

Role of Mercury(II) Acetate in Oxidation of Azide Ion by N-Bromosuccinimide in Aqueous Medium

T S VIVEKANANDAM & M S RAMACHANDRAN*

School of Chemistry, Madurai Kamaraj University,
Madurai 625 021

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Rate of oxidation of azide ion by N-bromosuccinimide (NBS) in aqueous medium is found to be proportional to $[N_3^-]$ and $[NBS]$ at constant $[Hg(OAc)_2]$. The product of oxidation is pure nitrogen. The reaction is independent of ionic strength. The reaction proceeds through an initial complex formation presumably between NBS and $Hg(OAc)_2$, the resulting complex acting as an active oxidant. The role of $Hg(OAc)_2$ as a scavenger of formed Br^- and as a catalyst has been established.

As a follow-up of our earlier work on the oxidation of azide ion^{1,2}, we report in this note the results of investigation on the kinetics of oxidation of azide by N-bromosuccinimide (NBS) in aqueous medium.

Stock solutions of NBS (Fluka, AG purum) and azide (Riedel) were always prepared afresh and standardised. The ionic strength (μ) of the medium was maintained between 0.15 and 1.20 mol dm⁻³ using $NaClO_4$. All the other reagents used were of AR (BDH) grade. All solutions were prepared in doubly distilled water. The reaction was followed by measuring the nitrogen gas evolved as described in our earlier publication² and for stoichiometric runs unreacted N_3^- was also determined cerimetrically.

The stoichiometry of the reaction was determined under the conditions $[N_3^-] \gg [NBS]$ after the completion of the reaction. The results showed that, in neutral medium, the stoichiometry in the presence and absence of $Hg(OAc)_2$ could be represented by Eq. (1).



The evolution of N_2 followed a perfect first order upto 60% of the reaction. The first order rate constants at various $[NBS]$, constant $[N_3^-]$ and $[Hg(OAc)_2]$ showed that the rate was directly proportional to $[NBS]$ (Table 1). Further at constant $[NBS]$ and $[Hg(OAc)_2]$, the rate was directly proportional to the $[N_3^-]$ (Table 1). The plot of $1/k_{obs}$ versus $1/[N_3^-]$ was linear with a definite positive intercept showing the formation of a complex intermediate in the reaction. At constant $[N_3^-]$ and $[NBS]$ addition of $Hg(OAc)_2$ increased the rate, which reached a constant value at $[Hg(OAc)_2] = [NBS]$ (Table 2). The plot of k_{obs} versus $[Hg(OAc)_2]$ was linear with an intercept only when

Table 1—Rate Constants of Reaction Between N_3^- and NBS in Neutral Medium

$[Hg(OAc)_2] = 0.01 \text{ mol dm}^{-3}$; temp. = 30°C			
$[N_3^-]$ (mol dm ⁻³)	$[NBS]$ (mol dm ⁻³)	μ (mol dm ⁻³)	$k_{obs} \times 10^3$ (s ⁻¹)
0.15	0.005	0.15	3.15
0.15	0.006	0.15	3.04
0.15	0.007	0.15	3.04
0.15	0.008	0.15	3.17
0.15	0.010	0.15	3.12
0.15	0.005	0.55	3.15
0.15	0.005	0.75	3.04
0.15	0.005	0.95	3.09
0.06	0.005	1.20	0.94
0.09	0.005	1.20	1.97
0.12	0.005	1.20	2.83
0.15	0.005	1.20	3.10
0.18	0.005	1.20	4.33
0.21	0.005	1.20	4.58
0.24	0.005	1.20	4.83
0.28	0.005	1.20	5.18

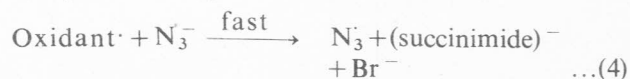
Table 2—Rate Dependence on $[Hg(OAc)_2]$

$[N_3^-] = 0.15 \text{ mol dm}^{-3}$; $[NBS] = 0.005 \text{ mol dm}^{-3}$; $\mu = 0.55 \text{ mol dm}^{-3}$; temp. = 30°C

$[Hg(OAc)_2] \times 10^4$ (mol dm ⁻³)	$k_{obs} \times 10^3$ (s ⁻¹)	$[Hg(OAc)_2] \times 10^4$ (mol dm ⁻³)	$k_{obs} \times 10^3$ (s ⁻¹)
5	0.44	40	2.50
10	0.65	45	2.80
15	0.98	50	3.10
20	1.20	65	3.10
25	1.60	80	3.15
30	1.92	100	3.10
35	2.20		

$[Hg(OAc)_2] \ll [NBS]$. Under the condition $[Hg(OAc)_2] > [NBS]$, k_{obs} remained constant, implying some interaction between NBS and $Hg(OAc)_2$. The addition of succinimide had negligible effect on the rate. The rate was independent of the ionic strength of the medium. The reaction became fast in the presence of H^+ ion and the rate could not be measured.

In the light of the above experimental results, the following tentative mechanism can be proposed (see Scheme 1).





Scheme 1

The intermediate (N_6) in step (5) has been identified earlier by Hayon and Simic in the photolysis of azide ion³. The Br^- ion in step (4) may be removed⁴ by $\text{Hg}(\text{OAc})_2$ either as HgBr_2 or HgBr_4^{2-} .

Based on Scheme 1, the rate law can be represented by Eq. (6).

$$3 \frac{d[\text{N}_2]}{dt} = - \frac{d[\text{NBS}]}{dt} = k_{\text{obs}} [\text{NBS}] [\text{N}_3^-] \quad \dots(6)$$

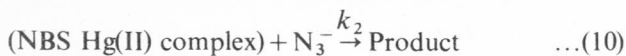
$$= \frac{k_1 K [\text{NBS}] [\text{N}_3^-]}{1 + K [\text{N}_3^-]} \quad \dots(7)$$

$$k_{\text{obs}} = \frac{k_1 K [\text{N}_3^-]}{1 + K [\text{N}_3^-]} \quad \dots(8)$$

This accounts for the observed kinetics and the values of K and k_1 are found to be $4.75 \pm 0.20 \text{ dm}^3 \text{ mol}^{-1}$ and $5.30 \pm 0.15 \times 10^{-3} \text{ s}^{-1}$ respectively.

It may be pointed out that all kinetic studies have been made in the presence of $\text{Hg}(\text{OAc})_2$ in order to avoid any possible oxidation by Br_2 which may be produced by the reaction: $\text{NBS} + \text{Br}^- \rightarrow \text{Br}_2 + (\text{succinimide})^-$. The effect of added $\text{Hg}(\text{OAc})_2$ is rather perplexing. If it was acting as a trapping agent for Br^- formed in step (4), then a decrease in its concentration should have resulted in either an increase in the rate constant or at least k_{obs} should have remained constant. This is contrary to our observation. The observed decrease in the rate constant with decrease in $[\text{Hg}(\text{OAc})_2]$ can be explained by assuming that $\text{Hg}(\text{OAc})_2$ is involved in the rate-determining step. The interaction of Hg^{2+} with N_3^- is ruled out.

Since $\text{Hg}(\text{II})$ salts are known⁵ to form complexes with N and O donors we envisage that NBS forms a complex with $\text{Hg}(\text{OAc})_2$ (Eq. 9), which acts as an oxidant. Under this condition, the reaction scheme will be given by Eqs (10) and (11).



The rate will be given by Eq. (12).

$$\begin{aligned} - \frac{d[\text{NBS}]}{dt} &= k_{\text{obs}} [\text{N}_3^-] [\text{NBS}]_{\text{T}} \\ &= k_2 [\text{N}_3^-] [\text{NBS Hg(II) complex}] + \\ &\quad k_3 [\text{NBS}]_{\text{free}} [\text{N}_3^-] \quad \dots(12) \end{aligned}$$

If the equilibrium constant K_1 is large, then all the $\text{Hg}(\text{OAc})_2$ will be in the form of complex. Therefore, at constant $[\text{N}_3^-]$, $[\text{NBS}]$ and when $[\text{Hg}(\text{OAc})_2] < [\text{NBS}]$, the k_{obs} is given by Eq. (13).

$$k_{\text{obs}} = \frac{(k_2 - k_3) [\text{Hg(II)}]}{[\text{NBS}]_{\text{T}}} + k_3 \quad \dots(13)$$

This equation explains the effect of $\text{Hg}(\text{OAc})_2$ on the observed kinetics. The values for k_2 and k_3 are $3.26 \times 10^{-3} \text{ s}^{-1}$ and $0.16 \pm 0.02 \times 10^{-3} \text{ s}^{-1}$ respectively. The value of k_2 is exactly equal to the value of k_{obs} at $[\text{N}_3^-] = 0.15$; $[\text{NBS}] = 5 \times 10^{-3}$ and $[\text{Hg}(\text{OAc})_2] = 0.01 \text{ mol dm}^{-3}$ (Table 1). This proves the validity of our assumption. Therefore the reactive species of the oxidant is NBS-Hg(II) complex and the values of k_1 and K in Eq. (8) correspond to oxidant NBS-Hg(II) complex since all the kinetics are carried out under the condition $[\text{Hg}(\text{OAc})_2] \gg [\text{NBS}]$. This clearly shows that in the oxidation of N_3^- by NBS, $\text{Hg}(\text{OAc})_2$ acts as a catalyst by forming a complex with NBS.

The effect of H^+ can be explained by the fact that HN_3 is the active species and HN_3 reacts more readily and rapidly with NBS than N_3^- as observed in the oxidation of N_3^- by periodate⁶.

From the temperature dependence of the k_{obs} the activation parameters for overall reaction have been computed (under the condition $[\text{Hg}(\text{OAc})_2] \gg [\text{NBS}]$) as $\Delta H^\ddagger = 58.8 \text{ kJ mol}^{-1}$ and $-\Delta S^\ddagger = 102.1 \text{ J deg}^{-1} \text{ mol}^{-1}$. A comparison of overall $-\Delta S^\ddagger$ for this oxidation with that of the oxidation² of azide by Br_2 suggests that the active oxidant species is not the NBS molecule since the magnitude for the reaction between a negative ion and a dipolar molecule⁷ would be very less, of the order of zero.

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References

- 1 Ponnuraj V, Ramachandran M S, Vivekanandam T S & Chandra Singh U, *Bull chem Soc. (Japan)*, **51** (1978) 460.
- 2 Vivekanandam T S, Chandra Singh U & Ramachandran M S, *Int J chem Kinet*, **13** (1981) 199.
- 3 Hayon E & Simic M, *J Am chem Soc.*, **92** (1970) 7486.
- 4 Bailor (jr) J C, *The chemistry of co-ordination compounds* (Reinhold, New York) 1965, 4.
- 5 Aylett B J, *Comprehensive inorganic chemistry*, Edited by J C Bailor, H J Emeleus, Ronald Nyholm & A F Trotman-Dickenson (Pergamon, Oxford) 1973, 324.
- 6 Vivekanandam T S & Ramachandran M S, *Indian J Chem.* (In press).
- 7 Laidler K J, *Chemical kinetics*, (McGraw-Hill, New York) 1965.