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The Gas Chromatographic Analysis of Bis(chloromethyl) Ether in Air

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Synopsis. Bis(chloromethyl) ether was converted into bis(ethylthiomethyl) ether by a reaction with sodium ethanethiolate in a hexane solution; the latter sulfur-containing compound was then analyzed by means of a gas chromatograph equipped with a flame photometric detector.

Bis(chloromethyl) ether (BCME) is known to be one of the impurities present in chloromethyl methyl ether, which is a commercial chloromethylating reagent widely used in the production of anion-exchange resins, membranes, and other aromatic products.

Because of its strong carcinogenicity at the 100 ppb level concentration in air, possible industrial exposure to BCME has been of great concern, and so several analytical techniques for monitoring the ppb level of BCME in air have been developed. These analytical methods include gas chromatography and high-resolution mass spectroscopy.[1-5]

BCME is known to be unstable in humid air, and a recent kinetic study of its hydrolysis in an aqueous solution showed that BCME was hydrolyzed very fast, with a half-life of the order of 10 s;[6] this unstability of BCME has presented difficulty in the process of concentrating the air sample in the preparation of the analytical sample used in the analysis described above.

Collier[5] used an enriching column packed with Porapak Q resin, which retains only the organic material, to concentrate the ppb level of BCME in air, and Solomon[2] used the 2,4,6-trichlorophenyl ether derivative of BCME (2,4,6-$Cl_3C_6H_2$-$OCH_2OCH_2OCH_3$) in the analysis by means of a gas chromatograph equipped with an electron-capture detector.

In this study, BCME was converted into bis(ethylthiomethyl) ether (BETME), and the latter sulfur-containing derivative was detected by means of a flame photometric detector (FPD). FPD's selective and sensitive detectability of the sulfur compounds permits the selective detection of the sulfur-containing derivative of BCME in a contaminated sample obtained by the concentration of an air sample containing foreign compounds other than BCME.

BETME can be prepared simply by the reaction of BCME and sodium ethanethiolate (NaSEt) in a hexane solution; this sulfur compound is not only stable to the hydrolysis, but also the presence of water in the reaction mixture does not interfere with the BETME formation reaction.

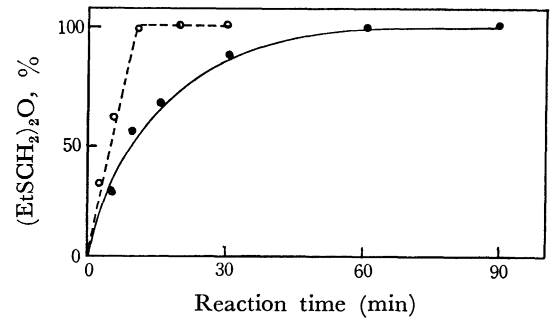

Fig. 1. Reaction rate of the $(EtSCH_2)_2O$ formation reaction.
——: At room temp,
----: at reflux temp of hexane solution.

As is shown in Fig. 1, the reaction of BCME with sodium ethanethiolate proceeds in the course of 1 h at room temperature. The reaction rate can be accelerated with a higher reaction temperature; at the reflux temperature of the hexane solution the reaction can be completed within 10 min. No side reactions have been observed in either reaction. However, the use of freshly prepared sodium ethanethiolate is recommended to keep the reaction rate rapid. The sodium ethanethiolate, even when kept in a desiccator, gradually loses its reactivity in the reaction with BCME, and after one month's storage a large depression of its reactivity was observed.

The presence of water does not change the course of the reaction, as is shown in Table 1, but it decreases the rate of the reaction. In the presence of 960% of water to BCME (mole ratio), 3 h stirring at room temperature was required to complete the reaction. However, no side reaction was observed in this case.

Excellent linearity and reproducibility were observed

TABLE 1. THE EFFECT OF WATER IN THE BCME/NaSEt REACTION

Run	NaSEt	BCME	H_2O added μl	H_2O added mol × 10^{-5}	H_2O/BCME %	H_2O/NaSEt %	$(EtSCH_2)_2O$/IS[a]
1	100 × 10^{-5} mol	23 × 10^{-5} mol	0	—	—	—	2.40
2			1	5.5	24	5.5	2.42
3			2	11	48	11	2.36
4			10	55	240	55	2.39
5			20	110	480	110	2.37
6			40	220	960	220	2.41

a) n-Pr_2S was used as an internal standard.

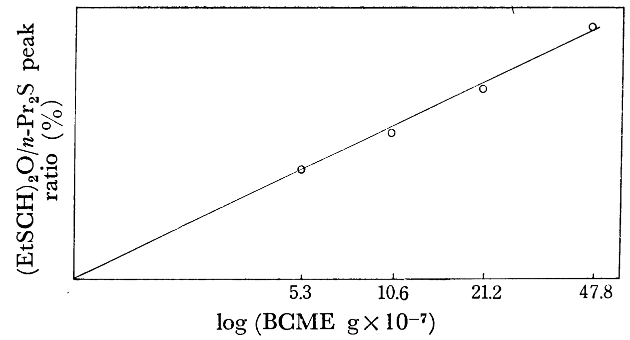

Fig. 2. Calibration curve of bis(ethylthiomethyl) ether.

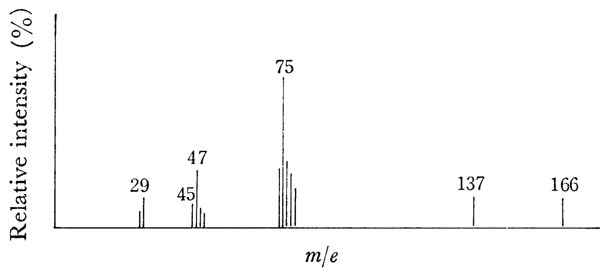

Fig. 3. Mass spectrum of bis(ethylthiomethyl) ether.

in the preparation of the calibration curve (Fig. 2); this fact indicates this analytical method can be applied practically. The mass spectra of the product obtained by the BCME/NaSEt reaction have been shown to be consistent with the assignment of bis(ethylthiomethyl) ether (Fig. 3).

Experimental

Bis(ethylthiomethyl) Ether. A solution of sodium methoxide in methanol (10%) was mixed with a slightly excessive molar amount of ethanethiol. The solution was stirred for 10 min and then evaporated to dryness under a vacuum. The solid residue was pulverized, and a solution of BCME in hexane was added (mole ratio of NaSEt/BCME=2.5). The reaction mixture was stirred for 1 h at room temperature, or refluxed for 10 min.

Gas Chromatography. Micro Tek Instruments Corp. A Model 160 gas chromatograph equipped with a flame photometric detector was used. The analytical column was 1 m× 3 mm i.d. Teflon column packed with 25% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W AW(60—80 mesh). The column oven was kept at 150 °C (isothermal). The carrier gas was a chromatographic grade nitrogen at a flow rate of 60 ml/min.

Mass Spectrometry. The mass spectra of bis(ethylthiomethyl) ether were obtained using a JMS-Q 10 Gas Chromatograph-Mass Spectrometer operated at an ionizing potential of 70 eV.

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