Molecular Structure of Epibromohydrin and Glycidol by Electron Diffraction

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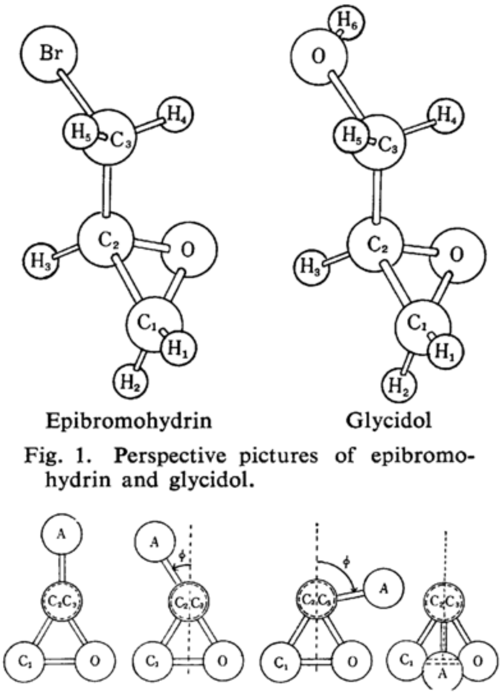
The molecular structure of ethylene oxide⁽¹⁾, propylene oxide and epichlorohydrin⁽²⁾ has been studied previously by the electron diffraction method. As for the size of the CCO ring, the electron diffraction results have agreed almost perfectly with that of microwave spectrum study of ethylene oxide⁽³⁾. The C–C distance was 1.46±0.03 Å and the C–O distance were about 1.44 Å, whereas the values by microwave spectroscopy were 1.472 Å and 1.436 Å, respectively.

In propylene oxide and epichlorohydrin, the C–C (methyl) distance was about 1.52 Å and the angle between C–C (methyl) and CCO ring plane was about 58°. The chlorine atom in epichlorohydrin was the farthest apart from the CCO ring.

In the present paper the structures of epibromohydrin and glycidol are reported especially in regard to the configuration of the bromine atom and of the oxygen atom of alcohol in each molecule.

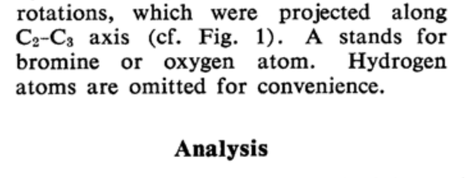
Experimental

Epibromohydrin was prepared according to the procedure described in "Organic synthesis"⁽⁴⁾. The boiling point was 61°C at 50 mmHg. Glycidol was prepared from glycerol monochlorohydrin by the procedure of Nef⁽⁵⁾. The boiling point was 52°C at 10 mmHg. The apparatus of electron diffraction and the procedures of experiment were the same as those of the previous reports⁽¹·²⁾. Visual intensity curves are shown in Figs. 3 and 5.



Epibromohydrin Glycidol

Fig. 1. Perspective pictures of epibromohydrin and glycidol.



$\phi=0$ $\phi=33°$ $\phi=-80°$ $\phi=180°$

Fig. 2. Various configurations of epibromohydrin and glycidol showing internal rotations, which were projected along C_2-C_3 axis (cf. Fig. 1). A stands for bromine or oxygen atom. Hydrogen atoms are omitted for convenience.

Analysis

Radial distribution and theoretical intensity curves were calculated using the same formulas

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1) M. Igarashi, This Bulletin, **26**, 330 (1953).

2) M. Igarashi, ibid., **28**, 58 (1955).

3) G. L. Cunningham, A. W. Boyd, R. J. Myer, W. D. Gwinn and W. I. Le Van, *J. Chem. Phys.*, **19**, 676 (1951).

4) Organic Synthesis, **14**, 42; **16**, 31.

5) J. U. Nef, *Ann.*, **335**, 231 (1904).

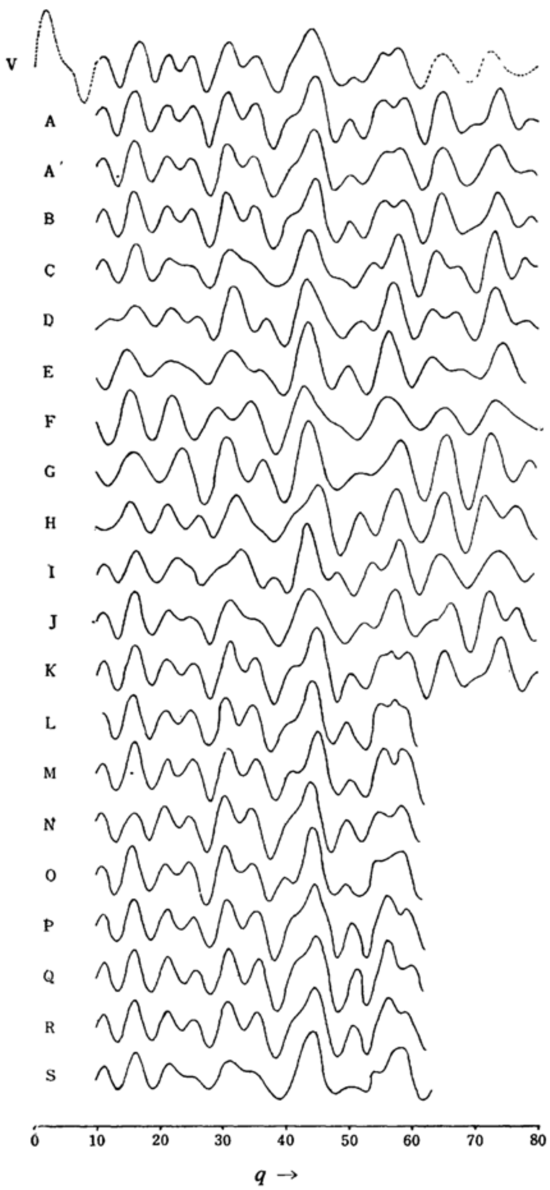

Fig. 3. Visual intensity curve (V) and theoretical intensity curves for the models from A to S (Table I) of epibromohydrin. Curve A′ is drawn using thermal factor $b_{ij}= =0.0002$ instead of zero in curve A for the atomic pairs $C_1\cdots Br$ and $O\cdots Br$.

as before[2]. Making reference to the previous reports[1-3], some parameters of the molecular models for the theoretical intensity curves were assumed as follows: the CCO ring size and C-H distances adjacent, attached to the ring, are equal to those of ethylene oxide, the other C-H distances 1.09 Å, the angles C_2C_3Br and C_2C_3O are both 109.5°, and the angle between C_1C_2 and $C_3C_2H_3$ plane is 21° (Fig. 1). Other parameters such as C_2-C_3 distance and its inclination from the ring plane, C_3-Br and C_3-O distances, and the angles of internal rotation (Fig. 2) were examined.

Epibromohydrin.—The visual intensity curve in the region of $q=60\sim80$ was uncertain, therefore in the correlation method the maxima and minima in the region of $q=10\sim60$ were compared with the theoretical intensity curves, and radical distribution curves were calculated, using several different intensity values in the former region. On account of the damping factor $\exp(-aq^2)$ the positions of the peaks in radial distribution curves were not so much affected by the intensity in such a region. The radial distribution curve is nearly consistent with models A and K (Table I).

Molecular models for the theoretical intensity curves were constructed in the following ranges: C_2-C_3: 1.50~1.58 Å, C_3-Br: 1.88~1.96 Å, angle between C_2-C_3 and CCO ring: 45~70°, rotational angle ϕ around C_2-C_3 axis: 0~360° (Table I).

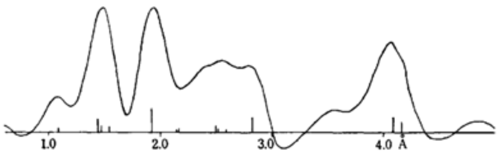

Fig. 4. Radial distribution curve of epibromohydrin. Vertical lines show the interatomic distances of model A.

The theoretical intensity curves of the models in which the rotational angles drawn in Fig. 2 are smaller than ±15° have features which resemble the observed. But as those having the other rotational angles are very far from the observed, these models can be rejected. C_2-C_3 and C_3-Br bond distances and the inclination of C_2-C_3 were examined mainly by the $q_{\text{calcd}}/q_{\text{obs}}$ values (Table I).

The results are as follows: C_2-$C_3=1.53\pm0.03$ Å, C_3-Br$=1.91\pm0.02$ Å, angle between C_2-C_3 and CCO ring is 58±8°, rotational angle ϕ is 0±15°, i. e. the bromine atom is almost trans against the midpoint of C_1-O.

Glycidol. — Theoretical intensity curves of the models in which the rotational angles are about 0° and 80° have features which resemble the observed, although the maximum of the model of 80° at about $q=33$ is not predominant compared with that of 0° (Fig. 5). The models of the other ϕ values such as G, H, L and M may be excluded because the apperances of the intensity curves at about $q=30$ and 50 are very different in comparison with the observed.

The radial distribution curve RD_1 calculated using the visual intensity curve which is shown by the solid line in Fig. 5 and spliced by the

TABLE I. MODELS FOR EPIBROMOHYDRIN AND q_{calcd}/q_{obs} VALUES

Model	C_2-C_3 Å	C_3-Br Å	Inclination of C_2-C_3	Rotational angle, ϕ	Mean value of q_{calcd}/q_{obs}	Average deviation
A	1.54	1.92	58°	0°	0.993	0.015
B	1.54	1.92	58°	15°	0.996	0.017
C	1.54	1·92	58°	33°	—	—
D	1.54	1.92	58°	90°	—	—
E	1.54	1.92	58°	147°	—	—
F	1.54	1.92	58°	180°	—	—
G	1.54	1.92	58°	−147°	—	—
H	1.54	1.92	58°	−90°	—	—
I	1.54	1.92	58°	−33°	—	—
J	1.54	1.92	58°	−15°	0.998	0.015
K	1.50	1.92	58°	0°	1.003	0.015
L	1.58	1.92	58°	0°	0.991	0.015
M	1.54	1.88	58°	0°	1.005	0.019
N	1.54	1.96	58°	0°	0.986	0.015
O	1.54	1.92	45°	0°	0.987	0.015
P	1.54	1.92	65°	0°	0.998	0.019
Q	1.54	1.92	70°	0°	1.011	0.016
R	1.54	1.92	65°	15°	—	—
S	1.54	1.92	65°	33°	—	—

TABLE II. MODELS FOR GLYCIDOL AND q_{calcd}/q_{obs} VALUES

Model	C_2-C_3 Å	C_3-O Å	Inclination of C_2-C_3	Rotational angle, ϕ	Mean value of q_{calcd}/q_{obs}	Average deviation
A	1.54	1.43	58°	0°	0.998	0.016
B	1.50	1.40	58°	0°	1.005	0.020
C	1.54	1.46	58°	0°	0.992	0.022
D	1.58	1.43	58°	0°	—	—
E	1.50	1.43	58°	0°	1.005	0.013
F	1.50	1.43	58°	−15°	1.006	0.008
G	1.50	1.43	58°	−33°	—	—
H	1.50	1.43	58°	−60°	—	—
I	1.50	1.43	58°	−75°	—	—
J	1.50	1.43	58°	−80°	1.003	0.008
K	1.50	1.43	58°	−90°	1.010	0.005
L	1.50	1.43	58°	−120°	—	—
M	1.50	1.43	58°	180°	—	—
N	1.50	1.43	58°	33°	1.007	0.011
O	1.54	1.43	58°	−85°	0.998	0.007
P	1.50	1.40	58°	−85°	1.010	0.008
Q	1.54	1.46	58°	−85°	0.995	0.008
R	1.50	1.43	50°	0°	—	—
S	1.50	1.43	50°	85°	—	—
T	1.50	1.43	65°	0°	—	—
U	1.50	1.43	65°	85°	—	—

theoretical intensity of model E at small q values has a slight peak at about 3.0 Å, which might be regarded as a ghost and a somewhat larger peak at about 3.6 Å, which should correspond to the configuration $\phi=0°$.

But another radial distribution curve RD_2 calculated using the dashed intensity curve in the region of about $q=35$ instead of solid intensity curve and the theoretical intensity curve of model J at small q values in Fig. 5, shows a more predominant peak at about 3.0 Å which corresponds to the existence of the configuration of about $\phi=80°$ (Fig. 6).

Whether the configuration of the oxygen atom of alcohol is at about $\phi=0°$, or about $\phi=80°$, or at the both positions, could not be determined by the present visual method.

The parameters other than the internal rotation were examined in the following ranges: C_2-C_3: 1.50∼1.58 Å, C_3-O: 1.40∼1.46 Å, angle

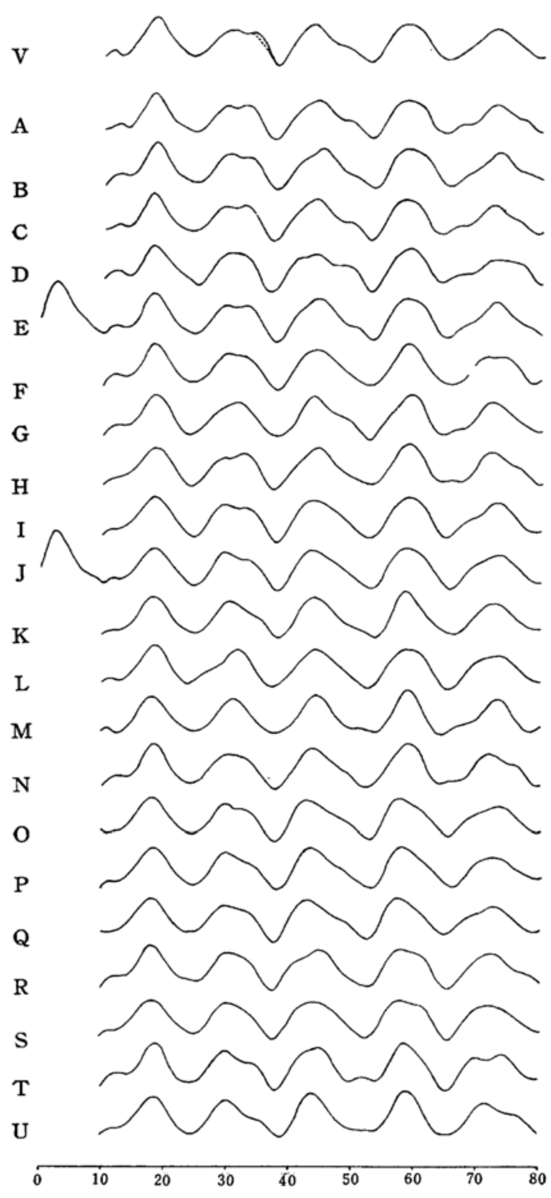

Fig. 5. Visual intensity curve (V) and theoretical intensity curves for the models from A to U (Table II) of glycidol.

between C_2–C_3 and CCO ring: 50~65° (Table II).

As the features of the theoretical intensity curves of the models in which C_2–C_3 inclinations against CCO ring plane are 50° and 65° are considerably different from the visual, both models can be excluded as inadequate. C_2–C_3 and C_3–O bond distances were examined mainly by the $q_{\text{calcd}}/q_{\text{obs}}$ values (Table II). The results are as follows: C_2–C_3=1.53±0.03 Å, C_3–O=1.43±0.03 Å, angle between C_2–C_3 and CCO ring is 58±5°.

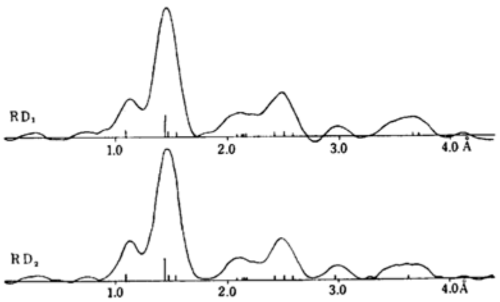

Fig. 6. Radial distribution curves of glycidol. Vertical lines show the interatomic distance of models A (RD_1) and O (RD_2).

Discussion

As mentioned in the previous report[2] about epichlorohydrin and the present report about epibromohydrin, chlorine and bromine atoms in these compounds are almost at the trans position against the midpoint of C_1–O, i. e. these atoms are fathest apart from the CCO ring.

Therefore it can be thought that there is a strong steric repulsion between chlorine atom or bromine atom and ethylene oxide ring.

If the same steric repulsion is present between oxygen atom of alcohol and ethylene oxide ring and moreover no intramolecular hydrogen bond between two oxygen atoms, the oxygen atom of alcohol will be at trans too. Contrarily, if there is a stronger intramolecular hydrogen bond than the steric repulsion, the oxygen atom of alcohol will be nearer to the oxygen atom in the ring than the trans position and ϕ will be equal to about 80°.

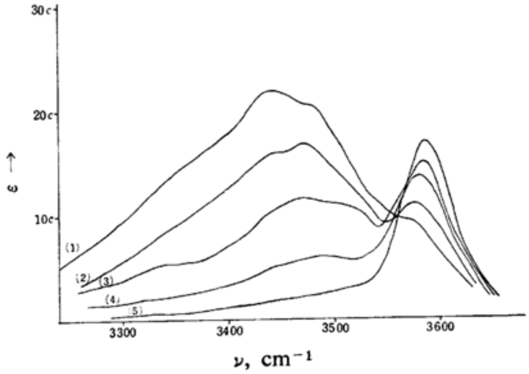

Fig. 7. Infrared absorption spectra of glycidol in carbon tetrachloride solutions. ε is molecular extinction coefficient, c is the concentration of satulated solution at room temperature and ν is wave number. Curves from (1) to (5) are absorption spectra of solutions of the following concentratrations; (1): c, (2): 1/2 c, (3): 1/5 c, (4): 1/18 c, (5): 1/54 c.

Unfortunately as the theoretical intensity curves of both the models rather resemble each other in the features which are characteristic of internal rotations, the above two cases could not be determined unambiguously.

However infrared absorption spectrums of glycidol in dilute carbon tetrachloride solutions using lithium fluoride prism did not show a deviation of O-H stretching vibration by which the intramolecular hydrogen bond can be recognized (Fig. 7). It may be supposed that in the vapor state at room temperature there exists no intramolecular hydrogen bond either, so the oxygen atom of alcohol will be almost at trans against the midpoint of C_1-O.

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