A Kinetic Study of Chlorine-isotopic Exchange between Lithium Chloride and Di- and Tri-nitro-derivatives of *m*- and *p*-Dichlorobenzenes

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The kinetics of chlorine-isotopic exchange between di- or tri-nitro-derivatives of *m*- or *p*-dichlorobenzene with $Li^{36}Cl$ have been measured. Second-order rate constants for 1,3-dichloro-4,6-dinitrobenzene increase in the sequence of solvents: isopropyl alcohol $\ll$ acetylacetone < sulpholan < dimethyl sulphoxide < 97 : 3 (v/v) diethyl ketone–n-butanol < acetone < hexamethylphosphoramide < diethyl ketone. No exchange was observed for dioxan or glacial acetic acid solutions. Water exerts a strong retarding effect on the rate of exchange of this substrate in acetone solution. Rate-constants relative to 1-chloro-2,4-dinitrobenzene = 1·00, at 298 K in anhydrous acetone solution were: 1,3-dichloro-2,4-dinitrobenzene 0·019, 1,4-dichloro-2,6-dinitrobenzene 0·61, 1,3-dichloro-4,6-dinitrobenzene 26, and 1,3-dichloro-2,4,6-trinitrobenzene 32,000. With 1,3-dichloro-2,4-dinitro- and 1,4-dichloro-2,6-dinitro-benzene only the 1-chloro-groups undergo exchange, under the conditions used.

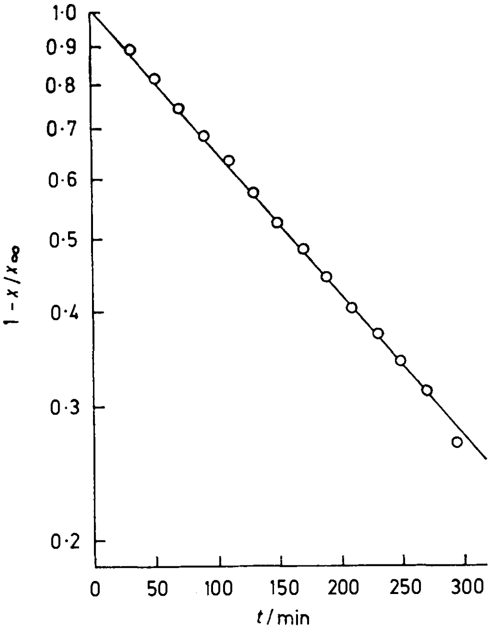
CHLORINE-36 (half-life 3×10^5 years) has been used in a study of chlorine-isotopic exchange between lithium chloride and dichloro-substituted aromatic compounds in homogeneous stable systems. This work continues our earlier investigation of monochloro-substituted aromatic derivatives.[1a] In all the cases examined simple isotopic exchange behaviour was observed. Semi-logarithmic plots of (1 — fraction exchange) against time (*t*) were rectilinear, and the time necessary for the fraction of exchange to reach a value of one-half ($t_{\frac{1}{2}}$) could readily be determined (Figure). From the half-times the constant rate of exchange R (g-atom dm^{-3} s^{-1}) of Cl atoms between LiCl and, for instance, $C_6H_4Cl_2$ could be derived from the expression (1). Values of R

$$R = \frac{2[C_6H_4Cl_2][LiCl]}{2[C_6H_4Cl_2] + [LiCl]} \cdot \frac{0{\cdot}693}{t_{\frac{1}{2}}} \qquad (1)$$

were related to second-order rate constants, $R = k_2[C_6H_4Cl_2][LiCl]$, and substitution of equation (1) leads to (2).

$$k_2 = \frac{2 \times 0{\cdot}693}{t_{\frac{1}{2}}(2[C_6H_4Cl_2] + [LiCl])} \qquad (2)$$

The effect of reactant concentrations on the rate constants for isotopic exchange is illustrated, for acetone solution, in Table 1. A small negative salt effect, and also a variable but generally small rate effect of substrate concentration, can be observed. Comparisons can,



Determination of rate of chlorine-isotopic exchange between 1,3-dichloro-2,4-dinitrobenzene and lithium chloride in dimethyl sulphoxide at 375·4 K; x and x_∞ are the count rates for identical conditions at times t and t_∞, respectively, corresponding to unit mass of the aromatic compound

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[1] (*a*) D. E. Caddy, P. H. Gore, S. D. Hammond, and D. F. C. Morris, *J.C.S. Perkin II*, 1972, 1807; (*b*) P. H. Gore, S. D. Hammond, and D. F. C. Morris, *Tetrahedron Letters*, 1970, 2747.

however, be made between rate constants obtained at different concentrations of reactants, since the effects on rates by substituents are much more powerful.

TABLE 1

Effect of reactant concentration on the rate constant for chlorine-isotopic exchange between LiCl and dichlorobenzenes in solution in acetone

Substituted 1-chlorobenzene	Temp. (K)	[Dichlorobenzene] (M)	[LiCl] (M)	10^3k_2 (dm^3 mol^{-1} s^{-1})
3-Chloro-4,6-dinitro (IV)	303·2	0·0258	0·0180	1·44
		0·0309	0·0180	1·46
		0·0258	0·0235	1·40
		0·0309	0·0235	1·12
4-Chloro-2,6-dinitro (II)	319·2	0·0293	0·0155	0·246
		0·0437	0·0155	0·219
		0·0293	0·0218	0·199
		0·0416	0·0218	0·180

Substituent Effects.—In Table 2 are collected kinetic data on chlorine-isotopic exchange obtained for several substrates and solvents. Nucleophilic displacement of nitro-groups, such as has been observed in related reactions,[1b] does not occur in these reactions. Relative rates of isotopic exchange in acetone solution were observed to follow the sequence: 1,3-dichloro-2,4-dinitrobenzene (I) < 1,4-dichloro-2,6-dinitrobenzene (II) < 1-chloro-2,4-dinitrobenzene (III) < 1,3-dichloro-4,6-dinitrobenzene (IV) < 1,3-dichloro-2,4,6-trinitrobenzene (Va). Here one observes a number of interesting substituent effects. In substrate (II) it may be inferred that the activated 1-chloro-substituent alone undergoes chlorine-isotopic exchange. The role of the 4-chloro-substituent is to increase the rate of the chlorine-isotopic exchange in 1-chloro-2,6-dinitrobenzene (VI)[1a] by a factor of *ca.* 20 (Table 3). This rate enhancement is presumably due to the inductive ($-I$) effect exerted by the chloro-substituent. A corresponding *p*-nitro-group, in contrast, effects a rate enhancement of *ca.* 10^6, by a combination of inductive ($-I$) and conjugative ($-M$) electronic processes.[1a] This rate increase results both from a substantial decrease of enthalpy of activation ($\Delta H^‡$) and an increase of entropy of activation ($\Delta S^‡$). When a chloro-group is substituted *meta* to the chlorine in 1-chloro-2,6-dinitrobenzene (VI), as in compound (I), a reduction by a factor of 3·2 in the rate of isotopic exchange is observed. This apparent anomaly may be explained by analogy with the profound rate-lowering effect of *meta*-alkyl groups on the chlorine isotopic exchange in 1-chloro-2,4,6-trinitrobenzene (Vb).[1a] It is probable that a *m*-chloro-group will cause a degree of twisting of the 2-nitro-substituent in 1-chloro-2,6-dinitrobenzene (VI) away from its near-coplanar conformation, resulting in a weakened mesomeric ($-M$) activation. If one allows for the opposite signs of the inductive ($\pm I$) effect of methyl and chloro-substituents, one finds that each of these groups exerts a 150—200 fold rate-lowering effect, *through steric causes*, *e.g.* on substrates (Va) and (Vc).

TABLE 2

Rate constants, and activation parameters, for chlorine-isotopic exchange between LiCl and dichlorobenzenes in homogeneous stable systems

Substituted 1-chlorobenzene	Solvent	[dichlorobenzene] (M)	[LiCl] (M)	10^3k_2 (dm^3 mol^{-1} s^{-1}) [Temp. (K)]	10^3k_2 (298 K) (computed)	Relative rate (acetone, 298 K)	E_a [a] (kJ mol^{-1})	$\log_{10}A$	$\Delta S^‡$ (298 K) (J K^{-1} mol^{-1})	$\Delta G^‡$ (298 K) (kJ mol^{-1})
2,4-Dinitro (III) [b]	Acetone	0·038	0·026		0·0291	1·00				
3-Chloro-4,6-dinitro (IV)	Acetone	0·026	0·023	0·380(292·2), 0·819(299·2), 1·40(303·2), 2·47(309·2), 4·03(314·2)	0·754	26	82·4	11·3	−37	90·9
	Isopropyl alcohol	0·023	0·024	0·000380(323·2), 0·000972(332·7), 0·00355(343·1), 0·0111(354·2)	0·000013		105·0	10·5	−52	118·3
	Dimethyl sulphoxide	0·021	0·061	1·08(312·4), 3·12(322·7), 5·53(328·5), 8·36(332·8)	0·219		86·7	11·5	−33	94·0
	Sulpholan	0·021	0·018	0·351(312·1), 0·685(318·2), 1·03(322·6), 2·79(332·1),	0·0702		89·0	11·4	−34	96·6
3-Chloro-2,4-dinitro (I)	Dimethyl sulphoxide	0·019	0·059	0·0197(354·9), 0·0251(357·6), 0·0446(364·0), 0·0742(368·2), 1·47(375·4)	0·00016	$1·9 \times 10^{-1}$ [c]	109·4	12·4	−16	111·7
4-Chloro-2,6-dinitro (II)	Acetone	0·032	0·019	0·0954(312·2), 0·173(317·2), 0·479(326·1), 0·563(328·7)	0·0178	$6·1 \times 10^{-1}$	98·4	11·6	−31	105·1
3-Chloro-2,4,6-trinitro (Va)	Acetone	0·0092	0·020	48·4(268·2), 80·0(273·2), 80·8(273·3), 86·3(273·4), 127(277·2)	943	$3·2 \times 10^4$	66·2	11·6	−32	73·2
	Isopropyl alcohol	0·0095	0·023	0·0577(306·5), 0·167(316·2), 0·370(322·7), 1·04(333·7), 2·39(342·2)	0·0211		91·0	11·3	−37	99·6

[a] $\Delta H^‡$ Values are smaller by *ca.* 2·5 kJ mol^{-1}. [b] Data from ref. 1*a*. [c] Using relative rate data for compound (IV) in solvents acetone and dimethyl sulphoxide.

Introduction of a 3-chloro-group in 1-chloro-2,4-dinitrobenzene (III) similarly causes a substantial rate-lowering effect (Table 2). The steric effect is exerted here on the 2-nitro-group and, to a smaller extent, on the 4-nitro-group. For 1,3-dichloro-4,6-dinitrobenzene (IV), which may be regarded as resulting from chloro-substitution at the other *meta*-position of substrate (III), a rate decrease (factor *ca.* 100) is converted into a rate increase (factor *ca.* 13). For compounds (II), (IV), and (Va) differences in rate constants (spanning five powers of magnitude) are seen to be mainly due to changes in the enthalpies of activation, since the entropy term ($\Delta S^{\ddagger}$) remains reasonably constant.

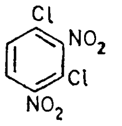
TABLE 3

Substituent effects on the rate constant, enthalpy of activation, and entropy of activation, of chlorine-isotopic exchange between LiCl and 1-chloro-2,6-dinitrobenzene in acetone solution

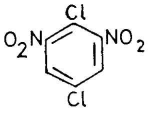
Substituent	10^3k_2 (298 K) (dm^3 mol^{-1} s^{-1})	Relative rate	$\Delta\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta\Delta S^{\ddagger}$ (J K^{-1}mol^{-1})
H [a]	$8{\cdot}69 \times 10^{-4}$	1·00	0	0
4-Cl [b]	$1{\cdot}78 \times 10^{-2}$	$2{\cdot}05 \times 10^{1}$	+15	+56
4-NO_2 [a]	$1{\cdot}88 \times 10^{3}$	$2{\cdot}16 \times 10^{6}$	−24	+39

[a] Data from ref. 1*a*. [b] Data from Table 2.

Experimental values for rate constants of exchange in acetone solution, together with values predicted from the data of simpler molecules, of di- and tri-chlorobenzene derivatives, containing one, two, or three activating nitro-groups, are collected in Table 4. The effect on rate of a *meta*-chloro-substituent was estimated from the data for 1-chloro-2,4-dinitrobenzene (III) and 1,3-dichloro-2,4-dinitrobenzene (IV), giving a value of 13 for the enhancement of rate (see above). One may expect this chloro-substituent to exert a direct ($-I$) activating effect on the exchange reaction. At the same time the nitro-group *ortho* to the new substituent will be rotated away from coplanarity, due to non-bonded interactions,[1,2] through *ca.* 40°. This twisting will result in a reduction in the contribution to the activation by this nitro-group through mesomerism of *ca.* 41%, since the extent of conjugation $= f(\cos^2 \theta)$ (θ = angle of twist).[3]



(I)



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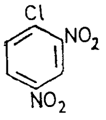

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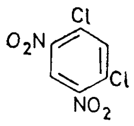

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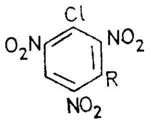
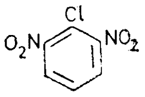


(V) a; R=Cl
b; R=H
c; R=Me



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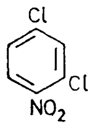
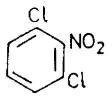


(VII)



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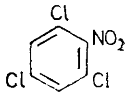

(IX)

TABLE 4

Observed and calculated rate constants for chlorine-isotopic exchange between derivatives of chlorobenzene and lithium chloride in acetone solution at 298 K

Structure	Substituted 1-chlorobenzene [a]	10^3k_2 (dm^3 mol^{-1} s^{-1}) Observed	Estimated	Method of estimation [b,c]
1	2-Nitro	$6{\cdot}34 \times 10^{-9}$ [d]		
2	4-Nitro	$4{\cdot}04 \times 10^{-7}$ [d]		
3	3-Chloro-2-nitro (VIII)		$8{\cdot}24 \times 10^{-8}$	(1 [e])
4	4-Chloro-2-nitro		$4{\cdot}81 \times 10^{-7}$	*f, g*
5	3-Chloro-6-nitro (VII)		$8{\cdot}24 \times 10^{-8}$ [h]	(1 [e])
6	3-Chloro-4-nitro (VII)		$5{\cdot}25 \times 10^{-6}$	(2 [e])
7	3,5-Dichloro-2-nitro (IX)		$1{\cdot}07 \times 10^{-6}$ [h]	(3 [e])
8	3,5-Dichloro-4-nitro (IX)		$6{\cdot}82 \times 10^{-5}$	(2 [e])
9	3-Chloro-2,4-dinitro (I)	$5{\cdot}50 \times 10^{-4}$ [e]	$1{\cdot}32 \times 10^{-1}$	(3 [i])
			$1{\cdot}94 \times 10^{-1}$	(6 [g])
10	3-Chloro-2,6-dinitro (I)	0 [j]	$3{\cdot}05 \times 10^{-3}$	(1 [e,g])
11	3-Chloro-4,6-dinitro (IV)	$3{\cdot}77 \times 10^{-1}$ [k]	$1{\cdot}32 \times 10^{-1}$	(5 [i])
			$1{\cdot}94 \times 10^{-1}$	(6 [g])
12	3-Chloro-2,4,6-trinitro (Va)	$4{\cdot}72 \times 10^{2}$ [k]	$1{\cdot}02 \times 10^{1}$	(9 [g])
			$4{\cdot}40 \times 10^{2}$	(10 [i])
			$6{\cdot}03 \times 10^{3}$	(9 [g,l])
			$4{\cdot}88 \times 10^{3}$	(10 [i,l])
			$2{\cdot}44 \times 10^{4}$	*m, e*

[a] Chlorine at C-1 is being exchanged. [b] Structure (column 1) to be modified, and the particular operation employed, *e.g.* (1 [e]) signifies: structure 1, modified as given under footnote *e*. [c] For conversion of data from one solvent to another, rate constants for substrate (IV) (Table 2) are compared. One thus obtains k_2(acetone)/k_2(sulpholan) = 0·754/0·0702 = 10·7, and k_2(acetone)/k_2(dimethyl sulphoxide) = 0·754/0·219 = 3·44. [d] Data from ref. 1*a*, extrapolated for change of solvent (footnote *c*). [e] A *m*-chloro-substituent, placed *ortho* to an activated nitro-group, enhances the rate: $\frac{1}{2}k_2$[for substrate (IV) (Table 2)]/k_2[for substrate (III) (ref. 1*a*)] = $0{\cdot}377/(2{\cdot}91 \times 10^{-2}) = 13{\cdot}0$. [f] Data for compound (II) (Table 2). [g] An *o*-nitro-substituent causes a rate enhancement of $3{\cdot}7 \times 10^{4}$ (ref. 1*a*). [h] Probably an underestimate (see text). [i] A *p*-nitro-substituent causes a rate enhancement of $1{\cdot}6 \times 10^{6}$ (ref. 1*a*). [j] Zero rate observed (see text). [k] Half rate constant for the compound (Table 2). [l] Using calculated values of k_2. [m] Starting from experimental value of $k_2 = 1{\cdot}88$ dm^3 mol^{-1} s^{-1} for compound (Vb) (ref. 1*a*).

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[2] P. M. Harris, P. T. Reed, R. E. Gluyas, U.S. Dept. Commerce Office Tech. Serv., 1959, PB Rept. 156,104 (*Chem. Abs.*, 1963, **58**, 2919); G. A. Gol'dev, G. S. Zhdanov, and M. M. Umanskii, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 311.

[3] B. M. Wepster, in *Progr. Stereochem.*, 1958, **2**, 102, 122; *cf.* J. E. Dubois and A. F. Hegarty. *J. Chem. Soc.* (*B*), 1969, 638.

A similar *meta*-chloro-substituent effect can be expected in proceeding from *p*-chloronitrobenzene to give (VII), and probably also for substrates (VIII) (from *o*-chloronitrobenzene) or (IX) [from compound (VII)]. However, by this predictive procedure the effect of the 3-chloro-group in substrate (VII) or the 5-chloro-group in substrate (IX) will be underestimated.

Estimates of the rates of isotopic exchange of the chlorine atoms in substrate (I) give values which are appreciably higher than those found experimentally. The high estimates stem from the fact that 3-chloro-substitution, as envisaged, can account for the steric effect on the 4-nitro-substituent, but takes no account of any additional steric effect exerted on the 2-nitro-group. Too large a rate of exchange is similarly predicted for substrate (Va) (Table 4), if one uses the *calculated* values for the rate constants of compound (I). An estimate can similarly be made for the rate constant of isotopic exchange of compound (Va) starting from the value of the *experimental* rate constant [1a] of 1-chloro-2,4,6-trinitrobenzene (Vb), *viz.* $k_2 = 1{\cdot}88$ dm^3 mol^{-1} s^{-1}. Simple *m*-chloro-substitution would here give us a rate constant for the molecule (Va) (two equivalent chlorine atoms) of $k_2 = 48{\cdot}9$ dm^3 mol^{-1} s^{-1}, which is too high an estimate by a factor of *ca.* 52 (Table 2). The need for detailed consideration of the substituent effects involved is apparent. This is emphasised by results from *X*-ray crystallographic studies on 1,3-dichloro-2,4,6-trinitrobenzene (Va) which show that (at least in the crystalline state) the 2-nitro-group is approximately orthogonal to the aromatic ring.[4]

For compound (I) one predicts that the 1-chloro-group undergoes exchange 53 times as fast as the 3-chloro-group. Such a difference in experimental values would be sufficiently great not to show up as a departure from the rectilinear plot actually obtained (see Figure). These simple exchange kinetics obtained in a complex case, where on structural grounds the two chloro-substituents [in (I)] are not expected to be chemically equivalent, can be explained in several ways. It could be that the rates of exchange of the two chlorines are identical, and remain so through a range of temperature; or, alternatively, that one chlorine atom alone undergoes exchange with lithium chloride. A third possibility, of a rapid intramolecular equilibration of the two halogens prior to exchange with lithium chloride, is ruled out on theoretical grounds. In view of the rate constants predicted (Table 4) we prefer the idea that only the 1-chloro-group in substrate (I) here undergoes the exchange reaction.

Solvent Effects.—The chlorine-isotopic exchange measured for 1,3-dichloro-4,6-dinitrobenzene (IV) exhibits a wide range of reactivity (spanning more than six powers of magnitude) depending on the solvent employed (Tables 2, 5, and 6). The sequence, which probably follows inversely the strengths of solvation of the lithium chloride reagent, increases thus: isopropyl alcohol $\ll$ acetonylacetone (hexane-2,5-dione) $<$ sulpholan $<$ dimethyl sulphoxide (DMSO) $<$ 97 : 3 (v/v) diethyl ketone–n-butanol $<$ acetone $<$ hexamethylphosphoramide $<$ diethyl ketone (pentan-3-one). No reaction was observed in dioxan or acetic acid solutions.

TABLE 5

Effect of different solvents on the rate of isotopic chlorine-exchange between LiCl and 1,3-dichloro-4,6-dinitrobenzene in homogeneous stable systems

Solvent	[1,3-Dichloro-4,6-dinitrobenzene] (M)	[LiCl] (M)	Temp. (K)	10^3k_2 (dm^3 mol^{-1} s^{-1})
Acetonylacetone	0·0218	0·0197	315·7	0·260
Diethyl ketone	0·0216	0·0010	315·2	40·9
Diethyl ketone (3% v/v n-butanol)	0·0230	0·0254	311·7	2·44
Hexamethylphosphoramide	0·0203	0·0213	315·2	39·9
Dioxan	No observable exchange			
Acetic acid	No observable exchange			

TABLE 6

Effect of added water on the rate of exchange between lithium chloride (0·02075M) and 1,3-dichloro-4,6-dinitrobenzene (0·0215M) in acetone at 303·8 K

% H_2O (v/v)	10^3k_2 (dm^3 mol^{-1} s^{-1})
0·0	1·22
0·05	1·12
0·1	1·05
0·2	0·87
0·3	0·73
0·4	0·58

For the reactivity of 1,3-dichloro-2,4,6-trinitrobenzene (Va) we have isopropyl alcohol $\ll$ acetone. Previously we had shown [1a] the solvent sequence for substrate 1-chloro-2,4,6-trinitrobenzene (Vb): methanol $<$ ethanol $<$ 4 : 1 (v/v) isopropyl alcohol–water $<$ n-propanol $<$ 9 : 1 (v/v) isopropyl alcohol–water $<$ isopropyl alcohol $<$ t-butyl alcohol $\ll$ acetone.

The effect of added water to solvent acetone was studied for the kinetics of chlorine isotopic exchange between lithium chloride and 1,3-dichloro-4,6-dinitrobenzene (IV) (Table 6). Even quite small percentages of water caused a significant reduction of the rate of exchange. Addition of 0·4% of water effectively halves the rate constant of this substrate at 303·8 K. This result compares with our previous findings [1a] on substrate (Vb) that addition of 6% of water causes a similar reduction in rate constant with isopropyl alcohol solvent. The effect on rate is clearly less pronounced when a solvent is already hydroxylic, *i.e.* when the change in solvent structure is likely to be smaller.

EXPERIMENTAL

Materials.—1,3-Dichloro-4,6-dinitrobenzene [5] had m.p. 101·5 °C (lit.,[5] 103—104 °C). 1,3-Dichloro-2,4-dinitrobenzene [6] had m.p. 68·5 °C (lit.,[6] 70—71 °C) (Found: C, 30·2; H, 0·8; N, 11·6. Calc. for $C_6H_2Cl_2O_4N_2$: C, 30·4;

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[4] J. R. Holden and G. Dickinson, *J. Phys. Chem.*, 1967, **71**, 1129.

[5] J. H. Boyer, R. S. Buriks, and U. Toggweiler, *J. Amer. Chem. Soc.*, 1960, **82**, 2213.

[6] C. B. Kremer and A. Bendich, *J. Amer. Chem. Soc.*, 1939, **61**, 2658; A. F. Holleman, *Rec. Trav. chim.*, 1920, **39**, 435.

H, 0·8; N, 11·8%). 1,4-Dichloro-2,6-dinitrobenzene[7] had m.p. 104 °C (lit.,[7] 104—105 °C). 1,3-Dichloro-2,4,6-trinitrobenzene[8] had m.p. 128° (lit.,[8] 128 °C).

Solvents.—The purification of solvents acetone, isopropyl alcohol, and sulpholan has been described.[1a] Pentan-3-one was fractionated through a 4 ft Vigreux column, then run down a cooled column (4 ft × 1·5 in) of activated molecular sieve (B.D.H. type 4A; 1/16 in pellets), and stored in a dark bottle in a dry box; water content (Karl Fischer[9]) *ca.* 50 p.p.m., n_D^{20} 1·3940; g.l.c. showed no impurities. Redistilled dimethyl sulphoxide, hexamethylphosphoramide, acetonitrile, or hexane-2,5-dione were dried over molecular sieve. Dioxan[10] was freshly distilled from sodium.

Kinetic Procedures.—The kinetic procedures and methods of calculation were those used earlier.[11]

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[3/700 *Received, 3rd April,* 1973]

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