

Role of the reaction of nitric oxide with oxygen in the decomposition of nitrous acid in aqueous acid solution

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The decomposition of nitrous acid in air-saturated aqueous acid has been monitored. Comparison with numerical integrations indicate that this decomposition occurs *via* reaction of dissolved oxygen with nitric oxide.

Studies of nitrosation and nitrous acid catalysed nitration in dilute aqueous acid are complicated by the decomposition of nitrous acid.¹⁻³ Under anaerobic conditions this proceeds *via* the two equilibria (a) and (b).

Flash photolysis,^{4,5} pulse radiolysis,^{4,5} ¹⁸O isotopic exchange,⁶ nitrosation⁷ and diazotisation⁸ have all been used in obtaining values for the individual rate constants involved. This large body of work has been reviewed by Schwartz and White^{9,10} who have recommended values based on the averages of the individual determinations.

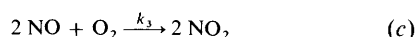
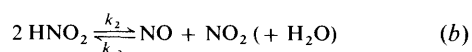
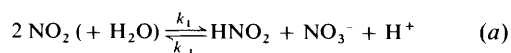
However, more recent studies using chemiluminescence NO_x detection¹¹ and the hexachloroiridate redox couple in HNO₂ solution¹² have questioned some of the values chosen.

In air-saturated solution the situation is more complex as dissolved oxygen present in solution has a considerable effect on both the rate and extent of the decomposition. There are apparently conflicting rate laws quoted for the reaction of nitrous acid with oxygen. Progrebnaya and co-workers¹³ found the reaction to be second order in nitrous acid and independent of oxygen concentration, whereas Damschen and Martin¹⁴ have reported that the reaction had a first-order dependence on oxygen and was third-order overall. To explain this anomaly the latter group proposed a mechanism involving the dimerisation of nitrous acid although it has not gained widespread support.

Instead, the reaction between nitric oxide and oxygen has been generally considered to be responsible for the effects of dissolved oxygen on the decomposition. This reaction produces nitrous acid as the sole product in aqueous solution which has been taken as evidence that the decomposition of nitrous acid could not proceed *via* step (c).

The NO₂ formed was considered¹⁴ rapidly to hydrolyse to equimolar amounts of nitrous acid and nitrate ion in marked contrast to the observed lack of any nitrate product. However, it has been suggested¹⁵⁻¹⁷ that the rate of (b) might allow formation of solely nitrous acid. This idea has been questioned by Wink *et al.*¹⁸ whose competitive trapping studies have provided evidence against the intermediacy of NO₂.

The work described in this paper was designed to ascertain whether Scheme 1, comprising steps (a)–(c) offers a complete explanation of the kinetics and products of the oxidation of nitrous acid and nitric oxide in dilute aqueous acidic solution.



Scheme 1

Table 1 Variation of k_{obs} for the decomposition of nitrous acid with initial HNO₂ concentration and acidity^a

[HNO ₂]/ 10 ⁻³ mol dm ⁻³	[H ⁺]/ mol dm ⁻³	$k_{\text{obs}}/$ 10 ⁻³ s ⁻¹	Mean $k^b/$ dm ⁶ mol ⁻² s ⁻¹
8.0	1.0	3.87 ± 3%	62.1
8.0	1.0	4.07 ± 3%	
8.0	0.1	3.95 ± 4%	
8.0	0.1	3.96 ± 5%	61.8
6.0	1.0	2.74 ± 4%	
6.0	1.0	2.82 ± 2%	77.2
6.0	0.1	2.81 ± 7%	
6.0	0.1	2.83 ± 4%	78.4
4.0	1.0	1.29 ± 4%	
4.0	1.0	1.37 ± 4%	83.1
4.0 ^c	1.0	1.42 ± 4%	
4.0	0.1	1.40 ± 4%	88.8
4.0	0.1	1.45 ± 4%	
2.0 ^d	1.0	0.400 ± 2%	89.1
2.0 ^d	1.0	0.445 ± 3%	
2.0 ^d	0.1	0.329 ± 1%	105.7
2.0 ^d	0.1	0.361 ± 2%	

^a Air-saturated aqueous solutions at 25.0 °C containing HCl (0.1–1.0 mol dm⁻³), HNO₂ (2–8 × 10⁻³ mol dm⁻³). ^b Apparent third-order rate constant. Wavelength used 385 nm except ^d 371 nm. ^c With added NaNO₃ (1 × 10⁻² mol dm⁻³).

It should be noted that this Scheme does not preclude the intermediacy of the species N₂O₃ and N₂O₄, present in mobile equilibrium with 2 HNO₂ and 2 NO₂ respectively, provided that these equilibria, under the conditions used, will be over towards the dissociated forms as all the evidence suggests. At the acidities used (0.1–1.0 mol dm⁻³ HCl), N^{III} and N^V are present almost exclusively as HNO₂ and NO₃ respectively.

Results

The kinetics of the decomposition in air-saturated solution were studied using full cells as previously² to prevent further ingress of oxygen by phase transfer from the air. When the decomposition was monitored under anaerobic conditions both the rate and extent of decomposition were dramatically reduced. In air-saturated aqueous acidic solution, with nitrous acid in large excess over dissolved oxygen, the decomposition to nitrate ion was found to follow a reasonable first-order kinetic form (Table 1). The extent of this decomposition conformed approximately to a stoichiometry of two moles of nitrous acid reaction with one mole of dissolved oxygen. The nitrous acid concentration fell by 6–24% of its initial value. The observed first-order rate constant for this decomposition was found to be virtually insensitive to varying either the acidity or the concentration of nitrate ion, and to increase almost as the

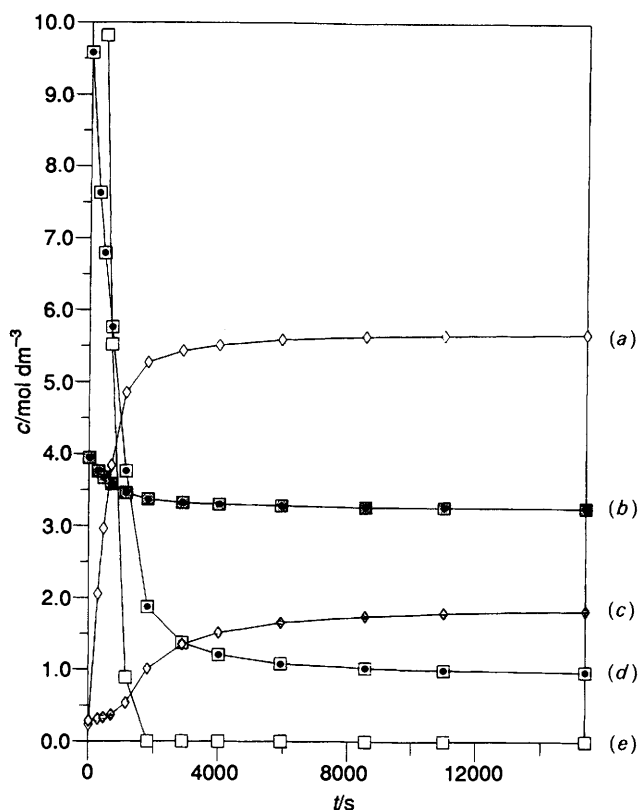


Fig. 1 Calculated concentration-time curves for inorganic species in aqueous HCl (1.0 mol dm⁻³) containing initially HNO₂ (4 × 10⁻³ mol dm⁻³) and O₂ (2.4 × 10⁻⁴ mol dm⁻³). (The other initial concentrations are zero but there are sharp initial rises in [NO] and [NO₂].) (a) 10⁴ [NO₃⁻], (b) 10³ [HNO₂], (c) 10⁴ [NO], (d) 10⁸ [NO₂], (e) 10⁵ [O₂].

square of the initial nitrous acid concentration. The apparent third-order rate constant ($k_{\text{obs}}/[\text{HNO}_2]_0^2$) for the reaction of HNO₂ with O₂ decreased from 100 to 60 mol⁻² dm⁶ s⁻¹ for a four-fold increase in [HNO₂] (last column in Table 1). Values increase at lower concentrations of HNO₂, and this, together with the observation that a plot of log rate constant *vs.* log [HNO₂] has a slope of 1.65, shows that the decomposition has a less than second-order dependence on initial nitrous acid concentration.

Discussion

Numerical integration using the computer package previously described¹⁻³ and based on Scheme 1 was found to explain the first-order kinetic form of the decrease in [HNO₂]. An illustrative set of computed concentration-time curves is shown in Fig. 1. The dependence of k_{obs} on [H⁺], [HNO₂] and [NO₃⁻] was well reproduced. No attempt to fit all five rate constants was undertaken. Instead it was decided to take four values based on those in the literature and vary only one parameter. Values for the rate constants k_1 and k_3 were considered reasonably well established in the literature and the following values were used after a small adjustment for temperature for k_1 , $k_1 = 1 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $k_3 = 2.1 \times 10^6 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$. k_2 was considered slightly less well established but its value was taken as $k_2 = 15 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, in order to simplify the numerical integration by not having too many fitting parameters. Determinations of k_{-1} in the literature vary by a factor of *ca.* 3. A value of $k_{-1} = 5 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ was chosen. The analysis was found to be quite insensitive to small deviations around this value. k_{-2} was thought much less well

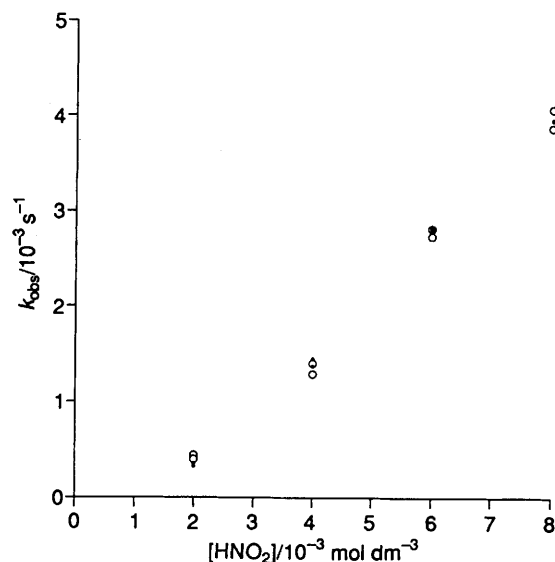


Fig. 2 Variation of k_{obs} with the concentration of H⁺ and HNO₂ in air-saturated aqueous solution containing HCl (0.1 mol dm⁻³, small dot, or 1.0 mol dm⁻³ open circle) and HNO₂

Table 2 Comparison between calculated and experimental results for HNO₂ decomposition^a

[HNO ₂]/ 10 ⁻³ mol dm ⁻³	[H ⁺]/ mol dm ⁻³	Mean $k_{\text{obs}}/$ 10 ⁻³ s ⁻¹	$k_{\text{calc}}/$ 10 ⁻³ s ⁻¹
8.0	1.0	3.97	4.14
8.0	0.1	3.96	3.93
6.0	1.0	2.78	2.58
6.0	0.1	2.82	2.49
4.0	1.0	1.33	1.35
4.0 ^b	1.0	1.42	1.36
4.0	0.1	1.41	1.27
2.0	1.0	0.423	0.362
2.0	0.1	0.345	0.374

^a Conditions as in Table 1. ^b With added NaNO₃ (1 × 10⁻² mol dm⁻³). Values used in the numerical integration: $k_1 = 1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{-1} = 5 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_2 = 15 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{-2} = 9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_3 = 2.1 \times 10^6 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

established in the literature and hence it was chosen as the parameter to be fitted.

The concentration of dissolved oxygen present varies between solutions of 1.0 mol dm⁻³ HCl and 0.1 mol dm⁻³ HCl with 0.9 mol dm⁻³ NaCl added to keep the ionic strength constant. Calculations based on literature data¹⁹ show that 1.0 mol dm⁻³ HCl contains 2.38 × 10⁻⁴ mol dm⁻³ dissolved oxygen whereas 0.1 mol dm⁻³ HCl-0.9 mol dm⁻³ NaCl contains 1.90 × 10⁻⁴ mol dm⁻³. Numerical integrations have shown that this *ca.* 30% drop in the initial concentration of dissolved oxygen has a negligible effect on k_{obs} , the observed first-order rate constant for the decomposition (Fig. 2).

The numerical integrations showed that a value of $k_{-2} = 9 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ was found to be best fitting to the experimental observations. A satisfactory fit to the experimental observations was obtained and is shown in Table 2. The less than second-order dependence on nitrous acid is well reproduced. The numerical integration was able to show that slight deviations around the stoichiometry of 2 HNO₂:1 O₂ were consistent with the effects of the equilibria in Scheme 1.

It should be noted that the value of k_{-2} found best-fitting is a little lower than the most recent determinations in the literature, however it is still a factor of three above that recommended by Schwartz and White.¹⁰

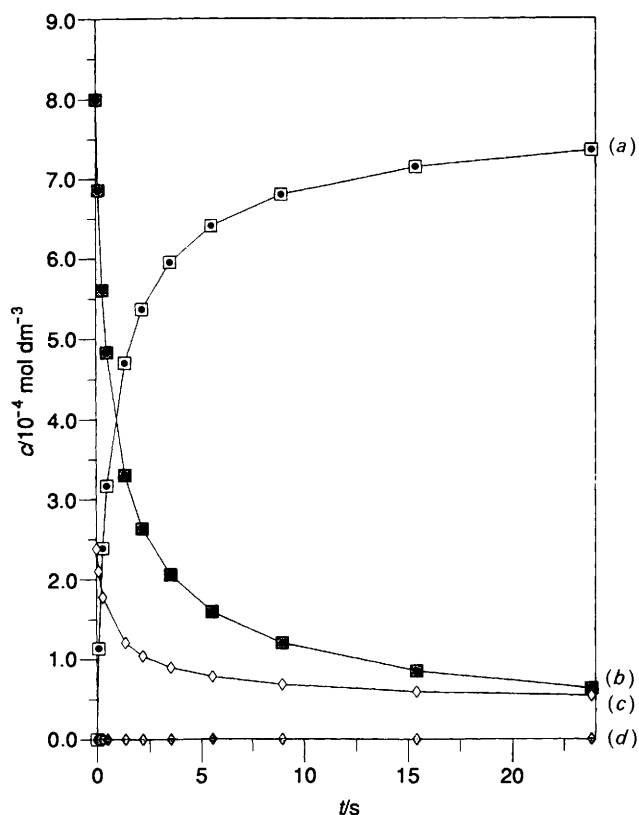


Fig. 3 Calculated concentration-time curves for inorganic species in aqueous HCl (1.0 mol dm^{-3}) containing initially NO ($8 \times 10^{-4} \text{ mol dm}^{-3}$) and O_2 ($2.4 \times 10^{-4} \text{ mol dm}^{-3}$): (a) $[\text{HNO}_2]$, (b) $[\text{NO}]$, (c) $[\text{O}_2]$, (d) $[\text{NO}_3^-]$

Scheme 1 can accommodate the findings of the previous investigators of the reaction of nitrous acid with oxygen if it is recognised that changes in initial oxygen and nitrous acid concentrations affect the nature of the rate determining step. At high ($ca. 5 \times 10^{-2} \text{ mol dm}^{-3}$) concentrations of oxygen step k_2 is rate determining whereas at lower oxygen concentrations ($ca. 2.5 \times 10^{-4} \text{ mol dm}^{-3}$), the oxygen containing term (k_3) is at least partially rate limiting. The first-order dependence on the oxygen concentration, in the experiments of Damschen and Martin¹⁴ is then further evidence of this step being rate determining at lower concentrations of oxygen.

Oxidation of nitric oxide in aqueous solution

Numerical integrations based on Scheme 1 with nitric oxide as the initial nitrogen species have been carried out. The speed of step (b) provides the explanation for the fact that nitrite is formed exclusively. Indeed the results of the calculations are the same if (a) is left out entirely. This follows because the rate constants k_1 and k_2 are of comparable magnitude, and if the concentration of NO greatly exceeds that of NO_2 then the k_2 step is the main sink for NO_2 .

It appears, therefore that the oxidation of NO in aqueous solution can be rationalised without the need to invoke any novel NO_x species as suggested by Wink and co-workers.¹⁸ That NO_2 is on the pathway is likely since it is the only product when NO is oxidised in CCl_4 .²⁰ The rate of this reaction is very close to that in aqueous solution strongly suggesting the same step is rate limiting in both media.

In conclusion, this study has confirmed that Scheme 1 gives a satisfactory representation of the observations regarding the rate and extent of decomposition of nitrous acid in dilute aqueous HCl. It is likely that the quantitative fit can be

improved as more accurate values for the individual rate constants become available. (Since this work was completed a smaller value of k_3 , $1.6 \times 10^6 \text{ mol}^2 \text{ dm}^3 \text{ s}^{-1}$ has been reported.²¹ Our present studies of the ascorbic acid-nitrous acid reaction, on which we will report soon, suggest a somewhat larger value of the same rate constant in 1M HCl.) No attempt has been made in this study to measure all the rate constants in Scheme 1 but to show that a careful selection, and in one case adjustment, of literature values leads to results consistent with experiment. This gives encouragement that the Scheme is a correct qualitative and satisfactory quantitative description of the inorganic reactions occurring when nitrous acid is used as a reagent in organic reactions in aqueous acid.

Experimental

Materials

Sodium nitrite and sodium nitrate were AR reagents. Hydrochloric acid solutions were made up by dilution of ampoules of AR grade HCl and maintained at constant ionic strength (1 mol dm^{-3}) by addition of AR sodium chloride.

Kinetics

An aqueous solution of sodium nitrite ($50 \mu\text{l}$) ($1 \mu\text{l} = 1 \text{ mm}^3$) was injected into a full 4 cm path-length UV cell containing hydrochloric acid generating a known concentration of nitrous acid *in situ*. Mixing was effected by having a small magnetic stirrer present in the solution. The decomposition was followed by UV spectroscopy at 371 or 385 nm. First-order rate constants were obtained from absorbance-time measurements over at least three half-lives by a non-linear least squares method. Comparison with decomposition under anaerobic conditions was achieved by flushing the cell with N_2 for 15 min prior to addition of the sodium nitrite. The fit to a first-order form is expressed as a percentage error, with a 3% error being approximately equivalent to an RMS error of 1×10^{-3} in absorbance. This gives a better idea of goodness of fit than RMS errors when the absorbance changes are small. Graphical examples of fits with 1% and 10% errors are in ref. 2.

Acknowledgements

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