# The synthesis of butene glycol ethers with aluminium triflate

#### Yvette M. Terblans, Michelle Huyser, Desmond A. Young, and Michael J. Green

Abstract: The use of aluminium triflate as a ring-opening catalyst for butene oxide (BuO) was evaluated in the presence of different alcohols such as methanol, ethanol, n-propanol, n-butanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol. The reaction with methanol was studied kinetically by varying the temperature, catalyst concentration, and methanol – butene oxide molar ratio. These reactions yielded two major products (2-methoxy-1-butanol and 1-methoxy-2-butanol) in a approximate ratio of 1:1. It was noted that at low catalyst concentrations (<5 ppm), low temperatures (<90 °C), and a MeOH–BuO molar ratio of 8:1, the selectivity of the reaction could be kinetically manipulated to shift the product ratio towards 1-methoxy-2-butanol, the  $\alpha$ -alkoxyalcohol. This result was confirmed by an experimental design program. Statistical calculations using the data from the experimental design identified a feasible region in which reactions with methanol could be carried out, which would lead to slightly higher selectivities to 1-methoxy-2-butanol. This region shows that the methanol – butene oxide ratio should be 8:1, the temperature between 80 and 85 °C, and the catalyst concentration between 3.9 and 5 ppm. These reaction conditions were used to carry out a test reaction with methanol and an extended series of alcohols. All the alcohols, except for 2-methyl-2-propanol, reacted with butene oxide under these conditions, with the selectivity to the  $\alpha$ -alkoxyalcohol higher than to the  $\beta$ alkoxyalcohol. To obtain a ring-opening reaction with 2-methyl-2-propanol, it was found that a higher catalyst concentration (approximately 10 ppm) and a lower alcohol - butene oxide ratio (6:1) at a temperature of 80 °C were necessary. This reaction led to a mixture of 1-tert-butoxy-2-butanol and 2-tert-butoxy-1-butanol with the selectivity to the  $\alpha$ -alkoxyalcohol being somewhat higher because of the steric influence of the bulky *tert*-butoxy group.

Key words: aluminium triflate, alcohols, butene oxide, ring opening,  $\alpha$ -alkoxyalcohol,  $\beta$ -alkoxyalcohol.

Résumé : On a évalué l'utilité du triflate d'aluminium comme catalyseur pour effectuer l'ouverture du cycle de l'oxyde de butène (BuO) en présence de divers alcools, dont le méthanol, l'éthanol, le n-propanol, le n-butanol, le 2-propanol, le 2-methyl-1-propanol et le 2-methyl-2-propanol. On a étudié la cinétique de la réaction avec le méthanol en faisant varier la température, la concentration de catalyseur et le rapport molaire méthanol - oxyde de butène. Ces réactions conduisent à la formation de deux produits principaux (le 2-méthoxybutan-1-ol et le 1-méthoxy-2-butanol) dans un rapport approximatif de 1 : 1. On a noté que, à de faibles concentrations de catalyseurs (<5 ppm), de faibles températures (<90 °C) et un rapport molaire MeOH-BuO de 8 : 1, la sélectivité de la réaction peut être manipulée d'une façon cinétique pour déplacer le rapport des produits en faveur du le 1-méthoxy-2-butanol, le  $\alpha$ -alkoxyalcool. Ce résultat a été confirmé par un programme de modélisation expérimental. Des calculs statistiques à l'aide de données de modélisations expérimentales ont permis d'identifier une région appropriée dans laquelle les réactions avec le méthanol pourraient se produire pour conduire à des sélectivités légèrement supérieures en le 1-méthoxy-2-butanol. Ces calculs montrent que le rapport méthanol - oxyde de butène devrait être de 8 : 1, la température entre 80 et 85 °C et la concentration en catalyseur entre 3,9 et 5 ppm. On a utilisé ces conditions pour évaluer la réaction avec le méthanol et une série importante d'alcools. Dans ces conditions, tous les alcools réagissent avec l'oxyde de butène, à l'exception de l'alcool tert-butylique, et dans tous les cas la sélectivité favorise le  $\alpha$ -alkoxyalcool par rapport au  $\beta$ -alkoxyalcool. Pour obtenir une réaction d'ouverture de cycle avec le 2-methyl-2-propanol, il est nécessaire d'utiliser une concentration en catalyseur plus élevée (environ 10 ppm) et un rapport alcool - oxyde de butène plus faible (6 : 1), à une température de 80 °C. Cette réaction conduit à un mélange de 1-tert-butoxy-2-butanol et de 2-tert-butoxy-1-butanol dans lequel la sélectivité en faveur du  $\alpha$ -alkoxyalcool est légèrement supérieure en raison de l'influence stérique du groupe *tert*-butoxy.

*Mots clés* : triflate d'aluminium, oxyde de butène, ouverture de cycle,  $\alpha$ -alkoxyalcool,  $\beta$ -alkoxyalcool.

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Scheme 1. Ring opening of butene oxide with an alcohol.



#### Introduction

Ring-opening reactions of epoxides with alcohols, which have been successfully carried out for many decades, can be either base- or acid-catalyzed (1). In recent years the use of triflate salts (also known as trifluoromethane sulfonate salts) has become increasingly popular as catalysts for these reactions. The catalytic acitivity of rare earth triflates (e.g.,  $Eu(CF_3SO_3)_3$ ,  $La(CF_3SO_3)_3$ ,  $Lu(CF_3SO_3)_3$ ,  $Nd(CF_3SO_3)_3$ ,  $Sm(CF_3SO_3)_3$ ,  $Sc(CF_3SO_3)_3$ ,  $Y(CF_3SO_3)_3$ , and  $Ce(CF_3SO_3)_4$ ) has been investigated for the ring opening of epoxides by alcohols (2). Scandium triflate was found to be an exceptionally active catalyst for the ring opening of epoxides.  $Yb(CF_3SO_3)_3$  has also been reported as a catalyst for intermolecular ring-opening reactions of epoxides with alcohols to give  $\beta$ -alkoxyalcohols in good to high yields with high regio- and stereo-selectivity (3).

Aluminium triflate is a Lewis acid that has been used as a catalyst in organic synthesis, for reactions including Friedel-Crafts acylation and alkylation (4, 5), the epoxidation of olefins with iodosylbenzene (6), the preparation of esters and lactones (7), as initiators for cationic polymerization (8), and as co-catalysts in the polymerization of olefins (9). Aluminium triflate has also been used as a catalyst for the ringopening reactions of epoxides in the presence of alcohols and amines (10-12). Some work has also been carried out in which different epoxides and alcohols have been employed (13). In a recent study, we described the reaction of butene oxide with methanol, catalyzed by aluminium triflate (14). We now report on a kinetic study in which the effect of reaction variables (i.e., catalyst concentration, temperature, and reagent molar ratio) on the rate of conversion of butene oxide and selectivity to the major products (the  $\alpha$ - and  $\beta$ alkoxyalcohols) was investigated. The study was further expanded to include reactions with ethanol, *n*-propanol, *n*butanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2propanol, with the aim of comparing the activity of  $Al(CF_3SO_3)_3$  as a ring-opening catalyst of butene oxide in the presence of different alcohols (Scheme 1).

Due to the fact that Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> is a Lewis acid, its use as a ring-opening catalyst for butene oxide leads to the formation of both isomers of the corresponding butene glycol ether, i.e.,  $\alpha$ - and  $\beta$ -alkoxyalcohols. Previous studies have shown that the two isomers form in a molar ratio of close to one with the  $\beta$ -alkoxyalcohol in a slight excess compared with the  $\alpha$ -alkoxyalcohol (10–12, 14). In a recent communication, three examples were provided in which the selectivity to the  $\alpha$ -alkoxyalcohol is higher when using butene oxide and several others in the case of styrene oxide (13). In this study we show that it is possible to slightly increase the selectivity to the  $\alpha$ -alkoxyalcohol with a simultaneous decrease in selectivity to the  $\beta$ -alkoxyalcohol by choosing the correct reaction conditions. Lower temperatures and catalyst concentrations were found to increase the selectivity to the



obtained from an experimental design program.

### Experimental

Unless otherwise stated, all chemicals used in this study were purchased from Sigma-Aldrich and used without further purification. Aluminium triflate was prepared as described in the literature (12). Stock solutions of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (500 ppm) were prepared in each alcohol and the desired quantity thereof was weighed for every reaction. Kinetic reactions were carried out in a Parr autoclave. Gas chromatography was carried out using a Shimadzu GC-17A equipped with a flame ionization detector and a PONA capillary column (50 m × 0.21 mm × 0.5 µm). Each sample was weighed into a GC vial and *n*-heptane was used as an internal standard.

## Typical experimental procedure for the ring opening of butene oxide

Methanol (192.25 g, 6 mol) and butene oxide (72.11 g, 1 mol) were combined in a 300 mL Parr reactor. On closing the reactor, it was flushed with nitrogen and evacuated to remove all air present. This flushing procedure was repeated three times.

A catalyst bomb was placed under vacuum prior to the run. The desired amount of the stock solution (2.644 g, 5 ppm) was weighed and transferred via a syringe to the bomb, which was then connected to the inlet of the autoclave. Next, a high-pressure nitrogen line was connected to the opposite side of the catalyst bomb after which stirring in the reactor commenced. The reactor was subsequently heated to 100 °C after which the catalyst solution was discharged into the reactor and a sample taken immediately (0 min) and weighed. The sample was weighed to determine the mass removed from the reactor. Further sampling from the reactor was carried out at the following intervals: 5, 10, 15, 20, 30, 60, and 120 min and each sample was weighed. Saturated NaOH–water solution (0.5 mL) was added to all samples to quench the reaction.

#### **Results and discussion**

#### **Butoxylation of methanol**

#### Catalyst concentration

In the first part of this study, the influence of catalyst concentration on the conversion of butene oxide and the selectivity to the major products (the  $\alpha$ - and  $\beta$ -alkoxyalcohols) was studied over a range of catalyst concentrations. Included in this was the uncatalyzed reaction. The conversion of butene oxide is shown in Table 1. The data showed that the rate of conversion of the uncatalyzed reaction (0 ppm) was

	Conversion (mol%	Conversion (mol%) of butene oxide					
Time	Al(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub>						
(min)	(0 ppm)	(1 ppm)	(5 ppm)	(10 ppm)			
5	3.00	16.00	74.00	85.00			
10	6.00	36.00	97.00	100.00			
15	11.00	46.00	100.00	100.00			
20	16.00	50.00	100.00	100.00			
30	21.00	61.00	100.00	100.00			
60	29.00	77.00	100.00	100.00			
120	41.00	88.00	100.00	100.00			

**Table 1.** Conversion of butene oxide at different Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalyst concentrations.

**Note:** T = 100 °C; MeOH–BuO = 6:1.

Table 2. Selectivity to products at different Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalyst concentrations.

	1-Methoxy-2-butanol		2-Methoxy-1-butanol	
Catalyst concentration (ppm)	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)
0	49.60	10.42	42.94	9.02
1	49.75	30.35	42.25	25.77
5	43.39	43.39	48.61	48.61
10	42.98	42.98	49.02	49.02

**Note:**  $T = 100 \,^{\circ}\text{C}$ ; MeOH–BuO = 6:1.

Fig. 1. Ring-opened intermediate.



significantly slower than those of the catalyzed reactions. The increase in the rates from 0 to 1 ppm and to 5 ppm can clearly be seen; thus, as the catalyst concentration was increased, the rate of conversion also increased. However, hardly any difference was observed in the rate of conversion when the catalyst concentration was increased from 5 to 10 ppm. At these two catalyst concentrations, the rate of the reaction was very fast and the reactions were completed after approximately 10 min. The low catalyst concentration needed for a fast reaction is due to the fact that the Lewis acid (Al(OCF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>) coordinates to the epoxide, which leads to further activation of the already active electrophile. It was also further demonstrated that the transfer of the Al(OCF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> from the ring-opened intermediate (Fig. 1) to the next butene oxide molecule is energetically favourable (14).

In these reactions two major products (the  $\alpha$ - and  $\beta$ alkoxyalcohols, 1-methoxy-2-butanol and 2-methoxy-1butanol) were formed. By-products such as dimers, diols, and in some instances, trimers, were also formed during these reactions with a total yield of dimers, diols, and trimers of approximately 8%, selectivity to dimers of approximately 4%, selectivity to diols of approximately 1%, and selectivity to the trimers of approximately 3%. All products were identified using GC–MS. It was noticed that the higher the catalyst concentration, the higher the concentration of by-products.

The selectivities to the  $\alpha$ - and  $\beta$ -alkoxyalcohols and yields of these products were calculated after 30 min of reaction

time and are tabulated in Table 2. Upon considering the influence of the catalyst concentration on the selectivity to the products, it is observed that the selectivity to 1-methoxy-2butanol was slightly higher than to 2-methoxy-1-butanol. However, as the catalyst concentration was increased above 2.5 ppm, the selectivity to the 2-methoxy-1-butanol was slightly higher than to 1-methoxy-2-butanol. This observation shows that as the catalyst concentration is increased, the formation of the sterically more hindered isomer becomes more facile.

#### *Temperature*

The second part of the study with methanol focused on the influence of reaction temperature on the rates of conversion, as well as the selectivity to the products. The conversion data are shown in Table 3.

The temperature data display a similar trend as the catalyst concentration data, i.e., the rate of conversion, increased as the reaction temperature was increased. The data also showed that the increase in the rate of conversion was not as significant when the temperature was increased from 100 to 120 °C, as was the case when it was increased from 60 to 80 °C and to 100 °C. This is due to the fact that the rates become very fast at the higher temperatures. It was also seen that the higher the temperature, the higher the concentration of by-products, i.e., dimers and trimers (total yield approximately 10%, selectivity to dimers approximately 7% and to trimers approximately 3%).

The selectivities to the alkoxyalcohols and the yields of these products were calculated after 30 min of reaction time. The data are shown in Table 4. It was observed that, although the ratio of the major products is approximately 1, at temperatures below 80 °C, the selectivity to 1-methoxy-2-butanol is slightly higher than to 2-methoxy-1-butanol, whereas the opposite is observed at temperatures above 80 °C. At 90 °C, the selectivity to 1-methoxy-2-butanol is

	Conversion	Conversion (mol%) of butene oxide					
Time (min)	60 °C	80 °C	90 °C	100 °C	120 °C		
5	16.05	16.68	31.67	59.18	88.80		
10	36.43	54.31	73.62	94.39	100.00		
15	53.47	79.95	97.22	99.55	100.00		
20	69.64	81.95	100.00	100.00	100.00		
30	74.33	89.17	100.00	100.00	100.00		
60	88.50	93.32	100.00	100.00	100.00		
120	95.86	97.15	100.00	100.00	100.00		

Table 3. Conversion of butene oxide at different temperatures.

**Note:**  $Al(CF_3SO_3)_3$  catalyst concentration = 5 ppm; MeOH-BuO = 6:1.

Table 4. Selectivity to products at different temperatures.

	1-Methoxy-2-butar	nol	2-Methoxy-1-butar	nol
Temperature (°C)	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)
60	56.01	41.63	43.99	32.70
80	55.17	49.20	44.83	39.97
90	46.00	46.00	45.94	45.94
100	43.39	43.39	48.61	48.61
120	43.33	43.33	50.67	50.67

**Note:** Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalyst concentration = 5 ppm; MeOH–BuO = 6:1.

**Table 5.** Conversion of butene oxide with  $Al(CF_3SO_3)_3$  at different methanol – butene oxide ratios.

	Conversion (n	Conversion (mol%) of butene oxide							
Time	MeOH-BuO	MeOH-BuO	MeOH-BuO	MeOH-BuO	MeOH-BuO	Me-BuO			
(min)	(4:1)	(6:1)	(8:1)	(10:1)	(12:1)	(14:1)			
5	76.69	59.18	57.44	55.53	56.75	57.03			
10	100.00	94.39	96.57	96.37	96.20	92.55			
15	100.00	100.00	100.00	100.00	100.00	100.00			

Note: T = 100 °C; catalyst concentration = 5 ppm.

virtually equal to the selectivity to 2-methoxy-1-butanol. These observations correlate well with those already observed for the catalyst concentration. It was observed that as the temperature is increased, the formation of the sterically more hindered isomer becomes more facile; the same trend is observed for the catalyst concentration.

#### Reactant molar ratio

The last part of the study with methanol focused on the influence of the molar ratio of the reagents on the rates of conversion, as well as the selectivity to the alkoxyalcohol products. The conversion data are shown in Table 5. In this study the ratio of MeOH–BuO was varied from 4:1 to 14:1.

It was observed that as the ratio of MeOH–BuO is increased, the rate of the reaction decreases, since the transfer of the  $Al(CF_3SO_3)_3$  from the ring-opened intermediate (Fig. 1) to butene oxide depends on the concentration of butene oxide in the reaction mixture. Since the increase in the MeOH–BuO ratio will lead to a lowering in butene oxide concentration, a drop in rate was observed as expected. It was observed that the lower the MeOH–BuO ratio, the higher the concentration of by-products such as dimers and

trimers (total yield approximately 10%, selectivity to dimers approximately 7% and to trimers approximately 3%).

The selectivities to the alkoxy alcohols and the yields of these products were calculated after 30 min and the data are shown in Table 6.

The data show that at lower MeOH–BuO ratios, the selectivity to 2-methoxy-1-butanol is slightly higher, however, this slight excess decreases and the selectivity to 1-methoxy-2-butanol starts to increase. At a 14:1 ratio of MeOH–BuO, the selectivity to the two products is virtually the same. This is due to the fact that at lower MeOH–BuO ratios, the formation of the sterically hindered product 2-methoxy-1butanol is more facile than at higher MeOH–BuO ratios.

#### Experimental design

All the results obtained from this kinetic study led us to formulate an experimental design program in which to optimize conditions that would lead to shifting the selectivity to the formation of more 1-methoxy-2-butanol and less 2methoxy-1-butanol. All work done in the experimental design program can be found in the Supplementary material<sup>2</sup> to the publication. After all the data had been accumulated

<sup>&</sup>lt;sup>2</sup> Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5044. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub\_e.shtml.

	1-Methoxy-2-buta	1-Methoxy-2-butanol		2-Methoxy-1-butanol	
MeOH-BuO molar ratio	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	
4:1	41.48	41.48	48.52	48.52	
6:1	42.54	42.54	47.46	47.46	
8:1	43.10	43.1	46.90	46.9	
10:1	44.12	44.12	45.88	45.88	
12:1	43.83	43.83	46.17	46.17	
14:1	44.93	44.93	45.07	45.07	

 Table 6. Selectivity to products at different methanol – butene oxide ratios.

**Note:** T = 100 °C; catalyst concentration = 5 ppm.

**Table 7.** Conversion of butene oxide with  $Al(CF_3SO_3)_3$  in the presence of different alcohols.

Time (min)	Conversio	Conversion (mol%) of butene oxide						
	MeOH	EtOH	n-PrOH	n-BuOH	i-PrOH	<i>i</i> -BuOH	t-BuOH	
5	31.73	20.94	17.00	13.87	11.63	5.63	0.80	
10	47.09	37.5	28.03	21.36	17.36	8.71	0.12	
15	59.00	46.27	38.03	29.47	21.10	9.57	0.03	
20	69.85	53.69	43.81	33.15	25.89	10.58	1.13	
30	80.13	64.77	49.53	39.04	28.45	3.24	0.07	
60	88.50	73.74	60.46	47.12	34.50	15.91	0.46	

and the relevant calculations had been carried out to determine the selectivities to 1-methoxy-2-butanol and 2methoxy-1-butanol, the data were statistically evaluated by fitting response surface models. A response surface model describes the response as a function of the influential variables and yields a regression model. The significance of the regression model is evaluated through an analysis of variance table. This was done for each time interval. As a similar result was obtained for each time interval, only the results obtained for the 5 min interval are discussed here; the rest of the statistical calculations can be found in the Supplementary material<sup>2</sup> to the publication.

The results obtained for the 5 min interval were evaluated to determine the simultaneous effect of the variables on the responses. An overlay plot (a three-point design plot) of the predicted trends from the models in Fig. 2 was used to determine this effect.

Figure 2 depicts the feasible region (white area demarcated by three blue lines) for temperature and catalyst concentration where the 1-methoxy-2-butanol – butene oxide ratio is greater than 0.45, the 2-methoxy-1-butanol – butene oxide ratio is smaller than 0.35, and the mass of butene oxide reacted is greater than 0.18 mol simultaneously. This feasible region is shown for a methanol – butene oxide ratio at its centre value (8:1). It is clear that the criteria are satisfied simultaneously for temperatures between 80 and 85 °C and catalyst concentrations between 3.9 and 5 ppm.

The statistical interpretation of the data indicates that for slightly higher selectivities to 1-methoxy-2-butanol and lower selectivities to 2-methoxy-1-butanol, lower temperatures and catalyst concentrations should be used. This would represent the feasible region as indicated by the overlay plot (T = 80-85 °C, catalyst concentration = 3.9–5 ppm, and MeOH–BuO ratio = 8:1).

#### **Butoxylations of various alcohols**

The results obtained from the methanol butoxylation reac-

Fig. 2. Overlay contour plot presenting a feasible area.



A: Temp

tions led to the expansion of the study to include other alcohols. The conditions identified for methanol were used to carry out reactions with ethanol, *n*-propanol, 2-propanol, *n*-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, to test the activity of  $Al(OCF_3SO_3)_3$  as an epoxide ring-opening catalyst in the presence of these alcohols. A reaction was also carried out with methanol at these reaction conditions, to verify that these were indeed suitable for slightly higher selectivities to 1-methoxy-2-butanol. The reaction conditions chosen were T = 80 °C, catalyst concentration = 4 ppm, and ROH–BuO = 8:1.

The conversion data obtained for the different alcohols are shown in Table 7.

The results show that an increase in the carbon chain length of the alcohol has an influence on the rate of the reaction: the longer the carbon chain, the lower the reaction rate. This was evident when the alcohol was changed from

Table 8. Selectivity to major products with different alcohols.

	α-Alkoxyalcohol	α-Alkoxyalcohol		β-Alkoxyalcohol		
Alcohol	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	$Sel \ \alpha \ : \ Sel \ \beta$	
MeOH	51.17	41.002 52	40.83	32.72	1.3:1	
EtOH	59.90	38.797 23	32.10	20.79	1.9:1	
PrOH	62.27	30.842 33	26.73	13.24	2:1	
n-BuOH	66.21	25.848 38	24.79	9.68	2.7:1	
i-PrOH	59.37	16.890 77	16.63	4.73	3.5:1	
i-BuOH	39.00	1.263 6	0	0	_	
t-BuOH	0	0	0	0	_	

 $C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$  *n*-alcohols. When the sterically more hindered alcohols (2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol) were used, the rate decreased even further, up to the point where negligible reaction was observed when 2-methyl-2-propanol was used.

The selectivities to the alkoxyalcohols were calculated after 30 min of reaction time and are shown in Table 8. The yields of these products were also calculated at this time, as well as the ratio of the selectivity of the  $\alpha$ -alkoxyalcohol to the the selectivity of the  $\beta$ -alkoxyalcohol (ratio Sel  $\alpha$  : Sel  $\beta$ ); these values are also shown in Table 8.

The nature of the alcohol plays a role on the product selectivity, clearly demonstrationg a greater selectivity for the  $\alpha$ -alkoxyalcohol with increasing chain length and (or) steric bulk of the alcohol. No products were formed when using *tert*-butanol.

At these conditions, irrespective of the alcohol used, the reactions favoured the formation of the  $\alpha$ -alkoxyalcohol above that of the  $\beta$ -alkoxyalcohol, in that more of the former and less of the latter were formed. The longer the carbon chain of the alcohol, the slower the rate of formation of the  $\beta$ -alkoxyalcohol. Results showed that even with methanol as the alcohol, 2-methoxy-1-butanol was only detected after 5 min. The ratio of 1-methoxy-2-butanol (the  $\alpha$ -alkoxyalcohol) to 2-methoxy-1-butanol (the  $\beta$ -alkoxyalcohol) was, on average, 1.3. With an increase of one carbon atom in the chain length of the alcohol to ethanol, 2-ethoxy-1-butanol, the  $\beta$ -alkoxyalcohol was only detected after 10 min. The ratio of the two monomeric products (1-ethoxy-2-butanol to 2-ethoxy-1-butanol;  $\alpha$ -alkoxyalcohol to  $\beta$ -alkoxyalcohol) was, on average, 1.9.

It should be noted that the reaction conditions used here were optimized for methanol as the alcohol and are not necessarily the optimum conditions when using the other alcohols. It was therefore decided to further investigate the reaction conditions for reaction with 2-methyl-2-propanol to determine whether any reaction will take place when  $Al(CF_3SO_3)_3$  is used as the catalyst. If any reaction was observed, these conditions would also be used to carry out reactions with 2-propanol and 2-methyl-1-propanol.

The reaction conditions chosen were T = 80, 100, and 120 °C, catalyst concentration = 10 ppm, and *t*-BuOH–BuO = 6:1. The butene oxide conversion data are shown in Table 9. As expected, it was observed that as the temperature was increased, the reaction rate increased. Interestingly, at the higher catalyst concentration of 10 ppm and a lower *t*-BuOH–BO ratio of 6:1, a reaction between *t*-BuOH and BO was observed at 80 °C. Previously, the butoxylation re-

 Table 9. Conversion of BuO with t-BuOH at different temperatures.

	Conversion (mol%) of butene oxide			
Time (min)	80 °C	100 °C	120 °C	
5	9.04	15.10	24.62	
10	13.60	28.05	45.32	
15	17.06	39.62	64.60	
20	22.14	45.17	78.29	
30	30.75	54.43	90.07	
60	44.33	71.72	98.64	
120	65.31	85.48	99.45	

Note:  $Al(CF_3SO_3)_3$  catalyst concentration = 10 ppm; *t*-BuOH–BuO = 6:1.

action attempted at T = 80 °C, *t*-BuOH–BO = 8:1, and a catalyst concentration of 4 ppm showed no activity. Although the possibility of impurities in the feedstock acting as catalyst poisons cannot be ruled out at this stage, it has previously been indicated that higher catalyst concentrations are required with longer chain and bulkier alcohols (13).

The selectivities to the major products, as well as their yields, were calculated after 30 min of reaction time. These results are shown in Table 10.

As the temperature was increased, the selectivity to the major products decreased. The ratio of the  $\alpha$ -alkoxyalcohol to the  $\beta$ -alkoxyalcohol was approximately 2:1 at all three temperatures. This is expected as the sterically hindered alcohol (*t*-BuOH) would prefer to attach to the primary carbon ( $\alpha$ -C) of butene oxide, rather than to the secondary carbon ( $\beta$ -C). This ratio is lower than expected (*n*-BuOH, 8:1) and can be rationalized as follows. The formed  $\beta$ -alkoxyalcohol is a primary alcohol and would react faster with the next molecule of BuO to produce dimers. Experimentally this is verified by large concentrations of the by-products such as dimers and trimers that are formed (yields between 15% and 20%). It can thus be concluded that an increase in the temperature leads to an increase in the conversion of the  $\beta$ -alkoxyalcohol to dimers and trimers.

As reactions with *t*-BuOH are generally known to be difficult because of the steric hinderance of the *tert*-butyl group, and as reaction conditions for the ring opening of butene oxide with *t*-BuOH were identified, it was decided to employ these reaction conditions in reactions with *i*-PrOH and *i*-BuOH, which have previously shown low activity. The influence of the different branched alcohols at the same set of reaction conditions on the rate of conversion of the butoxylation reaction is shown in Table 11.

	1-tert-Butoxy-2-butanol		2-tert-Butoxy-1-butanol	
Temperature (°C)	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)
80	62.20	19.13	26.80	8.24
100	59.50	32.39	27.50	14.97
120	51.00	45.94	29.90	26.93

**Table 10.** Selectivities to products at different temperatures with *t*-BuOH.

Note: Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalyst concentration = 10 ppm; t-BuOH–BuO = 6:1.

Table 11. Conversion of BuO with different branched alcohols.

	Conversion (mol%) of butene oxide			
Time (min)	t-BuOH	<i>i</i> -BuOH	<i>i</i> -PrOH	
5	15.10	33.89	35.67	
10	28.05	53.06	49.96	
15	39.62	70.50	71.80	
20	45.17	77.91	82.47	
30	54.43	86.42	88.02	
60	71.72	95.84	96.53	
120	85.48	99.09	99.65	

Table 12. Selectivity to products with different branched alcohols.

	α-Alkoxyalcohol		β-Alkoxyalcohol	
Alcohol	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)
t-BuOH	45.10	24.56	5.90	14.10
<i>i</i> -BuOH	52.1	45.026	33.90	29.30
i-PrOH	49.10	43.22	34.30	30.19

With *t*-BuOH, which is sterically more hindered than *i*-BuOH and *i*-PrOH, the rate of the butoxylation reaction with *t*-BuOH was slower. It was also observed that the rate with *i*-BuOH (a primary alcohol with branching) was similar to that with *i*-PrOH (a shorter chain secondary alcohol).

The selectivities to the major product and their yields were calculated at 30 min. These results are shown in Table 12.

For each of the three alcohols, the selectivity to the  $\alpha$ alkoxyalcohol (secondary alcohol) is higher than to the  $\beta$ alkoxyalcohol (primary alcohol). This was also previously observed when the chain length of the alcohol was increased. The selectivity with *t*-BuOH was lower than for the other two alcohols, which correlates with the slower reaction rate, as the sterically more hindered alcohol will react slower. The selectivity for *i*-BuOH is higher than for *i*-PrOH, as the former alcohol is a primary alcohol and the latter a secondary alcohol. In all of these reactions, byproducts were formed that are dimers and trimers.

#### Conclusion

The ring-opening reaction of butene oxide with different alcohols (methanol, ethanol, propanol, *n*-butanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol) can easily be achieved in the presence of low concentrations of  $Al(CF_3SO_3)_3$  as the catalyst. For short chain primary alcohols, e.g., methanol, ethanol, propanol, and *n*-butanol, very low catalyst concentrations (<5 ppm) and temperatures

(<80 °C) are required to achieve this ring-opening reaction. For branched alcohols such as 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, either slightly higher catalyst concentrations (approximately 10 ppm) or temperatures (approximately 120 °C) are required because of increased steric bulk and (or) hinderance.

It was also observed that the regioselectivity to the two major products ( $\alpha$ - and  $\beta$ -alkoxyalcohols) can be kinetically manipulated to slightly favour either the one or the other, by changing the reaction conditions. For the reaction with methanol, it was observed that by choosing the correct reaction conditions, i.e., low catalyst concentrations and temperatures, the selectivity is slightly shifted to the  $\alpha$ alkoxyalcohol and vice versa. By using these conditions for the other alcohols, it was observed that the regioselectivity is shifted towards the  $\alpha$ -alkoxyalcohol, except for 2-methyl-2propanol where no reactivity was observed. However, by choosing the correct set of reaction conditions for 2-methyl-2-propanol to obtain activity (catalyst concentration of approximately 10 ppm and an alcohol-BuO molar ratio of 6), it was observed that the  $\alpha$ -alkoxyalcohol is the preferred product. The same result is obtained when using 2-propanol and 2-methyl-1-propanol at the reaction conditions employed for 2-methyl-2-propanol.

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