

# *The indirect electrochemical epoxidation of butenes and ethylene in a bipolar trickle tower*

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1-Butene, *cis*-2-butene, *trans*-2-butene and ethylene have been epoxidized under conditions which give reasonable results for propylene. In all cases the selectivities are high, but the current efficiencies are low (< 65%) due to the bulk phase chemical reactions being slower than the electrochemical generation of oxidant. Under conditions where the rates of the chemical and electrochemical reactions match, the figures of merit would be comparable to those for propylene.

In the epoxidation the conformation of each butene isomer is preserved.

## 1. Introduction

The epoxidation of propylene in a bipolar trickle tower has been reported fairly extensively [1-5], but relatively little has appeared on other systems. Since the contacting pattern is so favourable in the case of propylene [2] and the selectivity for propylene oxide is so high (*c.* 97% across a wide range of conditions), [4, 5] a series of experiments was carried out on 1-butene and *cis*- and *trans*-2-butene, as well as ethylene. These experiments were unoptimized and the conditions chosen were those generally best for the epoxidation of propylene.

## 2. Experimental procedure

The tower consisted of a 65 mm i.d. glass pipe packed with layers of 12.5 mm long carbon (Morganite CYII5) Raschig rings, 20 per layer, in an 'in line' array [3]. Adjacent layers were separated by 0.9 mm thick monofilament polyester nets. There were 14 layers of rings which, together with the 5 mm thick perforated plate current feeders above and below the packing, made 15 cells in series. 52.5 V were applied across the tower, giving 3.5 V/layer, with polarity A [3] (top of each ring cathodic). The 1% NaBr electrolyte recycled continuously at 1300 cm<sup>3</sup> min<sup>-1</sup>.

The starting material was fed as a gas, concurrently.

The first experiment was carried out on a sample of 1-butene (supposedly 99%, BDH) and the course of the reaction was followed by gas chromatography (5% Tween 80, 2 m column in a Perkin Elmer F17 chromatograph) which revealed that three products were produced. At the end of the run the three organic products were isolated by distillation to yield approximately 4 cm<sup>3</sup> of two liquid phases (b.p. 50-80°), the lower layer of which was water saturated with the organic products. Separation of these products was achieved by preparative gas chromatography (Perkin Elmer 425 GC with a 7 m long, 1/4" diameter polypropylene glycol coated column), and the subsequent identification by NMR was confirmed by comparison with the retention times of authentic samples on both the Tween 80 and glycol columns. This showed the three products to be 1,2-epoxybutane, *trans*-2,3-epoxybutane and *cis*-2,3-epoxybutane (Table 2). Analysis of a 10 μm<sup>3</sup> sample of the original gas on a 2 m long Porapak Q column at 150° C showed three components in the approximate ratio of 40% 1-butene (retention time 5.65 minutes) to 60% *trans*-2-butene (6.20 minutes) plus *cis*-2-butene (6.50 minutes). The two peaks at 6.20 and 6.50 minutes were shown to be *trans*- and *cis*-2-butene by comparison with authentic

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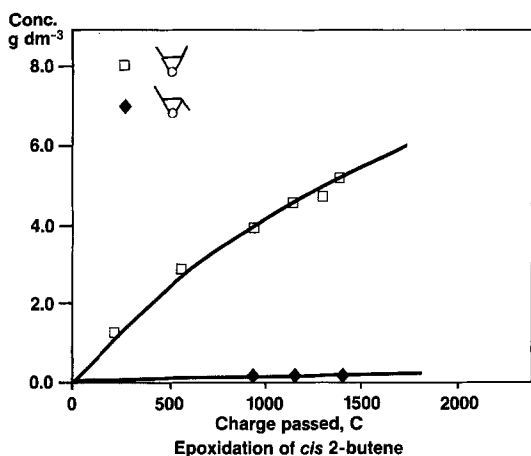


Fig. 1. Concentrations of *cis*- and *trans*-2,3-epoxybutane versus charge passed: feed *cis*-2-butene (99%).

samples, which showed only one peak each. A second bottle of '1-butene' showed the same distribution of isomers, so the supplier was changed (Matheson) and no further difficulty encountered.

### 3. Results and discussion

Figure 1 shows the results of epoxidizing *cis*-2-butene (99%, BDH); the selectivity was 98% to *cis*-2,3-epoxybutane at a concentration of  $4 \text{ g dm}^{-3}$ , with only 2% of the *trans* isomer and no detectable amount of 1,2-epoxybutane. The concentration of the *trans* isomer was almost certainly due to the presence of *trans*-2-butene

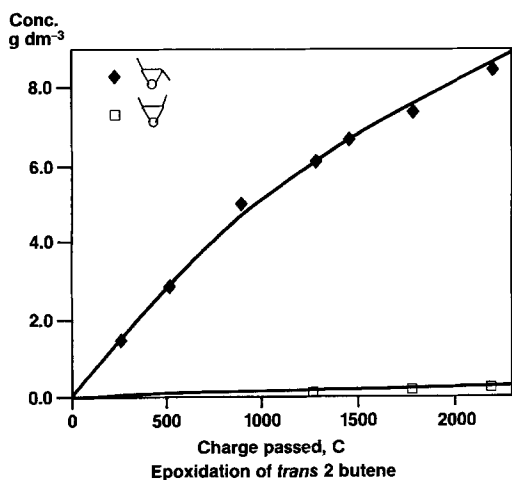
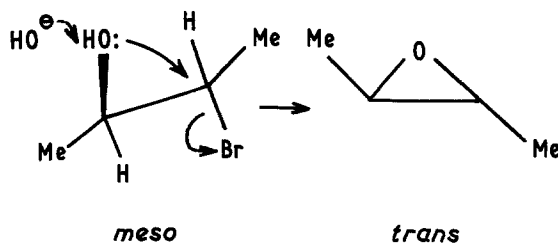


Fig. 2. Concentrations of *cis*- and *trans*-2,3-epoxybutane versus charge passed: feed *trans*-2-butene (99%).

as an impurity in the starting material. Likewise, Fig. 2 shows a selectivity of 98% to *trans*-2,3-epoxybutane from *trans*-2-butene (99%, Matheson); again, 1,2-epoxybutane was not detected. It is clear, therefore, that the conformation is preserved during epoxidation and that a mixture of butenes should give the same mole ratios of epoxides. This is reasonable in view of the probable mechanism; the addition of bromine and hypobromous acid is a two-step process via a bridged bromonium ion, the bromine and  $\text{OH}^-$  adding from opposite sides in *anti* addition so that the product from *trans*-2-butene is 100% *meso* bromohydrin. Similarly, *cis*-2-butene is converted into ( $\pm$ ) bromohydrin. The elimination occurs from the antiperiplanar conformation:



so that *trans*-2-butene goes to *trans*-2,3-epoxybutane with 100% selectivity, and *cis*- to *cis*-similarly.

Table 1 gives a summary of results for *cis*- and *trans*-2-butenes, together with those for propylene and ethylene under the same conditions. As discussed elsewhere [4], the current efficiency for propylene is worse than previously

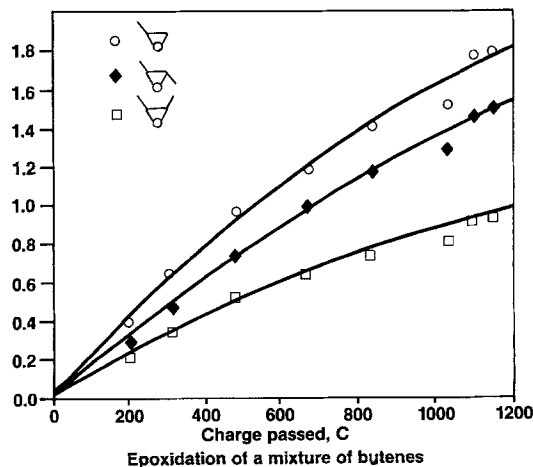


Fig. 3. Concentrations of *cis*- and *trans*-2,3-epoxybutane and 1-epoxybutane versus charge passed: feed a mixture of 1-butene and *cis*- and *trans*-2-butene.

Table 1. Figures of merit for the epoxidation of butenes and ethylene

Isomer	Current efficiency (%)	Space-time yield ( $\text{mol h}^{-1} \text{ m}^{-3}$ )		Energy consumption		Selectivity (%)		
		Measured	On basis of 100% c.e.	At 100% c.e.				
				Measured $\text{kWh kg}^{-1}$	$\text{kWh mol}^{-1}$		Measured $\text{kWh kg}^{-1}$	$\text{kWh mol}^{-1}$
<i>trans</i> -2,3-epoxybutane	65	76	117	4.0	0.29	2.60	0.19	98
<i>cis</i> -2,3-epoxybutane	54	74	137	4.8	0.35	2.59	0.19	98
propylene oxide	72	110	153	4.5	0.26	3.24	0.19	97
ethylene oxide	21	31	146	19.9	0.88	4.18	0.19	—

Table 2. Figures of merit for epoxidation of a mixture of butenes

Isomer	Current efficiency (%)		Space-time yield (mol h <sup>-1</sup> m <sup>-3</sup> )		Energy consumption (kWh kg <sup>-1</sup> )	Gas composition (%)
	Measured	Scaled to 100% total	Measured	On basis of 100% c.e.		
1,2-epoxybutane	25	41	26.5	43.5	4.3	41
<i>trans</i> -2,3-epoxybutane	23	38	24.3	40.1	4.3	38
<i>cis</i> -2,3-epoxybutane	13	21	13.8	22.3	4.2	21
Combined	61	100	64.6	105.9	4.3	100
1,2-epoxybutane	25	43	24.6	42.3	4.5	43
<i>trans</i> -2,3-epoxybutane	20	34	19.4	33.0	4.5	34
<i>cis</i> -2,3-epoxybutane	13	22	13.2	22.3	4.3	23
Combined	58	99	57.2	97.6	4.5	100

reported [1] because the reaction was run at higher current density in an attempt to increase the space-time yield and the depletion of propylene became the limiting factor, the excess bromine being reduced to bromide or oxidized to bromate. This is even more of a problem for the butenes, because of their lower solubilities in aqueous solution, and more particularly for ethylene due to its low solubility and the fact that its double bond is not activated by adjacent methyl groups. In fact, 40 times more bromate was formed (as shown by iodometric titration) in the case of ethylene than in the epoxybutane experiments for the same charge passed [6]. However, it has been shown [7] that pressurizing the propylene system alleviates propylene depletion in a flooded cell, and there is no reason to believe that it would not be effective in suppressing the parasitic reactions in the other cases. Interestingly, on the basis of 100% current efficiency (no excess bromine evolution), the figures of merit for the four species are comparable. No selectivity is quoted for ethylene oxide since, although no by-products were observed, the final concentration of ethylene oxide obtained in the reaction mixture was too low (1.2 g dm<sup>-3</sup>) for a definitive statement to be made. It is however, probably high (> 90%).

When allowance is made for the over-production of bromine (Table 2), the apparent current efficiency for each butene isomer is the same as its fractional composition in the gas phase, showing that the individual reactions proceed at essentially the same rate.

Since the adjusted performance figures are com-

parable to those for the propylene system, probably similar scale factors apply [4] so that it should be possible to achieve space-time yields in excess of 400 mol h<sup>-1</sup> m<sup>-3</sup> at 4.0 kWh kg<sup>-1</sup> in a moderately pressurized system.

### Conclusion

1,2-Butene, *cis*-2,3-butene and *trans*-2,3-butene can all be epoxidized in an unpressurized bipolar trickle tower with figures of merit less than, but comparable to, those for propylene. Ethylene, on the other hand, shows a much poorer performance due to its low rate of reaction with HOBr. Pressurization to increase the solubility of the gas, and an increase in temperature to increase the rate, would probably lead to similar figures for all the alkenes.

During the epoxidation of the butene isomers the stereochemistry is preserved and the reactions proceed at comparable rates, so that epoxidation can not be used as a means of separating the isomers.

### Acknowledgment

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