_3–O_2 distances and the valence angles of $C_1C_2C_3$, $C_2C_3O_1$ and $O_1C_3O_2$ in this molecule are essentially the same as the corresponding bond lengths and valence angles of acrylic acid which is obtained in a previous paper[2]. The C_2–C_M distance in this molecule is shorter than the normal C–C single bond distance 1.54 Å. This bond shortening is explained by the term hyperconjugation. The result of the theoretical calculation by Coulson and Crawford[4] shows that the bond compression energy of C–C single bond, from 1.54 to 1.52 Å, is 0.13 kcal./mol. In our preliminary calculation by a simple MO method** (neglecting overlap integral) acrylic and methacrylic acid, the values of bond order and free valence are shown schematically as follows:



When the values obtained here of the bond order and the bond lengths were treated following the method of Mulliken and others[5], the results compared favorably with the criterion regarding the bond order and the bond lengths which included the idea of hyperconjugation of them (the values concerned with C=C and C–C of acrylic acid, C=C, C–C and C–C_M (in methyl group) of methacrylic acid). In the above figure, the comparison of free valence shows that methacrylic acid has a tendency to possess somewhat greater sensibility than acrylic acid in radical reaction.

In the dimer of this acid, the circumstances are the same as in the case of the association of acrylic acid.

The author wishes to express his sincere gratitude to Professor A. Kotera, Mr. M. Igarashi and Mr. M. I'Haya of Tokyo University of Education for their kind guidance and encouragement throughout this work, and for the free use of the

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[4] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052.

** The well-known LCAO molecular orbital treatment is conducted as follows: the effect of the σ electron, assumed to be constant, is neglected, and the π-electrons are considered, as an approximation, to occupy the molecular orbital formulated below.

$$\Psi_i=\sum_{r=1}^{n} c_{ir}\phi_r$$

Then, we have the equatin:

$$(\alpha_r-E)C_r+\sum_{s\neq r}(\gamma_{rs}-S_{rs}E)C_s=0 \qquad (r=1,2,\cdots\cdots,n)$$

in which α is the coulomb integral, E's the energies of LCAO MO's, γ_{rs} the exchange integral and S_{rs} the overlap integral. The details of the calculations of the lower energy levels of these molecules and the empirical parameters adopted are essentially the same as in the case of the calculation of hyperconjugation by I'Haya except for the parameters assigned of oxygen atoms which are: α_O(carbonyl oxygen)$=\alpha_C+2.0$ and α_O(carboxyl oxygen)$=\alpha_C+1.5$. Here α_C is the coulomb integral of the carbon atom. According to Coluson's*** definition, the charge density (q_r) of π-electron on the atom r and the bond order (p_{rs}) of the bond between atoms r and s are given by the following equations:

$$q_r=2\sum_i C_{ir}^2$$

$$q_{rs}=2\sum_i C_{ir}\cdot C_{is}$$

where the summations are taken overall occupied MO's.

The calculation of the free valence F_r at atom r in a molecule followed the definition formulated by Coulson****

$$F_r=N_{\max}-N_r$$

The values of $N_{\max}$ is $3+\sqrt{3}$ and the N_r is

$$N_r=3+\sum_i p_{rs}$$

in which p_{rs} is the π-bond order of the r-s bond, where s is adjacent to r atom.

*** C. A. Coulson, *Proc. Roy. Soc.* (*London*), **A169**, 413 (1939).

**** C. A. Coulson, *Discussions Faraday Soc.*, **2**, 9 (1947).

[5] R. S. Mulliken et al. *J. Am. Chem. Soc.*, **63**, 41 (1941).

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