ELSEVIER

Thermochimica Acta 289 (1996) 177–187

thermochimica acta

Kinetics of the reaction of 4,4′-methylenedianiline with propylene oxide in ethylene glycol[1]

R.M. Machado *, J.W. Mitchell, J.P. Bullock, B.E. Farrell

Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, PA, 18195-1501, USA

Received 18 December 1995; accepted 30 April 1996

Abstract

The kinetics for the reaction of 4,4′- methylenedianiline, MDA, with propylene oxide in ethylene glycol as a solvent to generate secondary and tertiary aromatic alkanolamines were investigated. This reaction is important in converting glycolyzed, liquefied, recycled polyurethane foam, containing high levels of MDA and primary aromatic amines, into a high-performance, recycled polyol substitute that can be used in the manufacture of new polyurethane foams.

The kinetics were obtained using a combination of data from heat flow calorimetry and chemical analysis using HPLC. Reactions were run using a series of programmed propylene oxide feed additions to generate data-rich sets of global thermal rate data. Chemical analysis yielded the distribution of mono-,di-, tri-, and tetra-sustituted species. Using a weighted regression analysis the data sets for several experiments at different temperatures were analyzed simultaneously to obtain the kinetic parameters of a simplified reaction scheme that accurately described this system. The kinetic analysis shows that propylene oxide is a preferred epoxide to maximize the yield of secondary amines.

Keywords: Alkanolamines; Methylenedianiline; Polyurethane foams; Propoxylation; Propylene oxide; Reaction calorimetry; Recycling

1. Introduction

Polyurethane scrap foams can be converted into liquids suitable for use as a partial replacement of virgin polyols in the manufacture of polyurethane rigid foams.

---

* Corresponding author.

[1] This paper is a contribution to the special thematic issue "Reaction Calorimetry", edited by Ralph N. Landau.

PII S0040-6031(96)03027-4

This is accomplished by glycolysis, a process in which the scrap foam is contacted with low molecular weight glycols and selected catalysts at high temperature, 180–220°C, for a few minutes to a few hours [1–5]. The urethane and urea bonds that form the structure of the foam are reformed with the low molecular weight glycols to generate a complex mixture of low molecular weight urethane alcohols and primary aromatic amines. Foam made from diphenyl methane diisocyanate, MDI, will generate free primary amines including MDA and oligomeric amines based on MDA. The presence of primary amines makesv the reuse of the glycolyzed foam problematic as the subsequent foam synthesis reaction becomes difficult to control and the foam physical properties may be compromised [6]. The reaction of propylene oxide with the glycolyzed foam converts the primary aromatic amines to secondary aromatic alkanolamines. This modification improves the kinetics of the glycolyzed foam when it is reused to synthesize the next generation foam and improves the physical properties of the foam [6]. Controlling the conversion of the primary aromatic amines of MDA to secondary aromatic alkanolamines using propylene oxide is vital to the commercial application of this technology.

The reaction of MDA with various glycidyl ethers has been previously studied by Dobas et al. [7]. They found the reaction to be first order in the epoxide and first order in the amine. Aromatic diamines contain four amino hydrogens capable of reaction with epoxides. As described by Dobas et al., the structural separation of the amines in MDA makes their reactivity virtually independent so that the kinetics with epoxides can be reduced to a model with two independent second-order rate constants. The first rate constant characterizes the reaction of a primary amine with the epoxide to form a secondary amine and the second rate constant describes the reaction of the secondary amine to form the tertiary amine. For the glycidyl ethers, Dobas et al. that determined the ratio of the second-order rate constants, primary/secondary, ranged between 2.0 to 3.0 for temperatures between 60 and 80°C over a limited range of conversion (approximately 10%–70%).

In this study we report the fundamental kinetics of the reaction of MDA with propylene oxide in ethylene glycol. Compounds that act as hydrogen bond donors, such as ethylene glycol, protonate the epoxy ring and catalyze the reaction of the epoxide with amines [8]. Because of the relatively high concentration of the solvent in these studies, 80% by weight ethylene glycol, the catalytic effect of the solvent is considered to be lumped into the individual rate constants.

2. Reactor theory

Heat flow reaction calorimetry is well established as a method for obtaining the heat evolved during a chemical process and reaction kinetics [9–12]. The heat of reaction measured in this study was determined as described in the above references by systematically measuring the total heat flow to the reaction system and subtracting the sensible heating effects of the feed and the sensible heating effects due to variations of the reaction mass temperature.

The reaction calorimeter used in this study is a heat flow calorimeter. The heat flow from the reactor mass to the cooling medium is given by

$$Q_{\mathrm{flow}} = UA(T_{\mathrm{r}} - T_{\mathrm{j}}) \tag{1}$$

where T_{r} and T_{j} are the reacting fluid and reactor jacket coolant fluid temperatures, respectively. The lumped heat transfer coefficient, UA, is determined in a calibration experiment by placing a known amount of energy into the system via a heater, recording the temperatures, and calculating UA.

An overall energy balance on the reactor relates the measured heat flow to the heat effects internal to the reactor

$$Q_{\mathrm{flow}} = Q_{\mathrm{r}} + Q_{\mathrm{dos}} - Q_{\mathrm{loss}} + Q_{\mathrm{agit}} - Q_{\mathrm{accu}} \tag{2}$$

where Q_{r} is the heat released from chemical reaction, Q_{dos} is the sensible heat added from semibatch addition of any of the reactants, Q_{loss} is the heat loss to the environment, $Q_{\mathrm{agit}}$is the energy added through agitation, and Q_{accu} is the heat accumulated in the system due to temperature variations.

$$Q_{\mathrm{accu}} = mC_p\mathrm{d}T_{\mathrm{r}}/\mathrm{d}t \tag{3}$$

where m and C_p are the total mass and the heat capacity of the reaction fluid. The Q_{dos}, Q_{loss} and Q_{agit} terms are quatified in the calorimeter analysis,and the Q_{r} term is calculated over the course of the reaction. The reactive heat flow is related to the reaction rates via

$$Q_{\mathrm{r}} = \sum_{i=1}^{n_{\mathrm{r}}} \Delta H_i r_i V_{\mathrm{l}} \tag{4}$$

where r_i is the volumetric reaction rate for reaction i, ΔH_i is the individual heat of reaction, n_{r} is the total number of reactions, and V_{l} is the volume of the reacting (liquid) phase.

The individual reaction rates are a function of reactor temperature, T_{r}, the reactant concentrations of species j, C_j, and the kinetic parameters, $\boldsymbol{k}$, according to

$$r_i = f(T_{\mathrm{r}}, C_j, \boldsymbol{k}) \tag{5}$$

The quantity of each component species in the reaction mixture varies with time according to

$$\frac{\mathrm{d}N_j}{\mathrm{d}t} = \sum_{i=1}^{n_{\mathrm{r}}} (A_{j,i} r_i V_{\mathrm{l}}) + F_j \tag{6}$$

where N_j is the molar amount of component j in the reaction mixture, $A_{j,i}$ is the stoichiometric coefficient for component j in reaction i, and F_j is the molar rate of component j, fed semibatch to the reaction mixture. Once the initial conditions in the reactor are specified, the delay functions F_j defined, and a kinetic functionality proposed, the set of component ordinary differential equations can be solved to predict the temporal species concentration profiles. This in turn predicts Q_{r} as a function of time. In essence, once the experiment is defined, the reactive heat flow can be predicted mathematically as a function solely of the kinetic parameter space

$$Q_\mathrm{r} = g(\boldsymbol{k}) \tag{7}$$

This classic, unconstrained optimization problem may be solved by a variety of methods. In the present work, we apply a modified Gauss–Newton method [13] to perform the parameter regressions. This method is embedded in an overall kinetic regression package recently developed at Air Products and Chemicals, Inc. [14]. The overall objective function used in the analysis contains information on both the reactive heat flow and the analytical information

$$\Phi = \sum_{k=1}^{n_\mathrm{obs}} \{\boldsymbol{W}_\mathrm{q}(Q_{\mathrm{r}k,\mathrm{obs}} - Q_{\mathrm{r}k,\mathrm{reg}})\}^2 + \sum_{j=1}^{n_\mathrm{c}} \sum_{k=1}^{n_\mathrm{obs}} \{\boldsymbol{W}_\mathrm{c}(C_{j,k,\mathrm{obs}} - C_{j,k,\mathrm{reg}})\}^2 \tag{8}$$

where n_obs and n_c are the number of observations and components in the system respectively, the subscripts obs and reg indicate experimental observations and regressed predictions respectively, and $\boldsymbol{W}_\mathrm{q}$ and $\boldsymbol{W}_\mathrm{c}$ are user-defined weighting functions. For any specified kinetic function form, the objective function, Φ, is minimized with respect to the kinetic parameters.

3. Chemistry

Analytical methods limited the identification of the intermediate species to those classified only by the number of moles of propylene oxide, PO, reacted per mole of MDA. The species are identified as MDA, monosubstituted MDA, disubstituted MDA, trisubstituted MDA, and tetrasubstituted MDA. Isomers describing the degree of the alcohol on the reacted propylene oxide or the location of the propylene oxide substituents could be determined. This is reflected in the simplified mechanistic reaction steps that are formulated as a collection of six consecutive and series reactions illustrated below. Reaction rates for this process can be described by simple second-order reaction rate expressions, first order in both propylene oxide and the corresponding amine. The corresponding structures can be found in Table 1. It should also be noted that, under the conditions studied, propodxylated ethylene glycol was not found as a by-product.

$$\mathrm{A} + \mathrm{PO} \rightarrow \mathrm{M} \tag{9}$$

$$\mathrm{M} + \mathrm{PO} \rightarrow \mathrm{D12} \tag{10}$$

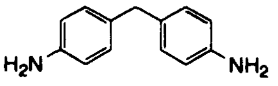
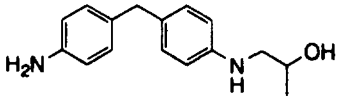
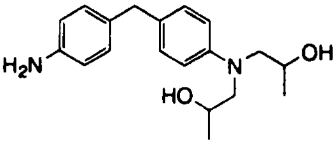
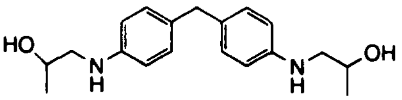
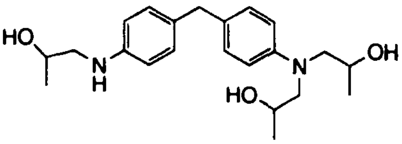
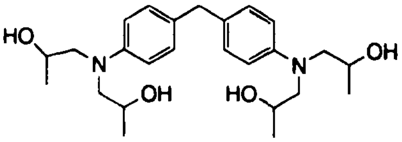
$$\mathrm{M} + \mathrm{PO} \rightarrow \mathrm{D11} \tag{11}$$

$$\mathrm{D12} + \mathrm{PO} \rightarrow \mathrm{T} \tag{12}$$

$$\mathrm{D11} + \mathrm{PO} \rightarrow \mathrm{T} \tag{13}$$

$$\mathrm{T} + \mathrm{PO} \rightarrow \mathrm{Q} \tag{14}$$

Table 1
Species with chemical structures

Species	Notation	Structure
Methylenedianiline, MDA	A	
Methylenedianiline, monosubstituted	M	
Methylenedianiline, disubstituted	D11	
Methylenedianiline, disubstituted	D12	
Methylenedianiline, trisubstituted	T	
Methylenedianiline, tetrasubstituted	Q	

4. Experimental

4.1. Materials

All reagents were purchased through Aldrich as reagent grade and used as received.

4.2. Analytical analysis

Quantitative Chemical analysis of the reaction samples was completed using a Hewlet Packard HPLC model 1090 with a Supelcosil LC-18 (5 μ) column operated at 40°C. Samples were diluted in acetone and a mobile phase of methanol/water was programmed to ramp between 50% methanol/50% water to 60% methanol/40% water over 40 min at 1 ml min^{-1}. A UV detector at 240 nm was used with internal standards for the MDA and for the tetrasubstituted MDA. Examples of two HPLC runs are illustrated in Fig. 1.

All chemical structures were verified using Thermalspray LC-MS on a VG Quattro triple quadruple mass spectrometer. The technique was able to verify the number of propylene oxide substituents on the MDA but was not able to resolve the isomer structures.

Response factors from the HPLC were obtained directly from internal standards for the MDA and tetrasubstituted MDA. The responses of the mono-, di- and tri-substituted species could not be verified independently since pure components were not available. However, they were obtained indirectly by adjusting the response factors until the predicted total mass in the reactor and the measured total mass in the reactor were identical for each of the four samples taken in each experiment. The values for the experiments were averaged and are reported in Table 2.

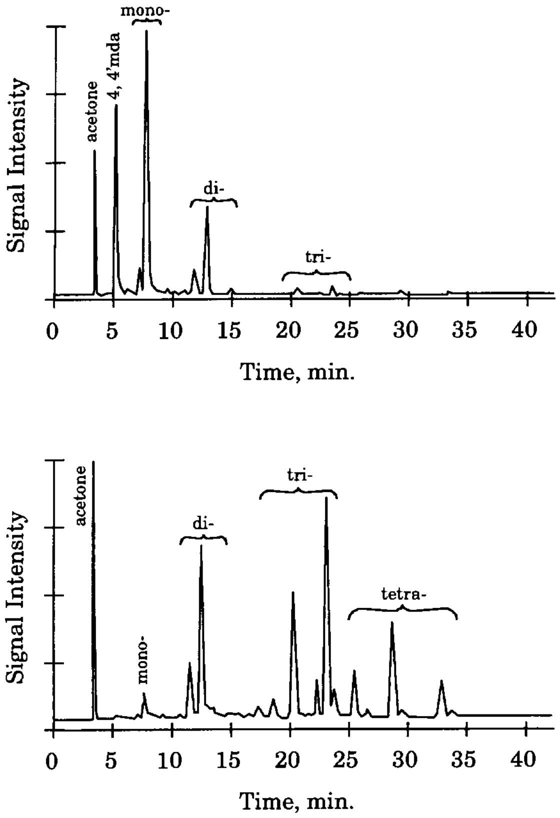


Fig. 1. HPLC traces at 240 nm for the addition of 1 mole propylene oxide to 1 mole of MDA (upper) and 3 moles of propylene oxide to 1 mole of MDA (lower).

Table 2
HPLC calibrations of substituted MDA

Species	Moles propylene oxide/mole MDA	Relative response factor at 240 nm
MDA	0	1.00[a]
Monosubstituted MDA	1	0.582[b]
Disubstituted MDA	2	0.529[b]
Trisubstituted MDA	3	0.427[b]
Tetrasubstituted MDA	4	0.289[a]

[a] Obtained from internal standards.
[b] Obtained from mass balance.

4.3. Thermal analysis

Thermal rate measurements were made with the Mettler Toledo RCI reaction calorimeter and the Mettler Toledo MP10, a 1-liter glass pressure reactor. Each experimental run began by charging 200 g (~ 1 mole) of 4,4' - MDA and 800 g of ethylene glycol to the reactor. The reactor head space was purged three times and pressurized to approximately 3×10^5 Pa with nitrogen. The reactor was operated at the system autogenous pressure and was monitored to ensure no leaks during the experiment. All reactions were isothermal within ±0.5°C at 70,85 and 100°C. Calorimetric calibrations were conducted at the begining and end of each ramped feed of propylene oxide. The propylene oxide was added in four separate feed ramps of approximately 60 (~ 1 mole) over 30 min for each addition. After each feed ramp and calibration, 12 samples of the reaction mass were removed from the reactor for analysis. Samples were not taken until the reaction exotherm had subsided and the propylene oxide was completely consumed.

5. Results and discussion

5.1. Thermal Analysis

The heat of reaction between MDA and propylene oxide was measured for 9 separate experiments and determined to be-105.0 kJ mole^{-1}of propylene oxide with an unbiased sample estimate of the standard deviation of 4.4 kJ mole^{-1}. The measurements were made over the temperature range 70–100°C. This average value was used in subsequent modelling and parameter estimations. The reactive heat profile for a propoxylation at 85°C is displayed in Fig. 2.

As the initial propylene oxide is added to the system, the reactive heat increases with the initiation of active reaction. After the first ramped dose of PO is completed, the reactive heat declines as the PO is consumed. With each subsequent dose of PO, the maximum heat release declines and the length of the reactive heat tail increases. This is due to both a reduction in concentration of the reactant MDA and the slower reaction rates for propoxylation of primary and secondary amine species. Using multiple feed

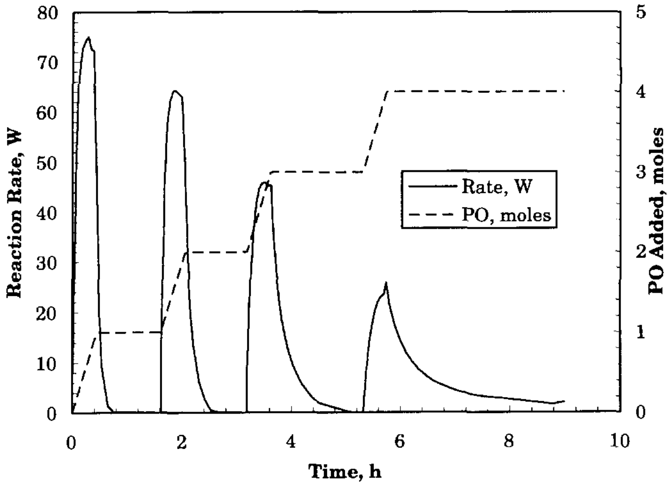


Fig. 2. Reaction rate and propylene oxide feed at 85°C.

ramps compared to only one feed ramp yields increased variation in the temporal thermal data and therefore a richer data set for kinetic analysis.

The data from the reactor studies were analysed to determine if a kinetic functionality could be established. The rate of each reaction is dependent on temperature and some function of composition. We tried a variety of kinetic models but found that a simple, mass-action-based, kinetic functionality describes the system quite well. For the six reactions specified above, the rate expressions are assumed to be

$$r_1 = k_1 C_A C_P \tag{15}$$

$$r_2 = k_2 C_M C_P \quad ; k_2 = k_1/2 \tag{16}$$

$$r_3 = k_3 C_M C_P \tag{17}$$

$$r_4 = k_4 C_{D12} C_P \quad ; k_4 = 2k_3 \tag{18}$$

$$r_5 = k_5 C_{D11} C_P \quad ; k_5 = k_1/2 \tag{19}$$

$$r_6 = k_6 C_T C_P \quad ; k_6 = k_3 \tag{20}$$

The kinetic constants (k_1 and k_3 in Arrhenius form) were determined via a single, global, non-linear regression using data from each of the three temperatures studied. Approximations for k_2, k_4, k_5 and k_6 are based on the structural similarity of the species and simple probability, based on the assumption that the two amine functional groups act independently. For example, k_2 is assumed to equal $k_1/2$ since there is only one primary amine functional group on the monosubstituted MDA, species M, whereas for reaction 1 Eq.(9), two primary amines are available from the MDA, species A. Fig. 3 compares the experimentally measured reactive heat profile to that predicted by the optimized model at 85°C. The agreement is quite good.

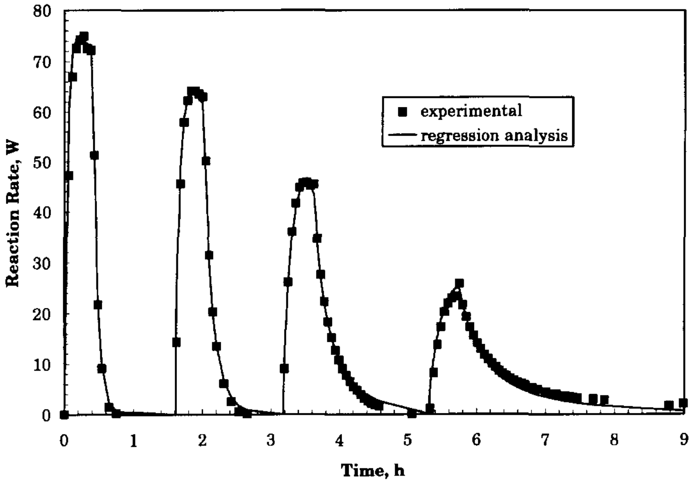


Fig. 3 Comparison of experimental and regression analysis for the reaction rate, Q_r, at 85°C.

The derived rate constants are thus given by

$$k_1 = 67.9\exp(-48200/RT) \tag{21}$$

$$k_3 = 7.70\exp(-48500/RT) \tag{22}$$

where k_i is the rate constant for reaction i in $m^3\ mol^{-1}\ s^{-1}$, R is the gas constant, 8.314 $J\ mol^{-1}\ K^{-1}$, and T is temperature in K.

The two rate constants have nearly identical activation energies and differ in overall magnitude by a factor of approximately 10.

Fig. 4 compares the model predictions, for component masses, to the experimental values over the entire range of collected data for the 85°C run. The disubstituted species are analysed as the sum of D11 and D12 species, which is represented as D.

While some scatter is evident, the predictions generally fall within the experimental/analytical errors. Overall, it appears that this kinetic model describes the propoxylation process quite well. The model may now be applied to optimize the process and to size a reactor for a specified load.

We can use the kinetic model to obtain a plot of the final composition of the mixture expressed as the mole fraction of amine functional groups versus propylene oxide, MDA stoichiometry. This is illustrated for the propoxylation at 85 °C in Fig. 5. From this plot, the level of propylene oxide can be selected to obtain the final desired composition of primary, secondary, and tertiary amine groups. At a feed ratio of propylene oxide to MDA equal to 3(a ratio of 1.5 moles of propylene oxide per mole of primary amine functional groups), the primary amines are practically eliminated: 50% of the amines are tertiary and 50% are secondary.

Because the activation energy of both k_1 and k_3 are essentially equivalent, this plot can be used over a broad temperature range.

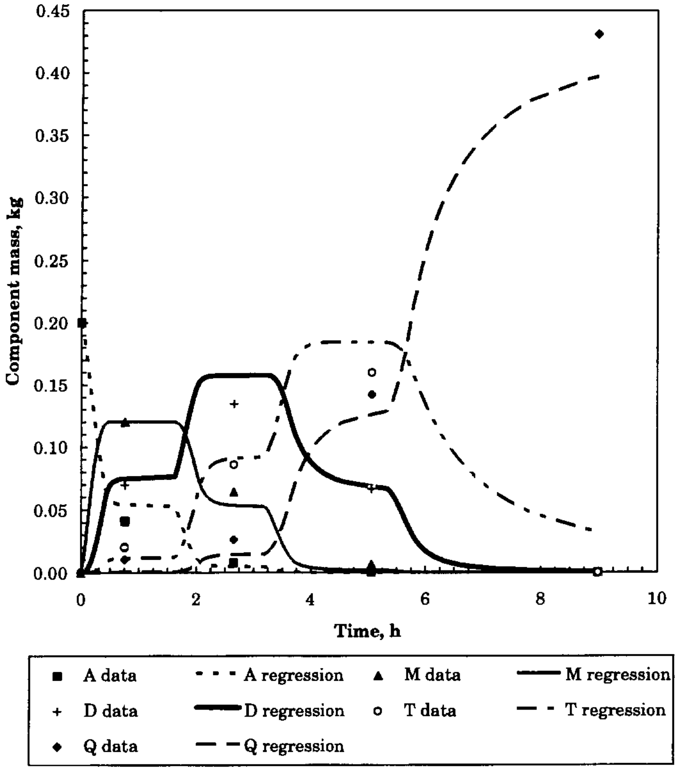


Fig. 4. Comparison of experimental and regression composition analysis for propoxylation at 85°C. (Note that D = D11 + D12.)

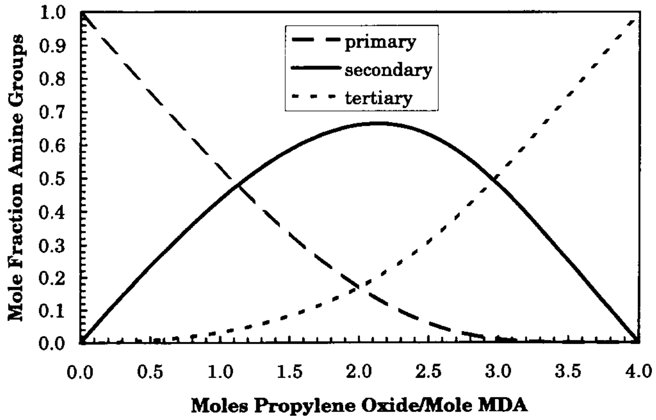


Fig. 5. Final distribution of amine functional groups in MDA as a function of the propylene oxide/MDA molar ratio at 85°C.

Finally, we can compare our results with Dobas et al [7]. The ratio of second-order rate constants for an individual primary amine group compared to a secondary amine group is given in our analysis as k_2/k_3. For propylene oxide we found this ratio to be approximately 5. Dobas et al. obtained a ratio of between 2 and 3 for various glycidyl ethers. This suggests that the stearic hindrance of the glycidyl ethers dominates the relative reaction rates much more so than for propylene oxide. To selectively reduce primary amines while maximizing the yield of secondary amines, smaller epoxides such as propylene oxide are preferred.

6. Conclusions

The simultaneous analysis and regression of reaction calorimetry rate data and analytical composition data for multiple experiments is a powerful and efficient methodology for obtaining fundamental kinetics. Also, using multiple feed ramps when investigating the kinetics yields data sets with a greater transient behaviour that are better suited for efficient kinetic analysis.

The reaction of methylenedianiline and propylene oxide can be described by a series of six second-order reactions with two independent rate constants both having similar activation energies. Compared to glycidyl ethers, propylene oxide is more selective in generating secondary amines and is preferred in processes to modify recycled polyols containing high levels of primary amines.

Acknowledgments

We would like to thank Dr. Dale Willcox of Air Products and Chemicals, Inc. for his valuable assistance in the mass spectroscopic analysis.

References

[1] H. Ulrich, A. Odinak, B. Tuckeer and A.A.R. Sayigh, Polym. Eng. Sci.,18 (1978)
[2] H. Ulrich, B. Tuker, A. Odinak and A. R. Gamache, Elastomers and Plastics, 11 (1979) 208.
[3] F. Simioni and S. Bisello, Cellular Polymers, 6 (1983) 281.
[4] J. Gerlock, J. Braslaw and M. Zinbo, Ind. Eng. Chem. Process Des. Dev., 23 (1984) 545.
[5] G. Bauer, Proceedings of the Polyurethanes World Congress 1991, p. 872.
[6] R.M. Machado and B.E. Farrel, US Patent 5,300,530 (1994).
[7] I. Dobas, J. Eichler and J. Klaban, Coll. Czech. Chem. Commun., 40 (1975) 2989.
[8] I.T. Smith, Polymer, 2 (1961) 95.
[9] Mettler Instruments AG, Greifensee, 1987.
[10] W. Hoffmann, Chimia, 43 (1989) 62.
[11] J.W.F. Stroessel and G. Kille, Chimia 44 (1990) 401
[12] R.N. Landau, D.G. Blackmond and Hsien-Hsin Tung, Ind. Eng. Chem. Res., 33 (1994) 814.
[13] P.E. Gill, W. Murray and M.H. Wright, Practical Optimization, Academic Press, London and New York, 1987.
[14] B.M. Yen, J.W. Mitchell, G.C. Achilles and R.M. Machado, GRaSP: A Generalized Kinetic Modeling Tool for Analyzing Complex Chemistry in Advanced Reactors, presented at Engineering Foundation: Reaction Engineering V Conf., St. Augustine, Florida, October 11,1995.