Bruce M. Bell[1]
John R. Briggs[1]
Robert M. Campbell[1]
Susanne M. Chambers[1]
Phil D. Gaarenstroom[1]
Jeffrey G. Hippler[1]
Bruce D. Hook[1]
Kenneth Kearns[1]
John M. Kenney[1]
William J. Kruper[1]
D. James Schreck[1]
Curt N. Theriault[1]
Charles P. Wolfe[1]

[1]The Dow Chemical Company, Midland, MI, USA.

Research Article

Glycerin as a Renewable Feedstock for Epichlorohydrin Production. The GTE Process

A significant improvement in a process to produce epichlorohydrin through the use of glycerin as renewable feedstock is presented. The glycerin to epichlorohydrin (GTE) process proceeds in two chemical steps. In the first step, glycerin is hydrochlorinated with hydrogen chloride gas at elevated temperature and pressure to a mixture of 1,3-DCH (1,3-dichlorohydrin, 1,3-dichloropropan-2-ol) and 2,3-DCH (2,3-dichlorohydrin, 2,3-dichloropropan-1-ol), using a carboxylic acid catalyst. In the second step, the mixture of dichlorohydrins is converted to epichlorohydrin with a base. This solventless process represents an economically and environmentally advantageous, atom-efficient process to an existing commodity chemical that can employ a renewable resource for its primary feedstock.

Keywords: Glycerin; Renewable; Feedstock; Green Chmistry; Epichlorohydrin Production

Received: March 12, 2008; *revised:* April 8, 2008; *accepted:* April 9, 2008

DOI: 10.1002/clen.200800067

1 Introduction

Epichlorohydrin is a high volume commodity chemical used largely in epoxy resins, although smaller quantities have, until recently, been employed for the manufacture of synthetic glycerin [1]. Although several routes are known for epichlorohydrin manufacture, most is made from propylene and chlorine as primary raw materials in a multi-step process. Shown in Fig. 1, this requires the allylic chlorination of propylene to allyl chloride followed by hypochlorination to give a 3:1 mixture of 1,3-DCH and 2,3-DCH, which is then treated with base to yield epichlorohydrin [1]. Although practiced on a very large scale, this process suffers from some undesirable features, particularly the low chlorine atom efficiency. Only one of the four chlorine atoms employed in the manufacture of epichlorohydrin by this route is retained in the product molecule, the remainder emerging as by-product hydrogen chloride or waste chloride anion. Additionally, inefficiencies in the chlorination and hypochlorination steps lead to the formation of unwanted chlorinated organics that are expensive to dispose of. Such factors have prompted the search for alternative routes to epichlorohydrin that are more atom-efficient and environment-friendly. The escalating cost of petrochemical raw materials such as propylene has also contributed to the accelerated search for processes that employ less expensive raw materials.

One such route that has been recently examined by us [2] and others [3, 4] is based on the conversion of glycerin through dichlorohydrins to epichlorohydrin. This two-step process, shown in Fig. 2, appears significantly simpler than the incumbent process, but the historically high cost of glycerin has prevented its development as a commercial process. Recently, however, glycerin has become increasingly available as a by-product of the manufacture of biodiesel, particularly in Europe. As a result, the available volume of renewable glycerin has risen, and the price has declined to a point where its use in the manufacture of commodity chemicals, such as epichlorohydrin, has become feasible. Several companies have announced plans to commercialize technology to manufacture epichlorohydrin from glycerin (Dow Chemical, *C&E News*, August 14, 2006, p. 3, Solvay www.solvaypress.com/pressreleases/0,52477-2-0,00.htm, Spolchemie www.spolchemie.cz/dwn/factsheet12.pdf). Epichlorohydrin is but one of several new opportunities that have been recognized as a viable use of increasingly plentiful, low cost glycerin [5], and exemplifies a more general trend of an expanding use of natural polyols for the manufacture of commodity chemicals [6].

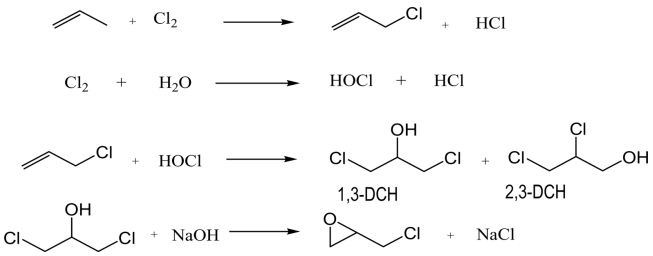

Figure 1. The dominant commercial route to epichlorohydrin is a multi-step process comprising the initial allylic chlorination of propylene to allyl chloride. This is then reacted with hypochlorous acid, made by dissolving chlorine in water, to yield a 3:1 mixture of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol in dilute aqueous solution. This mixture is reacted with base to give epichlorohydrin. Of the four equivalents of chlorine atoms employed, only one is retained in the desired product, the remaining three equivalents appearing as by-product HCl or waste chloride ion.

Correspondence: Dr. J. R. Briggs, The Dow Chemical Company, Michigan Operations, Bld 1776, C33.3, Midland, MI 48674, USA.
E-mail: briggsjr@dow.com

Abbreviations: GC, gas chromatography; **GTE**, glycerin to epichlorohydrin; **1-MCH**, 1-monochlorohydrin; **2-MCH**, 2-monochlorohydrin

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

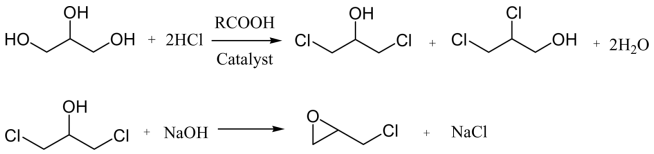

Figure 2. A route to epichlorohydrin that employs renewable glycerin as feedstock is a two-step process comprising initial hydrochlorination of glycerin with hydrogen chloride to give a 30 – 50:1 mixture of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol, followed by reaction with base. This process produces only one equivalent of waste chloride.

The carboxylic acid catalyzed hydrochlorination of glycerin to dichlorohydrins has been known for over a century [7], and the mechanism of the reaction was delineated some 50 years ago [8]. An extensive summary of the early literature up to 1930s can be found in a series of papers by Gibson [9]. In this paper, we will describe elements of the glycerin hydrochlorination step of the glycerin to epichlorohydrin (GTE) process, a technology that represents an economically and environmentally advantageous route to epichlorohydrin from a renewable carbon resource.

2 Experimental

Experiments were performed in a 100 mL, Hastalloy C(Parr autoclave equipped with a Magnedrive stirrer, a thermocouple, and internal cooling coils. Glycerol (Aldrich 99%, or Interwest Corporation) was added to the reactor, followed by carboxylic acid and water, and the reactor sealed. The mass of the reactor and contents were recorded. The reactor was stirred and water at ambient temperature cycled through the cooling coils. Hydrogen chloride gas (Airgas Corporation) at the desired pressure was admitted to the reactor, resulting in a 15 – 25°C exotherm. The reactor was heated to the desired temperature, and the reaction then allowed to proceed for the desired length of time, while hydrogen chloride gas was fed continuously at the set pressure as it was consumed by reaction. The mass of hydrogen chloride fed to the reactor was determined by the change in the mass of the cylinder throughout the reaction, or in some cases using a calibrated mass-flow controller. In some instances, samples were withdrawn from the reactor through a bottom valve for analysis. After the desired reaction time had elapsed, the hydrogen chloride feed was ceased, and the reactor and contents cooled to room temperature. The reactor was then vented and the mass of the reactor and contents were recorded.

All other chemicals used were of the highest purity commercially available and were used without purification.

Samples and standards were analyzed by gas chromatography (GC). Products for which no GC standard sample was available were identified by GC/mass spectrometry. The sample and standards were analyzed using an Agilent 6890 GC system with the following conditions:

Column:	DB-5. 30 m × 0.25 mm × 1.0 μm film, S/N: 9118515
Injection:	Split
Injection Volume:	0.2 μL
Detection:	FID
Carrier Gas:	He
Carrier Pressure:	24 psi
Split:	125 mL/min
Hydrogen:	30 mL/min
Air:	350 mL/min
Makeup:	25 mL/min
Injector Temperature:	200°C
Detector Temperature:	300°C

Temperature Program:

Initial Temperature:	40°C for 6 min
Ramp Rate:	10°C/min
Final Temperature:	180°C for 0 min
Ramp Rate A:	30°C/min
Final Temperature A:	300°C for 1 min

Response factors were calculated using the following equation:

$$\mathrm{RF} = \frac{(\text{Analyte Weight})/(\text{Analyte Area})}{(\text{Internal Standard Weight})/(\text{Internal Standard Area})} \times \text{Purity} \quad (1)$$

$$\text{wt\% concentration} = \mathrm{RF} \times \text{Area} \times \frac{\text{ISTD weight}}{\text{ISTD Area}} \times \frac{1}{\text{Sample Weight}} \times 100\% \quad (2)$$

The retention times of the major components (in minutes) are: 1,3-DCH (13.7); TCP (14.2); 2,3-DCH (14.6); 1-monochlorohydrin (1-MCH) (14.8); 2-monochlorohydrin (2-MCH) (15.5); glycerin (15.6 – 16.2).

3 Results and Discussion

Treating glycerin containing 2 wt % of a carboxylic acid catalyst with hydrogen chloride at slightly above atmospheric pressure (20 psi) and 120°C in a sealed vessel results in its conversion initially to mainly 1-MCH (1-MCH, 1-chloropropane-2,3-diol). Much smaller amounts of 2-MCH (2-MCH, 2-chloropropane-1,3-diol) are formed. In a much slower, low conversion reaction, the 1-MCH is converted mainly to 1,3-DCH with much smaller amounts of 2,3-DCH. The evolution of the major products in such a reaction is shown in the first plot in Fig. 3. The low conversion to DCHs obtained in a glycerin hydrochlorination process operated at atmospheric pressure appears to have resulted in a number of approaches to improve this process. Efforts adopted in the literature have included sparging hydrogen chloride gas through the reaction solution where upon water is also removed from the solution [10], employing an azeotroping agent to facilitate water removal [11], and employing multiple reaction stages with interstage water removal [4]. Sparging hydrogen chloride gas through the reaction solution, or the use of an azeotrope to remove water from the reaction medium is expensive and therefore less desirable on a commercial scale. In the first case, large excesses of hydrogen chloride gas are employed, and the hydrogen chloride that is recovered is contaminated with water and must be separated for reuse in the process, disposed of, or used for lower value applications. The use of an azeotroping agent to remove water results in a much more complex process in which the solvent must be separated from the water and hydrogen chloride and recovered for reuse. The use of multiple reaction stages results in increased equipment costs and process complexity.

Because the prior literature suggested that the glycerin hydrochlorination reaction exhibited an equilibrium limitation, we were led to explore the effect of higher hydrogen chloride concentration on the reaction conversion, rate, and selectivity. This was achieved

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

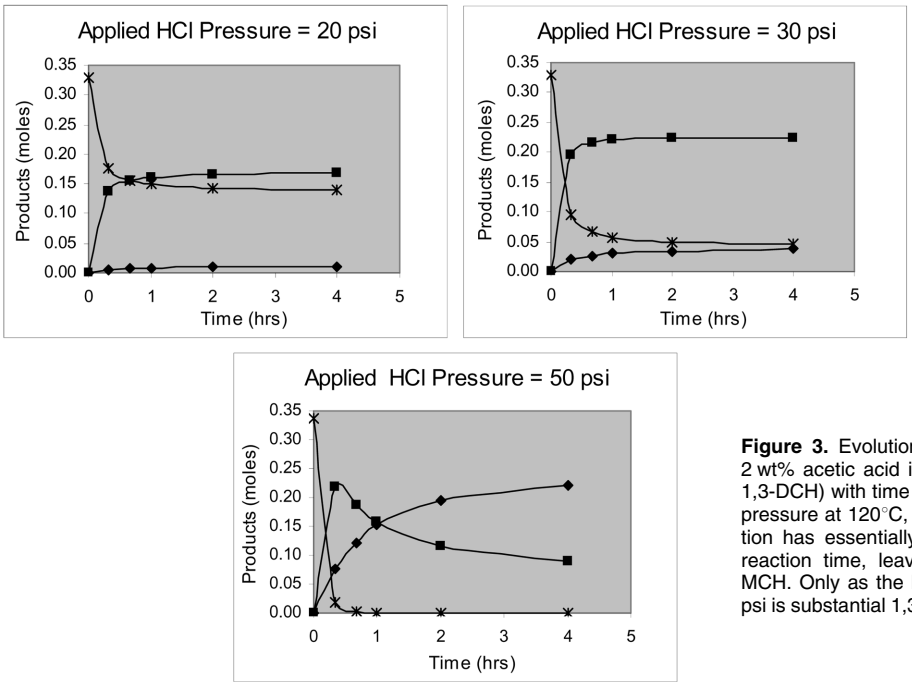

Figure 3. Evolution of major reaction products in a solution of 2 wt% acetic acid in glycerin (–*– Glycerin, –■– 1-MCH, –◆– 1,3-DCH) with time and as a function of applied hydrogen chloride pressure at 120°C, showing that at the lower pressures, the reaction has essentially achieved equilibrium by the end of the 4 h reaction time, leaving substantial unconverted glycerin and 1-MCH. Only as the hydrogen chloride pressure is increased to 50 psi is substantial 1,3-DCH produced.

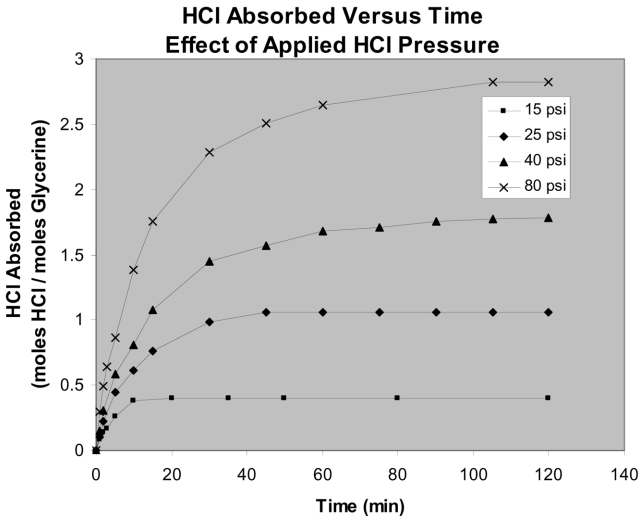

Figure 4. Plots of hydrogen chloride gas absorbed by a mixture of 85 wt % glycerin, 9 wt % water, and 7 wt % acetic acid at 90°C at different applied constant hydrogen chloride pressures show faster and greater uptake at higher pressure, suggesting an equilibrium limitation on the hydrochlorination reaction.

experimentally by employing higher applied pressures of hydrogen chloride gas. We expected that this would both speed up the hydrochlorination, and drive the reaction to higher conversion to the desired dichlorohydrins while minimizing the stoichiometric excess of hydrogen chloride required to achieve the desired, high conversion. Figure 4 shows the effect of hydrogen chloride pressure on the rate of hydrogen chloride uptake by a glycerin solution containing 2 wt % of acetic acid as catalyst.

Two features of the plots in Fig. 4 are striking. After a very rapid, initial consumption of hydrogen chloride by each reaction mixture, which we attribute to dissolution of hydrogen chloride in the glycerin, the rate of consumption of hydrogen chloride by the reaction increases with the applied pressure of hydrogen chloride. At each pressure, the rate of consumption of hydrogen chloride is initially fast but slows and largely ceases after a certain time. Thereafter, little or no additional hydrogen chloride is consumed by the reaction solutions even at extended reaction times. The total amount of hydrogen chloride taken up by the solutions also increases as the applied pressure increases. This behavior appears consistent with an equilibrium limited reaction that is driven to higher conversion at higher pressure.

Figure 3 shows the evolution of the major components of three reactions run at different applied hydrogen chloride pressures determined by gas chromatographic analysis of samples taken during the reactions. At P(HCl) = 20 psi, the initial consumption of glycerin and the formation of 1-MCH is rapid, but the reaction slows dramatically, and the formation of 1,3-DCH is limited. As the pressure is increased to 30 and 50 psi, it can be seen that the conversion of 1-MCH to 1,3-DCH becomes more significant. These plots confirm that the reaction is equilibrium limited at low pressure, and that this limitation can be largely overcome by increasing the applied hydrogen chloride pressure.

At even higher pressures, the reaction is fast and the formation of dichlorohydrins becomes very efficient. At 110 psi and 110°C, the hydrochlorination of wet glycerin (9 wt % water) in the presence of 5 mol% of acetic acid as catalyst is both rapid and efficient, so that after 4 h in a sealed vessel to which hydrogen chloride gas is fed on demand, the reaction product mixture comprises 93 mol% of dichlorohydrins and their acetate esters, in a ratio of 46:1 of 1,3-DCH to 2,3-DCH, and 6 mol% monochlorohydrins and their esters in a ratio of 1:2 of 1-MCH to 2-MCH. 2-MCH attains a higher concentration than 1-MCH at high conversions because, although it is formed more slowly than 1-MCH, it is also hydrochlorinated much more slowly than 1-MCH.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

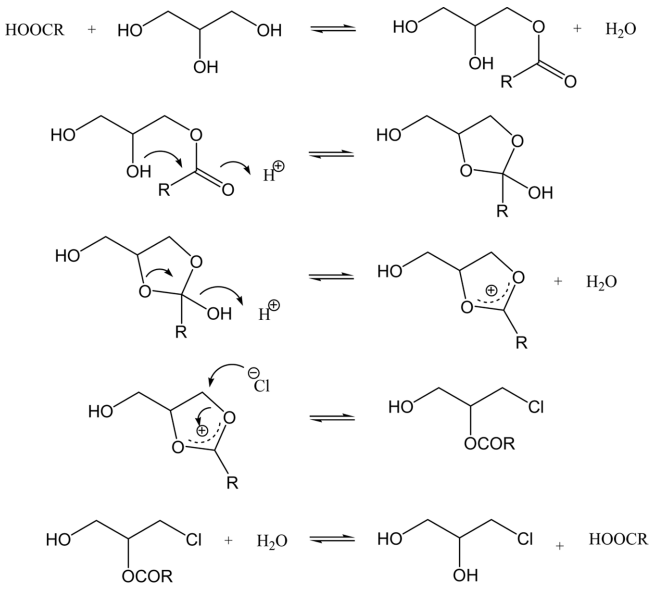

Figure 5. The mechanism of the carboxylic acid catalyzed hydrochlorination of glycerin to mono and dichlorohydrins, as presented in ref. [7]. Initial esterification preceeds ring-closure and loss of water to form an acetoxonium cation. Ring-opening of the acetoxonium cation by a chloride generates 1-MCH. Repetition of the process at the remaining two hydroxyl groups gives the desired 1,3-DCH product. This mechanism precludes the formation of 1,2,3-trichloropropane since two hydroxyls are required to form the acetoxonium cation.

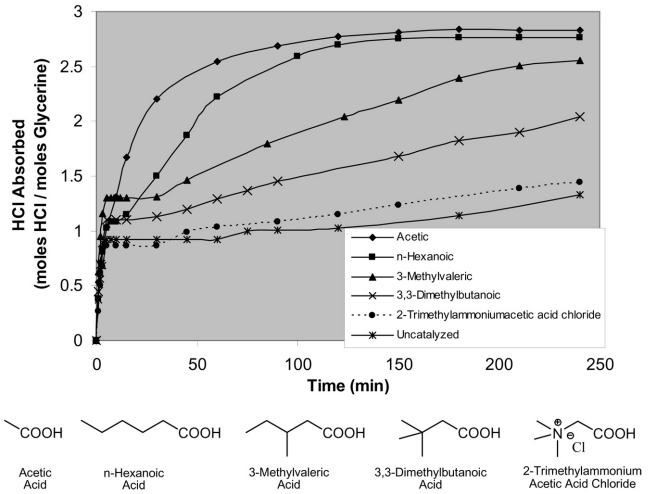

Figure 6. Plots of hydrogen chloride gas absorbed by 3 mol% carboxylic acid in glycerin at 100°C and 110 psi applied HCl pressure. As the carboxylic acid becomes more sterically hindered, the rate of HCl uptake declines.

A significant advantage of the GTE process compared with the incumbent propylene process of Fig. 1 is the improved regiochemistry observed in the dichlorohydrin products of the glycerin hydrochlorination reaction over that achieved during the hypochlorination of allyl chloride. This is manifested in the 1,3-DCH/2,3-DCH ratio, which is 30 – 50 in the GTE process, but only about 3:1 in the incumbent process. The value of improved 1,3-regioselectivity is that 1,3-DCH undergoes cyclization with base to form epichlorohydrin about 300 times faster than does 2,3-DCH [12]. This translates into smaller process equipment and/or shorter residence times. Shorter residence times can result in fewer reaction by-products, higher process efficiency, and a purer final product.

A second advantage of the high pressure GTE process is the intentional accumulation of water mitigates the formation of some by-products, including chlorinated ethers and chloroacetone [13]. This reduces the processing and waste disposal costs for these materials. Retaining water in the GTE process, while still achieving high levels of conversion of MCH to DCH is possible because the increased hydrogen chloride concentration significantly counteracts the equilibrium limitations seen at atmospheric pressure.

An important feature of the carboxylic acid catalyzed hydrochlorination of glycerin that makes the development of a commercial process viable is that the reaction effectively stops at the dichlorohydrin stage – there is no exhaustive hydrochlorination to TCP (1,2,3-trichloropropane). Should a significant rate to TCP occur in this chemistry, an efficient process to DCH would be very difficult to operate commercially because it would require the recovery of the desired DCH at relatively low concentration from the product mixture. Additionally, the formation of TCP would represent a loss of glycerin efficiency, and a significant economic loss because of the need for its disposal.

The absence of TCP in these hydrochlorination reactions is an inevitable consequence of the mechanism that is believed to be operative in this chemistry. A proposed mechanism of the carboxylic acid catalyzed hydrochlorination of polyols has been available for 50 years, and is shown in Fig. 5. In this mechanism, one hydroxyl group is esterified by the carboxylic acid catalyst. The cyclization of this ester with an adjacent hydroxyl group is followed by proton-assisted loss of water, and results in the formation of an acetoxonium cation. Ring opening of this acetoxonium cation with chloride ion, regioselectively at the primary position gives the observed major products. The intermediacy of the acetoxonium cation requires two available adjacent hydroxyls for this mechanism to be operative, and thus provides an explanation for why the glycerin hydrochlorination stops at the dichlorohydrin stage. Further confirmation of this mechanism is that under the hydrochlorination conditions either ethylene glycol or propylene glycol is only monohydrochlorinated to the chlorohydrin. This is particularly significant since these chlorohydrins can be employed for the synthesis of the corresponding epoxides by reaction with base. This makes the hydrochlorination reaction of a number of polyols, such as those derived from sugar hydrogenolysis, for example, particularly valuable for the conversion of the polyol into higher valued products which are currently manufactured using the epoxides.

It is known from the prior art that a variety of carboxylic acids are effective catalysts for the hydrochlorination reaction, although the vast majority of studies have employed acetic acid [6 – 8]. While acetic acid performs well in laboratory-scale batch reactions, and can be used in appropriately configured commercial processes, its volatility is too high for some recycle process configurations. Among the major products from the hydrochlorination of glycerin, the desired dichlorohydrins, 1,3-DCH and 2,3-DCH are the most volatile. This makes a recycle process, in which the DCHs are stripped from the product stream after reaction, and recycle of any unreacted glycerin or MCHs and catalyst back to reaction, particularly attractive. For this option to be viable, it is preferred that the catalyst, and its esters with the products or intermediates, should be less volatile than the DCHs, so that they remain in the stripper bottoms for easy recycle. Carboxylic acid catalysts containing six or more carbon

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

atoms meet this requirement. We have examined the structural features of a number of such carboxylic acids to delineate those structural features that lead to satisfactory catalytic performance in the hydrochlorination reaction.

Figure 6 shows the rate of hydrogen chloride uptake versus time in glycerin hydrochlorination reactions employing four different carboxylic acids, along with the corresponding plots for acetic acid and a reaction with no added catalyst. Of these five reactions, the acetic acid catalyzed reaction is fastest and total consumption of hydrogen chloride is greatest after 4 h. *n*-Hexanoic acid is initially slower, but after 4 h has consumed about the same amount of hydrogen chloride. Gas chromatographic analysis of the reaction products after these reactions confirms that the conversion to dichlorohydrins is essentially the same in these two cases. The plot of HCl uptake for the *n*-hexanoic catalyzed reaction appears to show an induction period which we attribute to mass-transfer limited esterification of the glycerin by the *n*-hexanoic acid catalyst, which is immiscible with the glycerin initially. The rate of hydrogen chloride uptake is slower for 3-methylvaleric acid and almost at the uncatalyzed rate in the case of 3,3-dimethylbutanoic acid. These rates appear to correlate with the steric bulk [14] of the carboxylic acids, with the less sterically hindered acids giving faster reactions. However, the pK_as for these acids also correlate with this steric parameter. To break this correlation, we also examined the performance of trimethylammonium acetic acid chloride (pK_a = 1.76) as a catalyst. The rate of HCl uptake in a reaction using this material as a catalyst is very slow, and quite similar to that observed with 3,3-trimethylbutanoic acid, even though its pK_a indicates it is by far the most acidic carboxylic acid catalyst of those acids shown in Fig. 6. This leads us to propose that it is the steric bulk of the catalyst that largely determines the catalyzed rate of hydrochlorination of glycerin.

4 Conclusions

The interest in the commercialization of a GTE process demonstrates the ascendancy of renewable feedstocks in the manufacture of commodity chemicals. The increasing availability of cheaper glycerin, as a result of the rapidly growing biodiesel industry, makes it a viable feedstock in this application. As recently as 2006, synthetic glycerin was manufactured from epichlorohydrin, but this has now completely ceased. Further development of technology for utilization of alternative, low-cost, renewable feedstocks, for example, sugar or cellulose, will likely result in the emergence of additional feedstock switches for existing commodity petrochemicals.

The GTE process is an economically advantaged route to epichlorohydrin that additionally features a number of environmentally desirable attributes compared to the incumbent process. These include a switch of chloride feedstock from elemental chlorine to hydrogen chloride, which can be obtained as the by-product from a number of commercial processes, including the incumbent epichlorohydrin process. Additionally, the GTE process exhibits improved atom efficiency, less waste water, and lower levels of chlorinated organic by-products, and, of course, the use of competitively priced, renewable glycerin feedstock.

Acknowledgements

We thank Erin O'Driscoll and Ernesto Occhiello for supporting this work.

References

[1] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, 3rd Edn., Wiley-VCH, Weinheim **1997**, p. 294, 299.
[2] PCT application WO 2006020234, published February 23, and assigned to **2006** to Dow Global Technologies, Inc.
[3] PCT application WO 2005054167, published June 16, **2005** and assigned to Solvay.
[4] PCT application WO 200521476, published March 10, **2005** and assigned to to Spolek.
[5] A. Behr et al., *Green Chem.* **2008**, *10 (1)*, 13 – 30.
[6] M. Schlaf, *Dalton Trans.* **2006**, *39*, 4645 – 4653.
[7] J. Carius, *Justus Leibigs Ann. Chem.* **1862**, *122*, 73.
[8] R. Boschan, S. Winstein, *J. Am. Chem. Soc.* **1956**, *78*, 4921.
[9] G. P. Gibson, *Chem. Ind.* **1931**, *20*, 949 – 975.
[10] J. B. Conant, O. R. Quayle, *Org. Synth.*, **1941**, *CV1*, 292 – 297.
[11] Dow Chemical Company, *US Patent 2,144,512*, January 24, **1939**.
[12] S. Carra, E. Santacesaria, M. Morbidelli, P. Schwarz, C. Divo, *Ind. Eng. Chem. Proc. Des. Dev.* **1979**, *18 (3)*, 424 – 427.
[13] Dow Global Technologies, Inc., *US Patent Appl. Publ. 20080015369, January 17,* **2008**.
[14] T. Komatsuzaki, I. Akai, K. Sakakibara, M. Hirota, *Tetrahedron* **1992** *48 (9)*, 1539.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim