# Catalytic Formation of an Amide Hydroperoxide and Hydrogen Peroxide using Rhodium Complexes and Dioxygen/Dihydrogen Mixtures

**Sujatha N. Gamage and Brian R. James***

*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6*

A rhodium(III) complex in *N,N*-dimethylacetamide solution under a 1 atm $O_2/H_2$ mixture catalyses concomitant formation of the hydroperoxide $MeC(O)N(Me)CH_2OOH$ and hydrogen peroxide.

Work from this laboratory has reported on the use of $O_2/H_2$ mixtures for selective oxidation of dimethyl sulphoxide (dmso) to the sulphone, and cyclo-octene to cyclo-octanone, catalysed by Rh or Ir complexes;[1] the systems are examples of 'reductive' dioxygen activation, where one oxygen atom of $O_2$ is reduced to $H_2O$ and the second oxygen atom is incorporated into the substrate, as in cytochrome-P450 oxygenations.[1,2] During attempts to detect a putative Rh–OOH intermediate in the sulphoxide oxidations (possibly formed by $O_2$ insertion into Rh–H),[1] we chose the basic, polar solvent *N,N*-dimethylacetamide (dma), because this is known to promote metal hydride formation.[3] The studies revealed instead a selective catalytic oxidation of the solvent to (*N*-methylacetamido)methyl hydroperoxide, $MeC(O)N(Me)CH_2OOH$, as well as accompanying hydrogenolysis of $O_2$ to $H_2O_2$.

Stirred dma solutions of *mer*-$RhCl_3(dmso)_3$,[4] (1.7—7.0) × $10^{-3}$ M, at 50 °C under $O_2/H_2$ mixtures at 1 atm pressure, absorb gas at a linear rate for about 1 h, and then the rate slowly decreases, as exemplified in Figure 1. This figure shows also a typical product distribution[†] as a function of time, and demonstrates that all the products are formed catalytically.

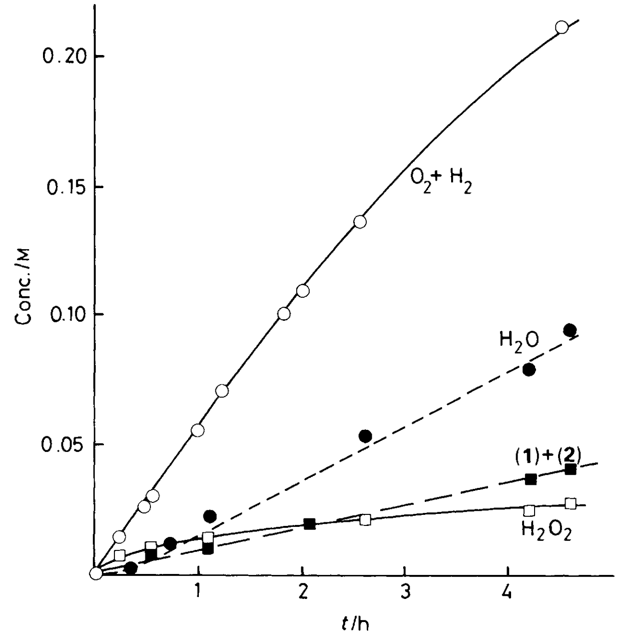


**Figure 1.** Concentration *vs.* time for: total gas uptake $O_2 + H_2$ (○); water (●); hydroperoxide + *N*-formyl, (**1**) + (**2**) (■); and hydrogen peroxide (□), for reaction mixtures containing 5.0 × $10^{-3}$ M $RhCl_3(dmso)_3$ in dma at 50 °C under a mixture of $O_2$ (260 Torr) and $H_2$ (500 Torr, 1.36 × $10^{-3}$ M).

---

[†] Product compositions were determined by a combination of GC, $^1H$ NMR, and chemical methods, as well as near IR absorption measurements at 1930 nm for water content.[5] The hydroperoxide (**1**) was prepared as a mixture of *cis*- and *trans*-isomers from dma by autoxidation induced by $Bu^tOOH$.[6] Full details[7] will be published elsewhere. $H_2O_2$ was determined as the difference between 'total peroxides,' measured iodometrically, both with and without prior treatment of the test solution with aqueous catalase solution.[6]

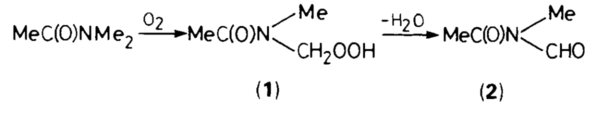
The amide oxidation product appears as a mixture of the hydroperoxide $RCH_2OOH$ (**1**) and the corresponding *N*-formyl compound RCHO (**2**) [R = MeC(O)N(Me)–] because (**1**) readily decomposes to the formyl (*e.g.* during work-up procedures or under the GC conditions used); maximum ratios of *ca.* 2:1 hydroperoxide:formyl are obtained for isolated products. The net amide oxidation is envisaged as in Scheme 1.

Of note, $H_2O_2$ is the major product for the first half-hour of reaction and throughout the reaction there is good mass balance.[‡] It seems likely from the product profiles that the $H_2O$ is formed from reaction (1) and by decomposition of the $H_2O_2$ which approaches a steady-state concentration; this decomposition ($\rightarrow H_2O + 1/2\ O_2$), presumably Rh-catalysed, does not affect the mass-balance calculations. The reaction then, in the earlier stages, catalytically generates $H_2O_2$ and (**1**).

The gas-uptake rates in the absence of either the Rh complex or the $H_2$, under corresponding conditions, are negligible. The catalysis is not free-radical in nature; the rates are reproducible (*vide infra*) and are not affected by radical inhibitors, and common autoxidation products from dialkylamides[6,8] are not seen.[§] Use of $H_2O_2$ or $Bu^tO_2H$ in the presence or absence of $RhCl_3(dmso)_3$ in dma at 50 °C produces amide hydroperoxide, but at much slower rates than when using the $O_2/H_2$ mixtures (by factors of 5—8).

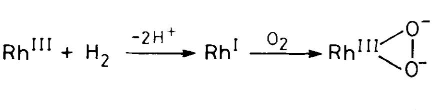
Considerable mechanistic details have been elucidated. In dma at 50 °C, $RhCl_3(dmso)_3$ reacts irreversibly with *ca.* 1 mol. equiv. $H_2$ at 1 atm ($t_{1/2} \sim 10$ min) to generate a non-hydridic species which must be $Rh^I$;[¶] removal of the $H_2$ and exposure to 1 atm $O_2$ instantly generates an *in situ* $Rh^{III}(O_2^{2-})$ species (i.r. 850 $cm^{-1}$), which can be formed also from reaction of $O_2$ with dma solutions of labile $Rh^I$ precursors such as $[RhCl(cyclo\text{-}octene)_2]_2$ in the presence of added dmso (3 mol/Rh) and $Cl^-$ (2 mol/Rh) [reaction (1)].

The kinetics of the catalytic reaction were readily ascertained from the initial, maximum rate of the gas-uptake plots (*cf.* Figure 1); the rates were unaffected by addition of water or a proton source, and were independent of the partial pressure of $O_2$ from 70 to 600 Torr. The other kinetic dependences are nicely rationalised in terms of the mechanism outlined in Scheme 2, which yields the rate-law shown in equation (2). The *K* equilibrium accounts for (a) a Rh dependence that decreases from first to half-order with increasing total [Rh], (b) an inverse dependence on added dmso (0.03—0.17 M), and (c) a first order dependence on [Rh] in the presence of excess (0.12 M) of dmso. The rate *vs.* $H_2$ plot increases linearly with $H_2$ pressure (120—700 Torr) but gives an intercept, the $k_2$ term, at zero $H_2$. Analyses of the rate dependences at 50 °C give internally consistent values for $k_1$ ($1.05\ mol^{-1}\ dm^3\ s^{-1}$), $k_2$ ($5 \times 10^{-4}\ s^{-1}$), and $K$ ($4 \times 10^{-3}$). The $k_1$ and $k_2$ rate constants, measured by consumption of $O_2$ and $H_2$, allow for calculation of the initial rates of formation of $H_2O_2$ and (**1**), respectively, and agreement with data from product distribution curves (*cf.* Figure 1) is excellent. The kinetically determined *K* value is comparable with that measured directly previously for a corresponding equilibrium with $RhCl_3(dmso)_3$ in dma (0.01 ± 0.005).[4]



(**1**) (**2**)

**Scheme 1**

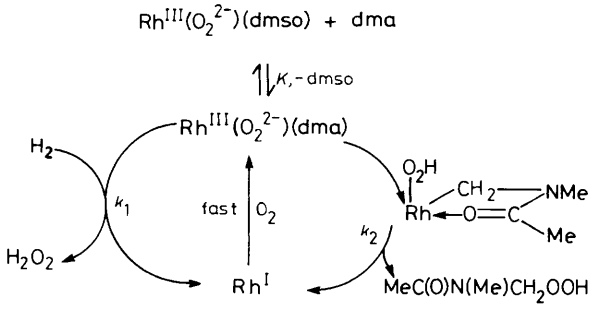

(1)

$$\text{Rate of gas uptake} = \frac{K[\text{dma}][\text{Rh}]_{\text{total}}}{K[\text{dma}] + [\text{dmso}]}\left(2k_1[H_2] + k_2\right) \quad (2)$$

A plausible route for the oxygen transfer to the amide is shown in Scheme 2. There is precedent in the literature for selective activation of C–H α to the nitrogen of a co-ordinated amide,[9] and for abstraction of a C–H hydrogen of co-ordinated substrate by co-ordinated peroxide with reincorporation of the $-O_2H$.[10]

The solution hydrogenolysis of $O_2$ to give $H_2O_2$ has precedent only in the patent literature where again homogeneous platinum metal catalysts, but in two-phase systems, have been utilised.[11] Heterolytic cleavage of $H_2$ by the Rh peroxide intermediate could generate RhH(OOH), which subsequently reductively eliminates $H_2O_2$ with generation of $Rh^I$ and continuation of the catalytic cycle *via* rapid $O_2$ uptake (Scheme 2).

It is clear that $H_2$ is not being used as an $O_2$-coreductant in the amide oxidation and, indeed, once the $Rh^{III}$–peroxide has been generated [reaction (1)], the suggested mechanism for the amide oxidation cycle requires no further $H_2$ consumption. Nevertheless, if the *in situ*-formed $Rh^{III}(O_2^{2-})$ in dma is subjected to 1 atm $O_2$ alone at 50 °C, the rate of $O_2$ uptake is negligible and the solution colour darkens somewhat within 30 min; catalytic activity can be regenerated by limited treatment with $H_2$,[¶] prior to admitting the $O_2/H_2$ atmosphere. The role of $H_2$ appears to be to retard conversion of the active peroxide catalyst into inactive forms, which we believe are di- or poly-nuclear species. There are several reports[12] on the aggregation of rhodium-based autoxidation catalysts to inactive forms; a bridged-peroxide is a much poorer nucleophile than a terminal peroxide,[13] and ability to abstract protons is decreased. Earlier work from this laboratory[14] has reported on the reaction of a $Rh_4Cl_4(CO)_4(O_2)_2(PR_3)_2$ species with $H_2$ in the presence of excess of phosphine to give $RhCl(CO)(PR_3)_2$ with probable liberation of $H_2O_2$. Such deactivation 'aggregation phenomena' could readily be incorporated into Scheme 2.



**Scheme 2**

---

[‡] *E.g.* in Figure 1, after 4.6 h the total gas uptake measured ($H_2 + O_2$) is 0.214 M; the concentrations of $H_2O_2$, (**1**), (**2**), and $H_2O$, are 0.026, 0.012, 0.029, and 0.094 M, respectively, and these require the respective consumption of 0.052, 0.012, 0.029, and 0.098 M gas uptake, *i.e.* a total of 0.191 M, in good agreement with the measured uptake [of the 0.094 M $H_2O$, 0.029 M comes from the conversion (**1**) → (**2**), Scheme 1, leaving 0.065 M to be formed from $H_2 + 1/2\ O_2$, *i.e. via* 0.0975 M gas uptake].

[§] Typically formaldehyde, formic acid, acetic acid, dimethylamine, and $CO_2$, formed *via* a photolysis or higher-temperature reaction.

[¶] In the absence of stabilising ligands, these $Rh^I$ solutions under $H_2$ slowly precipitate metal.

We thank the Natural Sciences and Engineering Council of Canada for financial support, and Johnson Matthey Ltd. for the loan of rhodium.

*Received, 2nd June 1989; Com. 9/02316J*

## References

1 M. T. Atlay, M. Preece, G. Strukul, and B. R. James, *Can. J. Chem.*, 1983, **61**, 1332; B. R. James, R. H. Morris, and P. Kvintovics, *ibid.*, 1986, **64**, 897.

2 I. Tabushi, *Coord. Chem. Rev.*, 1988, **86**, 1.

3 B. R. James, in 'Comprehensive Organometallic Chemistry,' vol. 8, eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, ch. 51.

4 B. R. James and R. H. Morris, *Can. J. Chem.*, 1980, **58**, 399.

5 D. K. Keyworth, *Talanta*, 1961, **8**, 461.

6 B. F. Sager, *J. Chem. Soc. (B)*, 1967, 428; 1047.

7 S. N. Gamage, Ph.D. dissertation, University of British Columbia, Vancouver, 1985.

8 N. N. Pozdeeva, T. I. Sapacheva, and A. L. Aleksandrov, *Izv. Akad. Nauk. SSSR., Ser. Khim.*, 1976, 1738.

9 J. M. Brown and P. J. Maddox, *J. Chem. Soc., Chem. Commun.*, 1987, 1278.

10 B. R. James, *Adv. Chem. Ser.*, 1980, **191**, 253.

11 For example: F. Moseley and P. N. Dyer, U. S. Pat. 4,336,240, 1982; R. C. Michaelson, U.S. Pat. 4,347,231, 1982; U.S. Pat. 4, 347,232, 1982.

12 E. C. Nyberg and R. S. Drago, *J. Am. Chem. Soc.*, 1981, **103**, 4966; M. T. Atlay, L. R. Gahan, K. Kite, K. Moss, and G. Read, *J. Mol. Catal.*, 1980, **7**, 31; H. Mimoun, M. M. Perez Machirant, and I. Seree de Roch, *J. Am. Chem. Soc.*, 1978, **100**, 5437; G. Read and P. J. C. Walker, *J. Chem. Soc., Dalton Trans.*, 1979, 883.

13 M. H. Gubelmann and A. F. Williams, *Struct. Bonding*, 1983, **55**, 1.

14 W. R. Cullen, B. R. James, and G. Strukul, *Inorg. Chem.*, 1978, **17**, 484; *Can. J. Chem.*, 1978, **13**, 1965.