The Kinetics of the Reactions of Picryl Chloride with Some Substituted Anilines. Part III.[1]

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Arrhenius parameters have been measured for the reactions of 3-X- and 3-X-5-nitroanilines (X = F, Cl, Br, or I) with picryl chloride in acetonitrile. In both series the span of the rate constants is small and although both log *A* values increase with increasing activation energies, the sequence of activation energies is different in the two series. The effect of the substituents in 3-fluoro-, 3-chloro-, and 3-iodo-5-nitroanilines on the free energies of activation is not additive.

RECENTLY we have examined the additivity of substituent effects in the reactions of symmetrically substituted 3,5-X_2-anilines, where X = NO_2, CF_3, SO_2CH_3,[2] and F, Cl, Br, and I,[1] with picryl chloride. The effects of the nitro, trifluoromethyl, methylsulphonyl, and bromine substituents were found to be additive, whilst the others were not. We have now extended these investigations to the 3-halogeno-5-nitroanilines. To avoid possible solvolysis of picryl chloride by hydroxylic solvents[2] at the high temperatures of reaction required by these nucleophiles, the reactions were studied in acetonitrile and this necessitated the determination of the Arrhenius parameters for the reaction of the 3-halogenoanilines in this solvent in order to obtain the requisite data for the calculation of additivity of the substituent effects. The Arrhenius parameters for the reaction of 3-nitroaniline with picryl chloride was also measured to establish the validity of the comparison of the present results with those of previous workers. The reactions were followed by the spectrophotometric determination of the products with the amine in large enough excess to ensure first-order kinetics. In all cases the optical densities at infinity agreed with the theoretical ones and the expected products were isolated from the reaction mixture. Values of the Arrhenius parameters are given in Table 1 and the rate constants calculated at various temperatures in Table 2.

TABLE 1

Arrhenius parameters for the reaction of picryl chloride with some substituted anilines in acetonitrile

Substituent	*E*/kcal mol^{-1} [a]	log *A*
3-F	10·5 ± 0·1	5·59
	(9·7 ± 0·03) [b]	(5·57) [b]
3-Cl	11·1 ± 0·03	5·95
	(10·4 ± 0·03) [b]	(6·24) [b]
3-Br	11·3 ± 0·07	6·13
	(10·8 ± 0·17) [b]	(6·53) [b]
3-I	9·4 ± 0·10	5·03
	(9·1 ± 0·08) [b]	(5·24) [b]
3-NO_2	11·1 ± 0·04	4·87
	(11·1 ± 0·07) [c]	(4·87) [c]
3-F-5-NO_2	13·1 ± 0·07	4·77
3-Cl-5-NO_2	11·9 ± 0·07	4·10
3-Br-5-NO_2	12·4 ± 0·03	4·38
3-I-5-NO_2	12·5 ± 0·08	4·51

[a] The errors quoted are the standard deviations from the mean. [b] Values in methanol from ref. 1. [c] Value in acetonitrile quoted in ref. 2.

The 3-*Halogenoaniline Series.*—The sequence of activation energies and log *A* factors for the four halogenoanilines is the same as that obtained by Ette and Hirst[1] for the reactions of these nucleophiles with picryl chloride in methanol as solvent. The activation energies are greater and the rates 3—6 times slower in acetonitrile than in methanol. In this respect they are similar to those obtained by Hirst and Rahman[2] for the reactions of 3-X-anilines (X = NO_2, CF_3, or SO_2Me) with picryl chloride. With the exception of 3-fluoroaniline for which the values are the same, the values of the log *A* factors are lower in acetonitrile than in methanol.

TABLE 2

Rate constants (l mol^{-1} s^{-1}) calculated at various temperatures for the reactions of picryl chloride with substituted anilines in acetonitrile

T/°C	0	25	100
Substituent	10^6k_2	10^5k_2	10^3k_2
3-F	1·54 × 10^3	7·80 × 10^2	2·74 × 10^2
3-Cl	1·17 × 10^3	6·5 × 10^2	2·80 × 10^2
3-Br	1·23 × 10^3	7·00 × 10^2	3·23 × 10^2
3-I	3·23 × 10^3	1·37 × 10^3	3·33 × 10^2
3-F-5-NO_2	1·95	1·46	1·24
3-Cl-5-NO_2	3·79	2·38	1·35
3-Br-5-NO_2	2·87	1·95	1·31
3-I-5-NO_2	3·24	2·22	1·54

The range of the rate constants is small; at 25° there is only a factor of two between the highest and lowest values, and these are 15—30 times smaller than that for aniline[2] itself. At 0°, the rate constant sequence is I > F > Br > Cl, but as the temperature increases the individual values become close together and at 100° there is only *ca.* 20% difference between the highest and lowest values. The values of log *A* increase with increase in activation energies and a plot of ΔH against ΔS is linear with a slope of 384 K. This pattern is very similar to that observed in methanol except that in methanol there is a greater variation of the rate constant sequence with temperature.

The 3-*Halogeno*-5-*nitroaniline Series.*—The introduction of a *meta*-nitro-group has a powerful deactivating effect, reducing the rate constants at 25° of the 3-halogenoanilines by 270—600. The magnitudes of these effects are similar to the 380-fold reduction in rate constant observed[2] when a 3-nitro-group is introduced into aniline. The span of reactivities is small, the difference between the highest and lowest value of the rate constants being approximately two-fold at 0° and

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[1] Part II, S. I. Ette and J. Hirst. *J.C.S. Perkin II*, 1974, 76.

[2] J. Hirst and Khali-Ur-Rahman, *J.C.S. Perkin II*, 1973, 2119.

ca. 22% at 100°. Within this temperature range the rate constant sequence Cl > Br > F is maintained but the position of iodine varies from Cl > I to I > Cl. As in the 3-halogenoaniline series, the log A factors increase with increasing activation energies, but the sequence of activation energies has changed from Br ~ Cl > F > I to F > I = Br > Cl. Neither the sequence of the Arrhenius parameters nor that of the rate constants are the same as those obtained in the symmetrical 3,5-dihalogenoaniline series.[1]

The same criterion as was used previously [2] has been applied to test the hypothesis of additivity of substituent effects on the free energies of activation. The rate constants and their statistical deviation at 25° for the 3-halogeno-5-nitroanilines calculated on this hypothesis * together with the rate constants (and their statistical deviations) obtained from the experimentally determined Arrhenius parameters are assembled in Table 3. According to this criterion, it is only in 3-bromo-5-nitroaniline that the substituent effects are additive. This result is similar to that obtained in the 3,5-dihalogenoaniline series [1] where bromine was the only substituent whose effect was additive. The present results for the fluoro- and chloro-substituents are however closer to being additive than those in the latter series.

TABLE 3

A comparison of the rate constants (l mol^{-1} s^{-1}) at 25° for the reactions of 3-X-5-nitroanilines with picryl chloride in acetonitrile calculated (i) on the assumption of additivity of the free energies of activation (k_c) and (ii) from the measured Arrhenius parameters (k_m)

X	F	Cl	Br	I
10^5k_c	2.18 ± 0.37	1.81 ± 0.09	1.95 ± 0.23	3.82 ± 0.65
10^5k_m	1.46 ± 0.17	2.38 ± 0.28	1.95 ± 0.10	2.22 ± 0.30

EXPERIMENTAL

Materials.—3-Fluoro-, b.p. 82·3° at 18 mmHg, 3-chloro-, b.p. 118·5° at 21 mmHg, 3-bromo-, b.p. 130° at 12 mmHg, and 3-iodo-aniline, b.p. 145° at 15 mmHg, were commercial samples purified by fractionation. Picryl chloride, m.p. 83—84° (lit.,[3] 84°) was prepared by the method of Boyer *et al.*[3]

3-*Fluoro*-5-*nitroaniline*.—3,5-Dinitrofluorobenzene was prepared from 3,5-dinitrobenzoic acid as previously described.[4] Selective reduction by Idoux's method [5] gave 3-fluoro-5-nitroaniline, m.p. 115—115·5° (lit.,[4] 115°).

3-*Chloro*-5-*nitroaniline*.—3,5-Dinitrochlorobenzene, prepared from 3,5-dinitroaniline by the Sandmeyer reaction, on selective reduction with sodium polysulphide gave 3-chloro-5-nitroaniline, m.p. 133—134° (lit.,[6] 133—134°).

3-*Bromo*-5-*nitroaniline*.—3,5-Dinitrobenzene was brominated by the method of Hirst and Udosien.[7] Selective reduction of 3,5-dinitrobromobenzene by Idoux's method gave 3-bromo-5-nitroaniline, m.p. 128° (lit.,[4] 129°).

3-*Iodo*-5-*nitroaniline*.—3,5-Dinitrobenzene was iodinated by the method of Arotsky *et al.*[8] Reduction of 3,5-dinitroiodobenzene with alcoholic ammonium sulphide gave 3-*iodo*-5-*nitroaniline*, m.p. 137° (Found: C, 27·2; H, 2·2; N, 10·6. $C_6H_5IN_2O_2$ requires C, 27·3; H, 1·9; N, 10·4%).

Kinetic Measurements.—Acetonitrile was purified by the method of Coetzee *et al.*[9] Details of the procedure for following the rates of the reactions by the spectrophotometric determination of the products formed have been given elsewhere.[2] The wavelengths used for the substituted anilines were: 3-F, 375; 3-Cl, 377; 3-Br, 392; 3-I, 382; 3-F-5-NO$_2$, 385; 3-Cl-5-NO$_2$, 383; 3-Br-5-NO$_2$, 385; and 3-I-5-NO$_2$, 350 nm. The initial concentrations of picryl chloride and amine were 10^{-2} and 10^{-1}M, respectively. The results at various temperatures are given in Table 4.

TABLE 4

Rate constants for the reactions of 3-halogeno- and 3-halogeno-5-nitro-anilines with picryl chloride in acetonitrile at various temperatures

Substituent:	3-F		3-Cl		3-Br	
	T/°C	10^4k_2/ l mol^{-1} s^{-1}	T/°C	10^4k_2/ l mol^{-1} s^{-1}	T/°C	10^4k_2/ l mol^{-1} s^{-1}
	−14·50	5·41	−10·70	5·54	−8·90	5·98
	−4·50	11·6	−0·30	12·4	0·30	12·4
	7·30	26·8	10·10	26·4	9·60	24·4
	16·20	47·9	19·50	49·4	18·90	45·8
Substituent:	3-I		3-F-5-NO$_2$		3-Br-5-NO$_2$	
	−19·20	9·42	74·40	3·61	74·40	3·74
	−10·10	18·8	85·60	6·54	85·20	6·42
	0·20	36·0	96·00	10·9	95·40	10·5
	10·10	63·5	105·90	17·4	105·40	16·3
Substituent:	3-Cl-5-NO$_2$		3-I-5-NO$_2$		3-NO$_2$	
	74·90	4·13	73·70	4·50	12·90	2·57
	86·10	7·07	82·20	6·95	22·90	4·95
	95·60	10·9	94·40	12·5	31·80	8·56
	106·20	17·1	105·7	20·7	45·50	18·9

Product Analysis.—Samples of the reaction mixture were left for sufficient time to ensure completion of the reaction. The solutions were concentrated, poured into 2N-sulphuric acid, and the products filtered off and recrystallised successively from glacial acetic acid and toluene. Satisfactory analytical figures were obtained in every case. The products isolated were: 3-fluoro-2′,4′,6′-trinitrodiphenylamine, m.p. 129—130° (lit.,[1] 135—136°); 3-chloro-2′,4′,6′-trinitrodiphenylamine, m.p. 136—137° (lit.,[10] 137—139°); 3-bromo-2′,4′,6′-trinitrodiphenylamine, m.p. 141—142° (lit.,[1] 144—145°); 3-iodo-2′,4′,6′-trinitrodiphenylamine, m.p. 151—152° (lit.,[11] 150—152°); 3-*fluoro*-2′,4′,5,6′-*tetranitrodiphenylamine*, m.p. 187—188° (Found: C, 39·1; H, 1·9; N, 18·75. $C_{12}H_6FN_5O_8$ requires C, 39·25; H, 1·65;

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* The values of $k_2 = 5.69 \pm 0.04 \times 10^{-4}$ s^{-1} determined directly at 25° for 3-nitroaniline, together with Hirst and Rahman's [2] value of $k_2 = 2.04 \pm 0.01 \times 10^{-1}$ s^{-1} for the rate constant for the reaction of aniline were used in these calculations. The errors quoted are standard deviations from the mean.

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N, 19·0%); 3-*chloro-2′,4′,5,6′-tetranitrodiphenylamine*, m.p. 203—204° (Found: C, 37·85; H, 1·6; N, 18·25. $C_{12}H_6ClN_5O_8$ requires C, 38·15; H, 1·45; N, 18·15%); 3-*bromo-2′,4′,5,6′-tetranitrodiphenylamine*, m.p. 201—202° (Found: C, 33·9; H, 1·85; N, 16·35. $C_{12}H_6BrN_5O_8$ requires C, 33·65; H, 1·4; N, 16·35%); and 3-*iodo-2′,4′,5,6′-tetranitrodiphenylamine*, m.p. 205—206° (Found: C, 30·6; H, 1·5; N, 14·85. $C_{12}H_6IN_5O_8$ requires C, 30·35; H, 1·25; N, 14·75%).

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