# 632. *Nitrosation, Diazotisation, and Deamination. Part VII.*[*] *The Reactivities of Some Aromatic Amines towards Dinitrogen Trioxide.*

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The rates of diazotisation in dilute perchloric acid of *p*-chloroaniline, *p*-aminophenyltrimethylammonium perchlorate, and *p*-methoxyaniline have been investigated. Dinitrogen trioxide has been shown to be the most important nitrosation carrier in their diazotisation. With *p*-aminophenyltrimethylammonium perchlorate acid-catalysis had to be suppressed to obtain a pure reaction with dinitrogen trioxide.

Rate constants, calculated upon the assumption that the molecular amine is the reactant, have been shown to obey the Hammett equation.

PREVIOUS papers in this Series elucidated the range of nitrosation mechanisms that give rise to diazotisation in dilute perchloric acid. It was shown that with a given amine the mechanism depended to a large extent on the acidity and the reactant concentration. The work described in the present paper is part of that being carried out to investigate how the nature of the amine influences the mechanism of nitrosation, with particular

[*] Part VI, *J.*, 1958, 88.

reference to the reactivity of different amines towards dinitrogen trioxide. For that purpose the kinetics of the diazotisation of three contrasting amines, *p*-chloroaniline, *p*-aminophenyltrimethylammonium perchlorate, and *p*-methoxyaniline, have been studied in detail.

An account of the diazotisation of aniline in an excess of perchloric acid has been given in Part II.[1] The overall kinetic order falls from 3 to 2 as the excess of acid is reduced because the order with respect to aniline falls from 1 to 0. The limiting kinetic equations for the reaction are:

$$\text{Rate} = k_3''[\text{Ar}\cdot\text{NH}_2][\text{HNO}_2]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Rate} = k_2''[\text{HNO}_2]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As shown in Part I [2] the existence of the two equations demonstrates that the nitrosation carrier is dinitrogen trioxide. The bracketed quantities are molecular rather than stoicheiometric, and the rate constants are molecular constants, *i.e.*, they are calculated from the concentrations of molecular amine and undissociated nitrous acid. Stoicheiometric constants are those calculated from the total concentrations of the ionised and un-ionised forms of the amine and the nitrous acid. The use of these rate constants is discussed in detail in Part I. Stoicheiometric constants are denoted by a superposed bar. The number of primes indicates the order in nitrous acid of the rate equation to which the stoicheiometric or molecular rate constant belongs.

Even in the most simplified system, that containing an excess of perchloric acid, several nitrosation carriers can exist,[2] *e.g.*, $NO^+$, $NO\cdot OH_2^+$, $NO\cdot NO_2$, $NO\cdot OH$. Thus, before the reactivities of different amines towards dinitrogen trioxide can be compared, it is necessary to chose experimental conditions in which diazotisation by carriers other than dinitrogen trioxide is negligible. How this is done will be made clear in the text. Then rate constants, obtained in conditions where equation (1) holds, can be used for the comparison of reactivities.

(1) *The Diazotisation of* p-*Chloroaniline.*—Values of the overall kinetic order, determined by the half-life method, are given in Table 1.

TABLE 1. *Diazotisation of* p-*chloroaniline: overall kinetic order in various concentrations of perchloric acid in excess.*

| | | | | |
|---|---|---|---|---|
| Free [H+] | 1·05 | 0·52 | 0·051 | 0·0049 |
| Order | 3·0 | 3·0 | 2·9 | 2·2 |

(a) *Second-order region.* The second-order reaction in the diazotisation of aniline has been found to obey equation (2) rather than equation (3) which was assumed by earlier workers without any evidence of the reactant orders:

$$\text{Rate} = k_2'[\text{Ar}\cdot\text{NH}_2][\text{HNO}_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

That *p*-chloroaniline is diazotised according to the same second-order equation as aniline is shown by the behaviour of the rate constants $\bar{k}_2''$ and $\bar{k}_2'$ in a run (Table 5) in which unequal concentrations of amine and nitrous acid were used. This has been confirmed by showing that doubling the amine concentration hardly affected the rate (Figure; runs 19 and 20).

When the reaction is no longer amine-dependent the rate-controlling process is the formation of the dinitrogen trioxide for which $\bar{k}_2''$ in Table 5 is the stoicheiometric second-order rate constant. The molecular rate constant calculated from the mean value of $\bar{k}_2''$, by using $4{\cdot}5 \times 10^{-4}$ mole $l.^{-1}$ for the acidity constant of nitrous acid, is 0·69 $sec.^{-1}$ $mole^{-1}$ l. This compares reasonably well with the value of 0·85 $sec.^{-1}$ $mole^{-1}$ l. found previously [1] because there was some slight amine-dependence in the excess of acid used in this run.

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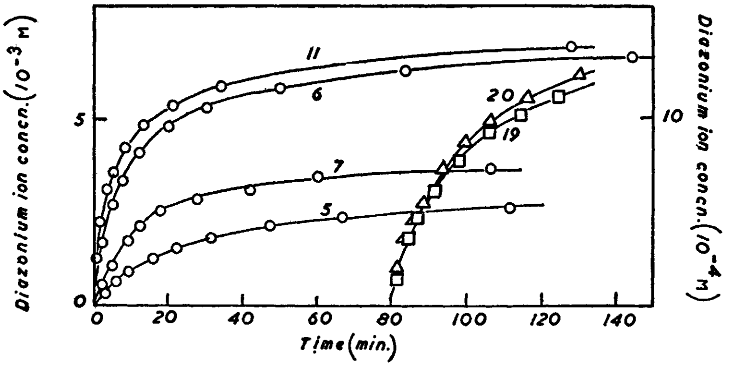
[1] Part II, Hughes, Ingold, and Ridd, *J.*, 1958, 65.

[2] Part I, *idem*, *J.*, 1958, 58.

(b) *Third-order region.* The Figure shows how doubling the amine concentration (runs 5 and 7) doubled the initial rate, whereas doubling the nitrous acid concentration (runs 6 and 7) quadrupled the initial rate. Doubling the perchloric acid concentration approximately halved the initial rate (runs 6 and 11) because it halved the free amine concentration. These results show that the kinetic equation (1) is operating.

*The effect of reactant concentrations on initial rates in the diazotisation of* p-*chloroaniline at* 0°. *The right-hand scale applies to runs* 19 *and* 20 *whose time zero is* 80.



*Initial stoicheiometric concentrations.*

| Run | Amine | [$HNO_2$] | [$H^+$] | Run | Amine | [$HNO_2$] | [$H^+$] |
|---|---|---|---|---|---|---|---|
| 5 | 0·00400 | 0·00400 | 1·05 | 11 | 0·00795 | 0·00795 | 0·525 |
| 7 | 0·00796 | 0·00398 | 1·05 | 19 | 0·00164 | 0·00164 | 0·0049 |
| 6 | 0·00797 | 0·00797 | 1·05 | 20 | 0·00328 | 0·00164 | 0·0049 |

Table 2 illustrates in detail the acid-dependence of the third-order stoicheiometric and molecular rate constants.

TABLE 2. *Diazotisation of* p-*chloroaniline: acid-dependence of the third-order stoicheiometric* ($\bar{k}_3'$) *and molecular* ($k_3''$) *rate constants* (*sec.*$^{-1}$ *mole*$^{-2}$ *l.*$^2$).

Acidity constant of $HNO_2$ = 4·5 × $10^{-4}$ mole $l.^{-1}$.
Acidity constant of amine cation = 1·55 × $10^{-4}$ mole $l.^{-1}$.

| Run | [$H^+$] | Amine as base (%) | Un-ionised nitrous acid (%) | $\bar{k}_3''$ | $10^{-4}k_3''$ |
|---|---|---|---|---|---|
| 6 | 1·05 | 0·015 | 100 | 33·7 | 22·5 |
| 11 | 0·52 | 0·03 | 100 | 51·5 | 17·2 |
| 14 | 0·051 | 0·30 | 99 | 272 | 9·16 |

The comparatively small increase in rate with hydrogen-ion concentration may be a salt effect. It is certain that there is nothing like first-order dependence on hydrogen-ion concentration, and that the ion $HN_2O_3^+$, claimed by Okano and Ogata [3] as a main agent in the diazotisation of aniline in much weaker acid, cannot be important here.

The observations that rate equations (1) and (2) both hold, and that when the excess of acid is reduced equation (1) gives way to equation (2), prove that the nitrosation carrier is dinitrogen trioxide. Therefore, the third-order rate constants given in Table 2 are measures of the reactivity of the amine towards dinitrogen trioxide.

(2) *The Diazotisation of* p-*Aminophenyltrimethylammonium Perchlorate.*—The overall reaction order was found to be 2·2 in 0·0051M-acid, and 2·5 in 0·129M-acid. Some runs have been carried out in more concentrated acid. These did not give the third-order kinetics expected for diazotisation by dinitrogen trioxide, and showed considerable acid-catalysis, both phenomena being probably due to some incursion of diazotisation by the

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[3] Okano and Ogata, *J. Amer. Chem. Soc.*, 1953, **75**, 5175.

nitrous acidium ion, which obeys equation (4) and therefore gives second-order kinetics in a constant excess of perchloric acid.[4]

$$\text{Rate} = k_3'[\text{Ar·NH}_2][\text{HNO}_2][\text{H}^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Diazotisation by dinitrogen trioxide has been favoured by using high nitrous acid concentrations, and, to ensure that the attack of the dinitrogen trioxide on the amine was rate-determining, the free amine concentration has been kept low by using moderate acid and low amine concentrations. Table 7 records first-order stoicheiometric rate constants for two runs, one with an excess of nitrous acid twice that of the other, the rate constants being $0·77 \times 10^{-3}$ and $2·7 \times 10^{-3}$ sec.$^{-1}$, respectively. Therefore, under these conditions, the reaction is closely of the second order with respect to the nitrous acid. Equation (1) is again the complete rate equation. The mean value of the third-order stoicheiometric rate constant is $3·5 \times 10^2$ sec.$^{-1}$ mole$^{-2}$ l.$^2$. If the acidity constant of the amine is taken to be $3·09 \times 10^{-3}$ mole l.$^{-1}$ the third-order molecular rate constant is found to be $1·4 \times 10^4$ sec.$^{-1}$ mole$^{-2}$ l.$^2$. This is a measure of the reactivity of the amine towards dinitrogen trioxide.

The proof of the validity of equation (1) shows that dinitrogen trioxide can play the dominating part in the diazotisation of this amine provided high enough nitrous acid concentrations are used. With such nitrous acid concentrations the third-order equation should give way to equation (2) as the excess of acid is reduced. This was happening when the order fell from 2·5 to 2·2 as the acid concentration was reduced from 0·129M to 0·0051M, although without detailed examination it is not possible to say how much of the second-order rate was due to the nitrous acidium ion.

Reilly and Drumm [5] have reported that the three amines, $p\text{-NH}_2\text{·C}_6\text{H}_4\text{·[CH}_2]_n\text{·NMe}_3^+$ ($n = 0, 1, 2$), are diazotised at the same second-order rate in 0·002M-hydrochloric acid. They claimed that the rates were equal because the amine cations were the reactants and sufficient acid was present to protonate the amines completely. From the now known value for the acidity constant of the amine with $n = 0$, it can be calculated that this is not so, and it seems likely that the main reaction they were studying was the formation of dinitrogen trioxide according to equation (2). It is likely, too, that catalysis by chloride ion markedly affected their results.

(3) *The Diazotisation of* p-*Methoxyaniline.*—Aniline (p$K_a$ 4·58) is only a little less basic than *p*-methoxyaniline (p$K_a$ 5·29), and so *p*-methoxyaniline would be expected to react similarly to aniline. A brief investigation, sufficient to show that this amine is diazotised by reaction with dinitrogen trioxide, has been carried out.

The total reaction order was found to be 3, and the stoicheiometric third-order rate constant $1·57 \times 10^2$ sec.$^{-1}$ mole$^{-2}$ l.$^2$, in 0·0175M-perchloric acid. In this acid the percentages of undissociated nitrous acid and molecular amine were 97·4 and 0·029 respectively; these gave a value of $5·56 \times 10^5$ sec.$^{-1}$ mole$^{-2}$ l.$^2$ for the molecular third-order rate constant.

TABLE 3. *Diazotisation of* p-*methoxyaniline: stoicheiometric and molecular second-order rate constants* (*sec.*$^{-1}$ *mole*$^{-1}$ *l.*).

$[\text{MeO·C}_6\text{H}_4\text{·NH}_2] = 0·01\text{M}$. $[\text{H}^+] = 0·002\text{M}$.

| Run | [HNO$_2$] | $\bar{k}_2''$ | $k_2''$ |
|---|---|---|---|
| 5 | 0·00025 | 0·597 | 0·895 |
| 4 | 0·0001 | 0·613 | 0·919 |

That the order in nitrous acid is two was confirmed by carrying out two runs with a large excess of amine in 0·002M-perchloric acid. The second-order plots were straight lines, and the values for the stoicheiometric and the molecular rate constants are given in

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[4] Part IV, Hughes, Ingold, and Ridd, *J.*, 1958, 77.

[5] Reilly and Drumm, *J.*, 1935, 871.

Table 3. Low nitrous acid concentrations were used in order to emphasise any acid-catalysed component of the reaction. Even so, the reaction was of the second order in nitrous acid, and not of the first order as has been found for the acid-catalysed mechanism. The presence of a very small acid-catalysed component is shown by the slight increase in the value of the second-order rate constant as the nitrous acid concentration is reduced. In an excess of acid as small as 0·002M, the rate-controlling step is expected to be the formation of the dinitrogen trioxide. The molecular rate constant for this has been found[1] to be 0·85 sec.$^{-1}$ mole.$^{-1}$ l. The molecular rate constants in Table 3 are very close to this; hence the same process is rate-controlling here. The slightly high values are due to the acid-catalysis.

(4) *Application of the Hammett Equation.*—If the attack of an amine on dinitrogen trioxide is a bimolecular nucleophilic substitution $S_N2$, it should be favoured by a high electron density on the nitrogen atom of the amino-group; and there should be a correlation between the basicity of the amine and its rate of reaction with dinitrogen trioxide.

$$\mathrm{XAr{\cdot}NH_2 + NO{\cdot}NO_2 \xrightarrow{\text{Slow}} XAr{\cdot}NH_2{\cdot}NO^+ + NO_2^-}$$

$$\mathrm{XAr{\cdot}NH_2{\cdot}NO^+ \xrightarrow[\text{fast steps}]{\text{Several}} XAr{\cdot}N_2^+ + H_2O}$$

The results with *p*-chloroaniline, *p*-aminophenyltrimethylammonium perchlorate, *p*-methoxyaniline, and aniline have been correlated by means of the Hammett equation,[6] $\log k/k^0 = \rho\sigma$, where $k^0$ is the rate constant for the unsubstituted member of a reaction series, $k$ is the rate constant for any member of the series, and $\rho$ and $\sigma$ have their usual meanings.

Third-order rate constants for the diazotisation of the amines investigated are given in Table 4. These are effectively rate constants for reaction with dinitrogen trioxide.

TABLE 4. *Third-order stoicheiometric ($\bar{k}_3''$) and molecular ($k_3''$) rate constants for the diazotisation of some aromatic amines together with their sigma constants.*

| Amine | Source | (H+) | $10^{-2}\bar{k}_3''$ | $10^{-5}k_3''$ | $\log k_3''$ | $\sigma$ |
|---|---|---|---|---|---|---|
| *p*-OMe ............... | p. 3119 | 0·0175 | 1·57 | 5·56 | 5·75 | −0·268[6] |
| Aniline ........... | Part II | 0·05 | 1·62 | 3·11 | 5·49 | 0 |
| *p*-Cl .................. | Table 2 | 0·051 | 2·72 | 0·916 | 4·96 | 0·227[6] |
| *p*-$NMe_3^+$ ........... | p. 3119 | 0·12 | 3·5 | 0·14 | 4·15 | 0·82 * |

* McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

From the slope of the straight line obtained when the logarithms of the molecular rate constants are plotted against σ, the reaction constant ρ can be calculated to be −1·6. The negative value implies that the reaction is favoured by a high electron density at the reaction centre.[6] Since the amino-nitrogen atom is the reaction centre in diazotisation the electron density on this atom must be a crucial factor. This can only mean that the molecular, basic amine interacts with the nitrosating agent in a bimolecular nucleophilic substitution. Were the conjugate acid of the amine the reactant, the positive pole would obscure, and probably make undectectable, reactivity changes due to substituents *para* to the reaction centre.

From Table 4 it can be seen that the reactivities of amines towards dinitrogen trioxide decrease rapidly as σ becomes more positive, *i.e.*, as the basicities of the amines decrease. Eventually, a stage must be reached when an amine is too weakly basic to react readily with dinitrogen trioxide. Then reaction with a more electrophilic nitrosation carrier must supersede that with dinitrogen trioxide if diazotisation is to occur. Acid-catalysis was important in the diazotisation of *p*-aminophenyltrimethylammonium perchlorate, and of *o*-chloroaniline,[4] and in the latter case was found to be due to reaction with the more

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[6] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, Chap. VII.

electrophilic nitrous acidium ion $NO \cdot OH_2^+$. Extrapolation of the results in Table 4 shows that *p*-nitroaniline, with a $\sigma$ constant of $-1{\cdot}27$,[6] is about ten times less reactive than *p*-aminophenyltrimethylammonium perchlorate towards dinitrogen trioxide. This is a sufficient reduction in reactivity, as is reported in the following paper, for *p*-nitroaniline, in similar conditions, to react mainly with the nitrous acidium ion.

## EXPERIMENTAL

*Kinetic Method, and Preparation of Solutions.*—All the runs were carried out at 0°. The rates of diazotisation have been followed by estimating the diazonium ion produced colorimetrically, as described in Part I.[2]

*p*-Chloroaniline and *p*-methoxyaniline were purified by conventional methods. Standard solutions were made up by dissolving these amines in water to which was added a slight excess of perchloric acid over that required to convert the amines into their perchlorates. The acid helped to dissolve the amines. It was allowed for in the calculation of the excess of perchloric acid used in the runs. *p*-Aminophenyltrimethylammonium chloride hydrochloride, prepared according to the method of Pinnow and Koch,[7] formed colourless plates, m. p. 219° (decomp.) (Found: Cl, 31·6. Calc. for $C_9H_{16}N_2Cl_2$: Cl, 31·8%). This chloride had to be converted into the perchlorate before use, to avoid catalysis by the chloride ions. This was done in solution: the perchlorate was not isolated. A known weight of the chloride was dissolved in water and stirred with an excess of silver oxide for 30 min. The oxide became grey as a coating of silver chloride formed. The chloride and the oxide were filtered off and washed rapidly with water: slow washing caused peptisation of the silver chloride. The solution of the quaternary hydroxide was transferred quantitatively to a volumetric flask, an equivalent amount of perchloric acid added, and the volume made up with water. There was no precipitate with silver nitrate (all the chloride had been removed).

To test whether there had been quantitative conversion into the perchlorate, samples A and B, of identical weights, of the chloride were taken, and B alone was converted into the perchlorate in solution. Sample A was just dissolved in water, the final volumes of the two solutions being the same. Identical solutions of A and B in 0·2M-perchloric acid were then made up, cooled to 0°, and diazotised in nitrous acid in sufficient excess to make the reaction go rapidly to completion. Equal samples were then withdrawn, coupled, and estimated colorimetrically:

| | | Spekker readings |
|---|---|---|
| A, solution ........................ | 0·0567M | 0·293 falling to 0·286 after 12 hr. |
| B, solution ........................ | 0·0567M | 0·284 ,, 0·276 ,, 12 hr. |

The smallness of the fall in the readings during 12 hr. showed that the diazonium ion was stable. Therefore it can be assumed that the readings are proportional to the initial amine concentrations. The readings show that about 3—4% loss of amine had occurred. Similar results were obtained with other solutions and were allowed for in the calculation of the amine concentrations in the runs.

*Conditions of Coupling.*—In the previous work 2 or 5 ml. samples of the reaction mixture, containing $\ngtr$0·05M-perchloric acid, were run into 27 ml. of the coupling solution consisting of R-salt (0·01M) and borax (0·025M or 0·05M) in water. There was thus no difficulty in the neutralisation of the perchloric acid. The present work has been done in perchloric acid from 0·002M to about 2M. Samples containing dilute acid were neutralised and coupled in the same way as before. Those containing more concentrated acid were neutralised in coupling solutions containing a quantity of borax calculated to ensure that the ratio borax : boric acid after neutralisation of the acid was constant from run to run and not far different from unity. Then the final pH was constant and about 8·5, a value at which coupling takes place readily. Runs in acid more concentrated than 2—3M are not possible by this method because a saturated borax solution is little more than 0·15M. The absorption of the dyes produced by the coupling of the diazonium ions varied a little with the coupling conditions, and whenever the excess of acid was varied drastically the calibration of the Hilger Spekker photo-electric absorptiometer, used to

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[7] Pinnow and Koch, *Ber.*, 1897, **30**, 2861.

estimate the colour densities, was checked. The calibration was made as described in Part I.[2] The calibration curves were approximately linear.

*Kinetic Results.*—Tables 5—7 contain representative examples of the kinetic results.

TABLE 5. *Diazotisation of* p-*chloroaniline at* 0°*: stoicheiometric second-order rate constants* (*sec.*$^{-1}$ *mole*$^{-1}$ *l.*) *calculated according to equations* (2) *and* (3).

Run 20

Stoicheiometric initial concentrations:

$[\mathrm{Ar{\cdot}NH_3^+}] = 0{\cdot}00328$, $[\mathrm{HNO_2}] = 0{\cdot}00164$, $[\mathrm{H^+}] = 0{\cdot}0049$M.

| $t$ (min.) | Reaction (%) | $\bar{k}_2''$ (eqn. 2) | $\bar{k}_2'$ (eqn. 3) | $t$ (min.) | Reaction (%) | $\bar{k}_2''$ (eqn. 2) | $\bar{k}_2'$ (eqn. 3) |
|---|---|---|---|---|---|---|---|
| 0 | 9·2 | — | — | 18·0 | 52·7 | 0·570 | 0·222 |
| 2·45 | 19·7 | 0·599 | 0·275 | 25·1 | 60·0 | 0·565 | 0·206 |
| 5·15 | 28·5 | 0·588 | 0·263 | 35·5 | 68·3 | 0·588 | 0·195 |
| 7·42 | 34·1 | 0·570 | 0·248 | 49·0 | 74·7 | 0·593 | 0·178 |
| 12·5 | 44·6 | 0·575 | 0·236 | 65·9 | 78·7 | 0·557 | 0·154 |

Mean value of $\bar{k}_2'' = 0{\cdot}578$.

TABLE 6. *Diazotisation of* p-*chloroaniline at* 0°*: stoicheiometric third-order rate constants in* 0·52M- *and* 0·051M-*acid.*

Run 11

[Reactants] = 0·00795M, $[\mathrm{H^+}]$ = 0·52M.

| $t$ (min.) | Reaction (%) | $\bar{k}_3''$ (sec.$^{-1}$ mole$^{-2}$ l.$^2$) |
|---|---|---|
| 0 | 16·4 | — |
| 1·33 | 28·3 | 49·3 |
| 3·28 | 39·0 | 50·5 |
| 5·00 | 45·4 | 51·2 |
| 7·90 | 53·0 | 51·7 |
| 12·5 | 60·8 | 52·6 |
| 20·7 | 67·7 | 51·6 |
| 33·5 | 74·2 | 53·5 |

Mean value of $\bar{k}_3'' = 51{\cdot}5$.

Run 14

[Reactants] = 0·00200M, $[\mathrm{H^+}]$ = 0·051M.

| $t$ (min.) | Reaction (%) | $\bar{k}_3''$ (sec.$^{-1}$ mole$^{-2}$ l.$^2$) |
|---|---|---|
| 0 | 11·4 | — |
| 3·00 | 22·6 | 272 |
| 5·93 | 24·8 | 265 |
| 16·2 | 45·6 | 270 |
| 27·2 | 55·1 | 283 |
| 38·1 | 60·7 | 285 |
| 48·0 | 63·8 | 277 |
| 88·8 | 71·0 | 250 |

Mean value of $\bar{k}_3'' = 272$.

TABLE 7. *Diazotisation of* p-*aminophenyltrimethylammonium perchlorate at* 0°*: stoicheiometric first-order rate constants during course of reaction in different concentrations of nitrous acid in excess.*

Run 12

[Amine] = 0·000231M, $[\mathrm{HNO_2}]$ = 0·00290M, $[\mathrm{H^+}]$ = 0·12M.

| $t$ (min.) | Reaction (%) | $10^3\bar{k}_1''$ (sec.$^{-1}$) |
|---|---|---|
| 2·58 | 34·8 | 2·76 |
| 4·07 | 47·3 | 2·63 |
| 5·42 | 58·7 | 2·73 |
| 7·40 | 70·9 | 2·79 |
| 10·5 | 79·5 | 2·53 |
| 15·0 | 87·6 | 2·33 |
| 24·5 | 93·6 | 3·02 |

Mean value of $\bar{k}_1'' = 2{\cdot}68 \times 10^{-3}$.

Run 12

[Amine] = 0·000115M, $[\mathrm{HNO_2}]$ = 0·00145M, $[\mathrm{H^+}]$ = 0·12M.

| $t$ (min.) | Reaction (%) | $10^3\bar{k}_1''$ (sec.$^{-1}$) |
|---|---|---|
| 3·62 | 15·1 | 0·751 |
| 4·88 | 20·8 | 0·794 |
| 7·28 | 29·1 | 0·787 |
| 9·42 | 35·9 | 0·786 |
| 12·7 | 45·2 | 0·788 |
| 15·9 | 53·6 | 0·803 |
| 20·4 | 60·8 | 0·765 |
| 27·4 | 71·2 | 0·757 |
| 37·6 | 80·0 | 0·715 |

Mean value of $\bar{k}_1'' = 0{\cdot}772 \times 10^{-3}$.

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