Kinetic Evidence for a Possible End-on Oxidative Addition of Dioxygen to a Five-Co-ordinate Iridium(I) Complex

By WYNAND J. LOUW,* THOMAS I. A. GERBER, and DIRK J. A. DE WAAL

(*National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria* 0001, *Republic of South Africa*)

Summary Kinetic measurements have shown dioxygen to react faster with the five-co-ordinate complex [(cod)Ir(phen)I] (cod = cyclo-octa-1,5-diene; phen = 1,10-phenanthroline) than with the four-co-ordinate complex [(cod)Ir(phen)]Cl to form the peroxide complex $[(cod)Ir(phen)O_2]X$ (X = Cl, I).

OXIDATIVE addition reactions of molecular oxygen and hydrogen to co-ordinatively unsaturated low-valent metal complexes are believed to proceed *via* a concerted three-centred mechanism.[1,2] Consequently, five-co-ordinate d^8-complexes should be inert towards O_2 and H_2, and reaction will only occur with initial dissociation of a ligand.[3] Our spectrophotometric (Cary 15) kinetic study of reaction (1)

$$[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})]\mathrm{Cl} + \mathrm{NaI} + O_2 \xrightarrow[\mu\ 0{\cdot}01\ \mathrm{M}]{\mathrm{MeOH},\ 40\ ^\circ\mathrm{C}} [(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})O_2]\mathrm{I} + \mathrm{NaCl} \qquad (1)$$

(cod = cyclo-octa-1,5-diene, phen = 1,10-phenanthroline) has shown that dioxygen reacts directly with the five-co-ordinate complex [(cod)Ir(phen)I].

The presence of NaI established the equilibrium (2) in

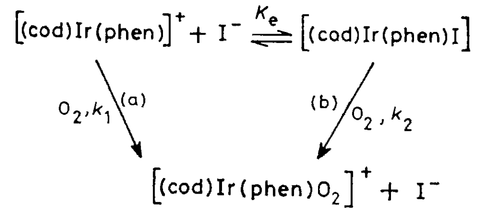
$$[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})]^+ + \mathrm{I}^- \overset{K_e}{\rightleftharpoons} [(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})\mathrm{I}] \qquad (2)$$

methanol solution.[4] A K_e value of 156 ± 9 l mol^{-1} was determined spectrophotometrically at μ 0·01 M (LiCl) and 40 °C. Oxygen-saturated methanol solutions were obtained by bubbling dioxygen through magnesium-distilled methanol, and the dioxygen concentration was determined by Winkler's method.[5] Diluted dioxygen solutions were prepared by mixing the saturated dioxygen solutions with nitrogen-saturated solutions. The end products of reaction (1), $[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})O_2]X$ (X = Cl, I) were isolated and fully characterised by micro-analysis, conductivity measurements, and i.r. spectroscopy (ν_{O-O} 850 cm^{-1}).

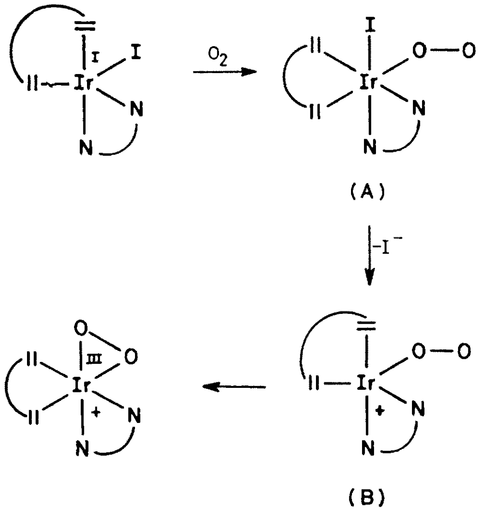
The reaction rate is first order in both [complex] and [dioxygen], and increases with increasing [NaI]. All the data conform to the rate law given in equation (3) which

$$k_{obs} = \{(k_1 + k_2K_e[\mathrm{I}^-])/(1 + K_e[\mathrm{I}^-])\}[O_2] \qquad (3)$$

can be derived from the Scheme 1. This rate law simplifies to $k_{obs} = k_1[O_2]$ and $k_{obs} = k_2[O_2]$ for $[\mathrm{I}^-] = 0{\cdot}0$ and $0{\cdot}53$ mol l^{-1}, respectively, and $[O_2] = (9{\cdot}41, 11{\cdot}29, 13{\cdot}17, 15{\cdot}06, 16{\cdot}94, 18{\cdot}82) \times 10^{-3}$ mol l^{-1} with $k_1 = (2{\cdot}86 \pm 0{\cdot}1) \times 10^{-2}$ l mol^{-1} s^{-1} and $k_2 = 0{\cdot}69 \pm 0{\cdot}004$ l mol^{-1} s^{-1}. Data were also obtained at $[\mathrm{I}^-] = (5, 8, 10, 12, 15, 100) \times 10^{-4}$ mol l^{-1} and $[O_2] = (9{\cdot}41, 11{\cdot}29, 13{\cdot}17, 15{\cdot}06, 16{\cdot}94, 18{\cdot}82) \times 10^{-3}$ mol l^{-1}. With rate law (3) as the model and using the SPSS non-linear least squares fit programme,[6] the following constants were obtained: $k_1 = (2{\cdot}36 \pm 0{\cdot}24) \times 10^{-2}$ l mol^{-1} s^{-1}, $k_2 = 0{\cdot}71 \pm 0{\cdot}01$ l mol^{-1} s^{-1}, and $K_e = 151{\cdot}8 \pm 6{\cdot}3$ l mol^{-1}. These values compare well with those given above. It is therefore clear that the five-co-ordinate [(cod)Ir(phen)I] complex is more susceptible to oxygenation than the four-co-ordinate [(cod)Ir(phen)]Cl complex.



SCHEME 1



SCHEME 2

Reaction path (a) (Scheme 1) is most probably a one-step reaction. Conversely, reaction path (b) must proceed *via* a multi-step process through one of three possible intermediates, *i.e.* (i) through the seven-co-ordinate complex $[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})\mathrm{I}(O_2)]$, (ii) through the 'dot complex' $[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})\mathrm{I}{\cdot}O_2]$,[2] or (iii) through an 'end-on' oxidative addition of dioxygen to [(cod)Ir(phen)I] shown in Scheme 2. In case (iii) intermediates (A) and (B) (Scheme 2) may be considered as either iridium(II) superoxide or iridium(III) peroxide species.

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[1] P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, 1966, **88**, 3511; L. Vaska, L. S. Chen, and W. V. Miller, *ibid.*, 1971, **93**, 6671; L. Vaska, L. S. Chen, and C. V. Senoff, *Science*, 1971, **174**, 587; L. Vaska and L. S. Chen, *Chem. Commun.*, 1971, 1080.

[2] L. Vaska, R. C. Patel, and R. Brady, *Inorg. Chim. Acta*, 1978, **30**, 239.

[3] A. J. Deeming in 'M.T.P. International Reviews of Science. Reaction Mechanisms in Inorganic Chemistry,' Inorganic Series One, Vol. 9, cons. ed., H. J. Emeleus, vol. ed., M. L. Tobe, Butterworths, London, 1972, pp. 144 and 148.

[4] G. Mestroni, A. Camus, and C. Zassinovich, *J. Organomet. Chem.*, 1974, **73**, 119; W. J. Louw and J. E. Singleton, *Inorg. Chim. Acta*, 1978, **27**, 21.

[5] L. W. Winkler, *Ber. Bunsenges. Phys. Chem.*, 1888, **21**, 2843.

[6] N. H. Nie, C. H. Hull, J. G. Jenkins, K. Steinbrenner, and D. H. Bert, 'Statistical Package for Social Sciences,' Second Edn., McGraw-Hill, New York, 1975.