

Mechanistic Investigation of the Oxidative Cleavage of the Carbon–Carbon Double Bond in α,β -Unsaturated Compounds by Hexachloroiridate(IV) in Acetate Buffer

BISWAJIT PAL

Department of Chemistry, St. Paul's Cathedral Mission College, 33/1 Raja Rammohan Roy Sarani, Kolkata 700 009, India

Received 18 June 2013; revised 27 August 2013; 16 September 2013; accepted 16 September 2013

DOI 10.1002/kin.20824

Published online 9 October 2013 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The hexachloroiridate(IV) oxidation of α,β -unsaturated compounds such as acrylic acid, acrylamide, and acrylonitrile ($\text{CH}_2=\text{CHX}$; X = $-\text{COOH}$, $-\text{CONH}_2$, and $-\text{CN}$) was carried out in NaOAc-AcOH buffer medium. The reaction follows complex kinetics, being first order in $[\text{Ir}^{\text{IV}}]$ and complex order in $[\text{CH}_2=\text{CHX}]$. H^+ ion has no effect on the reaction rate in the pH range 3.42–4.63. The pseudo-first-order rate constant decreases with a decrease in the dielectric constant and with a decrease of ionic strength of the medium. The oxidation rate follows the sequence: acrylonitrile > acrylamide > acrylic acid. A mechanism is proposed involving the formation of an unstable intermediate complex between the substrate and the oxidant which is transformed to the radical cation in a slow rate-determining step with the concomitant reduction of Ir(IV) to Ir(III). The radical cation subsequently decomposes to the aldehyde that appears as the ultimate product of the carbon–carbon double bond cleavage. The major product of oxidation was identified as HCHO by ^1H NMR. Activation parameters for the slow rate-determining step and thermodynamic parameters associated with the equilibrium step of the proposed mechanism have been evaluated. The enthalpy of activation is linearly

Correspondence to: Biswajit Pal; e-mail: palbiswajit@yahoo.com.

Contract grant sponsor: University Grants Commission, New Delhi, India.

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related to the entropy of activation, and this linear relationship confirms that the oxidation of all the α,β -unsaturated compounds follows a common mechanism. © 2013 Wiley Periodicals, Inc. *Int J Chem Kinet* 46: 31–40, 2014

INTRODUCTION

α,β -Unsaturated compounds are being used extensively for the preparation of synthetic polymers. The compounds with carbon–carbon double bond adjacent to a strong electron-attracting group is very important as they allow the access to a variety of synthetic intermediates as well as the natural products [1]. Considerable work has been carried out to cleave the carbon–carbon double bond of some unsaturated compounds by different oxidants [2–7]. Sen Gupta and Bhattacharjee [8] studied the oxidative behavior of cinnamic acid and substituted cinnamic acids by hexachloroiridate(IV) in dimethyl formamide–water mixtures and in the presence of perchloric acid. The reaction mechanism was proposed involving the formation of an unstable complex between iridium (IV) and the substrate, which subsequently decomposes to the respective products through the formation of free radicals. The oxidation of α,β -unsaturated compounds by $[\text{Fe}(\text{CN})_6]^{3-}$ [9] and $[\text{M}^{\text{III}}(\text{H}_2\text{TeO}_6)_2]^{5-}$ ($\text{M} = \text{Cu}$ or Ag) [10] takes place in alkaline medium via the free radical mechanism, but the same reaction by bromate ion in acid medium [11] proceeds by a one-step two-electron transfer process. Recently, nickel oxide hydroxide, a useful heterogeneous catalyst, was used for the catalytic oxidation of α,β -unsaturated carboxylic acids to give epoxy acids [12].

Hexachloroiridate(IV) ion is the most important halogen compounds of iridium(IV) and has octahedral d^5 configuration with low spin t_{2g}^5 arrangement. Owing to the presence of antiferromagnetic interactions in IrCl_6^{2-} having one unpaired electron, the magnetic moment (μ_{eff}) values are found to be low (1.6–1.7 BM), which disappears on dilution with isomorphous PtCl_6^{2-} salts [13]. The IrCl_6^{2-} ion has been much studied as a convenient one-electron oxidant and often reacts as an outer-sphere oxidant. The standard reduction potential for the $\text{IrCl}_6^{2-}/\text{IrCl}_6^{3-}$ system in acid medium is 0.867 V [14]. The kinetics and mechanism of the hexachloroiridate oxidation of various organic reductants such as L-cysteine [15], phenols [16,17], aryl alcohols [18], aromatic aldehydes [19], and glucose phosphates [20] have been studied in acid medium. Oxidation of thioglycolic acid by $[\text{IrCl}_6]^{2-}$ is studied by the use of bathophenanthrolinedisulfonate as a chelating agent [21]. The reaction is highly susceptible to trace metal–ion catalysis. In reference to the oxidative cleavage of acrylic acid and its derivative by pen-

tachlorohydroxyplatinate(IV) in alkaline medium, the results were interpreted on the basis of an inner-sphere mechanism where platinum(IV) is reduced to platinum(II) by the substrates in a one-step two-electron transfer process [22]. In this study, we have focused on the oxidation of unsaturated compounds such as acrylic acid, acrylamide, and acrylonitrile by hexachloroiridate(IV) in sodium acetate–acetic acid buffer medium to understand the possibility of cleaving the carbon–carbon double bond of the unsaturated compounds.

EXPERIMENTAL

Materials

Iridium(IV) solution was prepared in water by dissolving the requisite amount of Na_2IrCl_6 (Aldrich, St. Louis, MO, USA). The absorption spectra of iridium(IV) solution were recorded in the visible region in the concentration range $(0.3\text{--}4.15) \times 10^{-4}$ mol dm^{-3} in $\text{NaOAc}\text{--}\text{AcOH}$ buffer medium, and the spectral pattern remained unaltered with changes in the concentration of Ir(IV). An absorption maximum at 488 nm ($\epsilon = 4050$ dm^3 mol $^{-1}$ cm $^{-1}$) was obtained [23]. The concentration of Ir(IV) solution was determined at the absorption maximum of IrCl_6^{2-} [24]. Acrylamide (S. M. India, Hyderabad, India; solid extra pure, assay >99%) was used as supplied. Acrylic acid (Merck, Mumbai, India) and acrylonitrile (S. M. India, Hyderabad, India) were purified before use. Trace amount of hydroquinone monomethyl ether was present as a stabilizing species both in acrylonitrile and acrylic acid to prevent polymerization. Prior to the actual experimental processes, acrylonitrile (b.p. 77.3°C) was distilled at its boiling temperature to set it free from hydroquinone monomethyl ether (b.p. 243–246°C). Similarly, acrylic acid (b.p. 141°C) distilled at temperature near its boiling point to ensure the absence of the stabilizer in the distillate. NaClO_4 (Loba, Mumbai, India), NaCl (Loba, Mumbai, India), and KCl (Loba, Mumbai, India) were used without purification. 1,4-Dioxane (extra pure, AR; SRL, Mumbai, India) was purified prior to use. All other chemicals were of the highest available purity. The solutions were prepared in doubly distilled water.

Instrumentation

Spectral measurements were recorded using a Shimadzu 1700 UV–vis spectrophotometer. The kinetic

measurements were performed in a Systronics (India) visible spectrophotometer (model 106) with a thermostated cell compartment. Cyclic voltammograms were recorded by a bioanalytical system CV-27 instrument in a dry argon atmosphere using DMF as the solvent and a three-electrode configuration (scan rate: 200 mV/s) in the potential range +1.0 to -1.0 V. The working electrode was Pt, and the standard Ag/AgCl electrode was used as the reference. IR spectra were obtained on a Shimadzu IR-200 spectrometer. The elemental analyses were performed by the microanalytical laboratory using a Perkin-Elmer 240 C,H,N analyzer. Melting point determinations were carried out on a Gallenkamp melting point apparatus. ^1H NMR spectra were recorded on a 300-MHz Bruker DPX spectrometer.

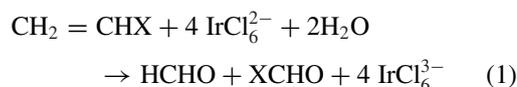
Kinetic Measurements

The kinetic investigations were performed under pseudo-first-order conditions, where $[\text{CH}_2=\text{CHX}]$ was present in large excess compared to $[\text{Ir}^{\text{IV}}]$. The progress of the reaction was monitored by measuring the absorbance of the reaction mixture at 488 nm using a cell of path length 1.0 cm. Except Ir(IV), other reactants and products were transparent at this wavelength. The cell compartment of the spectrophotometer was kept at constant temperature by circulating water from a thermostat through the thermospacer coils of the cell compartment. The plots from $\log A$ (A = absorbance) versus time were linear at least up to two half-lives. The pseudo-first-order rate constants (k_{obs}) were evaluated from the gradient of such plots. The reproducibility was within $\pm 5\%$.

Product Analysis

The reaction mixtures containing α,β -unsaturated compounds and iridium(IV) in buffer medium were allowed to stand for 6 h in a closed container and then distilled. The distillate was then subjected to the following tests: To one part of the distillate, an equal volume of 12 N H_2SO_4 was added and then treated with a pinch of solid chromotropic acid. The mixture was warmed on a water bath for a few minutes. A pink violet color [25] appeared immediately, which confirmed the presence of formaldehyde. Another part of the distillate was treated quantitatively with 2,4-dinitrophenyl hydrazine (DNP) solution in 4 N H_2SO_4 when a yellow DNP derivative of the product was precipitated. The yellow derivatives were purified and then analyzed. The melting point of the 2,3-dinitrophenyl hydrazone derivative was found to be 166–168°C [26] which was identical to that of the DNP derivative of

formaldehyde. C, H, N analysis of the DNP derivative yielded the following results: found C = 40.05, H = 2.8, N = 25.8%; calcd for $\text{C}_7\text{H}_6\text{N}_4\text{O}_4$: C = 40.0, H = 2.85, N = 26.6%. The yield of HCHO in each study was calculated from the respective DNP derivative. The values are found to be 48, 51, and 53% in the oxidation of acrylic acid, acrylamide, and acrylonitrile, respectively. The DNP derivative was further analyzed by ^1H NMR spectroscopy. The spectrum of the 2,4-DNP derivative of the reaction product in each study was recorded in CDCl_3 . The recorded spectral data reveal the characteristic signals such as a broad singlet at $\delta_{11.3}$ assignable for the presence of -NH moiety in the compound. The high δ -value for the -NH proton strongly supports the presence of intramolecular hydrogen bond between the proton of -NH moiety and any one O-atom of the NO_2 group at the ortho position. A doublet appearing at $\delta_{9.11}$ with $J = 2.35$ Hz was responsible for the aromatic proton flanked by two - NO_2 groups present in the compound. The appearance of a doublet of a doublet signal at $\delta_{8.34}$ with $J_1 = 9.45$ Hz and $J_2 = 2.13$ Hz was assigned to the aromatic proton, which is ortho to the 4- NO_2 group and para to the ortho - NO_2 group present in aryl moiety of the compound. A doublet observed at $\delta_{7.95}$ with $J = 9.5$ Hz corresponded to the aromatic proton at the meta position with respect to both the - NO_2 groups. All the signals assigned to the aromatic protons corroborated by the aryl moiety of the 2,4-dinitrophenyl hydrazone derivative of formaldehyde. However, a doublet at $\delta_{7.15}$ with $J = 10.73$ Hz and another doublet at $\delta_{6.75}$ with $J = 10.75$ Hz were assigned to the methylene protons. The coupling constant values in respect of methylene proton indicated the presence of a methylene moiety, i.e., geminal protons, which strongly supports the formation of hydrazone derivative from formaldehyde and 2,4-DNP. The above spectral analysis confirms that HCHO was formed as an oxidation product from all three unsaturated compounds. The stoichiometry of the reactions was studied at pH 4.32 in which the hexachloroiridate(IV) concentration was in large excess compared to the substrate concentration. The mixture was kept for 6 h, and the excess concentration of iridium(IV) was determined spectrophotometrically. The stoichiometry ($\Delta[\text{Ir}(\text{IV})] / \Delta[\text{CH}_2=\text{CHX}]$) was found to be 3.8 ± 0.3 . The results indicate that 4 mol of hexachloroiridate(IV) reacts with 1 mol of each unsaturated compound according to the following reaction:



where X = -CN, -CONH₂ and -COOH.

It may be noteworthy that XCHO was also formed as another product of oxidation in addition to formaldehyde. However, the absence of characteristic IR bands [27] assigned for $-\text{CN}$, $-\text{CONH}_2$, and $-\text{COOH}$ groups in the 2,4-DNP derivative of the respective products confirms that XCHO, which was formed initially together with HCHO, was converted to another molecule of formaldehyde through fast hydrolysis followed by subsequent decarboxylation. The formation of the product is in conformity with the results reported in earlier investigation [11]. It is to be noted that a major amount of HCHO existed as hydrated formaldehyde, i.e., $[(\text{CH}_2)_2(\text{OH})_2]$. The latter was then slowly evaporated on a water bath. Upon removal of the solvent and subsequent recrystallization from ether, a crystalline needles of 1,3,5-trioxane (m.p. 63°C , lit. m.p. 62°C [3]) was isolated.

The iridium-containing reaction product was examined spectrophotometrically, and the absorption spectrum was found to be identical to that of the pure IrCl_6^{3-} . Iridium(III) product was also determined following the reported procedure of Cecil and Littler [28]. After the kinetic experiments are completed, iridium(III) product was reoxidized by passing HCl free dry Cl_2 gas for 1 h through the solution. The absorbances of the resulting solution were measured at 460 and 488 nm [23]. Using the extinction coefficient values (2080 and $4050 \text{ mol}^{-1} \text{ cm}^{-1}$) of IrCl_6^{2-} at these wavelengths [23], the concentrations of iridium(III) species were determined. The results indicated that IrCl_6^{2-} was reduced to IrCl_6^{3-} , and the latter remained at $\sim 92\%$.

RESULTS

Effect of $[\text{Ir}^{\text{IV}}]$ and $[\text{CH}_2=\text{CHX}]$ on k_{obs}

The reactions were investigated at varying $[\text{Ir}^{\text{IV}}]$ in the range $(0.3\text{--}4.0) \times 10^{-4} \text{ mol dm}^{-3}$ at constant $[\text{CH}_2=\text{CHX}]$, pH, and temperature of $15 \times 10^{-2} \text{ mol dm}^{-3}$, 4.63, and 308 K, respectively. In all the kinetic experiments, $[\text{H}^+]$ was kept constant using acetic acid–sodium acetate buffer. The plots of $\log A$ versus time were found to be linear for different initial concentrations of Ir(IV), and parallel straight lines were obtained. The values of pseudo-first-order rate constant (k_{obs}) were found to be $(2.46 \pm 0.08) \times 10^{-4}$, $(3.12 \pm 0.12) \times 10^{-4}$, and $(3.68 \pm 0.11) \times 10^{-4} \text{ s}^{-1}$ for the oxidation of acrylic acid, acrylamide, and acrylonitrile, respectively. The results indicate that the reaction rate is first order with respect to Ir(IV). The effect of variation of the $\text{CH}_2=\text{CHX}$ concentration on the reaction rate was studied in the temperature range 298–313 K, keeping $[\text{Ir}^{\text{IV}}]$ and pH constant at $4.0 \times$

Table I Effect of Substrate Concentrations on the Pseudo-First-Order Rate Constants at Different Temperatures

Temperature (K)	$10^2 [\text{S}]$ (mol dm^{-3})	$10^5 k_{\text{obs}}^a$ (s^{-1})	$10^5 k_{\text{obs}}^b$ (s^{-1})	$10^5 k_{\text{obs}}^c$ (s^{-1})
298	5.0	5.63	5.72	6.04
	10.0	8.71	9.33	10.1
	15.0	9.97	11.9	13.6
	20.0	11.2	14.05	16.4
	25.0	12.1	15.3	18.8
	30.0	12.7	16.5	20.1
303	2.5	5.37	5.61	5.98
	5.0	8.84	9.56	10.7
	10.0	12.8	15.15	17.4
	15.0	14.9	18.5	22.4
	20.0	16.9	21.6	26.5
	25.0	17.9	23.3	29.9
308	2.5	10.8	11.0	11.3
	5.0	16.4	18.2	19.1
	10.0	21.6	27.8	30.7
	15.0	24.3	31.5	36.5
	20.0	26.5	35.3	41.7
	25.0	28.5	38.9	46.7
313	2.5	19.9	20.5	22.8
	5.0	27.8	32.4	34.3
	10.0	36.5	41.7	50.7
	15.0	38.9	48.6	55.5
	20.0	41.7	53.0	61.4
	25.0	44.9	58.3	68.6

$[\text{Ir}^{\text{IV}}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ and pH 4.63.

^a $\text{CH}_2 = \text{CHCOOH}$.

^b $\text{CH}_2 = \text{CHCONH}_2$.

^c $\text{CH}_2 = \text{CHCN}$.

$10^{-4} \text{ mol dm}^{-3}$ and 4.63, respectively. The value of k_{obs} increases with increasing $\text{CH}_2=\text{CHX}$ concentration (Table I). The plot of k_{obs} versus $[\text{CH}_2=\text{CHX}]$ at a fixed temperature did not pass through origin, which indicates that the reaction is complex order with respect to $\text{CH}_2=\text{CHX}$. The plots of $\log k_{\text{obs}}$ versus $\log [\text{CH}_2=\text{CHX}]$ at different temperatures for different substrates produced straight lines with slopes ranging from 0.45 to 0.69. But a Lineweaver and Burk plot of $1/k_{\text{obs}}$ versus $1/[\text{CH}_2=\text{CHX}]$ at each temperature produced a straight line ($R^2 \approx 0.99$) with a positive slope and positive intercept (Fig. 1), indicating the existence of a Michaelis–Menten type of intermediate complex between iridium(IV) and $\text{CH}_2=\text{HX}$ in a fast pre-equilibrium step [29,30].

Effect of pH

The effect of variation of $[\text{H}^+]$ (pH range 3.42–4.63) on the reaction rate was studied at constant $[\text{CH}_2=\text{CHX}]$,

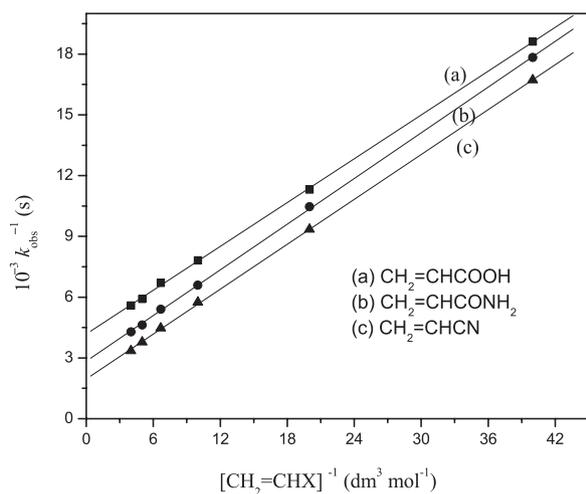


Figure 1 Variation of pseudo-first-order rate constants with the $\text{CH}_2=\text{CHX}$ concentration at 303 K. Plots of k_{obs}^{-1} versus $[\text{CH}_2=\text{CHX}]^{-1}$ at 303 K. $[\text{Ir}^{\text{IV}}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, pH 4.63.

Table II Effect of the H^+ Concentration on the Rate of Oxidation of α,β -Unsaturated Compounds by $\text{Ir}(\text{IV})$ at 303 K

pH	$10^5 k_{\text{obs}}^a \text{ (s}^{-1}\text{)}$	$10^5 k_{\text{obs}}^b \text{ (s}^{-1}\text{)}$	$10^5 k_{\text{obs}}^c \text{ (s}^{-1}\text{)}$
3.42	16.3	20.9	25.5
3.73	16.5	21.2	25.8
4.05	16.6	21.4	26.1
4.27	16.9	21.6	26.4
4.45	17.1	21.7	26.7
4.63	17.3	21.9	26.9

$[\text{CH}_2=\text{CHX}] = 20.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Ir}^{\text{IV}}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.12 \text{ mol dm}^{-3}$ and pH 4.63.

^a $\text{CH}_2=\text{CHCOOH}$.

^b $\text{CH}_2=\text{CHCONH}_2$.

^c $\text{CH}_2=\text{CHCN}$.

$[\text{Ir}^{\text{IV}}]$, ionic strength, and temperature of $20 \times 10^{-2} \text{ mol dm}^{-3}$, $4 \times 10^{-4} \text{ mol dm}^{-3}$, 0.12 mol dm^{-3} , and 303 K, respectively (Table II). The ionic strength was adjusted by the addition of sodium perchlorate. The pseudo-first-order rate constant was independent of $[\text{H}^+]$ in the pH range 3.42–4.63.

Effect of Salt

The influence of salts on the pseudo-first-order rate constant was studied by various salts such as sodium perchlorate, sodium chloride, and potassium chloride. The reactions were studied at different concentration of salts $[(0.5\text{--}4.0) \times 10^{-1} \text{ mol dm}^{-3}]$, but at constant $[\text{Ir}^{\text{IV}}]$, $[\text{CH}_2=\text{CHX}]$, pH, and temperature of 4

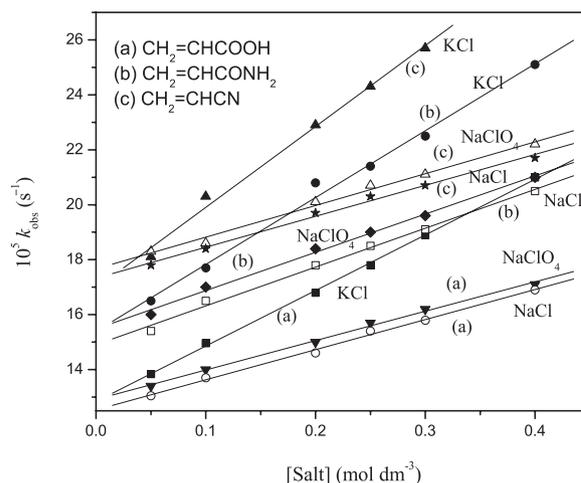


Figure 2 Effect of salt concentrations on the pseudo-first-order rate constants at 303 K. Plot of k_{obs} versus $[\text{salt}]$. $[\text{Ir}^{\text{IV}}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{CH}_2=\text{CHX}] = 10 \times 10^{-2} \text{ mol dm}^{-3}$, pH 4.63.

$\times 10^{-4} \text{ mol dm}^{-3}$, $10 \times 10^{-2} \text{ mol dm}^{-3}$, 4.63, and 303 K, respectively. The pseudo-first-order rate constant, k_{obs} , increased linearly with the increase in $[\text{salt}]$ (Fig. 2) in all the above cases. The results indicate that the anions do not seem to influence the pseudo-first-order rate constants. However, the pseudo-first-order rate constant values are greater in KCl than in NaCl or NaClO_4 of equal concentration.

Effect of the Dielectric Constant

The effect of variation of the dielectric constant of the medium on the pseudo-first-order rate constant was studied by the addition of 1,4-dioxane (0–40% v/v) keeping $[\text{Ir}^{\text{IV}}]$, $[\text{CH}_2=\text{HX}]$, pH, and temperature unchanged. The rate has been found to decrease with the decrease in the dielectric constant of the medium (Table III).

Test for Free Radicals

A literature survey reports that the metal ions such as iron(II) and mercury(II) were used earlier as a free radical trap [31]. In the present study, the possibility of induced polymerization was tested with the addition of mercuric chloride [40% (w/v)] to the reaction mixture where $\text{Ir}(\text{IV})$, $\text{CH}_2=\text{CHX}$, pH, and temperature were maintained at 4.0×10^{-4} , $10 \times 10^{-2} \text{ mol dm}^{-3}$, 4.63, and 303 K, respectively. An immediate precipitation due to the reduction of mercuric chloride to mercurous chloride was observed. This probably indicates that a reducing intermediate like free radicals

Table III Effect of Solvent Composition on the Pseudo-First-Order Rate Constant at 303 K

1,4-Dioxane (% v/v)	ε	$10^5 k_{\text{obs}}^a$ (s ⁻¹)	$10^5 k_{\text{obs}}^b$ (s ⁻¹)	$10^5 k_{\text{obs}}^c$ (s ⁻¹)
0	78.6	12.6	15.0	17.2
5	74.2	11.8	14.2	16.3
10	69.7	11.3	13.3	15.0
20	60.8	10.2	12.2	12.9
30	51.9	8.93	10.3	10.8
40	43.0	7.05	8.11	8.62

[CH₂=CHX] = 10.0 × 10⁻² mol dm⁻³, [Ir^{IV}] = 4.0 × 10⁻⁴ mol dm⁻³, and pH = 4.63.

^aCH₂=CHCOOH.

^bCH₂=CHCONH₂.

^cCH₂=CHCN.

were generated [32,33] during oxidation in each case. However, mercuric chloride failed to give mercurous chloride when either IrCl₆²⁻ or CH₂=CHX was treated separately.

Cyclic Voltammetry

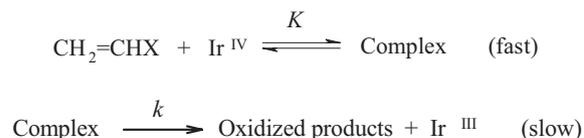
From the cyclic voltammetry study, it was found that the three substrates such as acrylic acid, acrylamide, and acrylonitrile had undergone oxidation at the potentials of -0.35, -0.31, and -0.226 V, respectively, at 298 K.

DISCUSSION

It is quite obvious from the literature [34] that IrCl₆²⁻ is highly photosensitive in the UV region, whereas it is not photosensitive in the visible region. Thus, photochemically induced reaction of IrCl₆²⁻ is insignificant under the present experimental conditions. It has been shown that hexachloroiridate(IV) is stable toward substitution or hydrolysis [35] over a wide range of acidities. Reductions of IrCl₆²⁻ by substrates are too slow to be studied at higher acidities (pH < 3.0). Again, the rapid reduction of IrCl₆²⁻ with HO⁻ takes place in alkaline solution [36]. Hence, the present reactions have been studied in the pH range 3.42–4.63 and it is suggested that IrCl₆²⁻ reacts with α,β -unsaturated compounds in the above-mentioned pH range.

The standard reduction potential for the IrCl₆²⁻/IrCl₆³⁻ system in acid medium is 0.867 V [14]. From the cyclic voltammetry study (the Results section), it is quite evident that all the three substrates are oxidized by IrCl₆²⁻.

The rate of the reaction is first order with respect to the oxidant concentration and fractional or-



Scheme 1 Reaction steps involved the oxidation of CH₂=CHX.

der (less than unity) in the substrate concentration. The Lineweaver and Burk type of plot of k_{obs}^{-1} versus [substrate]⁻¹ and the corresponding kinetic data indicates the formation of an intermediate 1:1 complex between the CH₂=CHX and Ir(IV). The intermediate complex decomposes in the rate-determining step to give the oxidation products along with Ir(III) (Scheme 1).

The addition of hexachloroiridate(III) does not inhibit the reaction rate, which indicates that the rate-determining step is not preceded by an equilibrium involving Ir(III). Assuming that the reaction takes place according to Scheme 1, the following rate equation may be deduced as follows:

$$-\frac{1}{[\text{IrCl}_6^{2-}]} \frac{d[\text{IrCl}_6^{2-}]}{dt} = k_{\text{obs}} = \frac{kK[\text{CH}_2=\text{CHX}]}{1 + K[\text{CH}_2=\text{CHX}]} \quad (2)$$

On rearranging, one can write

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} + \frac{1}{kK[\text{CH}_2=\text{CHX}]} \quad (3)$$

Equation (3) corroborates the linear plot of k_{obs}^{-1} versus [CH₂=CHX]⁻¹ with a positive slope and positive intercept, which is in agreement with the experimental observations. The value of the disproportionation constant (k) of the intermediate complex [formed between CH₂=CHX and Ir(IV)] at each temperature was calculated from the intercept of the above plots. Using the values of k at different temperatures, the value of the equilibrium constant (K) for the complex formation at each temperature was calculated from the slope of the linear plot (Fig. 1). The values of K and k for different substrates are recorded in Table IV. The linear plot of log k versus log K (Fig. 3) indicates that a similar mechanism is operative in all the oxidation reactions. Plots of log K versus 1/ T (Fig. 4) were linear, and the enthalpy change (ΔH^0) associated with the equilibrium step was evaluated followed by the determination of ΔS^0 using Eq. (4):

$$\log K = [\Delta S^0 - (\Delta H^0/T)] T/2.0303 R \quad (4)$$

Table IV Values of Equilibrium Constant Associated with Complex Formation and Dissociation Constant Associated with the Slowest Step for the Oxidation of Different $\text{CH}_2=\text{CHX}$ by Ir(IV) at 303 K

Substrate	K ($\text{dm}^3 \text{mol}^{-1}$)	$10^4 k$ (s^{-1})
$\text{CH}_2=\text{CHCOOH}$	11.6	2.39
$\text{CH}=\text{CHCONH}_2$	7.53	3.53
$\text{CH}_2=\text{CHCN}$	5.29	5.11

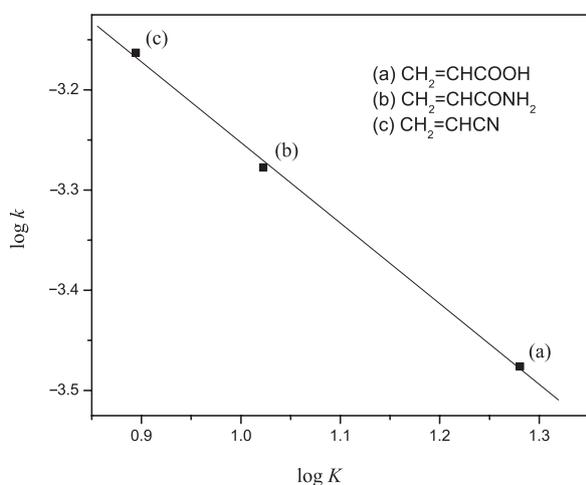


Figure 3 Variation of rate-limiting step constants (k) with the equilibrium constant (K) for the oxidation of different α,β -unsaturated compounds by Ir(IV) at 308 K. Plot of $\log k$ versus $\log K$.

Utilizing the k values at different temperatures, a plot of $\log(k/T)$ versus $1/T$ (Fig. 5) was done for each substrate, and the enthalpy of activation (ΔH^\ddagger), followed by the entropy of activation (ΔS^\ddagger) for the rate-determining step, was evaluated from Eq. (5):

$$\log(k/T) = [\log(k_B/h) + \Delta S^\ddagger/2.303 R] - \Delta H^\ddagger/2.0303 RT \quad (5)$$

The thermodynamic parameters associated with the equilibrium step and the activation parameters associated with the rate-determining step are presented in Table V. Since HCHO was found to be the reaction product and the $\text{CH}_2=\text{CH}$ - moiety is the common active reaction site in these substrates, a similar reaction mechanism may also be operative in the oxidation processes. The enthalpies of activation are linearly related to the entropies of activation (Fig. 6) ($R^2 = 0.99$) for all the reactions. The isokinetic temperature was found to be 350 K. The linear plot indicates that the oxidation of all the unsaturated compounds follows a similar reaction mechanism. The Exner plot of $\log k'$ versus

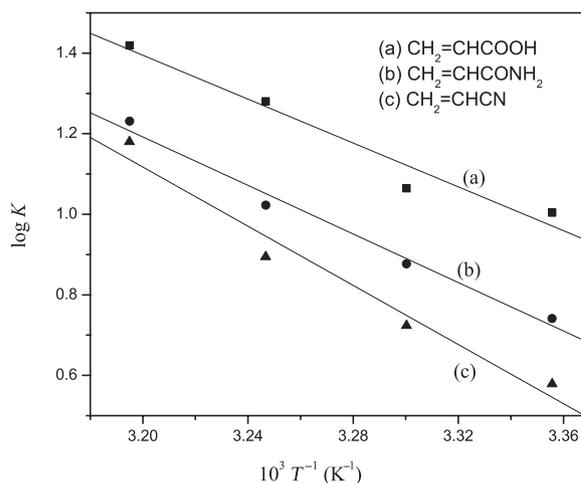


Figure 4 Variation of the equilibrium constant (K) with temperature. Plots of $\log K$ versus T^{-1} .

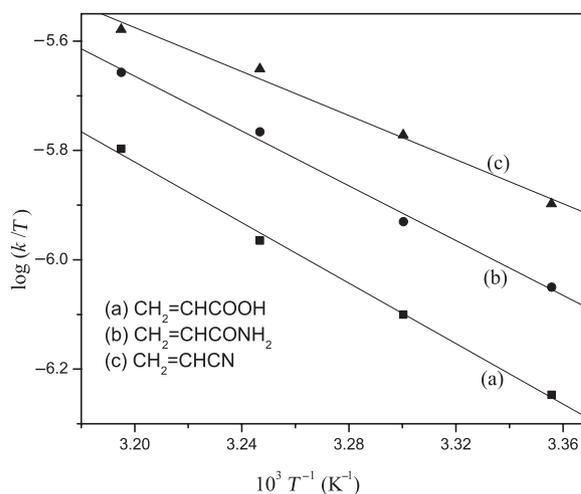


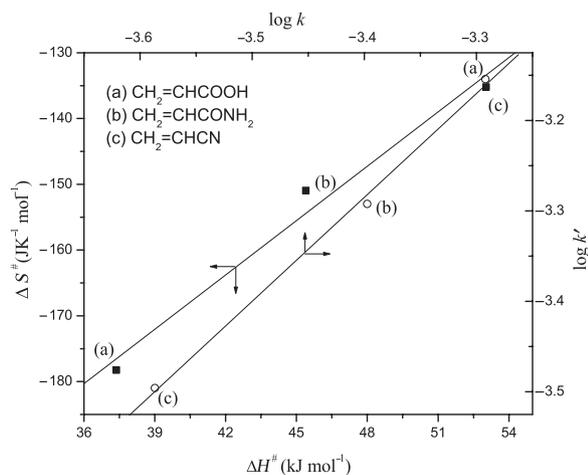
Figure 5 Variation of rate-limiting step constants (k) with temperature. Plots of $\log(k/T)$ versus T^{-1} .

$\log k$ (where k' and k are rate constants for the rate-limiting step at temperature 308 and 303 K, respectively) supports the above isokinetic behavior (Fig. 6) ($R^2 = 0.98$). The isokinetic temperature (β) has been found to be 348 K from the Exner plot [37], which is higher than the mean experimental temperature in the studied temperature range. The value of $\beta - T$, which is positive, indicates that the reactions are governed by their enthalpies of activation in the temperature range studied [38].

The unsaturated compounds (e.g., acrylamide, acrylonitrile), in general, are susceptible to radical-induced polymerization. Such a possibility may not be applicable under the present experimental conditions where the concentrations of the unsaturated compounds are

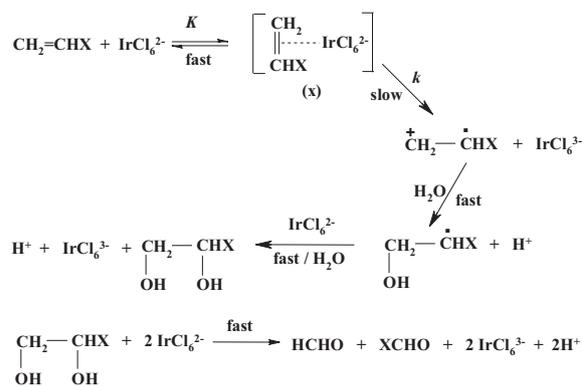
Table V Thermodynamic Data Associated with 1:1 Complex Formation and Activation Parameters Associated with the Slowest Step for the Oxidation of α , β -Unsaturated Compound by Iridium(IV)

Substrate	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (JK ⁻¹ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)
CH ₂ =CHCOOH	52 ± 8	193 ± 25	53 ± 2	-134 ± 7
CH ₂ =CHCONH ₂	58 ± 5	207 ± 16	48 ± 2	-153 ± 8
CH ₂ =CHCN	70 ± 9	246 ± 29	39 ± 3	-181 ± 9

**Figure 6** Isokinetic plots for the oxidations of some CH₂=CHX by Ir(IV) in acetate buffer. (i) Plot of ΔS^\ddagger versus ΔH^\ddagger ; (ii) plot of $\log k'$ versus $\log k$.

quite low [(2.5–25) × 10⁻² mol dm⁻³] [39,40]. Again, if these unsaturated compounds might have played a significant role in induced polymerization in the reaction mixture, it would have resulted in the decrease of the reaction rate with the increase in the concentration of the each substrate [40]. But no such decrease of the reaction rate with an increase in the substrate concentration was observed. Moreover, good linearity of the Lineweaver and Burk plot (k_{obs}^{-1} vs. [substrate]⁻¹) with a positive intercept and positive slope ($R^2 \approx 0.99$), indicating the positive dependence of substrate on the reaction rate, rules out the possibility of the polymerization.

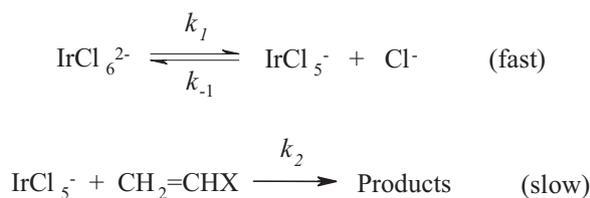
A detailed mechanism of the oxidation of α,β -unsaturated compounds by hexachloroiridate(IV) seems to take place through the intermediate formation of unstable complex between the substrate and iridium(IV) [41] as shown in Scheme 2. The existence of a similar type of Ir(IV) intermediate complex has already been reported [8,18]. The formation of metal complex with the carbon-carbon double bond has been shown in the oxidation of olefins by metal ion oxidants such as Ag(I) and Pd(II) [42,43]. The intermediate compound then disproportionates in the slow step by one-electron transfer from the substrate to Ir(IV) and thereby gener-

**Scheme 2** Overall reactions showing the electron transfer reaction between CH₂=CHX and Ir^{IV}.

ating the radical ion (⁺CH₂- $\dot{\text{C}}\text{H-X}$) and IrCl₆³⁻. The evidence for free radical intermediate was established by polymerization of HgCl₂ during the oxidation of α,β -unsaturated compounds by Ir(IV). The radical ion further reacts with Ir(IV) to give glycol in a fast step.

The absence of bands [27] due to the -OH group in the IR spectra of the final oxidation products suggests that the intermediate glycol undergoes rapid carbon-carbon bond cleavage by IrCl₆²⁻ in acid medium to give HCHO and XCHO (X = -CN, -ONH₂, and -COOH). Similar observation has also been reported by Nongkynrih and Mahanti [3] in the oxidation of styrene by quinolinium dichromate in acid medium, where the intermediate glycol was rapidly converted to the corresponding aldehyde. The product XCHO containing X = -CN or -CONH₂ groups hydrolyzes in a fast step to produce glyoxylic acid, and the latter subsequently decarboxylates to give another molecule of formaldehyde [22]. The reaction mechanism in this study has been found to be very much similar to that for the oxidation of styrene and cinnamic acid by Ir(IV) [8].

Based on the double reciprocal plot of k_{obs}^{-1} versus [CH₂=CHX]⁻¹, an alternative mechanism may also be suggested, where IrCl₆²⁻ dissociates to give IrCl₅⁻ and Cl⁻ followed by the reaction of IrCl₅⁻ with CH₂=CHX to afford the reaction products (Scheme 3).



Scheme 3 Alternative reaction path between $\text{CH}_2=\text{CHX}$ and Ir^{IV} .

On the basis of the proposed reaction mechanism (Scheme 3), the following rate expression can be determined:

$$-\frac{d[\text{IrCl}_6^{2-}]}{dt} = \frac{k_1 k_2 [\text{IrCl}_6^{2-}] [\text{CH}_2 = \text{CHX}]}{k_{-1} [\text{Cl}^-] + k_2 [\text{CH}_2 = \text{CHX}]} \quad (6)$$

However, the addition of chloride ion at constant ionic strength failed to inhibit the rate of reaction, suggesting that IrCl_5^- is not the reactive oxidant species. Thus, the reaction did not proceed following the above alternative reaction path between $\text{CH}_2=\text{CHX}$ and $\text{Ir}(\text{IV})$ (Scheme 3).

The $\text{p}K_a$ value of acrylic acid is 4.2. Since the experiments were carried out in the pH range 3.42–4.63, it is quite evident that the concentration of acrylic acid and that of acrylate ion does not differ widely. Here, either $-\text{COOH}$ or $-\text{COO}^-$ part of acrylic acid does not participate directly in the formation of unstable complex between the substrate and $\text{Ir}(\text{IV})$. In addition, as the concentrations of the free acid and its conjugate base do not differ significantly in the said pH range, there is no noticeable influence of either $-\text{COOH}$ or $-\text{COO}^-$ group of the substrate on the formation of radical cation in the rate-determining step. This may account for the fact that the rate constant for acrylic acid is independent of pH in the studied range. This may also be supported by the work of Sen Gupta and Bhattacharjee [8], where a similar type of pH independence was observed in the oxidation of cinnamic acid (unsaturated carboxylic acid) by iridium(IV) in acid medium.

The increase in the reaction rate in KCl over NaCl or NaClO_4 indicates that K^+ ion plays an important role on the pseudo-first-order rate constant. One explanation for this increase may be attributable to the fact that the IrCl_6^{2-} ion partially associates with K^+ ion, and thereby forming the associated $\text{Ir}(\text{IV})$ complex [8]. The associated species may be more reactive than the free IrCl_6^{2-} in the oxidation of the substrate. A similar type of positive salt effects as well as the K^+ ion catalysis have been cited in the oxidations of styrene, substituted styrene [8], and diols [39] by chlorocomplexes of iridium(IV), where the reaction was shown

to occur between the neutral and charged species. The K^+ ion catalysis has also been observed in some other previous studies [44,45].

The reaction rate was found to be enhanced with an increase in solvent polarity (Table III). The result was expected if one assumed that the interaction took place between the π -electron cloud of the substrates' double bond and the negatively charged oxidant [40]. Moreover, in the rate-determining step the intermediate complex decomposes to a number of charged species, which might come from the polar transition state. Thus, a lowering of the dielectric constant of the medium disfavored the transition state and possibly this decreases the reaction rate.

The kinetic results of the present study suggest that among the different substrates acrylonitrile reacts at a faster rate than the other two substrates. The pseudo-first-order rate constant obtained in the oxidation of acrylamide lies between those obtained for acrylonitrile and acrylic acid. This may be attributed to the fact that the presence of the $-\text{CN}$ group in acrylonitrile facilitates the formation of radical cation, which is possibly reflected by the lower value of enthalpy of activation of acrylonitrile oxidation compared to other two substrates. Although the experimental conditions of the present study are different, the reaction is similar to the oxidation of these compounds by $[\text{Cu}(\text{H}_2\text{TeO}_6)_2]^{5-}$ and $[\text{Ag}(\text{H}_2\text{TeO}_6)_2]^{5-}$ [10] in the alkaline medium so far as the reactivity order of the substrates is concerned. The reaction mechanism in this study has been found to be different for the oxidation of similar compounds by $\text{Pt}(\text{IV})$ in alkaline medium [22], where $\text{Pt}(\text{IV})$ is reduced to $\text{Pt}(\text{II})$ in an inner-sphere mechanism. The values of thermodynamic parameters (ΔH^\ddagger , ΔS^\ddagger) and activation parameters (ΔH^\ddagger , ΔS^\ddagger) support the proposed reaction mechanism (Scheme 2). The fairly large negative values of the entropy of activation indicate that the transition state in the rate-limiting step was highly solvated, thereby resulting in an increase in electrostriction [46]. This is associated with an immobilization of a large number of solvent molecules, which results in a decrease in entropy in forming the transition state. All the kinetic evidences, systematic product analysis (both organic and inorganic products), and the stoichiometric runs support the oxidative cleavage of carbon-carbon double bond of unsaturated compounds by $\text{Ir}(\text{IV})$ following a similar reaction mechanism that leads to the formation of the common reaction products— HCHO and IrCl_6^{3-} .

CONCLUSIONS

The redox reaction between hexachloroiridate(IV) and each of three α,β -unsaturated compounds in acetate

buffer proceeds through the formation of a 1:1 intermediate complex followed by the formation of radical cation and IrCl_6^{3-} in one electron transfer process. The oxidation product was found to be HCHO in each case, which was identified by ^1H NMR spectroscopy as well as by a spot test.

The author thanks Dr. Anil Kumar Barik, Department of Chemistry, St. Paul's Cathedral Mission College, Kolkata, India, and Dr. Sankar Prasad Dey, Department of Chemistry, Srikrishna College, Bagula, Nadia, India, for helpful discussions.

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