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Chemical Ionization Mass Spectrometry of Epoxides

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Synopsis. The chemical ionization mass spectrometry of epoxides using methane as a reagent gas produces quasi-molecular ions, $(M+1)^+$. This ion has maximum abundance for most epoxides except 1,2-epoxybutane. The method is useful for determination of the molecular weight of epoxides.

Although the behavior of olefines in the photochemical reactions of NO_x–hydrocarbon–O_2 system has attracted interest from the viewpoint of photochemical smog formation,[1–3] all the products from the above reactions were not identified. Epoxides are produced from the reaction of O radical and olefines.[1]

CI mass spectrometry, recently developed,[4] gives abundant quasi-molecular ions ($m/e=(M+1)^+$ or $(M-1)^+$) for many organic compounds, the method being useful for molecular weight determination.[4,5] The present paper gives the results of CI mass spectrometry of the epoxides, as a part of our overall program of identification and analysis of all the products formed in the NO_x–hydrocarbon–O_2 system.

Experimental

A Shimadzu GC-MS apparatus was used. C_2—C_4 epoxides were used as reference materials. Commercial ethylene oxide (Takachiho Chemical Industries), propylene oxide, 1,2-epoxybutane, 2-methyl-1,2-epoxypropane (Wako Pure Industries) and *cis*- and *trans*-2,3-epoxybutane (Tokyo Kasei) were used. All the compounds were separated in the GC column (PEG 400) at room temperature using helium as a carrier gas (flow rate 30 ml/min) before introduction to the ionization chamber.

Results and Discussion

Figures 1—6 give the EI and CI mass spectra of epoxides. The CI patterns were obtained with methane as a reagent gas. Methane gave relatively simple mass spectra for nitrites and nitrates as compared with $i\text{-}C_4H_{10}$ as a reagent gas.[6] The spectra were obtained after subtraction of the background.

The operational conditions of the GC-MS apparatus are as follows. EI spectrum: Ion-source temperature 190 °C, Electron energy 70 eV, Pressure[††] 7×10^{-7} Torr. CI spectrum: Ion-source temperature 190 °C, Electron energy 350—500 eV, Pressure[††] 5×10^{-5} Torr.

The main reactant ions are CH_5^+ and $C_2H_5^+$ when methane is used as a reagent gas.[7] The proton and hydride transfer reactions of these ions are important for analytical purpose, since they generate the quasi-molecular $(M+1)^+$ and $(M-1)^+$ ions, respectively.

$$RH + CH_5^+/C_2H_5^+ \longrightarrow RH_2^+ + CH_4/C_2H_4 \qquad (1)$$

$$RH + C_2H_5^+ \longrightarrow R^+ + C_2H_6 \qquad (2)$$

All the compounds except 1,2-epoxybutane showed very simple CI mass spectra, giving $(M+1)^+$ ion most abundantly. 1,2-Epoxybutane also gives $(M+1)^+$ ion, but the peak at $m/e=55$ is the highest (Fig. 3). This might be related to the easier γ-cleavage of the 1,2-epoxybutane.[8] EI also gave rise to complex cleavage of epoxides, showing that CI is useful for determination of the molecular weight of epoxides.

A series of mass spectra of C_4H_8O isomers, 1,2-epoxybutane, *trans*- and *cis*-2,3-epoxybutane and 2-methyl-1,2-epoxypropane, are given in Figs. 3—6. Only 1,2-epoxybutane could be identified by the CI method, since it gives a different CI mass pattern. However, CI is useless to distinguish other three isomers. Ethylene oxide gives CI mass spectrum quite similar to that of its isomer, acetaldehyde, which is produced by the photochemical reaction of NO_x–hydrocarbon–air system.[†††]

Mass fragments other than stated above are as follows. $(2M+1)^+$ fragment ion appeared in ethylene oxide ($m/e=89$, Fig. 1) and *trans*- and *cis*-2,3-epoxybutane ($m/e=145$, Figs. 4 and 5). Such ions very often appear in the CI spectra.[9] Small amounts of $(M)^+$ and $(M-1)^+$ ions were found in C_3—C_4 epoxides. The peaks at $m/e=(M-17)$ are also common to all epoxides except ethylene oxides. This is the highest peak especially for 1,2-epoxybutane. For C_4 epoxides, the peak ($m/e=55$, Figs. 3—6) could be ascribed to $C_3H_3O^+$ or $C_4H_7^+$. C_3 epoxide (propylene oxide) gave the peak, $m/e=41$ (Fig. 2) which might be derived from C_2HO^+ or $C_2H_5^+$. This suggests alcoholic ion formation; certain alcoholic structures were found for ionized epoxides.[10] The peaks at $m/e=(M-13)$ exist in propylene oxide and 1,2-epoxybutane. They are tentatively assigned to $C_3H_7O^+$ for 1,2-epoxybutane and $C_2H_5O^+$ for propylene oxide. The peaks at $m/e=(M-29)$ are small, but appear in all the spectra except for ethylene oxide. They may be $C_2H_3O^+$ or $C_3H_7^+$ for C_4 ($m/e=43$, Figs. 3—6) and CHO^+ or $C_2H_5^+$ for C_3 ($m/e=29$, Fig. 2).

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[††] Pressure is monitored between the ionization chamber and the vacuum pump in the apparatus. The pressure is related only to the reagent gas pressure.

[†††] Acetaldehyde is passed into the solution containing 2,4-dinitrophenylhydrazine in order to precipitate its hydrazone. Ethylene oxide precipitate no hydrazone in the same solution. The precipitate can be analyzed by means of GC[11] or LC.[12] The application to air pollution analysis is under investigation in this laboratory.

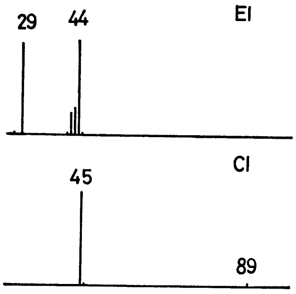

Fig. 1. Mass spectra of ethylene oxide (MW 44).

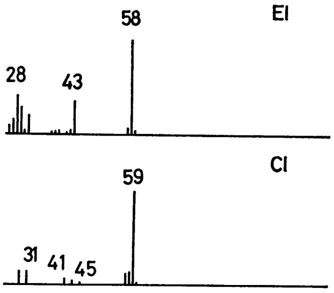

Fig. 2. Mass spectra of propylene oxide (MW 58).

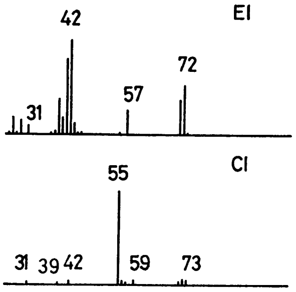

Fig. 3. Mass spectra of 1,2-epoxybutane (MW 72).

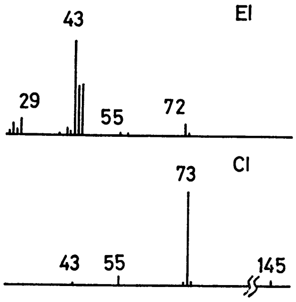

Fig. 4. Mass spectra of *trans*-2,3-epoxybutane (MW 72).

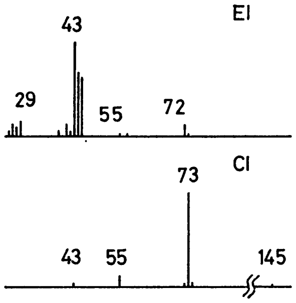

Fig. 5. Mass spectra of *cis*-2,3-epoxybutane (MW 72).

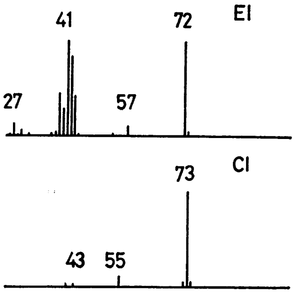

Fig. 6. Mass spectra of 2-methyl-1,2-epoxypropane (MW 72).

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