Nitrophenylcarbenes. Part III.[1] Kinetics of the Decomposition of 4-Nitrobenzyl Chloride and Dimethyl-4-nitrobenzylsulphonium Ion in Sodium Hydroxide. A Reinvestigation[2]

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The reactions of 4-nitrobenzyl chloride and dimethyl-4-nitrobenzylsulphonium salt in sodium hydroxide solution both give high yields (66—74%) of 4,4′-dinitrostilbene. These reactions are sensitive to air or oxygen but when carried out under an atmosphere of nitrogen overall third-order kinetic behaviour was found; each reaction being first order in hydroxide ion and second order in the nitrobenzyl compound. The evidence presented shows that α-elimination is unlikely in these reactions but S_N2 or radical mechanisms are more likely.

THE reaction of 4-nitrobenzyl chloride with sodium hydroxide to yield 4,4′-dinitrostilbene is in contrast with reactions of other substituted benzyl chlorides which give the expected benzyl alcohols.[3] Hanna and Iskanda[4] who studied the kinetics of the reaction reported that the reaction was first order in hydroxide ion and first order in the nitro-compound and therefore concluded that α-elimination leads to 4-nitrophenylcarbene, which subsequently reacts to yield 4,4′-dinitrostilbene. A similar mechanism was postulated by Thornton and his co-workers[5,6] who studied the reaction of dimethyl-4-nitrobenzylsulphonium ion with sodium hydroxide, and who reported 4,4′-dinitrostilbene as the sole product. Kinetic data and observed sulphur-isotope effect[5] was reported to be in accord with the postulated mechanism (Scheme 1)

$$\begin{aligned} \mathrm{ArCH_2X + OH^-} &\rightleftharpoons \mathrm{Ar\bar{C}HX} \\ \mathrm{Ar\bar{C}HX} &\xrightarrow{\text{slow}} \mathrm{ArCH + X^-} \\ \mathrm{ArCH + Ar\bar{C}HX} &\longrightarrow \mathrm{Ar\bar{C}HCHXAr} \\ \mathrm{Ar\bar{C}HCHXAr} &\longrightarrow \mathrm{ArCH{=}CHAr} \end{aligned}$$

$$\mathrm{Ar = 4\text{-}O_2NC_6H_4;\ X = Cl, \overset{+}{S}Me_2}$$

SCHEME 1

Although the mechanism is in agreement with the reported kinetic data, several difficulties remain. First, it is rather surprising to find that the postulated carbene does not react with water or hydroxide ion which are present in high concentrations. Secondly, for the reactions of a series of nitrobenzyl derivatives with sodium

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[1] (*a*) Part I, S. H. Goh, *J. Chem. Soc.* (*C*), 1971, 2275; (*b*) Part II, G. L. Closs and S. H. Goh, *J.C.S. Perkin I*, in the press.

[2] Taken in part from S. H. Goh, Ph.D. Thesis, University of Chicago, August 1968.

[3] (*a*) C. A. Bischoff, *Ber.*, 1888, **21**, 2071; (*b*) L. M. Litvinenko, I. F. Leuchenko, and A. N. Androsov, *Zhur. obshchei Khim.*, 1958, **28**, 2046.

[4] Y. Iskanda and S. B. Hanna, *J. Chem. Soc.*, 1961, 217.

[5] C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, 1961, **83**, 4033.

[6] I. Rothberg and E. R. Thornton, *J. Amer. Chem. Soc.*, 1964, **86**, 3296, 3302.

hydroxide, one finds that the above two reactions are the only exceptions to give 100% yields of 4,4′-dinitrostilbene. The other compounds generally yield one or a variety of other products, *e.g.* 4-nitrobenzyl bromide and iodide both give the alcohol and 4-nitrobenzyl ether,[7] dimethyl-3-nitrobenzylsulphonium ion yields 43% of 3,3′-dinitrostilbene oxide,[6] 4-nitrobenzylpyridinium ion gives 4-azoxybenzaldehyde,[8] and methyl-4-nitrobenzylphenylsulphonium ion gives 19% of 4-nitrobenzyl alcohol and 19% of dinitrostilbene.[6]

Our interest in the structure and reactivity of arylcarbenes has led us to study some of these nitro-substituted species, including the generation of the same species by α-elimination methods. A reinvestigation of the products from the action of sodium hydroxide on 4-nitrobenzyl chloride and dimethyl-4-nitrosulphonium ion has revealed that these reactions are sensitive to traces of air.[1b] This paper reports the kinetics of these reactions and discusses possible mechanisms.

RESULTS AND DISCUSSION

Carbanions from 4-*Nitrobenzyl Chloride and Dimethyl*-4-*nitrobenzylsulphonium Toluene*-p-*sulphonate*.—The unusual reactivity of 4-nitrobenzyl compounds is due to the high acidity of the benzylic protons, which in fact have been demonstrated to exchange rapidly with deuterium in sodium deuterioxide solution.[4,5] Since the carbanion is an important intermediate in reactions under basic conditions it was of interest to generate it and study its subsequent decomposition. Dilute solutions of 4-nitrobenzyl chloride in t-butyl alcohol containing an excess of potassium t-butoxide gave a yellow solution with absorption at 375 nm and extinction coefficient of 4×10^4. The spectrum resembles that of the carbanion of 4-nitrotoluene [9] which has $\lambda_{max.}$ 362 nm (ε 4×10^3). In the same way 4-nitrobenzyl bromide gave a carbanion with $\lambda_{max.}$ 378 nm (ε 3×10^4) and dimethyl-4-nitrobenzylsulphonium toluene-*p*-sulphonate gave a red solution, $\lambda_{max.}$ 500 nm (ε 3×10^4). The carbanions so generated were unstable and decomposed at room temperature over 10—30 min. Under these conditions, the product was a black material and not 4,4′-dinitrostilbene and the reactions were not investigated further.

Detection of Free Radicals.—The reactions of the above nitro-compounds are dependent on the reaction conditions. It would not be surprising if radicals were involved since it is known that nitroaromatics can spontaneously generate radicals [10] in the presence of base to give complex products. Dilute solutions (0·01M) of 4-nitrobenzyl chloride with excess of potassium t-butoxide (0·1M) also gave a weak e.s.r. spectrum. At a higher concentration (0·05—0·1M) of the nitro-compound a brown precipitate formed and an intense e.s.r. signal was observed with the coupling constants a_{N} 11·8, $a_{o\text{-H}}$ 6·3, $a_{m\text{-H}} < 1$, and $a_{\alpha\text{-H}}$ 2·3 G. Since this spectrum is different from the known spectra of radical-ions of 4-nitrotoluene, 4,4′-dinitrobibenzyl, and 4,4-dinitrostilbene [11] or that of 4-nitrobenzyl chloride radical-anion, which is known to be unstable,[12] it may be that of the radical anion of t-butyl 4-nitrobenzyl ether.

Strong e.s.r. signals were also obtained from 0·1—0·2M solutions of 4-nitrobenzyl chloride, bromide and the dimethylsulphonium toluene-*p*-sulphonate in 1·5M-methanolic potassium hydroxide. The recorded spectra in each case indicated that more than one radical species were present and were not investigated further.

The detection of paramagnetic species in low concentration in these reactions is consistent with the suggestion that a radical mechanism is possible.[13] This however does not demand that the radical or radical-ion is the key intermediate but it could well represent a by-product.

Kinetics of the Reaction of 4-*Nitrobenzyl Chloride with Sodium Hydroxide*.—4-Nitrobenzyl bromide may be expected to react in a similar way as the chloride; the bromide ion being a better leaving group than chloride it may be expected to react faster if the loss of halogen in the carbanion is the rate-determining step, as in Scheme 1. The kinetics of the reaction of 4-nitrobenzyl bromide (0·04M) and sodium hydroxide (0·375M) at 20·2° in 60% dioxan–water was found to be pseudo-first order with rate coefficient $k_1 = 3·85 \times 10^{-4}$ s^{-1}. The reaction of the corresponding chloride was found to be sensitive to air; under the same conditions but in the presence of air the reaction was also first order in the nitro-compound, $k_1 = 2·45 \times 10^{-4}$ s^{-1}. A comparison of these two results shows that the bromide is not significantly more reactive than the chloride. This argues against the α-elimination mechanism for both these reactions since the replacement of chlorine with bromine should not only facilitate carbanion formation but also enhance carbene formation.[14] The products from 4-nitrobenzyl bromide was however not 4,4′-dinitrostilbene but 4-nitrobenzyl alcohol and 4-nitrobenzyl ether. These products can be accounted for by S_N2 attack by hydroxide ions, the formation of the ether accounting for the slightly enhanced rate at the end (90%) of the reaction.

The kinetics of the decomposition of 4-nitrobenzyl chloride was investigated further since it was found that traces of air interfere with the reaction. Although the kinetic experiments reported previously were made with rather dilute solutions (0·01M) of 4-nitrobenzyl chloride, no difficulties due to air interference were mentioned. Two kinetic runs were repeated under similar conditions and the results are plotted in Figure 1 and show that the reaction under nitrogen is distinctly slower and is not

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[7] A. A. Abdullah, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 1969, 1178.

[8] S. B. Hanna, *Chem. Comm.*, 1965, 487.

[9] J. M. Miller and H. Pobiner, *Analyt. Chem.*, 1964, **36**, 238.

[10] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, 1967, **89**, 300.

[11] (*a*) G. A. Russell and E. J. Geels, *J. Amer. Chem. Soc.*, 1965, **87**, 122; (*b*) G. A. Russell and E. G. Janzen, *ibid.*, 1967, **89**, 300.

[12] (*a*) G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, 1968, **90**, 347; (*b*) M. Mohammad, J. Hajdu, and E. M. Kosower, *ibid.*, 1971, **93**, 1792.

[13] (*a*) N. Kornblum and R. Seltzer, *J. Amer. Chem. Soc.*, 1961, **83**, 3668; (*b*) N. Kornblum, R. C. Kerber, and W. G. Urry, *ibid.*, 1965, **87**, 4520.

[14] J. Hine, ‘ Physical Organic Chemistry,’ McGraw-Hill, New York, 1962, ch. 24.

TABLE 1

Reaction of 4-nitrobenzyl chloride (0·05M) with excess of sodium hydroxide in 50% aqueous dioxan at 25 °C under nitrogen

[NaOH]/M [a]	$10^2\,k_2$/l mol^{-1} s^{-1}	$10^2\,k_3$/l^2 mol^{-2} s^{-1} [b]
0·25	1·16 ± 0·06	5·0 ± 0·3
0·375	1·8 ± 0·1	4·8 ± 0·3
0·375	1·7 ± 0·1	4·7 ± 0·2
0·500	2·7 ± 0·2	5·5 ± 0·5

[a] Initial concentration. [b] k_3 is k_2 divided by the mean of the initial concentration of sodium hydroxide and that after two half-lives.

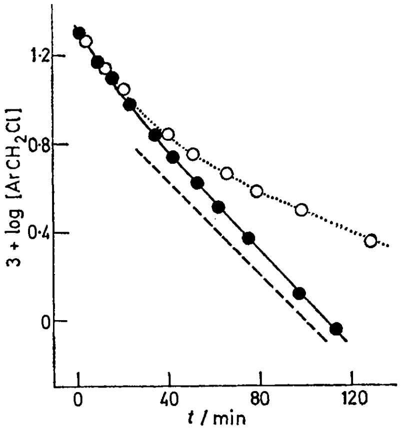


FIGURE 1 Reaction of 4-nitrobenzyl chloride (0·02M) with excess of sodium hydroxide (0·375M) in 50% aqueous dioxan at 25·0 °C. ○, Reaction under nitrogen; ●, reaction in the presence of air; ----, calculated slope from the data of ref. 4

pseudo-first order. In the presence of air, however, approximately first-order kinetics are observed in agreement with the results of Iskander and Hanna.[4]

To minimize the effect of interference by traces of air further kinetic experiments were conducted using a higher concentration (0·05M) of 4-nitrobenzyl chloride. Reactions under nitrogen and excess of sodium hydroxide (0·50M) show second-order kinetics (Figure 2). There is also a dependence on hydroxide ion concentration and the results given in Table 1 show that the overall kinetic order is three, first order in hydroxide ion and second order in 4-nitrobenzyl chloride.

Other kinetic results under various conditions are given in Table 2, those conducted in the presence of air show reasonable agreement with the data reported previously.[4]

The kinetics of the decomposition of dimethyl-4-nitrobenzylsulphonium ion in aqueous sodium hydroxide when re-examined was also found to be sensitive to air. Results for experiments using 0·1M-sodium hydroxide and 0·1M of the sulphonium salt at 55° show that the reaction is third order under nitrogen and approximately second order in the presence of air (Figure 3).

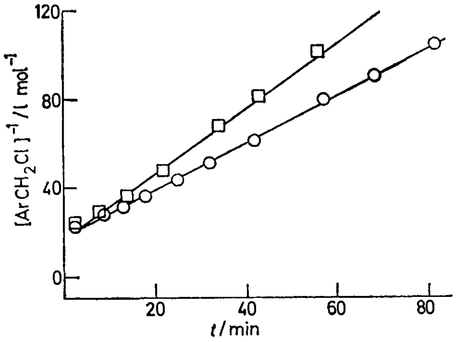


FIGURE 2 Kinetics of the reaction of 4-nitrobenzyl chloride (0·05M) with excess of sodium hydroxide in 50% aqueous dioxan under nitrogen at 25·0 °C. □, In 0·50M-sodium hydroxide; ○, in 0·375M-sodium hydroxide

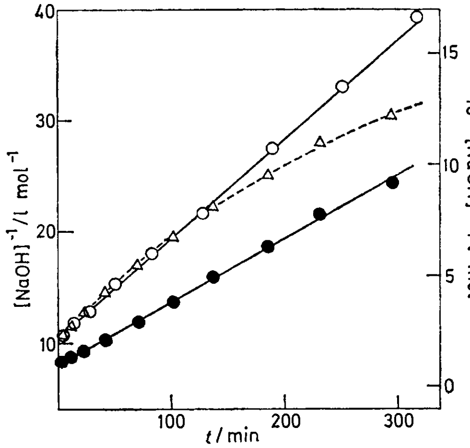


FIGURE 3 Reaction of dimethyl-4-nitrobenzylsulphonium perchlorate (0·1M) with sodium hydroxide (0·1M) at 55·0 °C; 1·0M in sodium chloride. ○, 1/[NaOH] *vs.* time in air; △, 1/[NaOH] *vs.* time under nitrogen; ●, 1/[NaOH]^2 *vs.* time under nitrogen

Under the conditions of the kinetic studies the products were mainly 4,4′-dinitrostilbene, amounting to 66% and 74% for reactions of 4-nitrobenzyl chloride and

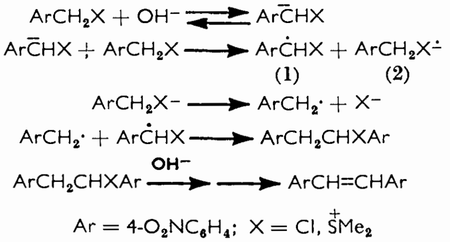
TABLE 2

Rate coefficients of the reaction of 4-nitrobenzyl chloride with sodium hydroxide under various conditions

Reaction conditions				Kinetic order	k_2 or k_3
[ArCH$_2$Cl]/M [a]	[NaOH]/M [a]	Temp. (°C)	Solvent [b]		
0·05	0·05	40 (N$_2$) [c]	50% Dioxan	3	$8{\cdot}02 \times 10^{-2}$ l^2 mol^{-2} s^{-1}
0·05	0·05	30 (N$_2$)	50% Dioxan	3	$3{\cdot}42 \times 10^{-2}$ l^2 mol^{-2} s^{-1}
0·05	0·05	30 (Air)	50% Dioxan	2	$1{\cdot}52 \times 10^{-3}$ l mol^{-1} s^{-1}
0·05	0·05	30 (O$_2$)	50% Dioxan	2	$3{\cdot}54 \times 10^{-3}$ l mol^{-1} s^{-1}
0·05	0·05	25 (N$_2$)	95% Ethanol	3	$1{\cdot}44 \times 10^{-2}$ l^2 mol^{-2} s^{-1}
0·05	0·30	25 (N$_2$)	85% Ethanol	2 [d]	$3{\cdot}85 \times 10^{-2}$ l mol^{-1} s^{-1}
0·1 [e]	0·1	55 (N$_2$)	Water	3	$2{\cdot}30 \times 10^{-2}$ l^2 mol^{-2} s^{-1}
0·1 [e]	0·1	55 (Air)	Water	2	$1{\cdot}38 \times 10^{-3}$ l mol^{-1} s^{-1}
0·1 [e]	0·1	40 (N$_2$)	Water	3	$6{\cdot}5 \times 10^{-3}$ l^2 mol^{-2} s^{-1}

[a] Initial concentration. [b] Aqueous organic mixed solvents. [c] N$_2$, air, or O$_2$ denotes that the reaction was carried out under nitrogen, air, or oxygen respectively. [d] Second order in 4-nitrobenzyl chloride. [e] Dimethyl-4-nitrobenzylsulphonium ion.

the sulphonium ion respectively.[15b] From the former reaction (under nitrogen) 10% of bis-(4-nitrophenyl)-acetylene was isolated while in the latter reaction 10% of *trans*-4,4′-dinitrostilbene oxide also formed. These results indicate that the carbene mechanism (Scheme 1) is not likely, in fact, the new kinetic results rule it out. The present data can however be explained by a radical mechanism similar to that postulated by Kornblum and his co-workers [13,15] for the related reactions of nitrobenzyl derivatives (Scheme 2).



$$\begin{aligned}
&\mathrm{ArCH_2X + OH^- \rightleftharpoons Ar\overset{-}{C}HX}\\
&\mathrm{Ar\overset{-}{C}HX + ArCH_2X \longrightarrow Ar\dot{C}HX + ArCH_2X^{\dot{-}}}\\
&\qquad\qquad\qquad\qquad\ \ (1)\qquad\quad (2)\\
&\mathrm{ArCH_2X^{\dot{-}} \longrightarrow ArCH_2\cdot + X^-}\\
&\mathrm{ArCH_2\cdot + Ar\dot{C}HX \longrightarrow ArCH_2CHXAr}\\
&\mathrm{ArCH_2CHXAr \xrightarrow{OH^-} \longrightarrow ArCH{=}CHAr}\\
&\mathrm{Ar = 4\text{-}O_2NC_6H_4;\ X = Cl,\ \overset{+}{S}Me_2}
\end{aligned}$$

SCHEME 2

The electron transfer is the rate-determining step in the mechanism; this will lead to an overall third-order kinetic behaviour, first order in hydroxide ion and second order in the nitro-compound. The mechanism also explains why side products, *e.g.* bis-(4-nitrophenyl)-acetylene, can form, *via* coupling of α-chloro-4-nitrobenzyl radical (1). Thus, the reaction is more complicated than previously assumed. The present results, however, do not eliminate a major competing S_N2 reaction of the carbanion and the reactant molecule which will give 4,4′-dinitrostilbene as well as third-order kinetics.

Sulphur Isotope Effects.—One of the pieces of evidence previously presented for the carbene mechanism [5] was that the observed sulphur isotope effect, k_{32}/k_{34} 1·0066, was consistent with such a mechanism. It was reasoned that the rate-determining formation of 4-nitrophenylcarbene (Scheme 1) should give an isotope effect close to 1·0177 obtained from S_N1 solvolysis of dimethyl-t-butylsulphonium iodide, since both the carbene and carbanion ion are high energy intermediates. But since the following reaction of the carbene and carbanion is rapid and irreversible and therefore should give rise to a negligible isotope effect, the overall sulphur isotope effect would be a half of 1·0177 giving a value of 1·0089, which is close to the observed value.

The sulphur isotope effect however cannot exclude the S_N2 mechanism since, based on the S_N2 reaction of hydroxide ion with dimethyltolylsulphonium ion which gives an isotope effect of 1·0096, the isotope effect for an S_N2 mechanism should be a half of this, giving a value of 1·0048. In the electron transfer mechanism (Scheme 2) a sulphur isotope effect could originate from the cleavage of the carbon–sulphur bond of the radical-anion (2) which if assumed to be similar to an S_N1 reaction should also lead to an isotope effect of 1·0089 as discussed above for the carbene mechanism. If on the other hand the electron transfer is the only slow step and the subsequent steps of Scheme 2 are fast and irreversible then a negligible sulphur isotope effect should be observed for the reaction.

It is clear from the above discussion that the sulphur isotope effect cannot provide unambiguous evidence for a particular mechanism of the reaction; the observed isotope effect of 1·0066 is in fact closer to that (1·0048) expected for an S_N2 reaction than that (1·0089) expected of a carbene mechanism.

Conclusions.—A reasonable mechanism of the reaction of 4-nitrobenzyl chloride or dimethyl-4-nitrobenzylsulphonium ion with sodium hydroxide should accommodate the following pieces of experimental evidence. (1) The major product is *trans*-4,4′-dinitrostilbene while side products, bis-(4-nitrophenyl)acetylene and 4,4′-dinitrostilbene oxide from the chloride and sulphonium salt respectively, are also formed. (2) The overall third-order kinetics, first order in hydroxide ion and second order in the nitro-compound excludes an α-elimination mechanism but agrees with the electron transfer mechanism as well as an S_N2 mechanism. (3) Radicals readily form and can be detected in such reactions. While this does not require a radical mechanism, it certainly makes such a mechanism appear more likely. Photochemical catalysis has also been reported for the decomposition of the sulphonium ion.[12a] (4) Cyclopropanes are not formed when the reaction is carried out in the presence of olefins although free 4-nitrophenylcarbene and the carbenoid species have been found to add readily to olefins. (5) The yields of 4,4′-dinitrostilbene from a series of 4-nitrobenzylsulphonium ions show a dependence on steric effects, being 74, 48, 21, and 19% when the leaving groups are dimethyl sulphide, methyl isopropyl sulphide, methyl tolyl sulphide, and methyl phenyl sulphide respectively. This would favour a direct S_N2 mechanism for dinitrostilbene formation but on the other hand does not exclude the electron transfer mechanism which should also be subject to steric effects.

By considering all the above pieces of evidence one can find that the electron transfer mechanism is the most plausible one but one cannot completely exclude a major competing S_N2 mechanism for dinitrostilbene formation.

EXPERIMENTAL

U.v. and visible spectra were recorded with a Cary 14 instrument and e.s.r. spectra with a Varian E3 instrument. Dimethyl-4-nitrobenzylsulphonium toluene-*p*-sulphonate, bromide, and perchlorate were made and purified as reported.[5,6] 4-Nitrobenzyl chloride and bromide were prepared [16] or purchased from Matheson, Coleman, and Bell.

Reactions with Strong Base.—Yellow solutions were obtained from dilute solutions (6×10^{-5}M) of 4-nitrobenzyl bromide or chloride and potassium t-butoxide (0·4M) in t-butanol. When observed directly in the u.v. spectrometer at 22 °C the absorption bands were observed to decay in

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[15] (*a*) N. Kornblum, R. T. Swiger, G. W. Earl, H. W. Pinnick, and F. W. Stuchal, *J. Amer. Chem. Soc.*, 1970, **92**, 1804, 5513; (*b*) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *ibid.*, 1967, **89**, 725.

[16] F. J. Alway, *J. Amer. Chem. Soc.*, 1902, **24**, 1060.

ca. 30 min. The products had ill-defined u.v.–visible spectra but were not 4,4′-dinitrostilbene. Dimethyl-4-nitrobenzylsulphonium toluene-*p*-sulphonate (5×10^{-5}M) in t-butanol–acetonitrile or t-butanol–dimethyl sulphoxide solutions containing potassium t-butoxide (0·03M) gave a red colour, $\lambda_{max.}$ 500 nm (ε 3×10^4), which also decayed over 15 min.

Detection of Radicals.—Radicals could be generated from 4-nitrobenzyl chloride and bromide and the sulphonium salt under various conditions. The reaction of 4-nitrobenzyl chloride (0·1M) and potassium t-butoxide (0·1M) in t-butanol under nitrogen gave an immediate precipitate and a strong e.s.r. signal. From dilute solutions, 0·01M in the nitro-compound, only a weak signal was obtained. Solutions (0·2M) of the above nitro-compounds in ethanol when mixed with an equal volume of potassium hydroxide (3M) also gave strong e.s.r. signals.

Kinetic Methods.—Solvents were deoxygenated by passing purified nitrogen gas through for 24 h. Bath temperature was thermostated to ±0·05 °C. The rates of reaction were determined by following the rate of liberation of halide ion and/or the rate of consumption of sodium hydroxide. For the determination of halide ion, aliquot portions were acidified by dilute nitric acid and then titrated by silver nitrate to a potassium chromate end-point. To determine hydroxide ion, aliquot portions were quenched in an excess of dilute acid and back-titrated with sodium hydroxide to a phenolphthalein end-point. Most experiments were carried out in duplicate.

Table 3 gives the results for the reaction of 0·04M-4-nitrobenzyl bromide with 0·375M-sodium hydroxide in 60% dioxan–water at 20·2 °C under nitrogen. Corresponding results for 4-nitrobenzyl chloride under the same conditions but in air gave $k_1 = 2{\cdot}45 \times 10^{-4}$ s^{-1}.

TABLE 3

t/min	2·5	31·0	52·0	75·0	96·0	113
10^2[ArCH$_2$Br]/M	3·78	2·17	1·38	0·83	0·53	0·34

$k_1 = 3{\cdot}58 \times 10^{-4}$ s^{-1}.

Table 4 illustrates a typical kinetic run for the reaction of 4-nitrobenzyl chloride (0·05M) with sodium hydroxide (0·05M) in 50% aqueous dioxan at 30 °C under nitrogen.

TABLE 4

t/min	3·8	32·5	60·0	103·5	153·0	217·0	293·0	344·0
10^2[NaOH]/M	4·80	4·20	3·76	3·34	2·94	2·72	2·46	2·32
10^2[ArCH$_2$Cl]/M	4·86	4·44	3·66	3·37	3·04	2·74	2·49	2·34

$k_3 = 3{\cdot}42 \times 10^{-2}$ l^2 mol^{-2} s^{-1}.

Other kinetic results are given in Figures 1—3 and Tables 1 and 2.

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