Kinetics and Mechanism of Addition of Parabanic Acid (Imidazolidine-2,4,5-trione) to Oxiranes

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Received 5 March 2002; accepted 16 October 2002

DOI 10.1002/kin.10104

ABSTRACT: The results of studies on the kinetics of reaction of 1 mol of parabanic acid (imidazolidine-2,4,5-trione) with 1 mol of ethylene oxide (oxirane) or propylene oxide (2-methyloxirane) carried out in the presence of triethylamine catalyst in dimethylsulfoxide solution are presented. A rate equation describing the reaction is presented and the mechanism proposed. The validity of the proposed mechanism is proved by instrumental analytical methods. The effect of temperature is also presented and the thermodynamic parameters of the reaction evaluated. © 2002 Wiley Periodicals, Inc. Int J Chem Kinet 35: 73–80, 2003

INTRODUCTION

Information on the kinetics of reactions of cyclic imides with oxiranes is rather scarce in literature as opposed to that on reactions of oxiranes with other active hydrogen-containing organic compounds, such as alcohols [1–3], thiols [4,5], phenols [6], carboxylic acids [7–11], and amines or amides [12–14], that are carried out in the presence of various catalysts and in different solvents [15–18]. The methodology of studying the kinetics of these reactions comprises three different approaches. One of them consists in following the amount of unreacted oxirane by measuring the partial pressure of ethylene oxide (oxirane) or propylene oxide (2-methyloxirane) over reacting mixture [19]. The second method involves chemical determination (usually by titration) of unreacted oxirane [20,21], and the third consists in following the volume contraction in reaction mixture [22]. The first method is not frequently used and because of technical problems can be applied only to systems where a large excess of oxirane is used. The chemical methods are not too accurate, particularly for systems with amine catalysts. The simplest and most convenient seems to be the dilatometric method, which is particularly useful for the imide–oxirane system studied in this work.

We used parabanic acid containing two imide groups. It reacts with oxiranes in two steps. First, N-hydroxyalkyl hydroparabanate (**I**) is formed and then N,N'-bis(hydroxyalkyl) parabanate (**II**) [23],

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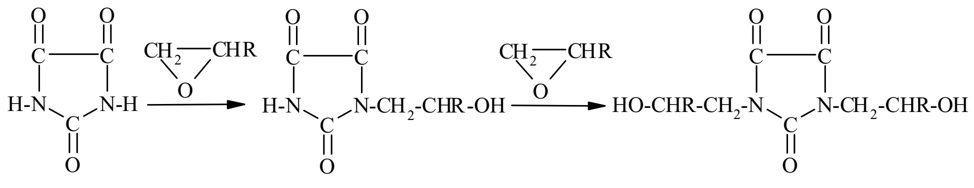
Contract grant sponsor: Polish Committee of Scientific Research.
Contract grant number: 4T09 B 010 22.

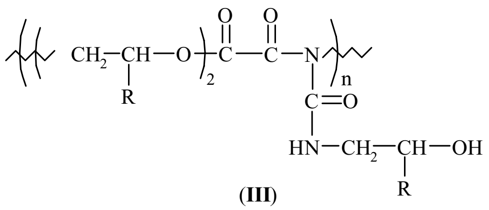
according to the following reaction:



(I) (II)

with R = $-$H, $-CH_3$.

It was found that the presence of triethylamine considerably reduces the reaction time. The optimal temperature for the reaction was 25–50°C. Further elevation of temperature leads to formation of polymeric products of the following structure [23]:



(III)

with R = $-$H, $-CH_3$.

In this work we have studied the kinetics of of reaction of 1 mol of parabanic acid with 1 mol of ethylene oxide or propylene oxide. The reaction products are the respective *N*-hydroxyalkyl hydroparabanates. We have limited ourselves to this molar ratio because in the presence of an excess of oxiranes, a more complex reaction mixture is obtained because of side reactions of oxirane with hydroxy groups and, at an even higher excess, to an opening of parabanic acid ring and formation of the earlier mentioned polymeric products (**III**). A report on the reaction of parabanic acid with an excess of oxiranes will be the subject of a forthcoming paper.

EXPERIMENTAL

Materials

Parabanic acid was obtained as described elsewhere [24]. Ethylene oxide and propylene oxide were reagent grade products supplied by Fluka (Switzerland). Triethylamine was a regent grade product of Avocado (Germany). Dimethyl sulfoxide (pure, Avocado) was dried on molecular sieves A4, a product of POCh (Poland).

Rate Measurements

In a 50-cm^3 measuring flask, a predetermined amount of parabanic acid was weighed (to within 0.1 mg). The content was then dissolved in ca. 30 cm^3 of dimethyl sulphoxide by placing the flask in a warm water bath. The solution was then brought to a desired temperature (30, 35, 40, 45, or 50°C (±0.05°C)) and a calculated amount of triethylamine was added to the flask. The volume was then adjusted using properly preheated dimethyl sulphoxide.

The effect of parabanic acid concentration on the rate of reaction was determined at constant oxirane concentration equal to 0.25 mol/dm^3, changing the acid concentration in the range 1.0–2.0 mol/dm^3 at 0.5 mol/dm^3 intervals.

The effect of catalyst concentration was studied at the constant parabanic acid (1.0 mol/dm^3) and oxirane (1.0 mol/dm^3) concentrations. The catalyst concentration was changed in the range 0.1–0.5 mol/dm^3 at 0.1 mol/dm^3 intervals.

The effect of temperature was studied at the constant parabanic acid (1.0 mol/dm^3), oxirane (1.0 mol/dm^3), and triethylamine (0.5 mol/dm^3) concentrations. Temperature was changed in the range 30–45°C in the case of ethylene oxide or 35–50°C for propylene oxide at 5°C intervals.

A dilatometer of total volume of ca. 45 cm^3 was used, equipped with a 40-cm long capillary of inner diameter 1 mm. Before it was filled it was kept at reaction temperature for at least 15 min. The reaction time was measured from the moment of mixing the reactants. The first reading of meniscus level was usually made after 10 min, which was needed to fill in the dilatometer and bring the mixture to reaction temperature. The next readings were made after constantly increasing time intervals until the meniscus level stabilized. The initial level of meniscus was calculated by extrapolating the readouts to the time $t = 0$. The values from the conversion range of oxirane 0.2–0.8 taken from smoothed readout curves at conversion intervals 0.05 were used to obtain rate equations.

The system with ethylene oxide (EO) was the reference one. The relative activity of propylene oxide, r_{PO}, was calculated as the ratio of rate constants k_{PO} and k_{EO} determined at the same temperature:

$$r_{PO} = \frac{k_{PO}}{k_{EO}} \qquad (1)$$

The Gibbs activation energy was calculated using the equation

$$\Delta G^{\neq} = RT \cdot \left(23.764 - \ln \frac{k}{T}\right) \qquad (2)$$

By plotting $\Delta G^{\neq}$ vs. T a straight line was obtained with activation enthalpy and entropy of the reaction as the coefficients of the line:

$$\Delta G^{\neq} = \Delta H^{\neq} - T \cdot \Delta S^{\neq} \qquad (3)$$

In Eqs. (2) and (3) T is the temperature of addition, k is the rate constant, R is the gas constant, and $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ are the Gibbs free energy, enthalpy, and entropy of activation, respectively.

Analytical Methods

Conductometry. The conductivity of the solutions of parabanic acid and triethylamine was measured at 20°C (±0.1°C) using a Radelkis OK-102/1 conductometer (Hungary). Solutions of parabanic acid, triethylamine, and mixtures thereof in water were prepared with the same total concentrations 0.5 mol/dm^3. A 20-cm^3 sample of each solution was placed in the measuring cell and its conductivity measured. Then the sample was diluted with another 20 cm^3 of water and the conductivity measured again. The procedure was continued until the system reached conductivity close to that of pure water. Conductivity of aqueous solutions of mixtures of parabanic acid and triethylamine in which molar ratios of components changed in the range from 0 to 1 in 0.1 intervals were also measured. The total concentration of the solutions was constant and equal to 0.25 mol/dm^3.

^{1}H NMR and IR Spectra

^{1}H NMR spectra were recorded using a BS-586A 80 MHz spectrometer (Tesla, Czechoslovakia). The solvent was d_6-DMSO, and hexamethyldisiloxane was the internal standard. IR spectra were recorded using a Paragon 1000 FT spectrometer (Perkin-Elmer). The samples were prepared in the form of KBr tablets.

RESULTS AND DISCUSSION

The study aimed at finding

- a general rate equation describing the reaction of addition of parabanic acid to ethylene oxide or propylene oxide;
- activation parameters of the reactions; and
- possible mechanism of the reactions.

The temperature range of the experiments was limited by the relatively low reaction rate, on one hand, and a danger of quick evaporation of volatile oxirane (boiling points 14 and 34°C for EO and PO, respectively) on the other. The study was carried out in DMSO solutions. The solvent dissolves parabanic acid very well.

Parabanic acid has been found to react with ethylene oxide (subscript B) following the first-order rate equation with respect to oxirane (Table I):

$$V = \frac{-\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} = k \cdot c_\mathrm{B} \qquad (4)$$

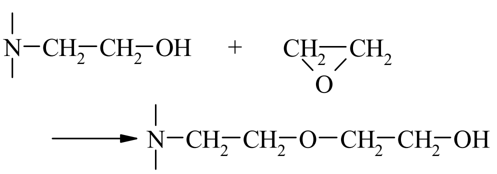
The relation is correct provided no subsequent reactions take place in the system, i.e., reactions of

Table I The Rate Constants k_n of the Reaction of Imide Groups of Parabanic Acid (AH) with Ethylene Oxide (B) in the Presence of Triethylamine Catalyst at 40°C as Calculated Assuming Reaction Order n with Respect to Ethylene Oxide

No.	t (min)	Oxirane Conversion, p	$k_{1/2}$ (10^{-5} s^{-1}mol$^{1/2}$ dm$^{-3/2}$)	k_1 (10^{-5} s^{-1})	$k_{3/2}$ (10^{-5} s^{-1}mol$^{-1/2}$ dm$^{3/2}$)
1	140	0.204	2.18	4.55	0.955
2	180	0.246	2.18	4.63	0.981
3	225	0.295	2.23	4.80	1.04
4	285	0.350	2.18	4.79	1.06
5	330	0.390	2.15	4.80	1.08
6	405	0.449	2.13	4.87	1.12
7	480	0.500	2.06	4.81	1.13
8	560	0.549	2.02	4.84	1.18
9	660	0.600	1.97	4.85	1.22
10	750	0.640	1.90	4.81	1.25
11	900	0.698	1.82	4.78	1.30
12	1050	0.740	1.74	4.76	1.35
13	1320	0.798	1.61	4.60	1.38

The initial concentrations were $c_{0\mathrm{AH}} = 2.0001$ mol/dm^3; $c_{0\mathrm{B}} = 0.2557$ mol/dm^3; $c_\mathrm{cat} = 0.5112$ mol/dm^3.

N-hydroxyalkyl groups with unreacted oxirane:



$$\text{N-CH}_2\text{-CH}_2\text{-OH} + \text{CH}_2\text{-CH}_2\text{(O)} \longrightarrow \text{N-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH} \tag{5}$$

To eliminate an effect of these reactions, a large excess of imide groups (subscript AH) with respect to oxirane was applied. Their concentration enter into the rate equation hidden in the rate constant k, according to equation

$$k = k' \cdot c_{\text{AH}}^{m} \tag{6}$$

By applying 8-, 12-, and 16-fold excess of imide groups with respect to ethylene oxide, the values of m and k' have been evaluated by the least-squares method (correlation coefficient $r = 0.9986$). By introducing Eq. (6) into Eq. (4) with $m = 1/2$ one obtains:

$$V = k' \cdot c_{\text{AH}}^{1/2} \cdot c_{\text{B}} \tag{7}$$

If Eq. (7) well described the reaction of addition of parabanic acid to ethylene oxide, the value of k' would have been the same as that of the same constant in Eq. (9) (later in the text), where no constancy of imide group concentration was assumed and correction was made according to

$$V = k'(c_{0\text{AH}} - pc_{0\text{B}})^{1/2}(1-p)c_{0\text{B}} \tag{8}$$

where "0" in the subscript denotes the initial concentration of reagents and p is the conversion of oxirane measured dilatometrically.

Thus, by integrating rate equation (8) one obtains

$$k' = \frac{1}{t}\left[\frac{1}{\sqrt{c_{0\text{AH}} - c_{0\text{B}}}} \times \left(\ln\left|\frac{-\sqrt{c_{0\text{AH}} - pc_{0\text{B}}} - \sqrt{c_{0\text{AH}} - c_{0\text{B}}}}{-\sqrt{c_{0\text{AH}} - pc_{0\text{B}}} + \sqrt{c_{0\text{AH}} - c_{0\text{B}}}}\right| - \ln\left|\frac{-\sqrt{c_{0\text{AH}}} - \sqrt{c_{0\text{AH}} - c_{0\text{B}}}}{-\sqrt{c_{0\text{AH}}} + \sqrt{c_{0\text{AH}} - c_{0\text{B}}}}\right|\right)\right] \tag{9}$$

From the data in Table II it follows that the values of k' calculated using the two methods are very close to each other. A difference becomes apparent only when there is a relatively small (eightfold) excess of imide groups with respect to oxirane. At this ratio of reagents, the effect of subsequent reactions of ethylene oxide with hydroxyethyl groups, that are slower than reactions of imide groups, starts to show up.

The effect of catalyst concentration was studied at the twofold excess of the active imide (AH) groups of parabanic acid with respect to ethylene oxide. The relation between catalyst concentration and the rate constant calculated according to Eq. (9) is

$$k' = k'' \cdot c_{\text{cat}}^{z} \tag{10}$$

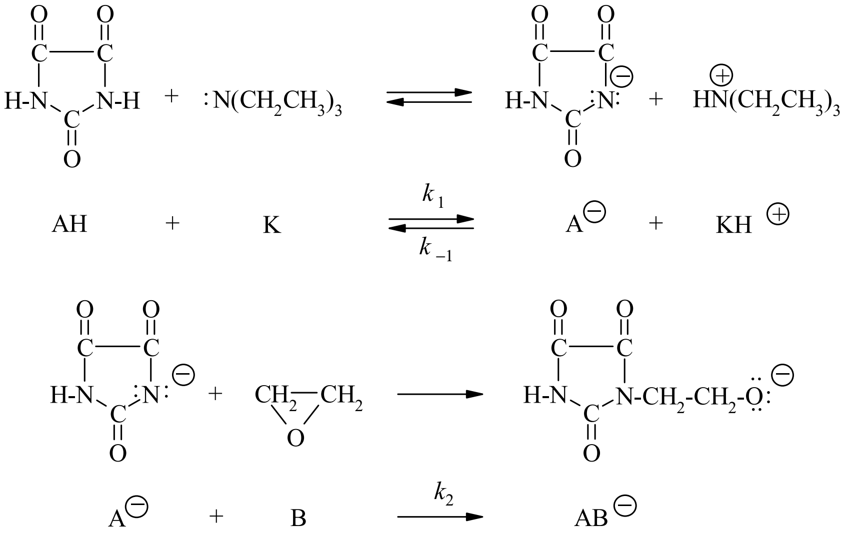
that can be used to calculate exponent z and the value of k''. The best fit was obtained for $z = 0.5$ ($r = 0.9992$).

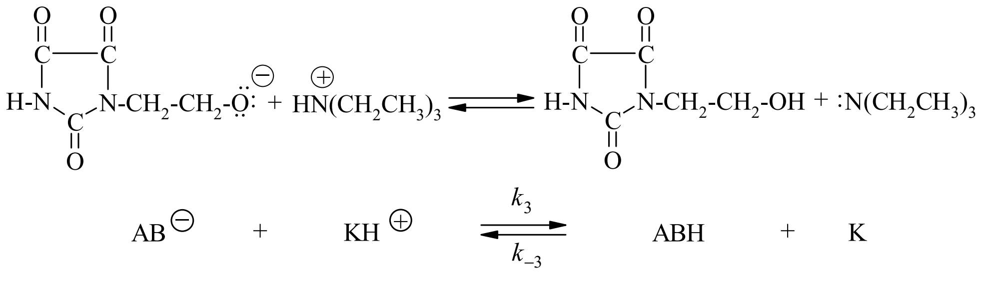
Hence, the general rate equation describing the reaction of addition of parabanic acid to ethylene oxide reads

$$V = k'' \cdot c_{\text{K}}^{1/2} \cdot c_{\text{AH}}^{1/2} \cdot c_{B} \tag{11}$$

(one should bear in mind that c_{AH} is twice the concentration of parabanic acid).

The reaction mechanism that is consistent with the rate equation (11) might read as follows:





The mechanism consists of three elementary reactions:

- formation of an adduct of parabanic acid with triethylamine that occurs in ionized form
- attack of parabanic ion upon oxirane molecule
- catalyst recovery

Assuming that the rate-limiting step is the reaction between anion and oxirane (the other two are quick since they involve proton exchange), the general rate equation should read

$$V_{\text{general}} = V_2 = k_2 \cdot c_{\text{B}} \cdot c_{\text{A}^-} \tag{12}$$

From the Bodenstein stationary rule it follows that

$$\begin{aligned}\frac{\mathrm{d}c_{\text{A}^-}}{\mathrm{d}t} &= k_1 \cdot c_{\text{AH}} \cdot c_{\text{K}} - k_{-1} \cdot c_{\text{A}^-} \cdot c_{\text{HK}^+} \\ &\quad - k_2 \cdot c_{\text{A}^-} \cdot c_{\text{B}} = 0\end{aligned} \tag{13}$$

Since

$$c_{\text{A}^-} = c_{\text{HK}^+} \tag{14}$$

one gets

$$-k_{-1} \cdot c_{\text{A}^-}^2 - k_2 \cdot c_{\text{B}} \cdot c_{\text{A}^-} + k_1 \cdot c_{\text{AH}} \cdot c_{\text{K}} = 0 \tag{15}$$

Hence,

$$c_{\text{A}^-} = \frac{k_2 \cdot c_{\text{B}} - \sqrt{k_2^2 \cdot c_{\text{B}}^2 + 4k_{-1} \cdot k_1 \cdot c_{\text{AH}} \cdot c_{\text{K}}}}{-2k_{-1}} \tag{16}$$

Table II The Rate Constants of the Reaction of Parabanic Acid with Ethylene Oxide at 40°C as Calculated from Rate Equations (7) and (9)

$c_{0\text{AH}}$ (mol/dm^3)	Imide to Oxirane Molar Ratio	k' (10^{-5} s^{-1} mol$^{-1/2}$ dm$^{3/2}$)	k' (10^{-5} s^{-1} mol$^{-1/2}$ dm$^{3/2}$)
4.000	16:1	4.77	4.80
3.000	12:1	4.09	4.09
2.000	8:1	2.96	3.31

$c_{0\text{B}} = 0.2500$ mol/dm^3, $c_{\text{cat}} = 0.5000$ mol/dm^3.

From the assumption on the slowest, rate-determining step, one has

$$k_2^2 \cdot c_{\text{B}}^2 \ll 4k_1 \cdot k_{-1} \cdot c_{\text{AH}} \cdot c_{\text{K}} \tag{17}$$

and

$$c_{\text{A}^-} = K_1^{1/2} \cdot c_{\text{AH}}^{1/2} \cdot c_{\text{K}}^{1/2} \tag{18}$$

By substituting Eq. (18) into Eq. (12) one obtains

$$V_{\text{general}} = k_2 \cdot K_1^{1/2} \cdot c_{\text{K}}^{1/2} \cdot c_{\text{AH}}^{1/2} \cdot c_{\text{B}} \tag{19}$$

with

$$k'' = k_2 \cdot K_1^{1/2} \tag{20}$$

which finally gives

$$V_{\text{general}} = k'' \cdot c_{\text{K}}^{1/2} \cdot c_{\text{AH}}^{1/2} \cdot c_{\text{B}} \tag{21}$$

The rate equation (21) is the same as found in experiment, thus confirming the assumption on the mechanism of reaction.

The mechanism has been verified by using instrumental methods. The adduct, which is in fact a salt, triethylammonium hydroparabanate, was prepared by reacting parabanic acid with triethylamine in tetrahydrofurane at room temperature.

Triethylammonium hydroparabanate is a crystalline substance of mp 149–150°C. Its structure has been confirmed by ^{1}H NMR and IR. In the ^{1}H NMR spectrum, the chemical shift of protons at —NH— groups of parabanic acid (Fig. 1a) is 11.7 ppm, whereas in the spectra of its adduct with triethylamine the shift is 10.2 ppm (Fig. 1b). This suggests the presence of ion pair or free ions. Furthermore, in IR spectrum of the adduct, bands of medium intensity appear at around 2500 cm^{-1} (cf. Figs. 2a and 2b) usually ascribed to triethylammonium cation. The conductometric measurements also indicate that ions appear in solutions of parabanic acid and triethylamine in water. For mixtures of parabanic acid and triethylamine the conductivity has

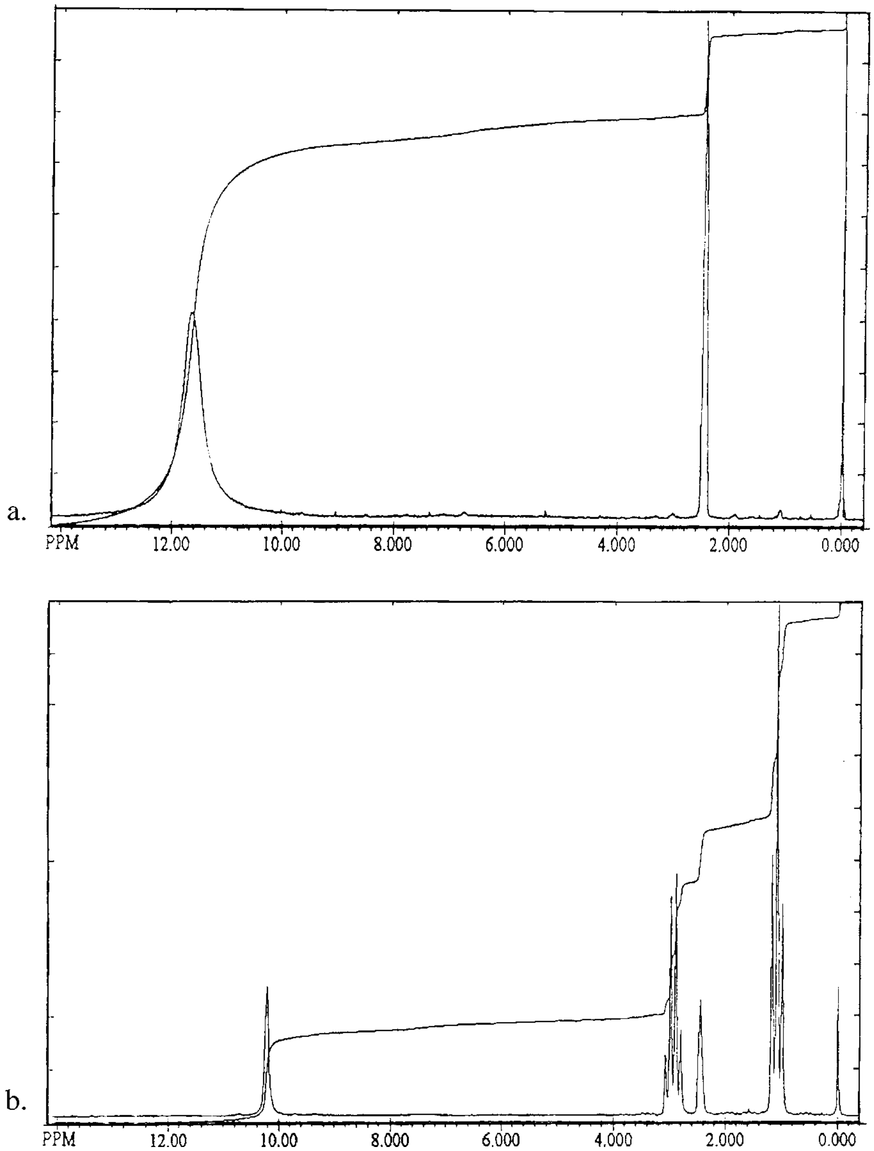
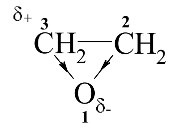
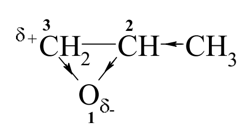


Figure 1 ^{1}H NMR spectra of parabanic acid (a) and triethylammonium hydroparabanate (b).

been found to be higher than the sum of conductivities of solutions of individual components. The highest conductivity was measured for equimolar mixtures of the components (cf. Fig. 3). Evidently, 1:1 salt was formed.

Equation (21) describing the rate of reaction of parabanic acid with ethylene oxide applies to the parabanic acid–propylene oxide system as well. By comparing the respective rate constants, one concludes that ethylene oxide is much more reactive in addition of parabanic acid than propylene oxide. The average relative activity of the second is only 0.55. By analyzing electron shifts one may also conclude that the reactivity depends primarily on the electropositive character of carbon atom 1 in oxirane molecules:





According to the induction effects shown in the scheme above, the electrophilic character of carbon atom 1 in propylene oxide is diminished by the donor action of methyl group. This may explain the reduced reactivity of propylene oxide as compared to that of ethylene oxide. It has been shown in Ref. [25] that parabanate anion attacks carbon C-3 of 2-methyoxirane

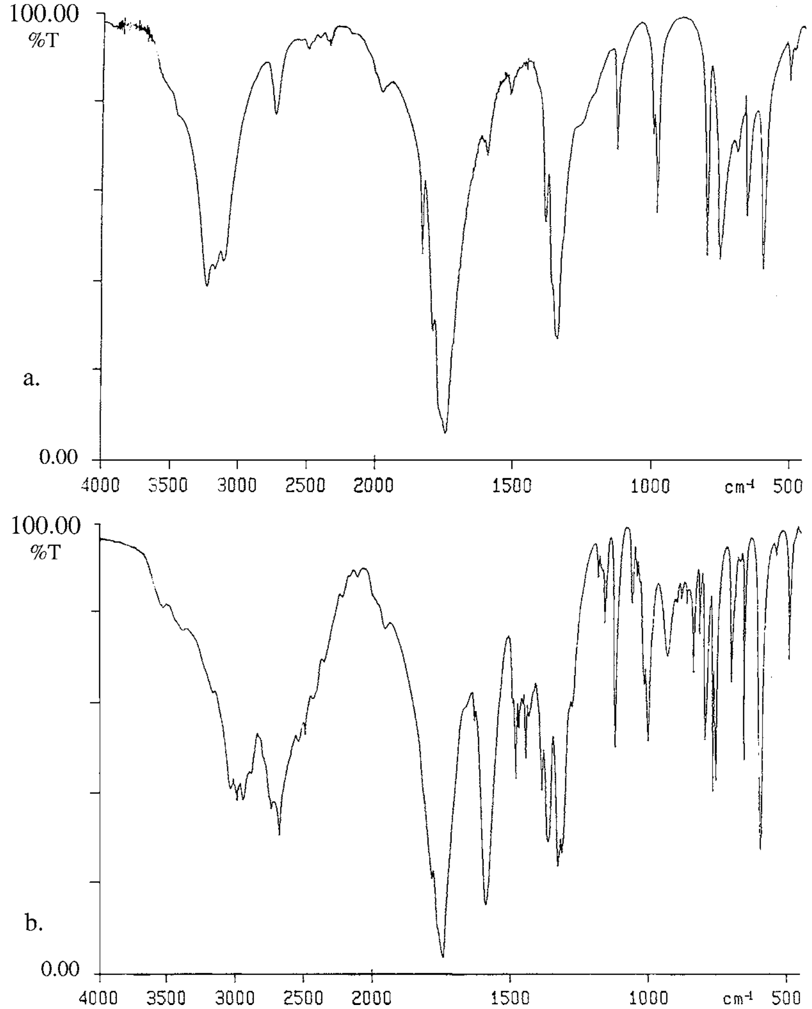


Figure 2 IR spectra of parabanic acid (a) and triethylammonium hydroparabanate (b).

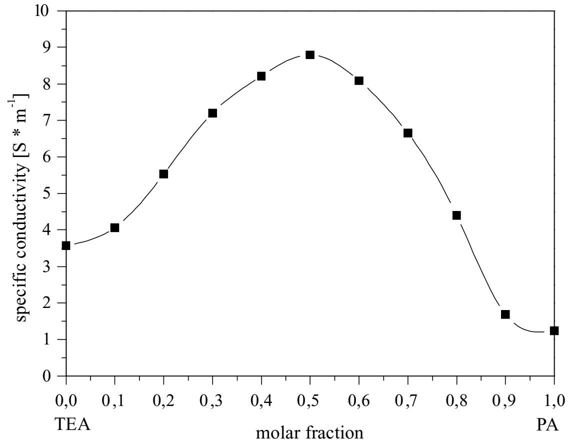


Figure 3 The conductivity of water solutions of mixtures of triethylamine (TEA) and parabanic acid (PA) vs. molar fraction of the components. Total concentration: 0.25 mol/dm^3.

and the resulting alcoholate has the structure N—CH$_2$—CH(CH$_3$)—O$^-$.

From the temperature effect on reactions of parabanic acid with oxiranes, the Gibbs free energy, $\Delta G^{\#}$, as well as enthalpy, $\Delta H^{\#}$, and entropy of activation, $\Delta S^{\#}$, have been evaluated (Fig. 4). The results of calculations are presented in Table III. The values of activation entropy suggest that the transition state of reaction consists of two components, in accord with the proposed mechanism of addition. Somewhat lower

Table III Activation Parameters of the Addition of Parabanic Acid to Ethylene Oxide or Propylene Oxide

Activation Parameter	EO	PO
$\Delta G^{\#}$ (kJ mol^{-1})	103.75	105.80
$\Delta H^{\#}$ (kJ mol^{-1})	71.4	68.9
$\Delta S^{\#}$ (J mol^{-1} K^{-1})	−107.9	−120.7

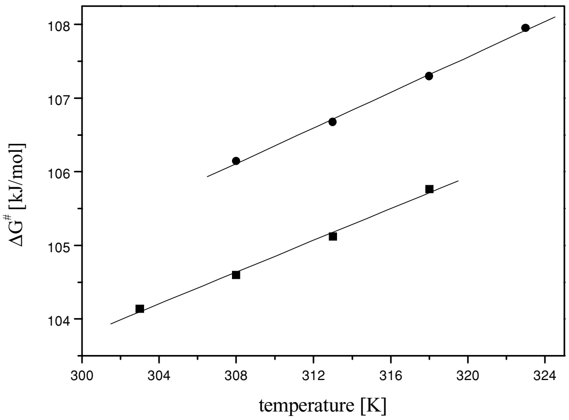


Figure 4 The Gibbs free energy of activation ($\Delta G^{\#}$) as calculated from Eq. (2) vs. temperature for the reaction of parabanic acid with ethylene oxide (■) and with propylene oxide (●).

activation entropy may be caused by a tighter packing of components in the transition state because of the presence of methyl group. A comparison of the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ suggests that the entropic terms controls both reactions.

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