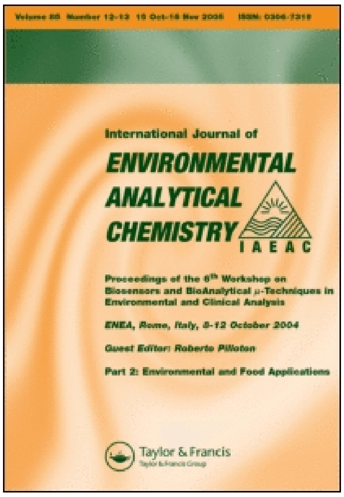

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Formation and Decomposition of Bis(chloromethyl) Ether in Aqueous Media

M. Alvarez[a]; R. T. Rosen[a]
[a] Chemical Research and Development Center, FMC Corporation, Princeton, New Jersey, U.S.A.

To cite this Article Alvarez, M. and Rosen, R. T.(1976) 'Formation and Decomposition of Bis(chloromethyl) Ether in Aqueous Media', International Journal of Environmental Analytical Chemistry, 4: 3, 241 — 246
To link to this Article: DOI: 10.1080/03067317608071118
URL: http://dx.doi.org/10.1080/03067317608071118

Intern. J. Environ. Anal. Chem., 1976, Vol. 4, pp. 241–246

Printed in Great Britain

Formation and Decomposition of Bis(chloromethyl) Ether in Aqueous Media

M. ALVAREZ and R. T. ROSEN

Chemical Research and Development Center, FMC Corporation, Princeton, New Jersey 08540, U.S.A.

(*Received August 11, 1975*)

KEY WORDS: Bis(chloromethyl) ether, hydrolysis, formation/decomposition rates, gas chromatography-mass spectrometry, hexamethylenetetramine.

Reports that bis(chloromethyl) ether (BCME) is carcinogenic have prompted numerous investigations into the formation and decomposition of the compound. In this study, it is shown that the compound forms rapidly in a chloromethylating medium (HCl-HCHO-$ZnCl_2$) at low levels (100 ppm) and attains a fairly steady concentration of 300–500 ppm. Methods for destroying BCME are discussed including the rates of destruction in homogeneous and heterogeneous media. Although BCME is considered reactive, it is not readily decomposed by water or aqueous base because of its low solubility. In homogeneous media such as MeOH-H_2O. the rate of hydrolysis is much faster. The reaction of BCME with aqueous ammonia is very fast and a reaction path to hexamethylenetetramine is suggested. Gaseous BCME reacts rapidly with aqueous systems, particularly alkaline solutions, due to greater contact efficiency.

INTRODUCTION

In 1973, workers at Rohm and Haas Corporation reported that bis(chloromethyl) ether (BCME) rapidly forms in moist atmospheres containing formaldehyde and hydrogen chloride[1]. This news was distressing since BCME previously had been reported to be carcinogenic.[2] Subsequent publications raised some question about vapor phase formation of BCME,[3–5] but the evidence did indicate that typical chloromethylating media generate the potential carcinogen.[3] The initial news release prompted investigations at our laboratories aimed at improving safety procedures. We report here some of our findings in the hope of contributing to safe laboratory practice.

RESULTS AND DISCUSSION

Formation

Analyses[6] of a typical chloromethylating medium (1 g paraformaldehyde, 6.2 g 37% HCl, and 8 mg $ZnCl_2$) showed that BCME formed at room temperature and reached a concentration of 100 ppm in solution within minutes of mixing. A concentration of 300–500 ppm was reached after 24 hours and remained fairly constant for several weeks. Although formation of BCME under these conditions is a minor side reaction, the hazardous nature of the compound warrants that unused or partially spent reaction mixtures be decomposed and that vapor streams be scrubbed to remove BCME.

TABLE I

Effect of treatment of BCME in the liquid and solution phase with various systems

System[a]	BCME taken µg/ml[b]	BCME, µg/ml, found in solution after		
		5 min	10 min	1–2 hour
H_2O[c]	28.7	~30	~30	~30
0.1% Na_2CO_3[c]	28.7	20–25	10–20	5–10
0.1% Na_2CO_3[c,d]	28.7	5–10	5–10	5–10
50% MeOH/H_2O	28.7		1–2	1–2
MeOH	28.7	30	30	<30
1% NaOH–50% MeOH	28.7	N.D.[e]	N.D.	N.D.
1% Na_2CO_3–50% MeOH	28.7	N.D.	N.D.	N.D.
1% NH_3	28.7	N.D.	N.D.	N.D.
1% NH_3	718.	N.D.	N.D.	N.D.
1% NH_3–50% MeOH	718.	N.D.	N.D.	N.D.

[a] All at 25°C unless otherwise specified.

[b] Theoretical concentration if no reaction had occurred and if systems were homogeneous.

[c] Heterogeneous system (BCME not in solution). Samples were vigorously shaken prior to analysis.

[d] Heated for 30 min at 50°C then cooled and analyzed.

[e] less than 1–2 ppm level in solution.

Hydrolysis of BCME

The stability of BCME was examined in various media (Table I). In pure water, BCME neither dissolved nor decomposed over a period of 1–2 hours.

In 0.1% Na_2CO_3, some hydrolysis occurred, but at a relatively slow rate. A faster, but still incomplete destruction of BCME was realized when 0.1% Na_2CO_3 at 50°C for 30 min was used. These results are not in disagreement with hydrolysis studies in which acetone was used to facilitate dispersion of BCME in the aqueous phases.[9] The hydrolyses here were slower than those reported because the BCME was not well dispersed. In homogeneous media such as 50% $MeOH/H_2O$, the concentration of BCME decreases rapidly although reaction in pure methanol is slow, while in alkaline methanol-water solutions, the decomposition of BCME is very rapid. These observations can be explained on the basis of heterogeneous phase reaction kinetics, i.e.,

$$\mathrm{ClCH_2OCH_2Cl}(l) \xrightarrow[\text{slow}]{k_1} \mathrm{ClCH_2OCH_2Cl\ (aq)} \qquad \text{(Eq. 1)}$$

$$\mathrm{ClCH_2OCH_2Cl(aq)} \xrightarrow[\text{fast}]{k_2} \mathrm{2HCHO(aq)+2HCl\ (aq)} \qquad \text{(Eq. 2)}$$

$$\mathrm{ClCH_2OCH_2Cl}(l)+\mathrm{H_2O} \xrightarrow[\text{slow}]{k_3} \mathrm{2HCHO(aq)+2HCl\ (aq)} \qquad \text{(Eq. 3)}$$

where the rate of solution (Eq. 1) is very slow as is the surface reaction (Eq. 3) of BCME with water. In homogeneous systems, only reaction 2 is involved.

A totally different observation was made when BCME was mixed with 1% NH_3 (aq). Unlike previous aqueous systems in which BCME failed to dissolve, 1% NH_3 caused rapid decomposition of BCME (Table I). Since the heterogeneous phase reaction of BCME with water is slow as is the rate of solution, it is probable that BCME (*l*) reacts with NH_3 (aq) at the liquid-solution interface[10] perhaps according to the following scheme:

$$\mathrm{BCME}(l)+\mathrm{NH_3(aq)} \rightleftharpoons \mathrm{NH_3(BCME)}$$

$$\mathrm{NH_3(BCME)} \xrightarrow{\text{fast}} \mathrm{H_2NCH_2OCH_2NH_2}$$

$$\mathrm{H_2NCH_2OCH_2NH_2} \xrightarrow[\text{fast}]{\mathrm{H_2O}} \mathrm{H_2NCH_2OH(aq)}$$

$$\mathrm{H_2NCH_2OH(aq)} \rightleftharpoons \mathrm{NH_3(aq)+HCHO(aq)}$$

$$\mathrm{NH_3(aq)+HCHO(aq)} \xrightarrow{\text{fast}} \mathrm{C_6H_{12}N_4}\ \text{(hexamethylenetetramine)}$$

The overall reaction, at least, does occur since formation of hexamethylenetetramine in this system was established by mass spectrometry, i.e., the mass spectrum of an extract was identical to that of authentic material. Hexamethylenetetramine or methenamine is much less toxic than

BCME and is used as a urinary antiseptic.[11] Consistent with the above explanation and published reports,[9,12] BCME could be readily removed from the vapor phase by scrubbing with 0.1% Na_2CO_3 (Table II). The greater efficiency of contact between gaseous BCME and the solution phase accounts for the rapid rate of destruction. Polarographic examination of the scrubber (E 1/2 = −1.75v vs. S.C.E. in 0.1 M NaOH) revealed a nearly stochiometric quantity of formaldehyde.

TABLE II

Effect of scrubber system on gaseous BCME

Scrubber[a]	BCME taken,[b] effective ppm (volume/volume) in air at 25°C	BCME found,[c] effective ppm (volume/volume) in air at 25°C
H_2O	47	N.D.
H_2O	936	5–7
0.1% Na_2CO_3	47	N.D.
0.1% Na_2CO_3	936	N.D.

[a] 200 ml indicated solution @ 25°C.

[b] Calculated on basis of BCME taken and amount of N_2 passed through the system; figures correspond to overall average air concentration during the experiment.

[c] Based on analysis of the MeOH trap and calculated on basis of air volume used.

CONCLUSIONS

BCME forms rapidly in chloromethylating media as illustrated by the system HCl-paraformaldehyde-$ZnCl_2$. Destruction of laboratory waste can be effectively accomplished with aqueous ammonia to give solutions containing hexamethylenetetramine and less than 1–2 ppm BCME (our limit of detection).

EXPERIMENTAL

Analyses

An LKB 9000 GC-Mass Spectrometer, equipped with an accelerating voltage alternator, was used. The GC column (10 ft × 1/4 in O.D. 3% Carbowax

20M on Chromosorb G AW-DCMS) was operated at 90°C with a helium flow rate of 20 ml/min. Other instrumental conditions were: flash heater, 100°C; source slit, 0.20, exit slit, 0.10; ionizing voltage, 22.5V, trap current, 60 μA; source temp., 310°C; separator temp., 270°C; and chart speed, 1 inch/min. The BCME had a GC retention time of 9 min. Simultaneous monitoring of the m/e 79 and 81 peaks was used.

Standard BCME

A sample of BCME was prepared from reagent grade chemicals (paraformaldehyde, hydrochloric acid, and chlorosulfonic acid) according to the literature.[13]

Stabilities

Media effects on the stability of BCME were studied by pipetting an aliquot of BCME (usually 2 μl) into 100 ml of the liquid phase under study contained in a stoppered flask. Samples of the reaction mixture were periodically removed for analysis by GC-MS/selective ion monitoring.

Scrubber techniques

The effectiveness of water and alkaline media as scrubber systems for plant and laboratory air was studied using the experimental arrangement shown below. Nitrogen at a flow rate of 100 ml/min as measured by a flowmeter (A) was used to volatilize an aliquot of BCME which was injected into an empty wash tower (B) through a septum port (C). The BCME was swept into a scrubber (D). After passing through a glass wool spray trap (E), the vapors were trapped in a bubbler (F) containing 20 ml MeOH at −78°C. The bubbler temperature was maintained with a dry ice-methanol bath (G). A total of 3 liter N_2 was passed through the train. The efficiency of the system was proved by running aliquots of BCME in MeOH with an empty scrubber (D). Effectively 100% recoveries were obtained.

To test the effect of scrubber solutions, the scrubber was filled with 200 ml of either H_2O or 0.1% Na_2CO_3 and an aliquot of BCME was injected at C (Figure 1). After 30 minutes (total N_2 = 3 liters), the bubbler trap was sampled at −78°C and analyzed. Sampling was done at low temperatures since separate experiments had shown that the rate of reaction of BCME with water in MeOH at −78°C is very slow (even with 10% H_2O in MeOH), and since further, water vapor from the scrubber would be expected to condense in the bubbler along with BCME. No attempt was made to dry the N_2-BCME-H_2O stream since experience had demonstrated that laboratory dessicants tend to trap low concentration vapor phase organics (including BCME) as well as water.[14]

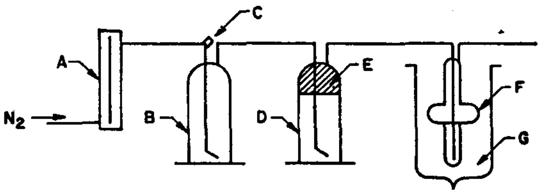

FIGURE 1

References and Notes

1. *Chem. and Eng. News*, Jan. 8, 1973, p. 13.
2. S. Laskin, M. Kuschner, R. T. Drew, V. P. Cappielle, and N. Nelson, *Arch. Environ. Health* **23**, (8) 135 (1971).
3. L. S. Frankel, K. S. McCallum, and L. Collier, *Environ. Sci. and Tech.* **8**, 356 (1974).
4. G. J. Kallos and R. A. Solomon, *Amer. Indust. Hygiene Assoc. J.* **34**, 469 (1973).
5. M. D. Hurwitz, *Amer. Dyestuff Reporter*, March, 1974, p. 62.
6. Initially, analyses were performed by gas chromatography-mass spectrometry utilizing low resolution single ion detection. Specific high resolution single ion detection has been reported for BCME (7). Since aromatic components caused minor interferences, the low resolution method was modified by using a specific-isotope-ratio detection technique (8).
7. L. Collier, *Environ. Sci. and Tech.* **6**, 930 (1972).
8. L. A. Shadoff, G. J. Kallos, and J. S. Woods, *Anal. Chem.* **45**, 2341 (1973).
9. J. C. Tou, L. B. Westover, and L. F. Sonnabend, *J. Phys. Chem.* **78**, 1096 (1974).
10. In alkaline media, the formation of hexamethylenetetramine helps drive the reaction to the right. There is evidence, however, that in the presence of HCl (aq), BCME can reform (3).
11. Merck Index, 8th Ed., 1968, p. 673.
12. L. A. Shadoff, G. J. Kallos, and J. S. Woods, *Anal. Chem.* **45**, 2341 (1973).
13. Organic Synthesis, Collective Volume 4, p. 101. (John Wiley and Sons, Inc.).
14. Alternatively, permeation techniques (5) could have been used for drying, but were not necessary in this work.