BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 949—950(1972)

Rotational Isomerism in Epihalogenohydrin

Michiro HAYASHI, Kazuki HAMO, Keiichi OHNO, and Hiromu MURATA
Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima

(Received August 19, 1971)

Thirty years ago, Ballaus and Wagner[1] studied the Raman spectra of epihalogenohydrin in the liquid state and discussed the molecular forms of these substances. Recently, several new investigations have been reported on the molecular forms of these substances.

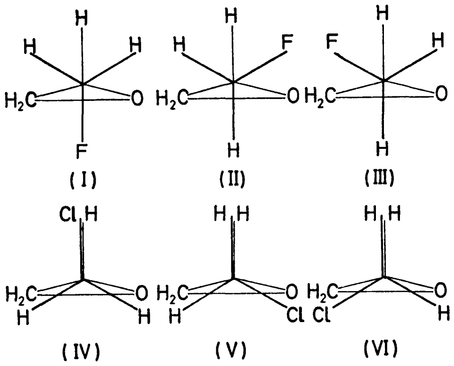

Fig. 1. Molecular forms of epihalogenohydrin.

For epifluorohydrin, the NMR study[2] and the microwave spectroscopy[3] have indicated that the most stable molecular form is the form I in Fig. 1, in which the fluorine atom occupies the *cis* position to the epoxide ring. For epichlorohydrin, however, the electron diffraction[4] has indicated that the preferred form is the form IV, in which the chlorine atom occupies the *trans* position to the epoxide ring.

Not only are the results of these investigations quite different, but the co-existence of the different isomers has never been proved explicitly. We have, therefore, investigated the vibrational spectra of epichlorohydrin, epibromohydrin, and epiiodohydrin in relation to the rotational isomerism, paying special attention to the problem of whether or not the isomers co-exist in the liquid state.

Experimental

Commercial propylene oxide, epichlorohydrin, and epibromohydrin were used without purification since the gas chromatograph showed no remarkable impurities. The epiiodohydrin was prepared from epichlorohydrin by an exchange reaction with KI in acetone.[1]

The infrared spectra were recorded in the region from 4000 to 200 cm^{-1} with a Perkin-Elmer 621 spectrophotometer in both the liquid and crystalline states. The solvent effects of the spectra were also examined using cyclohexane, acetone, and acetonitrile as solvents.

Results and Discussion

As is shown in Fig. 2, some of the spectra vanish in the crystalline state for epihalogenohydrin, while no remarkable change is seen for propylene oxide. The assignments of the observed spectra can be partially made if the spectra of epihalogenohydrin are compared with those of ethylene oxide[5] and propylene oxide.[6,7] Several strong infrared spectra found in the region below 750 cm^{-1} for these substances are regarded as originating from the CH_3 and CH_2X groups.

For propylene oxide, the observed strong bands at 370 and 415 cm^{-1} are assigned to two CCC deformation modes since the CH_3 torsional mode is known to be below 200 cm^{-1}.[7]

For epihalogenohydrin, three skeletal deformation modes may be expected in the region below 500 cm^{-1} for unique molecular form. As Ballaus and Wagner[1] have already pointed out, these skeletal deformations are found at the frequencies close to those of isobutyl

---

[1] O. Ballaus and J. Wagner, *Z. Physik. Chem.*, *B*, **45**, 272 (1939).

[2] W. A. Thomas, *J. Chem. Soc.*, *B*, **1968**, 1187.

[3] J. Bragin, K. L. Kizer, and J. R. Durig, *J. Mol. Spectrosc.*, **38**, 289 (1971).

[4] M. Igarashi, This Bulletin, **28**, 58 (1955).

[5] R. C. Lord and B. Nolin, *J. Chem. Phys.*, **24**, 656 (1956).

[6] M. C. Tobin, *Spectrochim. Acta*, **16**, 1108 (1960).

[7] W. G. Fateley and F. A. Miller, *ibid.*, **19**, 611 (1963).

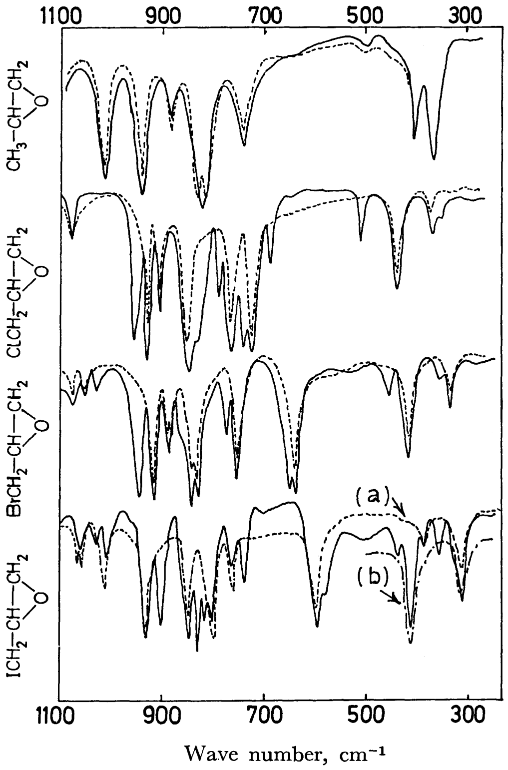

Fig. 2. The infrared spectra of propylene oxide and epihalogenohydrin:—in the liquid state, ----in the crystalline state; (a) in the most stable state, (b) in the metastable state.

halides. From a comparison with the observed spectra of isobutyl halides, the three skeletal deformation modes of epihalogenohydrin can be regarded as falling into two groups, one corresponding to two skeletal deformations of propylene oxide in the region over 300 cm^{-1}, and the other corresponding to the CCX deformation in the region below 300 cm^{-1}.

There are four infrared bands for epichlorohydrin and epibromohydrin and five for epiiodohydrin in this region in the liquid state, while two of them persist in the crystalline state. As is shown in Fig. 2, the frequency *vs.* intensity patterns of the infrared spectra observed around 400, 750, and 900 cm^{-1} show us that the isomers of epichlorohydrin and epibromohydrin in the crystalline state are probably similar to each other, but are different from that of epiiodohydrin. During the repetition of the crystallization procedure, a spectral pattern similar to those for epichlorohydrin and epibromohydrin was also obtained once in the region below 450 cm^{-1} for epiiodohydrin, as is shown in Fig. 2. However, the pattern was changed into an usual one by annealing the sample before recording the spectra around 750 and 900 cm^{-1}.

Although attempts at the reproduction of this special crystalline state have been unsuccessful thus far, these facts suggest that there exist two different crystalline states for epiiodohydrin and that the molecular form is similar to those of epichlorohydrin and epibromohydrin in the metastable crystalline state and is different in the most stable crystalline state.

The solvent effects of the infrared spectra were examined for the skeletal deformations around 400 cm^{-1} and for the C–X stretching modes in the region from 750 to 550 cm^{-1}, which can be easily assigned from the assignments for the similar molecules.[8,9]

For epichlorohydrin and epibromohydrin, the spectra vanishing in the crystalline state become stronger in the cyclohexane solution, while for epiiodohydrin, the spectra persisting in the most stable crystalline state become stronger.

From these results, it can be said that the form in the crystalline state is probably the more polar form for epichlorohydrin and epibromohydrin and the less polar form for epiiodohydrin, in relation to the other forms found only in the liquid state.

As is shown in Fig. 1, there are four other possible molecular forms besides the forms I and IV. Estimation from the bond moments indicates that the magnitudes of the dipole moments for the six different forms decrease in the order of $\mathrm{V} > \mathrm{I} \fallingdotseq \mathrm{II} > \mathrm{IV} \fallingdotseq \mathrm{VI} > \mathrm{III}$. However, we cannot conclude from these results alone which molecular forms in Fig. 1 correspond to the more polar form and the less polar form described above, though the co-existence of at least two different isomers in the liquid state is proved for these molecules.

---

8) S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and S. Tsuchiya, *J. Chem. Phys.*, **26**, 970 (1957).

9) J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **50**, 1164 (1954).