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Indirect electrochemical epoxidation of hexene in a liquid–liquid electrolyte

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Preliminary experiments have been carried out on the mediated electrolytic synthesis of 1,2-epoxyhexane from 1-hexene. The electrochemical cell was an undivided parallel-plate reactor under galvanostatic operation at 25° C and 1 atm. The electro-active Br_2/Br^- couple acted as the mediating species. A dispersion of 1-hexene droplets in aqueous sodium bromide solution was generated by use of a static mixer. Current efficiency for organic species and chemical yield of epoxide were determined in order to investigate qualitatively the dependence of the overall electrolyzer performance upon flow rate, organic volume fraction, dispersed droplet size, and current density. The cell effluent was analyzed by gas chromatography. Epoxide current efficiencies around 65% were obtained under operation conditions where the rate of bromine production by anodic reaction was sufficiently high so as to exceed the saturation concentration of hexene. Since the aqueous cell effluent was depleted of hexene, it was concluded that mass transfer from the organic phase into the aqueous phase was not able to replenish the electrolyte effectively.

Nomenclature

c_c	product concentration in aqueous phase (M)
c_d	product concentration in organic phase (M)
d	diameter of dispersed organic droplets (μm)
f	organic volume fraction
F	Faraday's constant, 96 487 C mol^{-1}
I	applied current (A)
n	number of electrons in electrode reaction
Q	total cell flow rate (l s^{-1})

1. Introduction

To enhance mass transfer to electrodes in solutions of sparingly soluble organics, a variety of techniques have been devised including the use of two-phase (liquid–liquid) electrolytes. In these, a mediating redox couple dissolved in the aqueous phase serves to carry charge from the electrode to reactant in the dispersed organic phase. Such mediated, or indirect, electrolytic processes tend to exhibit desirable features including high current density and space–time yield. However, most such systems have only been tested on a lab-scale; reliable numerical data and dimensionless scale-up criteria are still needed for accurate engineering evaluation at early stages of design. For this purpose, it would be helpful to have model chemical systems so that general design principles may be better understood. It is toward this goal that the present study represents an initial step. The purpose of the present investigation was therefore to identify and evaluate the usefulness of the hexane epoxide reaction sequence as a model system for the study of two-phase (liquid–liquid) electrolyte phenomena.

Feess and Wendt [1] discussed mass transport mechanisms in liquid–liquid electrolysis processes. A review of a large number of electro-organic reactions which have been reported for such systems is included. Advantages of two-phase processes include high conductivity of the electrolyte, availability of water as a reactant, and, in certain cases, protection of the product by extraction into the second phase.

Dworak and Wendt [2, 3] investigated the phenomenon of mass transfer between a dispersed liquid phase and an electrode, and concluded that organic droplets are not able to penetrate the boundary layer under highly turbulent flow conditions. Consequently wetting of the electrode is prevented. Mass transfer enhancement from a boundary layer disruption mechanism occurred only to a small extent in their experiments. Hence, it was concluded that the organic phase served primarily to maintain the saturation concentration of the organic reactant in the aqueous phase.

Lu and Alkire [4] investigated mass transfer in a parallel-plate cell with liquid–liquid flow. They found the presence of droplets of a second liquid phase causes substantial mass transfer enhancement, both by physical disruption of the boundary layer near the electrode as well as by extraction of reactants from droplets that are close to the electrode.

Different techniques for improving mass and current yields by using emulsion electrolytes have been described by Feess and Wendt [5]. Among others, they considered the case of mediated two-phase processes. Here, the overall production rate depends both on the volume-specific chemical reaction rate and on the volume-specific mass transfer rate, either of which can be rate controlling. Many types of electron transfer

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agents have already been used [6], and industrially promising applications have been compiled by Shono [7, 8].

2. System chemistry

The electrolytic conversion of olefin into epoxides via the bromohydrin route has been widely studied, particularly the oxidation of propylene. Recently, the epoxidation of butanes and ethylene has been investigated by Jansson and Ellis [9]. High selectivities and preservation of the isomer configuration were reported, but the current efficiencies remained less than 65% because of the slow bulk phase reaction compared to the fast electrode reaction.

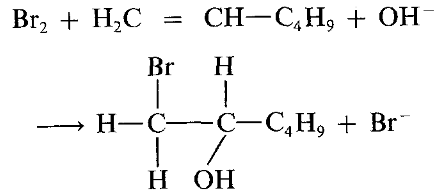
Melnikov *et al.* [10] have shown by the electrolysis of sodium bromide solution in the presence of alkenes that the chain length of olefins has little influence upon the selectivity of the formation of bromohydrin. A detailed description of the electrochemical epoxidation of propylene can be found in the work by Lisius [11]. The reaction path should remain the same for the epoxidation of 1-hexene.

The process, carried out in an undivided cell, used an aqueous solution of sodium bromide with sodium hydroxide to adjust electrolyte pH to a value of 12. Bromide concentrations of both 0.1 and 0.2 M were investigated. The initial steps are anodic oxidation of bromide and electrolysis of water at the cathode:

$$2Br^- \longrightarrow Br_2 + 2e^- \qquad (1)$$

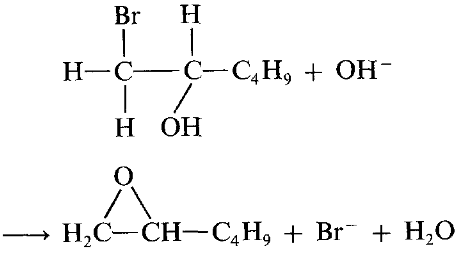
$$2H_2O + 2e^- \longrightarrow H_2 + OH^- \qquad (2)$$

The molecular bromine reacts with 1-hexene to form an unstable carbonium intermediate which, through subsequent nucleophilic addition of a hydroxide ion, forms 1,2-hexane bromohydrin, the desired primary product;



$$\mathrm{Br_2 + H_2C = CH{-}C_4H_9 + OH^-} \longrightarrow \mathrm{H{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{/}}{C}}{-}C_4H_9 + Br^-} \qquad (3)$$

The halohydrin then consumes another OH$^-$ ion and is converted into 1,2-epoxyhexane by base-catalyzed dehydrohalogenation:



$$\mathrm{H{-}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{/}}{C}}{-}C_4H_9 + OH^-} \longrightarrow \mathrm{\overset{\overset{\displaystyle O}{\diagup\;\diagdown}}{H_2C{-}CH}{-}C_4H_9 + Br^- + H_2O} \qquad (4)$$

Thus, the overall reaction is:

$$\text{1-hexene} + H_2O \longrightarrow \text{1,2-epoxyhexane} + H_2 \qquad (5)$$

Detailed discussions of possible side reactions are available elsewhere [11, 12] and are only summarized here. At high bromide concentrations, polybromides may form and the carbonium intermediate may react by nucleophilic attack to result in the major by-product, 1,2-dibromohexane, instead of the desired bromohydrin. Since the epoxide ring is susceptible to attack by water, it can hydrolyze to 1,2-hexanediol. At high pH values, bromine can hydrolyze in the bulk phase to yield hypobromous acid and subsequently to form the hypobromite ion.

Above the limiting current of the bromide ion, oxygen evolution occurs at the anode and serves thus to reduce the current efficiency:

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad (6)$$

3. Apparatus and procedure

The flow system, illustrated in Fig. 1, consisted of one aqueous and one organic reservoir, two pumps (March), one static mixer (Kenics, model 1/4″-40-14-0, 20 stainless steel elements), seven rotameters (Gilmont) and one settling tank. The fluid reservoirs were a 10-l and a 25-l Nalgene® tank, and the settling tank was a 4-l glass vessel. Polypropylene tubing and fittings connected all parts of the system, whereas the valves were made of Teflon® or glass [13].

The electrochemical cell was a parallel plate reactor that had been designed for the investigation of the propylene oxidation [11]. Each electrode consisted of a stainless steel backing plate on which a platinum foil (23 × 1.5 cm) was attached with conducting epoxy cement. Electrodes were embedded flush into two cell blocks made of plexiglass; the fluid passed the 23-cm direction of the electrode. The flow channel gap, formed by Teflon spacers, was 0.15 cm; by adjusting

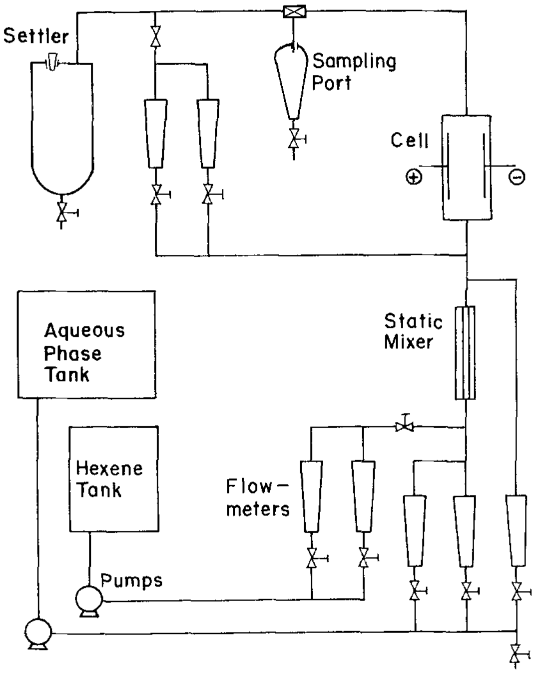


Fig. 1. Schematic diagram of the flow system.

the flow rate through the static mixer, a desired average drop size of the organic phase could be established. The mixer provided a narrow drop size distribution, and the mean droplet size was neither a function of the density of the dispersed phase nor of the volume fraction. Experiments were conducted in galvanostatic mode (PAR 371 and Lambda Regulated Power Supply, LK 351-FMOV) and were performed at 25° C and 1 atm pressure.

Concentrations of organic species were determined by gas chromatography (Varian, 3740). The column was a 6 foot 1/8-inch diameter silanized glass tubing packed with 5% carbowax 20 M on 80/100 mesh Chromosorb 101. Temperature programming was used to accelerate separation. The internal standard method was chosen to determine the sample composition with *p*-dioxane as the internal standard. A microprocessor/printer (Varian Instruments, CDS 401) was connected to the gas chromatograph for peak area integration and printout of the results.

Hexene, 1,2-epoxyhexane, and 1,2-hexanediol, which was not produced in accurately detectable amounts under the process condition investigated, were identified by comparison with purchased samples (Aldrol chemicals). Since the GC detector response factors of the other compounds were close to 0.5 with respect to *p*-dioxane, this value was assumed to apply also for the 1,2-dibromohexane and hexane bromohydrin. Dibromohexane and bromohydrin were identified by mass spectroscopy (LREIMS). Since the identification was accomplished by examination of the fragment ions, a slight uncertainty remained. Details are given elsewhere [14].

4. Results and discussion

The current efficiency for consumption of hexene was calculated according to Faraday's law:

$$\text{current efficiency} = [c_d f + c_c(1 - f)]\frac{nFQ}{I}$$

The results thereby took into account losses due both to competing electrode reactions and to chemical inefficiencies by unwanted bulk phase reactions. Some physical properties of 1-hexene are listed in Table 1.

Table 1. Physical properties of 1-hexene

Property	*Value*	*Ref.*
Density @ 25° C (g ml^{-1})	0.67	
Viscosity (g cm^{-1} s^{-1})	2.5 × 10^{-3}	[15]
Solubility in water (mM)	0.6 at 25° C	[16]
Boiling point @ 760 mmHg (° C)	63.5	
Flash point (° C)	−26	
Interfacial tension against 0.2 M aqueous sodium bromide solution (dynes cm^{-1})	33 at 25° C	Meas.

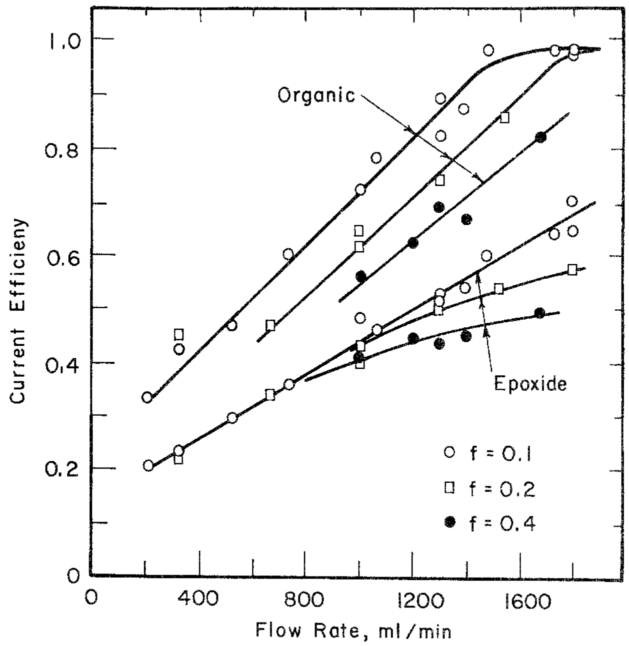


Fig. 2. Current efficiency as a function of total flow rate ([Br$^-$] = 0.2 M, pH = 12.0, i = 0.1 A cm^{-2}, d = 150 μm).

4.1. *Variation of flow rate*

The data shown in Fig. 2 illustrate the velocity dependence of epoxide and total organic current efficiency for different volume fractions of the dispersed organic phase. All other parameters were held constant. It can be seen that higher current efficiencies were obtained with increasing total flow rate and decreasing volume fraction of hexene. The total organic current efficiency finally attained a maximum of about 98%. The remaining loss was most likely due to hypobromite formation, because of high pH values [11]:

$$Br_2 + OH^- \longrightarrow HOBr + Br^- \qquad (7)$$

Mass transfer between dispersed hexene droplets and the continuous phase improved with increased flow rate. This effect should facilitate replenishment of the aqueous phase with organic reactant, and thus prevent a decrease of current efficiency caused by depletion of the solution during conversion in the cell. The same consideration is true for the transport of electro-active species from the bulk solution to the electrode surface. Losses at low flow rates can be attributed to the fact that the applied current density might be above the limiting current for the bromide/bromine couple so that oxygen is evolved.

The linear relationship between total organic current efficiency and flow rate, however, leads to the suggestion that the relation between bromine and 1-hexene concentration in the aqueous phase is the determining factor. The effective bromine concentration, which is the amount of bromine generated per unit volume of aqueous phase, is smaller at higher flow rates and at lower organic volume fractions for a given current density. Since there is only a limited amount of 1-hexene present in the aqueous phase, a higher fraction of the halogen is used up for the conversion of hexene thereby increasing the organic current efficiency; i.e. with decreasing bromine

Table 2. Ratio of effective bromine concentration to hexene saturation concentration at the first point of maximum current efficiency

	Volume fraction	*Current density* ($A\ cm^{-2}$)	*Flow rate* ($ml\ min^{-1}$)	*Ratio*
Fig. 2	0.1	0.1	1500	1.28
	0.2	0.1	1800	1.35
	0.4	0.1	2100 (extrapolated)	1.92
Fig. 3	0.1	0.033	550	1.19

concentration the amount which does not get consumed by organics also decreases. This suggestion is supported by the following two experimental observations. First, the maxima of the total organic current efficiency are reached at flow rates that correspond to effective bromine concentrations only slightly above the saturation concentration of hexene. (Data are given in Table 2.) Second, the aqueous cell effluent is entirely depleted of hexene at low flow rates.

One can conclude from these results that mass transfer of hexene across the phase boundary was, compared to the reaction rate, too slow to replenish the aqueous phase effectively.

For the same experimental conditions but at the lower current density of 0.033 A cm^{-2} the behavior of the epoxide current efficiency shown by the curved line in Fig. 3 was found. The graph agrees with the above-stated suggestion since the maximum value of the current efficiency is first attained at a flow rate (550 ml min^{-1}) where the effective bromine concentration barely exceeds the hexene saturation concentration (see Table 2). The decrease in current efficiency at higher flow rates was not expected and is difficult to explain. However, this effect may arise from sampling and analysis errors, as the product concentrations become increasingly smaller ($\sim 10^{-5}$ M) at high flow rates and at the applied low current densities.

The selectivity of the reaction sequence was found to be virtually independent of flow rates over the range studied (200–1800 ml min^{-1}, $[Br^-] = 0.2$ M, pH = 12, $i = 0.1$ A cm^{-2}, $f = 0.1$, $d = 150\ \mu m$). The chemical yield of 1,2-epoxyhexane was found to be 62%.

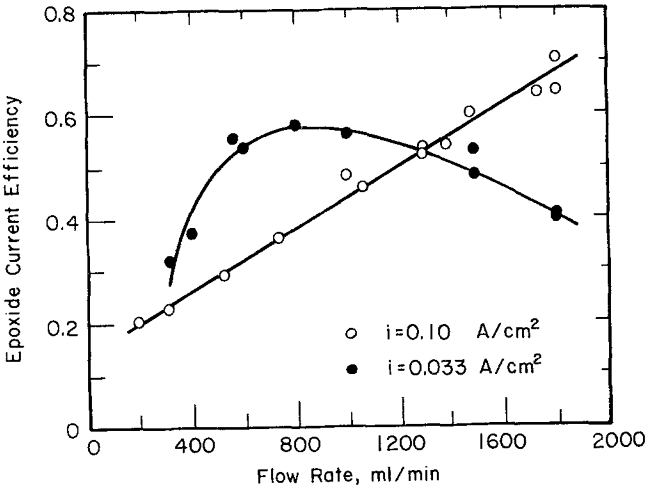


Fig. 3. Epoxide current efficiency as a function of total flow rate ($[Br^-] = 0.2$ M, pH = 12.0, $f = 0.1$, $d = 150\ \mu m$).

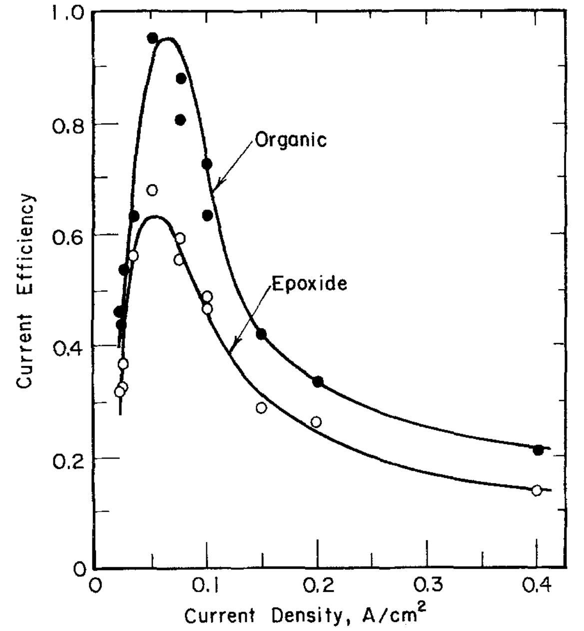


Fig. 4. Current efficiency as a function of current density ($[Br^-] = 0.1$ M, pH = 12.0, $Q = 1000$ ml min^{-1}, $f = 0.1$, $d = 150\ \mu m$).

4.2. *Effect of current density*

The current efficiencies for production of all organic species as well as just the epoxide product are shown in Fig. 4 as a function of current density. There is a distinct maximum at approximately 0.05 A cm^{-2}. At current densities below this value, little bromine is present in the vicinity of the anode and, consequently, only small amounts of bromohydrin and epoxide are produced. Thus, the concentration of OH^- ions remains high in the anode boundary layer; the situation thus favors formation of hypobromite ions. The decline of current efficiency above 0.05 A cm^{-2} is caused by generation of excess quantities of bromine (compared to the hexene saturation concentration) which then hydrolyzes according to Equation 7. Above the bromine limiting current additional losses still occur because of oxygen evolution.

If one takes the two sets of results depicted in Fig. 3 into acocunt, there is good reason to suggest that by increasing the flow rate the maximum value of the current efficiency will be improved and that, in addition, the maximum current efficiency will be shifted to higher current densities.

4.3. *Influence of droplet size*

The flow rate through the static mixer sets the average drop size of the organic phase. Correlations have been published that permit the calculation of average droplet size as a function of the viscosity ratio of the two phases, and of the Weber number [17].

The data presented in Fig. 5 indicate that better current efficiencies were obtained with smaller drops, where mass transfer rates are higher. A significant

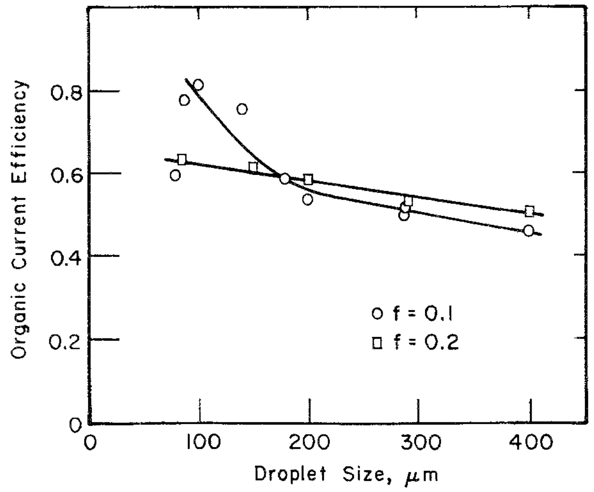


Fig. 5. Total organic current efficiency as a function of drop size ($[Br^-] = 0.2\,M$, pH = 12.0, $Q = 1200\,ml\,min^{-1}$, $i = 0.1\,A\,cm^{-2}$).

difference is observed at small droplet sizes between the two volume fractions studied, the increase in current efficiency being much more pronounced at the lower volume fraction. These results are in agreement with the previous discussion where depletion of dissolved hexene from the aqueous phase was suggested. Although the data are scattered it is reasonable to suggest that small droplets are not stable at high volume fractions, where coagulation occurs more easily. It was also found that the epoxide yield did not change appreciably upon variation of droplet size in the range of 75–400 μm.

5. Conclusions

Indirect electrochemical synthesis of 1,2-epoxyhexane was investigated because it appears to be a well-characterized model system for study of transport/reaction/scale-up in mediated systems containing two liquid phases. The effects of operating conditions on current efficiency and chemical yield were studied experimentally. The current efficiencies obtained were comparable to those reported by other authors [9, 11], who studied the epoxidation of shorter-chain gaseous alkenes.

Reasonably high current densities ($0.1\,A\,cm^{-2}$) were achieved without special attempts to optimize performance. Organic by-products were few in number and were easily detected by gas chromatography. For these reasons, the hexene epoxide system appears to be an excellent candidate for controlled studies on the complex interactions between mass transport phenomena and chemistry in liquid–liquid electrochemical processes. Of special interest would be more detailed studies of the chemical and transport processes occurring in the vicinity of the liquid–liquid interface since these evidently control the overall reaction rate and thus determine scale-up strategies.

Acknowledgement

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