

Kinetics of the Zinc Fluoborate- and Hydrogen Ion-Catalyzed Hydrolyses of Butadiene Diepoxides

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Synopsis

Optimum conditions for the etherification of cotton cellulose rather than hydrolysis or solvolysis of the diepoxide had been found to occur with zinc fluoborate catalysis when the diepoxide/catalyst molar ratio was 10-20, and water/diepoxide ratio was less than 100. Data in the literature on specific reaction rates of hydrolysis of butadiene diepoxide at approximately 1M in the presence of zinc fluoborate 0.05M were not available, nor were there such data for the H⁺ catalyzed-hydrolysis of the diepoxide at a pH = 3.25, which was the pH of the zinc fluoborate-butadiene diepoxide solution. Therefore, kinetics of the hydrolysis of the racemic mixture of the *d,l*-isomers (BDO) and of the *meso*-isomer of butadiene diepoxide (called BDE) catalyzed by dilute zinc fluoborate and by dilute HCl at 25-90°C. have been investigated. Rates of hydrolysis of both BDO and BDE were measured by following the change in oxirane oxygen content with time at 25, 40, 60, 75, and 90°C. Analysis of the experimental data at each temperature by the modified Swain method confirmed the assumption of consecutive first order reaction kinetics for the opening of the first and second oxirane rings for both Zn(BF₄)₂ and H⁺-catalyzed reactions. The relative rates (k_{2z}/k_{1z}) for the overall reaction with Zn(BF₄)₂ catalysis exceeded unity at each temperature, while the relative rates (k_{2H}/k_{1H}) with H⁺ ion catalysis was always less than unity. Thus, with Zn(BF₄)₂ catalysis, the second oxirane oxygen ring opened more rapidly than the first; but with H⁺ catalysis, the reverse was true. Correction of specific reaction rate constants of the Zn(BF₄)₂-catalyzed hydrolysis for the H⁺ control rates produced the same net result observed in the overall reaction; i.e., the corrected k_2'/k_1' was much greater than unity. The zinc fluoborate-catalyzed hydrolysis was much faster than the H⁺-catalyzed hydrolysis of both rings. Enthalpies, entropies, and free energies of activation for both oxirane rings were calculated. Large negative entropies of activation indicated an S_N² mechanism for both ring openings.

INTRODUCTION

Zinc fluoborate-catalyzed reactions between cotton cellulose and the *meso* form of butadiene diepoxide (BDE) or the racemic mixture of the *d,l*-isomers (BDO) resulted in only very small add-ons of diepoxide to cotton regardless of molar ratios of reactants used.^{1,2} In contrast, other diepoxides, such as vinylcyclohexene dioxide or the diglycidyl ether of 1,4-butanediol, could be reacted with cotton to give various add-ons, depending on molar ratios of reactants used.³ Neither BDO nor BDE could be

reacted with cotton from aqueous solutions in the presence of zinc fluoborate to produce crease resistant cottons unless concentrated solutions of BDO or BDE were used.² It was originally thought that the differences in rates of hydrolysis or solvolysis of the diepoxides in the presence of dilute zinc fluoborate or hydrogen ions might account for differences observed in cellulose-diepoxide reactions. Literature data on specific reaction rates for the hydrolysis of available diepoxides at approximately 1M in the presence of 0.05M $Zn(BF_4)_2$ were not available, nor were there such data for the H^+ ion-catalyzed hydrolysis of the diepoxides at pH = 2-3, which were the pH values of the zinc fluoborate-diepoxide solutions previously found to give optimum reaction conditions with cotton cellulose. Therefore, the kinetics of such hydrolyses of several diepoxides were investigated from room temperature up to 90°C. This paper presents a study of the kinetics of hydrolysis of BDO and BDE. The overall rates of hydrolysis in the presence of $Zn(BF_4)_2$ at a pH = 3.25 were measured at 25, 40, 60, 75, and 90°C. and were then corrected for the rates of hydrolysis in the presence of H^+ ion at pH = 3.25 at the same temperatures. Enthalpies, entropies, and free energies of activation for H^+ - and $Zn(BF_4)_2$ -catalyzed ring openings of both oxirane rings have been calculated.

EXPERIMENTAL

Materials

The *d,l*-butadiene diepoxide (BDO) was a research grade racemic mixture obtained from the Koppers Company. It was fractionally distilled at 120 mm. of pressure. That fraction collected at 85°C. and used in rate studies had an epoxide equivalent of 2.37 eq./100 g. as determined by the method of Durbetaki,⁴ and a boiling point of 145°C. at 760 mm.

One sample of the *meso* butadiene diepoxide (BDE) was obtained from the Union Carbide Corporation. Additional BDE was prepared from 1,4-dichloro-2,3-epoxybutane by the method of Starcher.⁵ The BDE used in rate studies was that fraction collected at 38°C. at 15 mm. It had an epoxide value of 2.34 eq./100 g. as determined by the method of Durbetaki⁴ and a boiling point of 138°C. at 760 mm. In addition, both BDE and BDO were characterized by their infrared spectra in CCl_4 solution. Characteristic spectra of both diepoxides have been published previously.⁶

The $Zn(BF_4)_2$ catalyst was obtained from the Harshaw Chemical Company as a 40% aqueous solution ($d_4^{25} = 1.0466$ g./cc.).

Reagent grade glacial acetic acid and 30% hydrobromic acid in glacial acetic acid were used. The HBr titrant was standardized daily against Na_2CO_3 as the primary standard.

Procedure

For the zinc fluoborate-catalyzed rate studies, known weights (approximately 5 g.) of BDO or BDE were dissolved in 45.00 ml. of conductivity water containing 0.5626 g. of $Zn(BF_4)_2$ and shaken in closed

flasks immersed in an oil bath thermostatically controlled to $\pm 0.05^\circ\text{C}$. The pH values of the reaction mixtures, measured with a Beckman Model GS pH meter to ± 0.02 pH unit, were found to be constant throughout the timed reactions. The pH values, followed from 0 to 24 hr. for the reaction mixtures at 25, 40, 63, 75, and 90°C . were 3.25 ± 0.02 .

For controlled rate studies in the absence of $\text{Zn}(\text{BF}_4)_2$, known weights (approximately 5 g.) of butadiene diepoxide were dissolved in 45.00 ml. of conductivity water which was adjusted to pH of 3.25 with HCl. These rate studies were made to determine if butadiene diepoxide at 1M in solutions of H^+ of pH 3.25 were hydrolyzed at the same rate as in the presence of 0.05M $\text{Zn}(\text{BF}_4)_2$ catalyst. Literature values for H^+ -catalyzed butadiene diepoxide hydrolysis rates^{7,8} were at different molar ratios of epoxide to H^+ ions and at different ionic strengths than needed in these investigations. The observed rates for the zinc fluoborate catalyzed reactions were corrected for these control rates.

For each rate experiment, aliquots were withdrawn with 1-ml. serological pipet at timed intervals and transferred to tared Erlenmeyer flasks. Weighed samples were analyzed for oxirane oxygen by the method of Durbetaki⁴ and corrected for blank determinations including water and catalyst in every case. All concentrations were expressed in milliequivalents of oxirane oxygen per gram of solution.

TREATMENT OF DATA

Cartesian graphs showing the change in concentration of oxirane oxygen with reaction time were plotted at each of the temperatures investigated. Initially, semilogarithmic graphs of the data were analyzed in attempts to detect changes in slope beyond the half-concentration point by the method of least squares. Unlike the study with vinylcyclohexene dioxide,⁹ in which the ratio of rates of opening of the first and second oxirane rings were 50:1 at 25°C ., the rates of opening of the two oxirane rings of butadiene diepoxide were not different enough to allow for the determination of k_1 and k_2 by statistical evaluation of the linear semilogarithmic plots. Therefore, the data were analyzed by the modified Swain method.^{10,11} Details of the method used have been previously described.⁹ Experimentally, it was found that the concentration versus time curves for the BDO and BDE at each temperature were identical. Therefore, for each temperature, one curve representing all measurements for both BDE and BDO could be used to determine time-percentage reaction relationships for the 15%, 35%, and 70% completion points needed for the Swain method. Figure 1 is typical of experimental data obtained at one temperature and plotted on a semilogarithm paper for convenience.

Enthalpies, entropies, and free energies of activation of both oxirane rings were computed from the rate constants for the overall reaction and for the H^+ ion catalyzed reaction. Rate constants of the zinc fluoborate-catalyzed reaction were corrected for H^+ catalysis.

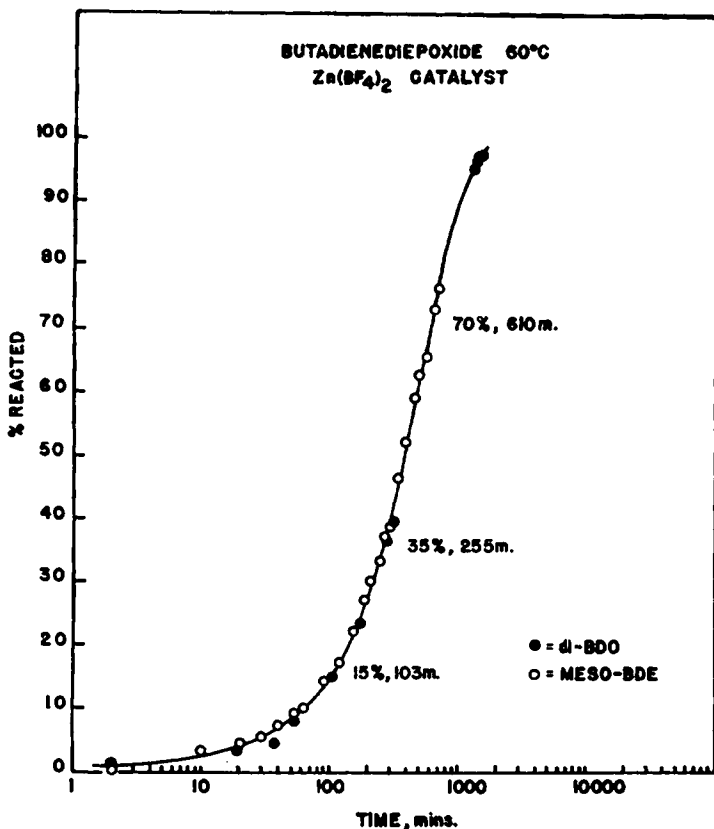


Fig. 1. Typical plot of per cent of oxirane oxygen reacted vs. time in minutes for the zinc fluoborate-catalyzed hydrolysis of butadiene diepoxide at 60°C.

RESULTS AND DISCUSSION

The specific reaction rate constants denoted by k_z and the relative rates for the overall reaction when butadiene diepoxide was catalyzed by $\text{Zn}(\text{BF}_4)_2$ are reported in Table I. Since it was experimentally determined that the change in oxirane oxygen content with time was the same for BDO and BDE at each temperature, the rate constants for the opening of the first (k_{1z}) and the second (k_{2z}) oxirane rings apply to reaction with the meso form as well as with the *d,l*-isomer. At each temperature, k_{2z} exceeds k_{1z} with the relative rates, k_{2z}/k_{1z} , ranging from 1.1 to 1.8. Thus, the second oxirane ring opens more rapidly than the first. However, as the temperature is increased from 25 to 90°C., the ratio k_{2z}/k_{1z} becomes less and approaches unity, indicating that at higher temperatures both rings tend to open at the same rate.

In the case of consecutive first-order reactions,

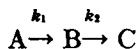


TABLE I
Rate Constants for Opening of First and Second Oxirane Rings in $\text{Zn}(\text{BF}_4)_2$ -Catalyzed Hydrolysis of Butadiene Diepoxide

Temp., °C.	Specific reaction rate constants		Relative rates k_{2s}/k_{1s}
	$k_{1s} \times 10^4$, min. ⁻¹	$k_{2s} \times 10^4$, min. ⁻¹	
25	1.14	1.82	1.60
40	5.52	9.69	1.76
60	28.73	33.85	1.18
75	80.57	91.09	1.13
90	320.63	371.16	1.16

A is the concentration of the diepoxide A , B is the concentration of the monoepoxide B after hydrolysis of the first oxirane ring, and C is the concentration of the final product C after the opening of both epoxide rings. Experimentally, C is not measured directly but bears a direct relationship to the oxirane oxygen content, T . Values of A , B , and T were computed from eqs. (1)–(3).

$$A = A_0 e^{-k_1 t} \quad (1)$$

$$B = [A_0 k_1 / (k_2 - k_1)] (e^{-k_1 t} - e^{-k_2 t}) \quad (2)$$

$$T = 2A + B \quad (3)$$

Figure 2 is a typical plot of the calculated concentrations A , B , and T as a function of time. In this instance, experimentally determined rate constants at 60°C. were substituted in the above equations. Observed values of T are shown as circles, and the standard error of estimate was determined to be 0.04. The agreement between experimental and theoretical data confirm the assumption of consecutive first order reactions at each temperature.

Enthalpies, entropies, and free energies of activation for the hydrolysis of the first and second oxirane ring openings are recorded in Table II. The apparent energies of activation (ΔH^*) were calculated from an Arrhenius plot, i.e., $\log k$ versus $1/T$, the equation of which was determined by the method of least squares. The enthalpy (ΔH^*) value for the opening of the second oxirane ring is significantly lower than that for the opening of the first oxirane ring of butadiene diepoxide. This is in direct contrast to results found with vinylcyclohexene dioxide where the apparent activation energy of the first oxirane ring opening was significantly smaller than the enthalpy of the second ring opening.⁹

Entropies of activation (ΔS^*) (Table II) were computed from the equation:

$$\Delta S^* = R[\ln k - \ln (KT/h) + (\Delta H^*/RT) - 1] \quad (4)$$

where k is the hydrolysis constant in sec.⁻¹; ΔH^* is the enthalpy of activa-

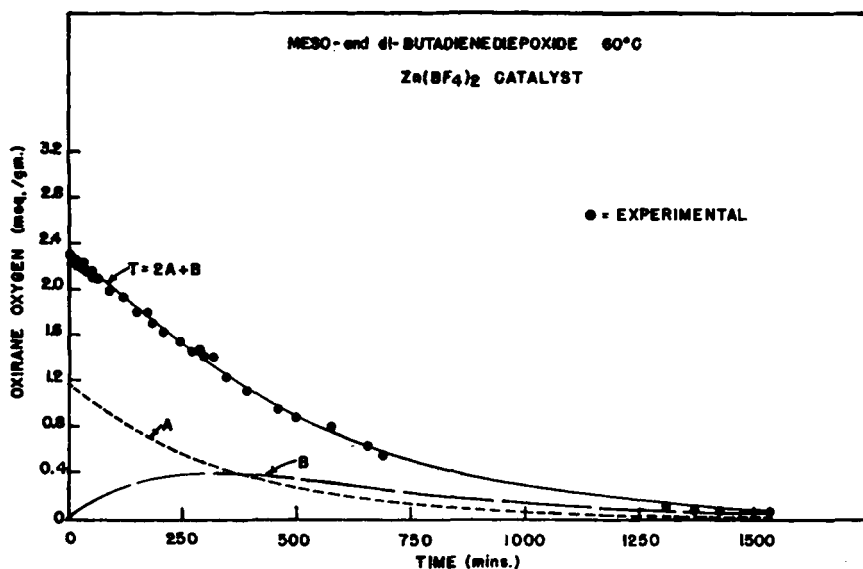


Fig. 2. Plot of calculated concentrations in meq./g. solution of diepoxide (*A*), monoepoxide (*B*), and total oxirane oxygen (*T*) as a function of time in minutes at 60°C. Curves calculated on assumption of consecutive first-order reactions.

tion; *R*, *K*, and *h* are the molar gas, Boltzman, and Planck constants, respectively.

Free energies of activation (ΔF^*) were calculated at each temperature from the equation:

$$\Delta F^* = \Delta H^* - T\Delta S^* \quad (5)$$

Included in Table II are the ΔH^* , average ΔS^* and ΔF^* at 25°C. values for the overall $\text{Zn}(\text{BF}_4)_2$ -catalyzed reaction. The data indicate a greater decrease in entropy of activation with the opening of the second oxirane ring of butadiene diepoxide; thus, indicating a more ordered transition state complex. This finding is also in direct opposition to results obtained with zinc fluoborate catalysis of vinylcyclohexene dioxide.⁹ As a result of the lower enthalpy but greater entropy of activation, the free energies of activation of the opening of both rings are approximately the same. Differences in free energies of activation of first and second ring openings

TABLE II
Enthalpies, Entropies, and Free Energies of Activation of Oxirane Oxygen Ring Openings in $\text{Zn}(\text{BF}_4)_2$ -Catalyzed Hydrolysis of Butadiene Diepoxide

Ring opening	Enthalpy ΔH^* , kcal./mole	Entropy ΔS^* , cal./mole-deg.	Free energy ΔF^* (25°C.), cal./mole
1st Oxirane	18.2	-25.93	25,883
2nd Oxirane	16.7	-29.75	25,573

become less as the temperature is increased, in agreement with the fact that the ratio k_{2H}/k_{1H} approaches unity at higher temperatures indicating that at higher temperatures both rings open at approximately the same rate.

To determine the rate of hydrolysis of butadiene diepoxide solutions catalyzed by H^+ ions in low concentration, similar studies were made on butadiene diepoxide solutions with the same pH as that of $Zn(BF_4)_2$ -catalyzed solutions (i.e., pH = 3.25). Specific reaction rate constants, denoted by k_H , and relative rates for the first and second oxirane ring openings are recorded in Table III. In contrast to $Zn(BF_4)_2$ catalysis, the specific rate constants for the opening of the first oxirane ring are greater than those for the second; and, hence, the ratio of k_{2H}/k_{1H} is less than unity. Thus, with H^+ ion catalysis, the first oxirane ring opens more rapidly.

TABLE III

Rate Constants for Opening of First and Second Oxirane Rings in Dilute HCl-Catalyzed Hydrolysis of Butadiene Diepoxide

Temp., °C.	Specific reaction rate constants		Relative rates k_{2H}/k_{1H}
	$k_{1H} \times 10^4$, min. ⁻¹	$k_{2H} \times 10^4$, min. ⁻¹	
25	0.46	0.11	0.24
40	3.49	0.35	0.10
60	19.70	2.97	0.15
75	50.08	21.49	0.43
90	140.99	48.25	0.34

The ΔH^* , average ΔS^* , and ΔF^* at 25°C. values for the H^+ ion-catalyzed reactions are shown in Table IV. The enthalpy of activation for the second oxirane ring opening of butadiene diepoxide with H^+ ion catalysis is significantly greater than that of the first, and the smaller decrease in entropy of activation of the second oxirane ring opening indicates a less ordered transition state complex. The free energy of activation of the second oxirane ring opening at each temperature exceeds that of the first oxirane ring opening. Thus, with H^+ ion catalysis, the first oxirane ring of butadiene diepoxide opens faster.

TABLE IV

Enthalpies, Entropies, and Energies of Activation of Oxirane Oxygen Ring Openings in H^+ Ion-Catalyzed Hydrolysis of Butadiene Diepoxide

Ring opening	Enthalpy ΔH^* , kcal./mole	Entropy ΔS^* , cal./mole	Free energy ΔF^* (25°C.), cal./mole
1st Oxirane	18.6	-25.98	26,281
2nd Oxirane	21.2	-21.19	27,492

Comparison of the data in Tables II and IV shows that for either system, the enthalpies, entropies, and free energies of activation of the first oxirane ring opening are essentially equal with the two catalysts. On the other hand, the differences between enthalpies, entropies, and free energies of activation noted with the two catalyst systems for the opening of the second oxirane ring indicate the influence of the degree of order of the activated complex upon the ease of opening of the second ring. The larger negative entropy in the case of the $\text{Zn}(\text{BF}_4)_2$ -catalyzed ring opening indicates a more ordered transition state complex, but the much lower enthalpies with the $\text{Zn}(\text{BF}_4)_2$ catalysis results in a smaller free energy of activation for the opening of the second oxirane ring with $\text{Zn}(\text{BF}_4)_2$ catalysis than with H^+ ion catalysis only.

TABLE V
Corrected Rate Constants for the Opening of First and Second Oxirane Rings in $\text{Zn}(\text{BF}_4)_2$ -Catalyzed Hydrolysis of Butadiene Diepoxide

Temp., °C.	Specific reaction rate constants		Relative rates k_2'/k_1'
	$k_1' \times 10^4$, min. ⁻¹	$k_2' \times 10^4$, min. ⁻¹	
25	0.69	1.71	2.48
40	2.04	9.34	4.59
60	9.03	30.87	3.42
75	30.49	69.61	2.28
90	179.64	322.89	1.80

Values of the specific reaction rate constants of the $\text{Zn}(\text{BF}_4)_2$ catalyzed hydrolysis have been corrected for H^+ ion catalysis, and these data are shown in Table V. The corrected specific reaction rate constants, k' , are equal to $(k_z - k_H)$, where k_z denotes the overall specific rate constants from Table I and k_H denotes those from Table III. Relative rates have also been included. The corrected rate constants show k_2' to exceed k_1' at every temperature, giving the same net results obtained with the overall reaction. Thus, the $\text{Zn}(\text{BF}_4)_2$ -catalyzed hydrolysis is much faster than the H^+ ion-catalyzed hydrolysis of both ring openings, and k_2'/k_1' values are always greater than unity.

The fact that the $\text{Zn}(\text{BF}_4)_2$ catalysis results in a faster rate of opening for the second oxirane ring while the H^+ ion catalysis results in a faster rate of opening for the first oxirane ring of butadiene diepoxide suggests a difference in mechanisms. A possible explanation is that after the first hydrolysis step, the hydroxyl group alpha to the epoxide can form a five-membered ring through an intramolecular hydrogen bond with the oxirane oxygen. Such bonding would make it harder for H^+ ions to protonate or activate the remaining oxirane oxygen as indicated by largest experimental ΔF^* for this step. However, chelation of Zn^{++} ions between OH^- and oxirane oxygen may occur in 1,2-epoxy-3,4-butanediol, thus

bringing Zn^{++} ions closer to the oxirane oxygen in a more ordered arrangement, as indicated by the largest negative entropy of activation in this case. Further studies will be made to determine if it is the Zn^{++} ion or the BF_4 ion which is responsible for observed differences in rates between HCl and $Zn(BF_4)_2$ -catalyzed reactions.

Epoxides are known to hydrolyze by either an S_N1 or an S_N2 mechanism. In either case, the epoxide reacts instantaneously with the H^+ ion or other Lewis acid. In the former, the rate determining step is the slow opening of the conjugated acid of the epoxide ring to form a carbonium ion, which then combines, in the fast step, with the anion of the solvent (water) molecule to form the product. In the S_N2 mechanism, the conjugate acid of the epoxide ring reacts bimolecularly with a solvent molecule (water) to form the diol. Under the experimental conditions of these investigations, both types of mechanisms should follow first order kinetics; but orientation is important only in the S_N2 mechanism. In this investigation, the hydrolysis of butadiene diepoxide followed consecutive first order reaction kinetics; and large negative entropies of activation were observed with the opening of both oxirane rings. These large negative entropies demonstrate the importance of the orientation factor and have been interpreted as indicating an S_N2 mechanism for the opening of the two rings of butadiene diepoxide. These results are in agreement with those obtained earlier for the hydrolysis of vinylcyclohexene dioxide under similar conditions where the concentration of epoxide is large with respect to concentration of catalyst. Additionally, it has been found that the ΔH^* , ΔS^* , and ΔF^* values for the first oxirane ring of butadiene diepoxide are the same as the corresponding values for the opening of the *exo* or vinyl oxirane ring of vinylcyclohexene dioxide. This is to be expected because of the similarity of conditions existing at the time of the opening of the *exo* or vinyl oxirane ring of vinylcyclohexene dioxide and at the onset of hydrolysis of BDO. This is, after the *endo* oxirane ring of vinylcyclohexene dioxide has been opened, the *exo* or vinyl oxirane ring is adjacent to a saturated ring, a condition which prevails when hydrolysis is initiated in butadiene diepoxide.

Results of these findings are in accord with observations in this laboratory on the Lewis acid-catalyzed reactions between cotton cellulose and diepoxides. The oxirane rings of butadiene diepoxide, like those of several other diepoxides, open readily in the presence of hydrogen ions, particularly in relatively concentrated solutions of strong acids, but these diepoxides do not react with cotton when catalyzed by H^+ ions only. The fact that these same diepoxides will react with cellulose when catalyzed by certain fluoborates, particularly zinc fluoborate in the absence of large concentrations of H^+ ions, indicates that reaction with cellulose requires conditions which will favor an S_N2 mechanism over an S_N1 mechanism. It is only by an S_N2 mechanism that the cellulose molecule can compete with the solvent molecule in a bimolecular reaction with the conjugate acid of the epoxide.

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Trade names have been used to identify materials used in this investigation, and such use does not imply endorsement or recommendation by the U. S. Department of Agriculture over other products not mentioned.

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Résumé

On rencontre les conditions optima pour l'éthérisation de la cellulose de coton de préférence à l'hydrolyse ou la solvolysse du diépoxyde lors de la catalyse au fluoborate de zinc pour un rapport de diépoxyde catalyseur de 10 à 20 et pour un rapport eau/diépoxyde inférieur à 100. On ne possède pas les données de la littérature concernant les vitesses spécifiques de la réaction d'hydrolyse du diépoxyde de butadiène à approximativement 1 M en présence de fluoborate de zinc à 0.05 M; il en est de même pour les données de l'hydrolyse du diépoxyde sous catalyse H^+ à un pH = 3.25 (ce qui est le pH de la solution du diépoxyde de butadiène/fluoborate de zinc). Dès lors on a étudié les cinétiques d'hydrolyse du mélange racémique d'isomères *d,l*-BDO) et d'isomères-*meso* du diépoxyde de butadiène (appelés BDE) catalysée par du fluoborate de zinc dilué et par HCl dilué de 25° à 90°C. Les vitesses d'hydrolyse des BDO et BDE ont été mesurées en suivant les changements de concentration en oxygène dans les oxiranes en fonction du temps à 25, 40, 60, 75 et 90°C. L'analyse des données expérimentales à chaque température par la méthode modifiée de Swain confirme l'hypothèse de cinétiques de réactions consécutives de premier ordre pour l'ouverture du premier et du second noyau d'oxirane pour les réactions catalysées $Zn(BF_4)_2$ et H^+ . Le rapport des vitesses (k_{22}/k_{12}) pour la réaction complète sous catalyse $Zn(BF_4)_2$ excède l'unité pour toutes les températures, tandis que le rapport des vitesses (k_{2H}/k_{1H}) sous catalyse par H^+ est toujours inférieur à l'unité. Donc sous catalyse $Zn(BF_4)_2$ le deuxième noyau d'oxirane s'ouvre plus rapidement que le premier; mais avec la catalyse H^+ le contraire est vrai. La correction des constantes de vitesse de la réaction spécifique de l'hydrolyse catalysée par $Zn(BF_4)_2$ pour contrôler les vitesses de H^+ , produit le même résultat que celui qui est observé dans la réaction complète, p.ex.: le rapport corrigé k'_2/k'_1 était beaucoup plus grand que l'unité. L'hydrolyse catalysée par le fluoborate de zinc était beaucoup plus rapide que l'hydrolyse des 2 noyaux catalysée par les H^+ . Les enthalpies, entropies et les énergies libres d'activation des 2 noyaux d'oxiranes ont été calculées. Les valeurs fortement négatives des entropies d'activation indiquent un mécanisme S_N^2 pour les 2 ouvertures des noyaux

Zusammenfassung

Die beste Bedingung für die Verätherung von Baumwollzellulose (eher als Hydrolyse und Solvolyse des Diepoxyds) ist Zinkfluoborat-katalyse mit einem Molverhältnis des zu katalysierenden Diepoxyds von 10 bis 20 und einem Wasser-Diepoxydverhältnis <100 . Weder über die Reaktionsdaten der Hydrolyse von Butadiendiepoxyd bei ungefähr $1 M$ in Anwesenheit von Zinkfluoborat $0,05 M$ noch über die H^+ -katalysierte Hydrolyse von Diepoxyd bei $pH = 3,25$, dem pH -Wert der Zinkfluoboratbutadiendiepoxydlösung konnten Angaben in der Literatur gefunden werden. Daher wurde die Hydrolysenkinetik einer racemischen Mischung von *d,l*-Isomeren (BDO) und von *Meso*-Isomeren von Butadiendiepoxyd (BDE) bei Katalyse mit verdünntem Zinkfluoborat und verdünnter HCl von 25° bis $90^\circ C$. untersucht. Die Hydrolysen-geschwindigkeit von BDO und BDE wurde durch Messung der Änderung des Oxiran-Sauerstoffgehaltes mit der Zeit bei $25, 40, 60, 75$ und $90^\circ C$. bestimmt. Die Analyse der Untersuchungsergebnisse bei jeder Temperatur nach der modifizierten Methode von Swain bestätigte die Annahme einer Kinetik von Folgereaktionen erster Ordnung für die Öffnung des ersten und zweiten Oxiranringes sowohl für $Zn(BF_4)_2$ als auch für H^+ -katalysierte Reaktionen. Die Relativgeschwindigkeit (k_{2z}/k_{1z}) der Bruttoreaktion bei $Zn(BF_4)_2$ -Katalyse war bei jeder Temperatur grösser als eins, während die Relativgeschwindigkeit (k_{2H}/k_{1H}) bei H^+ -Ionenkatalyse immer kleiner als eins war. Daher öffnete sich der zweite Oxiran-Sauerstoffring mit $Zn(BF_4)_2$ als Katalysator schneller als der erste, im Gegensatz zur H^+ -katalysierten Reaktion. Die Korrektur der spezifischen Reaktionsgeschwindigkeitskonstanten der $Zn(BF_4)_2$ -katalysierten Hydrolyse für die H^+ -bestimmte Geschwindigkeit ergab dasselbe Nettoresultat wie die Bruttoreaktion; d.h. das korrigierte k_2'/k_1' war sehr viel grösser als eins. Die Zinkfluoborat-katalysierte Hydrolyse verlief viel schneller als die H^+ -katalysierte Hydrolyse beider Ringe. Enthalpie, Entropie und freie Energie der Aktivierung beide Oxiranringe wurde berechnet. Die grosse negative Aktivierungsentropie spricht für einen S_N^2 -Mechanismus bei der Öffnung beider Ringe.

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