

Research Article

Synergistic Effect of [Ru(III) + Ir(III)] in N-Bromosuccinimide Reaction with Certain Aliphatic Ketones: A Kinetic Study

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Dramatic rate enhancements have been observed in the oxidation of acetone (MMK), ethyl methyl ketone (EMK), and isobutyl methyl ketone (IBMK) by N-bromosuccinimide (NBS) in the presence of a mixture of metal ions [Ru(III) + Ir(III)]. The rate of oxidation in the the [Ru(III) + Ir(III)] system is much faster than either in the Ru(III) or in Ir(III) catalyzed system. The order in [NBS] was found to be zero both in catalyzed as well as uncatalyzed reactions. However, the order in [ketone] changed from unity to a fractional one in metal ion catalyzed systems. On the basis of kinetic features, the most plausible mechanism involving the oxidation of [Ir(III)-ketone] by Ru(III) to give [Ir(V)-ketone] and Ru(I) in the rate limiting step is proposed. Ru(I) thus formed is oxidized by NBS to Ru(III) in a fast step is discussed and individual rate parameters were evaluated.

1. Introduction

Bimetallic catalysts often exhibit improved properties than either of the single metal catalysts. This is generally called the synergistic effect. The presence of the synergistic activity of platinum and rhodium in bimetallic catalysts and possible reasons for the effects has been discussed in the literature [1–10]. The synergistic activity of certain mixed catalyst systems, namely, [Ag(I) + Mn(II)], [Ag(I) + Cu(II)], [Ru(III) + Mn(II)], [Ir(III) + Mn(II)] and [Ru(III) + Os(VIII)], and so forth, has been the subject of interest in the field of homogenous redox reactions by several workers [4–10] in recent years.

N-bromosuccinimide (NBS) has been used as a versatile oxidizing agent and analytical reagent in acid and alkaline media [11–24]. In recent past microconcentrations (10^{-6} to 10^{-5} M) of Ru(III) and Ir(III) have been employed as an efficient catalyst in N-bromosuccinimide (NBS) oxidations and other redox systems [25–31]. Recently we have reported that Ru(III) 34 catalyzed the oxidation of aliphatic ketones by NBS in aqueous acetic acid [27], wherein trace amount of Ru(III) is used as a catalyst. However, kinetic studies involving the mixture of metal ions as a catalyst also appeared to be scanty in NBS oxidations. Preliminary experiments

involving the mixture of Ru(III) and Ir(III) as a catalyst in NBS-aliphatic ketone redox system in aqueous acetic acid medium containing H_2SO_4 indicated that the reaction rate is much greater than the sum of the reaction rates when metal ions such as Ru(III) and Ir(III) are separately employed as a catalyst. These striking features have become stimulus for us to take up a systematic kinetic study comprising the catalytic oxidation of certain aliphatic ketones by NBS by using Ir(III) alone and a mixture of [Ru(III) + Ir(III)] as homogeneous catalysts. Less than millimolar Ru(III) and Ir(III) have been used in the composition of mixed catalysts in this study.

2. Experimental

Reagents used in this study were analytical grade. Stock solutions of ketone and NBS were prepared by dissolving appropriate amounts of samples in doubly distilled water. The solution of NBS was standardized iodometrically against sodium thiosulphate by a known procedure [12]. Succinimide (NHS) was prepared by a known method and recrystallised from alcohol and the stock solution was prepared by dissolving the required quantity in distilled water. Solutions of all the other reagents were prepared

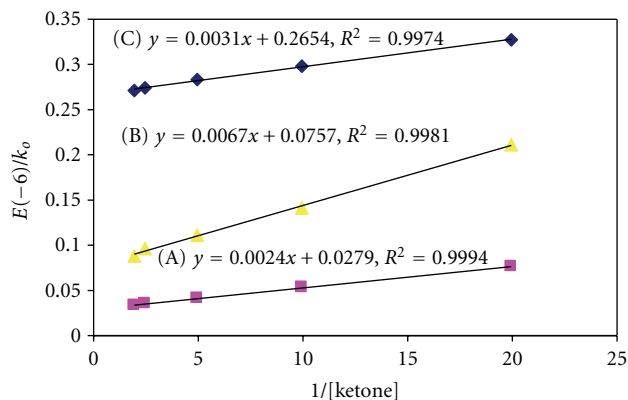


FIGURE 1: Plot of $1/k_o$ versus $1/[\text{ketone}]$. (A) Acetone, (B) EMK, and (C) IBMK; 10^3 [NBS] = 5.00 mol dm^{-3} ; 10^2 $[\text{H}^+]$ = 5.00 mol dm^{-3} ; HOAc = 10% (v/v); 10^5 [Ru(III)] = 2.09 mol dm^{-3} ; 10^6 [Ir(III)] = 6.67 mol dm^{-3} ; 10^2 $[\text{Hg}(\text{OAC})_2]$ = 2.00 mol dm^{-3} ; Temp. = 300 K.

by dissolving the requisite amounts of samples in doubly distilled water. Sulphuric acid (H_2SO_4) and KHSO_4 or NaClO_4 were used to provide the required acidity and to maintain the ionic strength (μ), respectively.

3. Kinetic Measurements

All kinetic measurements were performed under pseudo-first-order conditions with [ketone] at least 10-fold in excess over [NBS] at a constant ionic strength (μ) and desired temperature. The reaction was initiated by mixing previously thermostated solutions of NBS and Ketone, which also contained the necessary quantities of acid and NaClO_4 . The progress of the reaction was followed by the iodometric determination of the unreacted [NBS] in aliquots (5 mL each) of the reaction mixture withdrawn at regular time intervals. The initial rates (V) were evaluated from the tangential slopes of the plots of [NBS] versus time. The initial rate (V) values were reproducible within $\pm 5\%$. The oxidation product was identified as a 1,2-dicarbonyl compound according to standard procedures cited in the literature.

The effect of dissolved oxygen on the rate of the reaction was studied by preparing the reaction mixture and following the reaction under nitrogen atmosphere. No significant difference between the results obtained under nitrogen atmosphere and those obtained in the presence of air were observed. However, fresh solutions were used during the experiments.

4. Results and Discussion

4.1. Salient Kinetic Features of the Study. (1) When [NBS] is taken for greater than [EMK], the stoichiometry of the reaction has been found to be $2[\text{NBS}] : 1[\text{EMK}]$. The reaction kinetics indicated “zero”-order dependence on [NBS] and fractional in [Ketone] which could be seen from data presented in Table 1 and Figure 1. Further, the plots of $1/\text{rate}$

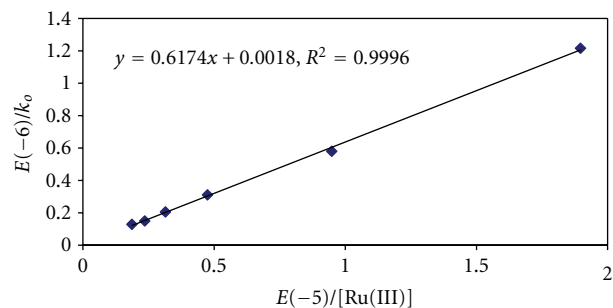


FIGURE 2: Plot of $1/k_o$ versus $1/[\text{Ru(III)}]$. 10^3 [NBS] = 5.00 mol dm^{-3} ; [EMK] = $0.100 \text{ mol dm}^{-3}$; HOAc = 10% (v/v); 10^2 $[\text{H}^+]$ = 5.00 mol dm^{-3} ; 10^7 [Ir(III)] = 5.05 mol dm^{-3} ; 10^2 $[\text{Hg}(\text{OAC})_2]$ = 2.00 mol dm^{-3} ; Temp. = 300 K.

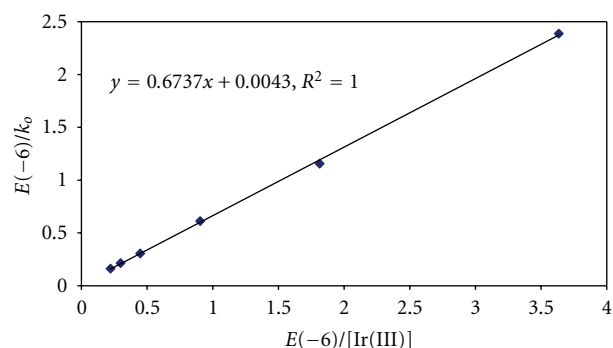


FIGURE 3: Plot of $1/k_o$ versus $1/[\text{Ir(III)}]$. 10^3 [NBS] = 5.00 mol dm^{-3} ; [EMK] = $0.100 \text{ mol dm}^{-3}$; HOAc = 10% (v/v); 10^2 $[\text{H}^+]$ = 5.00 mol dm^{-3} ; 10^5 [Ru(III)] = 2.09 mol dm^{-3} ; Temp. = 300 K 10^2 $[\text{Hg}(\text{OAC})_2]$ = 2.00 mol dm^{-3} .

as a function of $1/[\text{Ketone}]$ were linear with positive slope and definite intercept on $1/\text{rate}$ axis (Figure 1) indicating a complex formation of ketone with the catalysts.

(2) At constant $[\text{H}^+]$, ionic strength (μ), [EMK], [NBS], and [Ir(III)] order in [Ru(III)] was one as could be seen from the constancy of $[k_o/[\text{Ru(III)}]]$ values over a wide concentration range of Ru(III). Further, the plot of $1/\text{rate}$ versus $1/[\text{Ru(III)}]$ has been found linear passing through origin and with a positive slope (Table 2 and Figure 2).

(3) At constant $[\text{H}^+]$, ionic strength (μ), [EMK], [NBS], [Ru(III)], and temperature order in [Ir(III)] was also unity, which could be evidenced from the constancy of $[k_o/[\text{Ir(III)}]]$ values over a wide variation of [Ir(III)]. The plot of $1/\text{rate}$ versus $1/[\text{Ir(III)}]$ was linear passing through origin and with a positive slope (Table 3 and Figure 3).

(4) A ten-fold concentration variation of additives such as $[\text{KHSO}_4]$, $[\text{NaClO}_4]$, or $[\text{H}_2\text{SO}_4]$ did not alter the rate of oxidation to any significant extent in the present study.

(5) Rate data presented in Table 4 depicts that an increase in the [HOAc] increased the rate of oxidation. The increase in the rate of oxidation with increase in the polarity of the medium suggests that the transition state is more polar than the reactants. Laidler-Eyring's plot of $\log k_o$ against the inverse of the relative permittivity ($1/D$) indicated fairly good

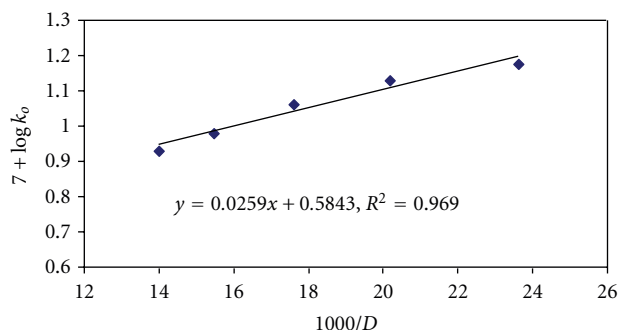


FIGURE 4: Effect of variation of solvent [% HOAc (v/v)] in NBS-EMK in [Ru(III) + Ir(III)] catalyzed reaction; Laidler-Eyring's plot of $\log k_o$ versus $1/D$. 10^3 [NBS] = 5.00 mol dm^{-3} ; [EMK] = $0.100 \text{ mol dm}^{-3}$; 10^2 [Hg(OAc) $_2$] = 2.00 mol dm^{-4} ; Temp. = 300 K ; 10^6 [Ru(III)] = 5.25 mol dm^{-3} ; 10^7 [Ir(III)] = 5.50 mol dm^{-3} .

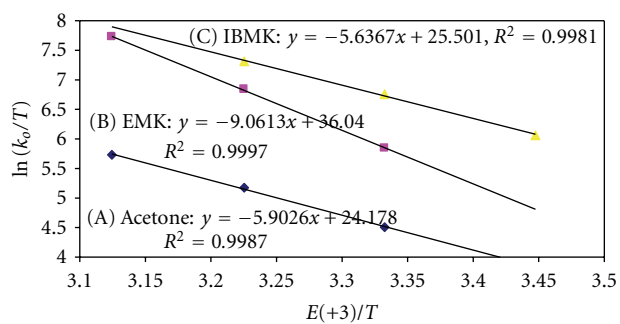


FIGURE 5: Eyring's plot of $\ln(k_o/T)$ versus $10^3/T$.

linearity ($R^2 = 0.969$) with a positive slope ($m = 0.025$). The value of m suggests that the transition state is more polar than the reactants. Thus considerable charge separation takes place in the transition state of the reaction.

(6) A four-fold change (0.02 to 0.08 M) in the concentration of mercuric acetate did not affect the rate of reaction to any considerable extent.

(7) Addition of olefin monomers such as acrylamide or acrylonitrile to the reaction system did not alter the reaction rate or indicate polymer formation ruling out the participation of free radical intermediates in the oxidation mechanism.

5. Mechanism of Oxidation

The rate of oxidation in [Ru(III) + Ir(III)] catalyzed system has been found to be greater than the sum of the reaction rates where Ru(III) and Ir(III) are employed separately as catalysts. Such a trend points out the synergistic activity of [Ru(III) + Ir(III)] on the rates of oxidation (Table 1). Further, the reaction kinetics in [Ru(III) + Ir(III)] catalyzed system is also similar to those when Ru(III) or Ir(III) is employed separately as catalysts. Observed reaction kinetics coupled with the linearity of reciprocal plot between $1/\text{rate}$ versus $1/[\text{ketone}]$ (Figure 1) suggests the formation of a precursor prior to the rate limiting oxidation step. At this point

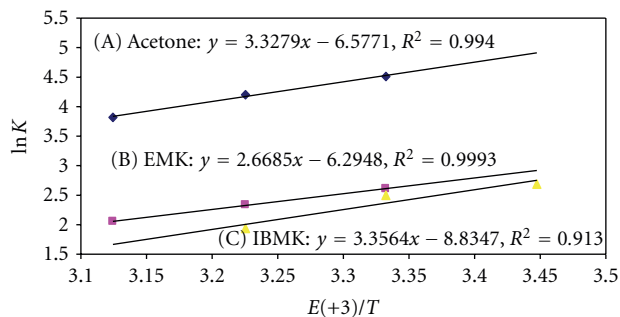
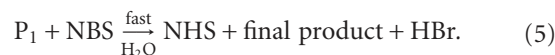
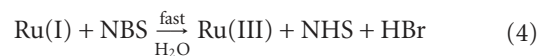
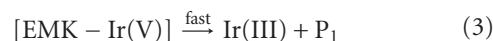
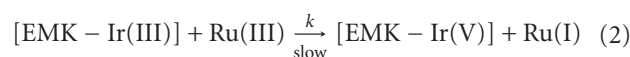


FIGURE 6: van't Hoff's plot of $\ln K$ versus $1/T$.

it is also pertinent to note that reaction rates are at least five to six times higher in Ir(III) catalyzed system as compared to Ru(III) catalyzed system. These observations probably indicate the formation of [EMK - Ir(III)] precursor prior to the slow decomposition step. Ru(III) being moderately good oxidizing agent may partake in the slow step to oxidize [Ir(III) - EMK] adduct and to give [Ir(V) - EMK] adduct as in Scheme 1 in ethyl methyl ketone (EMK) is as a typical example.

Scheme 1. Consider



A rate law for the above mechanism could be written as

$$\text{Rate} = \frac{k K [\text{Ru(III)}][\text{Ir(III)}][\text{EMK}]}{1 + K[\text{EMK}]} \quad (6)$$

Reciprocals of this equation yield

$$\frac{1}{\text{Rate}} = \frac{1}{k K [\text{Ru(III)}][\text{Ir(III)}][\text{EMK}]} + \frac{1}{k [\text{Ru(III)}][\text{Ir(III)}]} \quad (7a)$$

This can be further simplified as

$$\frac{1}{\text{Rate}} = \frac{1}{k [\text{Ru(III)}][\text{Ir(III)}]} \left\{ 1 + \frac{1}{K[\text{EMK}]} \right\} \quad (7b)$$

According to (7a) and (7b), plots of $1/\text{rate}$ versus $1/[\text{Ru(III)}]$, $1/\text{rate}$ versus $1/[\text{Ir(III)}]$ and $1/\text{rate}$ versus $1/[\text{EMK}]$ should be straight lines with positive slopes, the former two passing through origin and the later making an intercept on $1/\text{rate}$ axis. Such plots have been realized in the present study, keeping in with the proposed mechanism and validity of the rate law (Figures 2–4). The formation constant (K) value for

TABLE 1: The effect of variation of [NBS] and [EMK] in NBS-EMK system uncatalyzed and catalyzed by metal ions.

10^3 [NBS] mol dm ⁻³	[EMK]	$10^6 k_o$ mol dm ⁻³ s ⁻¹			
		Uncatalyzed	[Ru(III)]	[Ir(III)]	[Ru(III)] + [Ir(III)]
2.00	0.400	0.099	1.28	7.51	11.5
4.00	0.040	0.098	1.27	7.53	11.4
5.00	0.040	0.098	1.29	7.50	11.6
8.00	0.040	0.098	1.28	7.52	11.5
5.00	0.080	0.195	2.22	11.40	17.8
5.00	0.100	0.245	2.63	12.8	20.0
5.00	0.200	0.486	4.00	16.7	27.0
5.00	0.400	0.975	5.85	19.6	32.2

10^2 [Hg(OAc)₂] = 2.00 mol dm⁻³; HOAc = 10% (v/v); 10^2 [H⁺] = 5.00 mol dm⁻³; 10^5 [Ru(III)] = 2.09 mol dm⁻³; 10^6 [Ir(III)] = 6.67 mol dm⁻³; Temp. = 310 K.

TABLE 2: The effect of variation of Ru(III) in NBS-EMK system in the presence of Ir(III).

10^5 [Ru(III)] mol dm ⁻³	$10^6 k_o$ mol dm ⁻³ s ⁻¹	k_o /[Ru(III)]
0.525	0.813	0.155
1.05	1.62	0.154
2.09	3.24	0.155
3.15	4.86	0.154
4.18	6.45	0.154
5.25	8.10	0.154

10^3 [NBS] = 5.00 mol dm⁻³; [EMK] = 0.100 mol dm⁻³; HOAc = 10% (v/v); 10^2 [H⁺] = 5.00 mol dm⁻³; 10^7 [Ir(III)] = 5.05 mol dm⁻³; Temp. = 300 K. 10^2 [Hg(OAc)₂] = 2.00 mol dm⁻³.

TABLE 3: The effect of variation of [Ir(III)] in NBS-EMK system in the presence of Ru(III).

10^6 [Ir(III)] mol dm ⁻³	$10^6 k_o$ mol dm ⁻³ s ⁻¹	k_o /[Ir(III)]
0.275	0.406	1.48
0.550	0.816	1.48
1.10	1.62	1.48
2.20	3.21	1.46
3.30	4.80	1.45
4.40	6.41	1.46

10^3 [NBS] = 5.00 mol dm⁻³; [EMK] = 0.100 mol dm⁻³; HOAc = 10% (v/v); 10^2 [H⁺] = 5.00 mol dm⁻³; 10^5 [Ru(III)] = 2.09 mol dm⁻³; Temp. = 300 K. 10^2 [Hg(OAc)₂] = 2.00 mol dm⁻³.

TABLE 4: The effect of variation of solvent [% HOAc (v/v)] in NBS-EMK in [Ru(III) + Ir(III)] catalyzed reaction.

HOAc % (v/v)	10	20	30	40	50
$10^{-6} k_o$ mol dm ⁻³ s ⁻¹	0.850	0.950	1.15	1.35	1.50

10^3 [NBS] = 5.00 mol dm⁻³; [EMK] = 0.100 mol dm⁻³;
 10^2 [Hg(OAc)₂] = 2.00 mol dm⁻³; Temp. = 300 K;
 10^6 [Ru(III)] = 5.25 mol dm⁻³; 10^7 [Ir(III)] = 5.50 mol dm⁻³.

[Ir(III) – EMK] adduct in mixed catalyzed system (Table 5) is by and large similar to that in Ir(III) catalyzed system. This observation also points out the validity of the proposed

mechanism and rate law. Enthalpy (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) have been obtained from Eyring's plot (plot of $\ln(k_o/T)$ versus $10^3/T$, as shown in Figure 5), while the Gibbs-Helmholtz equation was used for the calculation of the free energy of activation (ΔG^\ddagger)

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger. \quad (8)$$

Enthalpy (ΔH) and entropy (ΔS) of the precursor formation are computed from vant Hoff's plot (plot of $\ln(k/T)$ versus $10^3/T$, as shown in Figure 6). The free energy of the precursor formation (ΔG) was calculated using vant Hoff's reaction isotherm and entropy (ΔS) from the Gibbs-Helmholtz equation as usual

$$\Delta G = -RT \ln K. \quad (9)$$

Activation parameters involving (k) and thermodynamic parameters involving (K) are compiled in Table 5 accordingly.

5.1. Comparison of Catalytic Activity. In general, the reaction rates of catalyzed reactions are ten to twenty times greater than uncatalyzed systems under similar conditions. The rate of a mixed catalyzed system is much more than the sum of the rates when Ru(III) and Ir(III) are employed separately as catalysts. The catalytic activity is indicated by a trend [Ru(III) + Ir(III)] > [Ir(III)] > [Ru(III)]. This can be further seen from the magnitude of decomposition constant (K) which is 10^3 times greater over Ir(III) and 10^4 times to Ru(III) systems (Tables 1 and 5). These results certainly point out the synergistic activity of [Ru(III) + Ir(III)]. The decomposition constant values of mixed catalysis one far higher than those recorded in the presence of Ru(III) or Ir(III). The order of reactivity reveals the order IBMK > EMK > MMK. The formation of the precursor complex between metal ion and substrate can be supported from fairly a good magnitude of formation constants coupled with large negative ΔG and ΔS values (Table 5). Fairly good positive entropy of activation ΔS^\ddagger values (Table 5) may suggest that the precursor is further undergoing a chemical change due to a reaction with another reagent.

TABLE 5: Kinetic and thermodynamic parameters.

Parameter	T (K)	MMK	EMK	IBMK
K ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	290	—	—	1.23×10^5
	300	0.268×10^5	1.02×10^5	2.55×10^5
	310	0.541×10^5	2.86×10^5	4.59×10^5
	320	0.975×10^5	7.16×10^5	—
ΔH^\ddagger kJ mol ⁻¹		49.1	75.8	46.8
ΔG^\ddagger kJ mol ⁻¹		48.0	44.7	42.4
ΔS^\ddagger J K ⁻¹ mol ⁻¹		3.67	104	15.0
K $\text{dm}^3 \text{mol}^{-1}$	290	—	—	14.5
	300	90.0	13.4	12.0
	310	66.0	10.2	6.85
	320	45.0	7.69	—
$-\Delta H$ kJ mol ⁻¹		27.7	22.4	28.1
$-\Delta G$ kJ mol ⁻¹		11.2	6.00	6.20
$-\Delta S$ kJ mol ⁻¹		55.0	53.0	73.0

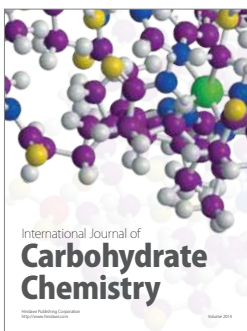
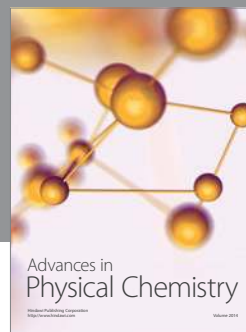
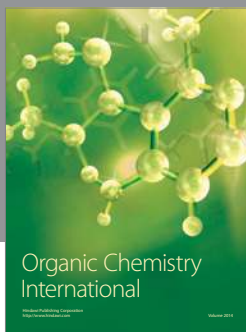
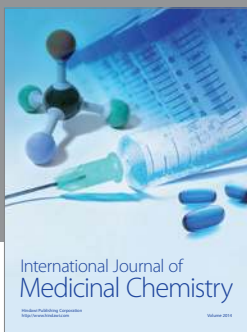
Acknowledgments

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