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Kinetics of Chlorination of Certain Aromatic Compounds Using N-Chlorosuccinimide

S MOHAMED FAROOK*†, S SIVAKAMASUNDARI & S VISWANATHAN

Department of Chemistry, University of Madras, Madras 600 025

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Kinetics of chlorination of anisole, *p*-cresol, *p*-chlorophenol and acetanilide by N-chlorosuccinimide (NCS) have been studied in dry acetic acid in the presence of LiCl. Kinetic results reveal that NCS chlorination of these substrates follows a mechanism which is different from that of chlorination by molecular chlorine or bromination by structurally related N-bromosuccinimide (NBS).

The kinetics of chlorination of organic substrates by N-chloroacetanilide[1] and oxidation by N-chlorosuccinimide[2] (NCS) are well studied, but not much[3] has been reported on the kinetics of chlorination by NCS. The title work has been undertaken with a view to comparing the results of chlorination by NCS with those of chlorination by molecular chlorine[4,5] and bromination by N-bromosuccinimide (NBS)[6], which structurally resembles NCS.

Acetic acid (BDH, LR) was purified by literature method. NCS was recrystallised from dry benzene, m.p. 148-49°. LiCl was prepared from lithium carbonate, recrystallised, dried at 130° and kept in a dessicator. Anisole, *p*-cresol and *p*-chlorophenol were purified by distillation and acetanilide by recrystallisation.

No reaction occurred between anisole and NCS when the reaction was carried out in dry acetic acid for 6 hr at 50°. Though acids like $HClO_4$ and H_2SO_4 did initiate the reaction, the kinetic runs were not reproducible and the reaction was instantaneous when LiCl was added along with these acids. However, in the presence of LiCl alone, the reaction took place at a measurable rate and data were reproducible. Hence all the runs were carried out in the presence of LiCl ($0.05\,mol\,dm^{-3}$).

Kinetic runs were carried out in specially devised tubes to avoid loss of chlorine. The reactions were initiated by mixing thermally equilibrated mixtures of substrate and LiCl with NCS, quenching it with KI after the desired interval of time and estimating the unreacted NCS iodometrically. Blank runs were carried out during each experiment. NCS solution was quite stable in dry acetic acid and no free chlorine could be detected ($\lambda_{max} = 317.5\,nm$) spectrophotometrically even after 8 to 10 hr.

The kinetic results can be summarised as follows: (i) The total order of the reaction was one as found by the fractional life period method. Integral first order plots were linear upto 90% of the reaction and $k_{obs} \times 10^4$ remained constant at $4.17 \pm 0.03\,s^{-1}$ for a wide variation in reactant concentrations (from 0.05 to $0.0015\,mol\,dm^{-3}$). (ii) Order in substrate was found to be zero for all the four substrates studied. (iii) The reaction was first order each in NCS and LiCl. (iv) Added neutral salts like $NaClO_4$ retarded the rate of the reaction. (v) The effect of solvent on the reaction was studied using several acetic acid-water and acetic acid-nitrobenzene mixtures as solvents. While nitrobenzene had no effect on the rate of the reaction added water retarded the reaction. (vi) Added succinimide (100-fold variation in concentration) did not have any effect on the rate of the reaction. (vii) The stoichiometry of the reaction for all the substrates was found to be 1 : 1. The products of chlorination of anisole, acetanilide and *p*-chlorophenol were isolated and indentified by direct comparison with authentic samples as *p*-chloroanisole, *p*-chloroacetanilide and 2,4-dichlorophenol respectively. (viii) Polymerisation tests completely ruled out the possibility of radical intermediates. (ix) Activation energy remained constant for the different substrates (Table 1).

The kinetic data reveal that the chlorination of the substrates studied presently follows a mechanism which is different from that of chlorination by molecular chlorine or bromination by NBS. In the case of chlorination by molecular chlorine[4,5] the reaction is second order, first order in chlorine and first order in substrate. The rate-determining step is the formation of a σ-complex between the substrate and chlorine. The structural changes in the substrates are directly reflected in the activation energy. In the present case

Table 1—Activation Parameters for the Chlorination by NCS

[NCS] = [substrate] = $0.00625\,mol\,dm^{-3}$; [LiCl] = $0.05\,mol\,dm^{-3}$; solvent = 100% Acetic acid

Substrate	$k_{obs} \times 10^4 (s^{-1})$				E_a kJ mol^{-1}
	20°	30°	40°	50°C	
Anisole	1.86	3.99	8.47	15.21	56.17
p-Cresol	1.88	4.05	8.96	17.92	58.73
p-Chlorophenol	1.44	3.29	6.88	14.27	59.31

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†Present address: Department of Chemistry, Avvaiyar Government College for Women, Karaikal 609 602.

not only the total and individual orders are different, but the activation energy also remains constant (58.07 ± 1.9 kJ mol $^{-1}$). Since the order in substrate is zero and the activation energy remains unaffected for widely differing substrates, the rate-determining step may not involve substrate molecule. The mechanism may be given by Eqs (1) and (2)

$$\mathrm{NCS + LiCl \xrightarrow[\text{slow}]{\text{solvent}} Succinimide + Li^+ + Cl_2} \quad \ldots (1)$$

$$\mathrm{ArH + Cl_2 \xrightarrow[\text{fast}]{} ArCl + H^+ + Cl^-} \quad \ldots (2)$$

That the first step is not an equilibrium step is proved by the fact that addition of even 100-fold excess of succinimide does not alter the rate. The formation of molecular chlorine in reaction (1) has been confirmed in a separate experiment in the absence of substrate. The slow evolution of chlorine in the reaction was detected spectrophotometrically by recording the absorbance at 317·5 nm at regular time intervals.

In the case of bromination by NBS though the activation energy remains constant the observed individual orders are zero in NBS and one in substrate irrespective of the substrate and the total order is one. Also addition of bromide to NBS liberates molecular bromine instantaneously contrary to the steady evaluation of Cl_2 by NCS in the presence of chloride. The difference in NBS and NCS halogenation mechanisms may be due to the difference in electronegativities[7] of the halo substituents. This renders the rupture of N – Br bond in NBS easier than that of N – Cl bond in NCS. Thus step (1) becomes slow and rate-determining in NCS chlorination.

The involvement of molecular chlorine as active oxidising species in the chlorination by NCS is proved by the fact that in the absence of LiCl and the presence of added $AgClO_4$ (7.3×10^{-3} mol dm $^{-3}$) which is a scavanger[8] of Cl^-, no reaction occurs even in the presence of 2 mol dm $^{-3}$ $HClO_4$.

It is also found that only in case of reactive substrates like anisole, *p*-cresol etc. the chlorination follows the above mechanism. With substrates like *p*-bromoacetanilide and *p*-chloroanisole, the mechanism is entirely different. In these cases the rate depends on the [substrate] and there is accumulation of chlorine in the system since step (2) is not fast compared to step (1). Hence the mechanism of NCS chlorination depends on the nature of the substrate.

Since added nitrobenzene does not affect the rate, the rate retardation by added water is not due to dielectric effect but is believed to be due to specific solvation effect. Water may directly solvate the halide ions thereby reducing their nucleophilic reactivity towards NCS.

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