Activation Parameters of the Oxidation of Tetraphenylborate Ion by Hexahaloiridate(IV) Complexes

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The oxidation of BPh_4^- by $IrCl_6^{2-}$ and $IrBr_6^{2-}$ has been studied as a function of temperature. The rate law of the oxidation is $-d[Ir(IV)]/dt = 2 k_2 [IrX_6^{2-}] \cdot [BPh_4^-]$ where k_2 (25 °C) is 87.0 (±2.3) and 74.4 (±3.1) $M^{-1} s^{-1}$, respectively for $IrCl_6^{2-}$ and $IrBr_6^{2-}$ as oxidant. The activation enthalpies and entropies obtained are 11.9 (±0.5) Kcal/mole, and −9.73 (±1.0) e.u. for $BPh_4^- + IrCl_6^{2-}$, and 13.5 (±0.5) Kcal/mole and −4.70 (±1.0) e.u. for $BPh_4^- + IrBr_6^{2-}$.

Introduction

Since Wittig [1] reported the preparation of lithium tetraphenylborate in 1949, considerable research has centered upon anionic organoboron compounds. Due to their analytical applications, the most thoroughly investigated have been the tetraphenylborates. The insolubility and high crystallinity of many tetraphenylborate salts have resulted in the extensive use of tetraphenylborate ion for the analysis of various metallic ions [2], as well as the precipitating counter anion for several organic and organometallic cations.

Tetraphenylborate ion has also found some use in the synthesis of organic [3] and organometallic [4] compounds. However, monoaryl-, alkynyl-, alkenyl- and enoxytrialkylborate ions have been of greater synthetic importance due to their greater reactivity. In general, tetraphenylborate ion is chemically inert to all but strong protonic acids [5] and to oxidation. Oxidation has been accomplished by photochemical [6, 7] and electrochemical [8—10] methods, as well as by a number of oxidizing agents including oxygen [5, 8], ferric ion [11], cupric ion [12], ceric ion [9], molecular halogens [11], and hexachloroiridate(IV) [13].

Kinetics studies of the oxidation of tetraphenylborate ion is a neglected area of research with only one journal publication [13]. This study by Abley and Halpern used hexachloroiridate(IV) as the oxidant at $\mu = 0.5$ M and had provided the products and stoichiometry of the reaction. This work extends the kinetics study to determine the needed activation parameters for this reaction as well as for the reaction using hexabromoiridate(IV) as the oxidant. At $\mu = 0.10$ M, the activation energies data are obtained for comparing the energy of free radical generation of several anionic substrates when the oxidant is IrX_6^{2-}.

Experimental

Chemicals

The sodium tetraphenylborate (Eastman) was recrystallized once from acetone/toluene and dried *in vacuo* as described by Cox *et al.* [14]. K_2IrCl_6 (Alfa) and K_2IrBr_6 (McKay) were used without further purification. Sodium perchlorate was prepared by neutralizing Na_2CO_3 (Spectrum) with seventy percent perchloric acid (Alfa). The solution was degassed by bubbling argon through it for one hour to expel CO_2. The pH was adjusted to ~5 with Na_2CO_3 and allowed to stand for several days after which it was suction filtered. This solution was standardized gravimetrically. The water used was distilled once, run through a column of mixed ion exchange resin from Illinois Water Treatment Company, followed by a final distillation in an all-glass apparatus. The water was finally degassed by boiling for one hour. Due to the reactants instability in solutions, all solutions were freshly prepared before each set of kinetic runs.

Apparatus

The ultraviolet and visible spectra of the solutions were recorded on a Pye-Unicam SP8-100 spectrophotometer. A Beckman Research Model pH meter was used to make pH measurements. Standardization was done with standard buffer solutions from Beckman. The kinetics were done with a Durrum D-100 stopped-flow spectrophotometer coupled to a Nicolet Explorer IIIA digital oscilloscope. Desired traces were transferred to graphing paper using an MFE 715M X—Y recorder. The temperature was kept constant by using a Masterline 2095 circulating water bath.
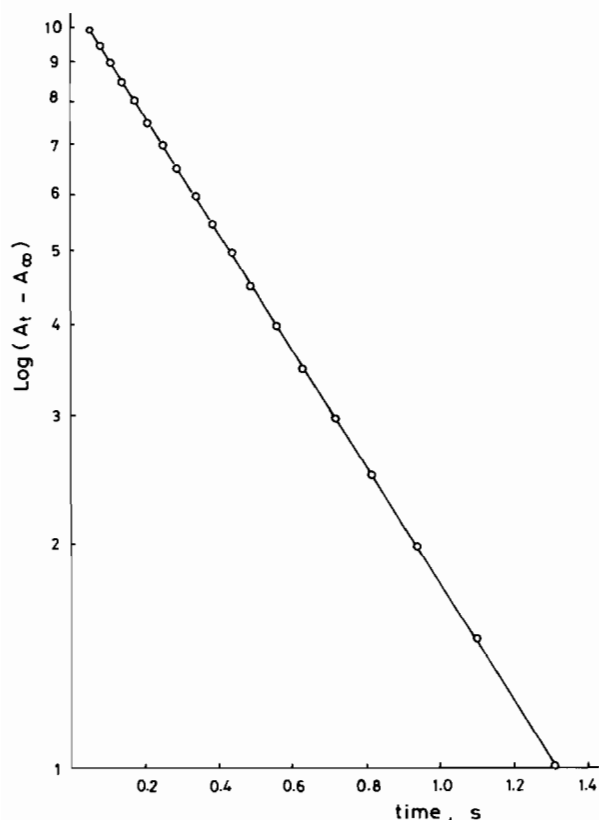
Fig. 1. Pseudo-first-order plot of the reaction between BPh_4^- and $IrCl_6^{2-}$. $[BPh_4^-] = 5.20 \times 10^{-3} M$, $[IrCl_6^{2-}] = 1.06 \times 10^{-4} M$, 35 °C, pH ~ 5, and $\mu = 0.10 M$; $k_{obs} = 1.81 \ s^{-1}$.

TABLE I. Second Order Rate Constants as a Function of Temperature.[a]

Temperature	$IrCl_6^{2-} + BPh_4^-$ [b]	$IrBr_6^{2-} + BPh_4^-$ [c]
15 °C	46.2 ± 4.1	35.8 ± 3.3
20 °C	64.0 ± 2.1	56.1 ± 2.6
25 °C	87.0 ± 2.3	74.4 ± 3.1
30 °C	134 ± 12	122 ± 4.9
35 °C	187 ± 10	169 ± 5.7

[a]Unit for $k_2 = M^{-1} \ sec^{-1}$; $\mu = 0.1 \ M$; pH ~ 5.   [b]$[IrCl_6^{2-}] = 9.90 \times 10^{-5}$ to $1.10 \times 10^{-4} \ M$; $[BPh_4^-] = 1.50 \times 10^{-3}$ to $9.00 \times 10^{-3} \ M$.   [c]$[IrBr_6^{2-}] = (1.90$ to $8.2) \times 10^{-5} \ M$; $[BPh_4^-] = 1.50 \times 10^{-3}$ to $9.00 \times 10^{-3} \ M$.
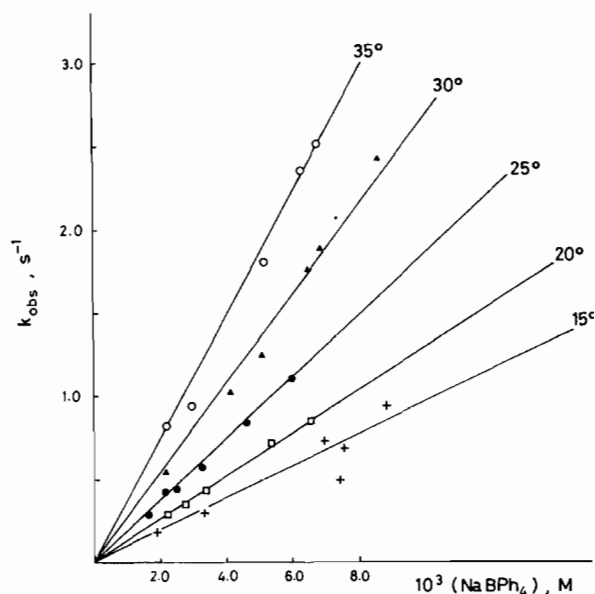
Fig. 2. k_{obs} *versus* $[BPh_4^-]$ for the $IrCl_6^{2-}$ system. 15–35 °C, pH ~ 5, $\mu = 0.10 \ M$, $[IrCl_6^{2-}] = 9.90 \times 10^{-5}$ to $1.10 \times 10^{-4} \ M$.

Kinetic Procedure

Kinetic runs were monitored by following the decrease in absorbance of $IrCl_6^{2-}$ (488 nm) and $IrBr_6^{2-}$ (575 nm) as a function of time. All runs were done under pseudo-first-order conditions in which the sodium tetraphenylborate was in at least ten-fold excess over the oxidants. The net ionic strength was kept constant at 0.10 M with sodium perchlorate. Plots of $\log(A_t - A_\infty)$ *versus* time were made on semilogarithmic paper and the pseudo-first-order rate constants were calculated. An example of these plots is shown in Fig. 1.

Results and Discussion

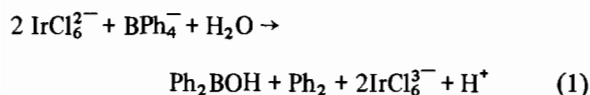The stoichiometry of the reaction has been determined previously [13], that is,

$$2 \ IrCl_6^{2-} + BPh_4^- + H_2O \rightarrow$$

$$Ph_2BOH + Ph_2 + 2IrCl_6^{3-} + H^+ \qquad (1)$$

Under pseudo-first-order conditions with $[BPh_4^-]$ in large excess, all plots of $\log (A_t - A_\infty)$ *versus* time were linear over at least three half lives establishing the first-order dependence in oxidant concentration. When $[BPh_4^-]$ was varied at constant $[IrCl_6^{2-}]$ concentration, plots of k_{obs} *versus* $[BPh_4^-]$ were linear with zero intercepts. Figure 2 is a temperature dependence plot of the reaction with $IrCl_6^{2-}$ as a function of $[BPh_4^-]$. Thus, the rate law can be expressed as:

$$-d[IrCl_6^{2-}]/dt = k_{obs} = 2k_2[BPh_4^-][IrCl_6^{2-}] \qquad (2)$$

The values of k_2 were calculated from the slopes of these linear plots and are listed in Table I. Similar measurements were carried out for $IrBr_6^{2-}$. The results are tabulated in Table I. Comparison of the k_2 (87.0

TABLE II. Second-Order Rate Constants as a Function of pH.[a]

pH	$IrCl_6^{2-} + BPh_4^-$	$IrBr_6^{2-} + BPh_4^-$
2.7	90.5	79.2
5.1	87.0	74.4
8.6	92.3	71.7
	ave = 89.3	ave = 75.7

[a]$[IrX_6^{2-}] = 1.00 \times 10^{-4}$ M; $[BPh_4^-] = (1.30-9.10) \times 10^{-3}$ M, $\mu = 0.10$ M and 25 °C.

TABLE III. Activation Parameters for the Oxidation of Anions by IrX_6^{2-}.

Reaction	$\Delta H^{\ddagger}$, Kcal/mole	$\Delta S^{\ddagger}$, e.u.
$IrCl_6^{2-} + BPh_4^-$	11.9 ± 0.5	−9.73 ± 1.0
$IrBr_6^{2-} + BPh_4^-$	13.5 ± 0.5	−4.70 ± 1.0
$IrCl_6^{2-} + SCN^-$ [a]	15.22 ± 0.6	−16.5 ± 2.0
$IrBr_6^{2-} + I^-$ [a]	7.90 ± 0.55	−24.0 ± 1.9

[a]Reference 17.

± 2.3 M^{-1} s^{-1}) at $\mu = 0.10$ M and 25 °C with those reported at $\mu = 0.50$ M ((1.2 ± 0.3) × 10² M^{-1} s^{-1}) [13] for the $IrCl_6^{2-}$ system shows that the rate of reaction is significantly increased at higher ionic strength. The reactions were also studied at pH 2.7, 5.1, and 8.6, (Table II) and no significant rate change was observed agreeing with previous findings.

The mechanism that has been proposed [13] for the oxidation of tetraphenylborate ion by IrX_6^{2-} (X = Cl, Br) shows that the rate determining step is the generation of the free radical $BPh_4\cdot$ as shown in eqn. 3:

$$BPh_4^- + IrX_6^{2-} \xrightarrow{k_2} BPh_4\cdot + IrX_6^{3-} \qquad (3)$$
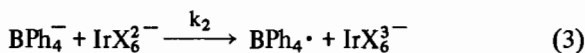
This is followed by the rapid reaction of $BPh_4\cdot$ and IrX_6^{2-} to give BPh_4^+ which then breaks up into biphenyl and BPh_2^+. The BPh_2^+ ion undergoes hydrolysis to yield Ph_2BOH.

The formation of the Ph_2 and Ph_2BOH when BPh_4^- undergoes a two-electron oxidation has been shown by Geske [8] in voltammetric and chronopotentiometric studies with platinum electrodes in acetonitrile.

Later work by Geske [9] using pentadeuterio-tetraphenylborate ion, $B(C_6D_5)_4^-$, indicated that two phenyl radicals in the transition state of the oxidized tetraphenylborate ion undergo intramolecular dimerization:
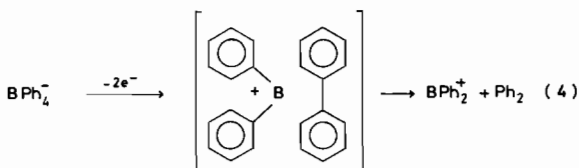
The absence of benzene as a product suggests that no phenyl radicals are liberated into solution because they would abstract hydrogens from the solvent.

With the formation of biphenyl it is logical to consider the formation of diphenylboronium ion, BPh_2^+. Davidson and French [15] reported the
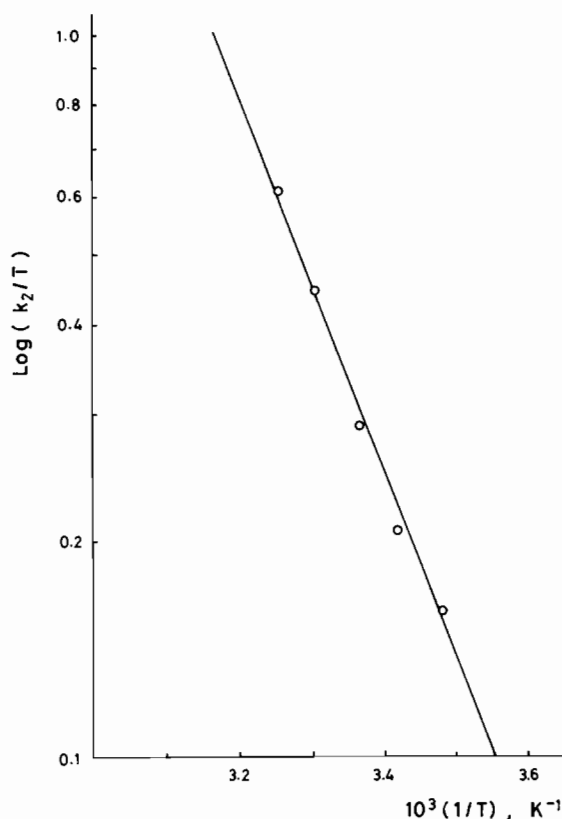

Fig. 3. Log (k_2/T) *versus* $1/T$ for the oxidation of BPh_4^- by $IrCl_6^{2-}$. 15–35 °C, pH ~ 5 and $\mu = 0.10$ M; slope = −2.60 × 10³.

existence of BPh_2^+ in both methylethylketone and nitrobenzene solutions. They suggested that this boronium ion is analogous to a carbocation and the electron-deficient boron center could receive a lone pair of electrons from the oxygen atom of a water molecule. Thereby BPh_2^+ is hydrolyzed by water to form diphenylboronous acid, Ph_2BOH, and hydrogen ion.

The values for the activation parameters given in Table III are calculated from the slopes of log

$k_2 T^{-1}$ vs. $1/T$ plot. Figure 3 shows the temperature dependence plot for $IrCl_6^{2-}$ + BPh_4^-. In both cases, excellent linear plots are obtained. The difference in $\Delta S^{\ddagger}$ (-4.70 ± 1.0 e.u. for $IrBr_6^{2-}$ and -9.73 ± 1.0 e.u. for $IrCl_6^{2-}$) reflects the steric effect of the bulkier $IrBr_6^{2-}$ complex in the activated complex. It is also expected that $IrCl_6^{2-}$ being a better oxidizing agent than $IrBr_6^{2-}$ ($E^0 = 0.892$ V [16] vs. $E^0 = 0.843$ V [17]) the $\Delta H^{\ddagger}$ should favor the $IrCl_6^{2-}$ oxidation. The difference in $\Delta H^{\ddagger}$ for the two systems is 1.6 kcal/mole. These activation enthalpies can be compared with those for the oxidation of I^- and SCN^- by IrX_6^{2-} as well and an order based on $\Delta H^{\ddagger}$ on the ease of free radical generation can be established, that is, $SCN^- < BPh_4^- < I^-$ *.

Acknowledgement

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*The rate law for IrX_6^{2-} oxidation of I^- and SCN^- is $-d[Ir(IV)]/dt = \{k' + k''[X^-]\}[X][Ir(IV)]$; only the $\Delta H^{\ddagger}$ corresponding to k' term is used.

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