Kinetics and Mechanism of the Reaction of 4-Nitrobenzylidene Dichloride with Hydroxide Ion

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The reaction of 4-nitrobenzylidene dichloride with hydroxide ion in aqueous alcoholic solvents under nitrogen gives mainly dimeric type products, *viz.* tetrachloro-1,2-bis-(*p*-nitrophenyl)ethane, αα'-dichloro-4,4'-dinitrostilbenes and bis-(4-nitrophenyl)acetylene, and also a significant amount of 4-nitrobenzyl chloride. Kinetic evidence indicates that the reaction is second order with respect to 4-nitrobenzylidene dichloride. These results support an electron transfer or radical mechanism and rule out rate-determining free carbanion or carbene formation pathways.

THE reaction of nitrobenzyl derivatives in basic medium is of mechanistic interest because of the possibility of a number of pathways.[1-5] For example, the reaction of 4-nitrobenzyl chloride with sodium hydroxide to give a high yield of 4,4'-dinitrostilbene was originally presumed to proceed by carbene formation.[5] Careful reinvestigation [6,7] of this reaction, however, revealed that the reaction was very sensitive to air, in the absence of which the kinetic and product data were in agreement with an electron-transfer mechanism, as shown in

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

[6] G. L. Closs and S. H. Goh, *J.C.S. Perkin I*, 1972, 2103.

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Scheme 1. Recent studies[8-11] of the reaction of a number of nitrobenzyl derivatives with sodium hydroxide

$$\begin{array}{rcll}
\mathrm{ArCH_2Cl + OH^-} & \rightleftharpoons & \mathrm{Ar\bar{C}HCl} & \text{fast} \\
\mathrm{Ar\bar{C}HCl + ArCH_2Cl} & \longrightarrow & \mathrm{Ar\dot{C}HCl + ArCH_2Cl^{-\cdot}} & \text{slow} \\
\mathrm{ArCH_2Cl^{-\cdot}} & \longrightarrow & \mathrm{Ar\dot{C}H_2 + Cl^-} & \\
\mathrm{Ar\dot{C}HCl + Ar\dot{C}H_2} & \longrightarrow & \mathrm{ArCHClCH_2Ar \xrightarrow{OH^-} ArCH{=}CHAr} &
\end{array}$$

$$\mathrm{Ar = 4\text{-}O_2NC_6H_4}$$

SCHEME 1

also confirm the view that radicals may be a dominant feature of the reaction mechanism.

We have studied the reaction of 4-nitrobenzylidene dichloride with sodium hydroxide in the expectation that if carbene formation is feasible it would be more likely to occur in this system than from the reaction of 4-nitrobenzyl chloride, the chlorine group being well known to stabilise carbenes.[12] The products from this reaction had been reported in an earlier communication[13] and a detailed kinetic study is now reported.

RESULTS AND DISCUSSION

The reaction of 4-nitrobenzylidene dichloride with sodium hydroxide in aqueous alcoholic or methanolic solutions gave a mixture of products. Thus, in aqueous methanol dimeric type products, (1)—(3) account for *ca.* 36, 34, and 12% respectively. In addition it was also discovered that small amounts of 4-nitrobenzyl chloride (4) and methyl 4-nitrobenzyl ether (5) were formed with a total yield of *ca.* 12%. In aqueous ethanol 4,4'-dinitrostilbene (6) was also detected, presumably arising from the further reaction of 4-nitrobenzyl chloride (4).[7]

$\mathrm{ArCCl{=}CClAr}$ (1)	$\mathrm{ArCCl_2CCl_2Ar}$ (2)	$\mathrm{ArC{\equiv}CAr}$ (3)
$\mathrm{ArCH_2Cl}$ (4)	$\mathrm{ArCH_2OMe}$ (5)	$\mathrm{ArCH{=}CHAr}$ (6)
ArCCl (7)	$\mathrm{Ar\dot{C}HCl}$ (8)	$\mathrm{Ar\dot{C}Cl_2}$ (9)

$$\mathrm{Ar = 4\text{-}O_2NC_6H_4}$$

The formation of the stilbene (1) may be suggestive of the intermediacy of the carbene (7) but this is rendered unlikely because large quantities of tetrachloro-1,2-bis-(*p*-nitrophenyl)ethane (2) and the acetylene (3) were also formed. Thus these products (1)—(3) can readily be produced by the dimerisation and cross coupling of radicals (8) and (9) followed by elimination of hydrogen chloride in basic medium. The formation of product (2) in relatively high yields (34%) as compared with (3) (12%) seems at first surprising; however, this becomes reasonable when one observes that 4-nitrobenzyl chloride (4) or its derivatives (5) and (6) were also formed. It is reasonable to rationalise that 4-nitrobenzyl chloride (4) arose *via* hydrogen abstraction of the starting 4-nitrobenzylidene dichloride by the radical ArCHCl (8) leading to a more stabilised radical (9).[14] The pathways to the observed products may therefore be summarised by Scheme 2.

Verification of the operation of this mechanism will have to come from kinetic studies. However the large number of products formed has rendered the kinetic study more difficult. Furthermore, considering the many problems reported by previous workers studying other nitrobenzyl systems,[7-11] the present system appears to be particularly challenging. Initial titrimetric work revealed that chloride ion formation and

$$\begin{array}{rcll}
\mathrm{ArCHCl_2 + OH^-} & \rightleftharpoons & \mathrm{Ar\bar{C}Cl_2 + H_2O} & \text{fast} \\
\mathrm{Ar\bar{C}Cl_2 + ArCHCl_2} & \longrightarrow & \mathrm{Ar\dot{C}Cl_2 + ArCHCl_2^{-\cdot}} & \text{slow} \\
\mathrm{ArCHCl_2^{-\cdot}} & \longrightarrow & \mathrm{Ar\dot{C}HCl + Cl^-} & \\
\mathrm{2Ar\dot{C}Cl_2} & \longrightarrow & \mathrm{ArCCl_2CCl_2Ar} & \\
\mathrm{Ar\dot{C}Cl_2 + Ar\dot{C}HCl} & \longrightarrow & \mathrm{\xrightarrow{OH^-} ArCCl{=}CClAr} & \\
\mathrm{2Ar\dot{C}HCl} & \longrightarrow & \mathrm{\xrightarrow{OH^-} ArC{\equiv}CAr} & \\
\mathrm{Ar\dot{C}HCl + ArCHCl_2} & \longrightarrow & \mathrm{ArCH_2Cl + Ar\dot{C}Cl_2} & \\
\mathrm{ArCH_2Cl} & \longrightarrow & \mathrm{ArCH_2OMe \text{ or } ArCH{=}CHAr} &
\end{array}$$

SCHEME 2

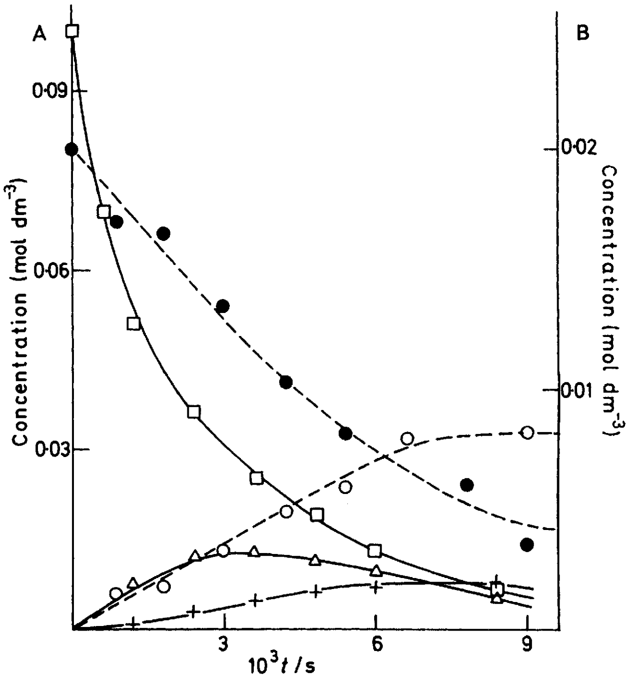

FIGURE 1 Reactions of 4-nitrobenzylidene dichloride with hydroxide ion under nitrogen: A, 4-nitrobenzylidene dichloride (0.1M) and potassium hydroxide (1.2M) in 95% methanol–water (v/v) at 25 °C, □ 4-nitrobenzylidene dichloride, △ 4-nitrobenzyl chloride, + methyl 4-nitrobenzyl ether; B, 4-nitrobenzylidene dichloride (0.02M) and sodium hydroxide (0.2M) in 95% ethanol-water (v/v) at 15 °C, ● 4-nitrobenzylidene dichloride, ○ chloride ion

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hydroxide ion consumption bear no simple stoicheiometric relationship to the amount of reactant consumed, hydroxide ion consumption being approximately one and a half times chloride ion liberation. The reactant and product profiles with reaction time are given in Figure 1, where it can be seen that a direct estimation of the reactant 4-nitrobenzylidene dichloride by ^1H n.m.r. offers a method of following the kinetics.

TABLE 1

Pseudo-second-order rate coefficients (k_2') for the reaction of 4-nitrobenzylidene dichloride with excess of potassium hydroxide under nitrogen

$[ArCHCl_2]$/M [a]	[KOH]/M [a]	T (°C)	Solvent [b]	$10^{-2}k_2'$/l mol^{-1} s^{-1} [c]	10^{-4} ' k_1 '/s^{-1} [d]
0.100	1.20	15.0	80% Methanol	1.16 ± 0.08 (0.995) [e]	3.13 ± 0.40 (0.985) [e]
0.040	1.20	15.0	80% Methanol	1.16 ± 0.07 (0.993)	1.27 ± 0.10 (0.987)
0.020	1.20	15.0	80% Methanol	1.23 ± 0.03 (0.999)	0.79 ± 0.03 (0.998)
0.100	1.20	25.0	95% Methanol	0.81 ± 0.04 (0.997)	1.59 ± 0.15 (0.986)
0.040	1.20	25.0	95% Methanol	0.78 ± 0.06 (0.997)	0.83 ± 0.05 (0.998)

[a] Initial concentration. [b] Aqueous organic mixed solvents. [c] Calculated from rate law k_2' $[ArCHCl_2]^2$. [d] Calculated pseudo-first-order coefficients ' k_1 ' based on rate law k_1 $[ArCHCl_2]$. [e] Correlation coefficient in parentheses.

The α-hydrogen of 4-nitrobenzylidene dichloride is fairly acidic. This was confirmed by experiment in which α-deuterio-4-nitrobenzylidene dichloride, when subjected to reaction in aqueous methanolic sodium hydroxide, was found to have exchanged off 94% of deuterium after 60% reaction. Likewise more than 90% deuterium incorporation was found when reaction of 4-nitrobenzylidene dichloride was carried out with sodium deuterioxide.[13] The carbanion $Ar\bar{C}Cl_2$ can be observed in strong base, *e.g.* potassium t-butoxide in t-butyl alcohol, $\lambda_{max.}$ 420 cm (ε 3 × 10^4), but under these conditions the carbanion decomposed rapidly over 10—30 min.

Kinetic experiments had to be carried out with carefully degassed aqueous methanolic solutions, the reaction being difficult to reproduce in the presence of traces of air. Excess base was maintained in the reaction medium so as to obtain pseudo-first- or pseudo-second-order kinetic behaviour. Initial experimental data for up to 90% reaction showed that the reaction is neither first-order nor perfectly second-order in 4-nitrobenzylidene dichloride although the reaction was definitely much faster at higher concentrations of the reactant. Further kinetic experiments were devised to observe the kinetic behaviour for the initial part of the reaction (up to one half-life) and over a range of concentration of the reactant (0.02—0.10M) while keeping the base concentration constant (1.2M). The results conclusively revealed that the rate of reaction was dependent on the initial reactant concentration, being faster at higher concentration. This is indicative of a higher order reaction, in fact, when plotted reasonable pseudo-second-order plots were obtained, as shown in Figure 2. The pseudo-second-order rate coefficients obtained are given in Table 1. The observed kinetic behaviour rules out a number of mechanistic pathways which require pseudo-first-order kinetics, *e.g.* rate-determining formation of carbene or free carbanion (Scheme 3).

Second-order kinetics are consistent with a mechanism in which the rate-determining step is electron transfer from the carbanion to the reactant molecule. Further, the deviation from second-order kinetics in the later stage of the reaction is not too surprising for two reasons. First, the proposed mechanism involves electron transfer from carbanion to a neutral nitro-compound acceptor.

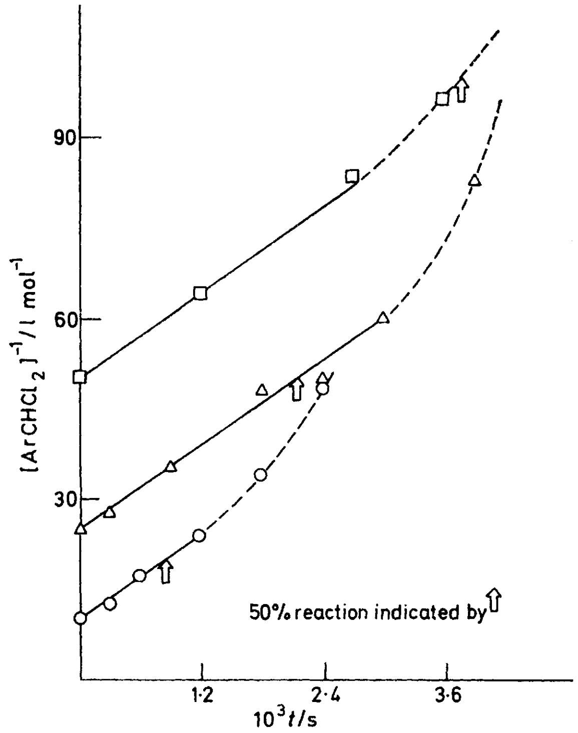
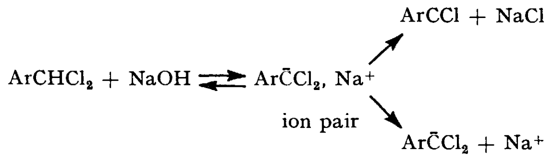


FIGURE 2 Kinetics of the reactions of 4-nitrobenzylidene dichloride (○, 0.1; △0.04; □ 0.02M) with potassium hydroxide (1.2M) in 80% methanol–water (v/v) under nitrogen at 15 °C

Products are formed increasingly with the progress of the reaction and being soluble nitro-compounds they can be effective electron acceptors and will accelerate the reaction. Secondly, the small but significant amount of 4-nitrobenzyl chloride formed by radical abstraction (Scheme 2) will lead to the consumption of reactant $ArCHCl_2$ and will inevitably complicate the kinetics.



SCHEME 3

Furthermore, under the reaction conditions 4-nitrobenzyl chloride also generates carbanions which will in all probability participate in the reaction.

The reaction rate was also examined under various conditions and the results are given in Table 2. By comparing the percentage of 4-nitrobenzylidene dichloride under fixed conditions and with additives it was found that the reaction is very sensitive to air, catalysed by light, accelerated by added nitroaromatic compounds, and can be slowed down by some radical inhibitors.

TABLE 2

Effect of additives on the rate of reaction of 4-nitro-benzylidene dichloride (0.06M) and potassium hydroxide (0.6M) in 95% methanol–water at 25° for 19 h

Additive and reaction conditions	% Reaction *
No additive	60
Reaction in the dark	60
Potassium nitrate (0.01M)	60
Trace of air	72
In air	95
Irradiation by 200 W tungsten lamp	97
4-Nitrobenzyl chloride (0.03M)	72
m-Dinitrobenzene (0.06M)	96
α-Methylstyrene (0.12M)	41
1,1-Diphenylethylene (0.03M)	23
2,6-Di-t-butyl-*p*-cresol (0.003M)	45

* Percentage reaction is based on 4-nitrobenzylidene dichloride. All reactions were duplicated and performed under nitrogen, unless otherwise stated.

In the light of the above experimental observations it is clear that the radical mechanism is operative. There is also sufficient corroboration available in the literature [15-20] for the electron transfer pathway and it is in fact a dominant feature of many reactions of nitroaromatic systems in basic media. Earlier work by Russell [17] has demonstrated that the formation of 4-nitrotoluene radical anion in potassium t-butoxide can be second- order in nitrotoluene. Bethell *et al.*[15] and Guthrie *et al.*[16] also discovered that the reactions of some other arylalkyl halides also follow a similar kinetic behaviour. Kornblum [18-20] further showed that radical-chain reactions may also arise in certain nitroaromatic systems. In the present system, however, it is not necessary to invoke radical-chain reactions as competing pathways. Likewise a competing S_N2 process need not occur and Scheme 2 sufficiently describes the mechanism of the reaction.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Hitachi–Perkin-Elmer R-20B instrument. U.v.–visible spectra were recorded on a Pye–Unicam SP 700A u.v.–visible spectrophotometer. Mass spectra were recorded on A.E.I. MS-3074 instrument. Halide ion and hydroxide ion determination were carried out by electrometric titration with a Radiometer TTT2 automatic titrator.

Preparation of 4-*Nitrobenzylidene Dichloride.*—4-Nitrobenzaldehyde (45.3 g, 0.3 mol) was heated with an excess of phosphorus pentachloride (73 g, 0.35 mol) on a steam-bath for 6 h after which the mixture was poured into an excess of crushed ice. The crude product was then filtered and recrystallised from absolute ethanol to yield pure 4-nitrobenzylidene dichloride (47 g, 76%) as almost colourless crystals, m.p. 42 °C (lit.,[21] 46 °C).

Reactions with Strong Bases.—Solvents t-butyl alcohol, dimethyl sulphoxide, and *NN*-dimethylformamide were dried by distillation from calcium hydride under nitrogen. Yellow solutions were obtained by mixing dilute solutions (4×10^{-5}M) of 4-nitrobenzylidene dichloride and potassium t-butoxide (0.1M) in t-butyl alcohol under nitrogen. When observed directly in the spectrometer at 26 °C the absorption bands were observed to decay in *ca.* 30 min. The corresponding reaction in dimethyl sulphoxide and dimethylformamide gave reddish solutions, $\lambda_{max.}$ 507 nm (ε 3×10^4).

Product Analysis.—The products obtained from the reaction of 4-nitrobenzylidene dichloride and potassium hydroxide in 95% methanol–water (v/v) under nitrogen were chromatographed through Florisil and eluted with light petroleum, benzene, chloroform, and methanol successively. Tetrachloro-1,2-bis-(*p*-nitrophenyl)ethane was relatively insoluble and crystallised out readily, and its yield was estimated directly by weighing. Other products which had been previously characterised were determined by their n.m.r. spectra based on their characteristic aromatic proton absorptions. 4-Nitrobenzyl chloride and methyl 4-nitrobenzyl ether could be isolated by column chromatography followed by distillation or sublimation and their identities verified by comparison of their m.p./b.p., n.m.r., and mass spectra with those of authentic samples.

Preparation of α-*Deuterio*-4-*nitrobenzylidene Dichloride.*—4-Nitrobenzylidene dichloride (3.09 g), deuterium oxide (2 ml), and triethylamine (3.03 g) in dry tetrahydrofuran (8 ml) were stirred together for 23 h, after which the solvent was pumped off under reduced pressure. The mixture was extracted with light petroleum (b.p. 60—80°) and concentration of the extract followed by cooling gave the product as almost colourless needles. The n.m.r. spectrum of the product showed it to be only *ca.* 90% deuteriated. This product (1.85 g) was deuteriated for a further 25 h with triethylamine (2 g) and deuterium oxide (1 ml) in dry tetrahydrofuran (5 ml). The final product after crystallisation was shown by n.m.r. to be 96.6% deuteriated.

Isotopic Exchange Experiment.—The deuteriated 4-nitrobenzylidene dichloride (0.50 g) was dissolved in 95% (v/v) methanol–water (30.4 ml) under nitrogen, after which potassium hydroxide (2.5M, 9.6 ml) was syringed in. The reaction was maintained at 25 °C under nitrogen for 19 h (or *ca.* 60% completion) after which the mixture was acidified by concentrated hydrochloric acid. Excess of methanol was removed by rotary evaporation after which unchanged 4-nitrobenzylidene chloride was extracted with light petroleum followed by chromatography through silica

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gel (25 g) to yield crystals. The n.m.r. spectrum showed that the product now contained 94% hydrogen at the α-position.

Deuteriation of unlabelled 4-nitrobenzylidene dichloride in sodium deuterioxide was similarly found to occur rapidly.[13]

Kinetic Methods.—Solvents were deoxygenated by boiling under nitrogen for at least an hour. Solutions of 4-nitrobenzylidene dichloride and potassium or sodium hydroxide were kept under nitrogen and thermostatted to ±0.05 °C. Reactions were initiated by mixing the solutions, introduced by syringes, and the mixture carefully kept under nitrogen. For initial experiments the reaction was monitored by titration of chloride ion liberation and hydroxide ion consumption. The array of products formed, however, ruled out the feasibility of this method for kinetic study. An alternative method was developed in which the concentration of the 4-nitrobenzylidene dichloride was determined directly by n.m.r., using 2,4-dinitrotoluene as standard. Control experiments indicated that 4-nitrobenzylidene dichloride and 2,4-dinitrotoluene could be extracted almost quantitatively from reaction mixtures by light petroleum. Synthetic mixtures using the two compounds in various ratios indicated that 4-nitrobenzylidene dichloride (0.2—1 mmol) can be determined with reasonable precision. In a typical analysis, the reaction was quenched by an excess of hydrochloric acid (with cooling) and a known amount of 2,4-dinitrotoluene was added. Excess of methanol was removed by rotary evaporation after which the mixture was thoroughly extracted three times with light petroleum (20 ml). The solvents were then distilled off and the residue in carbon tetrachloride was used for n.m.r. determination. Results are shown in Figure 1.

Experiments in aqueous ethanol were found to be inconveniently fast. In aqueous methanol many kinetic runs were obtained and some results are shown in Figure 2 and Table 1. The rate of reaction was also investigated in various other conditions and results are given in Table 2.

We thank the University of Malaya for research grants. Thanks are also due to Chong Hooi Long and Teoh Sin Ewe for some experiments.

[7/1591 *Received*, 6*th September*, 1977]