678. *The Kinetics of the Reduction by Titanous Chloride of Nitrobenzene and its Substitution Products.*

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The reduction of nitrobenzene by titanous chloride in aqueous alcohol is of the first order with respect to each of these reactants and, over a certain range, inversely proportional (approximately) to the square of the hydrogen-ion concentration. The active species are thought to be $Ph\cdot NO_2H^+$ and a hydrolysed form of titanous ion. In the sequence $Ph\cdot NO_2(1) \longrightarrow Ph\cdot NO(2) \longrightarrow Ph\cdot NH\cdot OH(3) \longrightarrow Ph\cdot NH_2$, (2) and (3) are reduced many times more rapidly than (1), but condensation leads to a very rapid formation of azoxybenzene which, although it yields aniline quantitatively, is reduced much more slowly. The diversion of a considerable part of the reaction by way of the azoxy-compound leads to a fall in bimolecular constants, but the rate of titanous ion consumption at each stage can be quantitatively accounted for in terms of the reaction scheme given.

Substituents in the benzene nucleus have the effect expected from their electronic character if the rate-determining step is a transfer of electrons from titanous complex to nitro-compound.

In the majority of examples the joint effect of two substituents on the free energy of activation is calculable additively from their individual actions. Deviations are attributable to a saturation effect with two powerfully acting groups, or to chelate interactions.

The entropy of activation is not constant for the whole series of reactions but tends to rise with the activation energy.

The present study will deal first with the kinetics of the reduction of nitrobenzene by titanous chloride in aqueous alcohol, and secondly with the influence of other substituents in the benzene nucleus on the reaction.

Course of the Reaction.—According to the scheme put forward by Haber (*Z. phys. Chem.*, 1900, **32**, 193) the reduction of nitrobenzene goes through the stages

$$Ph\cdot NO_2 \longrightarrow Ph\cdot NO \longrightarrow Ph\cdot NH\cdot OH \longrightarrow Ph\cdot NH_2$$

and in appropriate conditions Ph·NO and Ph·NH·OH interact to give Ph·NO⁚NPh. The azoxybenzene is itself reduced to aniline by titanous chloride but more slowly than nitrobenzene.

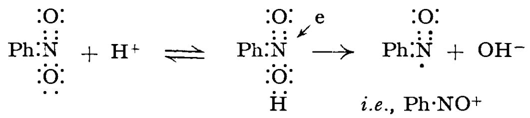
Under the conditions employed (concentration of Ti^{3+} 0·006—0·024N, $Ph\cdot NO_2$ 0·001—0·004M, hydrion 0·24—1·28N) the reduction of nitrosobenzene or of phenylhydroxylamine is very many times more rapid than that of nitrobenzene, and the interaction of these two compounds to give azoxybenzene is also extremely fast. On the other hand, the rate of reduction of azoxybenzene is only about one seventh as fast as that of nitrobenzene at the same molar concentration.

The rate of consumption of titanous chloride is proportional initially to the concentration of the nitrobenzene and to that of the titanous salt. The consumption of titanous salt does not yield a steady bimolecular constant but one which falls markedly with time. The total reducing agent used up is, however, that theoretically required for the formation of aniline. The facts are accounted for if small concentrations of nitrosobenzene and of phenylhydroxylamine are built up and if interaction of the latter with the former competes with its reduction to aniline, the azoxy-compound formed being itself reduced to aniline but much more slowly.

Reacting Species.—The rate of reaction over the experimental range proves to be proportional to [titanous salt][nitrobenzene]/$[H^+]^2$. The predominant species from nitrobenzene may be assumed to be $Ph\cdot NO_2$ itself, but the reactant might be $Ph\cdot NO_2H^+$. If it were, the concentration, X, of the active species from the titanous salt would be inversely proportional to the cube of $[H^+]$. If the reactant is $Ph\cdot NO_2$ then X is proportional to $1/[H^+]^2$.

The rate-determining step in the reduction is the conversion of nitrobenzene into nitrosobenzene, which demands the transfer of two electrons. This reaction itself is almost certain to occur in two steps, only one of which is rate-determining. The simplest process, in view of the known basic character of nitrobenzene, involves the primary addition of a hydrion, according to the following scheme :

(1)



$$\mathrm{Ph{:}NO_2 + H^+ \rightleftharpoons Ph{:}NO_2H^+ \xrightarrow{e} Ph{:}NO + OH^-}$$

i.e., $\mathrm{Ph{\cdot}NO^+}$

(2) $\mathrm{Ph{\cdot}NO^+ + e \longrightarrow Ph{\cdot}NO}$ (rapid)

In this the rate-determining step would be the communication of the electron from the titanous species to the $\mathrm{Ph{\cdot}NO_2H^+}$.

On this basis the nitrobenzene is positively charged, and will react best with a titanous species not bearing a positive charge itself. If the equilibrium $\mathrm{Ti^{3+} + 3OH^- \rightleftharpoons Ti(OH)_3}$ is assumed, the concentration of the hydroxide, or of the TiO(OH) derived from it, would be inversely proportional to the cube of the hydrion concentration. The TiO(OH) would lose an electron in reduction to give $\mathrm{TiO(OH)^+}$, the titanic form. But it may not be permissible to assume, as is here tacitly done, that $\mathrm{Ti^{3+}}$ is the predominant species in solution, so that the conclusion must be regarded with reserve. In any case simple variants of the above scheme are conceivable. What is clear, however, seems to be that the major reducing species is a hydrolysed form of the titanous salt, present in acid solution only as a minor constituent.

Experimental Method.—The solvent consisted of a mixture of equal volumes of ethyl alcohol and water (42·5% of alcohol by weight). The nitro-compound was dissolved in absolute alcohol and the titanous salt in aqueous hydrochloric acid, the concentrations being such that mixing of the appropriate amounts led to the required initial concentrations of reactants (corrections for the contraction on mixture being made). The reaction was followed by determination of residual titanous ion. Samples were pipetted into standard ferric alum, the excess of which was titrated with titanous chloride solution, stored in an atmosphere of hydrogen. Reaction vessels and titration flasks were kept filled with carbon dioxide from a cylinder, and solutions were de-aerated before use. Pipettes were flushed out with carbon dioxide before use.

The hydrion concentration of the titanous solutions was determined electrometrically, acid–alkali titration indicators being useless.

Influence of Initial Concentrations.—Proportionality of initial rate to titanous salt concentration is shown in Table 1, to nitrobenzene concentration in Table 2, and (approximately) to $1/[\mathrm{H^+}]^2$ in Table 3. The rate plotted against the reciprocal of [acid]^2 gives a straight line, but with a small intercept on the rate axis which is allowed for in the third column of Table 3.

TABLE 1.

$[\mathrm{Ph{\cdot}NO_2}] = 0{\cdot}004\text{M}$, $[\mathrm{H^+}] = 0{\cdot}48\text{N}$.

$[\mathrm{TiCl_3}]$, N	0·024	0·018	0·012	0·006
Rate	6·4	4·6	3·0	1·4
$10^{-2} \times \text{Rate}/[\mathrm{TiCl_3}]$	2·67	2·56	2·50	2·33

Note. Rates are in arbitrary units (*i.e.*, titres of test portions). For absolute values see Tables of *k* values.

TABLE 2.

$[\mathrm{TiCl_3}] = 0{\cdot}024\text{N}$, $[\mathrm{H^+}] = 0{\cdot}48\text{N}$.

$[\mathrm{Ph{\cdot}NO_2}]$, M	0·004	0·003	0·002	0·001
Rate	6·4	4·8	3·2	1·5
$10^{-3} \times \text{Rate}/[\mathrm{Ph{\cdot}NO_2}]$	1·60	1·60	1·60	1·50

Additions of titanic salts or of aniline had no effect on the rate, so that the fall in the bimolecular constant is not due to retardation by products. Thus : Ti^{3+} 0·012N, $Ph{\cdot}NO_2$ 0·002M, rate = 1·50 units; with addition of 0·012N-Ti^{4+}, rate = 1·48; with addition of 0·002M-$Ph{\cdot}NH_2$, rate = 1·55 units. Addition of large amounts of sodium chloride showed that the effect of changed hydrogen chloride concentration was mainly due to variation of hydrion rather than of chlorine-ion concentration, but revealed also a rather complex general salt effect which was not investigated further. The glass surface of containing vessels was without influence.

TABLE 3.

$[TiCl_3]$ = 0·012M. $[Ph{\cdot}NO_2]$ = 0·002M.

Acid, N	0·24	0·337	0·48	1·28
Rate	5·2	2·8	1·5	0·45
10 (Rate – 0·27) [Acid] ^{2}	2·84	2·87	2·82	2·95

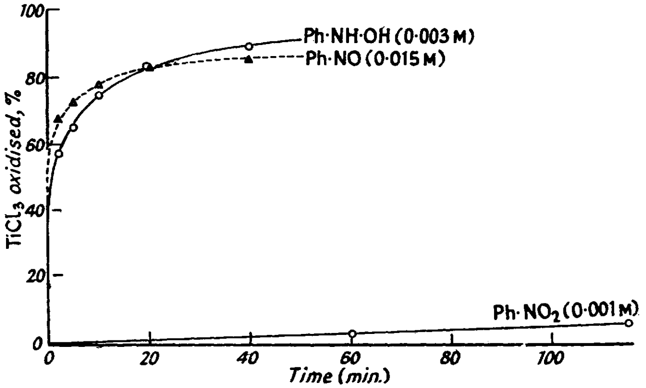


FIG. 1.
$TiCl_3$ 0·006N.
Acid 1·0N.
At 18°.

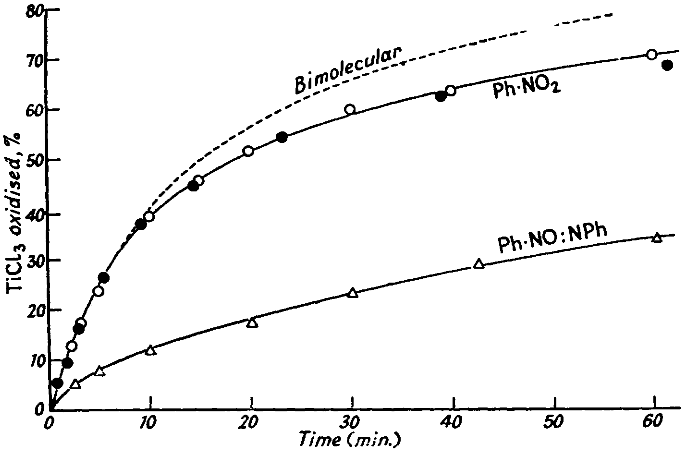


FIG. 2.
25°; $Ph{\cdot}NO_2$ 0·004M, $Ph{\cdot}NO{:}NPh$ 0·004M, Ti^{3+} 0·024N, *acid* 0·48N.

Second-order Velocity Constants.—These are not steady but drop as the reaction proceeds. The drop in the velocity constants can be inferred immediately from Fig. 2, and is also shown in Table 4.

TABLE 4.

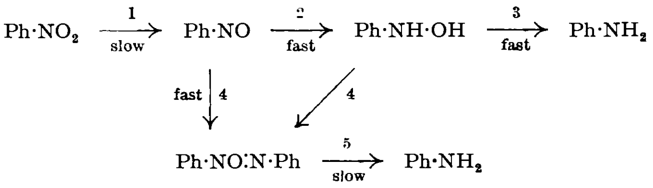
Time (min.)	1·75	4·05	7·00	11·4	20·0	34·0
$TiCl_3$ oxidised, %	10	20	30	40	50	60
k (bimol.)	2·65	2·57	2·55	2·40	2·08	1·84

End-points.—With sufficient titanous chloride for complete reduction the reaction reaches the theoretical end-point.

Reaction Rates of Intermediate Reduction Steps.—Nitrosobenzene and phenylhydroxylamine are reduced very many times more rapidly than nitrobenzene, as shown in Fig. 1. (Titanous salt concentration 0·006N, and hydrion 1·0N in each case. Nitrobenzene 0·001M nitrosobenzene 0·0015M, phenylhydroxylamine 0·003M.) Azoxybenzene is reduced much more slowly than nitrobenzene (Fig. 2).

The rapid interaction of nitrosobenzene and phenylhydroxylamine under the reaction conditions was shown by the following experiment. Equivalent quantities (0·004M) were mixed and allowed to stand for a few minutes in a solution of the same pH as the normal reaction mixture. Titanous salt equivalent to the total was then added and the reaction followed in the normal way. A considerable part of the rapidly reducible material was found to have disappeared during the interaction of the two compounds and to have been replaced by a compound which was much more slowly reduced. This was presumably the azoxy-compound.

Form of Reaction–Time Curves.—Nitrosobenzene and phenylhydroxylamine are both reduced with very great speed. Their interaction is also very fast so that it is difficult to predict what proportion of the reaction will take place by way of the azoxy-compound in the system



$$\begin{tikzcd}
\mathrm{Ph{\cdot}NO_2} \arrow[r, "1", "\text{slow}"'] & \mathrm{Ph{\cdot}NO} \arrow[r, "2", "\text{fast}"'] \arrow[d, "4", "\text{fast}"'] & \mathrm{Ph{\cdot}NH{\cdot}OH} \arrow[r, "3", "\text{fast}"'] \arrow[dl, "4"] & \mathrm{Ph{\cdot}NH_2} \\
 & \mathrm{Ph{\cdot}NO{:}N{\cdot}Ph} \arrow[r, "5", "\text{slow}"'] & \mathrm{Ph{\cdot}NH_2} &
\end{tikzcd}$$

Certain empirical trials were therefore made. Values were assumed for the appropriate velocity constants and the reaction–time curves were calculated by arithmetical computation for successive small time intervals (the integration of the differential equation being intractable). The results appeared to show that practically all the reduction followed the course 1, 2, 4, 5. The evidence is given in Fig. 2. Here the rate of reduction of azoxybenzene is shown to be 3·6 times as slow, in terms of titanous ion consumed, as that of an equimolar solution of nitrobenzene. If 1 g.-mol. of nitrobenzene gives azoxybenzene it uses up only one half as much of the reducing agent as 1 g.-mol. of the azoxy-compound giving aniline. Thus in a test of the assumption that azoxybenzene is an intermediate stage for practically all the nitrobenzene it must be assumed that k for process 1 is $2 \times 3{\cdot}6 = 7{\cdot}2$ times as great as k for process 5. The assumed reaction scheme now simplifies to

$$\mathrm{Ph{\cdot}NO_2} \xrightarrow{k_1} \mathrm{Ph{\cdot}NO{:}N{\cdot}Ph} \xrightarrow{k_1/7{\cdot}2} \mathrm{Ph{\cdot}NH_2}$$

k_1 is chosen to give the correct initial slope for the reaction–time curve of nitrobenzene. Computation then gives the points shown by full circles in Fig. 2, the open circles showing the experimental values. The dotted line shows the bimolecular curve. The assumption that azoxybenzene is a major intermediate appears to be justified. The result is a little surprising since although nitrosobenzene and phenylhydroxylamine interact rapidly, the direct reduction of the latter to aniline is also very rapid. What is possible, however, is that the labile odd-electron intermediate which is presumably formed transitorily between nitrosobenzene and phenylhydroxylamine may interact with nitrobenzene even more readily than these compounds react with one another, and give a binuclear substance easily reducible to the azoxy-compound. This matter seems worthy of further investigation.

For the present purpose, however, the important question is to establish the correct basis for the comparison of the various substituted compounds. According to the ratio in which the routes 1, 2, 3 and 1, 2, 4, 5 are followed as the result of the first rate-determining step, the titanous equivalent of the nitro-compound will vary, and this ratio might be different for the different derivatives studied.

Reaction–time curves for 15 compounds varying widely in reactivity were therefore plotted with the time-scales adjusted to give coincidence at one standard value of the ordinate. As shown in Figs. 3 and 4, all the curves then become nearly superposable. From this may be inferred that the ratio does not vary appreciably from one compound to another. [This conclusion is consistent with the result of Brandt and Mahr (*J. pr. Chem.*, 1931, **131**, 118; 1935, **142**, 161), who found the influence of substituents on the rate of interaction of nitroso-compounds and phenylhydroxylamines to be similar to that found in the present work on the rate of reduction of the nitro-compound.]

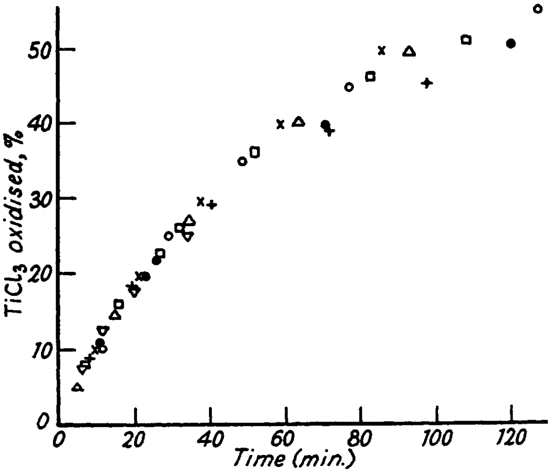


FIG. 3.

Nitrobenzene (30°) × 1·0, o-*nitrophenol* (16°) × 4·3, m-*nitrophenol* (30°) × 0·98, p-*nitrophenol* (25°) × 0·129, o-*nitrotoluene* (35°) × 0·217, m-*nitrotoluene* (25°) × 0·44, p-*nitrotoluene* (35°) × 0·827.

The initial rate of reduction expressed in terms of titanous ion consumption can therefore validly be used for comparison of the various nitro-compounds, independently of the (provisional) conclusion that the rate-determining step corresponds stoicheiometrically to the change nitro-compound ⟶ azoxy-compound.

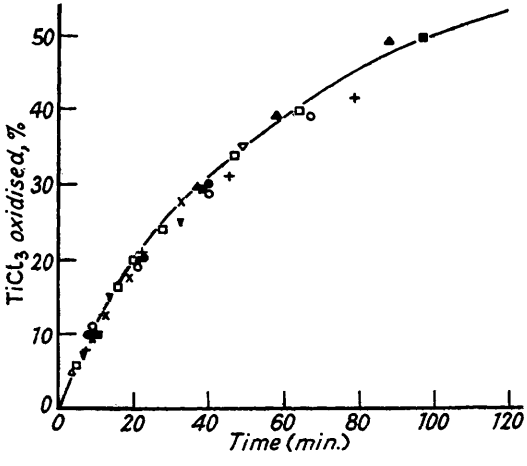


FIG. 4.

o-*Chloronitrobenzene* (20°) × 0·249, p-*chloronitrobenzene* (20°) × 0·933, m-*chloronitrobenzene* (15°) × 0·95, o-*nitroaniline* (25°) × 0·457, m-*nitroaniline* (5°) × 0·385, p-*nitroaniline* (25°) × 1·10, m-*dinitrobenzene* (15°) × 4·4, p-*dinitrobenzene* (15°) × 9·8.

Activation Energies.—These were calculated either directly from the initial rates at a series of temperatures (usually four) or indirectly as follows. Times required for given percentages of reaction at different temperatures were read off from curves and their logarithms were plotted against $1/T$. They gave good linear plots and the values of E were calculated by the method of least squares. A series of activation energies showing a small systematic trend were thus obtained and extrapolation to zero reaction then gave the value corresponding to the initial rate (cf. Table 5). Where both were used the two procedures yielded concordant results.

TABLE 5. *Typical variations of* E *with* % *of reaction.*

Nitrobenzene		*m*-Nitrophenol		*p*-Chloronitrobenzene		*o*-Nitroaniline	
Reaction, %	*E*	Reaction, %	*E*	Reaction, %	*E*	Reaction, %	*E*
10	18,100	10	16,600	10	18,600	10	17,300
20	18,700	20	18,500	20	19,700	20	17,700
30	19,800	30	19,500	30	20,500	30	18,700
40	21,200	40	19,800	40	20,800	Extrapolated	17,000
50	23,400	50	19,900	Extrapolated	17,300		
Extrapolated	17,500	Extrapolated	17,000				

TABLE 6. *Reduction of substituted nitrobenzenes by titanous chloride.*

Substituent	$k_{20°}$, l. g.-mol.$^{-1}$ sec.$^{-1}$	(ΔF^*) (cal.)	Change in (ΔF^*) due to substituent (cal.)	Measured *E*, cal./g.-mol.
(H)	$6·78 \times 10^{-2}$	1567	—	17,700
o-OH	1·119	−103	−1670	16,500
m-OH	$6·93 \times 10^{-2}$	1554	− 13	17,000
p-OH	$1·58 \times 10^{-2}$	2415	+ 848	19,500
o-CH_3	$7·43 \times 10^{-3}$	2854	+1287	25,000
m-CH_3	$8·4 \times 10^{-2}$	1443	− 124	17,500
p-CH_3	$3·87 \times 10^{-2}$	1893	+ 326	20,000
o-Cl	$7·43 \times 10^{-2}$	1514	− 53	18,500
m-Cl	$5·08 \times 10^{-1}$	536	−1031	16,500
p-Cl	$2·42 \times 10^{-1}$	826	− 741	17,300
o-NH_2	$1·00 \times 10^{-1}$	1341	− 226	17,000
m-NH_2	$3·72 \times 10^{-1}$	577	− 990	16,900
p-NH_2	$1·58 \times 10^{-1}$	1074	− 493	16,500
o-NO_2	$5·97 \times 10^{-1}$	300	−1267	17,600
m-NO_2	$7·75 \times 10^{-1}$	149	−1418	18,200
p-NO_2	1·171	−312	−1879	15,500
o-OCH_3	$1·1 \times 10^{-2}$	2622	+1055	21,600
m-OCH_3	$7·81 \times 10^{-2}$	1482	− 85	17,800
p-OCH_3	$1·4 \times 10^{-2}$	2483	+ 916	20,600
o-CO_2H	$1·58 \times 10^{-1}$	1074	− 493	17,200
m-CO_2H	$2·33 \times 10^{-1}$	849	− 718	16,200
p-CO_2H	1·081	−46	−1613	17,100

TABLE 7. *Reduction of substituted nitrobenzenes by titanous chloride.*

Substituents		$k_{20°}$	(ΔF^*), cal.:		Change in (ΔF^*) due to substituent:	
			By experiment	Predicted	By experiment	Predicted
o-CH_3	*m*-NH_2	$6·15 \times 10^{-2}$	1624	1864	+ 57	+ 297
m-CH_3	*o*-NH_2	$1·75 \times 10^{-1}$	1015	1217	− 552	− 350
p-CH_3	*m*-NH_2	$2·91 \times 10^{-1}$	719	903	− 848	− 664
m-CH_3	*p*-NH_2	$2·24 \times 10^{-1}$	872	950	− 695	− 617
o-CH_3	*m*-CH_3	$1·0 \times 10^{-2}$	2682	2730	+1115	+1163
m-CH_3	*p*-CH_3	$4·83 \times 10^{-2}$	1765	1769	+ 198	+ 202
o-CH_3	*p*-CH_3	$6·0 \times 10^{-3}$	2979	3170	+1412	+1603
o-CH_3	*o*-CH_3	$1·83 \times 10^{-3}$	3671	4141	+2104	+2574
m-Cl	*p*-Cl	$6·65 \times 10^{-1}$	239	795	−1328	−1772
o-Cl	*m*-Cl	$3·32 \times 10^{-1}$	644	483	− 923	−1084
o-Cl	*m*-NH_2	$2·66 \times 10^{-1}$	771	524	− 796	−1043
m-NO_2	*m*-NO_2	1·33	−166	−1269	−1733	−2836
o-NH_2	*m*-OCH_3	$1·43 \times 10^{-1}$	1133	1256	− 434	− 311
p-NH_2	*m*-OCH_3	$1·56 \times 10^{-1}$	1082	1989	− 485	− 578
m-NH_2	*p*-OCH_3	$6·3 \times 10^{-2}$	1610	1493	+ 43	− 74
o-OH	*m*-CO_2H	1·83	−352	− 821	−1919	−2388
p-OH	*m*-CO_2H	$8·3 \times 10^{-1}$	108	1697	−1459	+ 130
m-CO_2H	*p*-CO_2H	1·43	−208	− 764	−1775	−2331
m-CO_2H	*o*-CO_2H	$6·82 \times 10^{-1}$	223	356	−1344	−1211
m-Cl	*m*-Cl *p*-OH	$1·46 \times 10^{-1}$	1121	353	− 446	−1214
m-Cl	*m*-Cl *p*-NH_2	$2·83 \times 10^{-2}$	2076	− 988	+ 509	−2555
m-NO_2	*m*-CO_2H	$9·3 \times 10^{-1}$	42	− 569	−1525	−2136

Influence of Substituents in the Benzene Ring on the Reduction of the Nitro-group.—All the compounds listed in Table 6 were examined in the way described for nitrobenzene, and for those in Table 7 rate determinations were made at least at a standard temperature.

E (*i.e.*, ΔH^*) is the activation energy derived from the Arrhenius equation and ΔF^*, the so-called free energy of activation, derived from the formula $\Delta F^* = -\boldsymbol{R}T \ln k$, expressing the conventional thermodynamic analogy $k = e^{\Delta S^*/\boldsymbol{R}}e^{-\Delta H^*/\boldsymbol{R}T}$, so that $\Delta F^* = \Delta H^* - T\Delta S^*$. For polynitro-compounds the observed rates are for purposes of comparison divided by the number of nitro-groups.

Discussion.—(a) *Energy–entropy relations.* Fig. 5 shows log k (for 20°) plotted against E. If the entropy of activation is constant, the activation energy plotted against log k gives a straight line of slope $-2{\cdot}303\boldsymbol{R}T$. Fig. 5 shows that in the region of lower activation energies there is some tendency for this relation to be satisfied, although there is a quite considerable and apparently random scatter of the points about the mean line. As the activation energy rises, however, the drop in log k is less than the linear relation predicts, the sharp upward course of the curve corresponding to a definite and systematic increase in the entropy with the energy of activation.

In comparable series of reactions of substituted benzene derivatives a constant entropy of activation has several times been found—for example, in benzoylation of amines, and in alkaline hydrolysis of benzoic esters. A ln k–E relation somewhat similar to that shown in Fig. 5 was found for the benzoylation reaction, and also for the combination of pyridine with methyl iodide, when the variable parameter was not the substituent but the solvent (Pickles and Hinshelwood, *J.*, 1936, 1353).

FIG. 5.

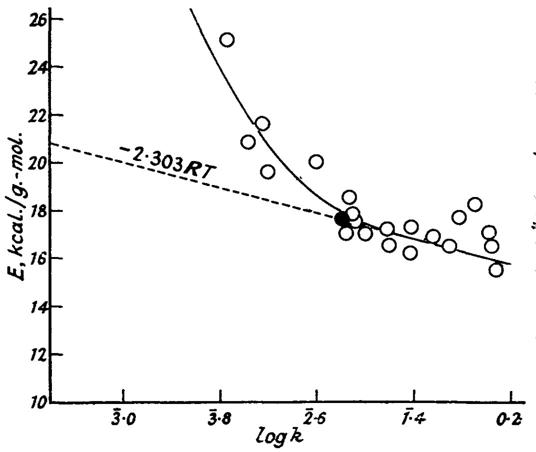
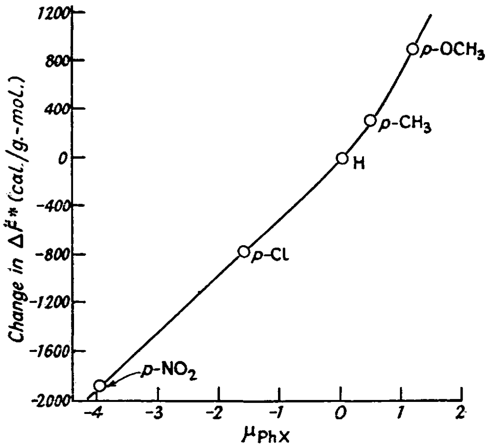


FIG. 6.



In view of the non-constancy of the entropy of activation in the present example, the free energy of activation was thought to be a more suitable quantity for the measure of substituent effects, and in particular for the testing of additive relations among them. It has, moreover, the advantage of being more accurately measurable, which is of importance in the present case where the values of E are subject to some experimental uncertainty. If, however, the logarithm of the non-exponential factor is a linear function of E, as it not infrequently is, then of course additivity in the free energy would imply a similar additivity in the activation energy.

(b) *Electronic influence of substituents.* In general, the electron-attracting substituents increase the rate of reduction and electron-repelling substituents lower it, the most rapid reactions being shown, for example, by trinitrobenzene and by dinitrobenzoic acid, and the slowest by methyl derivatives of nitrobenzene.

If the rate-determining step is a transfer of electrons from the reducing agent, such an influence is understandable. On the other hand, if the preliminary co-ordination of a hydrogen ion with the nitro-compound is necessary, as was suggested above, these same influences will operate in the opposite direction. This conflict may well account for the fact that the range of ΔF^* variation is here less than in the benzoylation of amines (Stubbs and Hinshelwood, *J.*, 1949, S 71), the ratio of the rates for the fastest and slowest nitro- or methyl-substituted reactants being there about 10^5 and here less than 10^3.

In general, the usual complex interplay of inductive, electromeric, and steric effects is discernible. Nevertheless, ΔF^* plotted, where possible, for *para*-compounds, $X{\cdot}C_6H_4{\cdot}NO_2$, against the dipole moments of the corresponding C_6H_5X yields a smooth curve (Fig. 6). For the corresponding *ortho*-compounds the curve is irregular but lies generally above that of the *para*-compounds (lower rates corresponding to a fairly general steric retardation), and for the *meta*-compounds the curve is even more irregular.

The greatest acceleration by a single substituent is caused by a *p*-nitro-group, that of an *ortho*-group being smaller presumably as a result of an adverse steric effect. The greatest retardation is observed with *o*-methyl groups where steric and inductive effects combine. Amino-groups behave as electron-attracting groups, being present largely as NH_3^+. The fact that the acceleration is less with the *ortho*- and *para*-groups than with the *meta*-groups is evidently due to the partial compensation by the mesomeric effect (which corresponds to retardation). The action of OCH_3 is mainly mesomeric and correspondingly nearly zero in the *meta*-compound.

Additive Effects of Substituents.—Table 6 shows the changes in ΔF^* caused by single substituents. These values can be used to predict the change in ΔF^* caused by two or more substituents on the assumption of a simple additivity of effect. Table 7 compares these predicted values with the change in ΔF^* from direct rate determinations.

The error in ΔF^* may amount to ±100 cals. and the error in predicted values can therefore be ±200 cals. In a large number of cases there is correspondence between the directly determined and predicted values which, though it is less striking than was found in the benzoylation of substituted anilines, is close enough to be significant.

The examples where the additive relation fails most noticeably are with

(*p*-OH, *m*-CO_2H); (*m*-Cl, *m*-Cl, *p*-OH); (*m*-Cl, *m*-Cl, *p*-NH_2)

on the one hand, and with

(*m*-NO_2, *m*-NO_2); (*m*-NO_2, *m*-CO_2H); (*m*-CO_2H, *p*-CO_2H)

on the other.

In the first set two groups capable of exerting electromeric effects are adjacent to one another and mutual interference is not surprising. In the dichloronitrophenol for example, there is the possible formation of a chelate ring between Cl and OH (Sidgwick and Callow, *J.*, 1924, **125**, 527) and this might seriously alter the effect which the individual groups normally exert. There may well be interaction between an adjacent OH and CO_2H also. For dichloronitroaniline two chelate rings are possible and it is interesting that this example reveals the greatest discrepancy between directly determined and predicted values.

In the second set the departure from additivity seems to depend upon a certain saturation. Thus with trinitrobenzene there is considerably less than the predicted change in ΔF^*. Here, as in the other two examples quoted, two of the most powerfully acting groups fail to exert the expected effect as though there is a limit to the total amount of disturbance which can be transmitted through the ring and manifested at the seat of reaction.

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