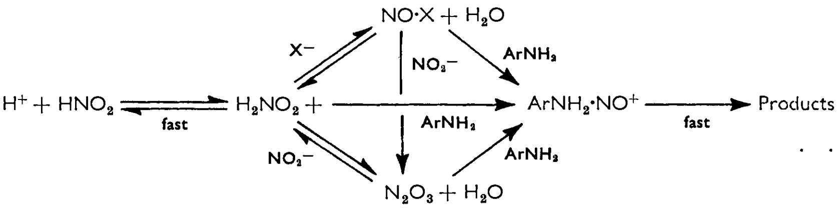
590. *Mechanism of the Azide–Nitrite Reaction. Part I.*

By G. Stedman.

Nitrous acid and hydrazoic acid react in the presence of excess of perchloric acid at 0° by two main paths. One involves formation of nitrosyl azide by a nucleophilic attack of the azide ion on dinitrogen trioxide; the other involves formation of nitrosyl azide by a nucleophilic attack of hydrazoic acid on the nitrous acidium ion. In each case nitrosyl azide subsequently breaks down rapidly to nitrogen and nitrous oxide. The results are in good agreement with the general theory of nitrosation in diazotisation and deamination put forward by Hughes, Ingold, and Ridd.[1] No evidence for nitrosation by the nitrosonium ion was found.

Hughes, Ingold, and Ridd[1] showed that a consistent account of the mechanism of diazotisation and deamination in dilute mineral acid is given by the following series of reactions. Similar schemes should apply to reactions of nitrous acid with other nucleophilic reagents.



. . . (1)

In this scheme there are two possible rate-determining steps. One is the formation of a nitrosating agent, the other is the reaction between the nitrosating agent and the substrate, in this case an amine. Which step is rate determining in any particular case depends on the concentration and reactivity of the free amine. The nitrosamine that is obtained as the primary product undergoes a subsequent rapid rearrangement and reaction to give the final products. Hughes, Ingold, and Ridd showed that the nitrous acidium ion, dinitrogen trioxide, nitrosyl iodide, nitrosyl bromide, and nitrosyl chloride could all act as nitrosating agents.[1] They were unable to find evidence for nitrosation by the nitrosonium ion, the most reactive of possible nitrosating agents, under the mildly acid conditions they used (pH ≈ 2).

Seel and Schwaebel studied the kinetics of the reaction between nitrous acid and hydrazoic acid in acetate buffers:[2]

$$HNO_2 + HN_3 \longrightarrow N_2 + N_2O + H_2O \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

They found that the rate of reaction was independent of the concentration of the azide, and could be fitted to the rate law $v = k[H^+]^2[NO_2^-]$. This result was interpreted as

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[1] Hughes, Ingold, and Ridd, *J.*, 1958, 58.

[2] Seel and Schwaebel, *Z. anorg. Chem.*, 1953, **274**, 169.

showing that reaction occurred by a rate-determining formation of the nitrosonium ion from the nitrous acidium ion, followed by a rapid reaction with azide ions:

$$H_2NO_2^+ \xrightarrow[\text{slow}]{} NO^+ + H_2O \xrightarrow[\text{fast}]{N_3^-} N_3NO \xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Bunton, Llewellyn, and Stedman showed that Seel and Schwaebel's results could equally well be explained as a rate-determining formation of nitrosyl acetate, which reacted rapidly with azide in a subsequent fast step:[3]

$$CH_3{\cdot}CO_2^- + H_2NO_2^+ \xrightarrow[\text{slow}]{} CH_3{\cdot}CO_2{\cdot}NO + H_2O \xrightarrow[\text{fast}]{N_3^-} N_3{\cdot}NO + CH_3{\cdot}CO_2^- \xrightarrow[\text{fast}]{} N_2 + N_2O \quad (4)$$

It was decided to investigate the reaction between nitrous acid and hydrazoic acid in the absence of nucleophilic buffers for evidence of the nitrosonium ion as a reaction intermediate. In the present work solutions were buffered with an excess of perchloric acid. The perchlorate ion is a very weak nucleophilic reagent, and does not intervene chemically in the mechanism of diazotisation and deamination.[1]

There is much evidence from kinetic studies that nucleophilic anions and nitrous acid interact to form nitrosyl compounds in aqueous solution.[1,3] Measurements of the visible-light absorption of solutions of nitrous acid in concentrated hydrochloric acid, nitric acid, and perchloric acid lead to the same conclusion.[3,4] Lucien has recently isolated nitrosyl azide in low yield at low temperatures.[5] It readily breaks down to nitrogen and nitrous oxide. Clusius and Effenberger have shown by means of labelling with nitrogen-15 that the nitrogen and nitrous oxide formed in the reaction between nitrous acid and hydrazoic acid have the isotopic composition corresponding to nitrosyl azide's being a reaction intermediate:[6]

$$H{-}\overset{a}{N}{=}\overset{b}{N}{=}\overset{a}{N} + H\overset{c}{N}O_2 \longrightarrow \overset{a}{N}{=}\overset{b}{N}{=}\overset{a}{N}{-}\overset{c}{N}{=}O \longrightarrow \overset{a}{N}{\equiv}\overset{b}{N} + \overset{a}{N}{\leftarrow}\overset{c}{N}{=}O \quad . \quad . \quad . \quad . \quad (5)$$

On the basis of this evidence, the present results were interpreted by assuming that nitrosyl azide was formed in the reaction, and that this rapidly broke down to nitrogen and nitrous oxide. Evidence to be presented later shows that the breakdown of nitrosyl azide to the reaction products in aqueous solution is much more rapid than the rate of hydrolysis by solvent. The various forms of rate equation observed were interpreted in terms of different mechanisms all leading to the formation of nitrosyl azide.

Results.—The kinetics of reaction were studied at several concentrations of excess of perchloric acid from 0·0029 to 0·173M, equimolar amounts of nitrous and hydrazoic acid being used. By varying the initial concentration of the reactants, the total order of reaction with respect to both components was found. The appropriate equation is

$$\log t_{\frac{1}{2}} = C - (n - 1) \log [\mathrm{a}]$$

where n is the overall kinetic order, [a] is the initial concentration of each reactant, $t_{\frac{1}{2}}$ is the half-life of the reactants, and C is a constant.[1] The results, given in Table 1, show that the reaction is of second order over the acidity range studied. Second-order rate constants are also given.

The second-order rate constants for these runs and also for a number of runs carried out at other acidities, given in Table 4, are plotted against $[H^+]$ in the Figure. The second-order rate constants, k_2, were calculated from the normal integrated form of the rate equation. Reaction is clearly acid catalysed. Below $[H^+] = 0{\cdot}04$M, $k_2 = 0{\cdot}80 + 33{\cdot}7\,[H^+]$ sec.$^{-1}$ mole^{-1} l.; above $[H^+] = 0{\cdot}10$M, $k_2 = 33{\cdot}7$ sec.$^{-1}$ mole^{-1} l. The reason for this change in the dependence of k_2 on $[H^+]$ is given later.

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[3] Bunton, Llewellyn, and Stedman, *Spec. Publ. Chem. Soc.*, No. 10, p. 113.

[4] Schmid and Maschka, *Z. physik. Chem.*, 1941, **49**, *B*, 171.

[5] Lucien, *J. Amer. Chem. Soc.*, 1958, **80**, 4458.

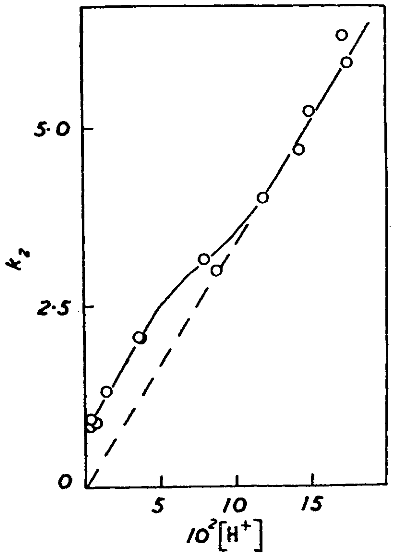
[6] Clusius and Effenberger, *Helv. Chim. Acta*, 1955, **38**, 1834.

TABLE 1. *Dependence of total reaction order on acidity at* 0°

10^2[H$^+$] (M)	0·29	1·42	3·64	7·9	17·3
10^3[a] (M)	2·00	2·04	2·04	0·800	0·851
$t_{1/2}$ (sec.)	744	357	240	372	204
10^3[a] (M)	0·800	0·407	0·407	0·160	0·341
$t_{1/2}$ (sec.)	1735	1830	1332	1842	456
10^3[a] (M)	0·400	—	—	—	—
$t_{1/2}$ (sec.)	3440	—	—	—	—
Total reaction order, n	2·0	2·0	2·1	2·0	1·9
k_2 (mean) (sec.$^{-1}$ mole^{-1} l.)	0·85	1·41	2·13	3·14	6·34

$[a] = [HNO_2] = [HN_3]$.

Reaction at Low Concentrations of Excess of Perchloric Acid.—The order of reaction with respect to the individual components, nitrous acid and hydrazoic acid, was determined by varying the relative concentrations of each, and comparing the initial rates of reaction. The results are given in Table 2.



Azide–nitrite reaction: second-order rate constant as a function of excess of perchloric acid concentration.

TABLE 2. *Initial rates of reaction at low acidity.* 0°

Run No.	21	22	23	24	29	30
10^4[HN$_3$]	4·02	1·61	1·61	4·02	20·00	4·00
10^4[HNO$_2$]	8·04	8·04	4·02	4·02	4·00	4·00
10^3[H$^+$]	2·32	2·32	2·32	2·32	4·7	4·7
$10^7 v_0$ (sec.$^{-1}$ mole l.$^{-1}$)	4·8	4·7	0·83	1·1	1·71	1·23

v_0 = Initial rate.

The reaction is of second order in nitrous acid, and nearly of zero order in hydrazoic acid, *i.e.*, $v = k_2[HNO_2]^2$. The slight dependence of rate on azide concentration is a real effect, due to a small amount of reaction going by a mechanism with a rate equation $v = k_3^{HN_3}[H^+][HNO_2][HN_3]$. It is this mechanism that is responsible for the acid catalysis of the reaction.

The rate equation $v = k_2[HNO_2]^2$ is interpreted as a rate-determining formation of dinitrogen trioxide, followed by a rapid reaction with either azide ion or hydrazoic acid:

$$NO_2^- + H_2NO_2^+ \xrightarrow[\text{slow}]{} N_2O_3 + H_2O \xrightarrow[\text{fast}]{\text{azide}} N_3{\cdot}NO + NO_2^- \xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \; . \; . \quad (6)$$

The formation of dinitrogen trioxide from two molecules of nitrous acid has been written as a nucleophilic substitution of a nitrite ion at the nitrous acidium ion, the form suggested by Hughes, Ingold, and Ridd.[1] It differs from the conventional formulation shown in eqn. (7), only in a rapid, pre-equilibrium proton transfer. The rate of reaction (6) is given by $v = k_3^{NO_2^-}[H^+][HNO_2][NO_2^-]$, where $k_3^{NO_2^-} = k_2/K_{HNO_2}$ and K_{HNO_2} is the dissociation constant of nitrous acid.

$$2HNO_2 \longrightarrow N_2O_3 + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

A comparison of the second-order rate constants, k_2, for the formation of dinitrogen trioxide, obtained by a number of workers is shown in Table 3.

TABLE 3. *Second-order rate constants for the formation of dinitrogen trioxide at* 0°.

	$[HNO_2]$ (M)	μ (M)	k_2 (sec.$^{-1}$ mole^{-1} l.)	Ref.
Diazotisation of aniline	0·001	0·01	0·85	*a*
Diazotisation of aniline			0·92	*b*
Diazotisation of other aromatic amines............	0·001	0·01	0·80	*c*
Diazotisation in acetate and phthalate buffers...	0·0002	0·1	0·78	*a*
Oxygen exchange between nitrous acid and water	0·01—0·1	0·3—2·0	0·5	*d*
Azide–nitrite reaction	0·002	0·01	0·80	This paper

μ = Ionic strength.

References: *a*, ref. 1. *b*, Schmid and Woppmann, *Monatsh.*, 1952, **83**, 346. *c*, Larkworthy, personal communication. *d*, ref. 3.

The kinetic form of the rate equation, and the agreement between the second-order rate constant obtained in this work and those found in other investigations are sufficient to establish that a rate-determining formation of dinitrogen trioxide is involved.

The subsequent fast step in which dinitrogen trioxide reacts with azide to form nitrosyl azide involves the azide ion, and not hydrazoic acid:

$$N_3^- + N_2O_3 \longrightarrow N_3{\cdot}NO + NO_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

This is shown by the dependence of the rate of reaction on acidity. If the reaction path is that described above, then the occurrence of a rate-determining formation of dinitrogen trioxide depends on there being a sufficiently high concentration of the reacting azide species to trap all of the molecules formed in eqn. (6). Hydrazoic acid is a weak acid: $K_a = 1{\cdot}0 \times 10^{-5}$ mole l.$^{-1}$ at 0°.[7] In our work the presence of excess of perchloric acid ensured that nearly all of the azide was present as undissociated hydrazoic acid. On increasing the concentration of excess of perchloric acid the concentration of hydrazoic acid remains essentially unaltered, while that of the azide ion decreases inversely. Thus, if dinitrogen trioxide reacts with hydrazoic acid increasing acidity will have no effect on the rate of reaction. If dinitrogen trioxide reacts with azide ion, then on increasing the acidity sufficiently a point will be reached where the concentration of azide ions will not be great enough to trap all of the dinitrogen trioxide molecules formed; some will react with water, and the reaction rate will decrease. In the limiting case nearly all of the dinitrogen trioxide molecules will react with water, and only a small fraction with azide ions. The mechanism will then be of the form shown in eqn. (9), the rate law will be $v = k_3[HNO_2]^2[N_3^-]$, and the specific rate will drop to a low value.

$$\begin{aligned} NO_2^- + H_2NO_2^+ &\underset{\text{fast}}{\rightleftharpoons} N_2O_3 + H_2O \\ N_2O_3 + N_3^- &\xrightarrow[\text{slow}]{} N_3{\cdot}NO + NO_2^- \\ N_3{\cdot}NO &\xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9) \end{aligned}$$

The "kink" in the plot of k_2 against $[H^+]$ (Figure) is due to just such a factor, reduction of the azide ion concentration below the critical value needed to compete effectively with water for dinitrogen trioxide, and corresponds to a change from the second-order kinetic

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[7] Stedman, following paper.

form $v = k_2[\mathrm{HNO_2}]^2$ to the third-order form $v = k_3[\mathrm{HNO_2}]^2[\mathrm{N_3}^-]$. The reason that the overall kinetics of the reaction between nitrous acid and hydrazoic acid remain of second order, as shown in Table 1, is that the transition from second-order to third-order kinetics for reaction *via* dinitrogen trioxide is accompanied by a large decrease in the specific rate, and this is overshadowed by the large contribution to the total rate due to another mechanism with a rate equation $v = k_3^{\mathrm{HN_3}}[\mathrm{H}^+][\mathrm{HNO_2}][\mathrm{HN_3}]$ which is also of second order with respect to the reagents. A similar change in kinetic form is observed in the diazotisation of aniline in dilute perchloric acid, on varying the acidity.[1]

As explained above, it is impossible to isolate the third-order rate equation, for reaction between an equilibrium concentration of dinitrogen trioxide and azide ions. To do so, it would be necessary to work with a very low concentration of azide ions, less than 10^{-7}M. This would entail working at a high acidity to suppress the ionisation of hydrazoic acid sufficiently, and under these conditions there would be a large contribution to the total rate by a mechanism with a rate equation $v = k_3^{\mathrm{HN_3}}[\mathrm{H}^+][\mathrm{HNO_2}][\mathrm{HN_3}]$. It is, however, possible to form an estimate of the relative reactivities of water and azide ion towards dinitrogen trioxide. From the Figure it can be seen that the transition from second order to third-order kinetics occurs between $[\mathrm{H}^+] = 0{\cdot}04$ and $[\mathrm{H}^+] = 0{\cdot}12$M. The mid-point of this range is $[\mathrm{H}^+] = 0{\cdot}08$M and the average azide concentration for these experiments was *ca.* 0·0004M. Nearly all of this was present as hydrazoic acid. Knowing the dissociation constant of hydrazoic acid,[7] one can calculate that the value of $[\mathrm{N_3}^-]$ is *ca.* 10^{-7}M. This concentration competes with approximately equal effectiveness to 55·5M-water for dinitrogen trioxide. The rates of reaction being assumed proportional to the concentrations of the reacting species, the relative reactivities of water and of the azide ion towards dinitrogen trioxide are $(10^{-7}/55{\cdot}5) : 1$; *i.e.*, $2 \times 10^{-9} : 1$. This value may be regarded only as an estimate of order of magnitude.

The Acid-catalysed Reaction.—The previous discussion has shown that up to $[\mathrm{H}^+] = 0{\cdot}04$M, there is a constant contribution to the rate of reaction of $0{\cdot}80[\mathrm{HNO_2}]^2$, because at these low acidities, and at the azide concentrations used, there was a sufficient concentration of azide ions to trap all of the dinitrogen trioxide formed. Above $[\mathrm{H}^+] = 0{\cdot}12$M this mechanism makes a negligible contribution to the total rate under the conditions used (equal concentrations of nitrous acid and hydrazoic acid). Table 4 contains the observed second-order rate constants including corrections for reaction *via* dinitrogen trioxide. The corrected rate constants k_2^* are those for the acid-catalysed reaction.

TABLE 4. *Acid catalysis of the azide–nitrite reaction* 0°.

$10^3[\mathrm{H}^+]$ (M)	2·3	2·9	14·2	36·4	37·1	79
k_2 (sec.$^{-1}$ mole^{-1} l.)	0·98	0·85	1·41	2·13	2·12	3·14
k_2^* sec.$^{-1}$ mole^{-1} l.)	0·18	0·05	0·61	1·33	1·32	2·34
$10^2k_2^*/[\mathrm{H}^+]$ (sec.$^{-1}$ mole^{-2} l.^{2})	—	—	4·3	3·7	3·6	—
$10^3[\mathrm{H}^+]$ (M)	88	120	143	149	173	176
$k_2 = k_2^*$ (sec.$^{-1}$ mole^{-1} l.)	3·0	4·07	4·75	5·23	6·33	5·90
$k_2^*/[\mathrm{H}^+]$ (sec.$^{-1}$ mole^{-2} l.^{2})	—	3·4	3·3	3·5	3·7	3·4

$k_2^* = k_2 - 0{\cdot}8[\mathrm{HNO_2}]^2$ for $[\mathrm{H}^+] < 0{\cdot}04$M. $k_2^* = k_2$ for $[\mathrm{H}^+] > 0{\cdot}12$M. $[\mathrm{HNO_2}] = [\mathrm{HN_3}] = 0{\cdot}0002 - 0{\cdot}0004$M.

The results show that the rate equation for the acid-catalysed reaction is $v = k_2[\mathrm{H}^+][\mathrm{Reactant}]^2$, where $[\mathrm{Reactant}] = [\mathrm{HNO_2}] = [\mathrm{HN_3}]$. In order to obtain the order with respect to the individual components, it is necessary to vary their relative concentrations. Table 5 contains some results for experiments in which this was done. Pairs of runs were

TABLE 5. *Order of the acid-catalysed reaction with respect to individual components.*

$10^2[\mathrm{H}^+]$ (M)	3·27	3·27	13·45	13·45	17·26	17·26
$10^4[\mathrm{HN_3}]$ (M)	2·84	1·42	12·5	2·5	17·3	3·45
$10^4[\mathrm{HNO_2}]$ (M)	2·84	2·84	2·5	2·5	3·46	3·46
10^6v_0 (sec.$^{-1}$ mole l.$^{-1}$)	0·069 *	0·034 *	1·44	0·24	3·22	0·69

v_0 = initial rate. * Values corrected for reaction *via* dinitrogen trioxide.

carried out at various concentrations of excess of perchloric acid, in which the value $[HNO_2]$ was kept constant, while $[HN_3]$ was varied. The initial rates of reaction were then compared.

These results show that at $[H^+] = 0{\cdot}173, 0{\cdot}1345$, and $0{\cdot}0327$M, the acid-catalysed reaction is of first order in $[HN_3]$. [For measurements at 0·0327M-acid, it was necessary to correct the observed initial rate for reaction *via* a rate-determining formation of dinitrogen trioxide, of $v = 0{\cdot}8[HNO_2]^2$ (sec.$^{-1}$ mole l.$^{-1}$).] As the total reaction order is two, as shown in Table 1, the full rate equation is $v = k_3^{HN_3}[H^+][HNO_2][HN_3]$ with $k_3^{HN_3} = 33{\cdot}7$ sec.$^{-1}$ mole^{-2} l.^{2}.

This rate equation corresponds to a mechanism in which the rate-determining step is a bimolecular reaction between hydrazoic acid and the nitrous acidium ion:

$$H_2NO_2^+ + HN_3 \xrightarrow[\text{slow}]{} N_3{\cdot}NO + H_3O^+ \xrightarrow[\text{fast}]{} N_2 + N_2O + H_3O^+ \quad . \; . \; . \; . \; . \quad (10)$$

This mechanism is formally similar to that found by Hughes, Ingold, and Ridd for the diazotisation of *o*-chloroaniline in dilute perchloric acid.[1] Hydrazoic acid appears to be a weaker nucleophilic reagent towards the nitrous acidium ion than is *o*-chloroaniline, the third-order rate constant for the latter being 175 sec.$^{-1}$ mole^{-2} l.^{2}. It is important to establish that the acid catalysis of the azide nitrite reaction is due to reaction between hydrazoic acid and the nitrous acidium ion, because Ridd found evidence for an acid catalysis of dinitrogen trioxide formation[1] (though the extent of the acid catalysis is less than in the present work).

The form of the rate equation, $v = k_3^{HN_3}[H^+][HNO_2][HN_3]$, is also consistent with a reaction between hydrazoic acid and an equilibrium concentration of nitrosonium ions:

$$H_2NO_2^+ \underset{\text{fast}}{\rightleftharpoons} NO^+ + H_2O \xrightarrow[\text{slow}]{HN_3} N_3{\cdot}NO + H_3O^+ \xrightarrow[\text{fast}]{} N_2 + N_2O + H_3O^+ \quad . \; . \; . \quad (11)$$

Hughes, Ingold, and Ridd have rejected mechanisms of this type in their studies of diazotisation,[1] by comparing their rates of reaction with the rate of oxygen exchange between nitrous acid and water.[3] Direct evidence from a study of the reaction between nitrous acid and hydrazoic acid in water enriched in oxygen-18 shows that chloride, bromide, and azide ions form the corresponding nitrosyl compounds by nucleophilic substitutions at the nitrous acidium ion and not at the nitrosonium ion.[7] It therefore seems very unlikely that the acid-catalysed reaction between nitrous acid and hydrazoic acid involves the nitrosonium ion.

These conclusions differ somewhat from those recorded by Seel *et al.*,[8] who suggest that nitrosyl azide is formed by reaction of hydrazoic acid, rather than azide ions, with a introsyl compound:

$$NO{\cdot}X + HN_3 \longrightarrow N_3{\cdot}NO + HX \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

The present work suggests that the alternative view is correct, *i.e.*, that nitrosyl compounds react with the azide ion and not with hydrazoic acid. The only exception observed is in the case of the highly reactive nitrous acidium ion.

EXPERIMENTAL

Materials.—Sodium azide was recrystallised from water and dried *in vacuo* over phosphorus pentoxide. " AnalaR " sodium nitrite was dried over phosphorus pentoxide. " AnalaR " perchloric acid, 60%, was used without further purification. All solutions were made up with boiled-out distilled water.

Kinetic Measurements.—The solutions containing sodium nitrite and sodium azide were made up in conical flasks and cooled to 0° in ice–water. Two initial samples were withdrawn for analysis. Reaction was started by adding the requisite quantity of ice-cold, concentrated

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[8] Seel, Wölfle, and Zwarg, *Z. Naturforsch.*, 1958, **13***b*, 136.

perchloric acid (usually between 0·8 and 3·6M) from a pre-cooled pipette. Samples were withdrawn with an ice-jacketed pipette at suitable time intervals, and reaction was stopped by adding the sample to a known excess of concentrated sodium hydroxide solution. Care was taken to exclude carbon dioxide from all solutions, as sodium carbonate interfered with the analysis procedure.

Spectrophotometric Analysis.—Solutions were analysed by measuring the optical density at several wavelengths in the range 2450—2300 Å, a Unicam S.P. 600 with silica cells being used at fixed slit-widths. Beer's law was obeyed. Care was always taken to check that the ratios of the optical densities at several wavelengths did not change during the course of a run (with initially equal concentrations of azide and nitrite). This provided a check on the absence of side reactions, and the validity of the analytical method. Blanks were always run to check light absorption due to traces of carbonate in the solution.

The author of this and the following paper thanks Professor Sir Christopher Ingold, F.R.S., and Professor E. D. Hughes, F.R.S., for their interest and for helpful discussions. He is also indebted to Dr. C. A. Bunton and Dr. J. H. Ridd.

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[*Received, February* 11*th*, 1959.]