Molecular Structures of Propylene Oxide and Epichlorohydrin by Electron Diffraction

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In the previous report[1], it was stated that the molecular structure of ethylene oxide was reinvestigated by electron diffraction and the results coincided better with those of the microwave investigation[2] than those of the early electron diffraction study[3].

In the present paper electron diffraction studies about the structures of propylene oxide and epichlorohydrin are reported.

Propylene oxide and epichlorohydrin have a ring of ethylene oxide and the chief aim of these studies is to know the configuration of $-CH_3$ in propylene oxide and $-CH_2Cl$ in epichlorohydrin with respect to the ring.

Procedure

Propylene oxide was prepared from lime and propylenechlorohydrin which had been obtained from propyleneglycol and hydrogen chloride gas (b. p. 35–36°C). Epichlorohydrin was purified by distillation of the commercial product (b. p. 115°C).

Electron diffraction photographs were prepared by the apparatus described in the previous report[1]; the camera distance at that time was about 9 and 10 cm., and the wave length of the electron beam was about 0.055 Å. Visual intensity curves V_1 (propylene oxide) and V_2 (epichlorohydrin) were drawn from measurements of the photographs (Figs. 1 and 2). The q values of maxima and minima are shown in Tables III and IV.

TABLE I

STRUCTURE OF ETHYLENE OXIDE BY MICROWAVE INVESTIGATION[2]

C−C	1.472Å	C−O	1.436Å
C−H	1.082Å		
∠H−C−H	116°41'	∠H_2−C−C	159°25'

TABLE II

MODELS FOR PROPYLENE OXIDE (A, B, C, D) AND EPICHLOROHYDRIN (E, F, G, H, I, J, K)

Model	C_2-C_3 Å	Angle between C_2-C_3 and C_1C_2O plane	Configuration of Cl atom in epichlorohydrin
A	1.54	58°	
B	1.50	58°	
C	1.54	50°	
D	1.54	65°	
E	1.54	58°	*trans* against the midpoint of C_1-O
F	1.50	58°	
G	1.54	50°	
H	1.54	65°	
I	1.54	58°	*cis* against the midpoint of C_1-O
J	1.54	58°	*trans* against C_1
K	1.54	58°	*trans* against O

Triangle C_1C_2O, C_1-H and C_2-H are equal to those of ethylene oxide (Table I). $C_3-H=1.09$Å, $C_3-Cl=1.76$Å. Angles in $-CH_3$ and $-CH_2Cl$ are all equal to tetrahedral angle.

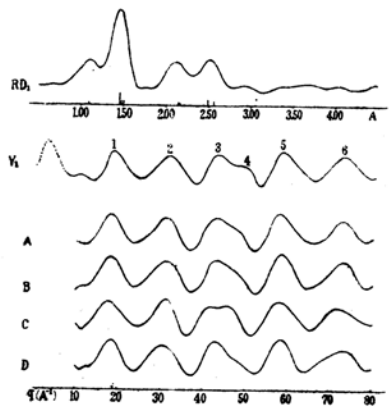


Fig. 1. Propylene oxide

1) M. Igarashi, This Bulletin, **26**, 330 (1953).
2) G.L. Cunningham, A.W. Boyd, R.J. Myer, W.D. Gwinn and W.I. Le Van, *J. Chem. Phys.*, **19**, 676 (1951).
3) P.C. Ackermann and J.E. Mayer, *J. Chem. Phys.*, **4**, 377 (1936).

TABLE III

PROPYLENE OXIDE

Max.	Min.	q_{obs}	q_{calc}/q_{obs} A	B	C	D
1		18.3	0.983	0.988	0.972	1.004
	2	25.05	0.943	0.947	1.003	0.947
2		31.45	0.982	0.992	0.982	0.970
	3	37.25	0.988	1.001	0.974	1.001
3		42.1	1.014	1.016	0.998	1.012
	4	45.85	(0.992)	(1.012)	(0.949)	(1.025)
4		49.4	(0.042)	(1.042)	(0.929)	(0.982)
	5	52.4	0.992	0.998	0.982	1.001
5		57.8	1.000	1.007	1.000	1.000
	6	65.4	1.025	0.987	1.006	0.983
6		72.2	1.004	1.007	0.991	1.015
	7	78.75	0.992	0.977	1.013	1.001
7		(84.0)				
Average, 10 features			0.994	0.994	0.991	0.994
Average deviation			0.015	0.012	0.012	0.017

TABLE IV

EPICHLOROHYDRIN

Max.	Min.	q_{obs}	q_{calc}/q_{obs} E	F	G	H
1		11.9	(0.908)	(0.950)	(0.908)	(0.915)
	2	14.45	(0 920)	(0.920)	(0.906)	(0.934)
2		17.1	0.977	0.954	0.971	0.983
	3	20.05	1.006	(1.021)	1.001	1.011
3		21.3	0.994	(1.008)	1.008	1.008
	4	23.25	1.002	1.006	0.998	1.024
4		26.25	**1.002**	**1.006**	**0.998**	**1.014**
	5	29.05	0.992	0.999	0.978	1.024
5		31.9	**0.991**	**0.998**	**0.982**	**0.994**
	6	34.7	0.994	1.008	0.988	1.000
6		37.05	1.007	1.001	1.001	1.001
	7	39.35	0.973	0.986	0.970	1.001
7		41.6	0.993	1.003	0.979	1.017
	8	44.0	0.991	0.998	0.984	1.000
8		46.95	**0.991**	**1.003**	**0.986**	**0.995**
	9	49.65	0.984	(1.016)	0.982	1.013
9		51.05	1.005	(1.019)	0.999	1.027
	10	53.2	1.004	(1.006)	0.996	1.021
10		56.8	**1.011**	**1.014**	**0.998**	**1.026**
	11	58.95	0.997	1.011	0.984	(1.017)
11		60.8	**0.995**	**0.998**	**0.998**	**1.003**
	12	64.7	0.998	1.003	0.998	1.003
12		70.0	1.023	1.024	1.011	....
	13	77.25	1.019	1.022	1.020	....
13		(82.25)				
Average			0.998	1.002	0.992	1.008
Average deviation			0.009	0.009	0.010	0.010

Values in Gothics were doubly weighted in computing averages.

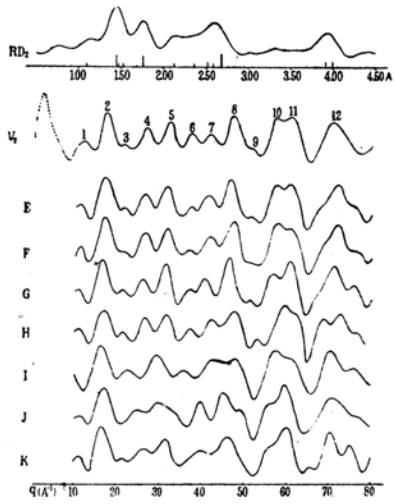
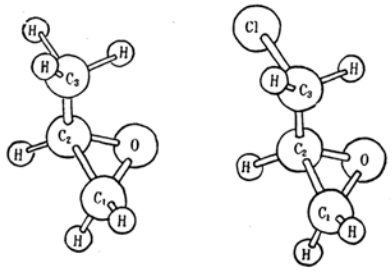


Fig. 2. Epichlorohydrin



Propylene oxide Epichlorohydrin

Fig. 3. Perspective picture of propylene oxide and epichlorohydrin molecules.

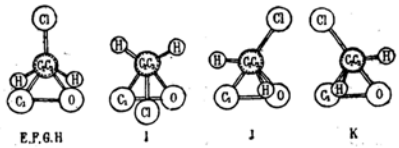


Fig. 4. Various configurations of epichlorohydrin.
H-atoms of C_1H and C_2H are omitted for convenience.

Analysis and Results

From the visual intensity curves V_1 and V_2, radial distribution curves RD_1 (propylene oxide) and RD_2 (epichlorohydrin) were drawn by using the formula,

$$rD(r)=\sum_{q=1,2,\cdots}^{q=80} V(q)\exp(-aq^2)\sin(\pi qr/10)$$

where $q=10s/\pi=(40/\lambda)\sin\phi/2$, ϕ the scattering angle, and a was determined such that $\exp(-aq^2)=0.1$ at $q=80$.

In RD_1 main peaks are at 1.10, 1.44, 2.11, 2.51 and 2.92 Å, which seem to correspond to the distances C−H, (C_1-C_2, C−O, C_2-C_3), ($C_1\cdots$H, O···H), ($C_1\cdots C_3$, $C_3\cdots$O) and long range (C···H, O···H), respectively.

In RD_2 main peaks are at 1.14, 1.45, 1.76, 2.13, 2.60 and 3.93 Å, which seem to correspond to the distances C−H, (C_1-C_2, C−O, C_2-C_3), C_3−Cl, (C···H, O···H), ($C_1\cdots C_3$, $C_3\cdots$O, $C_2\cdots$Cl) and ($C_1\cdots$Cl, O···Cl), respectively.

Making reference to the radial distribution curves and the results of ethylene oxide, molecular models for the correlation method were constructed in the ranges as follows, C_1-C_2; 1.44–1.56 Å, $C_1-O=C_2-O$; 1.43–1.45 Å, C_2-C_3; 1.50–1.58 Å, angle between C_2-C_3 and C_1C_2O plane; 50°–70°.

Among them models A, B, C, D (propylene oxide) and E, F, G, H, I, J, K (epichlorohydrin) are described here (Table II and Figs. 3 and 4).

In models E, F, G and H, Cl atom is *trans* against the midpoint of C_1–O. Models I, J, K for epichlorohydrin in which Cl atom is in different configuration from those of E, F, G and H, are also used for comparison.

Theoretical intensity curves for these models were calculated from the equation,

$$I(q)=\sum_{i,j}(Z_iZ_j/r_{ij})\exp(-b_{ij}q^2)\sin(\pi qr_{ij}/10)$$

where r_{ij} is the distance between atoms i and j, and Z_i is the atomic number of atom i, apart from the value 1.25 for the hydrogen atom. The coefficient b_{ij} was assumed to be 0.00016 for bonded hydrogen terms, 0.0004 for unbonded hydrogen terms, and zero for all the others.

Propylene Oxide.—From the correlation between visual and theoretical intensity curves and the values q_{calc}/q_{obs} (Table III), model B seems to be the best among them.

The main results are as follows; $C_2-C_3=1.52\pm0.03$ Å, the angle between C_2-C_3 and C_1C_2O plane is equal to 58°±5°. This angle is almost equal to that between C−H and C_1C_2O plane of ethylene oxide studied by microwave spectrum[2].

Epichlorohydrin. — Theoretical intensity curves of models E, F, G and H which are *trans* in reference to Cl atom and the midpoint of C_1-O, are in good accordance with the visual intensity curve, though the max. 6 is a little weaker than visual. Among them E and F are better than the others according to the value q_{calc}/q_{obs} (Table IV). As the curves of H, I and J are very different from the visual, these configurations would scarcely be worthy of further consideration.

The main results are as follows; $C_2-C_3=1.52\pm0.03$ Å, the angle between C_2-C_3 and C_1C_2O plane is equal to 58°±5°. They are

equal to those of propylene oxide. The configuration of Cl atom is almost *trans* against the midpoint of C_1-O.

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