

Ir(III) Catalysis in N-Bromosuccinimide Oxidation of Lactic Acid in Perchloric Acid

B.N. SINGH*, Arjun Prasad and S.N. SINGH

*Department of Chemistry
Nalanda College, Bihar Sharif
Nalanda, Bihar, India*

Kinetic data on Ir(III) catalysed oxidation of lactic acid (LA) by N-bromosuccinimide (NBS) in perchloric acid in the presence of mercuric acetate as scavenger show first-order in each NBS, LA and Ir(III) and zero-order in $[H^+]$. Negative effect of succinimide, positive effect of chloride ions and zero effect of ionic strength have been observed. Mechanistic steps are discussed.

INTRODUCTION

N-Bromosuccinimide (NBS) is a potent oxidant and has been widely used in the quantitative estimations¹⁻³. Oxidation kinetics involving NBS and alcohols⁴, esters⁵ and a few ketones⁶⁻⁸ have been reported but there is no report on mode of Ir(III) catalysed NBS oxidations. This prompted us to study Ir(III) catalysed NBS oxidation of lactic acid in perchloric acid.

EXPERIMENTAL

All the chemicals were of AnalaR grade. Aqueous solution of NBS was always prepared fresh and its strength was checked by estimating its active bromine iodometrically. Ir(III) chloride (Johnson Matthey) solution was prepared by dissolving the sample in HCl of known strength. Reaction vessels were blackened from outside. Progress of the reaction was monitored by estimating the amount of unconsumed NBS at regular time intervals iodometrically.

RESULTS AND DISCUSSION

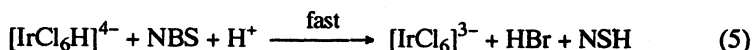
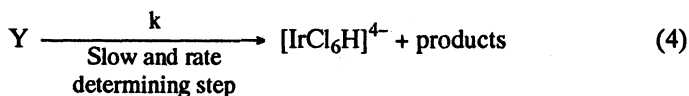
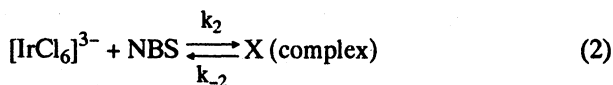
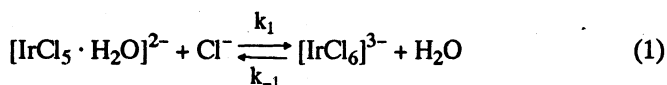
Table 1 records first-order constants for varying $[NBS]$. First order dependence on each lactic acid and Ir(III) was obvious from $\log K_1$ vs. $\log [lactic\ acid]$ or $\log [Ir(III)]$ plots, yielding straight lines with slopes nearly one. Zero-order kinetics in $[H^+]$ is obvious from constant values of first-order constant at different $[H^+]$ (Table 1). Successive additions of succinimide and chloride ions had negative and positive effects respectively while addition of mercuric acetate and sodium perchlorate had no effect.

TABLE 1

EFFECT OF VARIATION OF [NBS] AND [H⁺] ON REACTION RATEat 35°C [Lactic acid] = 5.00 × 10⁻² M [HClO₄] = 1.00 × 10⁻² M (unless otherwise stated)[Ir(III)] = 2.20 × 10⁻⁷ M, [KCl] = 4.00 × 10⁻² M[Hg(OAc)₂] = 4.00 × 10⁻³ M and μ (ionic strength) = 6.00 × 10⁻² M

[NBS] × 10 ⁴ M	2.50	5.00	7.50	10.00	12.50
k ₁ × 10 ⁵ min ⁻¹	17.82	17.76	17.86	17.80	17.88
^a [HClO ₄] × 10 ² M	1.00	2.00	3.00	4.00	5.00
k ₁ × 10 ⁵ · min ⁻¹	17.76	17.86 ^b	17.80 ^c	17.78 ^d	17.72 ^e
^a [NBS] = 10.00 × 10 ⁻⁴ M, μ = 7.20(b), 8.20(c), 9.20(d) & 10.20(e) × 10 ⁻² M					

Zero effect of mercuric acetate ensures pure NBS oxidation and thus mercuric acetate⁹ acts only as scavenger. Positive effect of chloride ions on reaction rate favours the equilibrium(I) to right side and thus [IrCl₆]³⁻ is the active species of Ir(III) chloride in acid media¹⁰. In acid media NBS as such, N⁺BSH and Br⁺ have been reported as possible reactive species⁷. If N⁺BSH or Br⁺ is taken as main active species, rate law, derived on either basis, does not conform to observed kinetics. Hence NBS as such is proposed as active species. The following scheme is proposed for the title reaction where NSH is succinimide.



Here Y stands for activated complex.

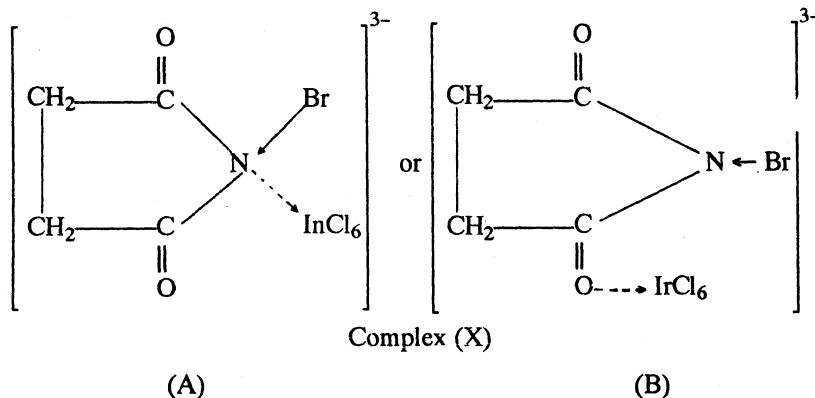
Application of the steady state treatment with the reasonable approximation yields the rate law (1).

$$-\frac{d[\text{NBS}]}{dt} = \frac{k^1[\text{NBS}][\text{LA}][\text{Ir(III)}]_T[\text{Cl}^-]}{k_{-3}[\text{NSH}] + kK_1[\text{Cl}^-]} \quad (1)$$

where $k^1 = K_1K_2k_3k$, $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$

The rate law (1) conforms to all kinetic observations.

The structure of the complex (X) formed in step (ii) is not known, but it may be assigned structures (A) or (B) to explain its hydride ion abstracting capacity.



In either case, the N-atom will become electron deficient which will facilitate shifting of electron pair of N-Br bond to N-atom, making Br slightly positive. Consequently, the electrophilic character and, hence, the hydride ion abstracting capacity of NBS is increased sufficiently after complexation leading to its interaction with lactic acid. The hydride ion transfer concept is also supported by Freeman and Scott¹¹.

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