Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

THE CHEMISTRY OF ETHYLENE OXIDE

III. REACTION OF ETHYLENE OXIDE IN AMINE SOLUTION[1]

By A. M. Eastham and B. deB. Darwent

Abstract

A kinetic study has been made of the reaction of ethylene oxide in pyridine solution in the presence of strong acids. The rate has been found to be dependent upon the concentration of acid and of oxide over a wide range of concentrations at 25°C. The specific rate constant, however, varies markedly with the nature of the acid anion and appears to decrease with increasing basic strength of the anion. The absence of large salt effects seems to indicate that the anion effect is of a physical rather than chemical nature and the results are therefore tentatively attributed to the nature of solutions of electrolytes in solvents of low dielectric constant.

Introduction

The results of some experiments on the reaction of ethylene oxide with amines in aqueous solution were reported in a previous paper (3). It was shown that in water the rate is a function of the concentrations of amine and oxide only, although the reaction must take the general form

$$R_3N + (CH_2)_2O + HX \rightarrow R_3\overset{+}{N}\text{-}CH_2CH_2OH + X^-$$

which, when R = H, becomes

$$NH_3 + (CH_2)_2O + HX \rightarrow H_3\overset{+}{N}\text{-}CH_2CH_2OH + X^- \rightarrow H_2N\text{-}CH_2CH_2OH + HX$$

However, in spite of the fact that the reaction proceeds through a proton transfer, no appreciable hydrogen ion or aminium (R_3NH^+) ion catalysis occurs over a very wide range of experimental conditions. Basic catalysis is also absent and the rate is given very closely by the equation

$$\frac{d\text{ product}}{dt} = k(\text{amine})\ (\text{oxide})$$

where the amine concentration is that of the free or unionized amine present in the solution. Apparently then, in aqueous solution water is the principal source of protons.

In view of the above results it was of interest to study this reaction in aprotic solvents where the concentration of proton-supplying substances could be controlled. In this paper we present the results of some experiments carried out with pyridine as both solvent and reactant, together with a few results obtained in diethylamine solution. Pyridine was chosen for most of the work because it is an excellent solvent for its own salts and because the formation of a pyridonium base permits the reaction to be followed accurately by simple acid–base titration. Unfortunately, however, pyridine cannot be used to study the

---

[1] *Manuscript received December 20, 1950.*
Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2464.

catalytic activity of water or other weakly acidic compounds because the pyridonium base formed in the reaction is stable only as the salt of a fairly strong acid (6). Accordingly, a few experiments were performed in diethylamine solution to obtain some idea of the catalytic activity of water.

Experimental

1. *Materials*

(*a*) Ethylene oxide—a commercial product having a purity of 99.5% or better was used without further purification. It was weighed in small sealed ampoules which were broken into the reaction mixture (4).

(*b*) Amines—all amines with the exception of pyridine were purified by careful fractional distillation after standing some days over solid potassium hydroxide.

(*c*) Pyridine—most of the pyridine used was purified by distillation, first from sodium hydroxide, then from aluminum chloride, and finally by careful fractionation (1, 2). Some of the dilatometric measurements were made, however, with pyridine carefully fractionated after standing over potassium hydroxide and barium oxide. There is some indication that the more rigorous purification gives slightly higher rates, but the differences unless otherwise noted are too close to the experimental error to be of much significance. In general, pyridine purified with barium oxide was used for the dilatometric experiments, while pyridine distilled from aluminum chloride was used for the experiments in which the reaction was followed by titration.

(*d*) Pyridinium salts were prepared by adding concentrated aqueous acids to a slight excess of pyridine and filtering the crystalline mass. The product was then dried over sulphuric acid in a vacuum desiccator at a few millimeters pressure, recrystallized from a suitable solvent, and finally dried again over sulphuric acid or phosphorus pentoxide. The acid content of the product was determined by potentiometric titration against standard sodium hydroxide and in all cases was found to be in excellent agreement with the theoretical value. In a few cases, where the pyridinium salts were too hygroscopic to be handled conveniently, solutions were prepared by adding the acid to the pyridine and titrating to establish the concentration. Thus, hydrogen chloride and hydrogen bromide solutions were prepared from the dry gaseous acids; sulphuric acid solutions were prepared by adding a few drops of concentrated acid to pyridine and assuming that the small amount of water present could be neglected.

2. *Methods*

All experiments were performed at 25°C. in a bath controlled to ± 0.002°. All titrations were made electrometrically with a Beckmann Model G pH meter.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

The reaction appears to be very clean since, when it is run to completion, analyses for quaternary base are essentially in quantitative agreement with the theoretical yields calculated from the ethylene oxide used. In pyridine solution the reaction was found to be of the second order, obeying the rate expression $d(\text{product})/dt = k(\text{oxide})(\text{acid})$; it was followed by a dilatometric method at acid concentrations above 0.1 *M* and by an analytical method below this concentration.

(*a*) *Dilatometric Method*

This method was essentially the same as that previously described (3). Dilatometers are suitable for use only with first order reactions and hence in pyridine solution were used only in the presence of a large excess of acid relative to ethylene oxide. For this reason the method was limited to those experiments in which the acid concentrations were above 0.1 *M*. In diethylamine solution the reaction is pseudo first order, since the proton required is regenerated and hence the concentration restrictions do not apply. Unfortunately, however, anhydrous diethylamine is a very poor solvent for its own salts and it was therefore necessary to restrict the experiments with this solvent to a few runs in which a small amount of water was added to the diethylamine. It was necessary to provide mercury seals for the dilatometers in these runs because no stopcock grease was found that would resist this solvent.

(*b*) *Analytical Method*

The reaction, in pyridine solution, actually consumes the acid "catalyst" so may be followed by determining the unreacted acid at intervals during the reaction. A sample of the reaction mixture was removed and quickly transferred to a small flask. This flask was fitted with a removable condenser to act as a spray trap and this in turn was connected to a vacuum system capable of reducing the pressure below one millimeter. The ethylene oxide and pyridine were rapidly distilled off at room temperature and the stable residue, consisting of pyridinium and pyridonium salts, was set aside for titration.

The condenser and flask were rinsed with water and the resulting solution titrated against a standard solution of sodium hydroxide using the internal electrodes of a Beckmann Model G pH meter. Conditions were usually chosen so that a sample of the initial acid solution required about 5 to 7 cc. of sodium hydroxide and titrations were accurate to about 0.01 cc. However, at low acid concentrations the end point of the titrations becomes poor with the result that the method is unsatisfactory for use with solutions less concentrated than 0.005 *M*. This is particularly true in the case of periodic acid which in water is a fairly weak acid. As a result the data for this acid are slightly more erratic than those for the stronger acids.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

Generally, four samples were taken on each run between 10% and 50% total reaction. In some cases reactions were carried close to completion but in no case was appreciable deviation from second order observed. It was assumed that one mole of ethylene oxide disappears with one mole of acid and the results so obtained were plotted against time using one of the usual second order rate expressions. The recorded rate was that given by the best straight line through the four points and was usually within 1–2% of the values calculated from the individual points.

3. Reaction Mixtures

Wherever possible, reaction mixtures were prepared by weighing the pyridine salt into a volumetric flask and making up to volume with pyridine. The solution was transferred to a vessel designed for filling the dilatometers or for withdrawing samples, and brought to the temperature of the bath. A weighed bulb of ethylene oxide was then broken into the mixture in the usual fashion.

Solutions of various amine perchlorates in pyridine were prepared by dissolving weighed quantities of pyridine perchlorate and amine in pyridine. The amount of amine added was slightly greater than that calculated as being necessary to transfer 98% of the protons from the pyridine. The calculations were based on the assumption that the distribution of the protons between the amines is given by the ionization constants of the amines as determined in dilute aqueous solution, and by the relative concentration of the amines.

Solutions in diethylamine were prepared by dissolving weighed amounts of water and of pyridine salt in the diethylamine. The more basic diethylamine was assumed to take up the protons, leaving a small amount of free pyridine in solution. The effect of this free pyridine should be very small in view of the large excess of diethylamine.

Results

The results obtained with the various acids in pyridine and diethylamine solution are shown in the accompanying tables and figures. Detailed results are given only for perchloric acid (Table I), since this acid was studied over the widest range of concentrations; the data show good agreement between the dilatometric and analytical methods and, more important, show that the rate constant holds over a very wide range of concentrations.

Essentially similar results, but with different values for the rate constant, were obtained with other acids. The data are illustrated graphically in Fig. 1 and the average values for the rate constants are given in Table II. It was not possible to study the catalytic activity of the halogen acids in this work because their reactions are complicated by the formation of halohydrins. In Table III are shown the data for sulphuric acid. For reasons given below, the rates for this acid have been calculated from both the normality and molarity of the acid.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

TABLE I

REACTION OF ETHYLENE OXIDE IN PYRIDINE SOLUTIONS OF PERCHLORIC ACID

Run	$HClO_4$ (moles/l.)	Oxide (moles/l.)	k_{obs} (min.$^{-1}$)	$k_{obs}/(H^+)$ (l.mol.$^{-2}$ min.$^{-1}$)
A. Dilatometric method				
265	1.65	0.0422	4.93×10^{-2}	2.98×10^{-2}
264	1.17	0.0581	2.71	2.31
262	0.778	0.0345	1.81	2.33
260	0.648	0.0360	1.49	2.30
300	0.614	0.0353	1.39	2.26
259	0.455	0.0384	1.01	2.20
276	0.411	0.0307	0.960	2.33 (contains 0.175 *M* $NaClO_4$)
301	0.302	0.0270	0.681	2.25
263	0.201	0.0210	0.428	2.14
266	0.200	0.0154	0.458	2.29
235	0.109	0.0374		(2.1) (Estimated only)
233	0.0750	0.0367		(2.7) (" ")
234	0.0555	0.0354		(2.6) (" ")
k average (dilatometric) = 2.27 × 10^{-2} between 1.2–0.2 M $HClO_4$				
B. Analytical method				
379	0.120	0.0969		2.47×10^{-2}
371	0.0911	0.0719		2.47
374	0.0710	0.0564		2.35
385	0.0500	0.0500		2.40
378	0.0305	0.0212		2.38
384	0.0155	0.0155		2.45
370	0.0153	0.0124		2.40
382	0.0100	0.0120		2.46
377	0.0101	0.00906		2.31
381	0.0100	0.00792		2.43
376	0.00815	0.00785		2.22
375	0.00502	0.00501		2.30
383	0.00334	0.00259		3.11
k average (analytical) = 2.39 × 10^{-2} between 0.1–0.005 M $HClO_4$				

TABLE II

CATALYTIC ACTIVITY OF STRONG ACIDS ON THE REACTION OF ETHYLENE OXIDE IN PYRIDINE

Acid	*k* (dilatometric) (l.mol.$^{-1}$ min.$^{-1}$)	*k* (analytical) (l.mol.$^{-1}$ min.$^{-1}$)	Solubility of acid in pyridine at 25°C. (moles/l.)
$HClO_4$	22.7×10^{-3}	23.9×10^{-3}	*ca.* 2.0
HIO_4	22.4	24.4	*ca.* 2.0
H_2SO_4		8.9 (?)	0.032
$C_6H_5SO_3H$		8.25	0.19
p-$C_7H_7SO_3H$	7.08	7.62	0.80
HNO_3	7.18	7.41	0.36

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

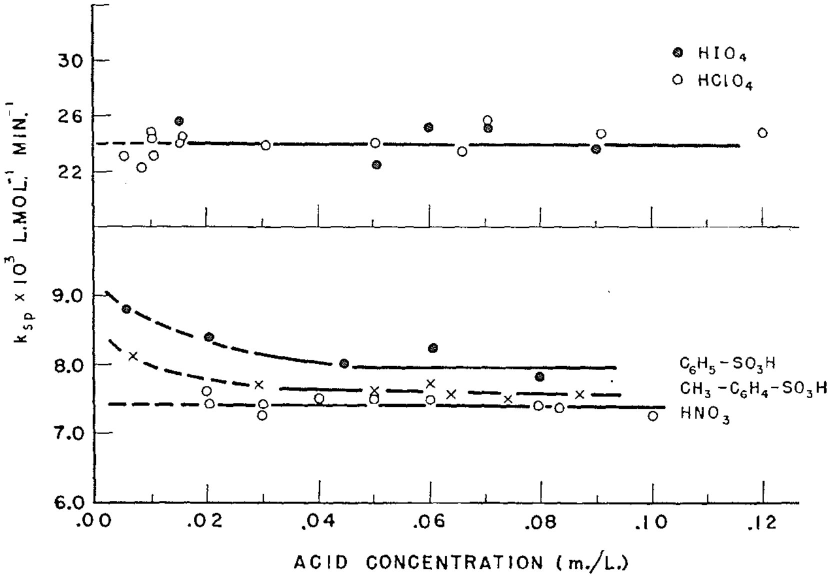


FIG. 1. *Rate of reaction of ethylene oxide in pyridine in the presence of strong acids (Analytical Method).*

TABLE III

REACTION OF ETHYLENE OXIDE IN PYRIDINE SOLUTIONS OF SULPHURIC ACID

Run	H_2SO_4 (moles/l.)	Oxide (moles/l.)	k_N*	k_M*
Analytical method				
427	0.0162	0.0256	4.0×10^{-3}	8.8×10^{-3}
428	0.00802	0.0122	4.2	8.9

* *k_N calculated from normality, k_M from molarity of H_2SO_4; all measurements made in the initial stages of the reaction only.*

The effect of sodium perchlorate on the perchloric acid catalyzed reaction is shown in Table IV. Salt effects are seen to be small.

Table V shows the results of some experiments in which small amounts of water were added to the pyridine–acid systems. The data are too limited to be of much significance but seem to indicate that the effect of water on the rate is small. As already mentioned, the catalytic activity of water alone cannot be studied in pyridine solution because the product is an unstable pyridonium hydroxide which undergoes further reaction. Some idea of the catalytic activity of water was obtained, however, in diethylamine solutions with the results shown in Table VI. Diethylamine in the absence of water is a very poor solvent for its own salts, so the studies were extended to include rate measurements in the system diethylamine–water–perchloric acid. The results shown in Fig. 2,

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

TABLE IV

SALT EFFECT ON THE PERCHLORIC ACID CATALYZED REACTION

Run	$HClO_4$ (moles/l.)	$NaClO_4$ (moles/l.)	ClO_4^- (moles/l.)	Oxide (moles/l.)	k (l. mol.$^{-1}$ min.$^{-1}$)
Analytical method					
426	0.01023	0.0877	0.0979	0.0192	25.8×10^{-3}
425	0.01023	0.0438	0.0540	0.0204	25.0
424	0.01023	0.0175	0.0277	0.0209	24.5
423	0.01023	0.0088	0.0190	0.0218	23.5
422	0.01023	none	0.0120	0.0219	23.6

TABLE V

EFFECT OF WATER ON THE ACID INDUCED REACTION OF ETHYLENE OXIDE WITH PYRIDINE

Run	Acid	Acid conc. (moles/l.)	Oxide (moles/l.)	Added H_2O (moles/l.)	k (l. mol.$^{-1}$ min.$^{-1}$)
396	$HClO_4$	0.0713	0.0713		2.40×10^{-2} (analytical method)
397	$HClO_4$	0.0713	0.0713	0.10	2.32 “
398	$HClO_4$	0.00517	0.00517	1.0	2.78 “
399	$HClO_4$	0.00811	0.00811	1.0	2.51 “
400	$HClO_4$	0.0119	0.0119	1.0	2.17 “
286	HNO_3	0.711	0.0312	1.0	8.03×10^{-3} (dilatometric method)
282	HNO_3	0.711	0.0410	1.0	8.40 “
284	HNO_3	0.213	0.0275	0.3	7.70 “
All runs	HNO_3				7.20 “
269	*p*-toluene sulphonic	0.528	0.0263	0.5	7.33 “
All runs	“				7.08 “

TABLE VI

REACTION OF ETHYLENE OXIDE IN DIETHYLAMINE SOLUTION IN THE PRESENCE OF WATER (DILATOMETRIC)

H_2O (moles/l.)	k_{obs}(min.$^{-1}$)
8.0	1.6×10^{-2}. . average of three runs
7.0	1.3. . . . . average of three runs
6.0	0.9. . . . . average of two runs
5.6	1.0 } by extrapolation to zero $HClO_4$ (see Fig. 2)
4.2	0.4
1.4	0.04

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

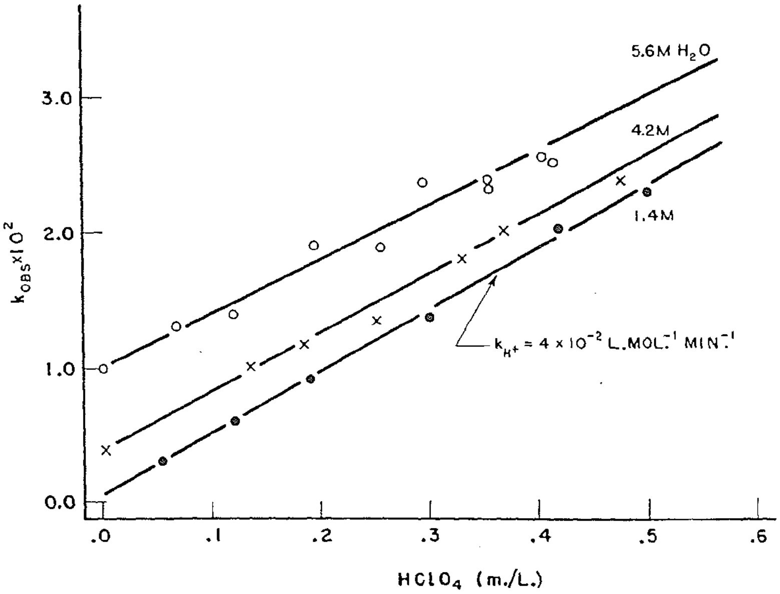


FIG. 2. *Reaction of ethylene oxide in diethylamine solution in the presence of both water and perchloric acid (Dilatometric Method).*

TABLE VII

EFFECT OF VARIOUS AMINES ON THE ACID INDUCED REACTION OF ETHYLENE OXIDE IN PYRIDINE SOLUTION (DILATOMETRIC)

Run	Acid	Acid conc. (moles/l.)	Amine	Amine conc. (moles/l.)	Oxide (moles/l.)	k_{obs} (min.$^{-1}$)	k_{obs}/acid (l. mol.$^{-1}$ min.$^{-1}$)
	$HClO_4$		Pyridine				2.27 × 10^{-2}
294	$HClO_4$	0.705	Triethyl-amine	0.788	0.0321	1.86 × 10^{-3}	2.64 × 10^{-3}
292	$HClO_4$	0.526		0.563	0.0322	1.47	2.80
291	$HClO_4$	0.423		0.450	0.0280	1.20	2.83
296	$HClO_4$	0.836	Ammonia	0.836	0.0322	2.75	3.28
293	$HClO_4$	0.644		0.644	0.0319	1.90	2.95
297	$HClO_4$	0.418		0.418	0.0342	1.14	2.73
278	$HClO_4$	0.658	Benzylamine	0.757	0.0224	2.18	3.01
279	$HClO_4$	0.508		0.565	0.0340	1.72	3.37
277	$HClO_4$	0.333		0.389	0.0306	1.14	3.42
287	$HClO_4$	0.878	Diethanol-amine	0.934	0.0328	2.96	3.38
288	$HClO_4$	0.526		0.560	0.0312	1.31	2.50
295	$HClO_4$	0.351		0.374	0.0330	0.797	2.70
	HNO_3		Pyridine				7.20 × 10^{-3}
298	HNO_3	0.870	Ammonia	0.870	0.0309	1.61 × 10^{-3}	1.85 × 10^{-3}
299	HNO_3	0.500		0.500	0.0259	0.87	1.74

although rather erratic, suggest that the catalysis by perchloric acid is not greatly affected by the presence of small amounts of water. Water itself gave very low rates at concentrations below about 2.0 *M*, presumably owing to a reduction of its effective concentration through association with diethylamine.

Since in the pyridine – perchloric acid system the proton source is presumably the pyridinium ion, it was of interest to examine the effect of the addition of small amounts of more basic amines in the reaction mixture. It might be expected that the rate of the reaction would be reduced in proportion to the basicity of the added amine, since the protons would be transferred to, and more firmly bound by, the more basic amines. The data of Tables VII and VIII indicate that the more basic amines do indeed reduce the rate but to about the same extent in all cases. It is possible, however, that the basic strengths of amines in pyridine solutions are not directly related to the ionization constants of the amines in water (7).

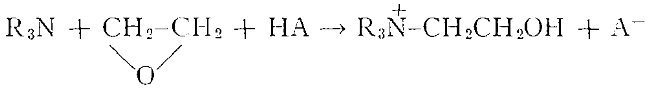
TABLE VIII

EFFECT OF THE VARIOUS AMINES ON THE ACID INDUCED REACTION OF ETHYLENE OXIDE IN PYRIDINE (SUMMARY)

Acid	Amine	Amine ionization constant	k (l. mol.$^{-1}$ min.$^{-1}$)
$HClO_4$	Pyridine	1.7×10^{-9}	2.3×10^{-2}
	Diethanolamine	7.6×10^{-7}	2.8×10^{-3}
	Benzylamine	2.0×10^{-5}	3.3
	Ammonia	1.9×10^{-5}	3.0
	Triethylamine	5.5×10^{-4}	2.8
HNO_3	Pyridine	1.7×10^{-9}	7.2×10^{-3}
	Ammonia	1.9×10^{-5}	1.8×10^{-3}

Discussion

In the previous paper it was shown that the reaction of ethylene oxide with amines probably occurs according to the equation:



$$R_3N + \underset{\diagdown\,O\,\diagup}{CH_2\text{–}CH_2} + HA \rightarrow R_3\overset{+}{N}\text{–}CH_2CH_2OH + A^-$$

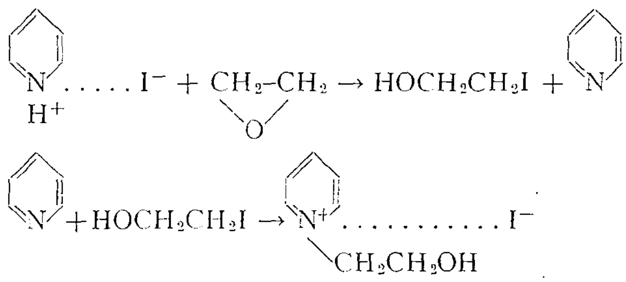
where R_3N = amine and HA a source of protons (acid). It is therefore not surprising that in pyridine solution the rate of the reaction has been found to be dependent upon the concentrations of oxide and of acid.

However, the results have also shown quite clearly that the rate constant for the reaction is sensitive to the nature of the acid anion present in the solution. This might suggest that the reaction in pyridine, like the reaction of ethylene oxide with neutral salts in water, is actually independent of the proton concentration, and proceeds through anion attack. Qualitative support for such a view is found in the hydriodic acid "catalyzed" reaction of ethylene oxide

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

in pyridine; this reaction is too complex for study at the present time but some results obtained during the course of this investigation indicate that the reaction probably proceeds, at least in part, according to the equations:

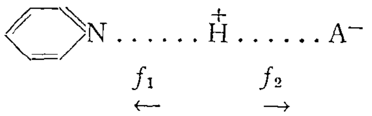


In the case of hydriodic acid the second step is slower than the first; in the case of an acid such as perchloric, however, the second step might well be very rapid and the over-all rate could conceivably be determined by the concentrations of oxide and of anion. There is, however, little reason to believe that anions such as perchlorate and nitrate actually do add to ethylene oxide and this view is supported by the very small increase obtained when sodium perchlorate is added to the perchloric acid catalyzed reaction (Table IV). For these reasons and from considerations of mechanisms, we at present prefer to regard the rate of the reaction as being determined by the concentrations of the oxide and of the proton source, and believe that the anion effect is due to the peculiarities of solutions of electrolytes in solvents of low dielectric constant. This view is amplified in the following paragraphs.

It is obvious that, because of the basicity of amine solvents, any strong acid, and even quite weak acids, may be expected to react completely to give, in pyridine, the pyridinium salt. The dependence of the rate constants upon the nature of the anion may be explained if we assume, in agreement with current theory, that in these solutions the pyridinium ion and the anion remain in more or less loose association.

$$\mathrm{Py} + \mathrm{HA} \rightarrow \mathrm{PyH^+} \ldots\ldots\ldots \mathrm{A^-}$$

If this is true then it is obvious that in reaction with ethylene oxide, the proton is removed, not from the free pyridinium, but from the $\mathrm{PyH^+} \ldots \mathrm{A^-}$ complex and the anion may then play a significant part in the case of proton transfer. This view is at least in qualitative agreement with the experimental data but requires that the proton be rather loosely bound in the complex



since, if the attractive force f_1 is large with respect to f_2, it would be impossible for the anion to exert so large an effect upon the rate. In support of the view that f_1 is small, it may be noted that Burgess and Kraus (1) have found that

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.

the pyridinium ion has an exceptionally high conductance, a fact which they attribute to the transfer of protons through the solvent. Furthermore, Fuoss *et al.* (5) have presented some evidence for the view that in toluene solution, amine picrates may exist in an equilibrium of the form

$$\begin{tikzcd}
R_3H.HPi \arrow[r, shift left, harpoon] \arrow[d, shift left, harpoon] & R_3NH^+.Pi^- \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon] \\
R_3N + HPi \arrow[u, shift left, harpoon] & R_3NH^+ + Pi^- \arrow[u, shift left, harpoon]
\end{tikzcd}$$

Experimentally we have found that the rate constants are, qualitatively, in the orders of the strengths of the catalyzing acids, and this is further support for the hypothesis that the protons are removed from ion pairs, since the value of f_2 will increase as the acid strength decreases.

It may be noted that the rate constants for the sulphonic acids seem to increase significantly at low concentrations (Fig. 1). This increase may possibly be due to an increase in the dissociation of the ion pairs in the system. Burgess and Kraus (1) have found a value of 5×10^{-5} for the dissociation constant of pyridinium nitrate ions which is so low that one would not expect any deviations from linearity with nitric acid at the concentration used here. However, they point out that the dissociation constants are determined largely by the diameters of the ions and hence it is likely that pyridinium benzene sulphonate, with its large ions, may be so much more highly dissociated than the nitrate that dilution effects become important at the concentration used in this work.

The cases of sulphuric and periodic acids merit some attention. Periodic acid in water appears to be very much weaker than perchloric acid—probably due to hydration to give H_3IO_5—but kinetically, in pyridine where no hydration is possible, it appears to be quite as strong as perchloric acid. Analyses of the pyridine salt of this acid show it to have the composition $C_5H_5N.HIO_4$.

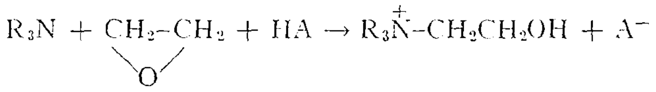
The rate constant for sulphuric acid has been assigned the value of 8.9×10^{-3} and this value is based on the assumption that it behaves as a monobasic acid in pyridine. The conclusion that sulphuric acid acts as a monobasic acid is supported by the following data, which were obtained in the course of this investigation:

(*a*) Pyridinium acid sulphate may be recovered unchanged by recrystallization from pyridine, and all our efforts at preparing the dipyridinium salt were unsuccessful.

(*b*) The acid sulphates of sodium, tetramethylammonium, and benzyltrimethylammonium are exceedingly insoluble in pyridine; when ethylene oxide reacts with pyridine solutions of sulphuric acid, precipitation of a reaction product occurs very early in the reaction.

It is evident from the foregoing discussion that the reaction of ethylene oxide in amine solutions is too complex to permit any definite conclusions on the reaction mechanism to be made at the present time. For the present our knowledge of the reaction may be summarized as follows:

(*a*) Since all amines behave essentially similarly, regardless of whether or not they have hydrogen attached to nitrogen, the reaction must take the general form



$$R_3N + \underset{\diagdown O \diagup}{CH_2{-}CH_2} + HA \rightarrow R_3\overset{+}{N}{-}CH_2CH_2OH + A^-$$

(*b*) In aqueous solution the reaction is largely independent of the source of hydrogen ions and takes the kinetic form

$$\frac{-d\text{ oxide}}{dt} = k(\text{oxide})(\text{amine})$$

No basic catalysis exists; acid catalysis is not impossible but if it exists will only be found under conditions such that appreciable amounts of free amine and oxonium ion will be present together in the solution.

(*c*) In pure amine solution the reaction is dependent upon, and rather sensitive to, the source of hydrogen ion; the reaction rate is given by the equation

$$\frac{-d(\text{oxide})}{dt} = k(\text{oxide})(\text{HA})$$

(*d*) In both aqueous and amine solution salt effects are small, suggesting the existence of an uncharged intermediate.

(*e*) The reaction rates, particularly in aqueous solution, show no relation to amine structure or basicity.

References

1. BURGESS, D. S. and KRAUS, C. A. J. Am. Chem. Soc. 70: 706. 1948.
2. CARIGNAN, C. J. and KRAUS, C. A. J. Am. Chem. Soc. 71: 2983. 1949.
3. EASTHAM, A. M., DARWENT, B. DEB., and BEAUBIEN, P. A. Can. J. Chem. 29: 575. 1951.
4. EASTHAM, A. M. and LATREMOUILLE, G. A. Can. J. Research, B, 28: 264. 1950.
5. FUOSS, R. M., EDELSON, D., and SPINRAD, B. I. J. Am. Chem. Soc. 72: 327. 1950.
6. Sidgwick's Organic chemistry of nitrogen. Clarendon Press, Oxford. 1937. p. 524.
7. TROTMAN-DICKENSON, A. F. J. Chem. Soc. 1293. 1949.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV WINDSOR on 11/10/14
For personal use only.