

Homogeneous Catalysis by Transition Metal Complexes

IV. The Use of Mixed Catalysts in the Oxidation of Cyclohexene

A. FUSI, R. UGO AND G. M. ZANDERIGHI

Istituto di Chimica Generale, Via Venezian, 21, The University, Milan, Italy

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The catalyzed oxidation of cyclohexene in benzene solution has been studied at 65°C using a mixture of two different homogeneous metal catalysts.

In order to obtain a reasonable selective formation of equimolecular amounts of cyclohexene oxide and 2-cyclohexen-1-ol, two types of catalysts have been mixed: catalysts A are catalysts of autoxidation (transition metal phosphine complexes or transition metal acetylacetonates), and catalysts B are catalysts of epoxidation (molybdenum complexes).

The conditions necessary to obtain reasonably good activities and selectivities are reported and discussed.

INTRODUCTION

Homogeneous metal catalyzed oxidations of olefins and other hydrocarbons by molecular oxygen have been the subject of a large number of investigations (1), in which cyclohexene has been often used as a useful model reactant (2). Moreover, the discovery of the formation of more or less reversible oxygen adducts of low oxidation state transition metal complexes has suggested the use of such metal complexes as catalysts for selective oxidation of olefins and other hydrocarbons (3-5). In this approach it has been supposed that the reactivity of coordinated oxygen could be similar to that of singlet oxygen or even of the peroxide ion.

However, it was observed that these metal complexes only catalyze autoxidation reactions, probably by decomposing the traces of hydroperoxides always present in unsaturated hydrocarbons (3-6). The evidence for direct activation of molecular oxygen, although claimed by some authors in a few cases (7), is very scanty. In short, low oxidation state metal complexes behave like other catalysts such as soluble metal salts (1) or metal acetylacetonates (2), although they often appear to be more active. Owing to the chain radical char-

acter of the autoxidation reaction catalyzed by these metal complexes, selectivity is poor and many oxidation products are obtained. Organic hydroperoxides and peroxides are probably formed as intermediates during this kind of oxidation and their presence has been supported by titration methods (3).

On the other hand, it has been reported that soluble metal complexes of V, Mo and W catalyze the selective epoxidation of olefins by organic hydroperoxides (8, 9).

The mechanism of this selective epoxidation is at present not understood in detail, although it appears that the formation of a metal-peroxide bond (10, 11) or a metal-hydroperoxide complex (12, 13) is an important step in the reaction.

EXPERIMENTAL METHODS

Reagents and Metal Complexes

Cyclohexene was purified as described in our previous paper (3).

Cyclohexene oxide was purified as reported earlier (3); 2-cyclohexen-1-one and 2-cyclohexen-1-ol were isolated and purified by preparative glc (see below) from a distilled fraction of an oxidation mixture

obtained by radical induced oxidation of cyclohexene.

Metal complexes were prepared according to well-known literature methods with the sole exception of $\text{Mo}_2\text{O}_3(\text{salen})_2$ (salen = *N,N'*-ethylene bis-salicylideneiminato). This red-brown complex was obtained by refluxing a benzene solution of stoichiometric amounts of $\text{Mo}(\text{CO})_6$ and salenH under a stream of oxygen. The initially yellow solution turned deep brown and after a few hours a red-brown powder separated, which was recrystallized from hot ethanol [mp = 220–225°C (dec.)]. Analyses for $\text{Mo}_2\text{O}_3(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)$: calcd: C, 49.8; H, 3.6; N, 7.3; found: C, 48.8; H, 3.8; N, 7.2.

Cyclohexene Oxidation

Weighed amounts of catalysts were placed in a 100 ml two-necked round bottomed flask equipped with a condenser and a screwed-in Sovirel serum-type cap. After evacuating, the flask was filled with O_2 , then, in O_2 flow, 10 ml of benzene (Carlo Erba R. S. spectroscopic grade) and 10 ml of cyclohexene (98.6 mmoles) were introduced. The solution obtained was 4.93 M in cyclohexene. The flask was equipped with a magnetic stirrer and placed in a thermostated bath at $65 \pm 2^\circ\text{C}$; 10 min later the internal and external pressures were balanced, the condenser being connected with a 300 ml burette filled with O_2 and equipped with a leveling-gauge. The reaction time varied from 5 hr to about 50 hr, depending on the desired degree of conversion. The oxidation was followed by analyzing reaction mixture samples.

Reaction Product Analyses

Samples taken from the reaction flask with a syringe were directly analyzed by glc (direct calibration method).

The details of the experimental conditions are reported in our previous paper (3).

Determination of Active Oxygen

The content of the active oxygen in the samples taken from the reaction flask with a syringe was obtained by the well-known

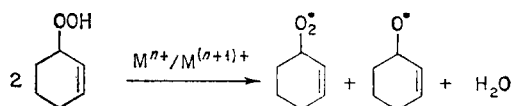
iodometric method (19). The end point of the titration was determined with great accuracy by the electrode polarization technique (20).

RESULTS

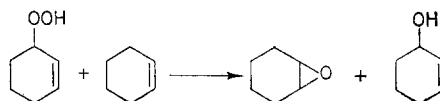
Background

Hydroperoxides of olefins, formed in the metal catalyzed radical chain autoxidation of olefins, are in a concentration which, in steady conditions, may be high enough to be considered as potential reagents for selective oxidation of the olefins themselves.

This has already been observed indirectly in the cyclohexene oxidation catalyzed by MoO_2^{2+} and VO^{2+} acetylacetonates (2) in which the metal complex does not act only as a radical initiator through a Haber-Weiss mechanism



but also catalyzes the direct epoxidation of olefins



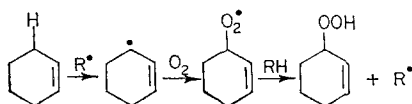
The high content of cyclohexene oxide in the reaction products (when compared with that obtained by thermal or radical autoxidation (14) or by autoxidation catalyzed by other metal acetylacetonates (2) such as those of Co^{3+} , Ni^{2+} , Cu^{2+}) is in agreement with such a selective oxidation.

An extended series of investigations on propylene oxidation catalyzed by many different molybdenum complexes is also in agreement with a certain selectivity towards the formation of the corresponding epoxide (15, 16).

Definition of the Two Classes of Catalysts

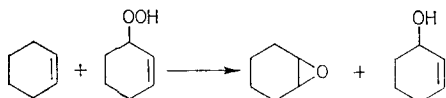
It therefore appears reasonable to propose the use of a soluble complex catalyst prepared by mixing two different kinds of metal complexes.

Type A catalyst should catalyze mainly the following radical reaction:

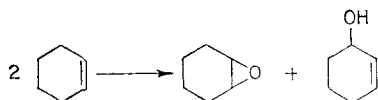


where R^\bullet is a radical formed by metal catalyzed cyclohexene hydroperoxide decomposition. It is known that cyclohexene is an olefin which produces the corresponding hydroperoxide with high selectivity in the radical catalyzed autoxidation (14). However, catalyst A should not be too active in catalyzing the radical decomposition of the hydroperoxide formed.

Type B catalysts should then catalyze the following reaction:



To sum up, in the presence of a completely selective mixed catalyst, one could obtain the following overall reaction:



The choice of type A and type B catalysts has been based on literature data. Type A catalysts were metal acetylacetonates (2) or low oxidation state metal complexes (3) which are known to be effective but not too active catalysts of cyclohexene radical autoxidation. Type B catalysts were molybdenyl or vanadyl soluble complexes which are known to be the most effective catalysts of selective epoxidation (8, 9).

The reaction products together with the selectivity which can be obtained when only type A or type B complexes are used as catalysts are reported in Table 1. Our results are in agreement with what has been reported so far in the literature (2, 3).

Type A catalysts are more active, but show lower selectivity (the formation of 2-cyclohexen-1-one may be used as a measure of the lack of selectivity) than

type B catalysts which display a higher selectivity.

Also, when type A catalyst is not too active, e.g., $\text{Pt}(\text{PPh}_3)_2\text{O}_2$, the concentration of active oxygen in the reaction mixture (which could be used as a rough measure of the concentration of the hydroperoxide) is high.

Investigation of the Action of Type B Catalysts in the Catalytic Mixture

We have investigated the action of many type B catalysts in the presence of a catalyst of type A of relatively low activity such as $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ (3) or $\text{Ni}(\text{acac})_2$ (2) and the results are given in Table 2.

We have observed that the use of $\text{MoO}_2(\text{acac})_2$ produces a much higher selectivity than does the use of $\text{Cr}(\text{acac})_3$ (this latter catalyst displays a rather high activity but a very poor selectivity). With $\text{VO}(\text{acac})_2$ the ratio of cyclohexene oxide to 2-cyclohexen-1-ol is not too far from unity, which is expected for a completely selective reaction, but the formation after a certain period of a relevant amount of 2-cyclohexen-1-one lowers the total selectivity of the system.

As a matter of fact the activity of the catalytic mixtures decreases with time so that we may define a "useful life of the catalyst" corresponding to the beginning of the loss of activity. Selectivity does not decrease with time in the same way but on the contrary an increase in selectivity is often observed (Table 2).

Another important observation is related to the amount of active oxygen found at different times in the reaction mixture. With systems of low selectivity the amount of active oxygen is higher than with those of higher selectivity (Table 2).

Once the way to control the reaction selectivity by the right choice of catalyst B was defined, we then continued our investigation using only the more selective molybdenyl complexes as type B catalyst.

Investigation of the Action of Type A Catalysts in the Catalytic Mixture

The results of an investigation of the use of many transition metal phosphine

TABLE I
COMPARISON OF THE DIFFERENT BEHAVIOR OF TYPE A AND B CATALYST

Catalyst	Reaction time (hr, min)	Conversion ^a (%)	Product distribution ^b					Active oxygen (%)	Molar ratio epoxide/alcohol	Selectivity ^d (%)	Useful life ^e (hr)
			Cyclohexene oxide (%)	2-Cyclohexen-1-one (%)	2-Cyclohexen-1-ol (%)	M ^c					
Type A Pt(PPh ₃) ₂ O ₂ ^f 6.74 × 10 ⁻⁴ M	1	0.4	Tr	Tr	Tr	100	0.020	—	—	None	
	20	16.3	3.9	21.1	35.6	39.4	0.360	0.11	5		
	46	52.6	8.3	20.0	18.3	53.4	1.400	0.45	15		
Type B MoO ₃ (acac) ₃ ^f 1.35 × 10 ⁻³ M	3	0.8	93.6	—	Tr	6.3	0.002	Very high	>>100	20	
	22	3.6	53	—	46.9	Tr	Tr	1.13	90		

^{a, b} These figures refer to initial (a) and converted (b) cyclohexene, respectively (moles).

^c Molarity of the peroxidic oxygen in the reaction mixture.

^d 100% selectivity means the formation of cyclohexene oxide and 2-cyclohexen-1-ol only and with molar ratio 1; the values reported are therefore approximate. These entries have the same meaning also in the other tables.

^e Useful life indicates the approximate period in which the catalytic system presents a ratio epoxide/alcohol near to 1, together with a significant amount of cyclohexene conversion.

^f acac = acetylacetonate; PPh₃ = triphenylphosphine.

TABLE 2
COMPARISON OF THE ACTIVITIES OF VARIOUS TYPE B CATALYSTS

Catalyst B	Reaction time ^a (hr, min)	Conversion (%)	Product distribution					Active oxygen (%)	Molar ratio epoxide/alcohol	Selectivity (%)	Useful life (hr)
			Cyclohexene oxide (%)	2-Cyclohexen-1-one (%)	2-Cyclohexen-1-ol (%)	Active oxygen (M)					
Cr(acac) ₃ ^b	1,20	0.5	—	—	—	100	0.030	—	—	—	
	8,10	40.5	5.2	49.3	23.5	22.0	0.470	0.22	10	—	
	11,45	53.4	4.7	52.3	19.7	23.3	0.625	0.24	10	—	
VO(acac) ₂ ^b	1,05	0.7	66.5	—	Tr	33.5	0.012	Very high	—	10	
	4,05	1.4	88.7	—	Tr	11.3	0.007	Very high	—	—	
	22,25	7.3	42.8	20.4	33.4	3.4	0.012	1.28	65	—	
MoO ₂ (acac) ₂ ^c	1,15	0.7	Tr	—	Tr	100	0.035	—	—	—	
	4,30	4.2	46.7	—	38.9	14.4	0.032	1.20	80	20	
	22,55	9.2	52.8	Tr	46.2	1.0	0.005	1.14	90	—	
MoO ₂ (acac) ₂ ^c	2	1.9	66.7	—	Tr	33.2	0.025	High	—	—	
	4	4.8	46.9	—	45.5	7.6	0.015	1.03	90	20	
	23	6.1	51.4	—	44.7	3.9	0.010	1.15	90	—	
VO(acac) ₂ ^c	1	3.4	23.8	Tr	49.9	26.2	0.045	0.48	45	—	
	5	5.3	33.4	21.8	41.2	3.7	0.010	0.81	65	20	
	22	6.3	39.4	18.9	41.7	Tr	Tr	0.95	80	—	

^a The three values refer to the initial, optimum or maximum reactivity and to the exhaustion or loss of selectivity of the catalytic system, respectively. This entry keeps the same meaning also in the other tables.

^b Catalyst A is Pt(PPh₃)₂O₂ 7.81 ± 0.95 × 10⁻⁴ M; molar ratio A/B = 1.

^c Catalyst A is Ni(acac)₂ 2.45 ± 0.20 × 10⁻³ M; molar ratio A/B = 2.

TABLE 3
COMPARISON OF THE ACTIVITY OF DIFFERENT TYPE A CATALYSTS AT VARIOUS A/B MOLAR RATIOS^a

Catalyst A	Molar ratio A/B	Reaction time (hr, min)	Conversion (%)	Product distribution						Active oxygen (%)	Molar ratio epoxide/alcohol	Selectivity (%)	Useful life (hr)
				Cyclo-hexene oxide (%)	2-Cyclo-hexen-1-one (%)	2-Cyclo-hexen-1-ol (%)	Cyclo-hexene oxide (%)		Active oxygen (%)				
Pt(PPh ₃) ₂ O ₂ 6.72 × 10 ⁻⁴ M	1	6	3.9	53.8	—	46.2	Not measured		1.16	90	25		
		11, 55	5.6	53.8	Tr	46.1	Not measured		1.16	90			
		30, 20	8.1	57.3	Tr	42.6	Not measured		1.34	85			
Pt(PPh ₃) ₂ O ₂ 1.99 × 10 ⁻³ M	3	5, 15	7.9	46.5	Tr	53.4	Not measured		0.87	90	25		
		8, 45	10.1	50.7	Tr	49.2	Not measured		1.03	95			
		29, 40	13.8	52.2	7.3	40.4	Not measured		1.29	80			
Pt(PPh ₃) ₂ O ₂ 3.99 × 10 ⁻³ M	6	5	9.2	27.9	19.9	52.2	Not measured		0.53	55	20		
		8, 25	15.9	39.4	14.1	46.5	Not measured		0.85	80			
		28, 25	23.5	48.0	19.0	40.0	Not measured		1.20	80			

TABLE 4
COMPARISON OF THE ACTIVITY OF DIFFERENT TYPE A CATALYSTS

Catalyst	Reaction time (hr, min)	Conversion (%)	Product distribution					Active oxygen (%)	Molar ratio epoxide/alcohol	Selectivity (%)	Useful life (hr)
			Cyclohexene oxide (%)	2-Cyclohexen-1-one (%)	2-Cyclohexen-1-ol (%)	Oxygen (M)					
Mn(acac) ₃ ^a	1	10.0	29.5	13.5	44.9	12.1	0.062	0.66	60	2	
	3	11.1	42.8	9.8	45.6	1.8	0.010	0.94	85		
	5	11.9	41.7	10.9	46.1	1.3	0.007	0.90	80		
Fe(acac) ₃ ^a	1	6.9	12.3	27.9	42.9	16.9	0.060	0.29	25	15	
	3	12.7	35.6	19.4	39.6	5.4	0.035	0.90	70		
	23	26.3	43.3	19.8	33.5	3.4	0.045	1.29	65		
Co(acac) ₃ ^a	1	12.6	40.8	13.1	39.3	6.7	0.045	1.04	80	2	
	7	31.3	46.5	20.1	31.2	2.2	0.035	1.49	60		
	25	55.4	43.9	33.3	22.8	Tr	Tr	1.93	45		
Co(acac) ₃ ^a	1	17.1	36.1	15.1	37.7	11.1	0.100	0.96	70	3	
	7	35.0	45.5	21.1	28.6	4.8	0.085	1.59	60		
	19	53.2	46.5	32.9	20.6	Tr	Tr	2.25	40		

Ni(acac) ₃ ^a	1	0.9	83.5	—	Tr	16.4	0.007	Very high	>>100	
	3	4.9	47.0	—	48.7	4.2	0.010	0.96	95	20
	24	8.0	48.9	Tr	49.7	1.3	0.005	0.98	100	
Mn(acac) ₃ ^b	1	8.2	Tr	24.7	42.5	32.7	0.140	Very low		10
	4	17.5	17.8	17.6	43.5	21.1	0.182	0.41	35	
(i)	20	35.9	35.5	18.1	32.0	14.3	0.252	1.11	65	
	1	7.4	22.5	20.6	38.2	18.7	0.072	0.59	45	
Fe(acac) ₃ ^b	4	13.5	37.0	11.9	43.1	8.0	0.057	0.86	75	15
(i)	20	22.1	42.4	16.0	40.1	1.5	0.017	1.06	80	
	1	11.9	7.6	28.0	32.7	31.7	0.160	0.23	15	
Co(acac) ₃ ^b	6	28.4	37.6	16.9	36.5	9.0	0.110	1.03	75	6
(ii)	30	62.3	45.8	31.7	17.7	4.8	0.105	2.59	35	
	2,30	11.0	12.3	21.8	43.0	22.9	0.135	0.29	25	
Co(acac) ₃ ^b	4	22.8	14.5	22.1	37.0	26.4	0.325	0.39	30	2
(i)	7	41.1	29.5	22.0	33.3	15.2	0.315	0.89	60	
	2	1.9	66.7	—	Tr	33.2	0.025	High	>>100	
Ni(acac) ₂ ^b	4	4.8	46.9	—	45.5	7.6	0.015	1.03	90	20
(ii)	23	6.1	51.4	—	44.7	3.9	0.010	1.15	90	

^a Catalyst B is MoO₃(acac)₂ 2.67 ± 0.03 × 10⁻³ M; molar ratio A/B = 1.

^b Catalyst B is MoO₄(acac)₃, (i) 1.45 ± 0.11 × 10⁻³ M, (ii) 1.08 ± 0.04 × 10⁻³ M; molar ratio A/B = 2. The induction period is much longer than with molar ratio A/B = 1; Cu(acac)₂ is inactive.

complexes of rather different activity (3) as catalyst A are reported in Table 3. When the catalyst A is too active on its own [e.g., $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ or $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (17)] the total conversion is high but the selectivity is low.

This trend was confirmed by increasing the molar ratio of catalyst A to catalyst B; in fact even in the case of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$, which is a catalyst of high selectivity, we have a drop in selectivity when this ratio approaches the value of six.

To sum up, a too effective action of catalyst A in the autoxidation part of the reaction may cause an evident loss of selectivity as expected when the radical decomposition of the intermediate 2-cyclohexen-1-hydroperoxide occurs too easily.

One interesting point must be mentioned: in the case of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $\text{MoO}_2(\text{acac})_2$ as catalysts the ratio of cyclohexene oxide to 2-cyclohexen-1-ol after a medium reaction time is much higher than one (about two or more). This is a rather unexpected result because it would support a direct and selective epoxidation with oxygen which has not been observed, for instance, when either $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ or $\text{MoO}_2(\text{acac})_2$ have been used separately.

Moreover, it has been reported that the amount of epoxide formed is higher when $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ is the only catalyst (17) than when $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ is used as the only catalyst (3). In the case of our catalytic mixtures we have observed a completely opposite trend (see Table 3).

An anomalously high formation of the epoxide has been observed in some other cases in the initial stages of the reaction (see, for instance, the case of the mixture $\text{Pt}(\text{PPh}_3)_2\text{O}_2\text{-VO}(\text{acac})_2$ of Table 2); however, after a certain period the ratio of epoxide to alcohol decreased to the expected value of about one.

We have extended our investigation to another class of catalysts of type A, namely the metal acetylacetonates.

In Table 4 are reported the data corresponding to a series of different mixtures of complexes. Once again we have lower selectivities with the most active catalysts. In the case of the very active cobalt acetyl-

acetonates we have also a very low useful life of the catalytic mixture.

In the case of the catalytic mixture $\text{Co}(\text{acac})_x$ ($x = 2,3$) + $\text{MoO}_2(\text{acac})_2$ a ratio of cyclohexene oxide to 2-cyclohexen-1-ol higher than one was obtained. Interestingly this anomalous high value has been always observed after a long reaction time (Tables 3 and 4) suggesting a slow formation *in situ* of a new and unknown selective catalyst; moreover, the precipitation of an insoluble brownish powder from the reaction mixture is in agreement with some transformation of the original metal complexes.

We have also observed that the useful life of the catalytic mixtures can be controlled by adding a further amount of type A complexes as soon as the catalytic activity begins to decrease. In fact the addition of an additional amount of the catalyst of type A (changing the value of the molar ratio A to B from 1 to 2) reproduces the initial value of the activity while the system maintains the same selectivity (Table 5).

Thus the loss of activity with time cannot be ascribed to the decomposition of the molybdenum part of the catalyst but rather to that of the catalyst A.

Stabilization of the Molybdenum Catalyst

A certain loss of selectivity has been observed only after very long reaction times (Table 5). This can be ascribed either to an irreversible transformation of the molybdenum catalyst or to the formation of a stable complex of molybdenum with some of the reaction products (12, 13).

We have investigated the use of different types of molybdenum complexes with the aim of increasing and stabilizing the properties of selective epoxidation of the catalytic mixture (Table 6). It was observed that a higher selectivity can be achieved by using a rather stable complex of molybdenum, e.g., $\text{MoO}_2(\text{oxinate})_2$ [oxinateH is 8-hydroxyquinoline]. Slightly lower selectivities were in fact obtained when $\text{Mo}(\text{CO})_6$, $\text{MoO}_2(\text{acac})_2$ or $\text{Mo}_2\text{O}_3(\text{salen})_2$ have been used [salen is the Schiff base of salicylaldehyde with ethylenedi-

TABLE 5
EFFECT OF THE VARIATION OF THE MOLAR RATIO A/B

Catalyst ratio A/B	Reaction time (hr, min)	Conversion (%)	Product distribution						Molar ratio epoxide/alcohol	Selectivity (%)	Useful life (hr)
			Cyclohexene oxide (%)	2-Cyclohexen-1-one (%)	2-Cyclohexen-1-ol (%)	Active oxygen					
			(%)	(%)	(%)	(%)	(M)				
1 ^a	1	8.2	33.2	11.6	41.5	13.7	0.057	0.80	65	20	
	3	11.0	43.0	8.0	44.6	4.4	0.025	0.96	85		
	21.30	16.9	44.7	11.3	42.9	1.1	0.010	1.04	85		
2 ^b	25	18.6	43.0	12.6	41.8	2.6	0.025	1.03	80	25	
	27	24.1	40.1	17.1	38.9	3.9	0.050	1.03	75		
	47	36.6	34.1	33.1	30.8	2.0	0.035	1.11	60		

^a Catalyst A is Fe(acac)₃; catalyst B is MoO₂(acac)₂ 2.67 × 10⁻³ M.

^b The ratio A/B = 2 has been obtained by adding again Fe(acac)₃ to the reaction mixture.

TABLE 6
 INFLUENCE OF DIFFERENT LIGANDS ON ACTIVITY AND SELECTIVITY OF TYPE B CATALYSTS, MOLAR RATIO A/B = 1

Catalyst B ^a	Reaction time (hr, min)	Conversion (%)	Product distribution						Molar ratio epoxide/alcohol	Selectivity (%)	Useful life (hr)
			Cyclohexene oxide (%)	2-Cyclohexen-1-one (%)	2-Cyclohexen-1-ol (%)	Active oxygen (%)		(M)			
			Tr	Tr	Tr	Tr	Tr				
MoO ₂ (acac) ₂ (a)	1	0.9	Tr	Tr	Tr	100	0.045	0.82	75	20	
	3	6.3	38.4	8.7	46.7	6.2	0.020	0.92	85		
	21,30	9.1	43.8	8.5	46.7	Tr	Tr				
MoO ₂ (oxinate) ₂ (a)	1	1.0	Tr	Tr	Tr	100	0.050	0.58	45	15	
	3	5.7	23.7	10.3	40.6	25.4	0.075	1.03	90		
	21,30	8.5	46.9	6.4	45.6	1.1	0.005				
MoO ₂ (acac) ₂ (b)	1	6.9	12.3	27.9	42.9	16.9	0.060	0.29	25		
	3	12.9	35.6	19.4	39.6	5.4	0.035	0.90	70	15	
	23	26.3	43.3	19.8	33.5	3.4	0.045	1.29	65		
MoO ₂ (oxinate) ₂ (b)	1	8.2	33.2	11.6	41.5	13.7	0.057	0.80	65		
	3	11.0	43.0	8.1	44.5	4.4	0.025	0.96	95	20	
	21,30	16.9	44.7	11.3	42.9	1.1	0.010	1.04	90		
Mo(CO) ₆ (b)	1	9.4	6.8	23.0	23.6	46.6	0.245	0.29	10		
	5	24.3	33.8	17.8	35.4	17.0	0.222	0.95	65	10	
	24	33.9	47.2	20.7	31.1	1.0	0.017	1.52	60		
Mo ₂ O ₃ (salen) ₂ (b)	1	5.5	37.0	Tr	57.9	5.1	0.015	0.64	75		
	5	11.6	37.4	9.9	48.6	4.1	0.025	0.77	20	20	
	24,30	26.0	40.0	20.1	38.4	1.5	0.020	1.04	80		

MoO ₂ (acac) ₂ (c)	1	12.6	40.8	13.1	39.3	6.7	0.045	1.04	80
	7	31.3	46.5	20.1	31.2	2.2	0.035	1.49	60
	25	55.4	43.9	33.3	22.8	Tr	Tr	1.93	45
MoO ₂ (oxinate) ₂ (c)	1	10.7	28.4	23.0	42.6	5.9	0.035	0.67	55
	3	12.6	33.4	20.3	44.8	1.4	0.010	0.75	65
	7	14.5	38.2	19.1	41.8	0.9	0.007	0.92	75
Mo(CO) ₆ (c)	1	14.4	5.4	37.3	30.6	26.7	0.200	0.17	10
	3	21.4	31.7	22.6	40.9	4.8	0.055	0.78	60
	5	22.7	35.9	23.6	39.3	1.2	0.015	0.91	70
Mo ₂ O ₃ (salen) ₂ (c)	1	7.9	27.8	21.3	43.9	7.0	0.030	0.63	55
	7	11.6	33.2	19.1	43.7	4.0	0.025	0.76	65
	24,30	19.9	43.5	17.2	37.4	1.9	0.020	1.16	75
MoO ₂ (acac) ₂ (d)	1	17.1	36.1	15.1	37.7	11.1	0.100	0.96	70
	7	35.0	45.5	21.1	28.6	4.8	0.085	1.59	60
	19	53.2	46.5	32.9	20.6	Tr	Tr	2.25	40
MoO ₂ (oxinate) ₂ (d)	1	14.2	28.2	20.8	41.6	9.4	0.070	0.68	55
	3	16.3	37.4	17.1	43.5	2.0	0.017	0.86	75
	5	17.1	37.9	16.8	44.1	1.1	0.010	0.86	75
Mo(CO) ₆ (d)	1	11.0	7.0	38.2	42.1	12.4	0.070	0.17	15
	3	25.9	21.6	26.9	35.6	15.9	0.210	0.60	40
	7	31.6	35.7	24.8	38.4	1.1	0.017	0.93	70
Mo ₂ O ₃ (salen) ₂ (d)	1	14.7	26.6	17.4	39.4	16.6	0.130	0.68	50
	5	25.6	40.2	18.5	36.8	4.5	0.060	1.09	70
	24,30	50.1	40.9	34.6	23.1	1.4	0.030	1.78	50

^a Catalyst A is: (a) Pt(PPh₃)₂O₂, (b) Fe(acac)₃, (c) Co(acac)₂, (d) Co(acac)₃; 2.07 ± 0.02 × 10⁻³ M. Oxine = 8-hydroxyquinoline; salen = N,N'-ethylene bis-salicylideneiminato.

amine]. The use of $\text{MoO}_2(\text{oxinate})_2$ to increase the stability of the molybdenum catalyst for olefin epoxidation with preformed hydroperoxides has already been reported (18).

Although we have not observed a real increase of the useful life (which, as was said above, is related only to the nature and concentration of catalyst A), we have obtained by the use of $\text{MoO}_2(\text{oxinate})_2$ a selectivity which is rather constant with time, as would be expected when the molybdenum catalyst maintains its properties during a long reaction time.

CONCLUSION

This investigation has shown that the use of a homogeneous mixture of metal complexes as oxidation catalyst can afford a quite high selectivity for epoxide formation, at least in cyclohexene oxidation. The selectivity is in fact much higher than in the case of a simple thermal oxidation (14) or of a simple metal ion catalyzed oxidation (1-3).

We have limited our investigation to catalytic systems obtained by mixing only two different classes of complexes that we have called class A (catalysts of autoxidation) and class B (catalysts of selective epoxidation). Moreover, we have limited the choice of type A catalysts to two classes of compounds (phosphine complexes of noble metals and transition metal acetylacetonates), although it is probable that better or comparable results may be obtained with other kinds of complexes (e.g., naphthenates of transition metals).

It appears that in our catalytic system the two complexes act separately to give rise to a stepwise mechanism of oxidation where we have clearly two different steps each corresponding to one well-defined catalyst.

As a result of our investigation we summarize below a few simple points which may be useful for the formulation of other similar complex mixtures of catalysts:

i. In order to obtain high selectivity for a long reaction time, it is necessary to use catalysts of autoxidation (type A) of low activity; of course this choice implies a

low total activity of the catalytic system.

ii. The use of molybdenum complexes as type B catalyst produces high selectivities; the complex $\text{MoO}_2(\text{oxinate})_2$ is the most effective.

iii. The molar ratio of catalyst A and B affects not only the activity but also the selectivity. The ratio must be about one in the case of catalysts of medium activity; lower values may give initially higher selectivities but slightly higher ratios do not produce either higher activities or selectivities (see, for instance, Table 7). Usually both activity and selectivity become rather constant and reproducible after a certain reaction time. When the activity of catalyst A is too high (see Table 4), as in the case of $\text{Mn}(\text{acac})_3$ or $\text{Co}(\text{acac})_3$, an excess of catalyst A must be avoided. On the other hand, when the catalyst A is of low activity the ratio A to B may be more than 2 without affecting too much the selectivity (see Tables 3 and 4).

iv. Values of the ratio of cyclohexene oxide to 2-cyclohexen-1-ol much higher than one have often been observed particularly with long reaction times. This result cannot be explained simply by assuming that the two homogeneous catalysts act separately in a two-step process first to produce the hydroperoxide (catalyst A) and then to react it selectively with the excess olefin (catalyst B). We cannot at the moment propose any satisfactory explanation of this departure from the two-step process but we suggest a transformation of the initial metal complexes to form in solution a more selective epoxidation catalyst. However, we have been unable to characterize and isolate it up to now. Evidence for some transformation of the initial complexes is the formation of insoluble powders with the time and also the loss of activity.

It is worthwhile to remember that this result is not completely understood. It has in fact been reported that, in propylene oxidation catalyzed by different molybdenum complexes (15, 16) at relatively low temperature, the selectivity for propylene oxide is much higher than 50% which would be the value expected if the two-step

TABLE 7
 INFLUENCE ON THE CATALYTIC ACTIVITY OF THE VARIATION OF THE MOLAR RATIO A/B FOR THE SYSTEM $\text{Fe}(\text{acac})_3/\text{MoO}_2(\text{acac})_2$

Catalyst A	Molar ratio A/B	Reaction time (hr, min)	Conversion (%)	Cyclohexene oxide (%)	Product distribution				Active oxygen (%)	Molar ratio epoxide/alcohol	Selectivity (%)	Useful life (hr)
					2-Cyclohexen-1-one (%)	2-Cyclohexen-1-ol (%)	2-Cyclohexen-1-ol (%)	(M)				
$\text{Fe}(\text{acac})_3$ $2.67 \pm 0.01 \times 10^{-3} M$	0.5	1	7.5	26.7	25.0	44.4	3.9	0.015	0.60	50	20	
		3	11.4	34.0	17.9	46.8	1.3	0.007	0.72	70		
		23	32.1	30.7	32.6	34.3	2.4	0.035	0.89	60		
	1	1	6.9	12.3	27.9	42.9	16.9	0.060	0.29	25	15	
		3	12.7	35.6	19.4	39.6	5.4	0.035	0.90	70		
		23	26.3	43.3	19.8	33.5	3.4	0.045	1.29	65		
2	1	7.4	22.5	20.6	38.2	18.7	0.072	0.59	45	15		
	4	13.5	37.0	11.9	43.1	8.0	0.057	0.86	75			
	20	22.1	42.4	16.0	40.1	1.5	0.017	1.06	80			

process was the only one involved in epoxidation.

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