JOURNAL OF CATALYSIS 41, 148–154 (1976)

Oxidation of Olefins Catalyzed by Dioxygen Complexes of Transition Metals

SHIGEAKI MUTO AND YOSHIO KAMIYA

Faculty of Engineering, the University of Tokyo, Hongo, Tokyo, Japan

Received May 29, 1975

In order to study the catalysis for the oxidation of α-methylstyrene and cyclohexene, some metal–dioxygen complexes were synthesized. The rate of oxidation was about half order with respect to the concentration of the dioxygen complexes. The oxidation rate of cyclohexene could be correlated with the reactivity for the redox decomposition of hydroperoxide formed as an intermediate during the course of the oxidation. From these results, it was concluded that the oxidation rate of cyclohexene was affected mainly by the reactivity of metal complexes for the hydroperoxide decomposition.

However, the oxidation rate of α-methylstyrene was suggested to depend on the coordinated oxygen molecule. It was observed that the oxidation rate of α-methylstyrene was lowered in basic solvents such as pyridine or ethanol. However, the chain initiation of α-methylstyrene catalyzed by $Ru(OH)(NO)(PPh_3)_2O_2$ increased dramatically in acetic acid. The correlation between the oxidation rate of α-methylstyrene and O–O bond length of the dioxygen complexes was also investigated.

INTRODUCTION

Recently the study on metal–dioxygen complexes has received considerable attention since new types of metal complexes, $IrX(CO)(PPh_3)_2$ and $RhX(PPh_3)_3$($X =$ halide, $PPh_3 =$ triphenylphosphine), which have an ability to coordinate oxygen molecule, were synthesized respectively, by Vaska (*1*) and Wilkinson (*2*). There has been catalytic interest in the oxidation of organic compounds using the dioxygen complexes and also biochemical interest as oxygen carrier which absorbs oxygen molecule reversibly in a similar manner as hemoglobin. In general, oxygen–oxygen bond length of a dioxygen complex (*3*) corresponds to that of excited oxygen molecule, suggesting that the dioxygen coordinated to a metal complex is activated considerably.

Although a number of applications (*4*, *5*) of these complexes to organic oxidations have recently been published, it seems important to distinguish the effect due to the activation of molecular oxygen from the effect due to hydroperoxide decomposition by a metal complex, when the autoxidation of hydrocarbon proceeds by hydrogen abstraction mechanism. It has been reported that the oxidation of ethylbenzene (*6*) and diphenylmethane (*7*) catalyzed by metal complexes gave acetophenone and benzophenone as major products, respectively. However, these are considered to be the decomposition products of hydroperoxides formed as intermediate. Further, oxidation of olefins has also been investigated. Lyons and Turner (*8*) reported that tetramethylethylene was oxidized by Rh- and Ir-complexes under an oxygen atmosphere to yield 2,3-dimethyl-2,3-epoxybutane and 2,3-

dimethyl-3-hydroxybutene-2 as major products and also 2,3-dimethyl-3-hydroperoxybutene-1 in as much as 10% yield simultaneously. Furthermore, oxidation of cyclohexene catalyzed by metal complexes or dioxygen complexes has been investigated by Collman *et al.* (*9*), Graham *et al.* (*10*), and Kaneda *et al.* (*11*). It was clarified that these reactions proceeded by radical mechanism, since there was no oxygen uptake in the presence of a free-radical inhibitor.

Previously (*12*), we have confirmed that α-copper phthalocyanine and metal acetylacetonates have a capability to activate oxygen molecule and a remarkable effect to initiate the chain of autoxidation of α-methylstyrene by addition mechanism. It seems that α-methylstyrene which proceeds entirely by addition mechanism (*13*) is the most suitable substrate to study the effect due to the coordinated oxygen molecule.

In this work, we studied the catalysis by metal–dioxygen complexes in the autoxidation of α-methylstyrene, where the reaction proceeds by addition mechanism to give polyperoxide, and of cyclohexene where the reaction proceeds by hydrogen abstraction mechanism to give hydroperoxide. Correlation between O–O bond length and reactivity for the oxidation of α-methylstyrene was also investigated.

EXPERIMENTAL METHODS

The infrared spectra were recorded as Nujol mulls on a Nippon Bunko IR-G spectrophotometer (4000–400 cm^{-1}), calibrated with polystyrene film. Melting points were measured on a Yazawa hot-stage apparatus. Triphenylphosphine was recrystallized from ethanol. Olefins were purified by treatment with activated alumina after distillation.

All the dioxygen complexes were prepared according to procedures in the literature (*14, 15*). The colors and ir data are given in Table 1. The stretching band of M–O bond which was expected in the 600–450 cm^{-1} region could not be assigned because of the overlapping with the strong bands of triphenylphosphine ligand (*16*).

The oxidation technique has been described previously (*17*). The oxidations were carried out under oxygen atmosphere at 60 or 50°C. The oxidation mixture of cyclohexene was treated with excess triphenylphosphine to reduce cyclohexenyl hydroperoxide to the corresponding alcohol, and then analyzed by gas chromatography after addition of a weighed amount of cyclohexanone (internal standard). A 2 m stainless steel column packed with 20% PEG 20 *M* and 20% DC-550 on Celite 545 was used. Hydroperoxide was analyzed by conventional iodometric method.

RESULTS AND DISCUSSION

Oxidation of α-Methylstyrene and Cyclohexene

Catalysis by metal complexes for the oxidation of α-methylstyrene and cyclohexene under an oxygen atmosphere was first investigated. Results are given in Table 2. With cyclohexene, the oxidation was carried out in chlorobenzene at 50°C. Usually the steady rate of the oxidation was observed after an induction period of several minutes. It was observed, as shown in Table 2, that most of the metal complexes used were remarkably effective for the oxidation of cyclohexene. On the other hand, certain complexes other than $RhCl(PPh_3)_3$, Co(Salen), and Co(Salchx) have shown little effect or even an inhibitory effect for the oxidation of α-methylstyrene. This suggests that the oxygen molecule attached to these metal complexes is not as activated as that of $M(acac)_2O_2$ published previously (*12*).

In Fig. 1, the log of the rate of oxygen absorption of α-methylstyrene is plotted against the concentration of dioxygen complexes. Although the rate of oxidation was about half order with respect to the con-

TABLE 1

COLOR AND IR DATA (cm^{-1}) FOR DIOXYGEN COMPLEXES

Formula	X	Color	ν (CO)	ν (NO)	ν (O–O)
$IrX(CO)(PPh_3)_2O_2$	= Cl	Orange	2000s		857s
	Br	Yellowish-brown	2000s		857s
	I	Brown	1999s		859s
$RuX(NO)(PPh_3)_2O_2$	= OH	Dark red		1760s	878s
	Cl	Brownish-black		1760s	880s
	Br	Dark brown		1759s	878s
	I	Dark brown		1756s	875s

centration of $Co_2(Salen)_2O_2$, the oxidation rate decreased with increasing concentration of the catalyst in the case of $RhCl(PPh_3)_2O_2$. This result shows that the termination effect due to the interaction between metal complex and peroxy radical is fairly great. Actually, as shown in Table 3, all of these complexes exerted a considerable effect on the autoxidation of α-methylstyrene initiated by α,α′-azobisisobutyronitrile (AIBN). The inhibitory effect of $RhCl(CO)(PPh_3)_2$ was the most remarkable. Cobaltous acetylacetonate and deconoate demonstrated additive properties in the catalytic activities of the metal salts and AIBN, respectively.

TABLE 2

OXIDATION OF OLEFINS CATALYZED BY METAL COMPLEXES

Metal complex	$-dO_2/dt$ (10^6 M/sec)	
	α-Methyl-styrene[a]	Cyclo-hexene[b]
None	0.66	—
$RhCl(PPh_3)_3$	2.05	8.17
$RhCl(CO)(PPh_3)_2$	0.13	—
$Ru(OH)(NO)(PPh_3)_2(CO)$	0.49	18.9
Co(Salen)	4.12	9.35
Co(Salpro)	—	1.09
Co(Salchx)[c]	3.13	19.1

[a] 0.005 M metal at 60°C.

[b] 0.01 M metal at 50°C in PhCl, 1:1 by vol.

[c] Bis-(salicylidene cyclohexyliminato) cobalt.

In Fig. 2, the log of the oxygen absorption rate of cyclohexene is plotted against the concentration of dioxygen complexes. The rate of oxidation is about half order with respect to both $RhCl(PPh_3)_2O_2$ and $Ru(OH)(NO)(PPh_3)_2O_2$. These results indicate that the dioxygen complexes have a considerable effect on the initiation reaction of autoxidation of cyclohexene as well as of α-methylstyrene. In cyclohexene oxidation, which proceeds by hydrogen abstraction mechanism, hydroperoxide is formed as an initial product during the course of the reaction. Most of the metal complexes used have shown a considerable effect on the decomposition of hydroperoxide. It seems, therefore, that the chain of the

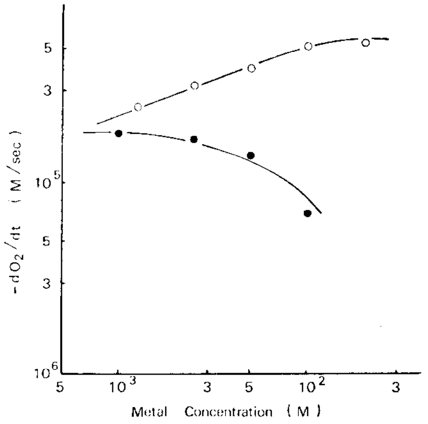

FIG. 1. The rate of oxidation of α-methylstyrene catalyzed by oxygen complexes as a function of metal concn at 60°C. (○) $Co_2(Salen)_2O_2$; (●) $RhCl(PPh_3)O_2$.

TABLE 3

INHIBITORY EFFECT OF METAL COMPLEXES ON THE OXIDATION OF α-METHYLSTYRENE INITIATED BY 0.03 *M* AIBN AT 60°C

Metal complex (0.01 *M*)	$-dO_2/dt \times 10^4$ (M/sec)
None	1.18
$RhCl(PPh_3)_3$	0.45
$RhCl(CO)(PPh_3)_2$	0.09
$Ru(OH)(NO)(PPh_3)_2(CO)$	0.23
$IrBr(CO)(PPh_3)_2$	0.30
Co(Salen)	0.59
$Co(acac)_2$	3.65
$CoDe_2$	1.47

cyclohexene autoxidation is initiated by redox decomposition of hydroperoxide catalyzed by metal complex, as observed by Lyons and Turner (*8*) and Fusi *et al.* (*18*).

Relation between the Decomposition Rate of Hydroperoxide and the Oxidation Rate of Cyclohexene

Variation of hydroperoxide concentration with reaction time during the oxidation of cyclohexene catalyzed by $RhCl(PPh_3)_2O_2$ is given in Fig. 3. At the beginning of the reaction, an amount of overall oxygen absorbed (3.43×10^{-2} *M* at 16.0 min) was a little higher than that of hydroperoxide formed (3.00×10^{-2} *M* at 16.3 min). As the reaction proceeded further, there was an appreciable decrease in the rate of formation of hydroperoxide. This result suggests that the chain initiation depends mainly on the redox decomposition of hydroperoxide.

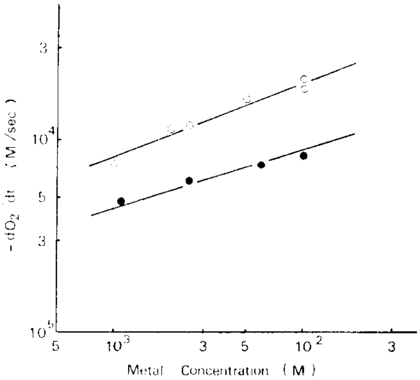

FIG. 2. The rate of oxidation of cyclohexene catalyzed by oxygen complexes as a function of metal concn at 50°C. (○) $Ru(OH)(NO)(PPh_3)_2O_2$; (●) $RhCl(PPh_3)_2O_2$.

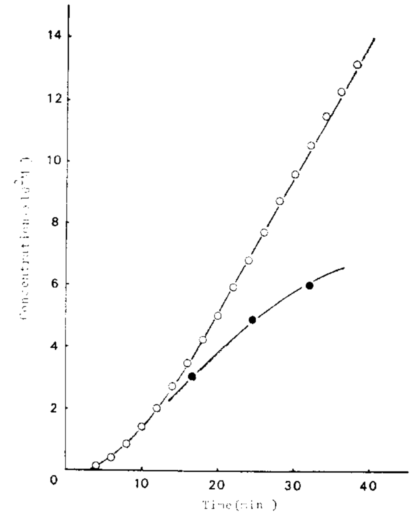

FIG. 3. Hydroperoxide accumulated in the oxidation of cyclohexene catalyzed by 0.005 *M* $RhCl(PPh_3)_2O_2$ at 50°C. (○) Oxygen absorbed; (●) hydroperoxides titrated.

The relation between the reactivity for the decomposition of hydroperoxide and the oxidation rate was also examined. Decomposition reactions were carried out at 50°C under a nitrogen atmosphere with 4×10^{-4} *M* metal complex, using tetralyl hydroperoxide (5.2×10^{-2} *M*) which has also the secondary hydroperoxy group and can be obtained in high purity (98.5% analyzed by iodometry). As is clar from Table 4, the rate constants (k_d) for the decomposition of hydroperoxide by $RhCl(PPh_3)_3$, $Ru(OH)(NO)(PPh_3)_2(CO)$, and Co(Salchx) are fairly proportional to the rates of oxidation of cyclohexene catalyzed by these complexes. It should be mentioned that the rate of oxidation was nearly half order with respect to the chain initiation.

From these results, it is suggested that the rate of the cyclohexene oxidation catalyzed by dioxygen complexes depends on

TABLE 4

Relation between Decomposition Rate of Hydroperoxide and Oxidation Rate of Cyclohexene Catalyzed by Metal Complexes

Metal complex	k_d ($\times 10^4$ sec^{-1})	$-dO_2/dt$ ($\times 10^5$ M/sec)
$RhCl(PPh_3)_3$	1.69	8.17
$Ru(OH)(NO)(PPh_3)_2(CO)$	10.4	18.9
Co(Salchx)	17.3	19.1

the reactivity of the complexes in the redox decomposition of cyclohexenyl hydroperoxide formed as an intermediate, as observed by Lyons and Turner (*8*), Collman *et al.* (*9*), and Fusi *et al.* (*18*). Thus the following initiation reactions due to metal complexes can be depicted,

$$RO_2\cdot + RH \longrightarrow ROOH + R^\cdot,$$

$$2ROOH \xrightarrow{ML_n} RO^\cdot + RO_2\cdot + H_2O,$$

where ML_n = metal complex.

In Fig. 4, the oxidation products of cyclohexene catalyzed by rhodium complex are plotted as a function of reaction time. The distribution is almost the same as that observed in the ordinary metal-catalyzed autoxidation.

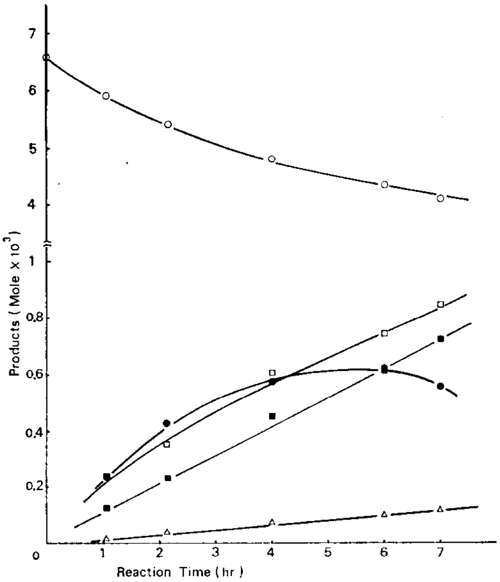

Fig. 4. The oxidation of cyclohexene catalyzed by 0.005 M $RhCl(PPh_3)_3$ in benzene at 60°C. (○) Cyclohexene; (□)2-Cyclohexene-1-ol; (■) 2-cyclohexene-1-one; (●) 3-hydroperoxy-1-cyclohexene; (△) cyclohexene oxide.

The Effect of Solvent on the Oxidation of α-Methylstyrene

In Table 5 is shown the effect of some solvents on the rate of oxygen absorption of α-methylstyrene. The values should be compared with half the rate of oxidation of neat α-methylstyrene, since the rate of initiated autoxidation is first order with respect to the concentration of the reactant. Chlorobenzene showed only the dilution effect, however, a basic solvent such as pyridine or ethanol strongly inhibited the autoxidation. A basic solvent may probably solvate metal complex and prevent coordination of oxygen molecule or substrate to metal center. On the other hand, the dioxygen complex of ruthenium, $Ru(OH)(NO)(PPh_3)_2O_2$, has a remarkable catalytic effect in acetic acid. This suggests that an electronic effect of protonation or ligand exchange may be operative on M–O or O–O bond of the dioxygen complex (*19*). More detailed studies on the catalysis of $Ru(OH)(NO)(PPh_3)_2O_2$ in acidic solvents will be reported elsewhere.

Correlation between Oxygen–Oxygen Bond Length and Reactivity

It was indicated that the dioxygen complexes had a small effect to initiate the chain of autoxidation of α-methylstyrene. Proba-

TABLE 5

EFFECT OF SOLVENT ON THE OXIDATION OF α-METHYLSTYRENE AT 60°C

Solvent	Catalyst (5 × 10^{-3} *M*)	$-dO_2/dt$ (×10^5 *M*/sec)		
		$Co_2(Salen)_2O_2$[a]	$RhCl(PPh_3)_2O_2$	$Ru(OH)(NO)(PPh_3)_2O_2$
None		5.35	2.05	0.49
Chlorobenzene	(1:1 by vol)	2.84	0.65	0.13
Acetic acid	(1:1 by vol)		0.47	3.45
Pyridine	(1:1 by vol)	0.21	—[b]	—[b]
Ethanol	(1:1 by vol)	1.20		

[a] Concentration; 1 × 10^{-2} *M*

[b] No oxidation occurred in 2 hr.

bly, oxygen molecule may be activated by coordination to metal complex. Since the O–O of dioxygen complex is fairly lengthened, it is of much interest to study the correlation between O–O bond length and the effect on chain initiation. However, as shown in Table 6, no satisfactory correlation could be observed. Both chloro- and iodo-compounds of Vaska's complex of which O–O bond lengths have been reported as 1.30 Å (*3*a) and 1.51 Å (*3*b), respectively, were inactive for the chain initiation of autoxidation. It is thought that O–O bond lengths of $RuX(NO)(PPh_3)_2O_2$ (X = OH, Cl, Br, and I) are considerably influenced by substituents as observed in Vaska's complexes (*3*). However, the rate of oxidation catalyzed by $RuX(NO)(PPh_3)_2O_2$ resulted in only a small change.

TABLE 6

OXYGEN–OXYGEN BOND LENGTH AND REACTIVITY FOR THE OXIDATION OF α-METHYLSTYRENE[a] AT 60°C

Dioxygen complex (5 × 10^{-3} *M*)	Bond length (Å)	$-dO_2/dt$ (×10^6 *M*/sec)
$IrCl(CO)(PPh_3)_2O_2$	1.30	—[b]
$IrI(CO)(PPh_3)_2O_2$	1.51	—[b]
$RhCl(PPh_3)_2O_2$	1.44	2.05
$Ru(OH)(NO)(PPh_3)_2O_2$		1.09
$RuCl(NO)(PPh_3)_2O_2$		0.52
$RuBr(NO)(PPh_3)_2O_2$		0.40
$RuI(NO)(PPh)_2O_2$		0.47

[a] Volume of substrate is 2 ml.

[b] No oxidation occurred in 2 hr.

The rate of oxidation of triphenylphosphine catalyzed by metal–dioxygen complexes is shown in Table 7. Although PPh_3 can be oxidized very easily by dioxygen complexes, it seems that no correlation holds between the rate of oxidation and O–O bond length.

From these results, it can be presumed that the rate of initiation by dioxygen complexes is strongly influenced by either stability of M–O bond or electronic effect of other ligands rather than O–O bond length.

Infrared absorptions due to dioxygen group coordinated to a metal complex have been reported (*1*b, *3*b, *19*). In general, characteristic band observed in the 830–900 cm^{-1} region can be assigned to the O–O

TABLE 7

RATE OF OXIDATION OF TRIPHENYLPHOSPHINE[a] CATALYZED BY VASKA'S COMPLEXES AT 60°C IN PhCl

Vaska's complex (1 × 10^{-2} *M*)	X	$-dO_2/dt$ (×10^6 *M*/sec)
$IrX(CO)(PPh_3)_2O_2$ =	Cl	4.53
	Br	3.55
	I	1.70

[a] Concentration of PPh_3, 0.5 *M*.

stretching, and the position of absorption varies with the bond length, i.e., bond strength. However, in ruthenium complexes the difference of substituent resulted in a change of only 5 cm^{-1} in the absorption (see Table 1) as observed in Vaska's complexes (*3*). From these results, it appears that the position of an absorption should not be correlated directly with the O–O bond length of a dioxygen complex.

ACKNOWLEDGMENT

We thank Dr. E. Niki of the University of Tokyo for his helpful discussions regarding this work.

REFERENCES

1. (a) Vaska, L., and DiLuzio, J. W., *J. Amer. Chem. Soc.* **83**, 2784 (1961); (b) Vaska, L., Science **140**, 809 (1963).

2. (a) Osborn, J. A., Jardine, J. H., Young, J. F., and Wilkinson, G., *J. Chem. Soc. A* **1966**, 1711; (b) Nappir, Jr., T. E., Meek, D. W., Kirchner, R. M., and Ibers, J. A., *J. Amer. Chem. Soc.* **95**, 4194 (1973).

3. (a) Laplaka, S. J., and Ibers, J. A., *J. Amer. Chem. Soc.* **87**, 2581 (1965); (b) McGinnety, J. A., Doedence, R. J., and Ibers, J. A., *Inorg. Chem.* **12**, 2243 (1967); (c) Kashiwagi, T., Yasuoka, N., Kasai, N., Kakudo, M., Takahashi, S., and Hagiwara, N., *Chem. Commun.* **1969**, 743; (d) Calligaris, M., Nordin, G., Randaccio, L., and Ripamonti, A., *J. Chem. Soc. A*, **1970**, 1069; (e) Rodley, G. A., and Robinson, W. T., *Nature (London)* **235**, 438 (1972).

4. Takao, K., Fujiwara, Y., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Jap. 43,* 1153 (1970).

5. James, B. R., and Ochiai, E., *Can. J. Chem.* **49**, 975 (1971).

6. Blum, J., Rosenman, H., and Bergman, E. D., *Tetrahedron Lett.* **38**, 3665 (1967).

7. Fine, L. W., Grayson, M., and Suggs, V. H., *J. Organometal. Chem.* **22**, 219 (1970).

8. Lyons, J. E., and Turner, J. O., *J. Org. Chem.* **37**, 2881 (1972).

9. Collman, J. P., Kubota, M., and Hosking, J. W., *J. Amer. Chem. Soc.* **89**, 4811 (1967).

10. Graham, B. W., Laing, K. R., O'Connor, C. J., and Roper, W. R., *J. Chem. Soc. D* **1972**, 1237.

11. Kaneda, K., Itoh, T., Fujiwara, Y., and Teranishi, S., *Bull. Chem. Soc. Jap.* **46**, 3810 (1972).

12. Kamiya, Y., *J. Catal.* **24**, 69 (1972).

13. Mayo, F. R., and Miller, A. A., *J. Amer. Chem. Soc.* **80**, 2465 (1958).

14. Pfeiffer, P., Breich, E., Lubbe, E., and Tsumaki, T., *Justus Liebigs Ann. Chem.* **503**, 84 (1933).

15. Laing, K. R., and Roper, W. R., *J. Chem. Soc. A* **1970**, 2149.

16. Takao, K., Fujiwara, Y., Imanaka, T., Yamamoto, M., Hirota, K., and Teranishi, S., *Bull. Chem. Soc. Jap.* **43**, 2249 (1970).

17. Kamiya, Y., Beaton, S., Lafortune, F., and Ingold, K. U., *Can. J. Chem.* **44**, 2020 (1963).

18. Fusi, A., Ugo, R. Fox, F., Pasini, A., and Cenini, S., *J. Organometal. Chem.* **26**, 471 (1971).

19. Nakamura, A., Tatsuno, Y., Yamamoto, M., and Otsuka, S., *J. Amer. Chem. Soc.* **93**, 6052 (1971).