

Vapor-Phase Chlorination of Dimethyl Ether

Vapor-phase photochemical reactions can give a low cost route to chlorinated dimethyl ethers

DIMETHYL ETHER IS commercially available by the catalytic dehydration of methanol (10) or as a by-product in the preparation of dimethylaniline from aniline and methanol (10). It is used as a refrigerant, solvent, extractant, and propellant for aerosol sprays (5). However, little investigation has been made into the reactions of dimethyl ether.

Chlorinated dimethyl ethers have been prepared, using formaldehyde in batch processes (1, 4, 6), or in a continuous process (9), or by liquid-phase chlorination of dimethyl ether (2, 3, 7, 8).

Both chloromethyl methyl ether and bis(chloromethyl) ether have been used as chloromethylating agents and as intermediates in organic synthesis. Considering the reasonable stability of these compounds and high reactivity of their halogen atoms, their reactions have been investigated surprisingly little.

Vapor-phase, photochemical chlorination of dimethyl ether proceeds readily at about 95° C. with high conversion of chlorine to chloromethyl methyl ether. Monochloroether may also be recycled through the same equipment to prepare dichlorinated products.

Using multiple injection of chlorine, dichlorination of dimethyl ether has been accomplished in a single pass. Yield of

bis(chloromethyl) ether from this reaction is about 70%.

Experimental

For the monochlorination of dimethyl ether, chlorine and dimethyl ether were metered directly into a mixing tee constructed of a 100-mm. length of 25-mm. borosilicate glass (Figure 1). The inlets were made of 7-mm. tubing. The dimethyl ether inlet was approximately 10 mm. from the inlet end and the chlorine inlet extended into the tee about 35 mm. After filling the tee with 1/8-inch glass helices, the exit was plugged with glass wool and, to exclude extraneous light, the entire tee was wrapped with tape which extended about 25-mm. down the reactor. An ultraviolet light, placed beneath the reactor and shielded from the mixing tee, activated the reaction. Extraneous light on the reactants before they were thoroughly mixed caused burning, explosions, or the formation of formaldehyde.

The premixed reactant gases were passed through a 10-mm. borosilicate glass tube reactor which had a volume of 28 ml. and which was nearly submerged in a water bath maintained at about 95° C. The bath controlled the exothermic reaction by removing heat and thus prevented yield losses to formaldehyde. Several reactors were used successfully without a water bath—light intensity and position as well as reactant flow

rates were carefully controlled to ensure a smooth reaction. The reaction mixture passed from the reactor to a water-cooled condenser where most of the chlorinated products were condensed. Part of the product was carried with the excess dimethyl ether to dry-ice traps.

The flow of dimethyl ether was adjusted at a rate of 450 to 900 ml. per minute and then the chlorine flow was regulated so that the molar ratio of dimethyl ether to chlorine was between 2.3 and 3.0. A smooth reaction normally ensued. However, burning, explosions, or the formation of formaldehyde resulted if the reaction zone became too hot or the mixing was inadequate so that high, localized concentrations of chlorine were present.

When recycling the chlorinated product, a smooth reaction was started which by-passed the flask containing the chloromethyl methyl ether. Then the dimethyl ether or nitrogen was passed through the chloromethyl methyl ether held at 60° C., to carry it into the reaction zone where a portion of it was chlorinated. The water bath could be eliminated in this reaction.

Since an excess of chlorine over dimethyl ether cannot be tolerated in a photochemical reaction, the direct vapor-phase dichlorination required an over-all excess of chlorine but with a deficiency present in any one portion of the reactor. The four reactor sections (Figure 2) consisted of 30 cm. of 10 mm. borosilicate

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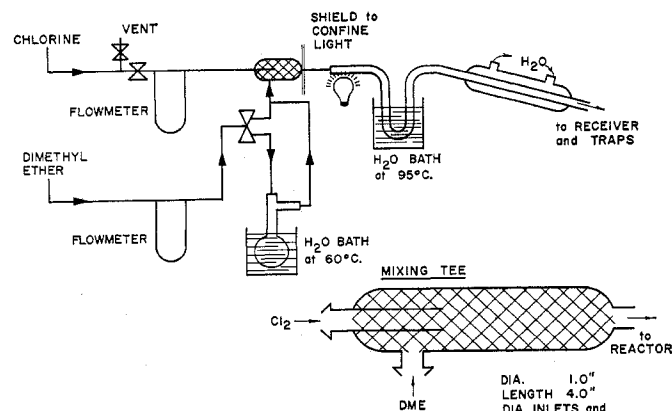


Figure 1. Monochlorination of dimethyl ether and recycle of the chlorinated product can be accomplished in the same reactor

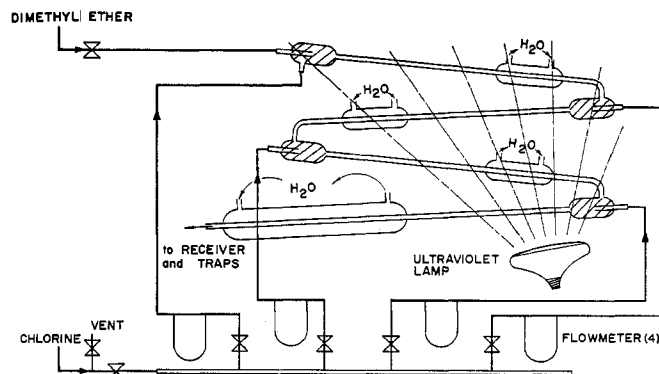


Figure 2. By multiple injection of chlorine, dimethyl ether is chlorinated in a single pass

Table I. Conversion to CME Decreases above 95° C.

Ml./Min.		DME/Cl ₂ , Mole Ratio	Temp., ° C.	Contact Time, Sec.	Conv. of Cl ₂ to CME, %
DME	Cl ₂				
600	200	3.0	90-100	1.55	90
680	300	2.3	90-95	1.27	87
600	200	3.0	95-100	0.91	85
900	300	3.0	250	0.73	80
900	300	3.0	330-350	0.62	74
600	200	3.0	230-270	0.62	70
450	150	3.0	290-310	0.52	59
900	300	3.0	325	1.55	35

glass tubing. The mixing tees were constructed as described for the monochlorination reaction (Figure 1). The condensers, made of 25 mm. tubing were 15 cm. long, but the final condenser was 60 cm. long.

About one fourth of the total chlorine flow was admitted to each mixing tee and the flow rates were such that essentially all of this chlorine reacted before more entered the system. Thus the ratio of chlorine to dimethyl ether and its chlorinated products was always 0.5 or less in each reactor section.

The dimethyl ether flow was adjusted at 500 to 1000 ml. per minute with the ultraviolet source on and then the chlorine flow was adjusted so that the total amount was about 1.5 times the ether flow. The product passed into a receiver and successively to wet-ice and finally dry-ice traps.

Results and Discussion

In a successful monochlorination, the reaction was conducted for 75 minutes which corresponded to a total of 1.0 mole of chlorine and 2.3 moles of dimethyl ether processed. The product recovered from the receiver contained 0.68 mole of chloromethyl methyl ether and 0.063 mole of bis(chloromethyl) ether. The material from the dry-ice traps contained no chlorine, 1.13 moles dimethyl ether, and 0.19 mole chloromethyl methyl ether. The recovery of chlorine was essentially quantitative and the recovery of dimethyl ether was 90%. The loss of dimethyl ether probably resulted from handling and process losses rather than by-product formation, because recovery in

some experiments indicated that conversions based on dimethyl ether were also probably quantitative.

Although conversion to chloromethyl methyl ether falls off at temperatures above 95° C. (Table I), the temperature must be above the boiling point of chloromethyl methyl ether. Otherwise, condensation on the reactor walls tends to yield overchlorination products. Theoretically, any ratio of dimethyl ether to chlorine greater than 1 to 1 can be tolerated. However, in the equipment used, mole ratios of less than 2.0 caused burning or explosions in the light-activated portion of the reactor.

Recycling with nitrogen as the diluent resulted in 65% of the chlorine being utilized in converting chloromethyl methyl ether to bis(chloromethyl) ether (Table II). When dimethyl ether was used as the diluent, the competition resulted in approximately 40% of the chlorine being converted to bis(chloromethyl) ether and 60% to chloromethyl methyl ether.

Four chlorinated products resulted from the direct dichlorination reaction: chloromethyl methyl ether; dichloromethyl methyl ether; bis(chloromethyl) ether; and dichloromethyl chloromethyl ether. The second and fourth of these products resulted in yield losses because they cannot be converted to the desired product. Consequently, it was not possible to operate at ratios of chlorine to dimethyl ether much greater than 1.6 without suffering yield losses to overchlorination products. The maximum conversion of chlorine to bis(chloro-

Table II. Monochlorinated Product Is Converted to BCE by Recycle

CME, Moles	Cl ₂ , Moles	Diluent		Conv. to BCE, %	Yield of BCE, %	Temp., ° C.
		Compd.	Moles			
1.34	0.58	DME	1.15	31	77	90
0.52	0.21	DME	0.21	47	73	...
0.27	0.09	N ₂	0.25	65	80	...

methyl) ether per pass occurs when the ratio of reactants is about 1.8. The yield of bis(chloromethyl) ether was fairly consistent at about 65 to 75% (Table III) regardless of the conversion, indicating that it is primarily controlled by the ratio of bis(chloromethyl) ether to dichloromethyl methyl ether.

Methods of Analysis

Composition of the product was usually determined by fractional distillation and by the refractive index of individual cuts. The distillation was conducted using a vacuum-jacketed column, packed with 1/8-inch glass helices, which, under total reflux, had 12 theoretical plates. The head of the column, designed for total reflux and variable drawoff, was usually operated at a reflux ratio of about 5 to 1.

Since the principal products boil at least 20° C. apart, separation by fractional distillation was quite effective. However, besides refractive indices, chlorine analyses and saponification equivalents were made on selected cuts as a check on the efficiency of separation. The three principal products obtained by the chlorination of dimethyl ether have saponification values of 1, 2, and 3 equivalents per mole which permits ready differentiation.

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Table III. Yield of BCE Is Relatively Independent of Reactant Ratio

Ml./Min.		Mole Ratio			Conv. of Cl ₂ to BCE, %	BCE Yield, %	Contact Time for 1st Jet, Sec.
DME	Cl ₂	Cl ₂ /DME	BCE/CME	BCE/DDE			
490	405	0.8	0.60	...	37	75	...
520	560	1.1	0.05	1.66	8	65	8.4
375	400	1.1	0.40	...	27	80	...
970	1200	1.2	0.18	1.79	23	65	4.3
710	860	1.2	0.23	3.85	30	79	6.0
610	780	1.2	0.28	2.80	32	74	6.8
455	605	1.3	0.31	1.87	32	65	9.1
580	830	1.4	0.51	1.83	40	67	7.0
325	480	1.5	0.60	1.93	43	66	13.8
715	1060	1.5	0.98	2.65	58	73	5.6
990	1560	1.6	0.98	2.43	52	68	3.7
530	860	1.6	1.24	2.98	57	74	7.2
605	1210	2.0	4.41	1.75	58	64	6.1

DME = dimethyl ether; BCE = bis(chloromethyl) ether; CME = chloromethyl methyl ether; DDE = dichloromethyl methyl ether.