# Kinetics of Phase-transfer Etherification Reactions of *p*-Chloronitrobenzene by Alkoxides

**Jaime de la Zerda Lerner, Sasson Cohen, and Yoel Sasson** *
*Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

The substitution reaction of chloride by alkoxide anions in *p*-chloronitrobenzene in a phase-transfer catalytic system has been studied and successfully performed in high yield and without the occurrence of side reactions. The effect of several parameters has been experimentally investigated. In particular, the poisoning effect of the chloride anion produced throughout the reaction is studied and a practical answer to successfully overcome this problem and increase yields is presented. A kinetic model based on the collected data is proposed.

The nucleophilic substitution of halogens by certain anions in aromatic compounds in which a nitro group is present at the *ortho*- or *para*-position with respect to the chloride is well known.[1] Such reactions are expected to be more effective as the attacking group shows more pronounced nucleophilicity. This would be, for instance, the case of alkoxide anions as compared with the hydroxide anion. It has been found[1] that methoxy and ethoxy anions react with *p*-chloronitrobenzene (PCNB) in such a fashion as to give the corresponding ethers or *p*-alkoxynitrobenzenes (PANB), equation (1).

$$\underset{\text{PCNB}}{p\text{-ClC}_6\text{H}_4\text{NO}_2} + \text{ROH} + \text{Na}^+\text{OH}^- \longrightarrow \underset{\text{PANB}}{p\text{-ORC}_6\text{H}_4\text{NO}_2}{}^+\text{Na}^+\text{Cl}^- + \text{H}_2\text{O} \quad (1)$$

Several alkoxides of substituted benzene compounds are important intermediates in the chemical industry *e.g.*, *p*-nitrophenetol, which is obtained from the ethoxylation of *p*-chloronitrobenzene—a starting material in the synthesis of *p*-phenetidine—is itself an intermediate useful in the production of phenatecin, phenecell, *p*-phenetylurea, ethoxyquin, and many dyestuff intermediates.

A number of important side reactions usually occur in such chemical systems, mainly due to the reduction of the nitro group by the alkoxide anion.[2] Various azoxy compounds are obtained. In a typical system in which PCNB is reacted with 96% ethanol in the presence of concentrated NaOH at 55 °C, the mixtures that appear in Table 1 are obtained.[3]

**Table 1.** Composition of reaction mixture of PCNB, alcohol, and base obtained without catalyst.[a]

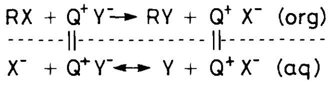
| Substance | Composition (%) 2 h | 10 h |
|---|---|---|
| PCNB | 10 | 4 |
| $p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{OH}$ | 4 | 5 |
| $p\text{-HOC}_6\text{H}_4\text{NO}_2$ | 0.5 | 0.3 |
| 4,4′-Dichloroazoxybenzene | 70 | 21 |
| 4,4′-Diethoxyazoxybenzene | 11.5 | 64.8 |
| 4,4′-Dihydroxyazoxybenzene | 4 | 4.9 |
| Total | 100 | 100 |

[a] *Conditions:* alcohol, 96% EtOH; base, 49% NaOH; *T* 55 °C.

These reduction reactions may be avoided by performing them in an oxygen atmosphere. Oxygen neutralizes the radical ion originally formed and thus avoids the formation of azo-compounds, though the formation of the desired product is slow and in low conversion yields. Furthermore, the presence of oxygen in the system stimulates the production of nitrophenol—another undesired by-product.

Several researchers have developed methods to avoid the side reactions mentioned and increase the reaction yield, mainly by the addition of different catalysts, such as sodium silicate, $\text{MnO}_2$, $\text{Co(OH)}_2$, $\text{H}_2\text{NCONH}_2$, $\text{HOCH}_2\text{CH}_2\text{NH}_2$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and the presence of oxygen or air enriched in oxygen.[4–7] In several cases, high conversions of the desired products are obtained, however, both the danger in the use of oxygen and the fact that the catalysts utilized are usually expensive confers limitations on the above methods when they are applied on an industrial scale.

Studies on the behaviour of the above system in phase-transfer catalytic conditions were undertaken by us and by other researchers,[8–10] and remarkable results in the form of high yields of desired products were obtained at relatively mild conditions. That is, it has been found that phase-transfer catalysis (PTC) contributes not only to higher reaction rates and conversions, but also favourably influences the selectivity of the system. A systematic kinetic study that could render a quantitative picture of the system behaviour has been lacking to date. This work presents an empirical-theoretical study on the effect of the various parameters that take part in this system.



**Scheme.** Nucleophilic substitution in a PTC system. RX is the halide, $Q^+$ is the quaternary amine cation and $Y^-$ is the substituting anion.

In principle, a nucleophilic substitution reaction promoted by phase-transfer catalysis would behave in the following fashion.[11] If RX is a given organic substrate and $Y^-$ is the nucleophile present in a separate aqueous phase, the presence of a phase-transfer catalyst (*e.g.*, a quaternary ammonium salt $Q^+X^-$ or 'quat') would permit the transfer of $Y^-$ from the inorganic to the organic phase and its reaction with RX would take place in the way described in the Scheme.

In particular, if the substituent is an alkoxide anion formed *in situ* in the system by the reaction of alcohol (ROH) and concentrated caustic base, and the substrate is PCNB, the following set of reactions would occur:

$$\text{ROH} + \text{OH}^- \underset{}{\overset{K_a}{\rightleftharpoons}} \text{RO}^- + \text{H}_2\text{O} \quad (2)$$

$$\text{Q}^+\text{X}^- + \text{OR}^- \overset{K_{\text{sel}}}{\rightleftharpoons} \text{Q}^+\text{OR}^- + \text{X}^- \quad (3)$$

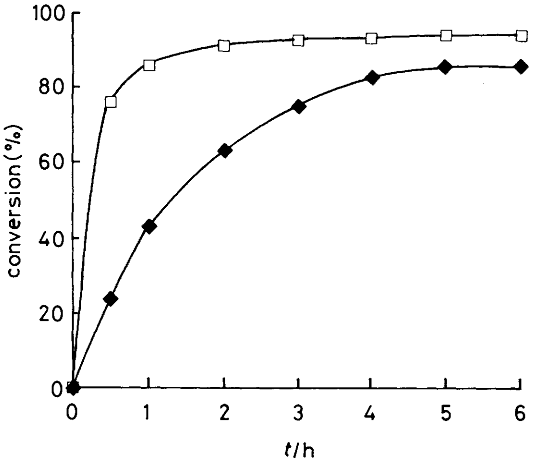


**Figure 1.** Kinetic profiles of reactions with methanol and pentanol. Conversion % is based on amount of PCNB reacted. □, methanol; ◆, pentanol.

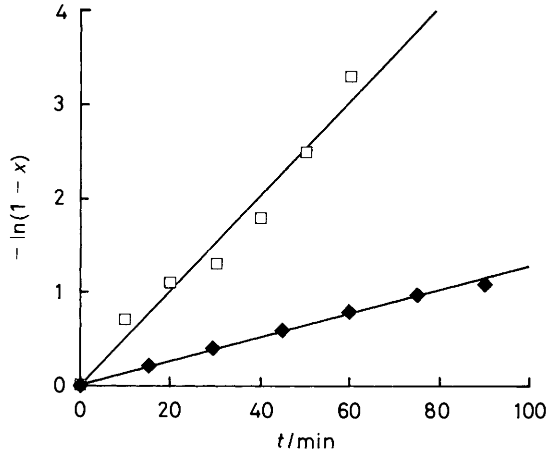


**Figure 2.** Correlation between kinetic data and a first-order reaction model; alkoxide sources are: □, methanol and ◆, pentanol, respectively.

$$\mathrm{PCNB} + \mathrm{Q^+OR^-} \xrightarrow{k} \mathrm{PANB} + \mathrm{Cl^-} \qquad (4)$$

where $K_a$ is the acidity constant of the alcohol, defined as

$$K_a = \frac{[\mathrm{OR^-}]}{[\mathrm{ROH}][\mathrm{OH^-}]} \qquad (5)$$

$K^{\mathrm{sel}}$ is the selectivity constant for extraction of $\mathrm{OR^-}$ with respect to that of $\mathrm{X^-}$, defined as[11]

$$K^{\mathrm{sel}} = \frac{[\mathrm{Q^+OR^-}][\mathrm{X^-}]}{[\mathrm{Q^+X^-}][\mathrm{OR^-}]} \qquad (6)$$

and $k$ is the rate constant of the final substitution reaction.

## Results and Discussion

A preliminary study of the kinetic behaviour of the system was first performed. This permitted the determination of the rate equation of the system in its simplest form and observed kinetic constant values ($k_{\mathrm{obs}}$) were attained. Then the study of the different parameters in the behaviour of the system was undertaken.

**Table 2.** Values of $k_{\mathrm{obs}}$ for the reaction as performed with four different primary alcohols.[a]

| Alcohol | $k_{\mathrm{obs}}$ |
|---|---|
| Methanol | $3.61 \times 10^{-4}$ |
| Ethanol | $1.685 \times 10^{-4}$ |
| Butanol | $1.712 \times 10^{-4}$ |
| Pentanol | $1.70 \times 10^{-4}$ |

[a] *Conditions:* 0.02 mol PCNB; 0.06 mol 45% NaOH; 0.25 g TBAB (8 mol%); 0.04 mol alcohol; $T$ 80 °C; magnetic stirring.

*Kinetic Behaviour.*—The substitution reaction can be reduced to the following [equation (7)]:

$$\mathrm{PCNB} + \mathrm{Q^+OR^-} \xrightarrow{k} \mathrm{PANB} + \mathrm{Q^+Cl^-} \qquad (7)$$

The simplest kinetic scheme that could describe the rate of this reaction ($r$) would be

$$r = \mathrm{d[PCNB]}/\mathrm{d}t = -k[\mathrm{PCNB}][\mathrm{Q^+OR^-}] \qquad (8)$$

*i.e.* a first-order reaction in both the substrate and the quat in its alkoxide form. If the base and the alcohol are in relatively great excess in the system, and since the quat is added in catalytic amounts, one could assume $[\mathrm{Q^+OR^-}]$ to be constant throughout the reaction, as a good first approximation, whatever the order in $\mathrm{Q^+OR^-}$. Thus one would have

$$r = k_{\mathrm{obs}}[\mathrm{PCNB}] \qquad (9)$$

where

$$k_{\mathrm{obs}} = k[\mathrm{Q^+OR^-}] \qquad (10)$$

Kinetic experiments with four different primary alcohols (methanol, ethanol, butanol and pentanol respectively) were performed in order to find out whether the reaction actually is first order in PCNB. PCNB (0.02 mol) was reacted with alcohol (0.04 mol) and NaOH (0.04 mol, 45% w/w) in the presence of tetrabutylammonium bromide (TBAB) (0.25 g, 8% w/w in relation to PCNB) at 80 °C. Results corresponding to MeOH and PeOH appear graphically in Figure 1.

Another set of kinetic experiments was performed with increased amounts of methanol and pentanol, respectively (0.06 mol) and NaOH (0.08 mol, 49% w/w) as compared with that of PCNB (0.02 mol) and TBAB (0.25 g, 8% w/w in relation to PCNB) at 80 °C. The values of conversion ($x$) obtained were used to calculate the corresponding values of $-\ln(1-x)$, which were found to correlate linearly very well with time (Figure 2) thus showing that the reaction is of overall first order in both cases. In fact, from the above data it can be also inferred that the reaction is of zero order with respect to $\mathrm{Q^+OR^-}$, since otherwise $k_{\mathrm{obs}}$ would not be constant and a linear relationship between the above logarithmic function and time would not be found. The actual values of $k_{\mathrm{obs}}$ obtained for the reactions appear in Table 2.

The value corresponding to methanol is more than twice the value obtained for any other alcohol. This may be due to the unique nature of this alcohol: ($a$) its acidity constant is about one order of magnitude higher than that for the other alcohols, thus rendering a relatively higher $\mathrm{Q^+OR^-}$ concentration; and ($b$) its being partially dissolved in the aqueous phase (as opposed to the other cases) may lead to a more intimate interaction between the base and the alcohol, thus rendering again a higher alkoxide concentration.

**Table 3.** Values of conversion for the reaction as performed with different alcohols.[a]

| Alcohol | Conversion (%) after 21 h |
|---|---|
| Methanol | 99 |
| Ethanol | 94 |
| Butanol | 91.3 |
| Pentanol | 90.3 |
| Hexanol | 90.8 |
| Propanol | 16 |
| Butanol | 0 |
| Phenol | 100 |
| Benzyl alcohol | 100 |

[a] *Conditions:* 0.1 mol PCNB; 0.3 mol 45% NaOH; 0.25 g TBAB; 0.3 mol alcohol; *T* 80 °C; magnetic stirring.

**Table 4.** Values of $k_{obs}$ for the reaction as performed with four different primary alcohols.[a]

| Alcohol | $k_{obs}$ (methanol) | $k_{obs}$ (pentanol) |
|---|---|---|
| TBAB | $2.82 \times 10^{-4}$ | $1.35 \times 10^{-4}$ |
| TBPB | $2.82 \times 10^{-4}$ | — |
| THxAB | $2.68 \times 10^{-4}$ | — |
| THpAB | $2.78 \times 10^{-4}$ | — |
| TEBA | $2.73 \times 10^{-4}$ | $8.6 \times 10^{-5}$ |
| TBNHSO$_4$ | $2.73 \times 10^{-4}$ | $1.20 \times 10^{-4}$ |
| Aliquat | $1.71 \times 10^{-4}$ | $1.08 \times 10^{-4}$ |
| TENOH | $1.11 \times 10^{-4}$ | $1.00 \times 10^{-4}$ |
| TMAC | $7.6 \times 10^{-6}$ | $8.9 \times 10^{-5}$ |

[a] *Conditions:* 0.02 mol PCNB; 0.04 mol 45% NaOH; 0.0006 mol quat (3 mol%); 0.04 mol alcohol; *T* 80 °C; magnetic stirring. TBAB = tetrabutylammonium bromide; TBPB = tetrabutylphosphonium bromide; THxAB and THpAB = tetrahexyl- and tetraheptyl-ammonium bromide respectively; TEBA = triethylbenzylammonium chloride; TBNHSO$_4$ = tetrabutylammonium hydrogen sulphate; aliquat = trioctylmethylammonium chloride; TENOH = tetraethylammonium hydroxide (25% in water); TMAC = tetramethylammonium chloride.

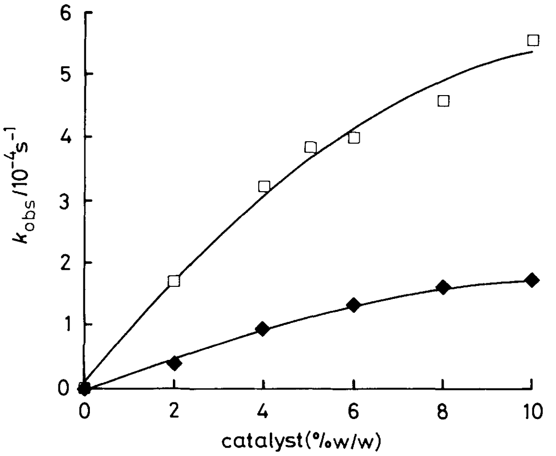


**Figure 3.** Influence of catalyst concentration on the observed rate constant $k_{obs}$. The catalyst is TBAB. □, methanol; ◆ pentanol.

*Study of Parameters.*—Several parameters were studied in detail in order to reach a broad understanding of the system, as well as to develop reaction conditions that render a high yield of product.

(*a*) *Nature of the alcohol.* Several alcohols were used and reaction conditions and results are summarized in Table 3.

Conversion in the case of the aromatic or benzyl alcohols is complete. With n-alcohols, conversion reaches 90–99%. For isopropyl alcohol (a secondary alcohol), conversion is much lower (16%), and in the case of t-butyl alcohol, there is no reaction at all under the given conditions. This behaviour can be explained if we consider the decreasing acidity of the alcohols.[12] In the case of t-butyl alcohol, steric hindrance is surely also a factor.

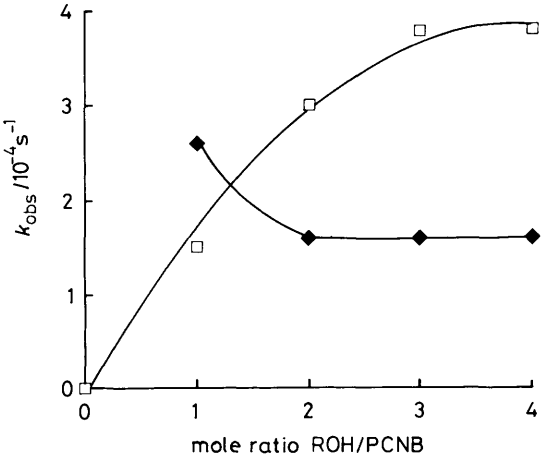


**Figure 4.** Influence of ROH/PCNB mole ratio on $k_{obs}$ for the etherification. □, methanol; ◆, pentanol.

(*b*) *Nature of the catalyst.* Two different alkoxide anion sources were studied—methanol and pentanol. The results are summarized in Table 4. The difference between the activity of the different catalysts can surely be attributed mainly to the different capacity of extraction of the alkoxide anion into the organic phase. As can be noticed, the highest $k_{obs}$ value obtained in both systems corresponds to the quat TBAB (and also TBPB for the case of methanol). This quat is more lipophilic than either TENOH or TMAC, and thus it may extract the alkoxide anions to the organic phase more easily than the latter. This would explain the higher $k_{obs}$ values for TBAB.

TMAC shows higher activity in the pentanol system. This may be due to the fact that this quat does not dissolve well in PCNB and thus stays mostly in the aqueous phase when methanol is used. On the other hand, TMAC dissolves in a mixture of PCNB and pentanol, thus becoming a more effective extractor of the alkoxide anion into the organic phase.

(*c*) *Concentration of the catalyst.* Methanol and pentanol systems were also utilized for this study. Results obtained for a series of experiments in which PCNB (0.02 mol) was reacted with alcohol (0.04 mol), 45% NaOH (0.04 mol) and TBAB in different amounts for different quat concentrations appear in Figure 3. In both cases, above a certain concentration of catalyst, the reaction rate changes very little. This is probably due to the fact that under the given stirring and temperature conditions, mass transfer of the active species into the organic phase reaches a limit due to interface saturation. At this point, addition of more catalyst will not help the reaction to proceed faster.

(*d*) *Alcohol/PCNB ratio.* Figure 4 describes the influence of the alcohol/substrate ratio in the reaction rate, found in a series of experiments in which PCNB (0.02 mol) was reacted with 45% NaOH (0.04 mol), TBAB (0.25 g, 8% w/w with respect to PCNB) and different amounts of alcohols, thus giving different ROH/PCNB mole ratios; *T* = 80 °C.

Two main features are apparent from the Figure 4.

(i) Beyond a certain alcohol/PCNB ratio, an increase in the value will not affect the reaction kinetics in either system. This means that, after the addition of a given amount of alcohol to the system, further addition of a similar amount will have much

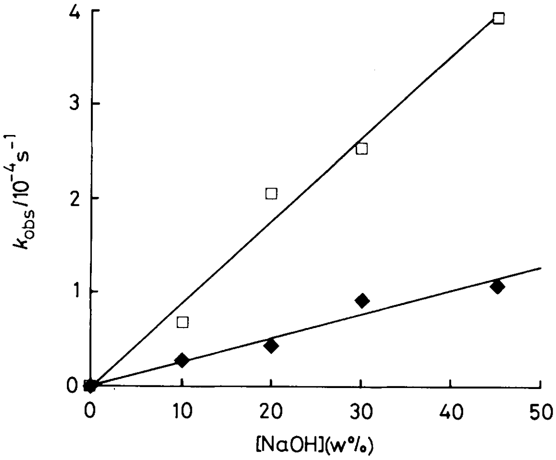


**Figure 5.** Relation between [NaOH] and the observed rate constant $k_{obs}$: □, methanol; ◆, pentanol.

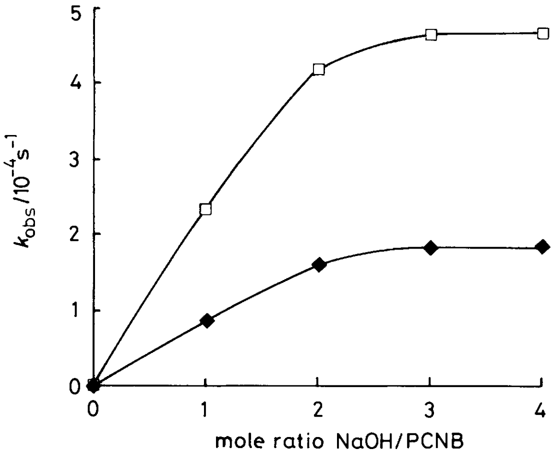


**Figure 6.** Influence of mole ratio NaOH/PCNB on $k_{obs}$ for the etherification. □, methanol; ◆, pentanol.

less effect than the first one in the formation of $RO^-$, and even less in that of the active species $Q^+OR^-$ [see equations (7)–(9)].

(ii) The activity of the system increases with an increase in the ratio in the case of methanol, as should be expected (more alcohol means more alkoxide and thus more $Q^+OR^-$).

For pentanol, however, the behaviour is, at first sight, rather unexpected. The activity decreases (although slightly) with an increase in the ratio, again, until a horizontal line is obtained. An explanation that seems to us plausible for this behaviour is that since pentanol, as opposed to methanol, dissolves completely in the organic phase, its dissolution causes a decrease in the PCNB and $Q^+OR^-$ concentration, thus reducing the reaction rate. Though an increase in the pentoxide anion concentration should be expected, this would nevertheless be much smaller than the parallel increase of methoxide anion in the methanol case, due to the lower acidity constant of the pentanol. Thus, the overall effect is a decrease in activity as the above ratio is increased.

(*e*) *Nature of the base.* Most experiments in this work were performed with NaOH as the base. Other bases were, however, also studied as follows: (i) $Ca(OH)_2$; (ii) $Na_2CO_3$; (iii) $NaHCO_3$; (iv) a mixture of $Na_2CO_3$ and $NaHCO_3$(1:1), and (v) KOH. In all cases the total base concentration was 45% w/w. Reactions were performed with methanol and pentanol, respectively.

In neither of the two systems did reaction occur with any of the above bases after 6 h except for KOH, which gave practically identical results as for NaOH (see Figure 1 above): $4.00 \times 10^{-4}$ $s^{-1}$ for the methanol system (*cf.* $3.94 \times 10^{-4}$ $s^{-1}$ for NaOH) and $1.62 \times 10^{-4}$ $s^{-1}$ for pentanol (*cf.* $1.60 \times 10^{-4}$ $s^{-1}$). These differences are insignificant. These results would mean that at such base concentrations, the activity of both bases is similar. And the other bases studied seem to be too weak to activate the system. It should be noticed that in the case of $Ca(OH)_2$ an emulsion was created, but even so, no reaction occurred.

(*f*) *Concentration of the base.* Figure 5 shows the effect of base concentration on $k_{obs}$, the NaOH/PCNB ratio being constant. Reactions were performed at 80 °C: PCNB (0.02 mol) was reacted with alcohol (0.04 mol), TBAB (0.25 g, 8% w/w with respect to PCNB), and NaOH (0.04 mol) in solutions at different concentrations.

The graphs in Figure 5 show an approximately linear dependence of $k_{obs}$ on [NaOH] in both systems. An increase in rate is expected for higher base concentrations since that implies higher $OR^-$ concentrations. One would expect that as concentrations become higher, the corresponding $OR^-$ (and thus $Q^+OR^-$) concentrations would increase at a slower pace than at the beginning, thus giving a curve that asymptotically would tend to straighten horizontally. Another effect may be taking part in the system as [NaOH] increases—the salting-out effect due to such an increase. Higher NaOH concentrations would 'push out' the $Q^+OR^-$ formed into the organic phase, thus accelerating the reaction. The overall effect makes the results more or less linear, at least within the working concentration range. Previous work[13,14] shows, surprisingly, a fifth-order dependency of rate on [NaOH].

(*g*) *NaOH/PCNB ratio.* The influence of the the mole ratio between NaOH and PCNB for a given concentration of 45% NaOH was studied. PCNB (0.02 mol) was reacted with alcohol (0.04 mol), TBAB (0.25 g, 8% w/w) with respect to PCNB) and different amounts of a 45% NaOH solution, rendering different NaOH/PCNB mole ratios. The results appear in Figure 6. An increase in the ratio from 1 to 2 considerably affects the reaction, both in methanol and in pentanol. But an increase above this value does not influence $k_{obs}$ further. The initial effect may be due to the fact that an increase in the amount of NaOH implies an increase in $Q^+OR^-$ concentration. But above a certain amount of alkoxide anion formed, most of the quat is already 'saturated' with alkoxide anion, so that a further increase in base will have no further effect on such a parameter, and thus on $k_{obs}$.

*Overall Kinetic Considerations.*—Equation (8), as written above, although correct in itself, is not of much practical use since it expresses the equation rate as a function of $[Q^+OR^-]$, which is a parameter that usually cannot be easily measured directly throughout a reaction process. Nevertheless, simple transformations may lead us to a more developed rate equation, as follows. From equation (5) we obtain equation (11). Now the

$$[RO^-] = K_a[ROH][OH^-] \qquad (11)$$

quat is distributed between the $Cl^-$ and the alkoxide anions, and we obtain equation (12) where $[Q]_{tot}$ is the concentration of the total amount of quat added to the system. Substituting equation (12) into equation (6) (where $Q^+X^-$ would

$$[Q^+Cl^-] = [Q]_{tot} - [Q^+OR^-] \qquad (12)$$

correspond to $Q^+Cl^-$) we obtain:

**Table 5.** Values of $k_{\text{obs}}/^{-1}$ for a system with or without NaCl.[a]

| Alcohol | no NaCl | with NaCl |
|---|---|---|
| Methanol | $4.67 \times 10^{-4}$ | $4.11 \times 10^{-4}$ |
| Pentanol | $1.85 \times 10^{-4}$ | $1.20 \times 10^{-4}$ |

[a] *Conditions:* 0.02 mol PCNB; 0.25 g TBAB (8 mol%); 0.06 mol 45% NaOH; 0.04 mol alcohol; *T* 80 °C; magnetic stirring. Amount of NaCl added to systems ('with NaCl') = 0.02 mol.

**Table 6.** Values of activation energies ($E_a$) for the system in which the alcohol is either methanol or pentanol.[a]

| Alcohol | $E_a$/kcal mol$^{-1}$ |
|---|---|
| Methanol | 7.0 |
| Pentanol | 11.0 |

[a] *Conditions:* 0.02 mol PCNB; 0.25 g TBAB; 0.08 mol 45% NaOH; 0.04 mol pentanol or 0.08 mol methanol; magnetic stirring.

$$K^{\text{sel}} = \frac{[\text{Q}^+\text{OR}^-][\text{Cl}^-]}{[\text{Q}^+\text{Cl}^-][\text{OR}^-]} \qquad (13)$$

Rearranging the above equation we obtain:

$$[\text{Q}^+\text{OR}^-] = \frac{[\text{Q}]_{\text{tot}}}{1 + [\text{Cl}^-]/(K_a K^{\text{sel}}[\text{ROH}][\text{NaOH}])} \qquad (14)$$

and finally, substituting the above equation into equation (8) we arrive at:

$$r = \frac{-k[\text{PCNB}][\text{Q}]_{\text{tot}}}{1 + [\text{Cl}^-]/(K_a K^{\text{sel}}[\text{ROH}][\text{NaOH}])} \qquad (15)$$

We may now study the validity of equation (15) by comparing it with experimental results. First, for the sake of simplicity let us define the variable *A*, which is a part of the denominator in

$$A = [\text{Cl}^-]/K_a K^{\text{sel}}[\text{ROH}][\text{NaOH}] \qquad (16)$$

equation (15). The following may therefore be noticed: (*a*) In the methanol system, the addition of alcohol increases its concentration in the aqueous phase (since this alcohol dissolves mainly in this phase), and thus *A* decreases. After a certain point, when $A \ll 1$, an additional increase in concentration of alcohol would not affect *A* further, and no further effect in rate should be noticed, as occurs in practice. (*b*) In the case of pentanol, its concentration in the aqueous phase is small and constant. Addition of pentanol dilutes the alkyl halide present and thus the rate decreases. (*c*) An increase in [NaOH] causes an increase in rate for both systems up to a certain point. This can be easily seen: as [NaOH] increases, *A* decreases until it becomes very small. From that stage on, a further increase in this parameter will not affect the overall value of *r*. (*d*) An increase in [Cl$^-$] should produce a decrease in rate (*A* increases and thus *r* decreases); this fact should be expected since catalyst poisoning would occur. Alkoxide anions are 'competing' for the quat cation, and an increase in the concentration of any other anion in the mixture would immediately cause a decrease in that quat available for the alkoxide anion, thus decreasing the reaction rate.[15] The experimental results (Table 5) confirm this fact.

This last set of data are of great practical importance since they give an essential clue as to the way in which the reaction can be led to complete conversion. The reason for which the reaction drastically slows down before completion is, it seems, such catalyst poisoning. Thus, if Cl$^-$ anions could be precipitated out of the aqueous phase in the form of a salt, then the ratio [Q$^+$OR$^-$]/[Q$^+$Cl$^-$] would also increase and so would the reaction rate.

This has been done in practice. Once a typical reaction had reached its highest conversion and stopped (as with either ethanol or pentanol described in Table 3, which reached 94 and 90.3% conversion, respectively), a few pellets of solid NaOH were added to the system. Complete conversion was reached in about 30 min. The added NaOH increases its concentration in the aqueous phase and produces the precipitaton of NaCl through a 'salting-out' effect, thus 'pushing' forward the reaction to completion.

Finally, the activation energies for both the methanolic and the pentanolic systems respectively, were determined. A series of experiments similar to those described above were performed at different temperatures. The conditions and results appear in Table 6. As can be seen, $E_a$ for methanol (7 kcal mol$^{-1}$) is considerably lower than for pentanol (11 kcal mol$^{-1}$). Since methoxide anion, as opposed to pentoxide ion, resides initially mostly in the aqueous phase, the mass transfer factor should be of greater importance in the case of methanol than for pentanol. This would mean that a lower activation energy should be expected in the case of the methanolic system, as has been actually found. It should be added, for the sake of comparison, that the value of $E_a$ for the methanolic system without catalyst is 24 kcal mol$^{-1}$.[16]

## Experimental

All catalysts used were made by Aldrich, and of purity >98%. The water content was determined by Karl–Fischer titrations.

Experiments were performed on a Magne-4 instrument Model 4620-4 of the Cole–Palmer Ins. Co., which consisted of a plate with four heads, each with its own thermostat and common stirring controller that allowed four simultaneous reactions to be performed. After the various reactants had been added to the system, samples were taken for analysis at different stages of the reaction with the organic phase. Samples were diluted in chloroform before being analysed. Analytical determinations were made by gas chromatography, using a GOW-Mac GC with a TC detector. The column used contained DC-200 10% in Chromosorb-A. The temperature of the oven was 200 °C and the flow of the carrier gas (He) was 30 cm$^3$ min$^{-1}$.

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