Oxidation of Tetraphenylborate by Hexachloroiridate(IV)

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Summary The reaction, $BPh_4^- + 2IrCl_6^{2-} + H_2O \rightarrow Ph_2BOH + Ph_2 + 2IrCl_6^{3-} + H^+$, has been shown to occur quantitatively in aqueous solution; the kinetics are interpreted in terms of a mechanism involving $BPh_4\cdot$ radicals which are also proposed as intermediates in certain electrochemical and photochemical reactions of BPh_4^-.

WE have found that BPh_4^- and $IrCl_6^{2-}$ react quantitatively in aqueous solution in accord with equation (1). The stoicheiometry was confirmed by (i) spectral titrations which exhibited sharp end points at $IrCl_6^{2-}:BPh_4^-$ ratios of 2·0 : 1, (ii) the quantitative (>95%) isolation of Ph_2 (identified by m.p., ^1H n.m.r., and g.l.c.), and (iii) quantitative estimation of Ph_2BOH by ^1H n.m.r., as well as conversion of the latter into the corresponding anhydride, Ph_2BOBPh_2, which was isolated and characterized by its m.p. (115°) and i.r. spectrum.

$$BPh_4^- + 2IrCl_6^{2-} + H_2O \rightarrow Ph_2BOH + Ph_2 + 2IrCl_6^{3-} + H^+ \qquad (1)$$

The kinetics of the reaction were studied by monitoring the $IrCl_6^{2-}$ concentration spectrophotometrically at 490 nm (ϵ 3·2 × 10^3). Kinetic measurements, encompassing the initial concentration ranges $1{\cdot}2 \times 10^{-4}$—$1{\cdot}5 \times 10^{-3}$M-$IrCl_6^{2-}$, $1{\cdot}1 \times 10^{-4}$—$1{\cdot}5 \times 10^{-3}$M-BPh_4^-, and 0—0·1M-$HClO_4$, yielded the rate-law, $-d[BPh_4^-]/dt = k[BPh_4^-][IrCl_6^{2-}]$ with $k = (1{\cdot}2 \pm 0{\cdot}3) \times 10^2\ l\ mol^{-1}\ s^{-1}$ at 25° (independent of the H^+ concentration), the ionic strength being maintained at 0·5M with $NaClO_4$.

The form of the rate-law, together with the virtually universal tendency of $IrCl_6^{2-}$ to react as a 1-electron outer-sphere oxidant,[1,2] favour the mechanism in equations (2)—(4), in which an intermediate $BPh_4\cdot$ radical, generated by the rate-determining electron-transfer step, undergoes a further (rapid) 1-electron oxidation to yield the observed products.

$$BPh_4^- + IrCl_6^{2-} \xrightarrow{k} BPh_4\cdot + IrCl_6^{3-} \qquad (2)$$

$$BPh_4\cdot + IrCl_6^{2-} \xrightarrow{fast} BPh_4^+ + IrCl_6^{3-} \qquad (3)$$

$$BPh_4^+ \xrightarrow{fast} [BPh_2^+] + Ph_2 \qquad (4)$$

$$[BPh_2^+] \xrightarrow{H_2O} Ph_2BOH + H^+$$

These results and conclusions are of interest in connection with several other aspects of boron chemistry. (1) Radical displacement reactions of boranes of the type,[3] $R\cdot + BR'_3 \rightarrow BR'_2R + R'\cdot$, in which the possibility of neutral tetraco-ordinated intermediates of the type $BR'_3R\cdot$ has previously been considered but not demonstrated.[4] (2) The electrochemical oxidation of BPh_4^-, which has also been found to yield Ph_2BOH and Ph_2 as products and which has previously been interpreted in terms of a primary 2-electron oxidation to BPh_2^+ and Ph_2.[5] Our results suggest that an alternative mechanism, involving successive 1-electron steps with the intermediate formation of $BPh_4\cdot$, is not unlikely. (3) The photochemical decomposition of the BPh_4^- which yields Ph_2BOH and a mixture of phenylcyclohexadienes in the absence of oxygen, as well as biphenyl in the presence of oxygen. The photochemical observations, in conjunction with our chemical oxidation studies, can be interpreted in terms of a mechanism involving the photochemical electron-detachment step (5), followed by ground-state reactions of the $BPh_4\cdot$ intermediate. The fact that Ph_2 is formed in quantitative yield by chemical oxidation of BPh_4^- with $IrCl_6^{2-}$, but in yields of only up to 77% (along with compensating yields of phenylcyclohexadiene) in the photochemical decomposition of BPh_4^- in the presence of air can be attributed to the (not unexpectedly) greater efficiency of $IrCl_6^{2-}$, compared with O_2, in intercepting and oxidizing $BPh_4\cdot$ (equation 3).

$$BPh_4^- \xrightarrow{h\nu} BPh_4\cdot + e^- \qquad (5)$$

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