

made to search for the existence of the dioxygen adduct proposed. No convincing evidence besides the reported kinetic data have yet been found, but it should be pointed out that dioxygen-molybdenum complexes are known to exist.¹³

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Kinetics of Oxidation of Hydrazinium Ion by Hexachloroiridate(IV)

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Kinetics of the oxidation of hydrazinium ion by hexachloroiridate(IV) have been studied spectrophotometrically in perchloric acid medium in the temperature range 30–45 °C. The reaction is first order with respect to iridium(IV) whereas the order with respect to hydrazinium ion is less than 1. Hydrogen ion decreases the rate of oxidation. The additions of salts have accelerating effects on the rate of reaction. The rate also increases with decreasing dielectric constant. The reaction is not retarded by the hexachloroiridate(III) ions produced in the reaction. The empirical rate equation is $-d[\text{IrCl}_6^{2-}]/dt = kK[\text{IrCl}_6^{2-}][\text{N}_2\text{H}_5^+]/([\text{H}^+] + K[\text{N}_2\text{H}_5^+])$. E_a and ΔS^\ddagger were found to be 96.8 kJ mol⁻¹ and -1.2 J K⁻¹, respectively. ΔH and ΔS° associated with K were found to be -69 kJ mol⁻¹ and -205 J K⁻¹, respectively.

Introduction

Hydrazinium ion is known to be a very powerful reducing agent.¹ The thermodynamic reducing strength of hydrazine is dependent on the nitrogen species to which hydrazine is oxidized. Hydrazine is quantitatively oxidized to nitrogen gas by 2-equiv oxidants^{2,3} whereas 1-equiv oxidation of hydrazine is approached⁴⁻⁶ when Mn^{III} , Fe^{III} , and Co^{III} are used as oxidants. However, the kinetics of the oxidation of hydrazinium ion by Ir(IV) has not been reported although the kinetics of the oxidation of cyclohexanone⁷ and some substituted phenols⁸ and quinols⁹ by Ir(IV) has been studied. The kinetics of oxidation of hydrazinium ion by PtCl_6^{2-} has been studied¹⁰ in the acid medium. The reaction has been shown to proceed through the formation of intermediate platinum(III) followed by the reaction of platinum(III) with another hydrazinium ion to give products of reaction. The present reaction was undertaken in view of the interesting results obtained with PtCl_6^{2-} . The oxidation of hydrazinium ion by IrCl_6^{2-} was carried out under various experimental conditions with a view to suggesting a possible reaction mechanism.

Experimental Section

Reagents. All inorganic materials were of AnalaR (BDH) grades. Hydrazine solution was standardized under the usual Andrews conditions¹¹ by using potassium iodate as mentioned in an earlier communication.¹⁰ Sodium hexachloroiridate, $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (Johnson-Mathey), was used to prepare solutions of iridium(IV), and such solutions in perchloric acid (0.1–1.0 M) were stable over periods of 24 h.^{12b} These were stored in the dark and used under subdued lighting conditions generally within 5–6 h of preparation. Standardization of hexachloroiridate(IV) solutions was effected spectrophotometrically at 488 nm (ϵ 4050 M⁻¹ cm⁻¹). Sodium perchlorate was prepared by the neutralization of perchloric acid with sodium hydroxide. All solutions were made in doubly distilled water. We purified the dioxane by distilling twice with metallic sodium, each time collecting the middle fraction.

Absorption Spectra. The absorption spectra of iridium(IV) solutions (in 0.1 M perchloric acid) in the concentration range (0.283–2.41) $\times 10^{-4}$ M were recorded in the visible region. The spectral pattern remained unaltered with changes in concentration of iridium(IV). An absorption maximum at 488 nm and a minimum at 460 nm were in good agreement with literature values.¹³ Beer's law has been found to be valid in this concentration range. The spectra of 1.0×10^{-4} M iridium(IV) were also recorded at different concentrations (viz., 0.04–2.24 M) of perchloric acid but without any change in the absorption maximum and minimum. It may be mentioned that the spectral pattern as well as λ_{max} of $\text{Ir}(\text{OH}_2)\text{Cl}_5^-$ is different from that of IrCl_6^{2-} indicating that IrCl_6^{2-} and not $\text{Ir}(\text{OH}_2)\text{Cl}_5^-$ acts as the oxidizing species. The IrCl_6^{3-} ion and its hydrolyzed product $\text{Ir}(\text{OH}_2)\text{Cl}_5^{2-}$ ion are transparent in the region of maximum absorption of IrCl_6^{2-} as indicated by Poulson and Garner.^{12a}

Kinetic Measurements. The reactions were studied under pseudo-first-order conditions, i.e., in the presence of a large excess of hydrazinium ion. Kinetic runs were performed at constant concentrations of iridium(IV), N_2H_5^+ , and HClO_4 at 1.04×10^{-4} , 8.0×10^{-3} , and 1.0×10^{-1} M, respectively, and measurements were carried out at 35 °C unless otherwise mentioned. The rate of the reaction was followed from the decrease in iridium(IV) concentration, the latter being reflected in the measurements of absorbance at 488 nm. The reactions were studied in the thermostated cell compartment of a Beckman DU spectrophotometer. Iridium(III) at that low concentration of 1.0×10^{-4} M and other products of the reaction were transparent at this wavelength. The cell compartment of the spectrophotometer was kept at constant temperature by circulating water from the thermostat into the surrounding water jackets. The reaction mixtures containing the oxidant in perchloric acid (and salt or solvent, if any) in one vessel and hydrazinium ion in the other vessel were separately equilibrated to bath temperature, mixed externally, and immediately transferred into a cell of path length 1 cm. The rate of decrease of iridium(IV) was followed for 50–80% conversion of the initial iridium(IV) concentration depending upon the concentration of hydrazinium ion and on the temperature. Generally, 6–8 readings were noted for each set with change in time, and pseudo-first-order rate constants (k_{obsd}) were obtained graphically from $\log A$ ($A =$

Table I. Effect of Initial Hexachloroiridate(IV) Concentrations on Pseudo-First-Order Rate Constants^a

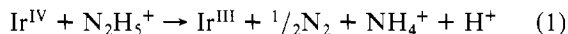
$10^4 [\text{Ir(IV)}], \text{M}$	0.30	1.04	1.44	1.91	2.30
$10^4 k_{\text{obsd}}, \text{s}^{-1}$	2.59	2.59	2.61	2.62	2.61

^a $[\text{N}_2\text{H}_5^+] = 8.0 \times 10^{-3} \text{ M}$ and $[\text{H}^+] = 1.0 \times 10^{-1} \text{ M}$.

absorbance) vs. time plots. The rate constants were reproducible to within $\pm 5\%$. Control of ionic strength, wherever necessary, was effected by the addition of sodium perchlorate.

Results

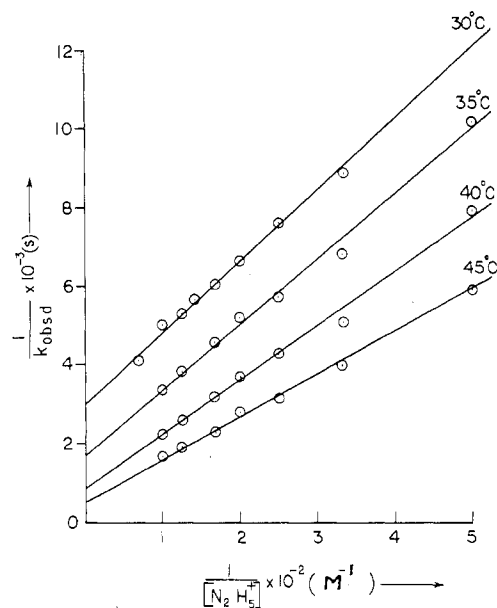
Stoichiometry. Brown and Higginson^{14a} earlier studied the stoichiometry of the reaction between hydrazinium ion and hexachloroiridate(IV) in the pH range 1.6–6.5 and found that, in excess iridium(IV), 3.5–3.8 mol of Ir(IV) is consumed/mol of N_2H_5^+ . In the present investigation, the kinetics of oxidation was studied for nearly 1 h in the pH range 0–1.7. Brown et al.^{14a} used hexachloroiridate(IV) and hydrazinium ion concentration in the regions 17–24 and 9.7–13.6 mM, respectively, unlike the present study where hydrazinium concentrations were in large excess compared to hexachloroiridate(IV) concentrations. However, we have also studied the stoichiometry in which hexachloroiridate(IV) and hydrazinium ion were in the ratios of 5:1 and 10:1 (pH 1.3), and the mixture was kept for 24 h. The excess of iridium(IV) was determined spectrophotometrically and the stoichiometry was found to be 3.7 ± 0.1 . It is likely that, in excess hexachloroiridate(IV), the reaction intermediates are further oxidized by the oxidant. However, in our kinetic studies, the hydrazinium ion concentration was in large excess compared to the oxidant concentration. The reaction mixture containing hydrazinium ion and hexachloroiridate(IV) of concentrations of 2.0×10^{-2} and $1.0 \times 10^{-3} \text{ M}$, respectively, was allowed to stand for several hours ($[\text{H}^+] = 1.0 \times 10^{-1} \text{ M}$). The excess hydrazinium ion concentration was determined.¹¹ The average of stoichiometries in three different experiments, which are 1.2, 0.95, and 1.04, indicates that 1 mol of hexachloroiridate(IV) reacts with 1 mol of hydrazinium ion according to eq 1. Consequently,



further oxidation of the intermediate species would not take place and the 1:1 stoichiometry of the reaction seems to be more justified under the conditions at which the present reaction was carried out. The formation of NH_4^+ was tested by the addition of Nessler's reagent as mentioned in the literature.^{14b}

Effects of Reactant Concentrations. The reaction was studied at varying concentrations of Ir(IV) but at constant $[\text{N}_2\text{H}_5^+]$, acidity, and temperature. The observed pseudo-first-order rate constant was found to be independent of iridium(IV) concentration (Table I). This indicates that the order with respect to iridium(IV) is unity. The effect of substrate concentration was studied at a constant $[\text{Ir(IV)}]$ and a $[\text{HClO}_4]$ of 1.04×10^{-4} and $1.0 \times 10^{-1} \text{ M}$, respectively, whereas the $[\text{N}_2\text{H}_5^+]$ was varied between the limits $(2.0\text{--}14.0) \times 10^{-3} \text{ M}$. Increase of substrate concentration enhances the rate of oxidation. Plots of $1/k_{\text{obsd}}$ vs. $1/[\text{N}_2\text{H}_5^+]$ at different temperatures are shown in Figure 1.

Effect of pH. The effect of changing the hydrogen ion concentration on the reaction was studied at 35 °C in the acid range $(2.0\text{--}50) \times 10^{-2} \text{ M}$ while the ionic strength was kept fixed at 1.0 M. Hydrogen ion has been found to have a decelerating effect on the rate. The plot of $1/k_{\text{obsd}}$ against $[\text{H}^+]$ did not show linear correlation with the acid concentration for the entire range used (Figure 2). However, the plot of $1/k_{\text{obsd}}$ against $[\text{H}^+]$ yields a straight line making an intercept in the y axis up to $[\text{H}^+] = 2.5 \times 10^{-1} \text{ M}$. The reaction rate becomes complex at higher acidities ($>2.5 \times 10^{-1} \text{ M}$) possibly because of the reaction of H^+ with IrCl_6^{2-} to give

**Figure 1.** Variation of pseudo-first-order rate constant with increase in hydrazinium ion concentration: plots of $1/k_{\text{obsd}}$ against $1/[\text{N}_2\text{H}_5^+]$ at different temperatures. $[\text{Ir(IV)}] = 1.04 \times 10^{-4} \text{ M}$ and $[\text{H}^+] = 1.0 \times 10^{-1} \text{ M}$.**Table II.** Effect of Salts on the Pseudo-First-Order Rate Constants^a

$10^2 [\text{NaClO}_4], \text{M}$	0	5.0	10.0	15.0	20.0	25.0
$10^4 k_{\text{obsd}}, \text{s}^{-1}$	2.59	2.63	2.76	2.88	2.95	3.03
$10^2 [\text{NaCl}], \text{M}$	0	5.0	10.0	15.0	20.0	25.0
$10^4 k_{\text{obsd}}, \text{s}^{-1}$	2.59	2.65	2.78	2.88	2.99	3.11
$10^2 [\text{Na}_2\text{SO}_4], \text{M}$	0	1.0	2.5	5.0	7.5	10.0
$10^4 k_{\text{obsd}}, \text{s}^{-1}$	2.59	2.67	2.78	2.87	3.01	3.15

^a $[\text{Ir(IV)}] = 1.04 \times 10^{-4} \text{ M}$, $[\text{N}_2\text{H}_5^+] = 8.0 \times 10^{-3} \text{ M}$, and $[\text{H}^+] = 1.0 \times 10^{-1} \text{ M}$.

Table III. Effect of Solvent Composition on the Pseudo-First-Order Rate Constants^a

% dioxane (v/v)	0	10	20	30	40
D	74.9	65.95	57.05	48.15	39.3
$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$	2.59	15.6	41.3	66.5	80.6

^a $[\text{Ir(IV)}] = 1.04 \times 10^{-4} \text{ M}$, $[\text{N}_2\text{H}_5^+] = 8.0 \times 10^{-3} \text{ M}$, and $[\text{H}^+] = 1.0 \times 10^{-1} \text{ M}$.

$\text{H}^+\text{IrCl}_6^-$ which may react with N_2H_5^+ to give the products of reaction. Alternatively, protonation of N_2H_5^+ to give $\text{N}_2\text{H}_6^{2+}$ at higher acidity followed by the reaction of $\text{N}_2\text{H}_6^{2+}$ with IrCl_6^{2-} cannot be totally ruled out.

Effect of Salts. The effect of addition of salts like sodium perchlorate, sodium chloride, and sodium sulfate on the pseudo-first-order rate constant was studied. The addition of salts does not seem to have any influence on the pseudo-first-order rate constant when $[\text{salt}] \leq 8.0 \times 10^{-3} \text{ M}$ although the acceleration in the rate of reaction was observed at higher concentrations of the salts (Table II). The plot of $\log k_{\text{obsd}}$ against μ (where μ = ionic strength) is linear (Figure 3).

Effect of Solvent. The effect of change of dielectric constant of the medium on the rate was studied by the addition of dioxane. The rate has been found to increase with the decrease in the dielectric constant of the medium suggesting a reaction between two oppositely charged ions (Table III). The values of dielectric constants (D) at different solvent compositions were taken from the works of Akerlof and Short.¹⁵

Effect of Temperature. The values of k (as referred to in eq 6) were found to be 3.3×10^{-4} , 5.9×10^{-4} , 11.1×10^{-4} , and $20.0 \times 10^{-4} \text{ s}^{-1}$ at 30, 35, 40, and 45 °C, respectively, whereas the values of K (as referred to in eq 5) were 16.4,

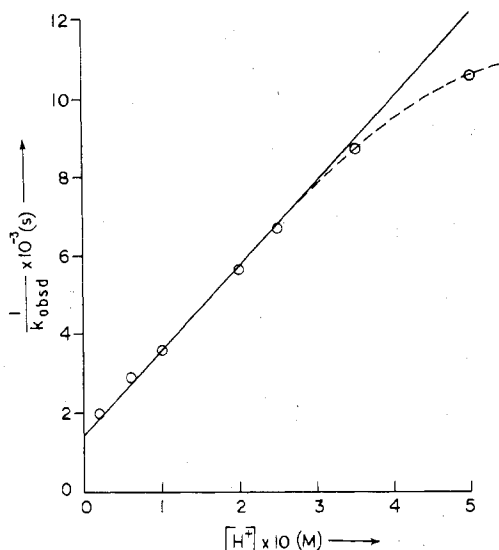


Figure 2. Effect of hydrogen ion concentration on the pseudo-first-order rate constant: plot of $1/k_{\text{obsd}}$ vs. $[H^+]$. $[\text{Ir(IV)}] = 1.04 \times 10^{-4} \text{ M}$, $[\text{N}_2\text{H}_5^+] = 8.0 \times 10^{-3} \text{ M}$, $\mu = 1.0 \text{ M}$, and temperature 35°C .

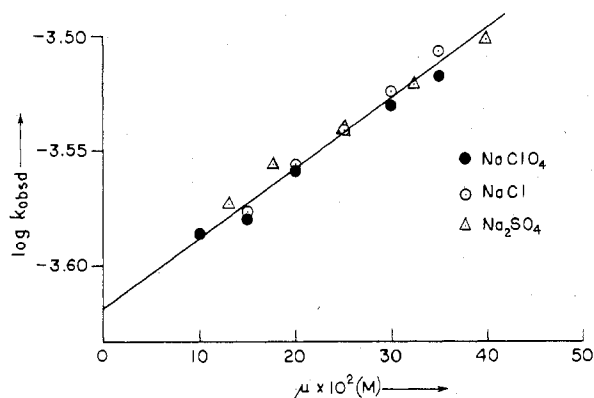


Figure 3. Influence of different salts on the pseudo-first-order rate constant: plot of $\log k_{\text{obsd}}$ against μ .

10.15, 6.55, and 4.55. A least-squares fit of the plot of $\log k$ against $1/T$ was used to evaluate the energy of activation which was calculated to be 96.8 kJ mol^{-1} . The value of PZ was calculated as usual,¹⁶ and the entropy of activation (ΔS^\ddagger) was obtained from eq 2 where k is Boltzmann's constant and

$$\text{PZ} = e^{-\frac{kT}{h}} e^{\Delta S^\ddagger/R} \quad (2)$$

h is Planck's constant. From the gradient of a plot of $\log K$ against $1/T$, the enthalpy change associated with the equilibrium step was found to be $-69.0 \text{ kJ mol}^{-1}$. Thermodynamic parameters associated with the equilibrium constant were then computed from the relations, $-\Delta G^\circ = RT \ln K$ and $\Delta G^\circ = \Delta H - T\Delta S^\circ$. The results have been recorded in Table IV.

Discussion

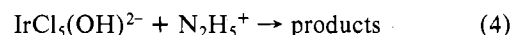
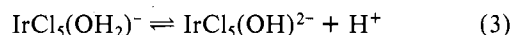
It has been mentioned in the literature^{7,8} that IrCl_6^{2-} is stable toward substitution or hydrolysis over a wide range of acidities. Again, at higher acidities ($[H^+] \geq 2.0 \times 10^{-2} \text{ M}$) hydrazinium ion will remain as an undissociated species, since the dissociation constant of hydrazinium ion is 1.02×10^{-8} at 25°C . It is, therefore, suggested that IrCl_6^{2-} oxidizes N_2H_5^+ . A few runs were carried out at constant reactant concentrations (as has been shown in Table II) but at different concentrations of IrCl_6^{2-} . The extraneous addition of iridium(III) in concentrations of 1.0×10^{-3} , 1.5×10^{-3} , and $2.0 \times 10^{-3} \text{ M}$ had

Table IV. Activation Parameters and Thermodynamic Values

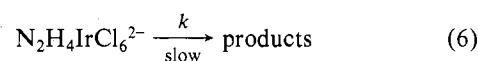
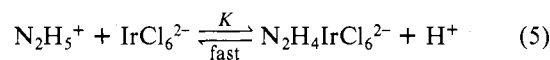
	step 6	step 5	
E_a , kJ mol^{-1}	96.8	$-\Delta H$, kJ mol^{-1}	69.0
$-\Delta S^\ddagger$, J K^{-1}	1.2	$-\Delta S^\circ$, J K^{-1}	204.8
ΔG^\ddagger , kJ mol^{-1}	97.0 ^a	$-\Delta G^\circ$, kJ mol^{-1}	5.5 ^a

^a The average value in the temperature range studied.

no kinetic effect; thus the fast, reversible reaction between IrCl_6^{2-} and N_2H_5^+ to give a free radical and IrCl_6^{3-} followed by the slow rate-determining step of the reaction between the free radical and IrCl_6^{2-} can be totally ruled out. Since fresh solutions of hexachloroiridate(IV) were used, the solutions being stable for 24 h,^{12b} it is unlikely that $\text{IrCl}_5(\text{OH})^{2-}$ oxidizes N_2H_5^+ according to the equations



The electron transfer from hydrazinium ion to hexachloroiridate(IV) takes place through the formation of an intermediate compound between N_2H_5^+ and IrCl_6^{2-} according to step 5. The intermediate compound decomposes to give the



products of reaction (step 6). The rate expression is given by

$$\frac{d[\text{IrCl}_6^{2-}]}{dt} = \frac{kK[\text{IrCl}_6^{2-}][\text{N}_2\text{H}_5^+]}{[\text{H}^+] + K[\text{N}_2\text{H}_5^+]} \quad (7)$$

Hence

$$k_{\text{obsd}} = \frac{kK[\text{N}_2\text{H}_5^+]}{[\text{H}^+] + K[\text{N}_2\text{H}_5^+]} \quad (8)$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k} + \frac{[\text{H}^+]}{kK[\text{N}_2\text{H}_5^+]} \quad (9)$$

Equation 9 explains both plots (Figures 1 and 2) of substrate and acid effects. The values of k and K at different temperatures were obtained from the plots in Figure 1 utilizing the relation $k = (\text{intercept})^{-1}$ and $K = (\text{intercept}) \times [H^+]/(\text{slope})$. With use of the values of k and K at different temperatures, the pseudo-first-order rate constants were calculated from eq 8 for various sets of experiments and were found to be in agreement with k_{obsd} values as shown in Table V. The agreement is satisfactory in view of the fact that considerable uncertainty is attached to the estimates of intercept/slope ratios. It is to be noted that the value of K indicates a complexation between iridium(IV) and hydrazinium ion. However, our attempts to detect the complex formation by taking a spectrum of a cooled solution of the reaction mixture were unsuccessful.

Hydrazinium ion has been shown to be oxidized by 1-equiv oxidants⁴⁻⁶ to N_2 and NH_4^+ whereas with 2-equiv oxidants^{2,3} only N_2 is formed. The presence of both N_2 and NH_4^+ in the solution indicates that Ir(IV) behaves as a 1-equiv oxidant in the present study. The complex which is formed in step 5 decomposes to give protonated hydrazyl radical (NHNH_3^+) and Ir(III). Two hydrazyl radicals dimerize and then decompose to give N_2 and NH_4^+ by fast steps. Davies and Kustin¹⁷ also showed that Mn(III) oxidizes hydrazinium ion in perchloric acid medium to give a protonated hydrazyl radical which then dimerizes quickly before further oxidation by Mn(III) takes place. The present work, therefore, supports the view of the previous workers who showed that iridium(IV)

Table V. Effect of Varying Concentration of Substrate at Different Temperatures^a

temp, °C	$10^3 \times [N_2H_5^+], M$	$10^4 \times k_{obsd}, s^{-1}$	$10^4 \times k_{calcd}, s^{-1}$	% error
30	3	1.12	1.10	-2.0
	4	1.31	1.32	+0.5
	5	1.51	1.50	-0.3
	6	1.65	1.66	+0.6
	7	1.77	1.78	+0.9
	8	1.88	1.89	+0.6
	10	1.98	2.07	+4.7
35	14	2.44	2.32	-4.8
	2	0.98	0.99	+1.2
	3	1.44	1.37	-4.5
	4	1.75	1.70	-2.6
	5	1.92	1.98	+3.1
	6	2.19	2.23	+1.6
	8	2.59	2.64	+1.7
40	10	2.97	2.96	-0.4
	2	1.27	1.29	+1.7
	3	1.92	1.82	-5.0
	4	2.34	2.31	-1.5
	5	2.69	2.74	+2.0
	6	3.14	3.13	-0.3
	8	3.84	3.82	-0.5
45	10	4.49	4.39	-2.1
	2	1.69	1.67	-1.6
	3	2.51	2.40	-4.4
	4	3.17	3.08	-2.7
	5	3.55	3.71	+4.4
	6	4.34	4.29	-1.1
	8	5.30	5.34	+0.7
	10	5.95	6.25	+5.1

^a $[Ir(IV)] = 1.04 \times 10^{-4} M$ and $[H^+] = 1.0 \times 10^{-1} M$.

behaves as a 1-equiv oxidant in the oxidations of some organic^{7,8,18} and inorganic compounds.¹⁹

The rates are found to depend not on the nature of the anions of the added salts but on the ionic strength. Again, for a reaction between ions of opposite charge, the rate would decrease with an increase in ionic strength. The results obtained in this study are, therefore, not in conformity with what might be predicted from the Brønsted-Bjerrum relation based on the Debye-Hückel theory. Added salts often exhibit specific effects, and numerous apparent anomalies are known

in the literature.²⁰⁻²² The anomalies may arise because of the ion pairing of the reactants in the reaction mixture. However, the equilibrium constant would be much smaller than that which has been obtained in this study, if the two ions associate by electrostatic interactions. Consequently, the ion pairing between the reactants may not take place. Alternatively, it may be that the activity coefficient of the activated complex is very much different²³ from that given by the simplifying assumption of the Debye-Hückel theory and hence opposite results are not unexpected.

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Registry No. $N_2H_5^+$, 18500-32-8; $IrCl_6^{2-}$, 16918-91-5.

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Oxygen-17 Nuclear Quadrupole Resonances in Molecular Oxygen Reversibly Bonded to Iridium Carrier

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A proton nuclear magnetic double-resonance technique has been used to detect the pure nuclear quadrupole resonances of ^{17}O - ^{17}O reversibly bonded to Vaska's iridium compound, $IrO_2Cl(CO)(P[C_6H_5]_3)_2$. Two sets of lines are observed, corresponding to $e^2qQ = 16.9$ MHz with $\eta = 0.7$ and to $e^2qQ = 15.6$ MHz with $\eta = 0.9$. The inequivalence of the charge distributions about each O atom which is revealed by these results, and which is not evident in the X-ray internuclear distances, may provide new insight into the mechanism of reversible oxygen bonding.

Introduction

In recent years some efforts to understand the electronic structure of the reversible dioxygen bond in the proteins hemoglobin and myoglobin have focused on relatively small

synthetic transition-metal compounds which also combine reversibly with one molecule of oxygen.¹ An early member of this class is Vaska's iridium compound² whose crystal structure determination³ confirmed that the dioxygen bond