A Kinetic Study of Chlorine-isotopic Exchange between Lithium Chloride and Nitro-derivatives of Chlorobenzene

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The kinetics of exchange between nitro-derivatives of chlorobenzene and lithium chloride labelled with ^{36}Cl have been measured. The second-order rate constants for 1-chloro-2,4,6-trinitrobenzene increase in the solvent sequence: methanol < ethanol < propan-2-ol–20% water < n-propanol < propan-2-ol–10% water < propan-2-ol < t-butyl alcohol ≪ acetone. 1-Chloro-2-nitrobenzene and 1-chloro-4-nitrobenzene were measured for sulpholan solutions in the temperature range 443—474 K. Other derivatives of chlorobenzene with two or three nitro-substituents gave convenient rate constants in acetone solution at normal temperatures. An *ortho*-nitro-substituent generally enhances the rate of chlorine isotopic exchange by *ca.* 4×10^4, and a *para*-nitro-group by *ca.* 10^6. The rate enhancement of nitro-groups in 1-chloro-2,4,6-trinitrobenzene is lowered by alkyl substitution in the 3- and 5-positions. A methyl or ethyl substituent reduces the rate of exchange by a factor of *ca.* 180, an isopropyl group by *ca.* $4{\cdot}5 \times 10^3$, a t-butyl group by *ca.* 8×10^4, and methyl groups at both *meta*-positions by *ca.* 3×10^5. The importance of steric factors in these reactions is discussed.

THE kinetics of isotopic exchanges of the type (1)

$$RX + MX^* \rightleftharpoons RX^* + MX \qquad (1)$$

where X* refers to a radioactive halogen atom, have been studied [1] for many aliphatic chloro-derivatives (R = alkyl, $X^* = {}^{36}Cl$). It is only recently [2] that detailed investigations of the exchange of radiochlorine with aromatic chloro-derivatives (R = aryl) have been attempted. All the earlier studies were sparse and unsystematic.[3-5] The kinetics of some related isotopic halogen exchanges, where $X^* = {}^{82}Br$ [6] or $X^* = {}^{131}I$,[7] have also been reported.

This paper deals with the kinetics of isotopic chlorine exchange reactions between lithium chloride ($Li^{36}Cl$) and monochloro-aromatic compounds containing one or more nitro-groups. The reactions were carried out in a variety of solvents and at temperatures ranging from 222 to 474 K, by use of techniques described elsewhere.[2,8] The rate data and derived thermodynamic parameters are summarised in Table 1. The reactions show a negative salt effect; however, a direct comparison can be made between rates obtained at different concentrations of lithium chloride, since the effect on rates by substituents is much more powerful.

Effect of Nitro-substitution on Chlorine-isotopic Exchange.—1-Chloro-2-nitrobenzene (I) and 1-chloro-4-nitrobenzene (II) are appreciably inert, giving measurable rates of isotopic exchange only at high temperatures. Sulpholan (2,3,4,5-tetrahydrothiophen 1,1-dioxide) was used as solvent in the temperature region 443—474 K.[9] Within this temperature range the *para*-isomer (II) reacts about $3\frac{1}{2}$ times as fast as the *ortho*-isomer (I). Extrapolated to 298 K (a procedure likely to introduce an error) a relative rate of *ca.* 65 is noted. No exchange

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[2] P. H. Gore, D. F. C. Morris, and T. J. Webb, *Radiochim. Acta*, 1966, **6**, 122.

[3] A. N. Bautysh, Ya. D. Zel'vinski, and V. A. Shalygin, *Zhur. fiz. Khim.*, 1962, **36**, 57.

[4] I. Barton Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *J. Amer. Chem. Soc.*, 1962, **84**, 158.

[5] C. W. L. Bevan and J. Hirst, *J. Chem. Soc.*, 1956, 254.

[6] (*a*) M. Sharan, *Indian J. Chem.*, 1969, **7**, 465; (*b*) J. J. Le Roux, C. S. Lu, S. Sugden, and R. W. K. Thomson, *J. Chem. Soc.*, 1945, 586.

[7] (*a*) A. M. Kristjanson and C. A. Winkler, *Canad. J. Chem.*, 1951, **29**, 154; (*b*) C. A. Marcopoulos, *J. Chem. Soc.*, 1965, 4613; D. L. Hill, K. C. Ho, and J. Miller, *J. Chem. Soc.* (*B*), 1966, 299; F. H. Kendall and J. Miller, *ibid.*, 1967, 119; E. Koros, M. Orban, and A. Meszticzky, *Magyar Kem. Folyóirat*, 1967, **73**, 463, and earlier papers.

[8] P. H. Gore, S. D. Hammond, and D. F. C. Morris, *Radiochem. Radioanalyt. Letters*, 1969, **1**, 3.

[9] Sulpholan decomposes only slowly at 529 K; *cf.* W. L. Mock, *J. Amer. Chem. Soc.*, 1970, **92**, 6918.

had been observed in earlier work [3] between 1-chloro-2-nitrobenzene (I) and lithium chloride in ethanolic solution up to 359 K.

A further rate increase of *ca.* 10^6 relative to compound (I) results for 1-chloro-2,4-dinitrobenzene (III), making it more convenient to measure the rates in acetone solution. The Arrhenius activation energy was found earlier investigation.[3] This estimate for the exchange half-time is likely to be low, since Miller [10] concludes that whereas a second nitro-group causes a decrease in activation energy of 105 kJ mol^{-1}, a first nitro-substituent (*ortho* or *para*) involves a decrease of 170 kJ mol^{-1}. 1-Chloro-2,6-dinitrobenzene (IV) reacts about 30 times more slowly than does the isomer (III); this difference

TABLE 1

Rate constants, and derived data, for chlorine-isotopic exchange reactions between substituted 1-chlorobenzenes and lithium chloride in homogeneous solution

Chlorobenzene derivative	Solvent	10^3[Substd. chlorobenzene] / mol dm^{-3}	10^3[LiCl] / mol dm^{-3}	10^6k_2 / dm^3 mol^{-1} s^{-1} (T/K)	10^6k_2 (298 K) (computed) / dm^3 mol^{-1} s^{-1}	E_{Arr} [a] / kJ mol^{-1}	$\log_{10} A$	$\Delta S^\ddagger$ (298 K) / J mol^{-1} K^{-1}	$\Delta G^\ddagger$ (298 K) / kJ mol^{-1}
2-Nitro (I)	Sulpholan	35	14	49·2 (457·2), 45·6 (458·2), 90·9 (467·0), 130 (471·2), 143 (473·2), 144 (473·2)	$5·92 \times 10^{-7}$	129·3	10·4	−53	142·8
4-Nitro (II)	Sulpholan	45	10	45·6 (443·2), 65·7 (447·2), 97·0 (450·6), 83·9 (452·2), 171 (459·2), 212 (461·7), 315 (466·4)	$3·77 \times 10^{-5}$	140·9	12·3	−18	143·9
2,4-Dinitro (III)	Sulpholan	65	13	3·1 (313·2)	$(5·9 \times 10^{-1})$				
	Acetone	38	26	101 (309·2), 177 (314·7), 272 (318·7), 327 (320·5), 382 (323·5) [b]	$2·91 \times 10^{1}$	85·8	10·5	−52	98·9
2,6-Dinitro (IV)	Acetone	38	20	5·41 (315·2), 6·94 (318·0), 12·1 (323·2), 19·1 (328·4)	$8·69 \times 10^{-1}$	83·4	8·6	−89	107·6
2,4,6-Trinitro (Va)	Acetone	50	25	439 (222·2), 1410 (229·7), 1760 (232·4), 2510 (234·7) 7210 (241·0), 32,800 (255·2) [c]	$1·88 \times 10^{6}$	59·1	10·6	−50	71·4
	Methanol	100	42	24·2 (307·7), 131 (323·0), 402 (333·2) [d]	7·37	93·9	11·3	−36	102·3
	Ethanol	100	100	141 (308·2), 240 (313·2), 398 (318·2), 750 (323·2) [e]	$4·14 \times 10^{1}$	91·3	11·6	−31	97·9
	n-Propanol	39	48	293 (313·2), 525 (318·2), 790 (323·2), 1310 (328·2)	$5·93 \times 10^{1}$	83·8	10·5	−53	97·1
	Propan-2-ol	31	49	467 (303·2), 773 (308·2), 1210 (313·2), 2230 (318·2)	$2·63 \times 10^{2}$	82·3	10·8	−46	93·5
	t-Butyl alcohol	19	14	1380 (313·2), 1820 (318·2), 3050 (323·2), 5120 (328·2)	$2·93 \times 10^{2}$	75·9	9·8	−66	93·1
	Propan-2-ol–10% H_2O	24	36	461 (313·2), 764 (318·2), 1280 (323·2), 2060 (328·2)	$8·76 \times 10^{1}$	85·5	10·9	−44	96·2
	Propan-2-ol–20% H_2O	24	45	396 (318·2), 625 (323·2), 1090 (328·2), 1680 (333·2)	$4·37 \times 10^{1}$	83·7	10·7	−56	100·3
3-Methyl-2,4,6-trinitro (Vc)	Acetone	16	21	2930 (285·4), 6030 (293·2), 11,500 (299·7), 16,200 (303·5)	$9·90 \times 10^{3}$	68·3	10·0	−62	84·4
3-Ethyl-2,4,6-trinitro (Vd)	Acetone	21	12	1240 (277·7), 2240 (283·0), 3570 (287·2), 6260 (292·8)	$1·08 \times 10^{4}$	72·6	10·8	−47	84·3
3-Isopropyl-2,4,6-trinitro (Ve)	Acetone	12	31	1830 (313·0), 2640 (318·1), 4200 (322·2), 6300 (326·9)	$4·03 \times 10^{2}$	77·1	10·1	−60	92·3
3-t-Butyl-2,4,6-trinitro (Vf)	Acetone	25	31	105 (312·9), 167 (317·7), 259 (322·5), 373 (326·3)	$2·30 \times 10^{1}$	79·8	9·3	−74	99·4
3,5-Dimethyl-2,4,6-trinitro (IXa)	Acetone	16	21	0·450 (318·2), 0·802 (322·6), 0·971 (324·7), 1·12 (326·8), 1·28 (326·8) [f]	$3·15 \times 10^{-3}$	104·6	10·8	−46	115·7
3-Ethyl-5-methyl-2,4,6-trinitro (IXb)	Acetone	9·6	21	0·139 (313·7), 0·249 (318·4), 0·301 (320·4), 0·621 (325·9) [f]	$1·72 \times 10^{-3}$	103·7	10·4	−54	117·3
3-Isopropyl-5-methyl-2,4,6-trinitro (IXc)	Acetone	11·3	15	0·173 (326·2) [f,g]	$(2·6 \times 10^{-3})$	(113)	(11·3)	(−37)	(122)

[a] $\Delta H^\ddagger$ values are smaller by *ca.* 2·5 kJ mol^{-1}. [b] Several further runs were made. [c] 25 Individual kinetic points within the temperature range 220·0—255·7 K. [d] Rate constants from Bevan and Hirst (ref. 5). [e] Rate constants from Gore, Morris, and Webb (ref. 2). [f] The reactions of the dialkyl derivatives (IX) were characterised by an initial faster part, which was probably due to a contaminant. The effect is accentuated in the kinetics, since only the first 5% of the reaction could be observed in a reasonable time. To produce realistic results for these unreactive compounds each experimental sample was used to calculate a rate constant. The results approached constant values with increasing time which were taken for k_2. [g] Other runs were conducted at 312·9, 317·9, and 322·2 K but the rate coefficients had not reached a constant value. Values of the apparent rate constants were taken from each run at a point of equal fraction exchange and used to estimate activation parameters.

to be *ca.* 86 kJ mol^{-1}, which is *ca.* 45—65 kJ mol^{-1} less than those found for the mononitro-derivatives (I) and (II) under different solvent and temperature conditions. An approximate activation energy of 120 kJ mol^{-1} was obtained for compound (III) in its isotopic exchange with lithium chloride in ethanolic solution.[2]

If one assumes that a first nitro-group exerts the same effect as a second nitro-group on the rate of isotopic chlorine exchange, the hypothetical k_{298} for chlorobenzene can be estimated as *ca.* 4×10^{-17} dm^3 mol^{-1} s^{-1}, equivalent to a half-time of exchange [concentrations as for compound (I)] of *ca.* 10^{10} years. It is not surprising that no exchange was observed in an is due almost entirely to the much lower entropy of activation for the former.

Substitution of a third nitro-group, to give 1-chloro-2,4,6-trinitrobenzene [picryl chloride (Va)], results in a further rate increase (in acetone solution) of *ca.* $6·5 \times 10^4$ (at 298 K). The rate-coefficients for the exchange reactions of compound (Va) vary considerably with the nature of the solvent. The rates increase in the sequence of alcohols: methanol < ethanol < n-propanol < propan-2-ol < t-butyl alcohol. As with other bimolecular reactions between a neutral molecule and an anion, the rates are faster in dipolar aprotic solvents than in

[10] J. Miller, personal communication, March 1967.

protic solvents. Clearly, the more strongly the Cl^- ion is solvated the slower the exchange reaction becomes.

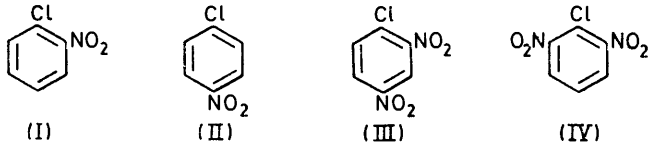
The effect on the rate-constant of isotopic chlorine exchange at 298 K of nitro-groups substituted *ortho* or *para* to chlorine is summarised in Table 2. A nitro-

TABLE 2

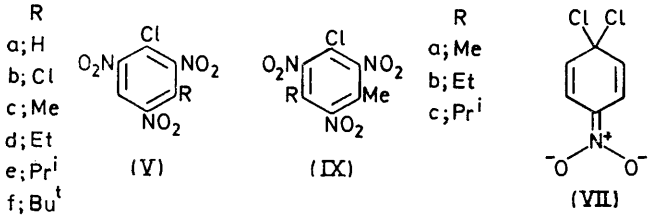
Effect on rate-constant of chlorine isotopic exchange of substitution by nitro-groups (corrected for change of solvent where appropriate)

Compound substituted	Position of substitution	
	ortho	*para*
(I)	$2{\cdot}9 \times 10^4$	$9{\cdot}9 \times 10^5$
(II)	$1{\cdot}6 \times 10^4$	
(III)	$6{\cdot}5 \times 10^4$	
(IV)		$2{\cdot}2 \times 10^6$
	Mean $3{\cdot}7 \times 10^4$	$1{\cdot}6 \times 10^6$

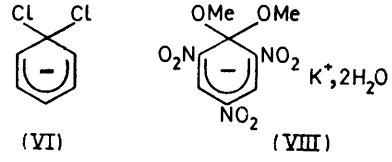
group enhances the rate more effectively at the *para*-position. The fact that substitution by two *ortho*-nitro-groups in compound (II) causes activation by each of the same order of magnitude suggests [11] that the polar influence of the substituent predominates over its steric effect.



(I) (II) (III) (IV)

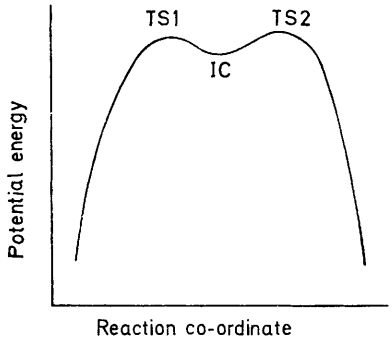


(V) (IX) (VII)



(VI) (VIII)

In nucleophilic aromatic substitutions activation by *o*- or *p*-nitro-substituents is effected by electron-withdrawal from the reaction site; this is equivalent to a lowering of the energy of the transition-states (TS1 and TS2; Figure) [close in structure to the σ-complex intermediate (IC) (VI) [12]], by resonance contributions of charged structures of the type (VII). Electron-withdrawal may result from a combination of inductive ($-I$) and conjugative ($-M$) effects.[13] With a nitro-group in the *ortho*-position the inductive effect will be relatively strong, and in the *para*-position relatively



Potential energy diagram for chlorine-isotopic exchange

weak. The $-M$ effect can be fully effective only when the nitro-group is coplanar with the aromatic nucleus,[14] and will be reduced, as a function of $\cos^2\theta$,[15] if the nitro-group is twisted away from coplanarity through an angle θ. A *p*-nitro-group, therefore, will exert a strong $-M$ effect. It is generally considered, however, that the influence on reactivity of an *o*-nitro-group is stronger than of a *p*-nitro-group.[14a,16] When, as in our work, the *p*-nitro-substituent is much more activating than is the *o*-nitro-group, the reversal is attributed to steric factors.[14b] A *p*-nitro-substituent is also more activating for the corresponding bromine isotopic exchange reactions,[6a] but for iodine isotopic exchange it is the *o*-nitro-compound which reacts at a higher rate.[7a] For other nucleophilic substitutions of chloronitrobenzenes the ratio $k_{ortho} : k_{para}$ is usually, *i.e.* with anionic reagents, within the range 0·15—0·41,[14b] but may be as low as 4×10^{-3},[17] or as high as 166.[18]

X-Ray crystallographic studies of 1-chloro-2,4,6-trinitrobenzene (Va) have shown [19] that the *p*-nitro-group is coplanar with the aromatic ring, whilst the *o*-nitro-groups are tilted at angles of 40 and 70° respectively. In a related study of 1,3-dichloro-2,4,6-trinitrobenzene

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[12] Evidence for the intermediate-complex mechanism is summarised in S. D. Ross, *Progr. Phys. Org. Chem.*, 1963, **1**, 38; W. E. Byrne, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, 1967, **32**, 2506, and subsequent papers; C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1968, **90**, 4982.

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[15] P. van Berk, J. O. M. van Langen, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1956, **75**, 1137; B. M. Wepster, in 'Progress in Stereochemistry,' eds. W. Klyne and P. B. D. de la Mare, Butterworths, London, 1958, vol. 2, pp. 102, 122; J. E. Dubois and A. F. Hegarty, *J. Chem. Soc.* (*B*), 1969, 638.

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[18] N. E. Sbarbati, T. H. Suarez, and J. A. Brieux, *Chem. and Ind.*, 1964, 1754.

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(Vb) the 4-nitro-group was found [20] to be rotated through 37°; the conformation of this nitro-group must be very similar to those of the 2-(6-)nitro-groups in 1-chloro-2,4,6-trinitrobenzene (Va). It is probable therefore that in solution the effective conformational angle of a nitro-group *ortho* to chlorine will be *ca.* 40°. The detailed structure of the intermediate complex in the exchange is more difficult to assess. Data exist, however, for closely related structures. Thus in the Meisenheimer complex (VIII) [21] isolated from the reaction of potassium methoxide with 1-methoxy-2,4,6-trinitrobenzene the three nitro-substituents were found to be all within 11° of coplanarity.[22] With allowance for the difference in geometry, and the less rigid arrangements of molecules in solution, it is nonetheless probable that *o*-nitro-groups will attain a greater degree of coplanarity as the transition state for chlorine exchange is being formed. The electronic charge can then be more effectively transferred to the *o*- and *p*-nitro-groups,[23] and an increase in resonance stabilisation results. This explains the marked lowering in the activation energy of the exchange reaction on nitro-substitution.

Effect of Alkyl-substitution on Chlorine-isotopic Exchange in 1-*Chloro*-2,4,6-*trinitrobenzene*.—Normally the polar effect of alkyl groups substituted *meta* to the seat of substitution is predominantly inductive,[24] *i.e.*, gently deactivating (*cf.* ref. 25). Alkyl substituents at the free *meta*-positions in 1-chloro-2,4,6-trinitrobenzene (Va), being positioned *ortho* to the activating nitro-groups, exert a secondary steric effect, which is seen (Table 3) to be powerfully deactivating on rate. Thus a methyl or ethyl group lowers the rate of isotopic exchange by a factor of *ca.* 180, an isopropyl group by *ca.* 4500, and a t-butyl group by *ca.* 80,000. This decrease in rate is associated with a progressive increase in activation energy; only in the case of the t-butyl derivative is there a significant decrease in the entropy of activation.

TABLE 3

The effect of alkyl-substitution on the rate constants and activation energies of chlorine-isotopic exchange of 1-chloro-2,4,6-trinitrobenzene and derivatives

Substnt. in parent 1-chloro-2,4,6-trinitrobenzene derivative	Alkyl substitution: Me k_{rel} [a]	Me ΔE_A [b] / kJ mol^{-1}	Et k_{rel} [a]	Et ΔE_A [b] / kJ mol^{-1}	Pr^i k_{rel} [a]	Pr^i ΔE_A [b] / kJ mol^{-1}	Bu^t k_{rel} [a]	Bu^t ΔE_A [b] / kJ mol^{-1}
H	$1{\cdot}9 \times 10^2$	+9·2	$1{\cdot}7 \times 10^2$	+13·5	$4{\cdot}7 \times 10^3$	+18	$8{\cdot}2 \times 10^4$	+21
3-Me	$3{\cdot}1 \times 10^5$	+36	$6{\cdot}3 \times 10^5$	+35	$3{\cdot}8 \times 10^6$ [c]	+45 [c]		
3-Et	$6{\cdot}3 \times 10^5$	+31						
3-Pr^i	$1{\cdot}5 \times 10^5$ [c]	+36 [c]						

[a] Ratio: k_2 of parent compound ÷ k_2 of substituted compound. [b] E_{Arr} for substituted compound − E_{Arr} for unsubstituted compound. [c] Based on extrapolated values.

A similar effect on the rate of reaction of 1-chloro-2,4-dinitrobenzene (III) with piperidine has been observed [24a] on introducing a methyl group between the two nitro-groups: the rate constant was lowered by a factor of 790, and the activation energy increased by 17·6 kJ mol^{-1}.

Introduction of a second alkyl group results in a further, and more dramatic, reduction in reactivity. The magnitude of the rate-lowering effect of placing a methyl, ethyl, or isopropyl group in the 5-position of 1-chloro-3-methyl-2,4,6-trinitrobenzene (Vc) is *ca.* 1000 times greater than it is in the 3-position of 1-chloro-2,4,6-trinitrobenzene (Va). An increase in the activation energy for the chlorine isotopic exchange of *ca.* 40 kJ mol^{-1} is involved. It is evident that the normal mesomeric activation by *o*- or *p*-nitro-groups is crucially affected by *meta*-alkyl substituents, and in particular by the bulky isopropyl or t-butyl groups. With one *meta*-alkyl group the *ortho*-nitro-group will probably become near-orthogonal, and the *para*-nitro-group will also be twisted away from coplanarity. It has been shown,[20] for example, that 1,3-dichloro-2,4,6-trinitrobenzene (Vb) in the crystalline state has its 2-nitro-group rotated through 75°, and the 4-nitro-group through 37° (see above), from the plane of the aromatic ring. A second alkyl group will in a similar way cause a further rotation away from the plane of the aromatic ring of both the 4- and the 6-nitro-groups. The consequence of the rotation of activating nitro-groups on reactivity has been discussed above. It is significant that the rate-constants are not very different for the dialkyl derivatives [(IXa), (IXb), and (IXc)]. The small differences in reactivity are simply explained on the basis of the $+I$ effects of alkyl groups.

EXPERIMENTAL

pK_a Values refer to apparent pK_a in water at 298 K, determined spectrophotometrically. U.v. absorption measurements were conducted in methanol. Molar extinction coefficient ε is in units m^2 mol^{-1}.

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Materials.—The following compounds were commercial products, purified by repeated crystallisation. In some cases purity was checked by g.l.c. 1-Chloro-2-nitrobenzene had m.p. 304 K (alcohol); $\lambda_{max.}$ at 252 and 295 (infl.) nm (ε 337 and 130). 1-Chloro-4-nitrobenzene had m.p. 356 K (alcohol); $\lambda_{max.}$ at 206, 215, and 272 nm (ε 744, 792, and 1024). 1-Chloro-2,4-dinitrobenzene had m.p. 321 K (alcohol); $\lambda_{max.}$ at 204, *ca.* 242, and 256 nm (ε 1430, 1130, and 1120). 1-Chloro-2,6-dinitrobenzene had m.p. 361 K (alcohol); $\lambda_{max.}$ at 291 nm (ε 130·6).

Substituted Picric Acids.—*m*-Cresol (or other phenol) was nitrated below 288 K by the literature method.[26] The crude acid was converted into its potassium salt, which was recrystallised several times (water), the acid regenerated by addition to its concentration aqueous solution of 10N-hydrochloric acid, and then finally purified by recrystallisation (alcohol). In this way were obtained: 3,5-dimethyl-2,4,6-trinitrophenol, m.p. 381 K (lit.,[26] 379·5 K); 3-ethyl-2,4,6-trinitrophenol, m.p. 358 K (lit.,[26] 358·5 K); 3-ethyl-5-methyl-2,4,6-trinitrophenol, m.p. 336 K (lit.,[26] 340 K); 3-isopropyl-2,4,6-trinitrophenol, m.p. 393 K (lit.,[26] 396 K) (Found: C, 40·5; H, 3·4; N, 14·6. Calc. for $C_9H_9N_3O_7$: C, 39·9; H, 3·35; N, 15·5%); *3-isopropyl-5-methyl-2,4,6-trinitrophenol,* m.p. 396 K (Found: C, 42·0; H, 3·8; N, 14·5. $C_{10}H_{11}O_7N_3$ requires C, 42·1; H, 3·9; N, 14·7%), pK_a 3·5, $\lambda_{max.}$ at 275 and 342 nm (ε 741 and 427); *3-t-butyl-2,4,6-trinitrophenol,* m.p. 444 K (Found: C, 43·0; H, 4·1; N, 14·5. $C_{10}H_{11}O_7N_3$ requires C, 42·1; H, 3·9; N, 14·7%), pK_a 3·5, $\lambda_{max.}$ at 271 and 340 nm (ε 1000 and 479).

Preparation of Picryl Chloride and Derivatives.[27]—Pyridine (7 ml) was added dropwise with cooling to phosphoryl chloride (30 ml). Dried picric acid (12 g) was then added, and the mixture gradually heated to 393—398 K and kept thereat for 1 h. The cooled mixture was then poured into water, the precipitate was collected, washed with water, and recrystallised (alcohol). In this way were prepared: 1-chloro-2,4,6-trinitrobenzene, m.p. 355 K (methanol), $\lambda_{max.}$ 225 nm (ε 1650); 1-chloro-3-methyl-2,4,6-trinitrobenzene, m.p. 422 K (alcohol) (lit.,[28] 422 K), $\lambda_{max.}$ 215 and 235 nm (ε 2440 and 1980); 1-chloro-3,5-dimethyl-2,4,6-trinitrobenzene, m.p. 487 K (lit.,[27] 491 K), $\lambda_{max.}$ (methanol) 288 and *ca.* 330 nm (ε 77·2 and 63); *1-chloro-3-ethyl-2,4,6-trinitrobenzene* (yield 51%), m.p. 362—363 K (Found: C, 35·3; H, 2·0; N, 15·4; Cl, 13·1. $C_8H_6ClN_3O_6$ requires C, 34·9; H, 2·2; N, 15·3; Cl, 12·9%), $\lambda_{max.}$ 211 and 233 (infl.) nm (ε 196 and 150); *1-chloro-3-ethyl-5-methyl-2,4,6-trinitrobenzene* (yield 3%), m.p. 391 K (Found: C, 37·0; H, 2·7; N, 14·4; Cl, 11·9. $C_9H_8ClN_3O_6$ requires C, 37·3; H, 2·8; N, 14·5; Cl, 12·3%); $\lambda_{max.}$ 288 and *ca.* 330 nm (ε 68 and 54); *1-chloro-3-isopropyl-2,4,6-trinitrobenzene* (yield 51%), m.p. 362—363 K (Found: C, 37·0; H, 2·6; N, 14·4; Cl, 11·9. $C_9H_8ClN_3O_6$ requires C, 37·3; H, 2·8; N, 14·5; Cl, 12·3%), $\lambda_{max.}$ 295 and *ca.* 335 (infl.) nm (ε 133 and 88); *1-chloro-3-isopropyl-5-methyl-2,4,6-trinitrobenzene* (yield *ca.* 5%), m.p. 390 K (Found: C, 39·4; H, 3·1; N, 14·2; Cl, 12·0. $C_{10}H_{10}ClN_3O_6$ requires C, 39·5; H, 3·3; N, 13·8; Cl, 11·7%), $\lambda_{max.}$ 280 (infl.) and *ca.* 330 nm (ε 62 and 41); *1-chloro-3-t-butyl-2,4,6-trinitrobenzene* (yield 50%), m.p. 369 K (Found: C, 40·1; H, 3·6; N, 14·2; Cl, 11·2. $C_{10}H_{10}ClN_3O_6$ requires C, 39·5; H, 3·3; N, 13·8; Cl, 11·7%), $\lambda_{max.}$ *ca.* 300 (infl.) and *ca.* 335 (infl.) nm (ε 113 and 75).

Solvents.—Acetone was AnalaR grade, fractionated through a 4 ft Vigreux column, then passed over 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 [29]) $< 8 \times 10^{-3}$%, $n_D^{293\ K}$ 1·3592. Propan-2-ol was magnesium-dried, water content 0·2 (±0·1)%, $n_D^{293\ K}$ 1·3778. Sulpholan was dried [30] over phosphoric oxide, twice distilled (b.p. 393 K/0·2 mm), then allowed to stand over molecular sieve, and again distilled from some sodium hydroxide pellets and activated charcoal, and kept in stoppered dark glass bottles in a dry-box at 303 K. The pure solvent had m.p. 301·7 K, $n_D^{303\ K}$ 1·4829, water content [29] <0·05%; the sulpholan was transparent above 200 nm, and contained <0·7 mole % of unsaturation (bromine titration).

Kinetic Procedures.—The experimental details of the kinetic methods [8] and calculation of results have been described.[2]

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