FORMATION OF BIS-CHLOROMETHYL ETHER IN TEXTILE - FINISHING OPERATIONS

by

Troy Marceleno, P.E.
Charles C. Yao, Ph.D.
Gordon C. Miller

for presentation at
American Chemical Society
Bicentennial Meeting
New York, New York
April 8, 1976

U.S. Department of Health, Education and Welfare
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations and Field Studies
Cincinnati, Ohio

Introduction

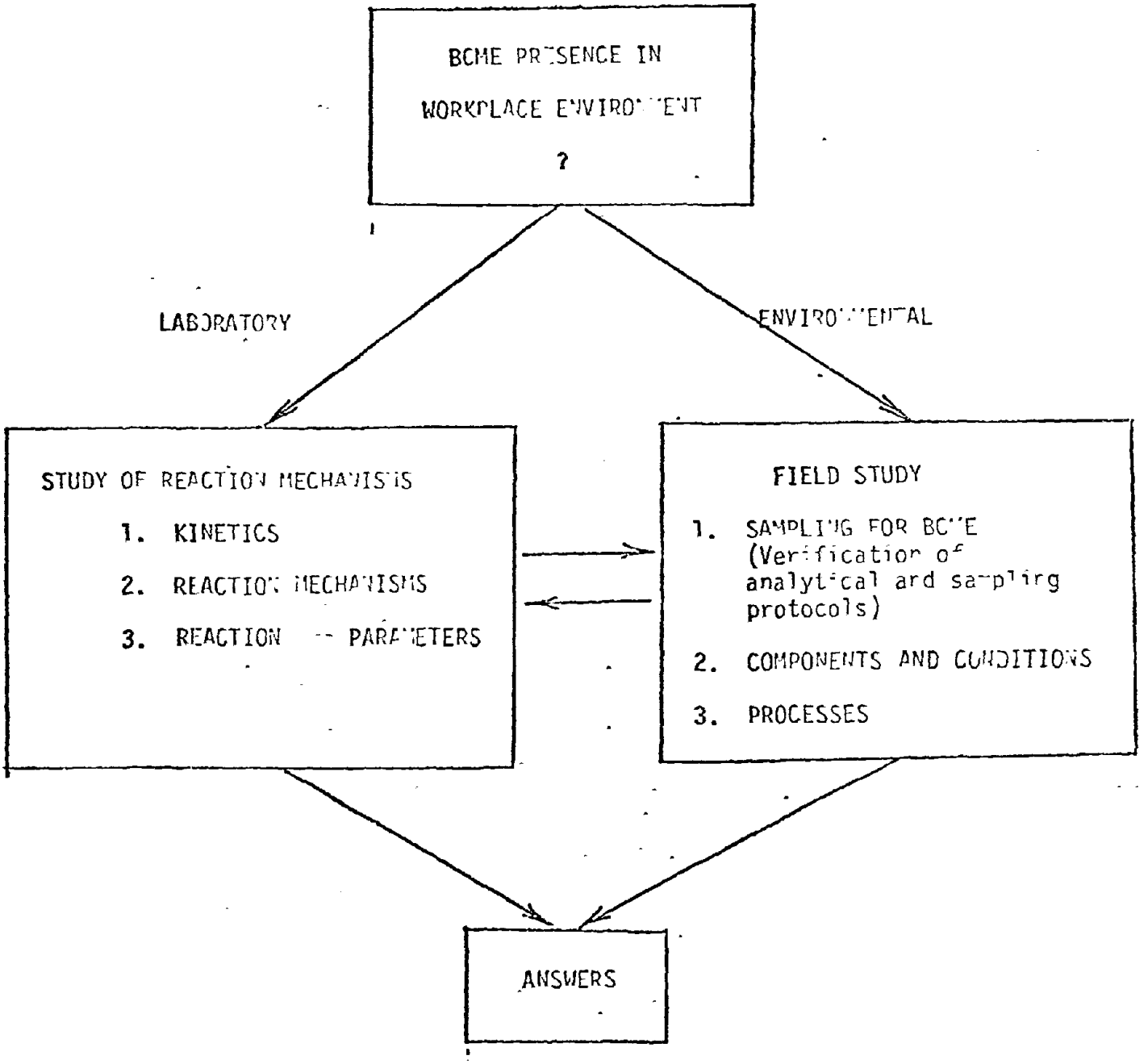
A great deal of concern and speculation has arisen lately on the presence of known carcinogens in the work environment [1], particularly the possible presence of Bis-chloromethyl ether (BCME), an active α haloether in textile manufacturing [2-4]. Formed from the reaction of formaldehyde (HCHO) and ionic chloride compounds, the toxicity of BCME was well established [5-10], however its role in the textile environment until now has been somewhat clouded. New evidence from on-site monitoring for BCME and various parameters at two textile plants and accompanying kinetic and reaction mechanism studies conducted by Bendix Special Projects for the National Institute for Occupational Safety and Health (NIOSH) has begun to resolve some of the uncertainty. Instrumental in this was the development of a two-prong attack centering on laboratory and environmental investigations (see Figure 1).

This report summarizes the preliminary project findings to date. The laboratory study centered on the kinetics and reaction mechanisms of BCME formation. The environmental effort involved the development and verification of existing and newly evolved sampling protocols and analytical techniques coupled with field monitoring of various work environments including textiles where a significant potential for BCME formation was thought to exist [2-4]. Sampling was not limited to the measurement of BCME but also included other possible contributing parameters. The concurrent studies allowed support and comparisons of results.

Summary and Conclusions

The effects of possible BCME formation may have a significant and far reaching impact on future work processes and work environments. Because of this,

FIGURE I


BCME PRESENCE IN
WORKPLACE ENVIRONMENT
?
LABORATORY
ENVIRONMENTAL
STUDY OF REACTION MECHANISMS
1. KINETICS
2. REACTION MECHANISMS
3. REACTION -- PARAMETERS
FIELD STUDY
1. SAMPLING FOR BCME (Verification of analytical and sampling protocols)
2. COMPONENTS AND CONDITIONS
3. PROCESSES
ANSWERS

the study of its role in the work environment requires a lengthy and detailed examination. The results presented are findings which have been developed up to this point and represent preliminary conclusions based on what has been determined from literature reviews, laboratory and field studies.

Surveys were also conducted at two textile plants in order to ascertain the presence and extent of BCME and its reactants, including environmental factors.

The following are preliminary conclusions based on the findings to date. As more work is conducted, some new finding will no doubt result.

1. The kinetic rate equation for BCME formation appears to be expotentially related to reactant concentration and will be a higher than first order reaction.

2. In the workplace environment, the relative abundance of water masks its effect in the rate equation but will still play an important role in the formation of BCME.

3. Because formation of BCME appears to be insensitive to temperature, the Arrhenius plot slope is relatively flat. Consequently, the energy of activation is relatively low which may allow the spontaneous formation of BCME at ambient conditions.

4. The presence of reactants needed for BCME appeared in low ppm levels in textile finishing operations.

5. Only traces of heavy metals were present in the textile finishing environment.

6. No BCME was detected above 0.1 ppb in the textile environment using separate gas chromatography and gas chromatography/mass spectrometer analysis.

KINETIC STUDY OF BCME REACTION MECHANISMS

Since 1887 it has been a standard practice to prepare BCME in the laboratory by mixing paraformaldehyde and concentrated hydrochloric acid and adding chlorosulfonic acid slowly to the mixture with cooling to obtain an 76 to 81% yield [11]. BCME also has been found as a major byproduct in the industrial preparation of chloromethyl methyl ether (CME) from paraformaldehyde, aluminum chloride, and water. Since the establishment of the carcinogenicity of BCME [5-10], attention has been directed not only to its detection but also to its mechanisms of formation in the industrial workplace. The following points demonstrate some of the important findings prior to the inception of this project.

• BCME was formed spontaneously from formaldehyde and hydrogen chloride in ppm range in humid air and that steady state was reached in less than 1 minute.

- Rohm and Haas Company, News Release, Dec. 27, 1972

• At ambient temperature and humidity, BCME is not formed in detectable amount (0.1 ppb) from formaldehyde and hydrogen chloride up to 200 ppm. At concentrations above 500 ppm, only low ppb levels of BCME were detected. The steady state was not attained at less than 18 hours. The reaction rate was independent of the humidity.

- G.J. Kallos and R.A. Solomon, Am. Ind. Hygiene Assoc. J., Nov., 469 (1973)

• BCME formation was exponentially related to the reactant concentrations, indifferent to the reactor surface. The yields were consistently low in dry atmosphere and insensitive to temperature.

- L.S. Frankel, K.S. McCallum, and Ledelle Collier, Environ. Sci. and Tech., 8(4), 356 (1974)

- BCME was not observed from the aqueous reaction of formaldehyde and hydrochloric acid at concentrations up to 2,000 ppm at ambient temperature for 18 hours:
  - J.C. Tou and G.J. Kallos, Am. Ind. Hygiene Assoc. J., July, 419 (1974)

POSTULATED MECHANISMS

The reaction can be discussed in terms of three different media.

- The gas phase reactions
- The condensed phase reactions (polar and nonpolar)
- Heterogeneous reactions (gas-liquid, gas-solid, and liquid-solid systems)

At the present time, only homogeneous reactions are being studied, each according to which one of the three components, water, formaldehyde, and hydrogen chloride, is present in excess, as shown in Figures2 to 4. The laboratory apparatus to effect some of this work are included in the Appendix.

In view of the multiplicity of reaction schemes and the variety of existing experimental parameters, it is a small wonder that the prevailing state of understanding regarding the BCME formation is rather complex and confusing. In order to resolve the selection and elimination process, kinetic study of the reaction in gaseous as well as in condensed phases were conducted. Reaction orders, rate constants and activation energies were determined. Some of the rate equations appeared manageable and have been integrated. Among them are the following:

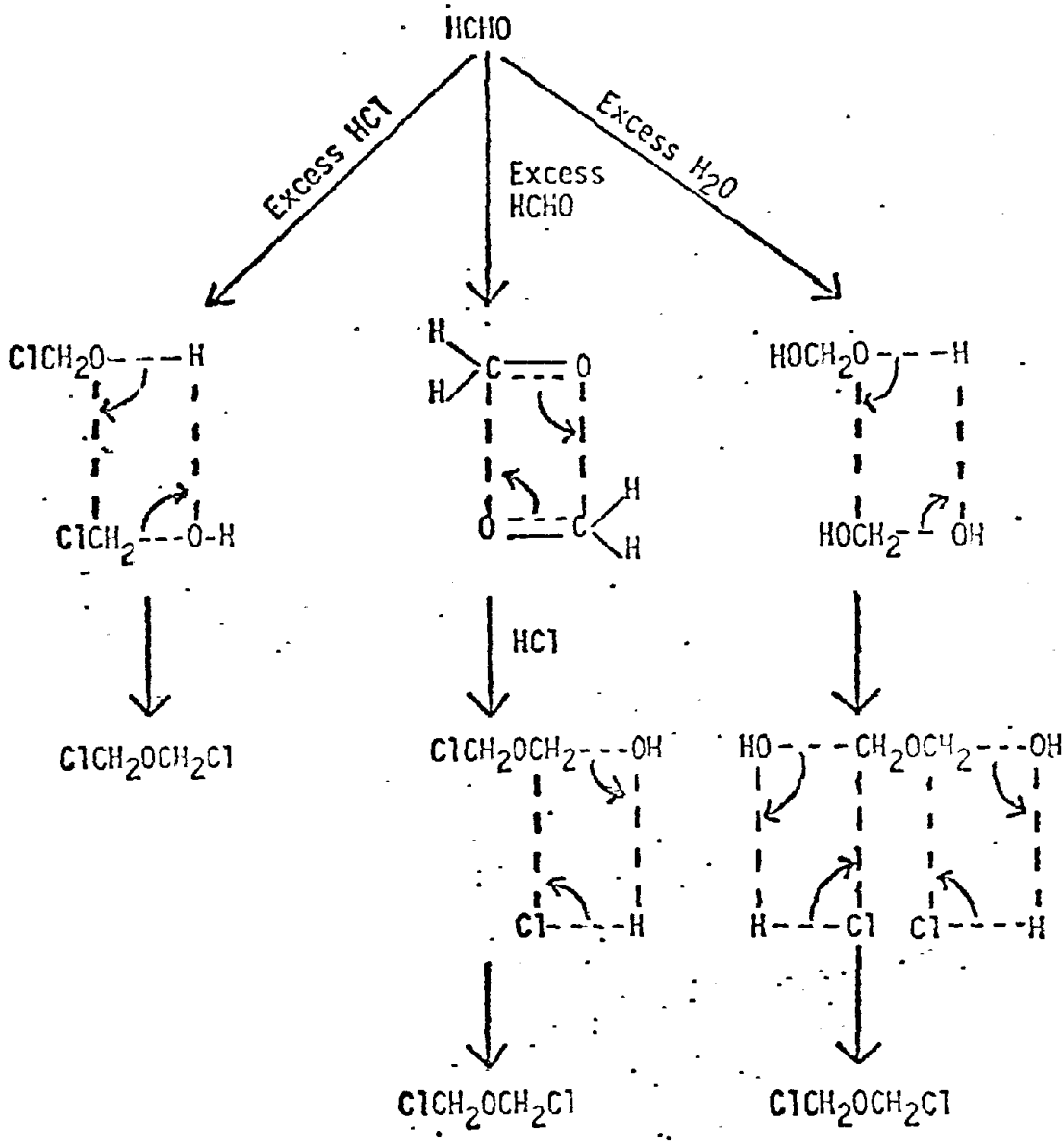


Figure 2 - Vapor Phase Reactions for BCME

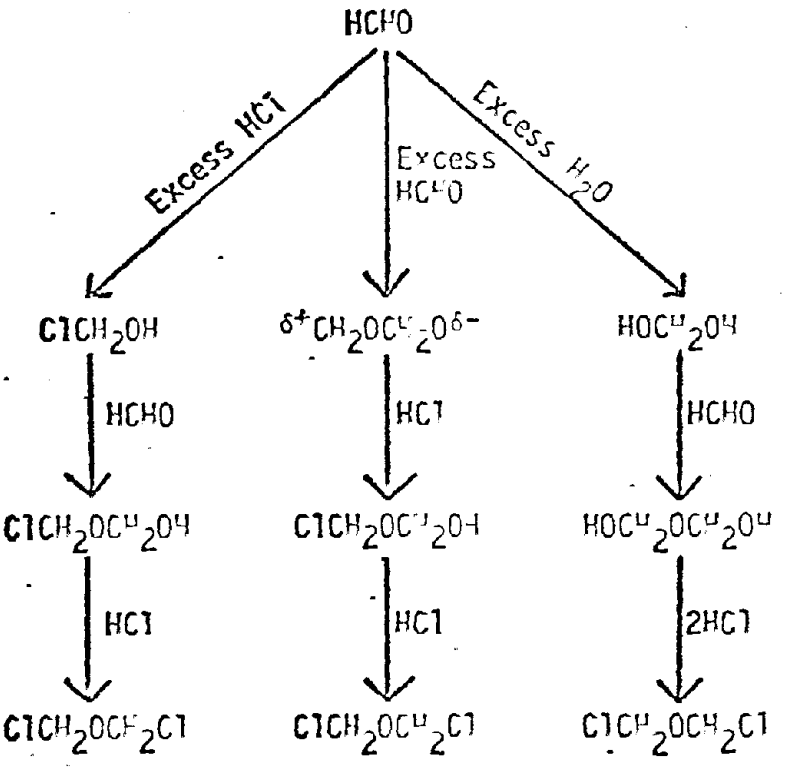


Figure 3 - Nonpolar Media Reactions for BCME

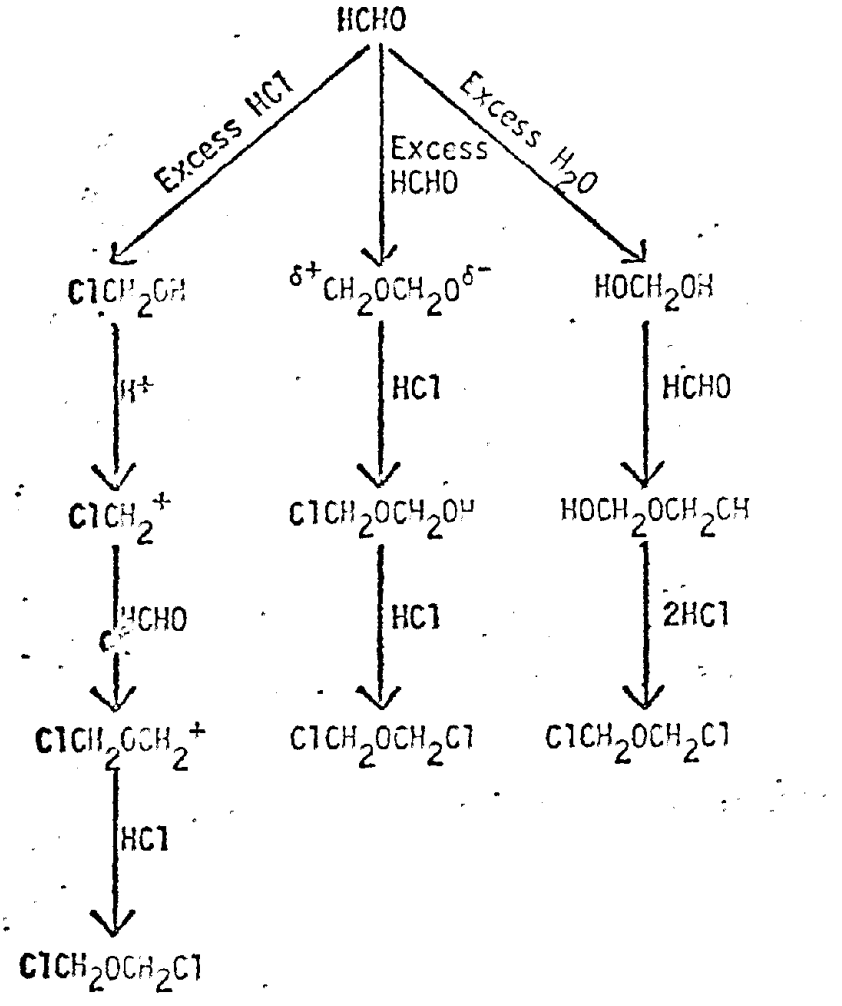


Figure 4 - Polar Media Reactions for BCME

A. Via Chloromethyl Alcohol Intermediate and 4-Center Transition State

$$HCHO + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClCH_2OH$$

$$2ClCH_2OH \xrightarrow{k_2} ClCH_2OCH_2Cl + H_2O$$

$$\frac{d[BCME]}{dt} = -\frac{d[ClCH_2OH]}{2dt} = k_2[ClCH_2OH]^2$$

$$= -\frac{K_e}{2}\frac{d[HCHO][HCl]}{dt} = k_2K_e^2[HCHO]^2[HCl]^2$$

$$-\frac{d[HCHO][HCl]}{dt} = 2k_2K_e[HCHO]^2[HCl]^2$$

When HCl is in excess,

$$-\frac{d[HCHO]}{dt} = k_{obs.}[HCHO]^2$$

$$-\int\frac{d[HCHO]}{[HCHO]^2} = \int k_{obs.}\, dt$$

$$\frac{1}{[HCHO]} = k_{obs.}\, t + \frac{1}{[HCHO]}$$

Therefore, the reaction is of a pseudo second-order kinetics with respect to formaldehyde.

When HCHO and HCl are at equivalent concentrations, x.

$$-\frac{dx^2}{dt} = 2k_2K_ex^4$$

$$-2x\frac{dx}{dt} = 2k_2K_ex^4$$

$$-\frac{dx}{dt} = k_2K_ex^3$$

$$-\int\frac{dx}{x^3} = k_2K_e\int dt$$

$$\therefore \frac{1}{x^2} = k_2K_et + \frac{1}{x_o^2}$$

Therefore, the reaction is of third-order kinetics.

B. Via Formaldehyde Dimer and 4-Center Transition State

$$2HCHO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{matrix} H_2C=O \\ | \quad | \\ O=CH_2 \end{matrix} \quad (T.S.)$$

$$\begin{matrix} H_2C=O \\ | \quad | \\ O=CH_2 \end{matrix} + 2HCl \xrightarrow{k_2} ClCH_2OCH_2Cl + H_2O \quad (BCME)$$

$$\frac{d[BCME]}{dt} = -\frac{d[HCl]}{2dt} = k_2[T.S.][HCl]^2$$

$$= k_2K_e[HCHO]^2[HCl]^2$$

When HCHO is in excess,

$$-\frac{d[HCl]}{dt} = k_{obs.}[HCl]^2$$

$$-\int\frac{d[HCl]}{[HCl]^2} = k_{obs.}\int dt$$

$$\frac{1}{[HCl]} = k_{obs.}t + \frac{1}{[HCl]_o}$$

Therefore, the reaction is of pseudo second-order kinetics with respect to hydrogen chloride.

C. Via $HOCH_2OH$ and 4-Center Transition State

$$HCHO + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCH_2OH$$

$$2HOCH_2OH \xrightarrow{k_2} HOCH_2OCH_2OH + H_2O$$

$$HOCH_2OCH_2OH + 2HCl \xrightarrow{k_3} ClCH_2OCH_2Cl + 2H_2O$$

$$\frac{d[BCME]}{dt} = k_3[HOCH_2OCH_2OH][HCl]^2$$

$$\frac{d[HOCH_2OCH_2OH]}{dt} = -k_3[HOCH_2OCH_2OH][HCl]^2 + k_2[HOCH_2OH]^2$$

Evidently, a condition of $k_3 >> k_2$ has to be assumed.

$$\frac{d[BCME]}{dt} = -\frac{d[HOCH_2OCH_2OH]}{dt} = -\frac{d[HOCH_2OH]}{2dt} = k_2[HOCH_2OH]^2$$

$$-\frac{K_e d[HCHO][HCl]}{2dt} = k_2 K_e^2 [HCHO]^2 [HCl]^2$$

$$-\frac{d[HCHO][HCl]}{dt} = 2k_2 K_e [HCHO]^2 [HCl]^2$$

When HCHO and HCl are at equivalent concentration, x.

$$-\frac{dx^2}{dt} = 2k_2 K_e x^4$$

$$-2x\frac{dx}{dt} = 2k_2 K_e x^4$$

$$-\frac{dx}{dt} = k_2 K_e x^3$$

$$-\int \frac{dx}{x^3} = k_2 K_e \int dt$$

$$\frac{1}{x^2} = k_2 K_e t + \frac{1}{x_o^2}$$

Therefore, the reaction is of third-order kinetics.

D. Condensed Phase Reaction

$$HCHO + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClCH_2OH$$

$$ClCH_2OH + HCHO \xrightarrow{k_2} ClCH_2OCH_2OH$$

$$ClCH_2OCH_2OH + HCl \xrightarrow{k_3} ClCH_2OCH_2Cl + H_2O$$

It is rather difficult to estimate the relative size of k_2 and k_3. In polar media, k_3 is likely to be greater than k_2, involving a SN1 type process, and the rate equation can be readily integrated. In a nonpolar media, k_2 might be greater than k_3 and it may be difficult to solve.

The information on hand regarding BCME formation is obviously complex, but the complexity is more apparent than real. All the experiments in the references cited above were carefully devised and accurately carried out. The data are therefore reliable and valuable. The prevailing state of perplexity and puzzlement seems, in the main, generated from the lack of a rigidly proven reaction mechanism, capable of satisfactorily explaining experimental facts from a variety of sources. The difficulties presented above will also serve to explain the discrepencies of results noted earlier by Marceleno [2-3] where BCME was found but where findings could not be duplicated. When this seemingly elusive reaction mechanism is finally established, these facts, contradictory though they may seem, can no doubt be explained in full, which in turn would strengthen the still sought-after mechanism. As a matter of fact, a faintly delineated image of solution is already in the offering. A few salient points are enumerated here.

1. Reaction Kinetics -- It was found that BCME formation is related exponentially to the reactant concentration. That is to say, the reaction is of higher than first-order kinetics. Keeping a picture of the reaction in mind, few would venture to expect otherwise.

2. Gas Phase Reactions -- The simplicity of use of plastic bags to maintain constant pressure in the kinetic study of gas phase reactions would have been remarkable. It was unfortunate and surprising to find that the HCHO permeation rate in the plastic bags was far greater than was anticipated as is shown in Figure 4. Because of this, all-glass systems were required for both liquid phase and gas phase reactions.

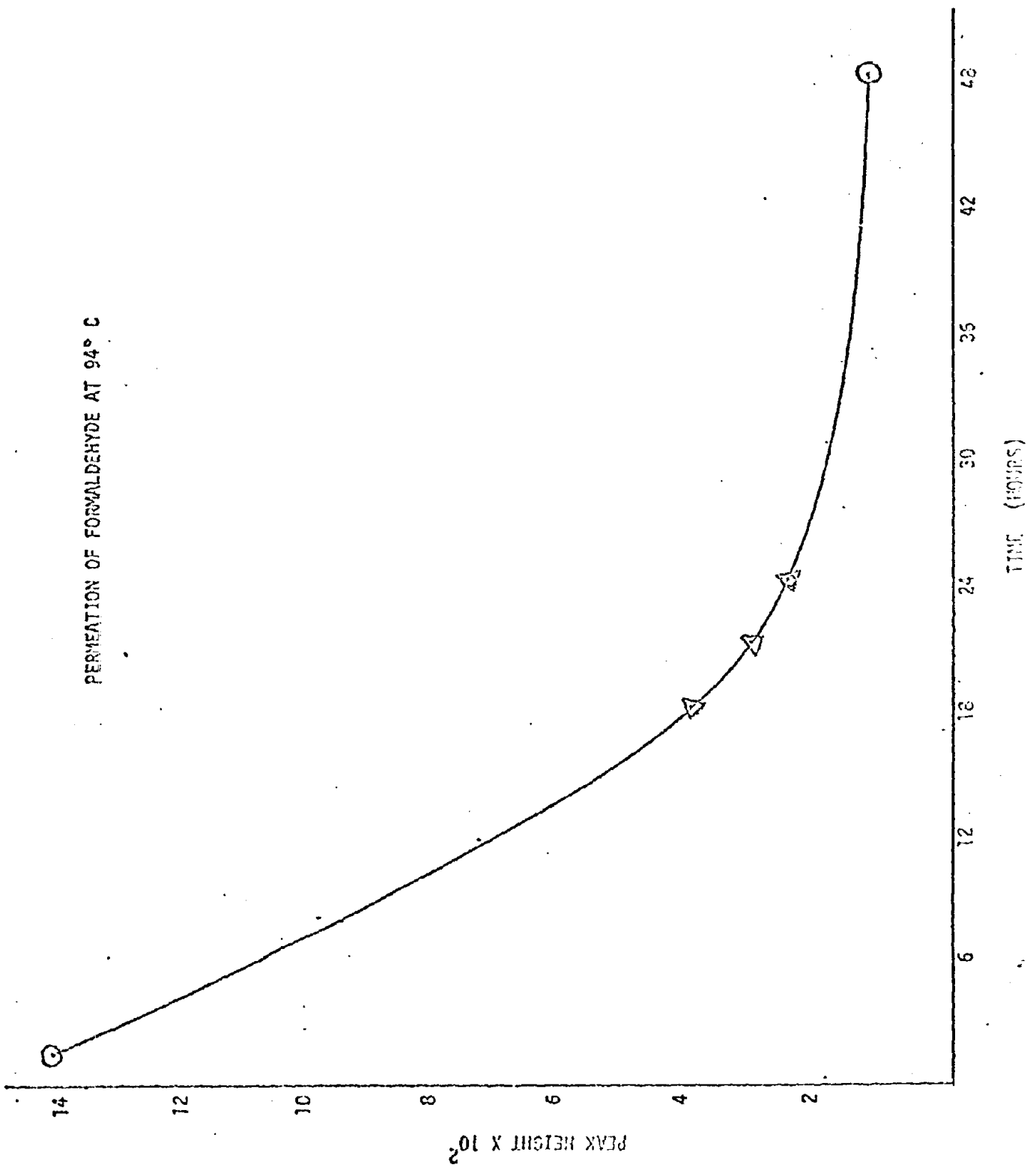


Figure 4. Permeation Rate of Plastic Bags.

Another problem encountered was in the use of HCl in the experimental systems since HCHO and BCME concentrations were to be determined by gas chromatography, any HCl present would be an interference. This was resolved by using a combination of carbosieve B and Porapak T in the chromatographic column.

3. Reversibility of Gas Phase Reaction -- In the gas phase reaction of HCHO and HCl, two stages were noticed. HCHO at first decreased, followed by an increasing trend. By keeping 4,670 ppm HCHO and 4,670 ppm HCl at 86°C for 28.3 hours, 0.65 ppm BCME was obtained (0.014 mole percent yield). On the other hand, 5.8 microliters BCME kept under vacuum at 91°C for 18.3 hours gave 12.94 percent HCHO. One problem encountered (and as yet unsolved) was the appearance of an unidentified component that has the same retention time as the peak found in a mixture of HCHO and HCl (see Figure 5).

4. BCME Formation from Hydrogen Chloride Versus Magnesium Chloride -- A mixture of equivalent amounts (0.1 mole) of HCHO and HCl in aqueous medium covered with hexane was stirred overnight in an ice bath, giving an 0.007 mole percent yield of BCME in the hexane layer. A similar run with magnesium chloride gaven an 0.027 mole percent yield.

5. The medium in which BCME is formed -- In the preceeding experiments aqueous as well as organic layers existed so that BCME could conceivably be formed first in the aqueous layer and subsequently diffused into the organic layer; or formaldehyde and hydrogen chloride could migrate into the organic layer and BCME be formed afterward. To resolve this issue, an attempt was made to identify the medium (polar or nonpolar solvent)

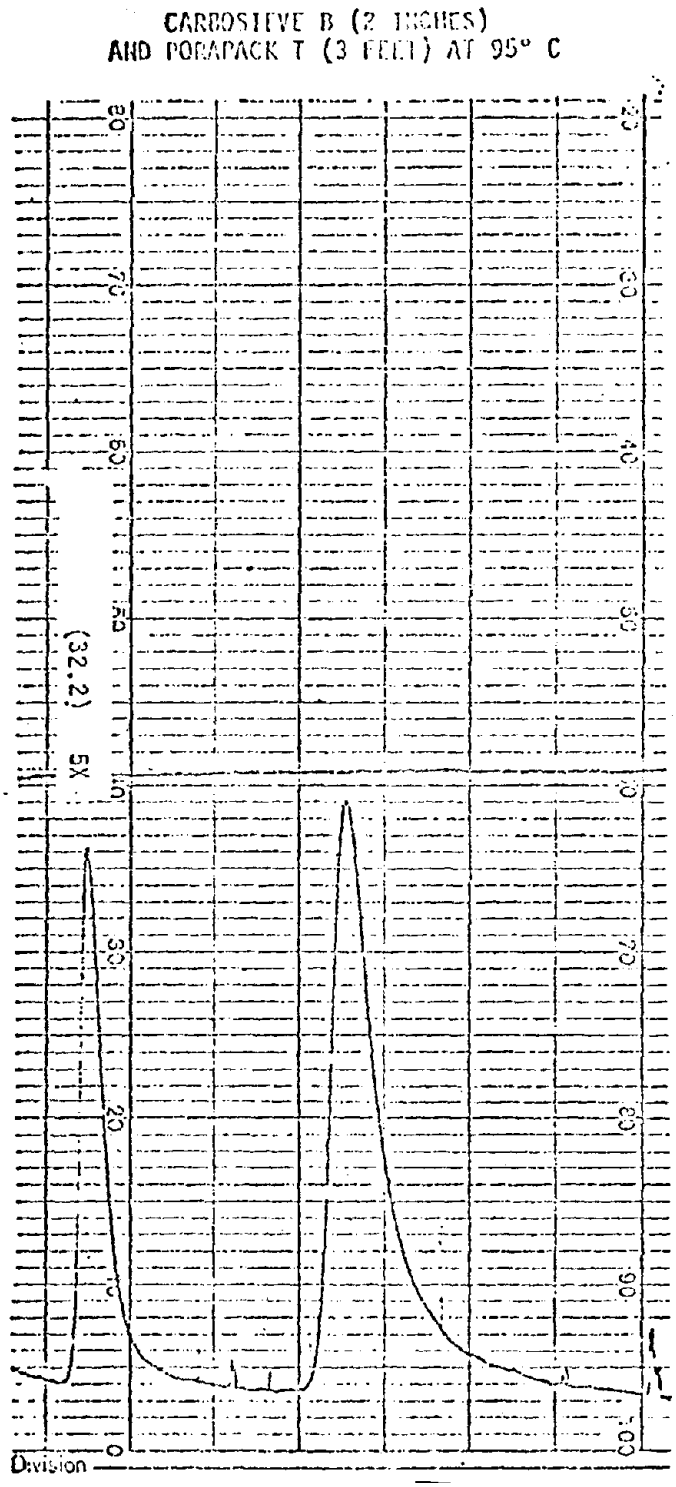


Figure 5. Chromatogram of BCME Thermal Decomposition.

in which BCME was formed by observing its kinetic order. As is shown in Figure 6, the BCME reaction proceeded rather fast and reached a low plateau at a very early stage. The curve appeared to be non linear and of nonzero order, indicating that the reaction most likely had taken place in the aqueous phase. If the plot had been linear and of zero order, the indication would be that it had taken place in the organiz layer.

6. Diffusion rate versus reaction rate -- Assuming that the diffusion rate of HCHO and HCl is greater than the reaction rate, the concentration of HCHO and HCl in the organic layer will be constant and the rate equation can be derived as follows:

$$\frac{d[BCME]}{dt} = k[HCHO]^x[HCl]^y$$

$$= k[HCHO]^o[HCl]^o$$

$$= k$$

$$d[BCME] = kdt$$

$$\int_0^t d[BCME] = k\int_0^t dt$$

$$[BCME]_t = -kt + [BCME]_o$$

$$[BCME]_t = kt$$

The reaction therefore is of zero order kinetics and a plot of BCME versus time will be a straight line passing through the origen.

7. Effects of Termperature and Chlorosulfuric acid on the formation of BCME -- Experiments similar to the preceding double layer reaction (at 0^oC) were performed at 30^oC and no BCME was formed.

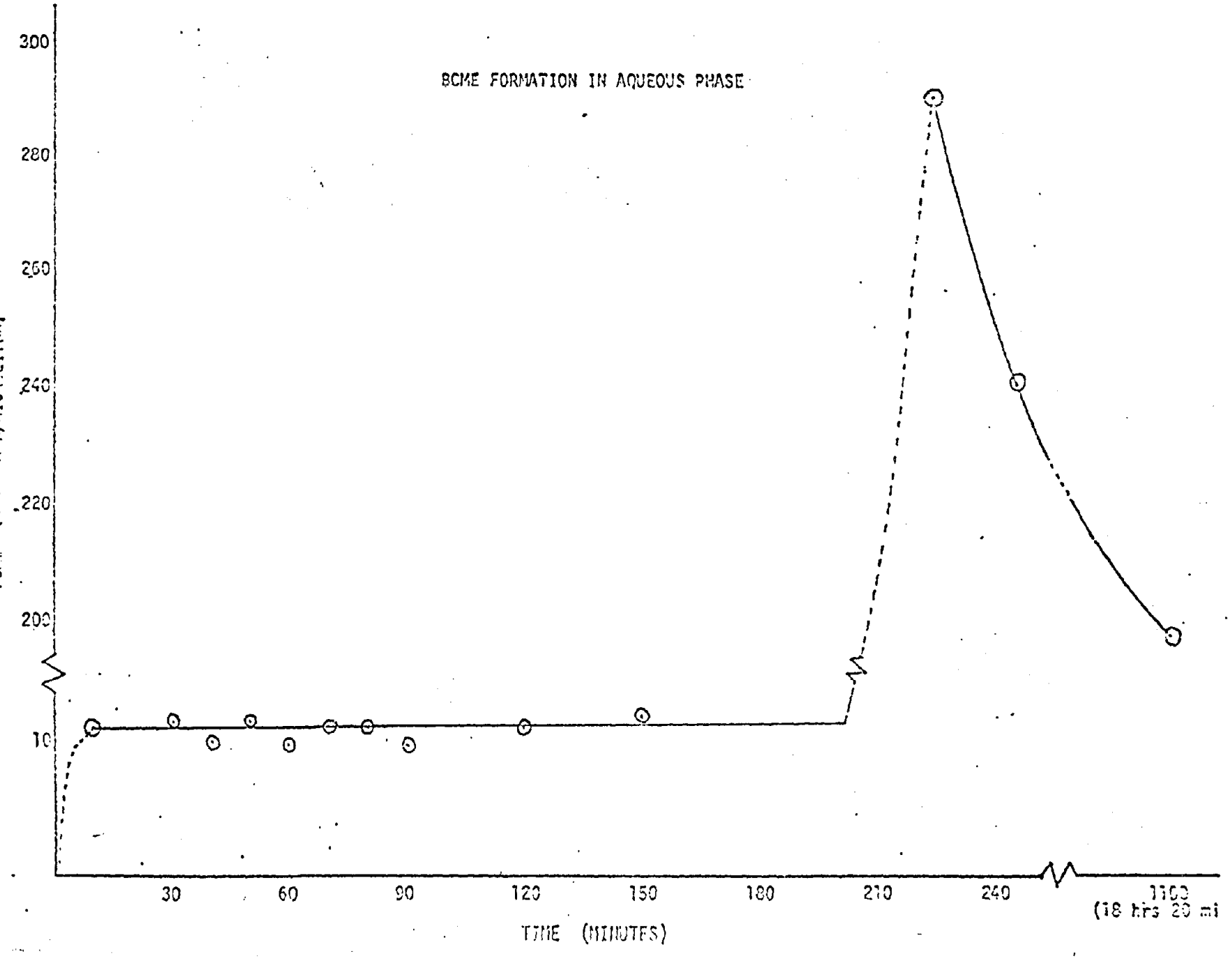


Figure 6. BCME Formation in the Aqueous Phase.

Similar experiments performed at 10°C gave an 0.0024 mole percent yield of BCME.

Addition of chlorosulfonic acid dramatically increased the yield (a 23-fold increase) as shown in Table 1 and Figure 6.

8. Effect of Moisture on the formation and decomposition of BCME -- It was reported that the yield of BCME in gas phase was consistently lower in dry atmosphere but not significantly different under various ambient humidity. It is therefore clear that the water molecules do participate in the formation of BCME. Furthermore, the experiments were carried out at 100 ppm levels and the ambient moisture content in the atmosphere was about 150 times in excess. This unsuspected presence of relative abundance of water naturally would mask its effect in the rate equation.

9. Reaction order of Formaldehyde -- It was reported that BCME formation is related exponentially to HCHO concentration. Obviously, the reaction is of higher than first order kinetics with respect to HCHO, a fact which would be anticipated from the mechanism schemes.

10. Spontanuity of Formation -- It was further found that the BCME formation was insensitive to temperature. This implies that the slope of Arrhenius plot is rather flat, and consequently the energy of activation for the BCME formation is relatively low. Therefore, the process might very well be spontaneous at ambient condition.

TABLE 1

Condensed Phase Reactions

Experiment	Covering Solvent	Reaction Temperature (° C)	Formaldehyde and Hydrogen Chloride (Mole)	BCME Yields (Mole %)	Yields After Adding Chloro-sulfonic Acid (Mole %)
II	Hexane	0	0.11	0.007	------
VII	Toluene	10	0.46	0.0024	0.0552
VIII	Benzene	30	0.10		------

The inherent difficulties of studying this type of problem are twofold: nonconventionality and uncertainty. At 100 ppm range, there are only 0.075 mg of water in a liter of air. A 50 percent relative humidity at ambient temperature ranges between 15,000 to 16,000 ppm. This unsuspected presence of a relatively huge amount of water in relation to reactant concentrations in the reacting system could not but mask the true picture of reaction. Consequently, the observed reaction rate would overshadow the true rate of reaction. This situation would, of necessity, not only confuse the experimental results but also undermine the confidence they deserve.

Field Survey

The selection of work environments for study were dictated by the following criteria: (1) the work environment's potential for BCME formation as indicated by the chemical components utilized; (2) the number of workers exposed; (3) representativeness of the plant to the industry in which it is classified; and (4) the ability or ease of measuring and ascertaining contributing factors to possible BCME formation. The first criteria was used to select industries; the others were used to select specific plants. Table 2 lists the industries selected.

TABLE 2

SELECTION OF INDUSTRIES FOR STUDY
BCME PROJECT

Production of Textiles (Finishing

Production of Dyes

Production of Formaldehyde-Type Resins

Production of Paper

Production of Fertilizers

Foundries

Laboratory Processes

The selection of textiles was considered of primary importance in this project. Previously, Marceleno and Bierbaum and Marceleno [3] had conducted preliminary pilot plant studies and sampling in several textile finishing operations with results that indicated the presence of BCME in the low (0.1 - 8.0 ppb) range. Subsequent meetings with industry representatives (American Textile Manufacturers Institute and Textile Workers Union of America) had attested to that selection.

Processes Studies

Textile finishing uses many substances which give various characteristics to fabric. Those used in permanent press treatment of fabric are considered perhaps the most important. In crease resistant finishing, cloth is treated with a resin-catalyst mixture, dried and cured. One of the most common mixtures includes glyoxal urea formaldehyde resins in conjunction with magnesium chloride catalysts. Because both free formaldehyde and chloride ions are present in this process in quantity, this process was chosen for study.

Two plants were studied: one, a finisher of heavy weight drapery and upholstery fabrics, and the other, a producer of currently fashionable knit fabrics. Each had a somewhat different process.

1. Drapery and Upholstery Fabrics

The finishing process in this plant utilized a conventional approach which is representative of the industry as a whole. The equipment, materials, and process are typical of what might be expected in other finishing plants around the country. The flow chart (Figure 7) indicates the major steps in the process.

The initial step is the mixing of the resin-catalyst materials which is done in a separate area of the facility. The mixture typically contains approximately 30 gallons of resin, 88 pounds of magnesium chloride, water, and small amounts of such things as various softeners and hand builders. The 250 gallon mix has a pH of about 6 and is typically at ambient temperature. Once mixed to specifications based on desired characteristics, the mix is sent down into the pad box. Here, the cloth is drawn through the resin-catalyst material. Most of the excess resin-catalyst is removed by drawing the cloth through a series of inward running rollers.

To remove moisture, the cloth is drawn through a series of ovens. The first, a predryer, quickly heats the fabric to approximately 250^{o}F for about 2 minutes. Allowed to cool slightly, the fabric is drawn into the dryer, more commonly called a "tenter frame" or simply "frame". Here, temperatures are again about 250^{o}F but the residence time is about twice as long. At this point, only the uncured resin is present in the fabric.

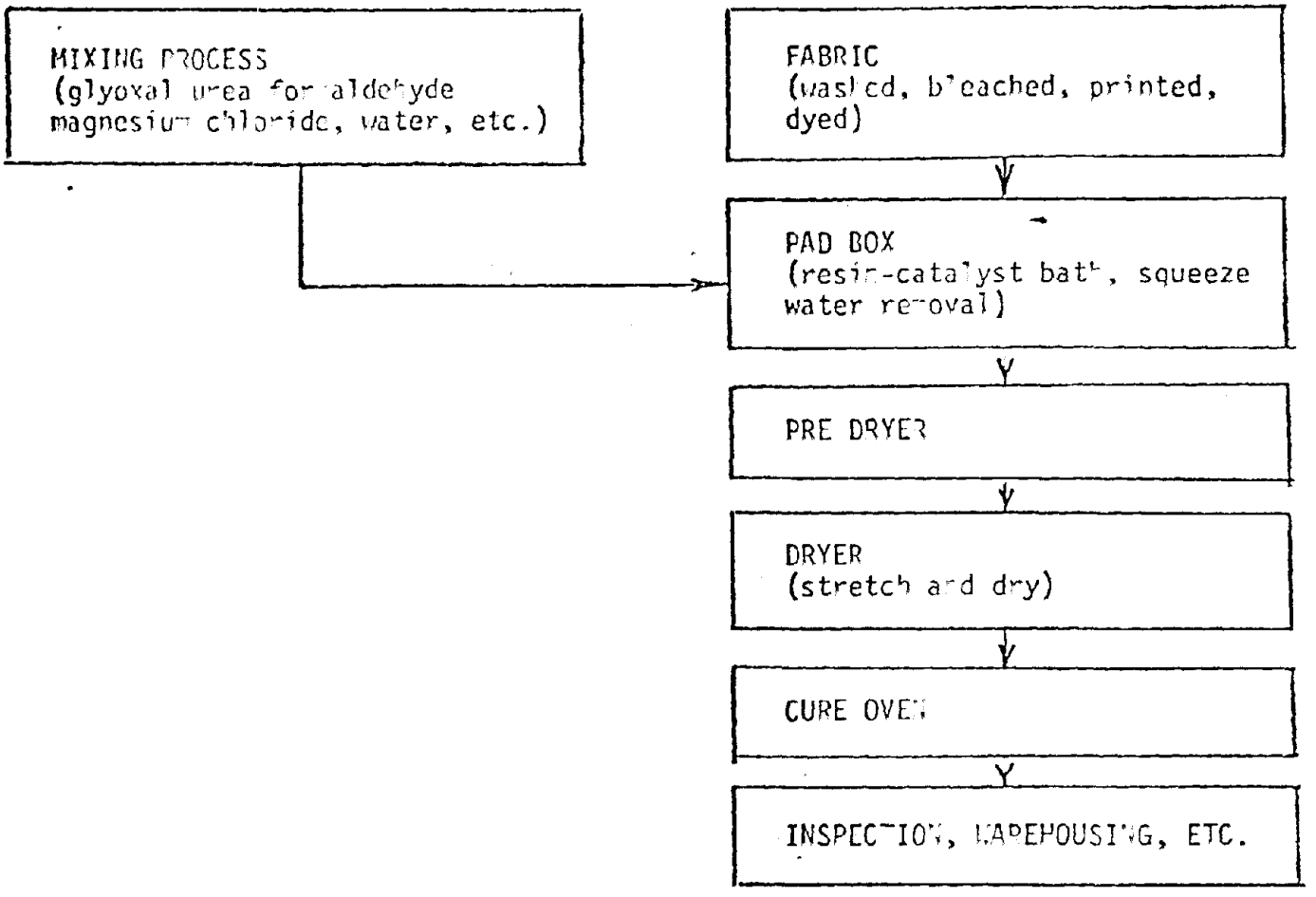


FIGURE 7 - Flow Charge of a Typical Finishing Process

The dried but uncrued resin-containing cloth is then subjected to a temperature of approximately 350°F for about 1 to 2 minutes. Using this resin-catalyst system, 350°F is satisfactory for curing the resin. Once this step is completed, the fabric has obtained the wrinkle resistant characteristics desired. The fabric is then ready for such things as inspection and warehousing.

2. Knitted Fabrics

Because of the means whereby knitted fabrics are made, two finishing processes were used in the other plant stuides. Knitted fabrics are made in a tubular form rather than in the more conventional flat cloth form seen in woven fabrics. Some users of knitted goods are equipped to work with the tubular fabric while others desire the flat cloth, open width form. Hence, two types of finishing are depicted in the flow chart in Figure 8.

The flat cloth (open width) finishing is essentially the same as that found in more typical finishing operations with several differences. One is the need for opening the tubular knitted fabric, a step which immediately precedes introduction of the fabric into the bath. Another is the lack of a separate predryer, dryer, cure oven system. All predrying, drying, and curing are conducted in the same dryer or tenter frame. A third difference in the process is the resin-catalyst mixture. It utilizes as much as 3 times the resin and catalyst quantity per 250 gallon batch as that used in a typical resin system. Other conditions are essentially the same including resin pH, temperatures, and residences times (slightly modified to be compatible with the equipment).

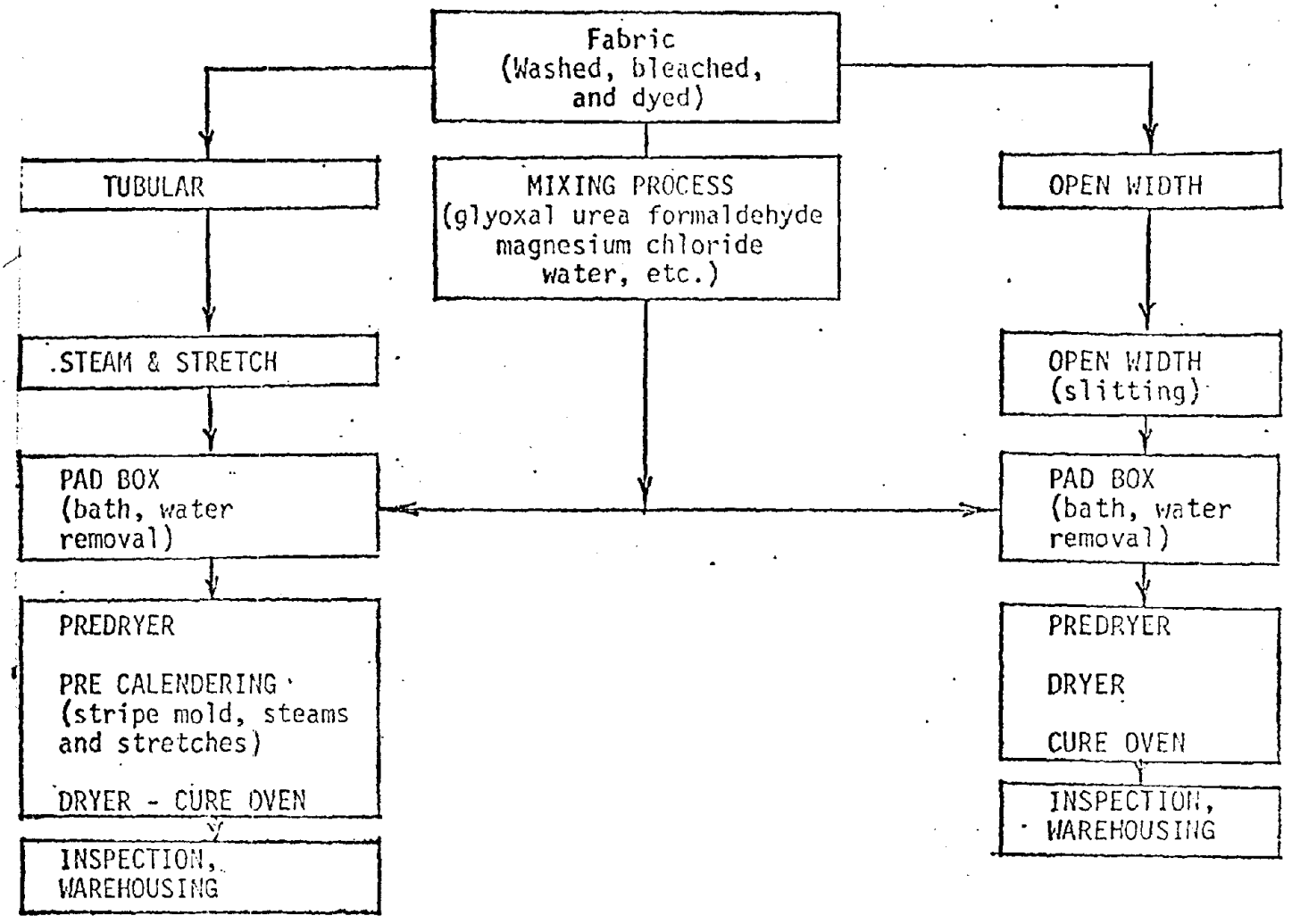


FIGURE 8 - Flow Chart of Two Knitted Finishing Processes

The second process used for tubular knits is somewhat different. The heavier concentration resin-catalyst mixture is used, but before the fabric is drawn through the mixture, it is subjected to both steaming and stretching. Fabric temperatures are typically 100°F when entering the resin-catalyst pad box. The fabric is squeezed between rollers to remove excess moisture and resin-catalyst material after running through the resin-catalyst containing pad box. The fabric is then drawn into a predryer and is heated to 250°F for about 2 minutes.

After leaving the predryer, the fabric is matched for stripes and moved to a precalendering operation. The fabric is then steamed and stretched again to specifications on width (while still in tubular form). At this point, the fabric is moved to the dryer-cure oven where is it subjected to temperatures of 350° to 400°F for several minutes. Once this step is completed, the cured fabric is ready for inspection and warehousing.

Parameters to be Studied

When investigating the possible formation of a substance such as BCME in the workplace, sampling must be conducted for not only BCME but also for other substances or conditions which are linked to it, along with physical parameters which may be influential in allowing or hindering formation. The substances and parameters selected for measurement are shown in Table 3.

Table 3

SUBSTANCES AND PARAMETERS MEASURED
BCME PROJECT

BCME

Formaldehyde

Chloride Ion (Hydrogen Chloride)

Metallic Dusts

Temperature

Humidity

Air Movement

Pressure

Lighting

By analyzing these substances and parameters along with process variables, more light can be shed on the conditions necessary for BCME formation.

Sampling and Analytical Methodology

Primary screening and analysis of samples were conducted on-site by means of a mobile laboratory which was equipped with a gas chromatograph, spectrophotometer, and pH meter. Thus, many analyses could be conducted in the field without the problems of laboratory analysis time lag. The advantages of this type of equipment capability are obvious.

Because of the field laboratory capability, two methods typically were used for sampling and analyzing BCME. The "Dow liquid media, derivative formation method" [12] was employed principally for field screening of potential BCME formation areas. If the "Dow" sample proved positive, a companion, side-by-side sample using a porous polymer (Porapak Q) sampling tube would be sent to the Kennedy Space Center Laboratories for gas chromatographic/mass spectrometric analysis [12-15]. In addition, four air samples were quantitatively analyzed by NIOSH. Table 4 shows the result of the MS/GC analysis.

Independent collection and analysis using separate methods was deemed necessary to confirm the presence of BCME. It also served to confirm negative results. Detection levels of 0.1 ppb were usually possible with the two methodologies above.

Formaldehyde was sampled and analyzed by the commonly used "Chromatropic Acid" method [16]. All samples were analyzed in the field laboratory.

Chloride ion was collected by bubbling workplace air through distilled water. Analysis of the chloride ion contact was made by using a calibrated specific ion electrode. These samples were also analyzed in the field.

Limited dust sampling was conducted to detect any significant metals which might be present. Spectrographic analyses were conducted on these samples.

TABEL 4

Qualitative Analysis of Four Textile Air Samples

Sample No.	Compounds Identified	
17	ethylene Oxide ethanol isopropyl alcohol vinyl acetate benzene ethyl propionate toluene	No BCME present
27	ethylene oxide ethanol isopropyl alcohol benzene ethyl propionate toluene	No BCME present
37	ethanol isopropyl alcohol vinyl acetate benzene toluene	No BCME present
43	ethanol isopropyl alcohol ethyl propionate toluene n-butyl propionate	No BCME present

The physical environmental parameters were measured using simple instrumentation such as thermometers, psychrometer, and velometers. Lighting was noted as incandescent, fluorescent, sunlight, etc. Noting physical parameters was conducted at each sampling site about midway through the sampling period. There were additional notings if conditions changed significantly.

Sampling for BCME was limited to area sampling. No personnel sampling was conducted because the primary goal was to detect the presence of BCME in the work environment. Samplers were placed where the potential for formation was considered to be optimum for the conditions noted during the actual survey. The sampling periods ranged from 3 to 4 hours.

Results

Concentrations of the two suspected components needed for BCME formation were in the low ppm range. Levels of formaldheyde approached 1.5 ppm in several areas in each facility studied. These levels are within the Occupational Safety and Health Administration (OSHA) accepted threshold limit values and do not, in themselves, appear to present a serious health hazard.

Chloride ion concentrations ranged up to about 1.1 ppm with slightly higher levels noted in the resin-catalyst mixing area. Again, no apparent health hazard is present (no known exposure limits are available). Dust determinations indicated that expected metals such as magnesium were present but in trace amounts. Other metals, were not present. The dust samples indicated high levels of nonmetallic substances such as sulfur and chloride aerosols.

The physical parameters which were measured indicated that the type conditions present were warmer and dryer than usual ambient air ($70^{o}F$, 50% relative humidity).

The presence of BCME was not detected in any samples. However, this does not eliminate the formation potential for other textile finishing processes or operations. Conditions and processes can vary and may play a very influential role in the BCME formation reaction. It is for this reason that, if the potential exists on an individual process, sampling should be conducted to assure that BCME formation is not occurring.

REFERENCES

1. Federal Register, Vol 39, No. 20, pp. 3756-3797, Tuesday, January 24, 1974.

2. Marcelcno, T. and Bierbaum, P.J., "A Preliminary Report on the Formation and Detection of Bis-chloromethyl Ether in the Industrial and Medical Environment," Present at the American Industrial Hygiene Conference, Miami, Florida, May 12-17, 1974.

3. Marceleno, T., Survey of Burlington, Industries, Inc., a NIOSH Survey Report, December, 1974.

4. Hurwitz, M.D., "Assessing the Hazard from BCME in Formaldehyde - Containing Acrylic Emulsions," Am. Dyestuff Reporter 63(3):62 (1974).

5. Van Duuren, B.L., Goldschmidt, B.M., Katz, C., Langseth, L., Mercando, G., and Sivak, A., "Alpha-Haloethers: A New Type of Alkylating Carcinogen," Archives of Environmental Health, Vol. 16 pp. 472-476 (April 1968).

6. Fiqueroa, W.G., Raszkowski, R., and Weiss, W., "Lung Cancer in Chloromethyl Methyl Ether Workers," New England Journal of Medicine, Vol. 288, No. 21, pp. 1096-1097, (May 1973).

7. Van Duuren, B.L., Sivak, A., Goldschmidt, B.M., Katz, C., and Melchionne, S., "Carcinogenicity of Halo-Ethers," Journal of the National Cancer Institute, Vol 43, No. 2, pp 481-486, (August 1969).

8. Laskin, S., Kuschner, M., Drew, R.T., Cappiello, V.P., and Nelson, N. "Tumor of the Respiratory Tract Induced by Inhalation of Bis (chloromethyl) Ether," Archives of Environmental Health, Vol 23, pp 135-136, (August 1969).

9. Leong, B.J., MacFarland, H.N., and Reese, W. H., "Introduction of Lung Ademonas by Chronic Inhalation of Bis-chloromethyl)Ether," Archives of Environmental Health, Vol 22, pp 663-666, (June 1971).

10. "Chemical Suspected in Six Cases of Lung Cancer," Occupational Health and Safety Letter, Vol 2, pp. 6 (1972).

11. Tischenko, Zhur, Russ. Fiz, Khim, Obshenhesstra, Vol 19, pp 464 (1887) (Abstract only).

12. Solomon, R.A. and Kallos, G.J., "Determination of Chloromethyl Methyl Ether and Bis-chloromethy Ether in Air at the Part Per Billion Level by Gas-Liquid Chromatography," Anal. Chem., 47(6), 955(1975).

13. Shadoff, L.A., Kallos, G.J., and Woods, J.S., "Determination of Bis(chloromethyl) Ether in Air by Gas Chromatography-Mass Spectrometry". Anal. Chem., 45(14), 2341(1973).

14. Collier, L., "Determination of Bis-chloromethyl Ether at the Ppb Level in Air Samples by High-Resolution Mass Spectroscopy", Environ. Sci. & Tech., 6(10), 931 (1972).

15. Evans, K.P., Mathias, A., Mellor, N., Silvester, R., and Williams, A.E., "Detection and Estimation of Bis-chlroomethyl) Ether in Air by Gas Chromatography-High Resolution Mass Spectrometry," Anal. Chem., 47(6), 821 (1975).

16. NIOSH Manual of Analytical Methods. NIOSH, Department of Health, Education, and Welfare, Publication Number (NIOSH) 75-121, U.S. Government Printing Office, Washington, D.C., 1974, pp 125-1-9.