# Aluminium triflate as catalyst for epoxide ringopening and esterification reactions — Mechanistic aspects<sup>1</sup>

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**Abstract:** Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> is a highly effective catalyst for the ring opening of epoxides with methanol, as well as for the esterification of carboxylic acids with alcohols. Factors that influence the rate of the ring opening of butene oxide with methanol and the esterification of acetic acid with *n*-propanol and ethanol were investigated. It was found that low concentrations (e.g., ~5 ppm) of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalyze the ring-opening reactions, whereas considerably higher concentrations are required for esterification reactions. Molecular modeling studies suggest that these differences can be rationalized in terms of the formation energies of the active intermediates of these reactions.

Key words: epoxide, ring opening, esterification, aluminium triflate.

**Résumé :** Le  $Al(CF_3SO_3)_3$  est un catalyseur très efficace pour effectuer des ouvertures de cycles d'époxydes avec le méthanol ainsi que pour l'estérification d'acides carboxyliques par les alcools. On a étudié les facteurs qui influencent la vitesse d'ouverture de cycle de l'oxyde de butène par le méthanol et d'estérification de l'acide acétique par l'éthanol et le propan-1-ol. On a trouvé que, à de faibles concentrations, environ 5 ppm, le  $Al(CF_3SO_3)_3$  catalyse les réactions d'ouverture de cycle alors que des concentrations beaucoup plus élevées sont nécessaires pour les réactions d'estérification. Des études de modélisation moléculaire suggèrent que ces différences peuvent être rationalisées en fonction des énergies de formation des intermédiaires actifs de ces réactions.

Mots clés : époxyde, ouverture de cycle, estérification, triflate d'aluminium.

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## Introduction

Esterification reactions between alcohols and carboxylic acids and ring-opening reactions of epoxides with alcohols have been successfully carried out for many decades. Traditionally, esterification reactions have been acid-catalyzed using mineral acids, e.g., HCl and  $H_2SO_4$ , as well as organic acids including *p*-toluene sulfonic acid and methane sulfonic acid. Epoxide ring-opening reactions can be either base- or acid-catalyzed (1).

In recent years, the use of triflate salts (also known as trifluoromethane sulfonate salts) as catalysts for both these types of reactions has become increasingly popular. Metal triflates and *N*-heterocyclic base triflates have been employed in the direct esterification of alcohols and carboxylic acids, as well as the transesterification of carboxylic acid esters

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Y.M. Terblans,<sup>2</sup> J.J. Huyser,<sup>3</sup> M. Huyser, M.J. Green, D.A. Young, and M.S. Sibiya. Homogeneous Catalysis and Organic Synthesis, SASOL Technology (Pty) Ltd., Research and Development Division, SASOL, 1 Klasie Havenga Road, Sasolburg, 1947, South Africa. and alcohols. Examples of the use of these catalysts in esterification reactions include the acylation of alcohols by anhydrides, which is catalyzed by a wide range of metal triflates (e.g.,  $Yb(CF_3SO_3)_3$ ,  $Bi(CF_3SO_3)_3$ ,  $In(CF_3SO_3)_3$ ,  $Sc(CF_3SO_3)_3$ ,  $Ce(CF_3SO_3)_3$ ) (2, 3). Rare earth triflates (lanthanide triflates), such as scandium triflate, have been successfully used to catalyze the reaction of alcohols with carboxylic anhydrides, activated esters, mixed anhydrides, acylurea, and N-hydroxysuccinimide at low temperatures. Reactions such as the esterification of aliphatic alcohols with carboxylic acids at room temperature and the direct polycondensation of dicarboxylic acids (succinic acids) with diols (ethylene glycol, 1,3-propanediol, and 1,4-butanediol) at 35-180 °C to synthesize polyalkylene succinates have also been reported (4). Scandium triflate has been used as a catalyst for the condensation of carboxylic acids with soluble polymers such as polyethylene glycol in toluene (5). Gadolinium triflate has been found to be a simple and efficient catalyst for the acetylation of alcohols and amines using acetic anhydride at ambient temperatures (6). Furthermore, the selective preparation of secondary esters from terminal vic-diols has successfully been achieved in a one-pot synthesis via the Yb(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalyzed formation and partial hydrolysis of cyclic orthoesters (7). N-Heterocyclic base triflates (e.g., diphenylammonium triflate (DPAT)) have been found to be excellent catalysts for sterically hindered esterification reactions in specific fluorous media under mild conditions using equimolar amounts of carboxylic acids and

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Scheme 1. Ring opening of butene oxide with methanol.



alcohols (8), as well as for the transesterification of carboxylic acid esters with a slight excess of alcohols via the use of trimethylsilyl chloride (TMSCl) as a co-catalyst (9). Other organic base triflates that have successfully been employed in esterification reactions include 4-(benzylamino-carbonyl)diphenylammonium triflate (BDPAT) (10) and polymer-supported 4-aminoforoyldiphenylammonium triflate (PS-AFDPAT) (11).

IR thermography has been used to screen the catalytic acitivity of rare earth triflates (e.g., Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, La(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, Lu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, Nd(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, Sm(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, Sc(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, Y(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, and Ce(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>) for the ring opening of epoxides by alcohols as well as the Baeyer–Villiger oxidation of cyclobutanones with hydrogen peroxide. In the case of the ring opening of epoxides, scandium triflate was found to be an exceptionally active catalyst, whereas in the case of the Baeyer–Villiger oxidation, it was again the most active, followed by neodymium triflate (12). Furthermore, it has been reported that Yb(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalyzes intermolecular ring-opening reactions of epoxides with alcohols to give  $\beta$ -alkoxy alcohols in good to high yields with high regio- and stereoselectivity (13).

Aluminium triflate has been used as a catalyst in organic synthesis for reactions such as the ring opening of epoxides in the presence of alcohols or amines (14–16), Friedel–Crafts acylation and alkylation (17, 18), the epoxidation of olefins with iodosylbenzene (19), and the preparation of esters and lactones (20). It has also been used as an initiator for cationic polymerization (21) and as co-catalyst in the polymerization of olefins (22).

We now report on the considerable difference in the required concentration of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> vs. KOCH<sub>3</sub> as catalysts for the ring opening of butene oxide (BuO) with methanol (MeOH) (Scheme 1) on the one hand, and the similar concentration requirements of Al( $CF_3SO_3$ )<sub>3</sub> and p-TSA as catalysts for the esterification of *n*-propanol (*n*-PrOH) or ethanol (EtOH) with acetic acid (Scheme 2) on the other hand. Low  $Al(CF_3SO_3)_3$  concentrations (e.g., ~5 ppm) are sufficient to obtain excellent conversions and high reaction rates when performing the ring-opening reaction of butene oxide with methanol, whereas much higher catalyst concentrations (e.g., ~1000 ppm or higher) are needed to obtain similar results for the KOCH<sub>3</sub> catalysed reactions. A related observation was that both acid (p-TSA) and  $Al(CF_3SO_3)_3$  catalysed esterification reactions of propanol and (or) ethanol with acetic acid require similar catalyst concentrations of ~1000 ppm to get reasonable activities. A molecular modeling study was undertaken with a view to rationalizing the experimental observations and to postulate a reasonable explanation for the low levels of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> needed in the ring-opening reactions. These calculations showed that  $\Delta H_{\rm f}$ values for the formation of the catalytically active species in the potassium methoxide and aluminium triflate catalyzed ring-opening reactions differ significantly, with  $\Delta H_{\rm f}$  = -3.3 kcal/mol (1 cal = 4.184 J) for the aluminium triflate re-

**Scheme 2.** Esterification of acetic acid with ethanol or *n*-propanol.



 $ROH = CH_3CH_2OH$  or  $CH_3CH_2CH_2OH$ 

action and  $\Delta H_{\rm f}$  = +12.8 kcal/mol for the potassium methoxide ring-opening reaction. It appears that the differences in catalyst concentrations required for the reactions under investigation are in line with the differences in the formation energies of the active intermediate.

### Experimental

### Materials

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 (16). For the ring-opening reactions, a stock solution of 500 ppm  $Al(CF_3SO_3)_3$  was prepared in methanol and the desired quantity thereof was weighed for every reaction. In the case of the esterification reactions, a fresh catalyst solution (of the desired concentration) was prepared in the alcohol substrate prior to each reaction.

### **Kinetic reactions**

Kinetic reactions were carried out in a Parr autoclave. The catalyst concentration was varied between 0 and 10 ppm for the ring-opening reactions and between 10 and 5000 ppm for the esterification reactions. In most cases, the esterification reactions were allowed to proceed to equilibrium, since none of the reaction products (including water) were removed. Gas chromatography was performed on a Shimadzu GC-17A, equipped with a flame ionization detector and a PONA capillary column (50 m  $\times$  0.21 mm  $\times$  0.5 µm). Each sample was weighed into a GC vial and heptane was used as an internal standard.

# Typical experimental procedure for the ring opening of butene oxide

Methanol (192.25 g, 6.00 mol) and butene oxide (72.11 g, 1.00 mol) were combined in a 300 mL Parr reactor. On closing, the reactor was degassed and flushed with nitrogen to remove all the air present. This flushing procedure was repeated three times.

A catalyst bomb was placed under vacuum prior to the run. The stock solution was weighed out (2.644 g, 5 ppm) and transferred via a syringe to this bomb, which was then connected to the inlet of the autoclave. A high-pressure nitrogen line was connected to the opposite side of the catalyst

bomb after which stirring of 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 amount 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 weighed. A satd. NaOH – water solution (0.5 mL) was added to all of the samples to quench the catalyst.

# Typical experimental procedure for the esterification reaction between n-propanol and acetic acid

Acetic acid (60.10 g, 1.00 mol) and propanol (60.21 g, 1.00 mol) were combined in a 300 mL Parr reactor. The reactor was closed and heated to an operating temperature of 100 °C while stirring at 900 rpm. Upon reaching this temperature, a solution of  $Al(CF_3SO_3)_3$  (0.05 g dissolved in 10.0 g of propanol, 5000 ppm) was charged into the reactor using a syringe. A sample was taken immediately and thereafter every 5 min for the first 30 min, after which samples were taken every 30 min. All samples were weighed.

#### Molecular modeling

All geometries were optimized with the DMol<sup>3</sup> DFT code in MaterialsStudio 3.0 (Accelrys, Inc.) (23) by applying the all electron nonlocal GGA/RPBE/DNP method, employing a med integration grid and 4.2 Å orbital cut-off values. All reported energies are electronic energies, which correspond to *G* at 0 K.

## **Results and discussion**

The epoxide ring-opening and esterification reactions were probed experimentally, as well as via molecular modeling. The ring-opening reaction of butene oxide with methanol was studied at different catalyst concentrations, temperatures, and methanol – butene oxide molar ratios. For comparison, the epoxide ring opening was also carried out with a base catalyst KOMe. The esterification reaction of acetic acid with *n*-propanol and ethanol was studied at different catalyst concentrations, whereas the influence of substrate concentrations was studied by varying the ethanol – acetic acid molar ratio.

A molecular modeling study was carried out to assist in formulating a reasonable explanation for the low levels of  $Al(CF_3SO_3)_3$  needed to catalyse the ring-opening reactions compared to using KOCH<sub>3</sub> as catalyst. In addition, calculations were carried out for the  $Al(CF_3SO_3)_3$  and Brønsted acid catalysed esterification reactions.

Model substrates were used for the calculations to save on computational time. Propylene oxide and methanol were used as models for the ring-opening reactions and acetic acid and methanol for the esterification reactions. In the calculations involving  $Al(CF_3SO_3)_3$ , possible stabilization effects involving, for example, methanol coordination or other solvation effects were not taken into consideration. KOCH<sub>3</sub> was used as the model for the base-catalysed epoxide ring-

**Table 1.** Conversion of butene oxide (mol%) at different  $Al(CF_3SO_3)_3$  catalyst concentrations.

	Catalyst concentration (ppm)			
Time (min)	0	1	5	10
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

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

**Table 2.** Conversion of butene oxide (mol%) at different temper-atures.

Time (min)	Temperature (°C)				
	60	80	100	120	
5	16.05	16.68	59.18	88.80	
10	36.43	54.31	94.39	100.00	
15	53.47	79.95	99.55	100.00	
20	69.64	81.95	100.00	100.00	
30	74.33	89.17	100.00	100.00	
60	88.50	93.32	100.00	100.00	
120	95.86	97.15	100.00	100.00	

**Note:** Al( $CF_3SO_3$ )<sub>3</sub> catalyst concentration = 5 ppm, MeOH:BuO = 6:1.

opening reactions and a protonated AcOH–MeOAc complex used to describe the acid-catalysed esterification reaction.

The limited objective of these simplified modelling studies was to calculate formation energies from geometry optimizations with a view to rationalizing the experimental results rather than the more time consuming location of transition states to obtain activation energies.

#### Ring opening of butene oxide

The conversion of butene oxide was calculated for each reaction carried out with  $Al(CF_3SO_3)_3$  and KOH as the catalyst and the data are presented in Tables 1–4. Graphs obtained from the data are shown in the Supplementary material to the publication.<sup>4</sup>

In the molecular modelling study, two steps in the catalytic cycle of the ring-opening reaction with  $Al(CF_3SO_3)_3$  and KOCH<sub>3</sub> were considered, i.e., the ring-opening step, as well as the regeneration of the active intermediate; these steps are shown in Schemes 3 and 4.

As can be seen from the data in Table 1, butene oxide was converted to the corresponding glycol ethers with  $Al(CF_3SO_3)_3$  concentrations of 10 ppm or less. When using 10 ppm of  $Al(CF_3SO_3)_3$ , 100% conversion was achieved within 10 min of reaction time. With a very low  $Al(CF_3SO_3)_3$  concentration of 1 ppm, 88% conversion was achieved within 2 h. In all of these reactions, both isomers of the glycol ether, i.e., 1-methoxy-2-butanol and 2methoxy-1-butanol, were formed as the main products.

<sup>&</sup>lt;sup>4</sup> Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3692. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub\_e.shtml.

	Methanol – butene oxide ratio						
Time (min)	4	6	8	10	12	14	
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	
20	100.00	100.00	100.00	100.00	100.00	100.00	
30	100.00	100.00	100.00	100.00	100.00	100.00	
60	100.00	100.00	100.00	100.00	100.00	100.00	
120	100.00	100.00	100.00	100.00	100.00	100.00	

**Table 3.** Conversion of butene oxide (mol%) at different methanol – butene oxide ratios with  $Al(CF_3SO_3)_3$ .

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

**Table 4.** Conversion of butene oxide (mol%) at different methanol – butene oxide ratios with KOH.

	Methanol – butene oxide ratio		
Time (min)	4	6	
5	70.01	50.72	
10	89.65	71.65	
15	98.48	85.12	
20	99.42	88.83	
30	99.70	92.28	
60	99.96	96.89	

Note: T = 160 °C, catalyst concentration = 100 ppm.

These products were formed in a ratio of approximately 1:1, with the yield of each ranging from 40%–47%. By-products like dimers, diols, and in some instances trimers were also formed during these reactions. All products were identified using GC–MS via comparison with the literature data (16).

The effect of temperature on the ring-opening reaction of butene oxide was as expected, in that the reaction rates and conversions increased as the temperature was increased (Table 2). It was found that as the reaction temperature was increased, the formation of by-products, especially dimers and trimers, increased over time.

It is seen from the data in Table 3 that as the ratio of MeOH:BuO was increased, the rate of the reaction decreased. As the ratio was increased from 4 to 6, a decrease in the rate was clearly observed. The decrease in the rate became less as the ratio was further increased to 8. With even further increases from 8 to 14, the decrease in the rate became even less. Similarly, when KOH was used as the catalyst, it was seen that as the ratio of MeOH:BuO was increased, the rate of the reaction decreased. However, these reactions had to be carried out with higher catalyst concentrations (100 ppm KOH compared to 10 ppm Al( $CF_3SO_3$ )<sub>3</sub>) and at higher reaction temperatures (160 °C for KOH compared to 100 °C for Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>). An explanation for this decrease in rate with an increase in MeOH:BuO ratio could be that the transfer of the  $Al(CF_3SO_3)_3$  to BuO to form the active intermediate is dependant on the concentration of BuO in the reaction mixture. Since the increase in the MeOH:BuO ratio will lead to a lowering in BuO concentration, it is to be expected that a drop in rate will be seen (Scheme 3).

The mechanism of the ring-opening reaction involves the coordination of the epoxide oxygen to the aluminum, thus forming the active intermediate, a strained three-membered epoxide ring. This is seen when geometry optimized structures of a "free" epoxide are compared with those of an epoxide coordinated to the aluminum. A C—O bond lengthening from 1.44 to 1.477 Å (O—C<sub> $\alpha$ </sub>) and 1.507 Å (O—C<sub> $\beta$ </sub>) is observed when Al is coordinated. Nucleophilic attack by methanol can then take place on either the C<sub> $\alpha$ </sub> or C<sub> $\beta$ </sub> position. Electronic factors will favor the C<sub> $\beta$ </sub> position (the O—C<sub> $\beta$ </sub> is longer than the O—C<sub> $\alpha$ </sub> bond) while steric factors will favor the C<sub> $\alpha$ </sub> position (less substituted). In the case of methanol as the nucleophile, these two factors contribute equally, as is evident by the product distribution of approximately 1:1 (Scheme 5).

As can be expected, the formation energies for the ringopening reactions are highly exothermic because of the release of the strained three-membered epoxide ring. In line with the Hammond postulate, it would be reasonable to assume that the activation energies for the ring-opening reactions would be low (the transition state for the ring-opening reactions should be very early and resemble the reagents because of the highly exothermic reaction). The interesting aspect about the base-catalysed ring-opening reaction is the high stability of the potassium salt of the product. The significance of this is that the regeneration of the active intermediate, KOCH<sub>3</sub>, represents a highly endothermic reaction. This will explain the high levels of KOCH<sub>3</sub> necessary to obtain a reasonable rate. The ring-opening reaction itself will be facile and the rate-determining step will be the regeneration of the KOCH<sub>3</sub> species to start the catalytic cycle again (Scheme 4). The  $Al(CF_3SO_3)_3$  catalysed reaction, on the other hand, does not have such a thermodynamic sink with the regeneration of the activated epoxide ring coordinated to the Al( $CF_3SO_3$ )<sub>3</sub> being only a slightly exothermic reaction (Scheme 3). Together with the low activation energy for the ring-opening reaction, this will explain the low levels of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> necessary to obtain very high rates. A reasonable explanation would then be that the difference in catalyst concentration needed for the ring-opening reaction is due to the highly endothermic and (or) unfavourable reaction for the regeneration of the KOCH<sub>3</sub> species compared to the facile reaction for the  $Al(CF_3SO_3)_3$ .

### **Esterification reaction**

The conversion of acetic acid at different acid catalyst concentrations with n-propanol is shown in Table 5 and for ethanol in Table 6. The results for the variation of the acetic acid – ethanol molar ratio are shown in Table 7. Graphs ob-

Scheme 3. Formation energies for the  $Al(CF_3SO_3)_3$  catalysed ring-opening reaction (1 cal = 4.184 J).



AI(OCF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>

H

Scheme 4. Formation energies for the KOCH<sub>3</sub> catalysed ring-opening reaction (1 cal = 4.184 J).



 $\Delta H_{\rm f}$  = -36.8 kcal/mol



 $\Delta H_{\rm f}$  = 12.8 kcal/mol

Scheme 5. Reaction mechanism for butene oxide ring opening.



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Scheme 6. Formation energies for the acid-catalysed esterification reaction (1 cal = 4.184 J).



$$\Delta H_{\rm f}$$
 = -8.8 kcal/mo



 $\Delta H_{\rm f}$  = -1.8 kcal/mol

**Table 5.** Conversion of acetic acid (mol%) at different  $Al(CF_3SO_3)_3$  catalyst concentrations with *n*-propanol.

	Catalyst concentration (ppm)				
Time (min)	5000	500	100	10	
10	50.73	26.73	19.17	7.38	
20	57.90	35.27	22.50	8.94	
30	60.78	41.18	29.79	12.12	
60	66.04			_	
90		55.94	41.82	25.84	
150	66.20	60.53	51.41	33.59	
210	66.6	61.21	56.92	38.64	

Note: T = 100 °C, *n*-PrOH : acetic acid = 1:1.

**Table 6.** Conversion of acetic acid (mol%) at different  $Al(CF_3SO_3)_3$  catalyst concentrations with ethanol.

	Catalyst con		
Time (min)	500	100	10
30	15.72	10.75	8.72
60	30.07	20.76	19.89
120	43.37	35.44	22.69
180	53.03	48.36	26.24

Note: T = 100 °C, EtOH : acetic acid = 1:1.

tained from the data are shown in the Supplementary material<sup>4</sup> to the publication.

In the molecular modelling study, two steps in the catalytic cycle of the esterification reaction with  $Al(CF_3SO_3)_3$  and an acid were considered, i.e., the esterification step as well as the regeneration of the active intermediate; these steps are shown in Schemes 6 and 7.

As esterification reactions are equilibrium reactions and are known to proceed very slowly in the absence of an acid catalyst (1), the addition of small quantities of the catalyst will ensure that they reach equilibrium much faster. This can clearly be seen upon comparing the data for the esterification reaction in Tables 5 and 6. It is evident that equilibrium (equilibrium conversion  $\cong 66\%$ ) is reached after 1 h,

**Table 7.** Conversion of acetic acid (mol%) with  $Al(CF_3SO_3)_3$  catalyst at different ethanol – acetic acid ratios.<sup>*a*</sup>

	Ethanol – acetic acid ratio			
Time (min)	1	4	8	
5	10.02	28.47	47.82	
10	15.10	34.28	57.21	
15	20.22	50.65	63.04	
20	25.43	55.72	71.54	
25	30.05	59.94	77.67	
30	32.97	64.99	84.41	
60	40.07	79.65	93.20	
90	45.10	85.43	97.80	
120	46.21	87.46	98.68	
150	49.80	90.46	98.63	

Note: T = 100 °C, catalyst concentration = 5000 ppm.

"These reactions were run to completion, hence the yields of ethyl acetate were  ${\cong}98\%.$ 

when using 5000 ppm of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> for the esterification reaction of acetic acid and *n*-propanol. However, equilibrium is not reached for this reaction even after 210 min when using 10 ppm of the catalyst. Similar results were observed for the esterification reaction of acetic acid and ethanol when 10 ppm of catalyst is used, as equilibrium is not reached after 180 min. The main products that were formed in the esterification reactions are the corresponding esters: *n*propyl acetate in the case of *n*-propanol and ethyl acetate in the case of ethanol. The equilibrium yields of the main products  $\cong$ 64%. Some by-products were also formed in low yields; these were identified as ethers (e.g., diethyl ether or dipropyl ether) via GC–MS.

In the esterification reaction, electron density is donated from the carbonyl oxygen atom of the carboxylic acid by coordinating to the aluminum, thus forming the active intermediate. Geometry optimized structures of the free acetic acid compared to one coordinated to aluminum show the C=O bond lengthening from 1.208 to 1.245 Å. Nucleophilic attack by the methanol then takes place on the carbonyl carbon of the carboxylic acid (Scheme 8). Scheme 7. Formation energies for the  $Al(CF_3SO_3)_3$  catalysed esterification reaction (1 cal = 4.184 J).



$$\Delta H_{\rm f}$$
 = -4.2 kcal/mol



 $\Delta H_{\rm f}$  = -2.8 kcal/mol

Scheme 8. Reaction mechanism for esterification.



Formation energies for the esterification reactions are, however, only slightly endothermic. In line with the Hammond postulate, it would thus be reasonable to assume the activation energies for the esterification reactions to be higher than those for the ring-opening reactions ( $\Delta H_{\rm f} =$ -4.2 kcal/mol for the esterification compared to  $\Delta H_{\rm f} =$ -27.3 kcal/mol for the ring-opening reaction).

Unlike the epoxide ring-opening reaction, the esterification reaction does not show any discrepancy between the  $Al(CF_3SO_3)_3$  and the acid-catalysed reactions. Similar formation energies are observed for both reactions and thus similar catalyst concentrations should give similar reaction rates; this was in fact the case.<sup>5</sup> The only difference will be the slight variation in the energy of the transition state for the  $Al(CF_3SO_3)_3$  and acid-catalysed reaction.

## Conclusion

The ring-opening reaction of butene oxide with methanol is easily achieved at low concentrations (10 ppm or less) of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> as the catalyst. When using 10 ppm of Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 100% conversion of butene oxide is achieved within 10 min. This is, however, not the case for the KOCH<sub>3</sub> catalysed ring-opening reaction, which requires at least a 1000 ppm catalyst concentration to achieve a reasonable rate. A plausible explanation is the energy difference in the regeneration of the active intermediate that is unfavourable for the KOCH<sub>3</sub> catalysed reaction, implying the necessity of higher catalyst loading to get similar rates. Esterification of acetic acid with *n*-propanol and (or) ethanol gave similar energies for both acid and Al(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> catalysed reactions,

<sup>&</sup>lt;sup>5</sup>On comparing the conversion of acetic acid using  $Al(CF_3SO_3)_3$  and a conventional acid catalyst in the esterification of 1-methoxy-2propanol with acetic acid, it was seen that the reaction rate with  $Al(CF_3SO_3)_3$  was only slightly faster than that with the acid catalyst when the same catalyst concentration was used.

thus explaining the need for similar catalyst loadings to give similar rates

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