

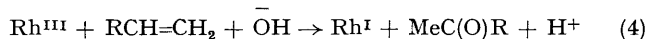
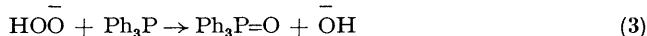
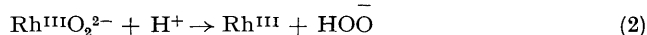
Oxygen Transfer from Group 8 Metal Dioxygen Complexes. Rhodium(I) Catalysed Co-oxygenation of Terminal Olefins with Triaryl-phosphine and -arsine Ligands

By REGINALD TANG, FRANK MARES, NOREEN NEARY, and DANNE E. SMITH

(Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960)

Summary Direct oxygen transfer in the intermediate rhodium dioxygen complex is the preferred mechanism for L_3RhCl catalysed co-oxidation of terminal olefins and the ligands L .

THE rhodium catalysed co-oxidation of terminal olefins and phosphines to alkan-2-ones and phosphine oxides was suggested by Read and Walker¹ to involve direct intramolecular oxygen transfer from the dioxygen unit of the intermediate rhodium dioxygen complex to the co-ordinated ligands. However, Sen and Halpern² recently presented evidence that oxidation of phosphines by molecular oxygen catalysed by tetrakis(triphenylphosphine)-platinum(0) involves Pt^{II} and HO_2^- as the true oxidants. They further suggested that a similar mechanism [a modified Wacker process, equations (1)–(4)] may account for the observed co-oxidation¹ of terminal olefins and triphenylphosphine since adventitious water (proton source), in catalytic quantities, cannot be excluded.² Even the recent report of Igersheim and Mimoun³ of exclusive incorporation of the labelled dioxygen into the product alkanone from the oxidant $[(Ph_3As)_4Rh(^{18}O_2)]^+ ClO_4^-$ cannot rigorously eliminate the route suggested by Sen and Halpern. Under these conditions, the ^{18}O content in the products necessarily corresponds to that in the dioxygen complex, regardless of the reaction mechanism, since the only source of oxygen is the complex.



This controversy prompted us to report our results on studies⁴ of novel modes of olefin and diene oxygenations.⁵ Thus, ^{18}O -enriched water (60%, 0.1 ml) was added to an otherwise dry reaction mixture containing benzene or toluene (6 ml), $(Ph_3P)_3RhCl$ (**1**) (0.22 mmol) or $(Ph_3As)_3RhCl$ (**2**) (0.088 mmol), oct-1-ene (6.4 mmol), dodecane (0.10 mmol, employed as internal standard for g.l.c. analysis of octan-2-one), and heptan-2-one (0.08 mmol, used as a calibrator for the expected ketone- $^{18}OH_2$ oxygen exchange). The reaction, carried out under 1 atm of O_2 and at 70 °C was monitored by withdrawing aliquots for: (a) g.l.c. analysis of octan-2-one; (b) g.l.c.-mass spectrometric analysis of ^{18}O content in the product, octan-2-one, and the calibrator, heptan-2-one; and (c) probe mass

spectrometric analysis of ^{18}O content of the oxidized ligand in the residue after vacuum evaporation of the volatile materials. Pertinent data for complex (**1**) are summarized in the Figure. In the first sample taken

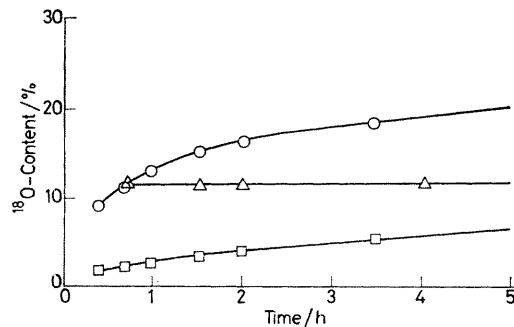


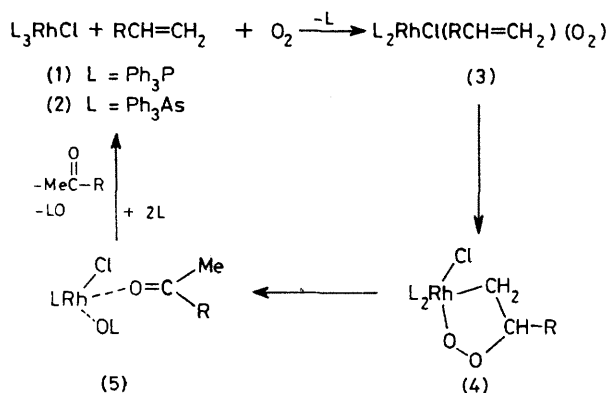
FIGURE. ^{18}O -Incorporation into octan-2-one (\circ), triphenylphosphine oxide (Δ), and heptan-2-one (\square). The yield of octan-2-one is 38% (1 h) and 50% (5 h) based on (**1**).

after 0.3 h the ^{18}O content in octan-2-one was 9.3% which corresponds to $\geq 85\%$ of the ketone oxygen being derived from molecular oxygen. Triphenylphosphine oxide contained 11.5% of ^{18}O throughout the run; this corresponds to $\geq 81\%$ of the oxygen originating from molecular oxygen. Similarly for complex (**2**), 9.1% of ^{18}O was present in octan-2-one after 0.3 h, which suggests that $\geq 85\%$ of the ketone oxygen is derived from molecular oxygen. The ^{18}O content of octan-2-one follows the same trend as that displayed in the Figure for complex (**1**). However, triphenylarsine oxide showed a much sharper increase in the ^{18}O content (13 and 33% in 0.3 and 2 h, respectively) when compared with triphenylphosphine oxide. This is expected since triphenylarsenic dihydroxide, the intermediate for oxygen exchange, is readily formed.⁶ Therefore, it can be concluded that neither a Wacker process[†] nor the sequence shown in equations (1)–(4) (both requiring 60% of ^{18}O incorporation, assuming rapid label equilibration between OH^- and $^{18}OH_2$) represents the major oxidation route. The slightly higher ^{18}O content in octan-2-one and phosphine oxide, as compared to controls, can be accounted for by postulating that the products, while still in the co-ordination sphere of the metal, exchange oxygen faster than those which have already dissociated.[‡]

We submit that the intermediates (**3**) and (**4**) previously suggested by Read and Walker¹ are involved in the oxidation. Complexes (**1**) and (**2**) are known to form $L_3RhCl(O_2)$ in the presence of oxygen,^{7,8} they exchange L for

[†] Based on the observation that added water slightly reduced the yield of the ketone, Read, *et al.*, suggested the absence of the Wacker process (ref. 1).

[‡] Under similar experimental conditions but in the absence of the metal complex no measurable ketone- $^{18}OH_2$ oxygen exchange is observed. Also, unco-ordinated triphenylphosphine oxide- $^{18}OH_2$ oxygen exchange is extremely slow with or without L_3RhCl ($\leq 4\%$ oxygen exchange in 10 h).



SCHEME

olefins in the presence of excess of olefin,^{8,9} and the iridium analogue of complex (3), (Ph₃P)₂IrCl(CH₂=CH₂)(O₂), has been isolated.¹⁰ Complexes of type (4) have been prepared and characterized in the case of Pt, Pd, and Rh for olefins bearing electronegative substituents.^{3,11} The observed partial incorporation of ¹⁸O into the products is consistent with the involvement of the intermediate (5). The intermediate (4) may collapse to alkan-2-one and a rhodium(III) oxochloride complex which, in turn, may be reduced concurrently or in a subsequent step by the ligand L. However, formation of a metal co-ordinated epoxide, by analogy with the chemistry of molybdenum peroxo complexes,¹² cannot be excluded. Indeed, preliminary data indicate that in methanol these metal complexes catalyze isomerization of oct-1-ene oxide to octan-2-one.

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- ¹ G. Read and P. J. C. Walker, *J.C.S. Dalton*, 1977, 883; G. Read, *J. Mol. Catalysis*, 1978, **4**, 83.
² A. Sen and J. Halpern, *J. Amer. Chem. Soc.*, 1977, **99**, 8337.
³ F. Igersheim and H. Mimoun, *J.C.S. Chem. Comm.*, 1978, 559.
⁴ Preliminary results of olefin and ligand co-oxygenation and the ¹⁸O-studies reported here were presented at the Gordon Research Conference—Organic Reactions and Processes, 1978, and the National Meeting, American Chemical Society, Miami, 1978.
⁵ F. Mares and R. Tang, *J. Org. Chem.*, 1978, **43**, 4631; R. Tang, H. J. Yue, J. F. Wolf, and F. Mares, *J. Amer. Chem. Soc.*, 1978, **100**, 5248.
⁶ G. O. Doak and L. D. Freedman, 'Organometallic Compounds of Arsenic, Antimony, and Bismuth,' Wiley-Interscience, New York, 1970, p. 183.
⁷ M. J. Bennet and P. B. Donaldson, *Inorg. Chem.*, 1977, **16**, 1581.
⁸ J. T. Mague and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1736.
⁹ J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.
¹⁰ H. van Gaal, H.G.A.M. Cuppers, and A. van der Ent, *Chem. Comm.*, 1970, 1694.
¹¹ R. A. Sheldon and J. A. Van Doorn, *J. Organometallic Chem.*, 1975, **94**, 115.
¹² H. Mimoun, I. Séré de Roch, and L. Sajus, *Tetrahedron*, 1970, **26**, 37.