*The Molecular Structure of Methyl Acrylate and Methyl Methacrylate**

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Investigations of methyl formate and methyl acetate by electron diffraction have been reported[1], but no information seems to have been proposed regarding the stereochemical structure of methyl acrylate and methyl methacrylate which are important materials for high polymeric products.

In the present work, structural studies on methyl acrylate and methyl methacrylate by the electron diffraction method are undertaken to determine the most probable location of the methyl group of ester in these two compounds and to inspect the effect of hyperconjugation on the C-C single bond between the methyl group and the α-carbon atom in methyl methacrylate.

Experimental

Samples were purified by careful distillation. Methyl acrylate, b. p. 84.5~85.5°C. Methyl methacrylate, b. p. 100~101°C. These were stocked over hydroquinone.

The electron diffraction photographs were taken in the usual manner using a camera similar to the one reported in the previous paper[2] (camera distance, ca. 9 cm., electron wavelength, 0.059~0.063 Å, determined by calibration with gold foil). Fifteen satisfactory photographs were obtained in the case of methyl acrylate and eight in the case of methyl methacrylate. The diffraction patterns were visually measured to an extent of about $q=80$ in both cases.

Interpretation of Diffraction Patterns and Results

For the calculation of theoretical intensity curves, the authorized formula[3] was used. The exponential term of the formula is omitted as a first approximation.

Methyl Acrylate.—In the models of this molecule only four parameters are changed. In these the C_3-O_2 distance in carboxyl bond is varied from 1.32 to 1.45 Å in steps of 0.02 or 0.04 Å, and the O_2-C_4 distance in methoxyl bond from 1.40 to 1.50 Å with the same increments. The angle of $C_3O_2C_4$ of methoxyl group varied from 105 to 130° in steps of 5° and the angle between $C_3O_2C_4$ plane and the plane composed of the other atoms in the molecule is varied from 0 to 60°. The other parameters of this molecule were assumed to be those of the most probable model of acrylic

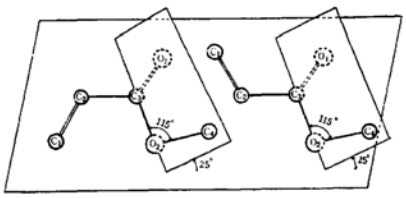

Fig. 1. Schematic models showing the skeletons and the numbering of atoms of methyl acrylate. The left model is *trans*-form and the right *cis*-form.

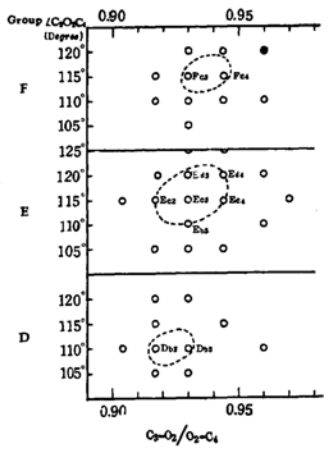

Fig. 2. Parameter chart for methyl acrylate.

* Partly presented at the 9th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1956.

1) A survey of the results of electron diffraction through 1949 is found in the tabulation by P. W. Allen and L. E. Sutton, *Acta Cryst.*, 3, 46 (1950).

2) T. Yuzawa and M. Yamaha, This Bulletin, 26, 414 (1953).

3) P. A. Shffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, 14, 659 (1946).

4) T. Ukaji, This Bulletin, 32, 1266 (1959).

acid[4]. Careful comparison was made between the visual intensity curve and the theoretical ones.

Fig. 2 shows the parameter chart for this molecule. The groupings of the models in the following discussions are made according to the qualitative similarity of the theoretical intensity curves. Groups D, E and F correspond to the models of which methyl groups are inclined by 20, 25 and 30°, respectively, to the molecular plane, and others are all rejected because of the disagreement with the visual curve.

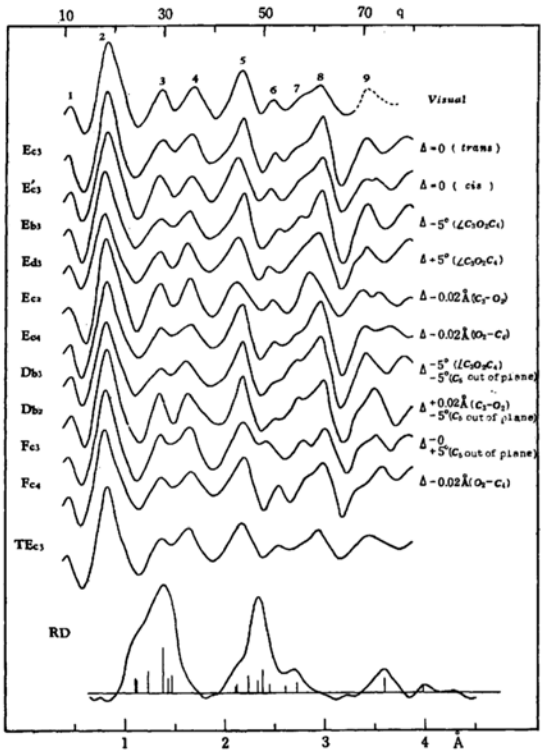

Fig. 3. Visual, theoretical intensity curves and radial distribution curve for methyl acrylate. The notations on the right hand side of this figure show that the models deviate from the most probable model, for example, $\Delta=0$ is the most probable model which has the following parameters; C_1-H =1.08, C_3-H (in methyl geoup)=1.10, C_1=C_2 =1.36, C_2-C_3=1.44, C_3=O_1=1.22, C_3-O_2=1.36, O_2-C_4=1.46 Å, $\angle C_2C_1H=\angle C_1C_2C_3=\angle C_2C_3O_1$ =120°, $\angle O_2C_4H$ (in methyl ester group)= 109.5°, $\angle O_1C_3O_2$=125°, $\angle C_3O_2C_4$=115° and C_4 atom is 25° out of plane configuration.

Of curves of the *trans*-form of the models E_{c2}, E_{b3}, E_{c3}, E_{d3} and E_{c4}, curve E_{c3} is in excellent agreement with the visual curve in all respects (Fig. 2). Curve E'_{c3} is taken as the typical one of which the model has a *cis*-configuration as regards C_1=C_2 and C_3=O_1. No remarkable discrepancies in the positions of maxima, minima and their intensity relations of the theoretical intensity curves are found throughout this work between the *trans*- and *cis*-configurations. Therefore, that of the *cis*'s of all the other models are omitted in Fig. 3. Curves E_{c3}, E_{b3}, E_{d3} and E_{c4} are given in order to show the limits of acceptability for the positions and relative intensities of the 5th, 6th and 8th maxima, and of the acceptable range of shapes of the 7th shelf. All curves with 4th maximum and minimum shifting inward and with the resolution of the 7th shelf greater than that in curve E_{b3} were rejected. Curve E_{d3} was the lower limit of acceptability for the 4th, 5th and 6th maxima shifting inward and for the prominence of the 7th shelf.

Curves D_{b2} and D_{b3} are given as acceptable curves of the D group. The height of the 5th maximum is slightly increased in both curves, and that of the 3rd maximum in the D_{b2} curve decreased, but that in D_{b3} increased. These discrepancies are not regarded as sufficient to justify the rejection of these models, and both models are considered to be acceptable borderline ones.

Of models in the F group, curves F_{c3} and F_{c4} are taken as representative ones. The features of the 6th maximum and the 7th shelf are both accepted as the limit of permission.

The effect of the thermal vibration on the theoretical curve was then examined. The vibration factor is listed in Table I. Curve TE_{c3} is a representative one showing this effect on the theoretical curve calculated from model E_{c3}. This curve has the same feature in all respects as the visual one has.

From the above considerations, model E_{c3} may be regarded as the most acceptable one, while the others are all accepted as borderline cases. The q_C/q_O values of these eight models are summarized in Table II. The weighing for each feature is indicative of its reliability in comparison with theoretical curves. Low weighing is given to the inner features, because these have generally been found to give less satisfactory agreement than do those at somewhat greater q values. Features for which reproducible measurements could not be obtained are also given lower weights. To the features farther out are assigned relatively low weights.

TABLE I. APPROXIMATE VIBRATION FACTORS USED IN THE CALCULATION FOR METHYL ACRYLATE

Factors	Atom pairs
0.00008	for C_3=O_1 and C_1=C_2
0.00012	for C_3-O_2, C_4-O_2 and C_2-C_3
0.00015	for $O_1'\cdots O_2$, $C_2'\cdots O_1$, $C_2'\cdots O_2$ and $C_1'\cdots C_3$
0.00030	for C-H, $O_1'\cdots C_4$ and $C_1'\cdots O_2$
0.00040	for $C'\cdots H$, $O_2'\cdots H$, $C_2''\cdots C_4$ and $C_1''\cdots O_1$
0.00045	for $C_1'''\cdots C_4$

TABLE II. q_C/q_O VALUES FOR METHYL ACRYLATE

Feature			q_C Model							
Max.	Min.	q_O	E_{c4}	E'_{c3}	E_{b3}	E_{d3}	E_{c2}	E_{c4}	D_{b3}	F_{c3}	Wt.
1		11.70	0.992	1.000	0.983	0.983	0.992	0.992	0.992	0.983	1
	1	14.25	0.986	0.986	0.976	0.975	1.013	0.990	0.983	0.997	1
2		18.70	1.003	1.000	0.974	0.979	1.000	1.005	0.974	1.000	2
	2	24.81	0.992	1.017	1.008	1.008	1.019	1.015	1.003	1.003	1
3		29.56	1.001	0.990	1.014	0.998	0.998	1.008	1.011	0.988	2
	3	32.55	0.999	1.004	0.984	0.984	0.992	0.999	0.968	0.992	1
4		36.00	1.000	0.992	0.979	0.976	0.987	1.000	0.967	0.981	2
	4	40.50	0.993	0.978	0.976	0.981	0.993	1.002	0.956	0.993	1
5		45.67	1.001	0.986	1.012	0.990	0.990	1.007	1.007	1.009	2
	5	49.44	1.011	0.995	1.011	0.995	1.011	1.011	1.005	1.001	1
6		52.20	1.001	0.990	1.019	0.983	1.002	1.006	—	0.978	1
	6	54.73	0.987	0.989	1.003	0.982	1.015	0.996	—	0.996	1
7		(57.50)	1.000	1.008	0.992	—	—	1.000	0.988	1.008	0
8		61.84	1.002	0.996	0.999	0.990	0.963	1.001	0.996	1.011	1
	8	66.15	0.997	0.998	1.002	0.998	1.005	1.001	0.998	1.008	1
Wt. mean			0.998	0.994	0.994	0.986	0.997	1.003	0.987	0.996	
Av. dev.			0.006	0.011	0.017	0.016	0.013	0.018	0.022	0.011	

TABLE III. APPROXIMATE VIBRATION FACTORS USED IN THE CALCULATION FOR METHYL METHACRYLATE

Factors	Atom pairs
0.00008	for $C_1{=}O_1$ and $C_1{=}C_2$
0.00012	for $C_3{-}O_2$, $C_4{-}O_2$, $C_2{-}C_3$ and $C_2{-}C_5$
0.00015	for $C_1'\cdots O_2$, $O_1'\cdots C_2$, $O_2'\cdots C_2$ and $C_3'\cdots C_4$
0.00018	for $C_1'\cdots C_3$, $C_3'\cdots C_5$ and $C_1'\cdots C_5$
0.00030	for C–H, $O_1'\cdots C_4$, $O_1''\cdots C_5$ and $O_2''\cdots C_1$
0.00040	for $C_2'\cdots H$, $O_2'\cdots H$, $O_1''\cdots C_1$, $O_2''\cdots C_5$ and $C_1'''\cdots C_4$
0.00050	for $C_4'''\cdots C_5$

TABLE IV. q_C/q_O VALUES FOR METHYL METHACRYLATE

Feature			q_C/q_O Model					Wt.
Max.	Min.	q_O	I	II	III	IV	V	
1		10.43	1.030	1.004	1.015	0.992	1.045	1
	1	14.26	1.013	0.982	0.978	0.972	0.982	1
2		18.08	0.999	1.013	0.999	1.001	1.006	2
	2	24.72	0.983	0.996	0.992	1.021	0.992	1
3		29.23	0.975	1.004	0.989	1.016	0.987	2
	3	32.18	0.988	1.011	0.979	0.995	0.979	1
4		35.80	0.987	1.002	0.978	0.957	0.971	2
	4	39.52	0.992	0.995	0.998	0.942	0.975	2
5		41.75	1.029	1.007	—	0.958	—	1
	5	43.08	1.010	1.015	—	0.963	—	1
6		45.05	1.021	1.021	1.011	1.003	0.999	2
	6	49.00	1.031	1.004	1.005	1.010	1.020	1
7		57.03	0.995	0.999	1.007	0.988	0.993	2
	7	59.59	1.002	0.993	1.006	0.987	0.974	1
8		61.41	1.023	1.003	1.014	0.989	0.998	1
	8	66.52	1.015	0.992	0.995	1.015	0.993	1
9		71.10	1.009	0.997	1.005	1.019	0.985	1
	9	75.03	0.999	0.984	0.999	1.010	0.973	1
Wt. mean			1.003	1.002	0.997	0.989	0.991	
Av. dev.			0.014	0.010	0.014	0.026	0.018	

The radial distribution function for this molecule is calculated by the use of the following equation, (RD curve in Fig. 3):

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

where $I_{(q)_O}$ is the intensity read from the visual curve. The value b is determined by setting $\exp(-bq^2)=0.1$ at $q=80$. The curve shows that the first peak corresponds to the C–H, C_3=O_1, C_2–C_3, C_3-O_2 (in carboxyl) and O_2–C_4 (in methoxyl) distance, the second and the third to the nonbonding atom pairs, i. e., $C'\cdots H$, $O'_2\cdots H$, $O_1'\cdots O_2$, $O_1'\cdots C_2$, $O_2'\cdots C_2$, $C_1'\cdots C_3$, $C_1'\cdots O_2$ and $C_2''\cdots C_4$, the fourth to the $C_1''\cdots O_1$, and the fifth to the $C_1'''\cdots C_4$, respectively. Owing to the complex nature of the peaks, no attempt was made to resolve the distances. It may be noted, however, that the position determined from the most acceptable model agrees fairly well with the peaks observed in this radial distribution curve.

The results obtained from the examination of theoretical intensity curves and the visual ones are as follows.

Assumption: C–H=1.08 Å, C–H (in methyl group)=1.10 Å, C_1=C_2=1.36 Å, C_2–C_3=1.44 Å, C_3=O_1=1.22 Å, $\angle CCH=\angle C_1C_2C_3=\angle C_2C_3O_1=120°$, $\angle O_1C_3O_2=125°$ and $\angle O_2C_4H=109.5°$ (in methyl group).

Results: C_3–O_2 (in carboxyl)=1.36±0.02 Å, O_2–C_4 (in methoxyl)=1.46±0.02 Å, $\angle C_3O_2C_4=115\pm5°$ and out-of-plane angle of methyl group is 25±5°.

Methyl Methacrylate.—On account of the many parameters involved, a complete analysis on the molecular structure of methyl methacrylate may be very laborious. The present analysis was based upon the following assumption: C–H (in methylene group)=1.08 Å, C–H (in methyl group)=1.10 Å, the hydrogen atoms in two methyl groups have tetrahedral configuration, C_1=C_2=1.36 Å, C_2–C_3=1.44 Å, C_3=O_1=1.22 Å, C_3-O_2 (in carboxyl)=1.36 Å, O_2–C_4 (in methoxyl)=1.46 Å, $\angle C_2C_1H=\angle C_1C_2C_3=\angle C_2C_3O_1=120°$, $\angle O_1C_3O_2=125°$, $\angle C_3O_2C_4=115°$ and the C_4 atom is inclined by 25° to the molecular plane. Therefore, in the models examined in this work, only two parameters are changed; the C_2–C_5 distance between C_5 atom of methyl group and α-carbon atom is varied from 1.45 to 1.54 Å in steps of 0.02 or 0.03 Å and the angle of $C_5C_2C_3$ from 110 to 130° in steps of 2 or 3°.

The theoretical intensity curves which are calculated through the above mentioned equation are carefully compared with the visual one. In Fig. 5, visual and theoretical intensity curves and also the radial distribution curve are shown. Curve B is the most acceptable one, and curves A and from C to E can be considered to show the limit of acceptability for the resolution and

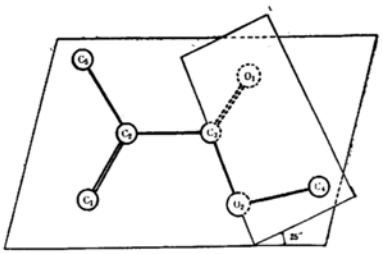

Fig. 4. Schematic model showing the skeleton and the numbering of atoms of methyl methacrylate. This model shows the *trans*-form.

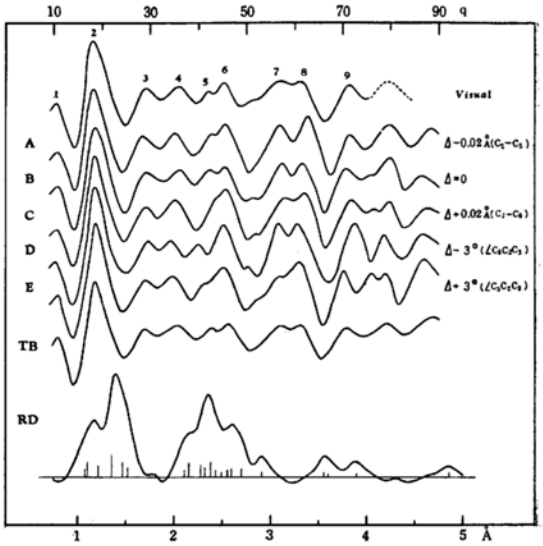

Fig. 5. Visual, theoretical intensity curves and radial distribution curve for methyl methacrylate. The notations on the right hand side of this figure show that the models deviate from the most probable one, for example, $\Delta=0$ is the most probable model which has the following parameters; C_1-H=1.08, C_4-H=C_5-H=1.10, C_1=C_2=1.36, C_2-C_3=1.44, C_3=O_1=1.22, C_3-O_2=1.36, O_2-C_4=1.46 Å, $\angle C_2C_1H=\angle C_1C_2C_3=\angle C_2C_3O_1=120°$, $\angle C_2C_5H=\angle O_2C_4H=109.5°$, $\angle O_1C_3O_2=125°$, $\angle C_3O_2C_4=115°$ and C_4 atom is 25° out of plane configuration.

for the relative intensities of the 7th and 8th maxima and the feature of the 5th shelf. Curve TB shows the effect of thermal vibration. The thermal vibration factors examined in this case are listed in Table III. The q_C/q_O values of these models are summarized in Table IV. The weighing of these features followed the same consideration as in the case of methyl acrylate.

The radial distribution curve (RD curve in Fig. 5) is drawn according to the above equation. The value of b is determined by setting $\exp(-bq^2)=0.1$ at $q=90$. The curve shows that the positions determined from the most acceptable model agree

well with the peaks observed in this radial distribution curve.

The results obtained from the above analyses in this molecule are as follows.

Assumption: All parameters of the most probable model of methyl acrylate were assumed, and the C_5 atom in the methyl group was coplanar, H atoms in this group were of tetrahedral configuration and C_5–H bond lengths were 1.10 Å.

Results: C_2–C_5 = 1.52±0.02 Å and $\angle C_5C_2C_3$ = 129±3°

Discussion of the Results

The results obtained from electron diffraction investigation of acrylic acid generally agree with the corresponding bond lengths and valence angles of acrolein and acetic acid which were obtained by electron diffraction study by Sutton et al.[5] and by Brockway et al.[6] On the basis of the above reason, it was assumed that the skeletons of methyl acrylate and methyl methacrylate were of the same dimension as in the case of acrylic acid.

Unfortunately, no data have appeared which make possible the valid comparison of the C=C, C–C and C=O distances in these esters with those in other compounds. However, the configuration of the methyl group in methyl acrylate agrees with that of methyl acetate. The values for the $C_3O_2C_4$ angle (115±5°) and for the out-of-plane configuration (25±5°) obtained in this work do not differ significantly from the values reported for methyl acetate.

Regarding methyl methacrylate, the value of C_2–C_5 distance obtained here is comparable with the recent value obtained by Keidel and Bauer[7] in the case of toluene, and with the results of I'Haya's theoretical calculation on hyperconjugation[8] of the methyl group in ethylacetylene.

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