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Selectivity in the electrochemical epoxidation of propylene

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The distribution of by-products produced during the indirect epoxidation of propylene in a bipolar trickle tower has been measured. The distribution changed with both propylene oxide concentration (time) and operating conditions, however, the selectivity with respect to the major product always remained high (*c*. 97%). Mechanisms giving rise to the important by-products are discussed.

1. Introduction

Selectivity has been identified [1] as a crucial factor in the economics of the indirect, electrochemical epoxidation of propylene. Due to its unique contacting pattern, the bipolar trickle tower is highly selective for the production of propylene oxide (*c*. 97% across a wide range of conditions [1–3]) but it is important to know the distribution of minor by-products. For example, Beck [4] has shown that about 3% of the product from the same reaction in the capillary gap cell is dibromopropane which leads to an irretrievable loss of bromine from the system and adds to the materials cost [1]. Also Ehdaie [5] identified propylene glycol as a major by-product (*c*. 1%) in the trickle tower which adds to the separations cost. As part of a larger study of the scale-up of propylene oxide production in the trickle tower, therefore, the distribution of concentrations of by-products was also monitored. The syntheses were run under batch recycle conditions, and it was found that the distribution changed with propylene oxide concentration rather than with time, although the total concentration of by-products remained constant at about 3% (up to about 34 gm dm^{-3} of propylene oxide).

2. Experimental procedure

The cells and syntheses have been fully described elsewhere [1].

Qualitative analysis of the by-products was provided by comparison of glc retention times with those of authentic compounds (where available), together with glc/ms carried out on an AEI MS 30 mass spectrometer coupled to a Pye Unicam GCD gas chromatograph. Quantitative analysis was carried out on a Perkin Elmer F17 GC using a 2 m, 10% Carbowax 20M on Chromosorb WAW DMCS column using the method of internal standards. The injector temperature was 225° C and the column temperature was programmed from 30 to 200° C at 20° C min^{-1}.

3. Results and discussion

Figure 1 is a typical chromatogram showing the number and relative quantities of by-products at a propylene oxide concentration of 33.7 g dm^{-3}. Ehdaie [5] reported dibromopropane and 1,2-propanediol as the by-products with never more than 1% of the glycol as the major by-product, but comparison of retention times with those of authentic compounds (Table 1) identified 2-propanol, 1-propanol, 1,2-dibromopropane and 1,2-propanediol, while glc/ms data confirmed the presence of 2-propanol and 1,2-dibromopropane as shown in Table 2 which lists the eight most abundant mass fragments for each of the peaks in Fig. 2.

The presence of dipropyl ethers was also indicated from the glc/ms data, Table 2, D, I, J and K. Ethers may generally be formed in two ways, either from alcohols in acid media or by Williamson's synthesis. The accepted mechanisms

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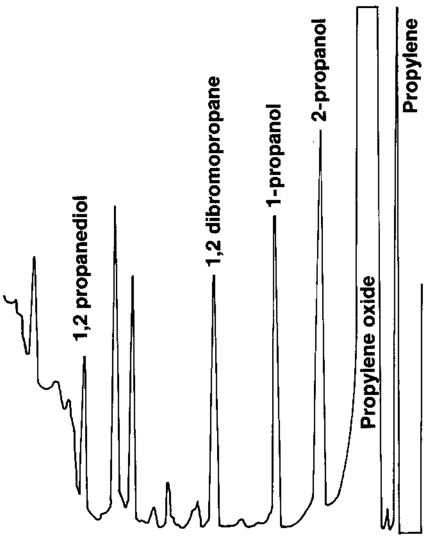


Fig. 1. glc trace showing the easily identified by-products at a propylene oxide concentration of 33.7 g dm^{-3}.

for their synthesis from alcohols are that straight chain primary alcohols react by bimolecular (S_N2) reaction, tertiary alcohol by unimolecular reaction, and secondary alcohols by either of these routes. Williamson's synthesis proceeds via the (S_N2) reaction of an alkoxide ion with an alkyl halide. A third possibility is that cyclic bromonium ions are generated, which can react with an alcohol which behaves as a nucleophile:

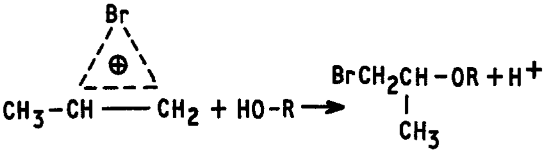


*Table 1. glc retention times for the propylene oxide systems**

Compound	*Retention time* (s)*
Propylene	30
Propylene oxide	60
Acetone†	104
2-Propanol	138
1-Propanol	201
1,2-Dibromopropane	288
1,2-Propanediol	492

* Time taken from injection: 2 m Carbowax 20 M (10%) on Chromosorb WAW DMCS (80–100 mesh), 30–200° C at 20° C min^{-1}, N_2 flow rate 30 cm^3 min^{-1}, injector temperature 225° C.

† Internal standard.

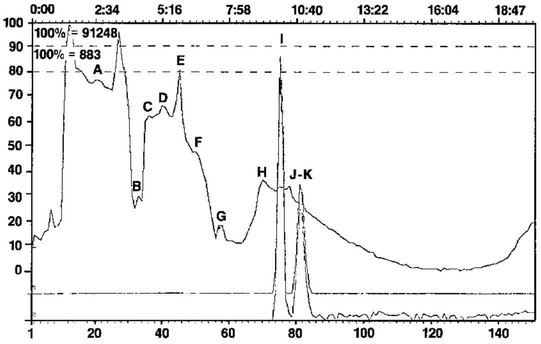
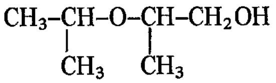


Fig. 2. glc trace from glc/ms of the same solution as in Fig. 1.

Thus, in a reaction mixture which contains 1-propanol, 2-propanol, 2-bromo-1-propanol, 1,2-dibromopropane and 1,2-propanediol, the number of ethers which may possibly be formed is very large, at least fifteen.

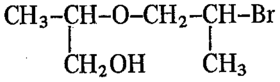
Compound D probably has the structure:



$$\underset{CH_3}{CH_3-CH}-O-\underset{CH_3}{CH}-CH_2OH$$

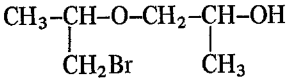
and is probably formed from the coupling of 2-propanol with 1-bromo-2-propanol. The evidence for this structure comes from the fragmentation pattern in the mass spectrum [2]. Likewise, the other compounds are identified as:

Compound I



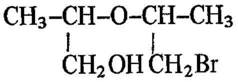
$$CH_3-\underset{CH_2OH}{CH}-O-CH_2-\underset{CH_3}{CH}-Br$$

Compound J



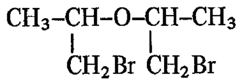
$$CH_3-\underset{CH_2Br}{CH}-O-CH_2-\underset{CH_3}{CH}-OH$$

Compound K



$$CH_3-\underset{CH_2OH}{CH}-O-\underset{CH_2Br}{CH}-CH_3$$

but no evidence was found of dibrominated ethers, such as:



$$CH_3-\underset{CH_2Br}{CH}-O-\underset{CH_2Br}{CH}-CH_3$$

As yet, compounds B, C, F and H are unidentified and B and C have defied identification even after an extensive computer-based library search had been carried out.

Although the number of by-products has been shown to be relatively large, their combined con-

Table 2. MS data for the compounds identified by GC/MS for the propylene oxide system

*GC Peak**	*Mass numbers of eight most abundant peaks (Intensity %)*								M^+ *(Intensity)*	*Compound*
A	45 (100)	43 (13.5)	41 (6.5)	44 (5.8)	59 (5.4)	27 (3.7)	42 (3.1)	39 (3.1)	60 (0.6)	2-propanol
B	88 (100)	77 (45.5)	58 (43.6)	45 (38.8)	33 (29.1)	34 (24.8)	62 (20.6)	87 (18.2)		Unknown
C	44 (100)	58 (88)	88 (80)	42 (38)	77 (34)	53 (22)	27 (17)	33 (16)		Unknown
D	43 (100)	45 (82.2)	59 (51.4)	75 (21.0)	40 (20.0)	41 (17.5)	61 (9.3)	27 (9.0)		See text.
E	121 (100)	123 (95.3)	41 (53.7)	39 (16.9)	45 (5.7)	42 (5.0)	122 (4.0)	124 (3.2)	203 (0.6) 201 (1.1)	1,2-dibromopropane
F	142 (100)	73 (36.5)	45 (23.7)	100 (18.4)	57 (11.3)	143 (9.4)	59 (16.3)	58 (6.3)		Unknown
G	45 (100)	28 (44.0)	32 (23.4)	43 (13.9)	123 (10.1)	125 (9.1)	41 (4.3)	40 (3.4)	138 (0.6) 140 (0.6)	1-bromo-2-propanol
H	45 (100)	28 (18)	43 (17)	61 (14)	32 (9)	57 (8)	87 (8)	31 (7)		Unknown
I	45 (100)	28 (19.8)	40 (17.7)	87 (17.0)	123 (10.7)	121 (10.3)	165 (10)	167 (10.0)		See text.
J	45 (100)	59 (35.5)	87 (23.2)	103 (21.5)	28 (18.6)	73 (18.3)	123 (17.0)	121 (16.8)		See text.
K	45 (100)	73 (59.0)	87 (37.8)	28 (26.1)	59 (22.4)	89 (20.9)	43 (19.6)	44 (18.7)		See text.

* See Fig. 2.

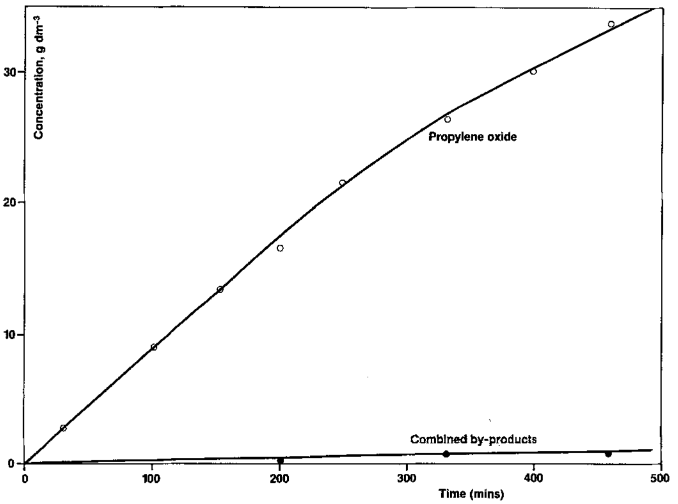


Fig. 3. Propylene oxide and total by-product concentrations as a function of time in a batch recycling synthesis, 1% NaBr, flow rate 1300 cm^3 min^{-1}, 4.0 V/cell, polarity B [1].

centration relative to propylene oxide is small, as shown in Fig. 3 (a response factor of unity was assumed for the unknowns, which introduces an error but probably one of much less than 50%). While the combined concentration remains approximately 3% of the propylene oxide concentration up to at least 34 g dm^{-3} (850 recycles) the distribution of by-products changes, as shown in Fig. 4. The amount of propanediol formed is low (approximately 0.02 g dm^{-3} at a propylene oxide concentration of 30 g dm^{-3}) and only increased to 0.60 g dm^{-3} after the reaction mixture had stood for four days at room temperature; hence, the rate of hydrolysis of propylene oxide to the diol is low in 1% NaBr solution at pH 10–11.

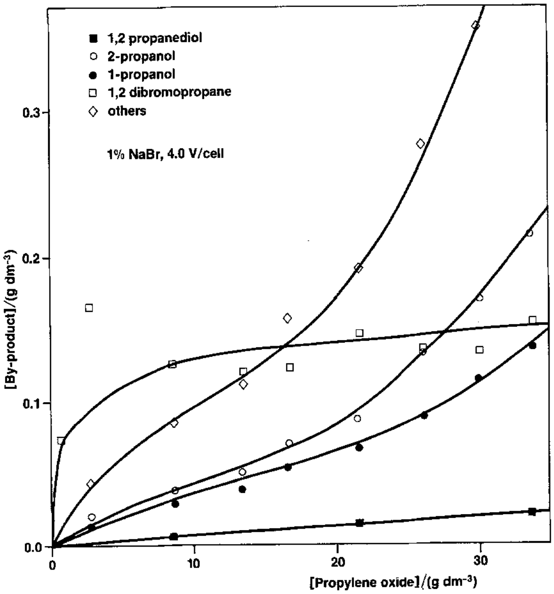
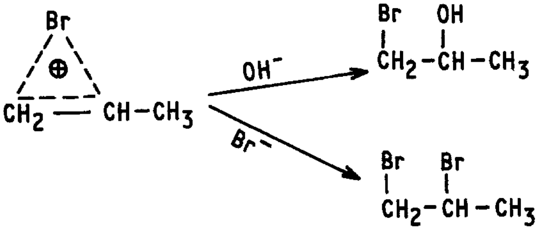


Fig. 4. Distribution of by-products as a function of propylene oxide concentration, 1% NaBr. Flow rate 1300 cm^3 min^{-1}, 4.0 V/cell, polarity B [1]. ■ 1,2-propanediol, ○ 2-propanol, ● 1-propanol, □ 1,2-dibromopropane, ◇ others.

Initially, the rate of formation of 1,2-dibromopropane was high but decreased with increasing propylene oxide concentration (hence time) and reached a value of just over 0.14 g dm^{-3} at a propylene oxide concentration of 30 g dm^{-3}. The reason for the initial high rate was almost certainly low pH. At the start of these (batch) experiments the solution was virtually neutral, favouring nucleophilic attack by bromide:



Increasing the current density (by increasing the voltage per cell) or the bromide concentration increased the concentration of dibromopropane, as expected (Fig. 5), but, once the working pH (between 10 and 11) had been reached, the production of dibromopropane virtually ceased, so in continuous production it would not constitute a major loss of bromine. Interestingly, the conditions necessary for higher concentrations of 1,2-dibromopropane have the effect of suppressing the formation of 1-propanol and 2-propanol, as shown

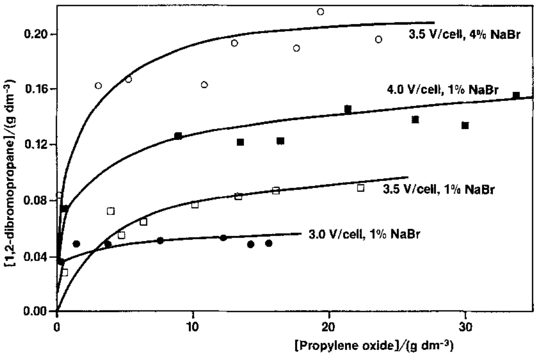
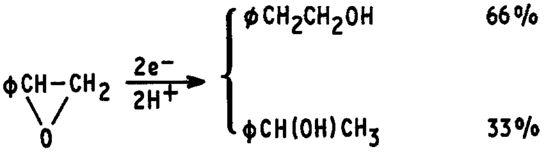


Fig. 5. 1,2-Dibromopropane concentration as a function of propylene oxide concentration under various operating conditions. Flow rate 1300 cm^3 min^{-1}, polarity B [1].

by Fig. 6 (*cf.*, Fig. 4). The secondary alcohol was always formed in larger amounts than the primary alcohol.

The mechanism by which the alcohols are formed is not obvious. The direct electrochemical reduction of epoxides has been observed [6], for example, styrene oxide can be reduced at − 2.35 V (versus Ag–AgI) at a mercury cathode in DMF with tetrabutylammonium perchlorate as the electrolyte,



but this is unlikely to occur in the present case due to the high potential required. Also, the propanol concentration was observed to decrease as the cell potential was increased; thus, the formation of propanol is probably not by direct electrochemical reduction of the product. Hydrogenation by cathodically produced hydrogen is also unlikely because of the inverse potential relationship, and, while hydration of alkenes is possible, it usually proceeds via a carbonium ion intermediate and requires strong acid and so is unlikely even in areas of poor mixing between the elements.

Propylene oxide can isomerize to propanal in dilute acid solutions, and small concentrations of propanal would not be detected in the presence of large concentrations of propylene oxide due to their similarity of properties. Propanal is readily reduced electrochemically to 1-propanol in weakly alkaline solutions on a number of cathode materials [7], and the suppression of alcohol formation at higher potentials and bromide concentrations could be explained by the competing electrochemical reduction of bromine to bromide which is enhanced under these conditions due to the depletion of propylene, which has been discussed elsewhere [1]. However, this does not explain the formation of 2-propanol. The analogous cathodic reduction of acetone to 2-propanol could not have occurred since no acetone was detected in these experiments.

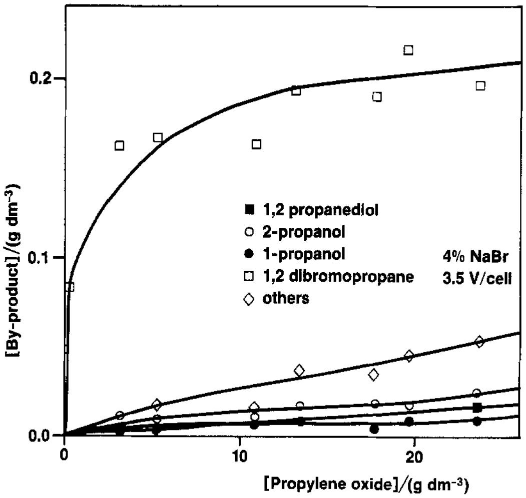


Fig. 6. Distribution of by-products as a function of propylene oxide concentration, 4% NaBr. Flow rate 1300 cm^3 min^{-1}, 3.5 V/cell, polarity B [1]. ■ 1,2-propanediol, ○ 2-propanol, ● 1-propanol, □ 1,2-dibromopropane, ◇ others.

A reaction sequence which could give rise to propanol isomers is the addition of HBr formed in the hydrolysis of bromine to propylene to give 1- and predominantly 2-bromopropane, followed by hydrolysis with cathodically generated hydroxide to give the corresponding alcohols. However, no bromopropane was detected as a by-product and this scheme does not fit the observed inverse relationship between applied potential and propanol concentration since more bromopropane, hence propanol, would be expected the higher the rate of evolution of bromine. Thus, the mechanism of propanol formation is uncertain; fortunately, 1- and 2-propanol are only formed in small amounts; 0.2 to 0.8% of the PO concentration up to propylene oxide concentrations of approximately 25 g dm^{-3}.

Conclusions

The distribution of by-products in the indirect, electrochemical epoxidation of propylene in a bipolar trickle tower changes with conditions, but, fortunately, their combined concentration never exceeds about 3% of the propylene oxide concentration. Further, the concentration of dibromopropane is always small, and, under the preferred operating conditions [1], is very small, so that loss of bromine from a continuously running system would not be serious. The economic consequences of this high selectivity have been discussed elsewhere [1].

References

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