

Effect of Nitro Group on Solvolysis of *o*-Nitro- & *p*-Nitro-benzal Chlorides

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Received 15 June 1983; revised 22 September 1983
and accepted 1 November 1983

The *para*-nitrobenzal chloride solvolysis faster in aqueous ethanol than the *ortho*-isomer, indicating lack of intramolecular nucleophilic participation by the *ortho*-nitro group in *o*-nitrobenzal chloride. Addition of silver nitrate diminishes the chloride ion concentration and accelerates the overall rate of solvolysis.

The capacity of the nitro group to act as an intramolecular nucleophile in various reactions is well recognized¹. To obtain information concerning the role of the nitro group the solvolysis rates of *o*- and *p*-nitrobenzal chlorides have now been measured in aqueous ethanol. The silver ion assisted solvolysis of these compounds is likely to provide appreciable carbonium ion character in the transition state and such a study may throw some light on the participation of the nitro group.

o-Nitrobenzal chloride, b.p. 169-70 /30 mm, *m*-nitrobenzal chloride, m.p. 64-66 and *p*-nitrobenzal chloride, m.p. 44-45° were prepared in the laboratory.

To avoid the change in the composition of the solvent and the concentration of the solvolysing reaction mixture at reaction temperatures of 70° and 80° C, known amounts of substrates in a known volume of solvent were taken in ampoules, which were sealed and equilibrated at the desired temperatures maintained with an accuracy of $\pm 0.1^\circ$ C. Seven to eight such ampoules per run were prepared. The ampoules were taken out at regular time intervals, broken, the contents poured into ice-cold water, shaken with ether (20-25 ml), aqueous phase separated and titrated against standard sodium hydroxide to phenolphthalein end point to determine the concentration of HCl liberated at different intervals of time. The rate constants were calculated from the slopes of the plots of time versus $x/(a-x)$.

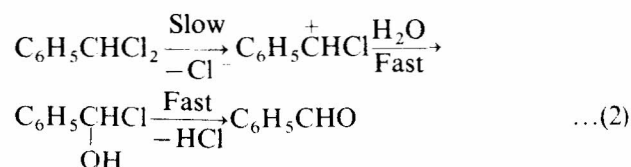
The individual rate constants (k_{Ag^+}) in the presence of silver nitrate were calculated² using Eq(1).

$$k_{Ag^+} = \frac{1}{2at} \frac{x}{(a-x)} \quad \dots(1)$$

where the symbols a , t and x have the usual meaning.

Andrews and Keefer³ observed that the $k_{(ortho)}/k_{(para)}$ ratio for solvolysis of nitroiodobenzene dichlorides

varied from 750-1000 at 15°C in acetic acid. The $k_{(ortho)}/k_{(para)}$ ratio of the solvolysis⁴ of *o*- and *p*-carboxybenzal chlorides in dioxane-water mixtures at 25°C varied from 0.83 to 110 depending upon the solvent composition. The higher ratio was attributed to the stabilization of the positively charged transition state rather than intramolecular participation. The solvolysis rate constants of *o*- and *p*-nitrobenzal chlorides in aq. ethanol are listed in Table I. The mechanism of hydrolysis of benzal chlorides seems to involve a rate-controlling formation of chlorocarbenium ion followed by a series of steps leading to an aldehyde⁵ (Eq. 2)



The *ortho*-nitrobenzal chloride is less reactive than the *para*-isomer in aqueous ethanol. The $k_{(ortho)}/k_{(para)}$ ratio is sufficiently low (0.62 at 80° C in 50% aqueous ethanol). The comparatively low reactivity of the *ortho*-isomer may partially be ascribed to steric hindrance as well as to the inductive electron-withdrawing effect of the *o*-nitro group.

The choice of solvent compositions, i.e. 50% and 60% aq. ethanol is crucial because of the poor solubility of the substrates in aq. ethanol containing less than 50% (v/v) ethanol and because of the sluggishness of the reaction in aq. ethanol containing more than 60% (v/v) ethanol.

As a matter of interest, the solvolysis rates of *m*-nitrobenzal chloride were also measured and the data are reported in Table I. From the results it is clear that the rate of solvolysis of *meta*-compound is higher than that of *ortho*- or *para*-isomer. This higher reactivity presumably can be considered as normal hydrolysis rate of this compound since it does not enter into resonance with the reaction site.

Added silver nitrate accelerates the reaction. The bimolecular rate constant (k_{Ag^+}) in the presence of silver nitrate for *ortho*-nitrobenzal chloride are again considerably less than those of the *para*-isomer. Therefore even under conditions which are likely to provide for appreciable carbonium ion character in the transition state, the effectiveness of the *o*-nitro group as a participating substituent is not adequate.

The energies and entropies of activation are summarized in Table I. The E_a values for the *ortho*-isomer are higher than those of the *para*-compound.

Table I—Rates and Thermodynamic Constants for the Solvolysis of Benzyl, Benzal and *o*-, *m*- and *p*-Nitro Benzal Chlorides in Aq. Ethanol, 50% (v/v)

Substrate	$k \times 10^6 \text{ (sec}^{-1}\text{)}$		$E_a \text{ (70}^\circ\text{)}$ (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
	70°	80°		
Benzyl chloride	70.7 ± 1.5 (50.7 ± 2.2)	195.8 ± 2.9 (137.6 ± 2.1)	102.5 ± 3.1 (100.5 ± 3.2)	82.5 ± 8.9 (91.0 ± 8.9)
Benzal chloride	1025 ± 14.1 (597.4 ± 9.0)	2340.3 ± 102.1 (1327.3 ± 41.8)	83.0 ± 3 (80.3 ± 2.0)	117.2 ± 9.0 (129.3 ± 8.1)
<i>o</i> -Nitrobenzal chloride	0.32 ± .01 (0.25 ± .01)	0.78 ± 0.01 (0.70 ± 0.02)	91.5 ± 1.3 (103.6 ± 5.4)	159.5 ± 4.0 (125.2 ± 16.5)
<i>m</i> -Nitrobenzal chloride	0.82 ± 0.02 (1.00 ± 0.03)	2.1 ± 0.01 (1.6 ± 0.06)	92.1 ± 8.4 (45.2 ± 6.5)	149.9 ± 24.9 (284.9 ± 18.8)
<i>p</i> -Nitrobenzal chloride	0.59 ± 0.02 (0.51 ± 0.02)	1.3 ± 0.09 (0.77 ± 0.02)	76.6 ± 8.9 (39.7 ± 4.7)	197.8 ± 25.8 (306.6 ± 2.1)

Values in parenthesis are in 60% (v/v) aq. ethanol.

indicating that the *ortho*-nitro group does not participate as an intramolecular nucleophile. It is difficult, however, to explain the observed differences in the entropies of activation of *ortho*- and *para*-isomers both in the absence and presence of silver nitrate. The high $-\Delta S^\ddagger$ values for the former case may be due to solvation of the transition state⁶ while small differences in the presence of silver nitrate could be attributed to large increase in rates of both the isomers.

References

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