Liquid-phase Metal-centred Autoxidation of Cyclo-octene promoted by Rhodium Species

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The rhodium(I)-promoted autoxidation of cyclo-octene, in benzene at 74 °C, gives non-catalytic yields of cyclo-oct-1-en-3-one and cyclo-octanone by a route independent of radical chains and a Wacker cycle. With added styrene, or in *NN*-dimethylacetamide, the oxidation is catalytic (6 mol of products per mol Rh). The oxidation is interpreted in terms of a rate-limiting metal-centred insertion of oxygen into an allylic carbon–hydrogen bond and subsequent reactions of the resulting cyclo-oct-1-en-3-ol.

AUTOXIDATION of styrene, catalysed by certain rhodium species, is not a radical-chain or a Wacker oxidation but probably involves attack of dioxygen on co-ordinated styrene.[1] Numerous attempts to autoxidise alkenes catalytically at metal centres have been unsuccessful [2-4] but James [5] reported a rhodium(I)–cyclo-octene complex able to adduct dioxygen and to yield unspecified quantities of cyclo-oct-1-en-3-one by a suggested metal-centred autoxidation. More detailed studies of this oxidation, reported here, show that catalytic yields of both cyclo-oct-1-en-3-one and cyclo-octanone can be obtained probably subsequent to initial oxygen-atom insertion into an allylic carbon–hydrogen bond.

EXPERIMENTAL

Materials.—Cyclo-octene (Koch-Light, puriss) was passed down an alumina column and distilled under nitrogen at 12 mmHg.† Other reagents were dried such that the water content of reaction mixtures was $<0.01\%$.

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† 1 mmHg $\approx 13.6 \times 9.8$ Pa, 1 atm = 101 325 Pa, $1\text{M} = 1$ mol dm^{-3}.

[1] J. Farrar, D. Holland, and D. J. Milner, *J.C.S. Dalton*, 1975, 815.

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[3] J. E. Lyons and J. O. Turner, *J. Org. Chem.*, 1972, **37**, 2881.

[4] K. Kaneda, T. Itoh, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1973, **46**, 3810.

[5] B. R. James and F. T. T. Ng, *Chem. Comm.*, 1970, 908; B. R. James and E. Ochiai, *Canad. J. Chem.*, 1971, **49**, 975; B. R. James, F. T. T. Ng, and E. Ochiai, *ibid.*, 1972, **50**, 590.

General Procedure.—Reaction mixtures (8.6 cm^3) contained metal complex (0.5 mmol of metal), cyclo-octene (4.5 mmol), and eicosane (0.2 g) as a chromatography standard. Benzene was the solvent unless otherwise specified. Typically, reaction mixtures were maintained at 74 °C in a thermostatted oil-bath under an atmosphere of oxygen. Water produced collected in the cooler parts of the reaction vessel and was washed into the bulk mixture with dry dioxan before analysis. Organic products were determined by gas chromatography (1.5 m column of 5% PEG 1 000 on Embacel at 130 °C). Cyclo-octanone was isolated, but other products were identified by combined g.l.c.–mass spectrometry. Other experimental details have been recorded.[1]

RESULTS

Radical Autoxidation.—After 22 h, with cobalt naphthenate as catalyst, cyclo-octene oxide (0.20 mmol), cyclo-oct-1-en-3-one (0.03 mmol), and cyclo-oct-1-en-3-ol (0.02 mmol) were formed. Addition of di-t-butyl-*p*-cresol (0.10 mmol) completely suppressed this oxidation and essentially no inhibitor was consumed.

Wacker Oxidation.—There was no reaction of cyclo-octene with $RhCl_3$ in aqueous dioxan (20% water) after 90 min.

Rhodium(I)*-promoted Reactions.*—In the presence of $[\{Rh(C_8H_{14})_2Cl\}_2]$ a brown precipitate began to form after 2 min. Within 30 min, cyclo-octene oxide (0.024 mmol), cyclo-octanone (0.260 mmol), cyclo-oct-1-en-3-one (0.265 mmol), cyclo-oct-1-en-3-ol (0.045 mmol), and water (0.260 mmol) were formed; cyclo-octene (0.590 mmol) and oxygen (0.420 mmol) had been consumed. At longer reaction times oxygen was continuously absorbed (0.75 mmol after 4 h) but no further organic products appeared and no more cyclo-octene was consumed. The catalyst was not regenerated on treatment with hydrogen at 1 atm. Identical yields of liquid products resulted with $[\{Rh(C_2H_4)_2Cl\}_2]$, but rapid evolution of ethylene from this complex prevented measurements of oxygen uptake. The complexes $[Rh(C_2H_4)_2(C_5H_5)]$ and $[\{Rh(cod)Cl\}_2]$ were inactive (cod = cyclo-octa-1,5-diene).

Effect of Water and Oxygen Concentrations.—The autoxidation rate was the same using air or oxygen and was also independent of the water content of the solvent with benzene (0.01—0.3% water) or dioxan (0.1—0.5% water). Molecular sieves (3A) did not affect the reaction.

Influence of Additives.—Addition of three concentrations of di-t-butyl-*p*-cresol (10.0, 1.0, and 0.1 mmol) to typical reaction mixtures all reduced the epoxide yield to about one third of its uninhibited value but the yields of other products were unaltered. Both cyclo-octanone and cyclo-octene oxide (0.4 mmol) were stable under the reaction conditions, in the presence or absence of cyclo-octene, and neither additive affected the oxidation. However, cod (1.0 mmol) completely suppressed the oxidation. Both cyclo-octanol and cyclo-oct-1-en-3-ol were unstable under the reaction conditions.* During 30 min, cyclo-octanol (0.4 mmol) gave cyclo-octanone (0.2 mmol), and cyclo-oct-1-en-3-ol (0.4 mmol) gave cyclo-octanone (0.2 mmol) and cyclo-oct-1-en-3-one (0.2 mmol).

*Oxygen-*18 *Tracer Study.*—After 3 min at 74 °C an otherwise typical reaction mixture saturated (0.3%) with $H_2{}^{18}O$ (1.4 mmol, 40% ^{18}O) gave cyclo-octanone (0.15 mmol) and cyclo-oct-1-en-3-one (0.15 mmol). Both products were free of ^{18}O (g.l.c.–mass spectrometry, which would have detected a level of 2% of the label).

Studies of the Precipitate.—Using $[\{Rh(C_2H_4)_2Cl\}_2]$ (0.20 g), after 16 h a red-brown precipitate (0.24 g) was formed (Found: C, 26.6; H, 3.75; Cl, 12.7; Rh, 36.2%). Cryoscopy in dimethyl sulphoxide (dmso) pointed to a molecular weight of *ca.* 252. Bands in the i.r. spectrum at 3 350 and 2 900 cm^{-1} indicated the presence of O–H and C–H groupings, respectively, but there was no evidence of a carbonyl group or of co-ordinated oxygen. Dissolution of the precipitate in *NN*-dimethylacetamide (dma), followed by g.l.c., showed the presence of cyclo-octene and a small quantity of ethylene. A temperature-programmed mass spectrum of the precipitate during 3 h showed water (40—170 °C), hydrogen chloride (130—190 °C), and ethylene (100—180 °C) to be evolved in the temperature ranges indicated.

Temperature Dependence.—With xylene as solvent, the product distribution was unaffected by temperature in the range 53—112 °C. Comparison of initial rates indicated an activation energy of 35 kJ mol^{-1}.

Reaction in dma.—With dma as solvent containing 0.2M-LiCl and inhibitor (10 mmol), there was no precipitate. After 46 h cyclo-octanone (1.42 mmol), cyclo-octenone (1.45 mmol), and cyclo-octenol (0.30 mmol) were formed.

Co-oxidation of Cyclo-octene with Styrene.—Reaction of styrene (1.0 g) and cyclo-octene (4.0 g) in xylene containing inhibitor (10 mmol) for 96 h gave acetophenone (0.30 mmol), cyclo-octenone (1.50 mmol), and cyclo-octanone (1.70 mmol).

Reactions with Cyclohexene.—Replacing cyclo-octene by cyclohexene in the general procedure, addition of $[\{Rh(C_2H_4)_2Cl\}_2]$ did not result in evolution of ethylene. After 16 h cyclohexanone (0.01 mmol) and cyclohex-1-en-3-one (0.01 mmol) were formed.

DISCUSSION

At reaction times of up to 30 min in benzene, the products assayed account for all the cyclo-octene and oxygen consumed. The major products are cyclo-octanone and cyclo-oct-1-en-3-one. The free-radical chain autoxidation of cyclo-octene yields mainly the epoxide,[6] and the reaction is completely suppressed by inhibitor. Epoxide is only a minor product of the rhodium(I)-promoted reaction and it is the only product even partially suppressed by added inhibitor. If the suppression of epoxide formation indicates the contribution of radical chains to the oxidation, only a small fraction (*ca.* 1%) of the cyclo-oct-1-en-3-one is likely to arise by this route in the Rh^I reaction. Cyclo-octanone is not formed in radical-chain oxidations of cyclo-octene, but it is analogous to products formed in Wacker oxidation of olefins. However, cyclo-octene is resistant to Wacker oxidation both by Pd^{II} [7] and by Rh^{III}. Moreover, the rate of the rhodium(I)-promoted oxidation is independent of both oxygen and water concentration, and added $H_2{}^{18}O$ is not incorporated into the products. Therefore, a Wacker cycle does not contribute significantly to the reaction.[1]

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* We are indebted to a referee for proposing both these alcohols as precursors of their corresponding ketones.

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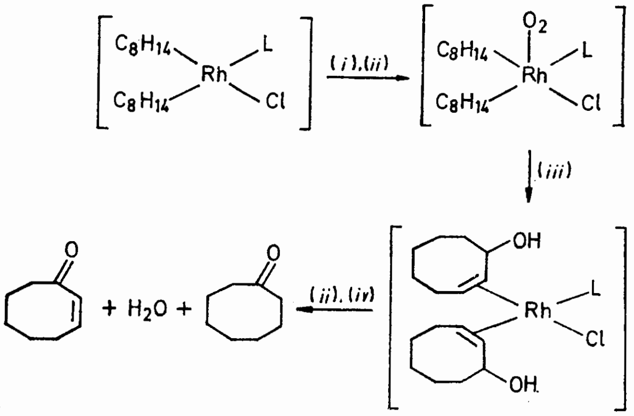
[7] R. Huttel, H. Dietl, and H. Christ, *Chem. Ber.*, 1964, **97**, 2037.

James[5] attributed cyclo-oct-1-en-3-one formation to hydrogen abstraction from the olefin by a Rh–O_2 adduct, followed by production and decomposition of an allylic hydroperoxide. The inability of di-t-butyl-*p*-cresol to inhibit cyclo-octenone formation rules out radical reactions in the bulk of the solution, but co-ordinated radicals must be considered and have been suggested. The inactivity of $[Rh(C_2H_4)_2(C_5H_5)]$ and $[\{Rh(cod)Cl\}_2]$ and the inhibiting action of cod indicate that co-ordination to the metal is essential for reaction.

The similarity of reaction rates of various organic peroxy-radicals with a given substrate is attributed to the remoteness of the organic group from the radicals' reactive centre.[8] Organic peroxy-radicals react *ca.* 4 000 times faster with the inhibitor than with cyclohexene,[8] and a comparable ratio is expected for inhibitor and cyclo-octene. A rhodium peroxy-species is also expected to show a marked preference for reaction with the inhibitor. A space-filling molecular model of the proposed[5] C_8H_{14}–Rh–O_2 intermediate indicates that the oxygen and allyl hydrogen atoms may be close to van der Waals contact and that the oxygen is not sterically restrained from reaction with inhibitor. The rates of reaction of organic peroxy-radicals, even with the inhibitor, are several orders of magnitude lower than those expected for encounter-controlled processes. If the reaction of the oxygen adduct to give cyclo-octenone is also slow compared with diffusion, the products of the appropriate rate constants with the local concentrations of olefin and inhibitor should give a measure of the competition between the two for the adducted oxygen. The local concentration of inhibitor is the same as that in the bulk solution (1.2M), but that of allyl hydrogen may be substantially greater than the bulk value. Van der Waals contact between oxygen and the allyl hydrogen is roughly equivalent * to a local concentration of 40M, but even this value seems too low to explain the insensitivity of cyclo-octenone yield to inhibitor if radicals are involved.

Cyclo-octanone formation is analogous to the production of ketones in other rhodium(I)-promoted olefin autoxidations.[1,9] These reactions allegedly resemble the dissociative 'oxygen insertion' proposed[10] for the $[Pt(PPh_3)_3]$-catalysed oxidation of triphenylphosphine. Co-oxidations of PPh_3 with terminal alkenes[9] on Rh^I, and with styrene[1] on Ir^I, yield phosphine oxide and ketones. These reactions seemingly occur by dissociation of a molecule of co-ordinated oxygen and transfer within the metal's co-ordination sphere of one of the oxygen atoms to the phosphine and the other to the olefin, but the mechanism by which the oxygen-accepting olefin rearranges to a ketone is not known. A similar reaction in a phosphine-free system may occur in the rhodium(I)-catalysed autoxidation of styrene.[1]

The effects of additives on the cyclo-octene reaction are instructive. All the products are formed at the shortest times accessible for sampling and the ratio of their yields is constant throughout the reaction. They are not formed by rearrangement of epoxide or dehydrogenation of cyclo-octanone, which are stable under the reaction conditions. Although added cyclo-octanol is converted into cyclo-octanone, it is probably not an intermediate. The dehydrogenation of cyclo-octanol is slower than is the oxidation of cyclo-octene to cyclo-octanone (when no cyclo-octanol is observed). Moreover, cyclo-octanol is the hydration product of cyclo-octene and addition of $H_2{}^{18}O$ to a typical reaction does not lead to labelled products. However, the fate of added cyclo-oct-1-en-3-ol strongly implies that it is the precursor of both major products. Cyclo-oct-1-en-3-ol is a minor product of the reaction and the added compound rapidly yields cyclo-octanone and cyclo-oct-1-en-3-one in the same ratio in which they are formed during the autoxidation. The insensitivity of the product spectrum to change in temperature suggests a common rate-limiting step, and this agrees with the proposed intermediacy of cyclo-oct-1-en-3-ol (Scheme). Up to 5% of the initial cyclo-octene is converted into cyclo-octenone. This cannot arise by oxygenation of cyclo-octadiene impurities because g.l.c. shows these to be present to the extent of only 0.1%. Moreover, water is the measured coproduct of cyclo-octenone. In the suggested rate-limiting step the co-ordinated oxygen dissociates and oxygen atoms insert into the allylic carbon–hydrogen bonds of two co-ordinated cyclo-octene molecules. The cyclo-oct-1-en-3-ol rapidly reacts further to yield cyclo-oct-1-en-3-one by dehydrogenation or cyclo-octanone by a rearrangement similar to that reported for allylic ethers.[11]



SCHEME (*i*), O_2; (*ii*), rapid; (*iii*), slow; (*iv*), $\frac{1}{2}O_2$

The phosphine–olefin co-oxidation has been likened[9] to the biological mono-oxygenations, and the cyclo-octene reactions resemble a dioxygenation. The low

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* An atom of the rhodium-bound oxygen could accommodate about four hydrogens in van der Waals contact. The value 40M is a quarter of that calculated for 'pure atomic hydrogen' assuming each hydrogen atom to occupy 6 cm^3 mol^{-1}.

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[9] C. W. Dudley, G. Read, and P. J. C. Walker, *J.C.S. Dalton*, 1974, 1926.

[10] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491.

[11] E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1973, **38**, 3224.

yield of epoxide is attributed to deactivation of the ethylenic bond on co-ordination to the rhodium. At reaction times longer than 30 min more oxygen is absorbed without further oxidation of the olefin. This additional oxygen appears in the brown precipitate which forms, but the nature of the precipitate is not known. The absence of catalysis is attributable to precipitate formation. With added styrene, or in dma, no precipitate forms, the spectrum of products from cyclo-octene is unchanged, and catalysis occurs (about six molecules of products are formed per rhodium atom).

The inactivity of cyclohexene to oxidation probably results from its inability to displace ethylene from $[\{Rh(C_2H_4)_2Cl\}_2]$. The low stability of cyclohexene-rhodium(I) complexes[12] has been reported, as has the low activity of cyclohexene in the phosphine-powered autoxidation.[13] The phosphine-driven oxidation of terminal alkenes is reported to give largely methyl ketones,[9] and preliminary studies show that these products are also formed under the conditions used for the cyclo-octene work. Since oxygen insertion into allylic carbon–hydrogen bonds, as proposed above, would convert terminal alkenes into ethyl ketones, the course of rhodium(I)-promoted autoxidations seems to be highly sensitive to the structure of the olefin. Investigation of this effect is in progress.

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