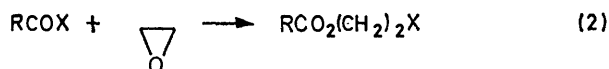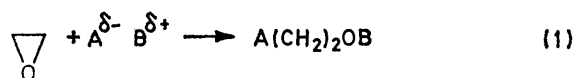# Acylation. Part XXXVII.[1] The Catalysed Benzoylation of Ethylene Oxides by Benzoyl Halides in Aprotic Solvents

By Derek P. N. Satchell * and Valeri F. Shvets, King's College, Strand, London, and Mendeleev Institute of Chemical Technology, Miusski Square, Moscow, U.S.S.R.

The benzoylation of ethylene oxide by benzoyl chloride in aprotic solvents occurs slowly at 70°, but is catalysed by acids and bases. At ethylene oxide concentrations $\gtrsim 1 \text{M}$ the only significant product is 2-chloroethyl benzoate. The hydrogen chloride catalysed reaction is zero order in oxide and obeys the rate equation $-d[\text{ethylene oxide}]/dt = k_2[\text{catalyst}][\text{benzoyl chloride}]$. The hydrogen chloride and excess of oxide lead rapidly to an equivalent quantity of 2-chloroethanol, the latter being acylated by the benzoyl chloride in the slow step. Added 2-chloroethanol also acts as a catalyst and leads to the same rate equation. Catalysis by tetraethylammonium chloride also involves a process zero order in ethylene oxide and a rate equation analogous to that found for catalysis by hydrogen chloride. The reaction orders, the effects of substituent changes in the reactants, and the known reactivities of alkoxide ions suggest a mechanism of benzoylation involving a rapid, initial association between ethylene oxide and the ammonium chloride to give a polar complex, which then attacks the benzoyl chloride in a slow step. Values of $\Delta S^{\ddagger}$ and E_a have been determined. The kinetic form of the pyridine catalysed reaction has also been studied briefly.

ETHYLENE OXIDES[2] will add a variety of reagents AB *via* heterolytic cleavage of a C–O bond [equation (1)]. These additions are both acid and base catalysed. Available kinetic evidence suggests that the C–O bond cleavage very often requires a transition state involving both electrophilic interaction at the oxygen atom and nucleophilic interaction at the carbon atom.[2,3] Kinetic studies of the acylation of ethylene oxides [equation (2)] have been limited to the acid and to the base catalysed additions of acetic anhydride in aprotic solvents.[4]

$$\text{(epoxide)} + A^{\delta-}-B^{\delta+} \longrightarrow A(CH_2)_2OB \qquad (1)$$

$$RCOX + \text{(epoxide)} \longrightarrow RCO_2(CH_2)_2X \qquad (2)$$

Under acid catalysis polymeric $\{Ac[O(CH_2)_2]_nOAc\}$, as well as monomeric, products are observed at high ethylene oxide concentrations. The base catalysed addition of acetic anhydride leads only to $AcO(CH_2)_2OAc$. Mechanisms which account for the observed products and the kinetic forms have been suggested. We report now on the kinetic form of the acid and the base catalysed addition of benzoyl chlorides, either in an excess of the benzoyl chloride, or in a chlorobenzene–nitrobenzene mixture, as solvent.
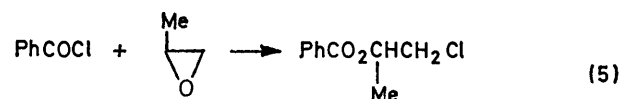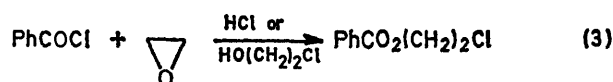
EXPERIMENTAL

Materials.—Benzoyl and *p*-methylbenzoyl chloride were distilled twice under vacuum, first from quinoline, then alone. They had b.p. 44° at 0·8 mmHg and 102° at 15 mmHg respectively. Nitrobenzene and chlorobenzene were distilled under vacuum, b.p. 108° at 30 mmHg and 45° at 30 mmHg respectively, and stored over a molecular sieve. Pyridine was distilled under nitrogen and had b.p. 115°. Redistilled 2-chloroethanol had b.p. 129°. Ethylene and propylene oxides, tetramethyl- and tetrabutyl-ammonium chlorides and tetraethylammonium chloride monohydrate were B.D.H. reagent grade materials and

were used without further purification. Tetraethyl-ammonium perchlorate was prepared from the chloride and silver perchlorate. Gaseous hydrogen chloride was supplied by Honeywell and Stein Ltd.

Reaction Products.—The reaction between ethylene oxide and benzoyl chloride was studied kinetically using hydrogen chloride, 2-chloroethanol, pyridine, and tetra-alkyl-ammonium chloride as catalysts. The corresponding study with propylene oxide used only the alkylammonium chloride as catalyst. We have examined the products in these systems, using an excess of benzoyl chloride as solvent, in preparative scale experiments. One of us has shown[5] that in catalysis by hydrogen chloride or 2-chloroethanol the reaction product is 2-chloroethyl benzoate (>95%) when the ethylene oxide concentration $\gtrsim 1 \text{M}$ [equation (3)]. At higher ethylene oxide concentrations some polymeric product is detected [equation (4)]. In the present kinetic experiments the oxide concentration was therefore always

$$PhCOCl + \text{(epoxide)} \xrightarrow[\text{HO(CH}_2)_2\text{Cl}]{\text{HCl or}} PhCO_2(CH_2)_2Cl \qquad (3)$$

$$PhCOCl + n\text{(epoxide)} \longrightarrow PhCO[O(CH_2)_2]_n Cl \qquad (4)$$

$$PhCOCl + \text{(Me-epoxide)} \longrightarrow PhCO_2\underset{\underset{Me}{|}}{C}HCH_2Cl \qquad (5)$$

$<1 \text{M}$. Our preparative experiments using base catalysis were as follows. (i) Ethylene oxide (14·9 g) was allowed to bubble (30 min) into a stirred mixture of benzoyl chloride (88·0 g) and pyridine (1·7 g). The temperature in the reaction vessel reached 90—100° and all the ethylene oxide was absorbed. Subsequent vacuum distillation led to 2-chloroethyl benzoate[6] (58·1 g, 93%), b.p. 94° at 0·8 mmHg, together with the excess of benzoyl chloride (40·5 g, 97%), b.p. 44° at 0·8 mmHg. The chloro-ester was identified by its n.m.r. spectrum in deuteriochloroform.

[1] Part XXXVI, B. Boopsingh and D. P. N. Satchell, *J.C.S. Perkin II*, 1972, 1702.

[2] 'The Chemistry of the Ether Linkage,' ed. S. Patai, Wiley, London, 1967.

[3] N. N. Lebedev and V. F. Shvets, *Kinetics and Catalysis*, 1968, **9**, 504; V. F. Shvets and Y. U. Likov, *ibid.*, 1971, **12**, 347, 883; N. N. Lebedev and Y. I. Baranov, *ibid.*, 1964, **7**, 619; and earlier papers.

[4] V. F. Shvets, to be published.

[5] V. F. Shvets, to be published.

[6] L. W. Jones and R. T. Major, *J. Amer. Chem. Soc.*, 1927, **49**, 1535.

No other product was detected. The fate of the pyridine catalyst is uncertain (see below). An exactly analogous preparation using tetraethylammonium chloride (1 g) in place of pyridine led to a similar yield of chloro-ester as the only detectable product. (ii) Propylene oxide (12·0 g) was added (40 min) to a stirred mixture of benzoyl chloride (61·0 g) and tetraethylammonium chloride (1 g). The temperature of the mixture reached 90—120°. Subsequent vacuum distillation led to 2-chloro-1-methylethyl benzoate [7]
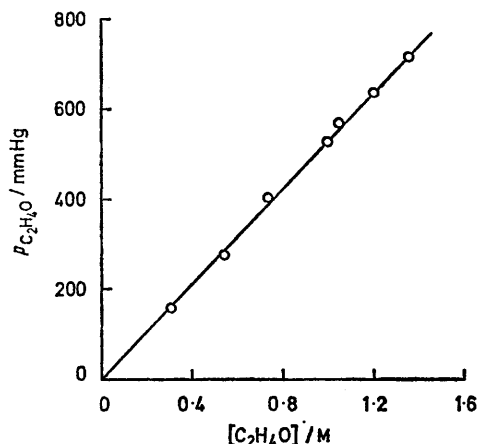

FIGURE 1 Calibration curve. $P_{C_2H_4O}$ = partial vapour pressure of ethylene oxide in benzoyl chloride at 70 °C

(37·8 g, 92%), b.p. 101° at 0·8 mmHg, and the excess of benzoyl chloride (31·0 g, 97%), b.p. 44° at 0·8 mmHg [equation (5)]. The product was again identified by its n.m.r. spectrum and contained <10% of 2-chloropropyl benzoate. It is evident, as is common in additions to substituted ethylene oxides,[2] that the chlorine atom adds preferentially to the carbon atom remote from the methyl substituent.

Kinetic Arrangements.—The various reactions were followed manometrically by Lebedev and Shvets' method,[3] the loss of ethylene oxide or, in certain cases the production of hydrogen chloride, being monitored. A typical calibration graph is shown in Figure 1. The temperature was usually 70° but a range of temperatures between 50 and 90° was also used. Runs were normally conducted using an excess of the benzoyl chloride (ε ca. 23) as solvent, but for all the experiments with p-nitrobenzoyl chloride, and for those which examined the reaction order in benzoyl chloride itself, a chlorobenzene–nitrobenzene mixture (4 : 6 v/v, ε ca. 23) was used. Reaction mixtures were placed in the all-glass apparatus and brought to the required temperature equilibrium using a thermostat bath accurate to $\pm0\cdot5°$. Reaction was usually initiated by the final addition of a small amount of the catalyst. The observed rate constants were normally reproducible to within $\pm4\%$.

RESULTS AND DISCUSSION

The Spontaneous Reaction.—Ethylene oxide (0·2—0·5M) dissolved in benzoyl chloride is acylated relatively slowly. It is removed in a zero-order process with rate constant $k_0 = (0\cdot47 \pm 0\cdot15) \times 10^{-4}$ at 90° and ca. $0\cdot2 \times 10^{-4}$ mol l^{-1} s^{-1} at 70°. The observed rates are somewhat irreproducible and it is probable that these 'spontaneous' rates really represent catalysis by adventitious hydrogen chloride in the solvent. Both

added water and hydrogen chloride are known to catalyse the acylation and to lead to a zero-order disappearance of ethylene oxide (see below).

The Chloride Ion Catalysed Reaction.—Details of reactions with ethylene oxide conducted at 70° using tetraethylammonium chloride as catalyst are in Table 1 and Figure 2. The loss of ethylene oxide was always an

TABLE 1
Tetraethylammonium chloride catalysed benzoylation of ethylene oxide at 70°. $[C_2H_4O]_{initial} = 0\cdot6$—$0\cdot9$M; solvent, benzoyl chloride (ca. 8·3M); k_0 = observed zero-order rate constant (mol l^{-1} s^{-1}); $10^4 k_0 = 0\cdot2$ for spontaneous benzoylation (see text); catalyst added as Et_4NCl,H_2O (see text for effect of H_2O)

$10^3[Et_4NCl]$	2·0	3·7	5·7	7·4	9·5	10·2
$10^4 k_0$	1·38	2·41	3·50	4·21	5·35	6·00
$10^2(k_0 - 0\cdot2)/[Et_4NCl]$	5·9	6·0	5·8	5·3	5·7	5·8

accurately zero-order process and the reaction is clearly of the first order in total catalyst concentration. Since the addition of tetraethylammonium perchlorate in relatively high (0·03M) concentrations did not significantly catalyse the acylation, the observed catalysis
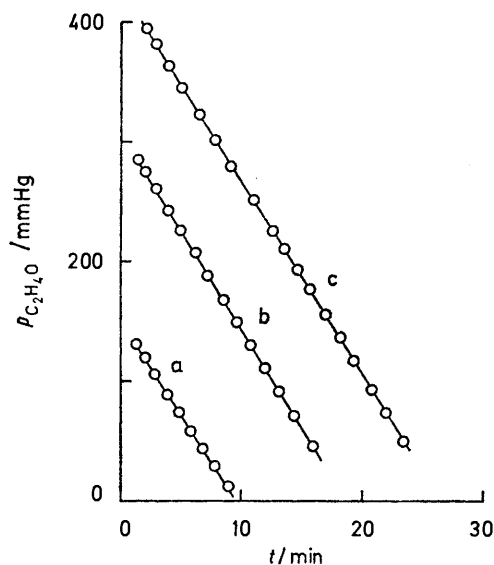

FIGURE 2 Zero-order disappearance of ethylene oxide. Solvent, PhCOCl; temperature, 70 °C; [Et$_4$NCl], 0·01M; [C$_2$H$_4$O]$_{initial}$ a, 0·326; b, 0·662; c, 0·900M; $P_{C_2H_4O}$ = partial vapour pressure of ethylene oxide

TABLE 2
Kinetic order in benzoyl chloride at 70°. $[C_2H_4O]_{initial} = 0\cdot65$—$0\cdot85$M; solvent, 4 : 6 v/v PhCl–PhNO$_2$; [Et$_4$NCl] = 0·01M; k_0 = observed zero-order rate constant (mol l^{-1} s^{-1})

[PhCOCl]	8·30	6·65	4·98	3·32	1·66
$10^4 k_0$	5·87	4·55	3·29	2·30	1·10
$10^5 k_0/$[PhCOCl]	7·0	6·9	6·6	6·9	6·7

by tetraethylammonium chloride is probably critically dependent on the basicity of the chloride ion. The reaction order in benzoyl chloride was examined in chlorobenzene–nitrobenzene mixtures (Table 2). This order is clearly unity and the overall second-order rate

[7] H. F. Mosley and A. G. Green, *Ber.*, 1884, **17**, 3015.

constant, k_2, in equation (6) is $6\cdot 8 \times 10^{-3}$ l mol^{-1} s^{-1}. (The spontaneous rate in the mixed solvent is assumed to make proportionately the same small relative contribution to k_0 as in pure benzoyl chloride.) The effects of

$$-\mathrm{d[C_2H_4O]}/\mathrm{d}t = k_2[\mathrm{C_2H_4O}]^0[\mathrm{PhCOCl}][\mathrm{Et_4NCl}] \quad (6)$$

temperature changes are shown in Table 3 and the effects of other tetra-alkylammonium chlorides on the ethylene oxide–benzoyl chloride reaction are given in Table 4. The sequence of catalytic effectiveness is $\mathrm{Me_4N} < \mathrm{Et_4N} \simeq \mathrm{Bu_4N}$.

Table 5 lists results of experiments using ethylene oxide with p-nitro- and p-methyl-benzoyl chlorides. The acylation with p-nitrobenzoyl chloride in chlorobenzene–nitrobenzene mixtures was shown to be of the first order in the p-nitro-compound, in keeping with the above result for benzoyl chloride. The comparison of reactivities in Table 5 is only approximate since the p-methyl derivative acted as its own solvent whereas

TABLE 3

Effect of temperature and Arrhenius parameters for the tetraethylammonium chloride catalysed benzoylation of ethylene oxide. $[\mathrm{C_2H_4O}] = 0\cdot 6\text{--}0\cdot 817\mathrm{M}$; solvent, benzoyl chloride ($ca.$ $8\cdot 3\mathrm{M}$); for k_0 (mol l^{-1} s^{-1}) and k_2 (l mol^{-1} s^{-1}) see Table 1 and text; in calculating k_2 any (relatively very small) contribution to k_0 from a spontaneous rate has been neglected

Temp. (°C)	54·1	60·8	65·1	70·0	76·5
$10^3[\mathrm{Et_4NCl}]$	8·0	8·4	7·9	8·3	7·5
10^4k_0	1·43	2·64	3·16	4·78	5·88
10^3k_2	2·1	3·8	4·7	6·9	9·4

$\Delta S^{\ddagger} = -29 \pm 1$ cal mol^{-1} K^{-1}, $E_a = 13\cdot 7 \pm 0\cdot 5$ kcal mol^{-1}.

TABLE 4

Effects of tetramethyl- and tetra-butylammonium chloride at 70°. Solvent = benzoyl chloride ($8\cdot 3\mathrm{M}$); k_0 (mol l^{-1} s^{-1}) and k_2 (l mol^{-1} s^{-1}) as Table 3; $10^4k_0 = 0\cdot 2$ for spontaneous rate at 70°

$[\mathrm{C_2H_4O}]_{\mathrm{initial}}$	0·65		$[\mathrm{C_2H_4O}]_{\mathrm{initial}}$	0·62	0·59
$10^3[\mathrm{Me_4NCl}]$	3·4		$10^3[\mathrm{Bu_4NCl}]$	5·9	8·3
10^4k_0	0·44		10^4k_0	3·6	4·9
10^3k_2	0·9		10^3k_2	6·9	6·8

TABLE 5

The reactivity of p-methyl- and p-nitro-benzoyl chlorides towards ethylene oxide at 70°. k_0 (mol l^{-1} s^{-1}) and k_2 (l mol^{-1} s^{-1}) as in Table 3; negligible contribution from spontaneous rate in these systems under conditions used

(i) p-Nitrobenzoyl chloride (solvent, 4 : 6 v/v chlorobenzene–nitrobenzene)

$[\mathrm{C_2H_4O}]_{\mathrm{initial}}$	0·15	0·29	10^4k_0	4·13	4·10
$[\mathrm{NO_2C_6H_4COCl}]$	1·84	1·84	10^3k_2	34·0	33·7
$10^3[\mathrm{Et_4NCl}]$	6·6	6·6			

(ii) p-Methylbenzoyl chloride [solvent, p-methylbenzoyl chloride ($7\cdot 02\mathrm{M}$)]

$[\mathrm{C_2H_4O}]_{\mathrm{initial}}$	0·62	0·57	10^4k_0	0·82	1·25
$10^3[\mathrm{Et_4NCl}]$	6·1	9·3	10^3k_2	1·8	1·9

$k_2(p\text{-NO}_2) : k_2(\mathrm{H}) : k_2(p\text{-Me}) = 33\cdot 9 : 6\cdot 8 : 1\cdot 9.$

the other two compounds were compared in a chlorobenzene–nitrobenzene mixture. We also assume, as is very probable, that the reaction products formed using

the p-nitro and p-methyl derivatives are analogous to that found using the parent chloride.

The reaction between propylene oxide and benzoyl chloride catalysed by tetraethylammonium chloride was briefly studied (Table 6). This acylation is also
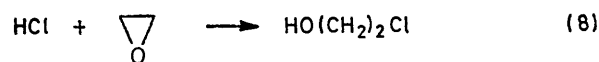
TABLE 6

The benzoylation of propylene oxide at 70°. $[\mathrm{C_3H_8O}]_{\mathrm{initial}}$ $ca.$ $0\cdot 8\mathrm{M}$; solvent, benzoyl chloride ($8\cdot 3\mathrm{M}$); k_0 (mol l^{-1} s^{-1}) and k_2 (l mol^{-1} s^{-1}) as in Table 3

$10^3[\mathrm{Et_4NCl}]$	11·0	7·40	10^4k_2	2·3	2·3
10^4k_0		0·208	0·140		

accurately zero order in oxide and probably of the first order in catalyst. Assuming that the order in benzoyl chloride is unity, the overall second-order rate constant, k_2 [$cf.$ equation (6)] is $2\cdot 3 \times 10^{-4}$ l mol^{-1} s^{-1} at 70°, this oxide therefore being about 30-fold less reactive than ethylene oxide.

The Water, Hydrogen Chloride, and 2-Chloroethanol Catalysed Reactions.—The fact that the catalysts anhydrous tetramethyl- and tetrabutyl-ammonium chlorides lead to behaviour very similar to that shown by tetraethylammonium chloride monohydrate suggests that the small quantity of water invariably added with the tetraethyl compound does not contribute importantly to the observed catalysis. However, since most of our experiments employed the tetraethyl compound, we have examined separately the effect of added water to check this point. In an excess of benzoyl chloride, water may be assumed to lead relatively rapidly to benzoic acid and hydrogen chloride, and the product hydrogen chloride to add to any ethylene oxide also present. The resulting 2-chloroethanol can then be acylated by the benzoyl halide, giving 2-chloroethyl benzoate [equations (7)—(9)], the same product as that

$$\mathrm{H_2O} + \mathrm{PhCOCl} \longrightarrow \mathrm{PhCO_2H} + \mathrm{HCl} \quad (7)$$

$$\mathrm{HCl} + \underset{O}{\triangledown} \longrightarrow \mathrm{HO(CH_2)_2Cl} \quad (8)$$

$$\mathrm{HO(CH_2)_2Cl} + \mathrm{PhCOCl} \longrightarrow \mathrm{PhCO_2(CH_2)_2Cl} + \mathrm{HCl} \quad (9)$$

obtained in the base-catalysed addition (see Experimental section). Thus added water, hydrogen chloride, or 2-chloroethanol will certainly be expected to catalyse the addition, and independent experiments show that they do so. In practice it is found that equivalent concentrations of these compounds lead to the same zero-order rate of removal of ethylene oxide (Figure 3). The curved region of the water reaction (Figure 3a) represents the build-up of the hydrogen chloride concentration via reaction (7). More details of the 2-chloroethanol catalysis at 90° are in Table 7. It is evident that the reaction is of the first order in catalyst [equation (10)]. A reasonable explanation of the observed reaction orders, and of the identical catalysis by 2-chloroethanol and hydrogen chloride, is to assume that reaction

$$-\mathrm{d[C_2H_4O]}/\mathrm{d}t = k_1[\mathrm{HO(CH_2)_2Cl}][\mathrm{C_2H_4O}]^0 \quad (10)$$
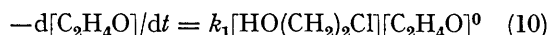
TABLE 7

2-Chloroethanol catalysis of the reaction between benzoyl
chloride and ethylene oxide at 70°. Solvent, benzoyl
chloride; k_0 = observed zero-order rate constant
(mol l^{-1} s^{-1})

[C$_2$H$_4$O]$_{initial}$	0·60	0·20	0·60	0·60
[HOC$_2$H$_4$Cl]	0·10	0·20	0·20	0·30
$10^4 k_0$	1·65	3·30	3·30	4·78
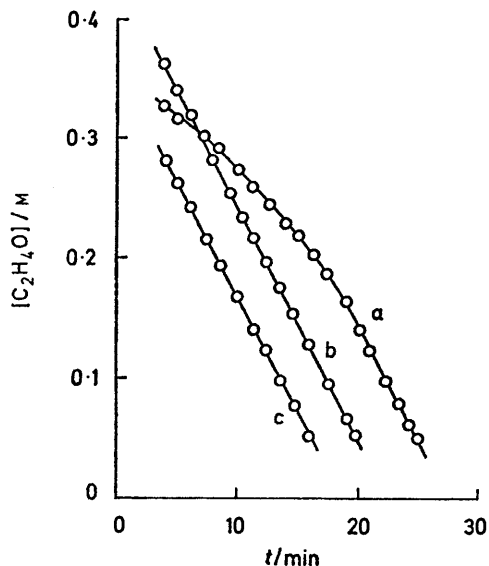
FIGURE 3 Catalysis by water, hydrogen chloride, and 2-chloro-
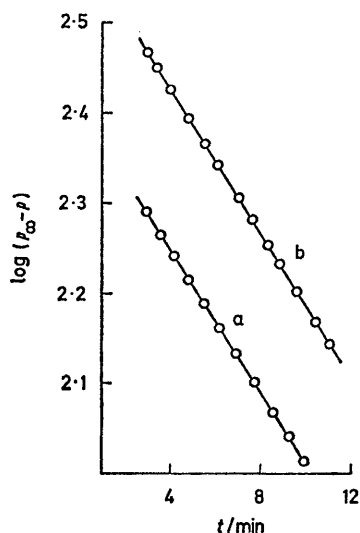ethanol. Solvent, PhCOCl; temperature, 90 °C; a, [H$_2$O]
0·211; b, [HCl] 0·196; c, [HOC$_2$H$_4$Cl] 0·201M

FIGURE 4 First-order production of HCl in reaction (9).
Solvent, PhCOCl; temperature, 90 °C; [HOC$_2$H$_4$Cl]$_{initial}$,
a, 0·075; b, 0·115M; p = partial pressure of HCl

(8) is much faster than reaction (9) and lies far to the
right. With hydrogen chloride, or 2-chloroethanol, in
deficit compared with the other reagents, this scheme
leads to the observed kinetic form: [catalyst] = [HCl] =
[HO(CH$_2$)$_2$Cl] and $-d[C_2H_4O]/dt = k_2$[PhCOCl][C$_2$H$_4$O]^0-
[catalyst] = k_1[catalyst].

The value of $k_1 = k_2$[PhCOCl] = $(16·0 \pm 0·5) \times 10^{-4}$

s^{-1} at 90°. This value shows that, as suggested above,
the accelerating effect of the concomitant water added
with the tetraethyl ammonium chloride in our experi-
ments on salt catalysis will have been negligible.

We have supported our interpretation of the hydrogen
chloride, 2-chloroethanol, etc., catalysis by direct measure-
ment (Figure 4) of the rate of reaction (9). This reaction
is of the first order in 2-chloroethanol and in an excess of
benzoyl chloride we have equation (11). Our average

$$-d[HO(CH_2)_2Cl]/dt = d[HCl]/dt = k_2(PhCOCl)-$$
$$[HO(CH_2)_2Cl] = k_1[HO(CH_2)_2Cl] \quad (11)$$

value for k_1 at 90° from these experiments is 15·4 ×
10^{-4} s^{-1} (in good agreement with the value obtained
from the runs involving ethylene oxide). In the presence
of 0·0107M-Et$_4$N$^+$Cl$^-$, k_1 rises to only 18·0 × 10^{-4} s^{-1} at
90°. It is clear therefore that the salt catalysis of the
acylation of ethylene oxide does not arise via a process
like (12), the adventitious 2-chloroethanol deriving from
adventitious water or hydrogen chloride. The salt
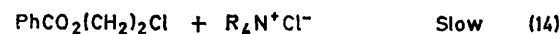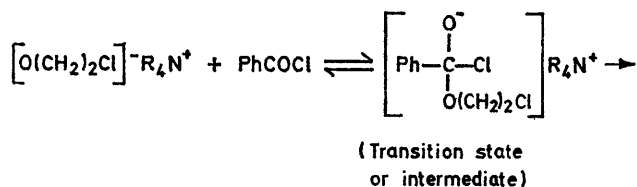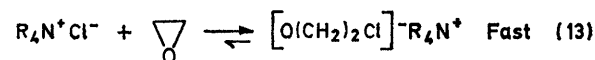catalysis is much too fast for processes (9) or (12) to be
important.

$$HO(CH_2)_2Cl + PhCOCl \xrightarrow{Et_4NCl} PhCO_2(CH_2)_2Cl + HCl \quad (12)$$
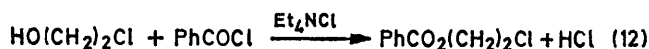
The Effect of Benzoic Acid.—Any benzoic acid, pro-
duced by the acylation of water [reaction (7)] added with
tetraethylammonium chloride, was also shown to
produce a negligible effect compared with that of the
salt (Table 8).

TABLE 8

Effect of benzoic acid at 70°. [C$_2$H$_4$O] = 0·60—0·80M;
solvent, benzoyl chloride; k_0 = observed zero-order
rate constant (mol l^{-1} s^{-1}); 10^3[Et$_4$NCl] = 7·8M

10^2[PhCO$_2$H]	0·0	2·88	3·61
$10^4 k_0$	4·50	4·27	4·03

Mechanism of Alkylammonium Chloride Catalysis.—
The effects on the benzoyl chloride–ethylene oxide re-
action of various compounds HX, and the mechanism of
the HX catalysis, have been dealt with above. None of
these matters complicates the catalysis by R$_4$N$^+$Cl$^-$.
This latter process exhibits the rate equation (6). The
effects of substituents in the benzoyl halide suggest that
the rate-determining step involves nucleophilic attack
on the carbonyl carbon atom. One obvious possibility
for the mechanism is therefore equations (13) and (14).
R$_4$N$^+$Cl$^-$ was always present in great deficit compared

$$R_4N^+Cl^- + \overset{O}{\underset{}{\triangle}} \rightleftharpoons [O(CH_2)_2Cl]^-R_4N^+ \quad \text{Fast} \quad (13)$$

$$[O(CH_2)_2Cl]^-R_4N^+ + PhCOCl \rightleftharpoons \begin{bmatrix} O^- \\ | \\ Ph-C-Cl \\ | \\ O(CH_2)_2Cl \end{bmatrix} R_4N^+ \rightarrow$$

(Transition state
or intermediate)

$$PhCO_2(CH_2)_2Cl + R_4N^+Cl^- \qquad \text{Slow} \quad (14)$$

with ethylene oxide, so that, if the equilibrium (13) lies well to the right, the reaction will appear as zero order in oxide and of the first order in both salt and benzoyl chloride, as found. This scheme, although simple and chemically straightforward, is very unlikely to be correct since previous work [8] strongly suggests that the rate of attack of species RO⁻ on PhCOCl in a medium with ε ca. 23 will, at 70°, be appreciably too fast to account for the rate constants observed in the present systems.

An alternative mechanism, chemically less simple, but compatible with all the kinetic evidence, is given in equations (15) and (16). As for reactions (13) and (14), with $R_4N^+Cl^-$ in deficit and the pre-equilibrium lying

$$R_4N^+Cl^- + \underset{O}{\triangledown} \rightleftharpoons \underset{O}{\triangledown}\underset{+}{Cl^-} \quad \text{Fast} \quad (15)$$
$$\underset{NR_4}{}$$
(Complex)

$$\underset{O}{\triangledown}\underset{NR_4}{Cl^-} + PhCOCl \longrightarrow \left[\begin{array}{c} \text{Cl}^- \\ \underset{O}{\triangledown} \underset{NR_4}{+} \\ Ph-C \\ \parallel \quad Cl \\ O \end{array} \right]$$
(Transition state)

$$\longrightarrow PhCO_2(CH_2)_2Cl + R_4N^+Cl \quad \text{Slow}, k \quad (16)$$
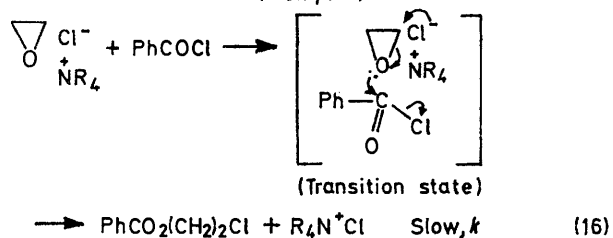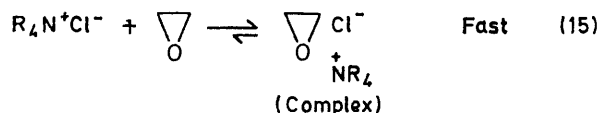
well to the right, the overall rate equation will be (17), as found.

$$-d[C_2H_4O]/dt = k[PhCOCl][C_2H_4O]^0[R_4N^+Cl^-] \quad (17)$$

This scheme accounts for the general effect of substituents in the benzoyl chloride, for the relative reactivity of the different tetra-alkylammonium chlorides (their polarities and dissociabilities will be in the sequence Me < Et < Bu), and for the fact that, although the dissociation constants of the salts would be expected [9] to have values giving significant amounts of free ions in the concentration range used, there is no evidence for any departure from strict first-order dependence on salt concentration which would be expected were free chloride ions effective alone. The scheme is probably also compatible with $\Delta S^{\ddagger}$ and with the observed lower velocity for propylene, compared with ethylene, oxide. This decrease is surprisingly large, but then little is known about substituent effects in ethylene oxide.[2] In general the suggested transition state is in keeping with current views concerning the opening of oxide rings.[2]

The Pyridine Catalysed Reaction.—Use of pyridine as catalyst led to an approximately zero-order removal of ethylene oxide, the plots revealing a slight acceleration

[8] M. L. Bender and M. C. Chen, *J. Amer. Chem. Soc.*, 1963, **85**, 30; N. N. Lebedev, V. P. Savel'yanov, Y. I. Baranov, and V. F. Shvets, *Theor. Exptl. Chem.*, 1968, **4**, 203.

with time (Figure 5a). Addition of more ethylene oxide at the completion of a pyridine catalysed run led, however, to an accurately zero-order loss of the added
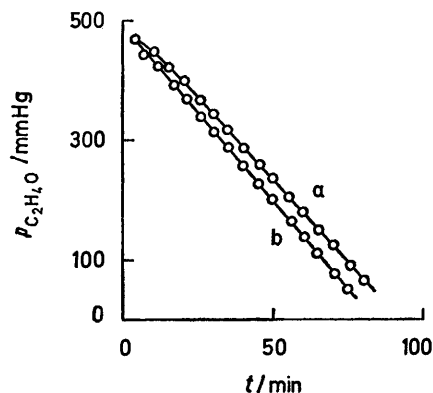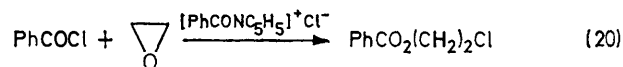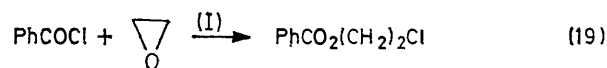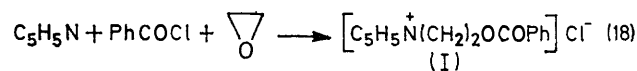

FIGURE 5 Pyridine catalysed benzoylation of ethylene oxide. Solvent, PhCOCl; temperature, 70 °C; $P_{C_2H_4O}$, partial pressure of C_2H_4O; a, $[C_5H_5N]$ 0·023, $[C_2H_4O]_{initial}$ ca. 1·0M; b, further addition of equivalent quantity of C_2H_4O to reaction mixture at completion of run a

oxide (Figure 5b). These results suggest that pyridine is converted into another, slightly more effective, catalyst during the reaction. It is difficult to be certain what this new catalyst is. One possibility, which suggests itself in the light of previous work,[10] is shown in equations (18) and (19). A semi-preparative scale reaction employing a high concentration of pyridine

$$C_5H_5N + PhCOCl + \underset{O}{\triangledown} \longrightarrow \left[C_5H_5\overset{+}{N}(CH_2)_2OCOPh\right]Cl^- \quad (18)$$
(I)

$$PhCOCl + \underset{O}{\triangledown} \xrightarrow{(I)} PhCO_2(CH_2)_2Cl \quad (19)$$

$$PhCOCl + \underset{O}{\triangledown} \xrightarrow{[PhCONC_5H_5]^+Cl^-} PhCO_2(CH_2)_2Cl \quad (20)$$

failed, however, to detect any of the salt (I). Since it is probable [11] that pyridine in an excess of benzoyl chloride exists largely as $[PhCONC_5H_5]^+Cl^-$, it is difficult to see why the reaction with oxide does not proceed as outlined in (20), the details being analogous to equations (15) and (16). This would not, however, lead to accelerating zero-order plots. We have not been able to resolve this anomaly and have not examined the pyridine catalysis further.

[9] R. A. Robinson and R. A. Stokes, ' Electrolyte Solutions,' Butterworths, London, 2nd edn., 1968.

[10] M. F. Sorokin, L. G. Shode, A. B. Shteinpress, and L. N. Finyakin, *Kinetics and Catalysis*, 1968, **9**, 548.

[11] D. P. N. Satchell and R. S. Satchell, ' The Chemistry of Acyl Halides,' ed. S. Patai, Wiley, London, 1972, ch. 4.