9. *The Reaction between* tert.*-Butyl Chloride and Sodium Thiophenoxide.*

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The reaction between *tert.*-butyl chloride and sodium thiophenoxide is kinetically of the second order, and results in the formation of *ca.* 90% of olefin and a small amount of *tert.*-butyl phenyl sulphide. This product is stable under the conditions of the measurements. The main reaction is considered to be a bimolecular elimination (*E*2), and is more rapid than the corresponding reaction between *tert.*-butyl chloride and either sodium phenoxide or sodium ethoxide. The theoretical significance of these results is discussed.

Sodium thiophenoxide is, in ordinary circumstances, more reactive by factors between 100 and 1000, and therefore has greater nucleophilic power, than either sodium ethoxide or sodium phenoxide in nucleophilic displacements at a carbon centre (for rate comparisons, cf. Quayle and Royals, *J. Amer. Chem. Soc.*, 1942, **64**, 226; de la Mare and Vernon, *J.*, 1952, 3331). On the other hand, the thiophenoxide ion is less basic than either the ethoxide or the phenoxide ion, if this property is measured by the degree of dissociation of the conjugate acid (thiophenol, $pK_a = 9{\cdot}3$ in 95% ethanol, Schwartzenbach and Rudin, *Helv. Chim. Acta*, 1939, **22**, 1360; phenol, $pK_a = 12{\cdot}8$ in 95% ethanol, *idem, ibid.*; ethanol, $pK_{\text{auto}} = 19{\cdot}0$; see Remick " Electronic Interpretations of Organic Chemistry," Wiley and Sons, New York, 1949, p. 251). The nucleophilic powers of anions, as judged from their rates of attack on a carbon centre, do not bear a direct relationship to their basic strengths, as judged from their equilibrium properties in combination with hydrogen (cf. Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273; Hughes, *Quart. Rev.*, 1951, **5**, 245; Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 331).

A better correlation would be expected between basic strength and rate of attack upon hydrogen. If an alkyl halide were chosen for which, with ethoxide ions, much bimolecular elimination accompanies substitution, a much smaller proportion of elimination should occur in its reaction with thiophenoxide ions. Ethylene dibromide exemplifies this behaviour (Hine and Brader, *J. Amer. Chem. Soc.*, 1953, **75**, 3964).

It is of interest to compare directly the effect of different anions on the rates of elimination from an organic halide. In another connection we were examining the reaction of *tert.*-butyl chloride with sodium thiophenoxide; Ipatieff, Pines, and Friedman (*J. Amer. Chem. Soc.*, 1938, **60**, 2731) found only chloride ions and unchanged thiophenol as products of this reaction. Re-examination has confirmed that the main process involves elimination, but a small proportion of the product of substitution can be isolated.

EXPERIMENTAL

Product Analysis.—*tert.*-Butyl chloride (28 g.; b. p. 51°/760 mm.) was refluxed with 1·7N-sodium thiophenoxide in ethanol (200 ml.). The volatile olefinic product (12·6 g.) was collected in a cold trap, and was then allowed to evaporate into carbon tetrachloride (250 ml.) containing bromine (60 g.). Reaction was very rapid. The excess of bromine was removed and the organic material was dried and fractionated, giving, after removal of the solvent, (*a*) 11·9 g., b. p. 150—155°/765 mm., n_D^{25} 1·5080, (*b*) 1·0 g., b. p. 155—160°, n_D^{25} 1·5098; (*c*) 2 g. of residue of high b. p. Refractionation of (*a*) gave a main fraction, b. p. 148—150°/763 mm., n_D^{25} 1·5068 (Found : C, 22·4; H, 3·8. Calc. for $C_4H_8Br_2$: C, 22·2; H, 3·7%). Suter and Zook (*J. Amer. Chem. Soc.*, 1944, **66**, 738) record, for 1 : 2-dibromo-2-methylpropane, n_D^{25} 1·5070.

The alcoholic reaction mixture was added to 2N-sodium hydroxide (500 ml.) and extracted with ether. The extract was washed with alkali and water, dried, and fractionated, giving 1·0 g., b. p. 90—92°/15 mm., n_D^{25} 1·5307, f. p. −13° (Found : C, 72·3; H, 8·9; S, 18·7. Calc. for $C_{10}H_{14}S$: C, 72·3; H, 8·4; S, 19·3%). The properties of this material accord with those recorded by Ipatieff, Pines, and Friedman (*loc. cit.*) for *tert.*-butyl phenyl sulphide, b. p. 73°/5 mm., n_D^{20} 1·5335.

Kinetic Experiments.—The following are details of an experiment in which the reaction of *tert.*-butyl chloride with sodium thiophenoxide in ethanol at 44·6° (5·53 ml. portions, in sealed tubes) was followed (*a*) by titration in ethanol with standard acid, lacmoid being used as indicator, in order to measure the total rate of production of hydrogen chloride; and (*b*) by titration in slightly aqueous ethanol with sodium hydroxide, phenolphthalein being used as indicator, in order to measure the rate of production of thiophenol which, under these conditions, is titrated as a weak acid.

Time (min.)	0·0	19·0	43·5	115	199	259	408	∞
Titre (ml. of 0·0878N-HCl; lacmoid)	45·68	44·90	44·00	41·85	39·70	38·20	35·60	25·60
Titre (ml. of 0·0878N-NaOH; phenolphthalein)	0·26	—	—	3·90	—	—	9·41	19·04
10^3k_2 (l. mole^{-1} min.$^{-1}$)	—	2·75	2·73	2·57	2·55	2·65	2·62	—
Elimination (%)	—	—	—	95	—	—	91	93·5

From values obtained similarly at 58·4° ($k_2 = 0{\cdot}0130$ l. mole^{-1} min.$^{-1}$) and at 68·0° ($k_2 = 0{\cdot}0388$ l. mole^{-1} min.$^{-1}$) at both of which temperatures there was also found at the end of the reaction 93% of elimination, it can be calculated that the Arrhenius parameters of the reaction are $E = 24{\cdot}8$ kcal. mole^{-1}, and $\log_{10} B = 14{\cdot}46$ l. mole^{-1} min.$^{-1}$.

The following mean rate coefficients show the dependence of rate upon salt concentration :

$$[\mathrm{SPh}^-] = 0{\cdot}23,\ k_2 = 0{\cdot}00312;\ [\mathrm{SPh}^-] = 0{\cdot}70,\ k_2 = 0{\cdot}00264 \text{ l. mole}^{-1} \text{ min.}^{-1}.$$

The values illustrate that the reaction is of the second order; the customary " dilution effect " results in a small increase in the rate coefficient when the concentration is decreased.

The following experiment was designed to test the stability of *tert.*-butyl phenyl sulphide. Samples (5·0 ml.) of *tert.*-butyl phenyl sulphide (0·0766M, in 0·432M-sodium ethoxide) were heated at 89·6°, and were titrated at intervals with 0·0948N-acid (phenolphthalein) with the following results :

Time (min.)	0·0	4·20	1680	3870	∞ (calc.)
Titre (ml. of 0·0948N-HCl)	22·80	22·60	22·50	22·25	18·76

Since thiophenol is titrated as a weak acid under these conditions, the calculated infinity titre is that expected for complete formation either of *tert.*-butyl ethyl ether, by reaction (i), or of thiophenol, by reaction (ii) :

$$\mathrm{Bu^tSPh + OEt^- \longrightarrow Bu^tOEt + SPh^-} \qquad \text{(i)}$$

$$\mathrm{Bu^tSPh + OEt^- \longrightarrow EtOH + CH_2{:}CMe_2 + SPh^-} \qquad \text{(ii)}$$

That *tert.*-butyl phenyl sulphide would survive, even under conditions much more drastic than those of the kinetic measurements, is shown by the small change in titre in the above experiment.

The following result shows that added *tert.*-butyl phenyl sulphide does not significantly affect the rate of solvolysis of *tert.*-butyl chloride. Samples (5 ml.) were removed from a solution containing *tert.*-butyl chloride (0·078N) and *tert.*-butyl phenyl sulphide (0·033M) in ethanol at 43·9°, and were titrated with 0·0217N-alkali, with lacmoid as indicator except where otherwise stated :

Time (min.)	0·0	1138	1150	1673	2788	5963	7118	7133	∞
Titre (ml.)	0·15	1·88	1·89 *	2·58	3·95	7·30	8·30	8·42 *	18·10
10^5k_1 (min.$^{-1}$)	—	8·5	8·2	8·7	8·5	8·5	8·5	8·5	—

* Titrated in pre-neutralised slightly aqueous ethanol with phenolphthalein as indicator.

The mean rate-coefficient ($8{\cdot}5 \times 10^{-5}$ min.$^{-1}$) is only slightly greater than the corresponding value ($8{\cdot}0 \times 10^{-5}$ min.$^{-1}$ at 44·6°; see also Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 849) obtained in the absence of *tert.*-butyl phenyl sulphide. Furthermore, the *tert.*-butyl phenyl sulphide is not converted into thiophenol in the course of the reaction, since the titrations with phenolphthalein as indicator agree with those obtained by using lacmoid. In the presence of 0·10M-thiophenol, the solvolysis at 44·6° was found to have a velocity coefficient $k_1 = 9{\cdot}2 \times 10^{-5}$ min.$^{-1}$, being thus insignificantly catalysed by added thiophenol. These small alterations in rate, observed when thiophenol or *tert.*-butyl phenyl sulphide are added, should probably be regarded as co-solvent effects.

In the presence of phenol, in amount equivalent to the alkali, the nucleophilic reagent is substantially the phenoxide ion, the equilibrium $\mathrm{OEt^- + PhOH \rightleftharpoons OPh^- + EtOH}$ lying largely to the right-hand side. A solution thus prepared of sodium phenoxide (0·50M) reacts with *tert.*-butyl chloride (0·19M) with an initial first-order rate-coefficient at 43·7° of $2{\cdot}6 \times 10^{-4}$ min.$^{-1}$, substantially constant over 70% of the reaction. The rate of reaction is therefore significantly increased by change of the reagent from ethanol to phenoxide ions. The products of this reaction have been shown by Lewis (*J.*, 1903, 329) to include 2-methylpropene and, as a main product of substitution, *p-tert.*-butylphenol, which no doubt is the result of production, in the unimolecular component of the reaction, of the *tert.*-butyl carbonium ion, which can then react with the phenoxide ion to give nuclear substitution (cf. Gelles, Hughes, and Ingold, *J.*, 1954, 2198).

The formal initial second-order rate-coefficient, corrected for the concomitant solvolysis, is, for the reaction of *tert.*-butyl chloride with 0·50M-phenoxide ions at 43·7°, $0{\cdot}33 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$. The rate of solvolysis is similarly accelerated ($k_2 = 0{\cdot}26 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$ at 43·7°) by the addition of 0·54M-sodium ethoxide. These values are, however, subject to uncertainty in the rate of solvolysis in the presence of the added base.

DISCUSSION

The elimination of hydrogen chloride from *tert.*-butyl chloride under the influence of sodium thiophenoxide appears to be considerably more rapid (by a factor of about a power of ten) than the corresponding reactions involving either sodium phenoxide or sodium ethoxide. This result is at first sight surprising, in view of the relatively weak basic properties of the thiophenoxide ion. Other possibilities for the reaction process therefore require careful scrutiny. It appears theoretically possible that the reaction might in fact be a substitution, followed by decomposition of the product, *tert.*-butyl phenyl sulphide.

$$\mathrm{Bu^tCl + SPh^- \longrightarrow Bu^tSPh + Cl^-} \qquad \ldots\ldots\ldots\ldots \quad (1)$$

$$\begin{tikzcd} \mathrm{Bu^tSPh} \arrow[r] \arrow[d, "\mathrm{Bu^tCl}"] & \mathrm{Me_2C{:}CH_2 + H^+ + SPh^-} \qquad \ldots\ldots\ldots \quad (2a) \\ \mathrm{Bu^t{}_2SPh^+\}Cl^-} \arrow[r] & \mathrm{2Me_2C{:}CH_2 + 2H^+ + SPh^- + Cl^-} \qquad \ldots\ldots \quad (2b) \end{tikzcd}$$

Route (2*a*) has been excluded experimentally; for *tert.*-butyl phenyl sulphide has been shown to be stable under the conditions of the measurements. Route (2*b*) is also excluded, for the following reasons. The sulphonium salt $\mathrm{Bu^t{}_2SPh^+\}Cl^-}$ does not accumulate during the course of the reaction, as has been shown by the fact that the development of thiophenol parallels the formation of total acid. Hence, if the sulphonium salt is formed at all, it must be formed and decomposed more rapidly than the overall measured rate of reaction between *tert.*-butyl chloride and thiophenoxide ions. Separate experiments showed, however, that *tert.*-butyl phenyl sulphide is stable in the presence of *tert.*-butyl chloride, and does not appreciably influence the rate of solvolysis of the latter compound.

Since the observed kinetic form [equation (3)] can be rewritten as in equation (4), the possibility should be considered that the elimination is actually a ternary reaction between *tert.*-butyl chloride, ethoxide ions, and thiophenol. From the dissociation

$$\mathrm{d[HCl]/d}t = k\mathrm{[Bu^tCl][SPh^-]} \qquad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$\mathrm{d[HCl]/d}t = k\mathrm{[Bu^tCl][OEt^-][PhSH]/[EtOH]} \qquad \ldots\ldots\ldots \quad (4)$$

constants of ethanol and thiophenol, however, it can be calculated that the concentrations of ethoxide ions and of thiophenol under the conditions of the reaction are each less than about 10^{-4}M. The adoption of such a view of the reaction would entail the corollary that 10^{-4}M-ethoxide ions in conjunction with 10^{-4}M-thiophenol is a better combination for elimination than M-ethoxide ion in conjunction with *ca.* 17M-ethanol. In other words, one would have to conclude that thiophenol, as compared with ethanol, catalyses electrophilically the removal of hydrogen chloride under the influence of sodium ethoxide by a factor of the order of 10^{10}. This seems to us to be especially unlikely, and we prefer the view that the reaction of *tert.*-butyl chloride with sodium thiophenoxide is indeed a bimolecular elimination (*E*2).

It is well known that nucleophilic power as measured by rate of attack on carbon is not well correlated with basicity. Anions of the type RS$^-$ (R = H, alkyl, or aryl) appear to give the most striking examples of this type of deviation from simple theory, and the phenomenon seems to be associated with descent of the Periodic Table, since it appears also in the comparisons (cf. de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200) between basicity and power of nucleophilic attack in the reaction of halide ions with alkyl halides. It seems possible that it is connected, in some way not yet fully understood, with the greater polarisability of elements of the higher periodic groups.

There are very few examples, as far as we are aware, of comparisons of rates of nucleophilic attack on hydrogen which include ions of the type RS^-. Hine's case (*J. Amer. Chem. Soc.*, **1950**, **72**, 2438) of the reaction between anions and chloroform involves, according to his preferred mechanism, a pre-equilibrium (5).

$$CHCl_3 + B^- \rightleftharpoons CCl_3^- + BH^+ \text{ (fast)} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$CCl_3^- \longrightarrow CCl_2 + Cl^- \text{ (slow)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$CCl_2 \longrightarrow \text{products (fast)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

The measured rate-coefficients, in this case, should therefore be proportional to the equilibrium constant for the first reaction (5) and would, by analogy with the situation in the equilibrium (8) be greater for $B = OH^-$ than for $B = SH^-$,

$$H_3O^+ + B^- \longrightarrow H_2O + BH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

independently of the relative rates of attainment of equilibrium.

We do not yet know whether an abnormally great reactivity of the thiophenoxide ion is a characteristic of synchronous reactions involving displacement of a nucleophilic group, as seems possible, or more generally of rate processes involving attack on covalently bound atoms, including hydrogen. But the present example serves to illustrate once again the difficulties involved in attempting to correlate, over a wide range of structural differences, the rates of reaction with equilibria.

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