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NUCLEOPHILIC REPLACEMENT OF A NITRO-GROUP IN AN AROMATIC COMPOUND BY CHLORINE

P.H.Gore, S.D.Hammond and D.F.C.Morris

Department of Chemistry, Brunel University, London, W.3, U.K.

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While displacements of nitro-groups from activated aromatic compounds are well known,[1,2] more unusual types of replacements have recently been reported.[3-6] We wish to report a further instance of the nucleophilic replacement of an aromatic nitro-group by chloride ion: only few examples of this type have been recorded.[5]

1,3,5-Trichloro-2,4,6-trinitrobenzene (λ_{max} in methanol: 208 and 300 nm; ϵ_{max} 4,130 and 96.9 $m^2 mol^{-1}$, respectively) on treatment with lithium chloride in acetone or <u>iso</u>propanol solution affords 1,2,3,5-tetrachloro-4,6-dinitrobenzene, a yellow compound m.p. 424K (Found: C, 24.3; H, 0.3; Cl, 45.6; N, 8.9. Calculated for $C_6O_4N_2Cl_4$: C, 23.5; H, 0; Cl, 46.4; N, 9.1%. λ_{max} in methanol: 208, 305 and 380 nm; ϵ_{max} 4,490, 233 and 154 $m^2 mol^{-1}$, respectively). The m.p. had been reported as 438K;[7] but identity of the product was confirmed by conversion[8] to the known 1-chloro-3,5-dinitro-2,4,6-trisanilinobenzene, m.p. 452K (Found: Cl, 8.3. Calculated for $C_{24}H_{18}O_4N_5Cl$: Cl, 7.5%). The kinetics of the reaction in acetone were followed spectrophotometrically at 380 nm; details are given in the Table. The reaction shows a marked negative

Table. Kinetic results for the reaction of 1,3,5-trichloro-2,4,6-trinitrobenzene (0.996 mmol dm^{-3}) with Lithium Chloride (1.62 mmol dm^{-3}) in Acetone Solution.

T (K)	k_2 ($dm^3 mol^{-1} s^{-1}$)
305.6	0.883
300.6	0.607
295.5	0.453
289.4	0.293
284.1	0.168

$A = 1.3\ (\pm\ 0.2) \times 10^9\ s^{-1}$

$E_A = 53.6 \pm 3.0\ kJ\ mol^{-1}$

$\Delta H^{\ddagger} = 51.1 \pm 3.0\ kJ\ mol^{-1}$

$k_2(298K) = 0.525\ dm^3 mol^{-1}\ s^{-1}$

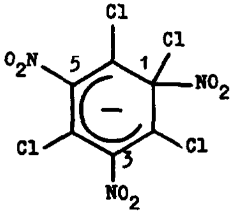
$\Delta S^{\ddagger} = -79 \pm 1\ JK^{-1} mol^{-1}$

$\Delta G^{\ddagger} = 74.6 \pm 4\ kJ\ mol^{-1}$

Errors represent 95% confidence limits

salt effect, but with a constant initial [LiCl] = 1.62 mmol dm^{-3} good second order kinetics were obtained.

In the trichlorotrinitrobenzene the three equivalent nitro-groups cannot be coplanar with the aromatic ring.[9-12] The σ-complex transition-state (I) for the reaction would permit relief of steric crowding at C_1. This would result in more effective charge-delocalisation involving the nitro-groups at C_3 and C_5,[13] and a closer approach to coplanarity of these nitro-groups.[14] It is therefore suggested that the present reaction involves a high-energy initial state, and a comparatively stable transition state. The remarkably low activation energy may thus be explained.



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