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HOMOGENEOUS BIMETALLIC CATALYSIS. THE SELECTIVE AUTOXIDATION OF CYCLOHEXENE

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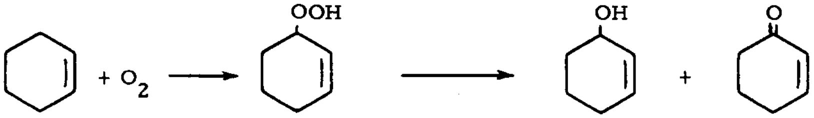
The autoxidation of olefins is known to be catalysed by various transition metal complexes. Several investigations[1] and a recent study by us[2] have well established the free radical character of this reaction, as well as the prior formation of an allylic hydroperoxide, decomposed subsequently by the catalyst. For instance cyclohexene is oxidized to give, in a typical free radical chain process, mainly 2-cyclohexen-1-ol and 2-cyclohexen-1-one.

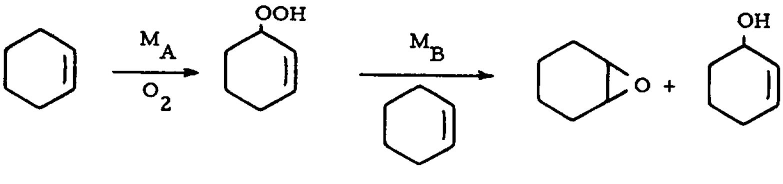


In the course of a detailed study of the decomposition of cyclohexene hydroperoxide catalyzed by Rh Cl (P $Ph_3)_3$, we observed that an autoxidation reaction carried out in the presence of a second transition metal compound led to quite a different decomposition path.

We now wish to report some results with cyclohexene pertaining to this new selective method of oxidation.

The results given in Table I, for some of the catalyst combinations used clearly show the different product distribution obtained with and without the second catalyst. This is specially emphasized in the epoxide percentage.

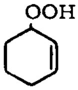
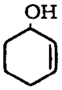
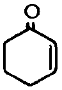
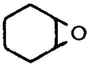
This difference in reaction path can be explained by two successive catalytic processes. The first one consists of a hydroperoxide formation as in a typical autoxidation process, the second, a selective olefin oxidation wherein the hydroperoxide is the oxidizing agent.



This scheme is well in accord with the previous studies carried out on the individual steps of the reaction ; metals listed have been used as catalysts in autoxidation and in epoxidation of olefins in the presence of hydroperoxides[1,3]. Such a sequence has been proposed by Gould and Rado[4] using only a type B catalyst (Mo, V) ; the results in Table I, however, show clearly that under our conditions no oxidation is achieved in the absence of catalyst A.

Furthermore, we have shown in a preliminary study on the various factors influencing the reaction[5] that the overall result reflects the stepwise process given above. For example, for the couple Rh/Mo the rate of oxygen absorption increases with the rhodium concentration, and the rate of epoxide formation increases with the molybdenum concentration. Both these observations have been previously made on the two separate reactions. The decrease in percent conversion upon addition of catalyst B can also be explained by this mechanism. The rate of formation of hydroperoxide is dependent on the concentration of free radicals, which is in turn influencedby the total concentration of hydroperoxide[2]. The consumption of hydroperoxide (step B) would thus have the effect of diminishing the rate of oxygen absorption.

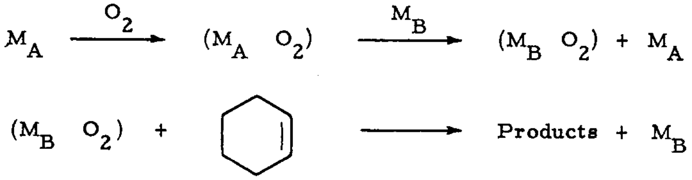
Table I. Autoxidation of cyclohexene[a] in nitrobenzene at atmospheric pressure and 60°.

Catalyst A[b]	Catalyst B[b]	Conversion[c] (%)	Products (%)[d]			
						
$RhCl(PPh_3)_3$	-	20	76	2	15	7
-	$MoO_5(HMPT)H_2O$	0	-	-	-	-
$RhCl(PPh_3)_3$	$MoO_5(HMPT)H_2O$	9	28	27	12	33
$RhCl(PPh_3)_3$	$V(acac)_3$	6	5	38	20	37
$RhCl(PPh_3)_3$	$Nb(OC_2H_5)_4$	18	72	5	13	10
$RhCl(PPh_3)_3$	$TiO(acac)_2$	19	72	1	15	11
$Fe(acac)_3$	$MoO_5(HMPT)H_2O$	4	15	39	5	41
$Co(acac)_3$	$V(acac)_3$	9	7	37	15	42
$Ni(acac)_2H_2O$	$MoO_5(HMPT)H_2O$	2	18	19	1	62
$IrClCO(PPh_3)_2$	$MoO_5(HMPT)H_2O$	19	31	27	22	20
$Pt(acac)_2$	$MoO_5(HMPT)H_2O$	3	0	46	3	48

[a] [cyclohexene] = 5 mole/l. [b] [cat. A] = [cat. B] = 2×10^{-3} mole/l.

[c] Measured after 4 hours. [d] Determined by glc using an internal standard.

Although these results as well as those given in Table I seem to favor the proposed scheme, one must point out that a second explanation is possible. The reaction could also be described in terms of an oxygen activation by catalyst A, followed by the transfer of the active oxygen to catalyst B. This species could then react with the olefinic substrate to give the oxidized products. Catalyst A would thus play the role of the oxygen carrier.



This second scheme is consistent with the ability of most metals listed as catalyst A to form oxygen adducts in a more or less reversible manner[6] ; furthermore, as we have already pointed out, most metals listed as catalyst B are known to be good epoxidation catalysts. A second argument which makes this scheme plausible relies on the fact that epoxidation catalysts are only active in the presence of peroxidic oxygen. This is possible if one considers the coordinated molecular oxygen on catalyst A to be in some electronically excited state comparable with a peroxidic linkage[7] .

In spite of these arguments in favor of the oxygen activation process, the presence of large amounts of alcohol and ketone in the products suggests strongly the hydroperoxide intermediacy. One must point out however that the possibility of both mechanisms being simultaneously operative remains plausible ; this is specially true in the cases where more epoxide is formed than alcohol and ketone.

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