The Kinetics of the Reactions of Picryl Chloride with Some Substituted Anilines. Part I

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Arrhenius parameters have been determined for the reactions of picryl chloride with 3-R, 4-R, and 3,5-R_2-anilines (where R = NO_2, CF_3, or SO_2Me) in methanol and acetonitrile. In acetonitrile for all three groups, and for the trifluoromethyl and methylsulphonyl groups in methanol, the rate sequence of the 3-substituted anilines is governed entirely by the entropy of activation. The results are discussed in terms of the electronic effects of the substituents and linear free energy correlations are made. The effects of *meta*-substituents are additive in acetonitrile.

THE electronic effects of nitro, trifluoromethyl, and methylsulphonyl groups when they are present in the substrate of bimolecular nucleophilic aromatic substitutions have been investigated by various workers, but the effect of the last two groups in the nucleophiles has received little attention, particularly when they are present in the *meta*-positions of aniline or phenoxide ion. Also very little work has been done on the additivity of substituent effects in this type of reaction. The influence of 3- and 4-nitro, -trifluoromethyl, and -methylsulphonyl groups and also of 3,5-dinitro and 3,5-bistrifluoromethyl substituents on the reactions of methoxide ions with fluorobenzene has been reported [1] and it is of interest to compare these results with those obtained for the correspondingly substituted anilines acting as nucleophiles in nucleophilic aromatic substituents.

The original intention was to study the reaction of 1-fluoro-2,4-dinitrobenzene with substituted anilines in methanol. When the nucleophile was 3-nitroaniline, however, the reaction at 100—130° was extremely slow and only went to 40% completion. When the substrate was changed to picryl chloride, the reactions of the monosubstituted anilines went to completion and good second-order rate constants were obtained. With 3,5-bistrifluoromethylaniline, the concentration of chloride ion liberated during a run rose to a maximum and then decreased to a constant value. This behaviour is similar to that observed by Bevan and Hirst [2] for the methanolysis of picryl chloride. These authors proposed that the methyl picryl ether formed undergoes a Zeisel-type of reaction forming picric acid and methyl chloride. On this basis it is assumed that the results observed with 3,5-bistrifluoromethylaniline are due to concurrent methanolysis. When the runs were followed by spectrophotometric determination of the product it was found that the reaction proceeded to 92% completion and that the product was stable under the conditions used. Hence rate constants for the anilinodechlorination can be

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[1] J. Hirst and S. J. Una, *J. Chem. Soc. (B)*, 1971, 2221.

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

obtained by employing first-order conditions. The product was isolated in 90% yield, in good agreement with the spectrophotometric value. 3,5-Bismethylsulphonylaniline was not sufficiently soluble in methanol for kinetic measurements to be made and as it was intended to test the hypothesis of additivity of substituent effects from the *meta*-position another solvent had to be used. Dimethyl sulphoxide reacts rapidly with picryl chloride to give a crystalline solid (*cf.* Experiment section) but all reactants were soluble in acetonitrile. In this solvent, spectrophotometric measurements under conditions ensuring first-order kinetics gave reproducible rate constants and the optical densities of solutions measured after the completion of the reactions agreed with the theoretical values. The change of solvent from methanol to acetonitrile may result in a change from the formation of the intermediate being the slow step to its decomposition being rate determining. In the latter case the reaction should be base catalysed.[3] The reaction of picryl chloride with aniline was studied over a 100-fold variation of the aniline concentration, but no base catalysis was found (Table 1). Rate constants calculated at 25° and Arrhenius parameters for the reactions of picryl chloride with aniline and substituted anilines in methanol and acetonitrile are given in Table 2.

TABLE 1

The effect of variation of concentration on the reaction of aniline with picryl chloride in acetonitrile at 22·30°. Initial concentration of picryl chloride 5 × 10^{-5}M

10^3 [Aniline]/M	1·00	10·0	100
$10k_2$/l mol^{-1} s^{-1}	1·79	1·82	1·84

TABLE 2

Rate constants at 25° and Arrhenius parameters for the reactions of picryl chloride with some substituted anilines in methanol and in acetonitrile

	Methanol			Acetonitrile		
Substituent	$10^6k_2^{25}$/l mol^{-1} s^{-1}	E/kcal mol^{-1} [a]	log (A/s^{-1})	$10^6k_2^{25}$/l mol^{-1} s^{-1}	E/kcal mol^{-1}	log (A/s^{-1})
3-NO_2	2·27 × 10^3	10·7 ± 0·07	5·20	541	11·1 ± 0·07	4·87
	(2·27 × 10^3) [b]	(10·9) [b]	(5·34) [b]			
4-NO_2	91·2 [c]	12·8 [c]	5·35 [c]	29·4	13·3 ± 0·1	5·22
3,5-$(NO_2)_2$	9·33 [c]	13·7 [c]	5·01 [c]	1·00	13·8 ± 0·17	4·12
3-CF_3	1·47 × 10^4	10·1 ± 0·07	5·57	2·57 × 10^3	11·0 ± 0·00	5·48
4-CF_3	5·25 × 10^3	10·2 ± 0·03	5·20	966	11·3 ± 0·13	5·27
3,5-$(CF_3)_2$	145	11·4 ± 0·17	4·52	25·6	11·8 ± 0·13	4·06
3-SO_2Me	6·67 × 10^3	9·9 ± 0·13	5·06	1·27 × 10^3	11·1 ± 0·13	5·24
4-SO_2Me	562	11·6 ± 0·07	5·25	159	12·9 ± 0·10	5·66
3,5-$(SO_2Me)_2$				11·5	12·2 ± 0·17	4·01
H	7·04 × 10^5			2·04 × 10^5	7·9 ± 0·27	5·06
	(6·77 × 10^5) [b]	(7·86) [b]	(5·59) [b]			

[a] The errors quoted are the standard deviations from the mean. [b] Values of ref. 2. [c] Values of ref. 13.

For aniline and the five *meta*-substituted anilines investigated in both methanol and acetonitrile, a plot of log k^{25}(MeOH) against log k^{25}(MeCN) is a straight line of slope 1·08, correlation coefficient (r) 0·9998, standard deviation (s.d.) 0·04 and for the *para*-substituted compounds (four points) a line of slope 0·99 (r 0·998; s.d. 0·13) is obtained. We take this as showing that the rate constants measured reflect the influence of the substituent on the nucleophilic power of the reagent and that there are no gross effects due to substituent–solvent interactions. All the rate constants in methanol are 3—5 times greater than those in acetonitrile. In this they differ from the results of Suhr[4] who reported that the reaction of 4-fluoronitrobenzene with piperidine was 16 times faster in acetonitrile than in methanol. In all cases the enthalpies of activation are either approximately the same or greater in acetonitrile than in methanol. This differs from S_N2-type Menschutkin reactions where there is a decrease in the enthalpy of activation in moving from a polar protic solvent to a dipolar aprotic one.[5]

Monosubstitution at the *meta*-position has a powerful deactivating effect, reducing the rate constants by between 50 and 300 times depending on the substituent and the solvent. The variation within the three groups though is fairly small, the rate constant ratios for 3-CF_3 : 3-SO_2Me : 3-NO_2 being 1 : 0·49 : 0·21 in acetonitrile and 1 : 0·45 : 0·15 in methanol. These results confirm the $-I$ sequence $NO_2 > SO_2Me > CF_3$ established from the rates of methoxydefluorination of 3-substituted fluorobenzenes by Hirst and Una,[1] but surprisingly in acetonitrile the rate constant sequence is governed entirely by the entropy of activation and in methanol the CF_3–SO_2Me sequence is determined by the entropy, while the position of the nitro-group is determined almost equally by the entropy and enthalpy of activation. Although surprising, these results parallel those for methoxydefluorination where the rate constant sequence for the three substituents is determined by the entropy of activation. In the 3,5-disubstituted aniline series, although the same rate constant sequence is observed, it is determined by the enthalpies of activation.

Comparison of the present results with those obtained[1] for methoxydefluorination of 3- and 4-substituted fluorobenzenes shows that the effect of moving a substituent from the 3- to the 4-position is less in the nucleophile than in the substrate. In methoxydefluorinations the *para* : *meta*-ratios are 2·3 × 10^3, 95, and 12 for nitro, methylsulphonyl, and trifluoromethyl groups. The present results show that moving these groups from the

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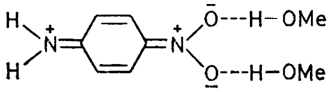
[3] J. F. Bunnett and R. H. Garst, *J. Amer. Chem. Soc.*, 1965, **87**, 3875.

[4] H. Suhr, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 893.

[5] P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg, *J. Org. Chem.*, 1971, **36**, 1792.

3- to the 4-position in aniline results in rate reduction factors of 18·4, 8·0, and 2·7 in acetonitrile and 24·5, 11·9, and 2·8 in methanol. These figures are explicable in terms of the transition state of aromatic substitutions, at least for the nitro and methylsulphonyl substituents. When these groups are present in the *para*-position of the substrate, in going from the initial state to the approximately quinoidal transition state, their full conjugative effect (mesomeric and electromeric) will come into operation. When they are present in the *para*-position of aniline, then in going from the initial to the transition state, only the mesomeric interaction between the amino-group and the substituent is destroyed and the electromeric effect of the substituents is never brought into operation.

There has been considerable controversy whether the substituent effect of the trifluoromethyl group contains a hyperconjugative component.[6] Hirst and Una,[1] basing their arguments on the ratios of the relative free energies of activation from the *meta*- and *para*-positions ($\delta\Delta G_p^*/\delta\Delta G_m^*$), claim to have found evidence for a hyperconjugative effect in the reaction of 4-trifluoromethylfluorobenzene with methoxide ion. In the methoxydefluorinations, the $\delta\Delta G_p^*/\delta\Delta G_m^*$ values for the nitro and trifluoromethyl groups are 1·84 and 1·41. For the substituted anilines the values for the nitro-group are 1·49 (acetonitrile) and 1·56 (methanol) and for the trifluoromethyl group 1·22 (acetonitrile) and 1·27 (methanol). If the greater value of the ratio for the nitro-group in methoxydefluorination is substantially due to an electromeric effect of the *para*-nitro group, then the exaltation observed for the trifluoromethyl group in this reaction indicates a $-E$ component in the activation by a *p*-trifluoromethyl group. The question remains however whether hyperconjugation is part of the trifluoromethyl group's substituent effect in the ground state. Recently Grynkiewicz and Ridd [7] obtained values of 1·31 and 1·07 for the $\delta\Delta G_p^*/\delta\Delta G_m^*$ ratios for the nitration of benzotrifluoride and benzotrichloride. On the basis of these figures they concluded that hyperconjugative electron withdrawal takes place in the benzotrifluoride leading to deactivation of the *para*-position to electrophilic attack. The figures we have obtained for this ratio (1·27, methanol; 1·22, acetonitrile) are similar to those obtained by Ridd for benzotrifluoride, and also to the value of 1·27 for the σ_p/σ_m ratio obtained by Sheppard [8] for the dissociation of 3- and 4-trifluoromethyl-substituted anilinium ions. Thus we conclude that the present results support the concept of hyperconjugative electron withdrawal by a *para*-trifluoromethyl group in the ground state. For all three groups investigated, the $\delta\Delta G_p^*/\delta\Delta G_m^*$ ratios are significantly larger in methanol than in acetonitrile. This is explicable if for the *para*-isomers the charge-separated forms of the mesomeric species are more stabilised by solvation in methanol than in acetonitrile [structure (I)]. A similar phenomenon has been observed and a similar explanation given, for the solvent variation of σ constants and ^{19}F-substituent n.m.r. shifts of substituents which produce charged forms by mesomeric interaction.[9]


(I)

For the *meta*-substituted anilines, plots of log k_2^{25} against the sum of Wepster's [10] σ^n constants* gave straight lines with ρ —3·46 (*r* 0·981; s.d. 0·37; seven points) in acetonitrile and ρ —3·50 (*r* 0·993; s.d. 0·22; six points) in methanol. These values are in agreement with Chapman's hypothesis [12] that ρ values between —3·1 and —3·5 are characteristic of displacement of chloride from an aromatic carbon atom by aromatic amines and that variations in the nature of the chloro-compounds are of secondary importance. They disprove, as was suggested [13] earlier, on the basis of more limited data, his suggestion that the high value of ρ —4·79 found by Litvinenko *et al.*[14] for the reactions of substituted anilines with picryl chloride in benzene at 25° is due to the peculiar nature of the substrate. The ρ values are similar to the value of 3·186 given by Wepster [10] for the ionization of substituted anilinium ions in 30% aqueous ethanol at 25°. The similarity is explicable if the transition state for the reactions of picryl chloride with substituted anilines approximates to that of the Meisenheimer complex-type intermediate formed in these reactions, and the conjugation of the amino-group with the benzene ring is destroyed, as in the formation of anilinium ions. Similar deductions concerning the transition state of aromatic nucleophile substitutions when phenoxide ions are the nucleophile have been made by Norman.[15]

The present results, together with those of Hirst and Una [1] enable a direct comparison to be made between the effects of the same *meta*-substituents in the substrate and the nucleophile. From the results quoted in their paper, a plot of log k_2 at 100° against $\Sigma\sigma^n$ gives a slope of 5·25 (*r* 0·998; s.d. 0·12). As the value of ρ increases with decrease of temperature, the value will be higher at 25°, showing that nucleophilic aromatic substitutions are much more sensitive to substitution in the substrate than in the nucleophile. Similar results, limited to the

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* The corrected value of 0·49 obtained by Sheppard [11] from the dissociation constants of substituted anilinium ions was used for the 3-CF_3 group.

[6] D. Holtz, *Chem. Rev.*, 1971, **71**, 139.

[7] G. Grynkiewicz and J. H. Ridd, *J. Chem. Soc.* (*B*), 1971, 716.

[8] W. A. Sheppard, *J. Amer. Chem. Soc.*, 1965, **87**, 2410.

[9] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davies, *J. Amer. Chem. Soc.*, 1963, **85**, 3146.

[10] B. M. Wepster, P. E. Verkade, and H. van Bekkum, *Rec. Trav. chim.*, 1959, **78**, 815.

[11] W. A. Sheppard, *J. Amer. Chem. Soc.*, 1962, **84**, 3072.

[12] N. B. Chapman, D. K. Chaudbury, and J. Shorter, *J. Chem. Soc.*, 1962, 1975.

[13] C. W. L. Bevan, J. Hirst, and W. O. Uwamu, *Nigerian J. Sci.*, 1968, **2**, 151.

[14] L. M. Litvinenko, I. G. Syroratka, T. S. Skoropisova, and S. V. Ostrovskaya, *Ukrain. khim. Zhur.*, 1959, **25**, 189.

[15] J. R. Knowles, R. O. C. Norman, and J. H. Prosser, *Proc. Chem. Soc.*, 1961, 341.

substituent effects of the nitro-group, have been obtained by Miller *et al.*[16] from the reactions of 1-chloro-2,4-dinitrobenzene and of picryl chloride with nitro-substituted phenols. These authors point out that the lower sensitivity to substitution in the nucleophile is to be expected since the substituent effects are relayed to an atom external to, although directly attached to, the benzene ring, whereas in substitution in the substrate they are relayed to one of the ring atoms. In the case of *meta*-substitution in the substrate and in aniline, there is an additional reason. If the transition state is close to the Meisenheimer complex-type intermediate then in this transition state the *ortho*- and *para*-carbon atoms of the substrate will have to accommodate considerably more charge than is conferred on the *ortho*- and *para*-carbon atoms by the ground-state mesomeric interaction of an amino-group with the benzene ring. Consequently there will be greater sensitivity in the substrate than in the nucleophile to changes in the charge density on these atoms produced by *meta*-substituents.

The results for the 4-nitro and 4-methylsulphonyl groups cannot be accommodated on the Hammett plot for *meta*-substituents either by the use of σ or σ^- constants. If the value of 0·62 obtained by Sheppard[11] for the σ^- constant of a 4-trifluoromethyl group from the dissociation of anilinium ions is used, then the result for this group does fall on the line defined by the *meta*-substituents. Originally a value of 0·74 was given for the σ^- constant of a 4-trifluoromethyl group by Roberts,[17] but this was subsequently corrected by Sheppard.[11] Hirst and Una[1] have however pointed out that for Hammett-type correlations in nucleophilic aromatic substitution, a 4-trifluoromethyl group when present in the substrate always required a σ^- value of 0·74 and used this as evidence in support of a hyperelectromeric element in the activating power of this group. When σ^- plots are made for the results for 4-nitro-, 4-methylsulphonyl-, and 4-trifluoromethyl-anilines and aniline, better correlations are obtained with 0·74 than with 0·62 as the value for the 4-trifluoromethyl group. The relevant figures are: for σ^- 0·74, ρ −3·01 [*r* 1·000; s.d. 0·04 (methanol)] and ρ −2·99 [*r* 0·999; s.d. 0·11 (acetonitrile)]; and for σ^- 0·62, ρ −2·98 [*r* 0·997; s.d. 0·15 (methanol)] and ρ −2·94 [*r* 0·989, s.d. 0·30 (acetonitrile)]. Hence the requirement of a σ^- value of 0·74 for a 4-trifluoromethyl group when present in the substrate cannot be taken as evidence of a hyperelectromeric effect.

As both the dissociation of anilinium ions and the reactions of picryl chloride with substituted anilines give Hammett plots, the latter reaction must also give Brönsted-like plots of the form $\log k_2^{25} = \alpha \log K_a +$ constant. When such plots are constructed, straight lines are obtained with the following characteristics for *meta*-substituted anilines: (a) slope 1·08; *r* 0·992; s.d. 0·26 (methanol, 5 points); and (b) slope 1·17; *r* 0·987; s.d. 0·35 (acetonitrile, 5 points). The points for 3,5-bistrifluoromethyl- and 3,5-bismethylsulphonyl-anilines could not be included as their dissociation constants in aqueous media are not known. For *para*-substituted anilines the results are: (a) slope, 1·03; *r* 0·995; s.d. 0·21 (methanol, 4 points); and (b) slope 1·02; *r* 0·995; s.d. 0·21 (acetonitrile, 4 points).

The dissociation constants used[18] were those for the anilinium ions in water, as a complete set of data for the dissociation constants in either acetonitrile or methanol were not available. The correlations are surprisingly good considering that Grunwald and Cesku[19] have shown that substituent effects on the base strength of aniline in water are qualitatively different from those in methanol and ethanol. Recently Biggi and Pietra[20] have obtained an α value of 0·63 for the reactions of primary n-alkylamines with 1-chloro-2,4-dinitrobenzene in 3 : 2 dioxan–water, the values of pK_a used in their correlation being determined in the same solvent mixture. The larger values of α reported here cannot be due to the different substrates used, as Bevan *et al.*,[13] in a survey of nucleophilic aromatic substitutions for which data for extended Brönsted plots were available, reported the reactions of seven different chlorides (including 1-chloro-2,4-dinitrobenzene) with substituted anilines giving α values >1. Again the correlations were done using pK_a values determined in water. It is unlikely that the large difference in magnitude is due solely to the fact that the correlations with substituted anilines were done using dissociation constants measured in water and not as should be the case, in the same solvent as for the rate measurements, as the values of α in methanol and acetonitrile, two widely different solvents, are very similar. The reason for the difference probably lies in the difference in the type of amine used, and it is significant that Biggi and Pietra observed that the point for aniline gave a positive deviation from their Brönsted-like plot.

The above linear free energy correlations indicate that the effect of *meta*-substituents is at least roughly additive. We wished to test this hypothesis more precisely, and while several methods[21] are available, they are applicable to the comparison of quantities that have been measured directly at the same temperature. The assumption of additivity of the free energies of activation leads to the expression $k_{XY} = k_X k_Y / k_H$, where k_H, k_X, k_Y, and k_{XY} are the rate constants for the unsubstituted, mono-, and di-substituted derivatives. Because of the large difference in reactivity, the rate constants for the four nucleophiles cannot be measured at the same temperature, so the procedure adopted is to calculate the rates at a common temperature by means of the Arrhenius equation. Errors in the Arrhenius parameters will lead to errors in the calculated value of k_{XY}, and the

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[16] G. D. Leahy, M. Liveris, J. Miller, and A. J. Parker, *Austral. J. Chem.*, 1956, **9**, 382.

[17] J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Amer. Chem. Soc.*, 1950, **72**, 408.

[18] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

[19] E. Grunwald and G. W. Ceska, *J. Amer. Chem. Soc.*, 1967, **89**, 1377.

[20] G. Biggi and F. Pietra, *J. Chem. Soc.* (*B*), 1971, **44**.

[21] P. D. Bolton, F. M. Hall, and J. Kudrynski, *Austral. J. Chem.*, 1968, **21**, 1541.

problem arises within what limits should agreement be expected between the measured and calculated values of k_{XY}. The procedure we have adopted is to calculate the value of k_{XY} and its statistical error at 25° assuming the additivity of the free energies of activation and to compare this with the value of k_{XY} and its statistical error calculated at 25° from the Arrhenius parameters of the reaction of the 3-X-5-Y-substituted aniline with picryl chloride. If there is agreeement between the two values within the limits imposed by the magnitudes of the statistical errors, the substituent effects are taken to be additive. In these calculations the biggest source of error was in the activation energies of aniline in the two solvents, and to eliminate this rate constants for the reaction of aniline with picryl chloride in methanol and acetonitrile were measured directly at 25°. Table 3 gives the results obtained from the measurements reported by us and in all cases in acetonitrile there is overlap between the statistical range of values of k_{XY} calculated on the assumption of additivity and the range obtained by calculation of k_{XY} from the Arrhenius parameters of the 3,5-substituted aniline. The figures for the trifluoromethyl group in methanol indicate non-additivity of the substituent effect. We reserve comment on this, particularly as the reaction of 3,5-bistrifluoromethylaniline with picryl chloride in methanol was the only one for which straightforward kinetics were not obtained.

TABLE 3

A comparison of the rate constants (k/l mol^{-1} s^{-1}) for the reactions of 3,5-disubstituted anilines with picryl chloride calculated (a) on the assumption of additivity of the free energies of activation [k_{XY}(calc.)] and (b) from the measured Arrhenius parameters for the reaction [k_{XY}(M)]

	Acetonitrile			Methanol
Substituent	CF_3	SO_2Me	NO_2	CF_3
10^6k_{XY} (calc.)	32 ± 2	$7{\cdot}9 \pm 2{\cdot}5$	$1{\cdot}4 \pm 0{\cdot}2$	310 ± 50
10^6k_{XY}(M)	26 ± 6	$12 \pm 2{\cdot}5$	$1{\cdot}0 \pm 0{\cdot}3$	150 ± 50

EXPERIMENTAL

Materials.—The preparation and/or purification of picryl chloride, aniline, 3-nitro-, 4-nitro-, and 3,5-dinitro-aniline [13] and 4-methylsulphonylaniline [1] have already been described. 3-Trifluoromethylaniline, b.p. 91° at 24 mmHg, 4-trifluoromethylaniline, b.p. 91·5° at 20 mmHg, and 3,5-bistrifluoromethylaniline, b.p. 89·5° at 22 mmHg, were commercial samples purified by fractional distillation. The purity was confirmed by g.l.c. 3,5-Bismethylsulphonylaniline, prepared by the method of Wepster *et al.*,[22] was purified by conversion into the hydrochloride, regenerated with caustic soda, and recrystallised from glacial acetic acid, m.p. 205° (lit.,[22] 207·5°).

3-*Methylsulphonylaniline*.—Methyl 3-nitrophenyl sulphone, m.p. 145° (lit.,[23] 146°), was prepared by the method of Twist and Smiles.[23] Reduction with tin and hydrochloric acid gave the amine, which was recrystallised from benzene, m.p. 72—73° (lit.,[22] 59·5°). In view of the discrepancy in m.p. the structure was confirmed by n.m.r. and elemental analysis (Found: C, 49·5; H, 5·4; N, 7·9; S, 18·5. Calc. for $C_7H_9NO_2S$: C, 49·1; H, 5·3; N, 8·2; S, 18·7%).

Product Analyses of the Reactions in Methanol.—Known volumes of the run mixtures were allowed to react to completion. As the products of the reactions of picryl chloride with 3-nitro- and 3- and 4-methylsulphonyl-aniline are insoluble in methanol, the completed reaction mixture was stored in a refrigerator overnight and then filtered through a weighed sintered glass crucible. The solid was washed thoroughly with cold aqueous methanol, dried under vacuum, and weighed. The solutions obtained from the reactions of 3-trifluoromethyl-, 4-trifluoromethyl-, and 3,5-bistrifluoromethyl-aniline were evaporated to half their original volume and an excess of 2N-HCl added. The precipitated products were filtered off, well washed with water, dried, weighed, and their m.p.s determined. Each product was then recrystallised successively from glacial acetic acid and toluene and the m.p. redetermined. The products obtained were: 2,3′,4,6-tetranitrodiphenylamine (99·3%), m.p. 213° (lit.,[24] 213°); 2,4,6-*trinitro*-3′-*trifluoromethyldiphenylamine* (99%), m.p. 152·5° (Found: C, 42·0; H, 2·0; F, 15·2; N, 15·0. $C_{13}H_7F_3N_4O_6$ requires C, 41·9; H, 1·9; F, 15·3; N, 15·05%); 2,4,6-*trinitro*-4′-*trifluoromethyldiphenylamine* (99·7%), m.p. 172·5° (Found: C, 42·25; H, 1·8; F, 15·2; N, 15·3%); 2,4,6-*trinitro*-3′,5′-*bistrifluoromethyldiphenylamine* (90%), m.p. 180·5° (Found: C, 38·3; H, 1·5; F, 25·8; N, 12·8. $C_{14}H_6F_6N_4O_6$ requires C, 38·3; H, 1·4; F, 25·9; N, 12·7%); 2,4,6-*trinitro*-3′-*methylsulphonyldiphenylamine* (99%), m.p. 239·5° (Found: C, 41·2; H, 2·7; N, 14·5; S, 8·4. $C_{13}H_{10}N_4O_8S$ requires C, 40·8; H, 2·6; N, 14·65; S, 8·4%); and 2,4,6-*trinitro*-4′-*methylsulphonyldiphenylamine* (98·2%), m.p. 240° (Found: C, 41·3; H, 2·45; N, 14·75; S, 8·3%).

Additional Products required for Spectrophotometric Determinations.—2,4,6-Trinitro-, 2,4,4′,6-tetranitro-, and 2,3′,4,5′,6-pentanitro-diphenylamine were prepared as already reported.[13] 2,4,6-*Trinitro*-3′,5′-*bismethylsulphonyldiphenylamine* was prepared by refluxing 3,5-bismethylsulphonylaniline (2 mol) dissolved in the minimum amount of acetonitrile with picryl chloride (1 mol) in methanol. On cooling the product crystallised out and was filtered off. It was recrystallized from glacial acetic acid and then from toluene, m.p. 281° (Found: C, 36·8; H, 2·5; N, 12·2; S, 14·0. $C_{14}H_{12}N_4O_{10}S_2$ requires C, 36·5; H, 2·6; N, 12·2; S, 13·9%).

Solvents.—The preparation of absolute methanol has already been described.[2] Acetonitrile was repeatedly distilled from fresh batches of phosphorus pentoxide until the phosphorus pentoxide no longer became coloured. It was then distilled from anhydrous potassium carbonate and finally fractionated. The water content was determined before each run by Karl Fischer titration and varied between 0·004 and 0·008%.

Kinetic Measurements.—With the exceptions of the reactions of aniline and 3,5-bistrifluoromethylaniline, all the rates in methanol were measured under second-order conditions with initial concentration of picryl chloride *ca.* 0·03M and those of the amine *ca.* 0·09M. The progress of the reaction was followed by potentiometric titration of the liberated chloride ions with silver nitrate solutions. Details of the techniques used have already been given,[13] the only modification being the use of an automatic titrator for the final titration. All other rates were measured under

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[22] J. Bolssens, J. A. C. Th. Brouwers, J. H. Choufoer, A. Kats, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1954, **73**, 819.

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

[24] F. van Duin and R. van Lennep, *Rec. Trav. chim.*, 1919, **38**, 368.

TABLE 4

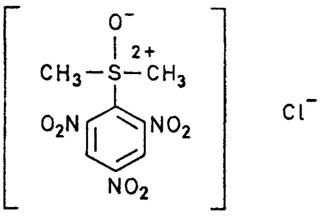
Rate constants * for the reactions of picryl chloride with substituted anilines in methanol and acetonitrile at various temperatures

	Methanol		Acetonitrile	
Substituent	t/°C	10^4k_2 / l mol^{-1} s^{-1}	t/°C	10^4k_2 / mol^{-1} s^{-1}
3-NO_2	31·76	33·9	40·19	13·0
	21·84	19·6	28·9	7·09
	11·57	9·65	19·04	3·58
	−0·72	4·13	9·90	1·92
3-CF_3	9·20	58·6	29·80	34·2
	−0·68	30·6	19·10	17·5
	−9·40	16·6	10·18	9·65
	−20·61	7·02	−0·10	4·62
4-CF_3	29·91	66·5	44·85	31·1
	20·34	38·0	37·00	19·9
	10·20	20·3	29·04	12·3
	−1·04	9·64	20·00	6·80
3-5-$(CF_3)_2$	90·00	44·9	127·3	40·1
	80·20	29·2	120·1	30·4
	70·11	17·9	109·9	20·3
	59·70	10·7	100·6	13·9
3-SO_2Me	29·93	86·8	40·19	33·5
	20·40	51·2	29·80	18·5
	10·15	28·0	19·04	9·31
	−1·80	12·7	9·90	5·00
4-SO_2Me	49·48	24·8	45·30	6·91
	39·40	13·8	37·62	4·16
	29·91	7·73	30·03	2·49
	20·36	4·12	21·00	1·29
3,5$(SO_2Me)_2$			130·30	24·3
			118·75	15·4
			110·75	11·2
			99·75	6·94
H			48·50	5270
			39·70	3770
			31·80	2660
			22·20	1770
4-NO_2			70·10	5·26
			62·80	3·44
			55·39	2·18
			48·90	1·45
3,5-$(NO_2)_2$			139·8	6·44
			129·5	4·23
			120·0	2·77
			110·0	1·74

* All kinetic runs were duplicated, the average values of the two sets of rate constants obtained agreeing to within ±2%.

first-order conditions by the spectrophotometric estimation of the products formed. With the exception of the reaction of aniline, samples were removed from the thermostat at known time intervals, diluted with a solution of 2N-sulphuric acid in methanol, and the optical density measured at the appropriate wavelength. The wavelengths used for the substituted anilines were: 3-NO_2, 355; 4-NO_2, 387; 3,5-$(NO_2)_2$, 350; 3-CF_3, 364; 4-CF_3, 369; 3,5-$(CF_3)_2$, 362; 3-SO_2Me, 364; 4-SO_2Me, 373; and 3,5-$(SO_2Me)_2$, 360 nm. The initial concentrations of picryl chloride and amine were 10^{-2}M and 10^{-1}M. The fast reactions of aniline in methanol and acetonitrile at 25° were measured at 369 nm by use of a Gilford recording spectrophotometer, with initial picryl chloride concentrations of 5×10^{-5}M. The results at various temperatures are given in Table 4.

Reaction of Picryl Chloride with Dimethyl Sulphoxide.—When picryl chloride is added to dimethyl sulphoxide, there is the immediate formation of a bright yellow colour. The intensity of the colour diminishes with time, and concurrent with this a white precipitate is formed. The white precipitate, which contains ionic chlorine, is insoluble in most organic compounds, while the yellow material is soluble in acetone. By analogy with the results of Smith and Winstein [25] we assumed the white material to be the sulphendiylium chloride (II) and the yellow material to be its oxygen-bonded isomer, but we have not been able to confirm this by elemental analysis.



(II)

[3/1210 *Received*, 11*th June*, 1973]

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[25] S. G. Smith and S. Winstein, *Tetrahedron*, 1958, **3**, 717.