A Study on the Molecular Structure of Acrylyl Chloride by Electron Diffraction[1]

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Mackle and Sutton[2] proposed a planar structure of acrolein molecule along with other related molecular dimensions, and there is Coulson's discussion[3] regarding the relation between the bond length and the bond order of the compound. Here, the molecular structure of acrylyl chloride was treated by means of electron diffraction method.

Experimental

The preparation of acrylyl chloride was as follows[4]. β-Chloropropionic acid was prepared by passing dry hydrogen chloride through acrylic acid which had been made by hydrolysis of methyl acrylate of commercial grade. It was treated with thionyl chloride at about 80°C to be converted into β-chloropropionic acid chloride. Then the β-chloropropionic acid chloride was gradually dropped onto a catalyser heated to about 200°C which was composed of alumina containing a few per cent. of aluminium chloride and barium chloride. By careful distillation of the chloride, a fraction boiling at 73 ± 1°C was collected.

The electron diffraction photographs were taken in the usual manner using a camera reported in the previous paper[5] (camera distance, ca. 9 cm.; electron wave length, 0.056–0.063 Å, determined by calibration with gold foil). Ten satisfactory photographs were obtained. The diffraction patterns were visually measured up to ca. 90 of q-values.

Analysis

The diffraction photographs were measured by the usual visual method, and the results were shown in Fig. 2 and Table II. The well known formulae for the calculation of the theoretical intensity curves are

$$I_{(q)}=\sum_i\sum_j\frac{Z_iZ_j}{r_{ij}}\exp(-a_{ij}q^2)\sin\frac{\pi}{10}qr_{ij} \quad (1)$$

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

where r_{ij} is the distance between the i-th and j-th atom, λ the electron wave length, θ the scattering angle, Z_i the atomic number of the i-th atom, and $<\Delta r_{ij}^2>$ the mean square amplitude of r_{ij}. The thermal vibration term was neglected for the first approximation, i.e. $<\Delta r_{ij}^2>=0$. It was assumed that all the atoms in this molecule were coplanar, and that the distance of C—H and the angle of CCH were 1.08 Å and 120°, respectively. The parameters

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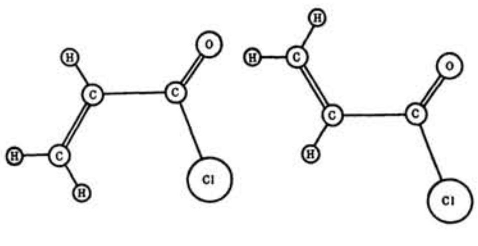
[1] Presented partly at the Symposium on the structral chemistry held on October 16, 1956, at Nagoya.

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

[3] C. A. Coulson, ibid., **42**, 106 (1946).

[4] H. Ueda, T. Sugita and Y. Tanaka, *The Report of the Institute of Synthetic Fiber*, **1**, 635 (1943).

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



trans-form *cis*-form

Fig. 1. Schematic models showing the *trans*- and *cis*-form acrylyl chloride.

C=C and C—C, used in the calculation of theoretical intensity curves, were varied from 1.32 to 1.40 Å and from 1.40 to 1.54 Å in steps of 0.02 or 0.03 Å, and C=O and C—Cl were varied from 1.18 to 1.24 Å and from 1.68 to 1.77 Å with the same increments, while the angles of CCC, CCO, and OCCl were varied from 110° to 130°, from 120° to 130° and from 110° to 130° in steps of 2° or 3°, respectively.

The effect of thermal vibration on the theoretical curves was examined, using the vibration factors a_{ij} listed in Table I, and the curves including thermal terms are shown in the dotted lines in Fig. 2.

A careful comparison was made between the visual intensity curve and the theoretical ones. The curves C_t and C_1 are in the best agreement with the visual one. The curves of several other models also resemble the visual, but they differ from it in the features of the fourth and the fifth maximum and the seventh shelf.

TABLE I

VALUES FOR a_{ij} USED FOR ACRYLYL CHLORIDE MODELS*

Atom Pairs	$a_{ij}\times 10^5$
C—H	15.0
C=O	0
C=C	0
C—C	0
C—Cl	12.0
C′···H	20.5
C′···O	5.0
C′···C	8.0
C′···Cl	15.0
C′···Cl	13.0
C″···O (*cis*-form)	20.5
C″···O (*trans*-form)	30.0
C″···Cl (*cis*-form)	28.0
C″···Cl (*trans*-form)	23.5

* All the values are assumed.

The theoretical intensity curves of the *trans*- and the *cis*-form (Fig. 2) remain almost unchanged throughout the features of intensity relation, except the discrepancies of the features of the fourth and the fifth maximum and the seventh shelf. Curves C_1, C_2, and C_3 are the curves of mixtures composed of three parts of the *trans*-form and one part of the *cis*-form, equal parts of the *trans*- and the *cis*-, and one part of the *trans*- and three parts of the *cis*-, respectively.

The fourth and the fifth maximum of the curves A and B are both shifted inward and the seventh shelf has a different shape, while in curve D the fourth maximum changes to a shelf and the sixth minimum shifts outward. Curve E shows that the intensity of the fourth and the eighth maximum is too great in comparison with the fifth and the ninth maximum, and the seventh shelf changes to a peak. Curve F was taken as the typical one for the models which had a greater angle of CCO, the fourth and the eleventh maximum shifting inward and the seventh shelf changing to a small peak. In curves G and H, the features of the fourth maximum and the seventh shelf disagree with the visual ones; in curves I and J the third, the fourth, and the fifth maximum are shifted inward. Curves K and L were made for the purpose of ascertaining the limit of acceptability for C=O distance, both curves being in good agreement with the visual ones in all respects, except the seventh shelf. Likewise, curves O and P were used to show the limit for angle CCC. These curves are rejected because of the disagreement with the visual ones, in the range $q>50$. In curve M, the fourthand the eighth maximum shifted outward, and the tenth maximum changed its position and turned out to be a shelf of the ninth maximum. In curve N, each of the fifth, the sixth, and the eighth minimum, and each of the fifth and the ninth maximum shifted inward; the tenth maximum almost disappeared.

From the above consideration, the models C_t and C_1 are regarded as the most acceptable fits, while the others are all accepted as borderline fits. Nine models are selected from them, and their q_c/q_o values are summarized in Table II.

The radial distribution function for this molecule (Fig. 3) was calculated using the following equation,

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

where $I_{(q)}$ is the intensity read from the visual curve. The value of b was determined by setting $\exp(-bq^2)=0.1$ at $q=90$.

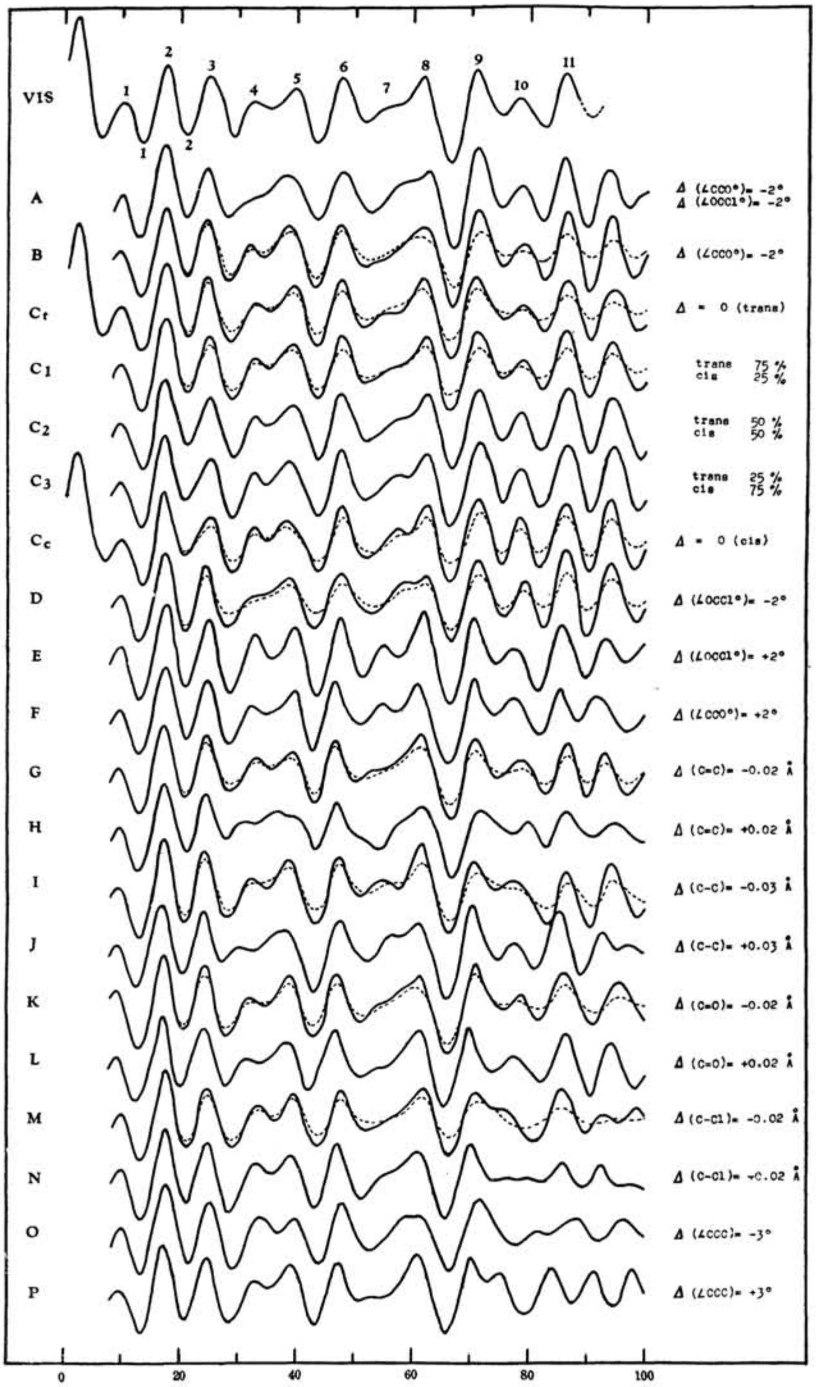


Fig. 2. Visual (VIS) and theoretical intensity curves for acrylyl chloride. The notations on the right hand side of this figure show that the models are deviated from the most probable model, for example, $\Delta=0$ is the most probable model which C—H=1.08, C=C=1.36, C=O=1.20, C—C=1.44, C—Cl=1.74 Å, ∠CCH=120°, ∠CCC =120° and ∠CCO=∠OCCl=125°.

TABLE II

q_c/q_o VALUES FOR ACRYLYL CHLORIDE

Feature		q_0	Model									Wt.
Max.	Min.		B	C_t	C_1	C_c	D	G	I	K	M	
1		10.36	0.923	0.912	0.922	0.965	0.941	0.927	0.946	0.913	0.951	0
	1	13.53	0.957	0.968	0.982	1.009	0.950	0.976	0.979	0.994	0.979	1
2		16.88	1.030	1.031	1.021	1.007	1.028	1.016	1.011	1.036	1.037	1
	2	21.17	0.990	1.000	0.997	0.987	0.992	0.999	0.994	0.999	1.027	1
3		25.07	0.997	0.983	0.987	1.015	0.977	0.981	0.983	0.989	0.997	2
	3	29.15	0.961	0.983	0.995	1.003	0.971	0.983	0.973	0.978	0.997	1
4		32.61	0.986	1.012	1.000	1.000	1.027	1.035	1.004	1.004	1.012	1
	4	36.86	0.922	0.975	0.974	0.943	0.958	0.970	0.963	0.950	0.996	1
5		39.89	0.969	0.991	0.989	0.963	0.974	0.992	0.985	0.985	1.002	2
	5	43.44	0.994	1.014	0.997	1.012	0.997	0.995	1.001	1.000	1.009	2
6		47.58	0.996	0.999	1.000	1.005	1.001	0.984	1.008	1.000	1.010	4
	6	51.14	1.008	1.008	1.007	1.009	1.028	0.987	0.997	1.005	1.026	1
7		(55.15)	—	1.015	0.997	1.042	1.056	0.988	1.015	0.993	—	0
8		61.82	1.000	1.000	1.003	1.009	1.009	1.000	1.003	0.995	1.011	1
	8	66.26	1.003	1.006	1.001	0.996	1.004	1.006	1.004	1.002	1.003	2
9		70.50	1.007	1.000	1.002	1.012	1.001	1.004	1.004	1.009	1.006	4
	9	75.00	1.003	1.003	1.003	1.003	1.010	0.995	0.998	1.009	0.984	1
10		78.38	1.007	1.002	1.002	0.998	1.008	1.010	0.998	1.010	0.963	1
11		86.29	0.998	0.996	0.998	1.001	1.001	1.007	1.008	1.004	0.994	1
Wt. mean			0.993	0.999	0.999	1.002	0.996	0.995	0.997	0.997	1.004	
Wt. mean sq. dev.			0.004	0.003	0.002	0.003	0.004	0.003	0.002	0.003	0.003	

The curve shows that the first and the second peaks correspond to the C—H, C=O, C=C and C—C distances, the third to the C—Cl, the fourth and fifth to the C′···H, C′···O and C′···C, the sixth to the C′···Cl, O′···Cl, C′′···Cl (in the *trans*-form) and C′′···O (in the *cis*-form), the seventh to the C′′···O (in the *trans*-form) and the eighth to the C′′···Cl (in the *cis*-form), respectively. Owing to the complex nature of the peaks, no attempt was made to resolve the distances. It may be noted, however, that the positions determined from the most acceptable model fairly well agree with the peaks observed in this radial distribution curve.

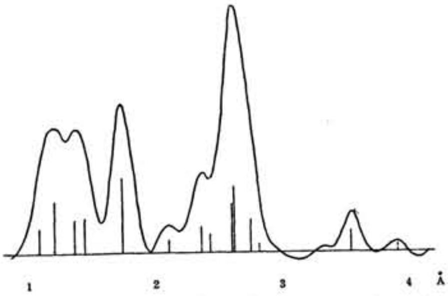


Fig. 3. Radial distribution curve for acrylyl chloride. The most probable interatomic distances are shown by the vertical lines.

In conclusion, the bond distances and bond angles obtained for acrylyl chloride of coplanar configuration are: C=C=1.36 ±0.02 Å, C—C=1.44±0.03 Å, C=O=1.20 ±0.02 Å, C—Cl=1.74±0.02 Å, ∠CCC=120 ±3°, ∠CCO=∠OCCl=125±2°. The *trans*-form is predominant in this molecule.

Discussion of the Results

An electron diffraction investigation of butadiene[6] gave values of 1.35±0.02 Å and 1.46±0.03 Å for the distances of C=C and C—C bond respectivery, and coplanar structure which predominantly had the *trans*-form; these results are in good agreement with the values of 1.36 Å and 1.46 Å in acrolein, respectively. These values agreed with those obtained by C. A. Coulson's theoretical calculation[3] on the C=C, C—C and C=O distances of butadiene, acrolein, and glyoxal. Bond shortening and bond elongation of C—C and C=C bonds in conjugated molecules were plausibly explained by the delocalization of π-electrons. Within the limits of accuracy of this investigation, the circumstances regarding the C=C, C=O distances and the predominance of the *trans* configuration are the same in the case of acrolein.

One of structural studies on acetyl

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

chloride⁽⁷⁾ shows that the carbon-carbon single bond distance is 1.50 Å and shorter than the normal distance 1.54 Å. Further, the single bond distance between chlorine atom and aromatic nucleus is shorter than the bond length of C—Cl 1.77 Å. From the results of this investigation, it may be considered that the corresponding C—C distance is shorter than that of acrolein, and the C—Cl distance is shorter than that of acetyl chloride.

The values for the C=O bond distance and the angles of CCO and OCCl (1.20 ±0.02 Å and 125±2°, respectively) obtained here are reasonablly compared with those of related compounds shown in reference to the view of the limit of accuracy of the present experiment.

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[7] Y. Morino et al., *J. Chem. Soc. Japan Pure Chem. Sec.*, **75**, 647 (1954).