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

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Arrhenius parameters have been measured for the reactions of picryl chloride with the following substituted anilines in acetonitrile: 3-methoxyaniline, 3-X-5-nitroanilines (X = CF_3, SO_2Me, or OMe), 3-X-5-methoxyanilines (X = F, Cl, Br, I, CF_3, SO_2Me, or OMe), and 3-X-5-methylsulphonylanilines (X = Cl, Br, or I). In both the methoxy-halogeno- and methylsulphonyl-halogeno-aniline series, the span of the rate constants is small and log *A* increases with increasing activation energy. The effects of the substituents in 3-methylsulphonyl-5-nitroaniline and in 3-methylsulphonyl-, 3-methoxy-, 3-trifluoromethyl-, 3-fluoro-, and 3-iodo-5-methoxyanilines on the free energies of activation is not additive.

RECENTLY [1] we examined the additivity of substituent effects in the reactions of 3-halogeno-5-nitroanilines with picryl chloride in acetonitrile. We have now extended our investigations to the series 3-X-5-nitroanilines (X = CF_3, SO_2Me, or OMe), 3-X-5-methoxyanilines (X = F, Cl, Br, I, CF_3, SO_2Me, or OMe), and 3-X-5-

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[1] Part III, T. A. Emokpae, J. M. Dosunmu, and J. Hirst, *J.C.S. Perkin II*, 1974, 76.

methylsulphonylanilines (X = Cl, Br, or I). The Arrhenius parameters for the reaction of 3-methoxyaniline with picryl chloride in acetonitrile have also been determined. The reactions were followed by spectrophotometric estimation of the products with the amines 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 mixtures. Values of the Arrhenius parameters are tabulated.

The introduction of a 3-methoxy-group into aniline reduces the rate constant of the reaction by a factor of 2.29, and the introduction of a second methoxy-group at the 5-position gives a further 1.75 fold reduction in the rate constant. The same deactivating effect of a 3-methoxy-group was observed by Peacock and Singh[2] in the reaction of substituted anilines with 1-chloro-2,4-dinitrobenzene in ethyl alcohol. Similarly a comparison of the results for 5-methoxy-3-nitroaniline with those for 3-nitroaniline given in Part III[1] shows that the introduction of a 5-methoxy-group into the 3-nitroaniline series reduces the rate constant by a factor of 3. Hence the overall effect of a *meta*-methoxy-group in these reactions is an electron-withdrawing one, in contrast to its effect when it is present in the substrate of aromatic nucleophilic substitution reactions. Bevan, Hirst, and Una[3] have shown that in the methoxydefluorination of substituted 3-nitrofluorobenzenes a 5-methoxy-group is deactivating.

Arrhenius parameters for the reactions of picryl chloride with some substituted anilines in acetonitrile and a comparison of the rate constants (l mol^{-1} s^{-1}) at 25 °C calculated (i) on the assumption of additivity of the free energies of activation ($k_{\text{calc.}}$) and (ii) from the measured Arrhenius parameters (k_{m})

Substituent	E/kcal mol^{-1} [a]	log A	$10^6k_{\text{calc.}}$	10^6k_{m}
3-CF_3-5-NO_2	14.3 ± 0.04	5.31	7.17 ± 0.06	6.76 ± 0.44
3-SO_2Me-5-NO_2	16.0 ± 0.06	5.94	3.85 ± 0.04	1.62 ± 0.16
3-OMe-5-NO_2	11.9 ± 0.09	5.12	$2.46 \pm 0.02 \times 10^2$	$2.47 \pm 0.38 \times 10^2$
3-Cl-5-SO_2Me	11.9 ± 0.10	4.43	$4.43 \pm 0.23 \times 10$	$5.08 \pm 0.86 \times 10$
3-Br-5-SO_2Me	12.9 ± 0.08	5.09	$4.74 \pm 0.56 \times 10$	$4.29 \pm 0.47 \times 10$
3-I-5-SO_2Me	10.9 ± 0.01	3.97	$9.27 \pm 1.57 \times 10$	$9.53 \pm 0.27 \times 10$
3-CF_3-5-OMe	10.9 ± 0.12	5.17	$1.12 \pm 0.01 \times 10^3$	$1.51 \pm 0.02 \times 10^3$ [b]
3-SO_2Me-5-OMe	11.6 ± 0.09	5.37	$6.02 \pm 0.07 \times 10^2$	$7.37 \pm 0.06 \times 10^2$ [b]
3-F-5-OMe	11.7 ± 0.10	6.21	$3.40 \pm 0.58 \times 10^3$	$4.23 \pm 0.11 \times 10^3$ [b]
3-Cl-5-OMe	11.2 ± 0.05	5.67	$2.83 \pm 0.13 \times 10^3$	$2.96 \pm 0.01 \times 10^3$ [b]
3-Br-5-OMe	11.5 ± 0.08	5.91	$3.02 \pm 0.36 \times 10^3$	$3.01 \pm 0.03 \times 10^3$ [b]
3-I-5-OMe	10.5 ± 0.08	5.37	$5.97 \pm 1.00 \times 10^3$	$4.73 \pm 0.03 \times 10^3$ [b]
3,5-$(OMe)_2$	9.9 ± 0.05	5.93	$3.88 \pm 0.03 \times 10^4$	$5.08 \pm 0.06 \times 10^4$ [b]
3-OMe	8.6 ± 0.07	5.25		$8.89 \pm 0.08 \times 10^4$ [b]
H	7.9 ± 0.27 [c]	5.06 [c]		

[a] The errors quoted are standard errors of the mean. [b] Values measured directly at 25°. [c] Values from ref. 4.

A comparison of the present results with those of Hirst and Rahman[4] shows that the introduction of 5-CF_3, 5-SO_2Me, and 5-NO_2 groups into 3-nitroaniline is powerfully deactivating, reducing the rate constants by factors between 80 and 540. The variation within the three groups, though, is fairly small, the rate constant ratios (5-CF_3 : 5-SO_2Me : 5-NO_2) are 1 : 0.24 : 0.15 at 25 °C, which are similar to those obtained when these groups are introduced into the 3-position of aniline. The rate constants give the expected $-I$ sequence $NO_2 > SO_2Me > CF_3$, but inspection of the Arrhenius parameters shows that this sequence is determined entirely by the entropy of activation and not the enthalpy. We have already[4] drawn attention to examples of this phenomenon and comparison of the present results with those reported in ref. 1 shows that when 5-NO_2 and 5-SO_2Me groups are introduced into 3-chloro- and 3-bromo-anilines, although the expected rate constant sequence $SO_2Me > NO_2$ is obtained, in both cases the sequence is due to the entropies of activation.

A comparison of the present results with those for the 3-halogenoanilines given in ref. 1 shows that the introduction of a 5-OMe group reduces the rate constant approximately two-fold (halogen = F, Cl, Br, or I) while the introduction of 5-SO_2Me reduces the value between 90- and 200-fold (halogen = Cl, Br, or I). In each series the span encompassed by the rate constants is small, and between 0—100 °C never exceeds a factor of three. The sequences of the rate constants are temperature variable, but are the same in both series, as is the sequence of activation energies, the magnitude of log A increasing with increase in activation energy. The general behaviour is the same as that previously observed[1] in the 3-halogeno- and 5-halogeno-3-nitroaniline series, and the sequence of activation energies, F > Br > Cl > I, is the same as that in the 3-halogenoaniline series, but different from the sequence in the 3-halogeno-5-nitroaniline series.

The same criteria as used previously[4] have been applied to test the hypothesis of additivity of substituent effects on the free energies of activation. The rate constants and their statistical deviations at 25 °C for the 3,5-disubstituted anilines calculated on this hypothesis * together with the rate constants (and their statistical deviations) either obtained from direct

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* The values of k_2 for trifluoromethylaniline ($2.60 \pm 0.04 \times 10^{-3}$), 3-methoxyaniline ($8.89 \pm 0.08 \times 10^{-2}$), and 3-methylsulphonylaniline ($1.38 \pm 0.01 \times 10^{-3}$) determined directly at 25 °C, together with the values for aniline and 3-nitroaniline given in ref. 1, were used in these calculations. The errors quoted are standard errors of the mean.

[2] D. H. Peacock and A. Singh, *J. Phys. Chem.*, 1936, **40**, 669.

[3] C. W. L. Bevan, J. Hirst, and S. J. Una, *Nigerian J. Sci.*, 1966, **1**, 27.

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

measurement at 25 °C or calculated from experimentally determined Arrhenius parameters are assembled in the Table. According to these criteria, the substituent effects are additive in 3-trifluoromethyl- and 3-methoxy-5-nitroanilines, 3-chloro-, 3-bromo-, and 3-iodo-5-methylsulphonylanilines, and 3-chloro- and 3-bromo-5-methoxyanilines, but not for the rest of the compounds investigated.

EXPERIMENTAL

Materials.—A commercial sample of 3-methoxyaniline was fractionally distilled and the fraction of b.p. 251° collected. Its purity was confirmed by g.l.c. A commercial sample of 3,5-dimethoxyaniline was recrystallised from water; m.p. 52—53°. Picryl chloride, m.p. 83—84° (lit.,[5] 84°), was prepared by the method of Boyer *et al.*[5]

3-*Nitro*-5-*trifluoromethylaniline*. Nitration of benzylidyne fluoride with potassium nitrate and sulphuric acid gave 3-nitrobenzylidyne fluoride, b.p. 202—204° (lit.,[6] 202.5°). Nitration of this product by the method of Finger and Reed [7] yielded 3,5-dinitrobenzylidyne fluoride, m.p. 48° (lit.,[7] 48—50°), which, on reduction with sodium polysulphide gave 3-nitro-5-trifluoromethylaniline, m.p. 80° (lit.,[3] 80°).

3-*Methylsulphonyl*-5-*nitroaniline*. Methyl 3-nitrophenyl sulphone, m.p. 146° (lit.,[8] 146°) was prepared by the method of Twist and Smiles.[8] The sulphone (20.1 g) was added to a cooled mixture of fuming nitric acid (96 cm^3) and 60% oleum (48 cm^3) and heated at 140 °C for 6 h. On cooling and pouring into crushed ice, 3,5-dinitrophenyl methyl sulphone was obtained, m.p. 248—250° (lit.,[8] 248—250°). Selective reduction by Idoux's method [9] gave 3-methylsulphonyl-5-nitroaniline, m.p. 200—201° (from water) (lit.,[3] 200—201°).

5-*Methoxy*-3-*nitroaniline*. 3,5-Dinitroanisole was prepared by refluxing for 30 min a solution of 1,3,5-trinitrobenzene (0.1 mol) in methanol (1 l) containing sodium methoxide [from sodium (0.15 mol)]. Reduction of one of the nitro-groups by Idoux's method gave 3-methoxy-5-nitroaniline, m.p. 119° (lit.,[10] 119—120°).

3-*Chloro*-5-*methylsulphonylaniline*. The diazonium salt obtained from 3-methylsulphonyl-5-nitroaniline on treatment with copper(I) chloride gave 3-*chloro*-5-*nitrophenyl methyl sulphone*, m.p. 142—144° (from methanol) (Found: C, 35.5; H, 2.5; N, 5.7. $C_7H_6ClNO_4S$ requires C, 35.7; H, 2.55; N, 5.95%). Reduction with tin and hydrochloric acid and repeated recrystallisation from water gave 3-*chloro*-5-*methylsulphonylaniline*, m.p. 114° (Found: C, 40.65; H, 3.7; N, 6.65. $C_7H_8ClNO_2S$ requires C, 40.85; H, 3.9; N, 6.8%).

3-*Bromo*-5-*methylsulphonylaniline*. Bromination of methyl 3-nitrophenyl sulphone by the method of Hirst and Udosien [11] gave 3-bromo-5-nitrophenyl methyl sulphone, m.p. 145—146° (lit.,[11] 145—147°). Reduction with tin and hydrochloric acid gave 3-*bromo*-5-*methylsulphonylaniline*, m.p. 132—133° (from water) (Found: C, 33.55; H, 3.4; N, 5.7. $C_7H_8BrNO_2S$ requires C, 33.6; H, 3.2; N, 5.6%).

3-*Iodo*-5-*methylsulphonylaniline*. The iodination of methyl 3-nitrophenyl sulphone by Arotsky's [12] method for the direct iodination of deactivated aromatic substrates gave 3-*iodo*-5-*nitrophenyl methyl sulphone*, m.p. 160—161° (from methanol) (Found: C, 25.8; H, 1.9; N, 4.4. $C_7H_6INO_4S$ requires C, 25.7; H, 1.85; N, 4.3%), identical with that obtained from the reaction of diazotised 3-methylsulphonyl-5-nitroaniline with potassium iodide. Reduction with tin and hydrochloric acid gave 3-*iodo*-5-*methylsulphonylaniline*, m.p. 139—140° (from water) (Found: C, 28.15; H, 2.95; N, 4.5. $C_7H_8INO_2S$ requires C, 28.3; H, 2.7; N, 4.7%).

3-*Bromo*-5-*methoxyaniline*. 1-Bromo-3-methoxy-5-nitrobenzene, m.p. 88° (lit.,[13] 88°) was prepared from 3-methoxy-5-nitroaniline by the Sandmeyer reaction. Reduction with tin and hydrochloric acid gave 3-bromo-5-methoxyaniline, m.p. 52° (lit.,[13] 52°).

3-*Iodo*-5-*methoxyaniline*. Addition of potassium iodide to a solution of diazotised 3-methoxy-5-nitroaniline gave 1-iodo-3-methoxy-5-nitrobenzene, m.p. 83° (lit.,[13] 84°). Reduction with hydrochloric acid and iron filings gave 3-iodo-5-methoxyaniline, m.p. 86—87° (lit.,[13] 86.5°)

3-*Fluoro*-5-*methoxyaniline*. 1-Fluoro-3-methoxy-5-nitrobenzene, m.p. 84° (lit.,[3] 85°), prepared from 3-methoxy-5-nitroaniline by the Balz-Schiemann reaction, on reduction with tin and hydrochloric acid gave 3-fluoro-5-methoxyaniline, b.p. 246°.

3-*Chloro*-5-*methoxyaniline*. 1-Chloro-3-methoxy-5-nitrobenzene, m.p. 99—101° (lit.,[13] 99—101°), obtained from 3-methoxy-5-nitroaniline by the Sandmeyer reaction on reduction with tin and hydrochloric acid gave 3-chloro-5-methoxyaniline, m.p. 31° (lit.,[13] 31°).

3-*Methoxy*-5-*trifluoromethylaniline*. 3,5-Dinitrobenzylidyne fluoride (0.3 mol) in dry methanol (720 cm^3) was added with stirring to sodium methoxide (0.37 mol) in absolute methanol (150 cm^3) and the mixture was refluxed for 90 min. Removal of the methanol left a residue which on extraction with petroleum gave 3-methoxy-5-nitrobenzylidyne fluoride, m.p. 32° (lit.,[14] 32.5°). Reduction with iron powder and ammonium chloride gave 3-methoxy-5-trifluoromethylaniline, m.p. 48° (lit.,[14] 48—49°).

3-*Methoxy*-5-*methylsulphonylaniline*. 1-Methoxy-3-methylsulphonyl-5-nitrobenzene was prepared from 3,5-dinitrophenyl methyl sulphone by the procedure used for the preparation of 3-methoxy-5-nitrobenzylidyne fluoride. A benzene solution of the crude material was placed on a column of activated alumina and eluted with 50% benzene–petroleum. Evaporation, and recrystallisation from methanol gave 1-*methoxy*-3-*methylsulphonyl*-5-*nitrobenzene*, m.p. 110° (Found: C, 41.55; H, 4.2; N, 6.2. $C_8H_9NO_5S$ requires C, 41.55; H, 3.9; N, 6.05%). Reduction of this compound with tin and hydrochloric acid gave 3-*methoxy*-5-*methylsulphonylaniline*, m.p. 124° (from water) (Found: C, 47.55; H, 5.75; N, 6.75. $C_8H_{11}NO_3S$ requires C, 47.75; H, 5.5; N, 6.95%).

Kinetic Measurements.—Details of the method of purification of acetonitrile and the procedure for following the rates of the reactions by spectrophotometric estimation of the products have been given elsewhere.[4] For the fast

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[5] R. Boyer, E. Y. Spencer, and G. F. Wright, *Canad. J. Res.*, 1946, **24B**, 202.

[6] G. C. Finger, C. Nachtrieb, and F. H. Reed, *Trans. Illinois State Acad. Sci.*, 1939, **31**, 132.

[7] G. C. Finger and F. H. Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1972.

[8] R. F. Twist and S. Smiles, *J. Chem. Soc.*, 1925, 1248.

[9] J. P. Idoux, *J. Chem. Soc.* (*C*), 1970, 435.

[10] H. Vermeulen, *Rec. Trav. chim.*, 1906, **25**, 12.

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[13] H. H. Hodgson and J. S. Wignall, *J. Chem. Soc.*, 1926, 2077.

[14] M. Hauptschein, A. J. Saggiomo, and C. S. Stokes, *J. Amer. Chem. Soc.*, 1955, **77**, 2284.

reactions of 3-methoxy- and 3,5-dimethoxy-anilines, the initial concentrations of picryl chloride and the amines were reduced to 1.00×10^{-3} and 1.00×10^{-2}M. The results at various temperatures are listed in Supplementary Publication No. SUP 21822 (3 pp.).*

Product Analysis.—Details of the procedure used to isolate the products have already been given.[1] The products obtained were: *3′-methoxy*-2,4,6-*trinitrodiphenylamine*, m.p. 118—119° (Found: C, 46.4; H, 3.3; N, 16.75. $C_{13}H_{10}N_4O_7$ requires C, 46.65; H, 3.0; N, 16.75%); 2,4,5′,6-*tetranitro*-3′-*trifluoromethyldiphenylamine*, m.p. 194—196° (Found: C, 37.6; H, 1.5; N, 16.65. $C_{13}H_6F_3N_5O_8$ requires C, 37.4; H, 1.45; N, 16.8%); 3′-*methylsulphonyl*-2,4,5′,6-*tetranitrodiphenylamine*, m.p. 266—267° (Found: C, 36.85; H, 2.4; N, 16.2. $C_{13}H_9N_5O_{10}S$ requires C, 36.55; H, 2.1; N, 16.4%); 3′-*methoxy*-2,4,5′,6-*tetranitrodiphenylamine*, m.p. 167—168° (Found: C, 40.9; H, 2.55; N, 18.2. $C_{13}H_9N_5O_9$ requires C, 41.15; H, 2.4; N, 18.45%); 3′-*chloro*-5′-*methylsulphonyl*-2,4,6-*trinitrodiphenylamine*, m.p. 222° (Found: C, 37.4; H, 2.4; N, 13.2. $C_{13}H_9ClN_4O_8S$ requires C, 37.45; H, 2.2; N, 13.45%); 3′-*bromo*-5′-*methylsulphonyl*-2,4,6-*trinitrodiphenylamine*, m.p. 231—233° (Found: C, 33.55; H, 2.25; N, 12.5. $C_{13}H_9BrN_4O_8S$ requires C, 33.85; H, 1.95; N, 12.15%); 3′-*iodo*-5′-*methylsulphonyl*-2,4,6-*trinitrodiphenylamine*, m.p. 238° (Found: C, 30.65; H, 2.05; N, 10.95. $C_{13}H_9IN_4O_8S$ requires C, 30.75; H, 1.8; N, 11.05%); 3′-*methoxy*-5′-*methylsulphonyl*-2,4,6-*trinitrodiphenylamine*, m.p. 178—179° (Found: C, 40.85; H, 3.0; N, 13.8. $C_{14}H_{12}N_4O_9S$ requires C, 40.8; H, 2.95; N, 13.6%); 3′-*methoxy*-2,4,6-*trinitro*-5′-*trifluoromethyldiphenylamine*, m.p. 158° (Found: C, 42.0; H, 2.55; N, 15.4. $C_{14}H_9F_3N_4O_7$ requires C, 41.8; H, 2.25; N, 15.15%); 3′-*fluoro*-5′-*methoxy*-2,4,6-*trinitrodiphenylamine*, m.p. 136° (Found: C, 44.55; H, 2.75; N, 16.1. $C_{13}H_9FN_4O_7$ requires C, 44.35; H, 2.6; N, 15.9%); 3′-*chloro*-5′-*methoxy*-2,4,6-*trinitrodiphenylamine*, m.p. 156° (Found: C, 42.45; H, 2.55; N, 15.5. $C_{13}H_9ClN_4O_7$ requires C, 42.35; H, 2.45; N, 15.2%); 3′-*bromo*-5′-*methoxy*-2,4,6-*trinitrodiphenylamine*, m.p. 166° (Found: C, 38.0; H, 2.35; N, 13.8. $C_{13}H_9BrN_4O_7$ requires C, 37.75; H, 2.20; N, 13.55%); 3′-*iodo*-5′-*methoxy*-2,4,6-*trinitrodiphenylamine*, m.p. 194° (Found: C, 33.65; H, 2.15; N, 12.45. $C_{13}H_9IN_4O_7$ requires C, 33.9; H, 1.95; N, 12.15%).

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.