

Kinetics of oxidation of hydrazinium ion by peroxomonosulphate in perchloric acid solution

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The kinetics of oxidation of hydrazine perchlorate by peroxomonosulphate is in agreement with the rate law

$$-\frac{d[\text{PMS}]}{dt} = \frac{k_1 K [\text{N}_2\text{H}_5^+] [\text{PMS}]_0}{1 + K [\text{N}_2\text{H}_5^+]}$$

The values of k_1 and K , where k_1 and K are rate and equilibrium constants respectively, have been determined to be $2.8 \times 10^{-4} \text{ s}^{-1}$ and $3.4 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ at 30° and $I = 1.0 \text{ mol dm}^{-3}$.

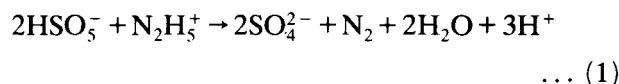
Peroxomonosulphate is an important oxidant in atmosphere¹. Hence it is necessary to investigate its redox chemistry employing a variety of inorganic substrates. Recently, the kinetics of the oxidation of hydroxylamine² and nitrite³ have been reported from this laboratory. Previously the oxidation of hydrazine with peroxodisulphate⁴ and peroxodiphosphate⁵ has been studied and as the reaction was slow, the use of catalysts such as silver(I) and copper(II) was necessary. Recently its oxidation with peroxomonophosphate⁶ has been studied and for one of the oxidation paths a mechanism involving the equilibrium between normal and active forms of H_3PO_5 has been proposed.

Experimental

Peroxomonosulphate (OXONE) having the formula $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (Aldrich) was standardised iodometrically^{2,3,7}. Hydrazine perchlorate was prepared by the reaction of hydrazine hydrate and perchloric acid. The reaction was initiated by mixing temperature equilibrated solutions of PMS and hydrazine perchlorate. The kinetics were followed by analysing aliquot portions for unreacted PMS iodometrically^{2,3,7}. The control experiment showed that hydrazine perchlorate did not interfere in the estimation of PMS.

Study of this reaction was beset with the problem of reproducibility ($\pm 15\%$). Hence, each kinetics run was repeated three times and average values of pseudo-first order rate constants have been used in all calculations.

For determining stoichiometry of the reaction, in some experiments $[\text{N}_2\text{H}_5^+]$, and in others $[\text{PMS}]$ was kept in excess. In the former set of experiments unreacted [hydrazine] was determined with iodate. In latter experiments, unreacted $[\text{PMS}]$ was determined iodometrically. The results were consistent with Eq. (1). With the concentrated reactant solutions, rapid evolution of nitrogen was seen. Incidentally, a similar stoichiometry has been noted with other oxidants^{5,6}.



Results and discussion

$[\text{PMS}]$ was varied in the range $(1.0-5.0) \times 10^{-3} \text{ mol dm}^{-3}$ under pseudo-first order conditions by maintaining the ratio $[\text{N}_2\text{H}_5^+]/[\text{HSO}_5^-]$ at > 3 which in equivalent terms (Eq. 1) becomes more than 6. Pseudo-first order rate constants, k_{obs} , were found not to depend on $[\text{PMS}]_0$. The results of $[\text{N}_2\text{H}_5^+]$ variation are shown in Fig. 1. On increasing $[\text{N}_2\text{H}_5^+]$, initially the rate shows a slight

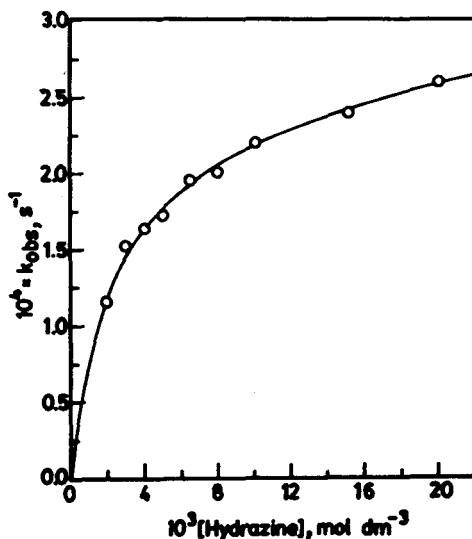


Fig. 1 - Dependence of pseudo-first order rate constant, k_{obs} , on $[\text{hydrazine}]$ at $[\text{PMS}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.01 \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ and temp. = 30°C .

increase but attains a saturation value at higher $[\text{N}_2\text{H}_5^+]$. From a log-log plot between k_{obs} and $[\text{N}_2\text{H}_5^+]$ an order of 0.33 in $[\text{N}_2\text{H}_5^+]$ was determined. k_{obs} values were found to fit the rate law (2).

$$-\frac{d[\text{PMS}]/dt}{[\text{PMS}]} = k_{\text{obs}} = \frac{k_1 K [\text{N}_2\text{H}_5^+]}{1 + K [\text{N}_2\text{H}_5^+]} \quad \dots (2)$$

where k_1 and K are rate and equilibrium constants respectively. From the double reciprocal plot of k_{obs} and $[\text{N}_2\text{H}_5^+]$ (correlation coefficient, 0.99), the values of K and k_1 were obtained to be $3.4 \times 10^2 \text{ mol dm}^{-3}$ and $2.8 \times 10^{-4} \text{ s}^{-1}$ respectively at 30° and $I = 1.0 \text{ mol dm}^{-3}$.

A variation in $[\text{H}^+]$, in the range 0.01 to 0.8 mol dm^{-3} with perchloric acid, and in the range $10^{-3} - 4 \times 10^{-4} \text{ mol dm}^{-3}$ with the help of perchloric acid and sodium acetate mixtures, showed the reaction to be insensitive to $[\text{H}^+]$. In fact k_{obs} increased by about 10% only when $[\text{H}^+]$ was varied from 4×10^{-4} to 0.8 mol dm^{-3} . Change in ionic strength (varied with sodium nitrate) had no effect on the rate. The overall energy of activation was determined to be 52 kJ mol^{-1} .

Some experiments were done to examine the effect of added metal ions such as Fe^{+3} , Mn^{+2} , Cu^{+2} , Co^{+2} , which are commonly found in trace amounts in water, and of added EDTA. Interestingly metal ions ($1 \times 10^{-6} \text{ mol dm}^{-3}$) and EDTA ($1 \times 10^{-4} \text{ mol dm}^{-3}$) did not affect the rate. Only Os(VIII) had a significant rate increasing effect.

The acid dissociation constant of N_2H_5^+ is reported⁸ to be quite low and hence hydrazine would predominantly exist as N_2H_5^+ in the range of acidity used in these experiments. Under the same conditions peroxomonosulphate will exist as HSO_5^- as its pK_a is reported⁹ to be 9.8. It is therefore reasonable to assume HSO_5^- and N_2H_5^+ to be reactive, since rate is independent of $[\text{H}^+]$.

The most unusual features of this reaction are the nature of dependence of rate on $[\text{N}_2\text{H}_5^+]$ and its independence on $[\text{H}^+]$. There are three possible ways in which the observed kinetics can be explained, first of which is Scheme (1) which involves the complex formation between hydrazine and a trace metal ion catalyst, M^{n+} , present in solutions as impurity. The absence of any effect



Scheme 1

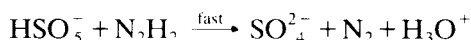
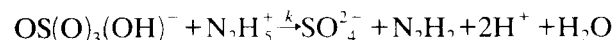
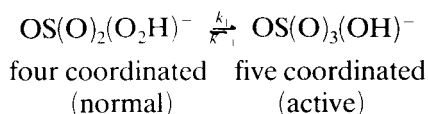
of commonly found trace metal ions and of EDTA rules out Scheme 1. The second possible mechanism assumes an ion-pair formation between N_2H_5^+ and HSO_5^- as in Scheme 2.



Scheme 2

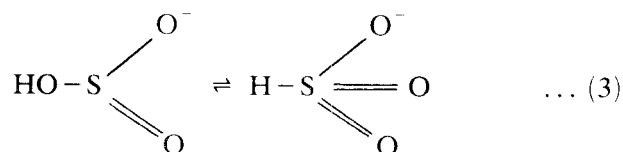
Under the condition $[\text{N}_2\text{H}_5^+] > [\text{HSO}_5^-]$, Scheme 2 leads to a rate law which would be equivalent to Eq. (2) through $k_1 = k$. Equation (2) predicts that when $K[\text{N}_2\text{H}_5^+] \gg 1$, k_{obs} will become independent of $[\text{N}_2\text{H}_5^+]$ as has been experimentally observed. In the other extreme condition ($1 \gg K[\text{N}_2\text{H}_5^+]$), the reaction will be characterized by a second order kinetics. As the second situation required using extremely low reactant concentrations, it could not be realised. However, in the intermediate region the order in N_2H_5^+ is found to be less than one as predicted.

The third possible mechanism involves the conversion of HSO_5^- into its more active form in a rapid pre-equilibrium as in Scheme 3.



Scheme 3

Scheme 3 is analogous to the one proposed by Dhas *et al.*⁶ for $\text{H}_3\text{PO}_5 - \text{N}_2\text{H}_5^+$ reaction. It has been argued⁶ that the conversion of normal form into active one is accompanied by structural changes and the penta-coordinated active form probably has trigonal bipyramidal/square pyramidal structure, which are more facile for attack by N_2H_5^+ . It is not out of place to point out that such tautomeric equilibria have been invoked in case of hypophosphorous and phosphorous acids earlier¹⁰⁻¹⁵. Incidentally in case of a sulphur compound, that is bisulphite ion, the evidence for a similar equilibrium (3) does exist¹⁶. This indirectly supports Scheme 3.



Scheme 3 will lead to a rate law which will be equivalent to rate law (2) and $K = k_1/k_{-1}$.

The oxidation of $N_2H_5^+$ by HSO_5^- (30°C) and H_3PO_5 (35°C) occurs by similar mechanism and the values of K and k_1 for two reactions are 3.4×10^2 , $2.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and 2.8×10^{-4} and $2.6 \times 10^{-4} \text{ s}^{-1}$ respectively. Keeping in view the temperature difference, the two oxidants do not differ substantially in their reactivity towards $N_2H_5^+$. A similar order of reactivity has been noted in the reaction of iodide¹⁷ with HSO_5^- and H_3PO_5 and of OH radicals¹⁸ with HSO_5^- and HPO_3^{2-} .

Acknowledgement

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