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Homogeneous vs. Heterogeneous Catalysis Oxidation of Liquid Cyclohexene Catalyzed by Ions and Oxides of Transition Metals

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Liquid-phase autoxidations of cyclohexene at 70° in the presence of soluble acetylacetonates of the first-row transition metals are compared with similar autoxidations in the presence of insoluble oxides of the same metals.

The distributions of volatile products (cyclohexene oxide, cyclohexenone, cyclohexenol, and cyclohexenyl hydroperoxide) closely follow the patterns observed for the decompositions of cyclohexenyl hydroperoxide in the presence of the same metal catalysts. Whereas several of the metals give nearly equal quantities of cyclohexenol and cyclohexenone, chromium(III) and iron(III) give significantly more ketone than alcohol, and vanadium and molybdenum give large proportions of epoxide. The pattern suggests that all of the observed oxidations are free-radical chain reactions having the same homogeneous propagation steps and yielding, as the principal primary product, cyclohexenyl hydroperoxide, which then undergoes metal-catalyzed decomposition

Strong parallelism is noted between the product distributions in the homogeneous oxidations and those in the heterogeneous oxidations involving the corresponding metals, leading to the conclusion that for the system studied, the atomic number and oxidation state of the transition metal in the catalyst is more important than the detailed catalyst structure in determining the course of the reaction

INTRODUCTION

Despite the enormous importance of metal oxide catalysts, there is considerable difference of opinion as to how much of their catalytic action arises from the specific properties of the individual metal ions in the oxides and how much stems from the collective character of the oxide network and from defects therein. On one hand, there is a very large body of work which attempts to correlate, with varying degrees of success, the action of oxide catalysts with such diverse experimental parameters as energies of gas absorption (*1*a), infrared bands (*1*b), conductivity (*1*c), electron spin resonance spectra (*1*d), magnetic susceptibility (*1*e), crystal parameters (*1*f), and electron work function (*1*g). An alternate view is that a metal ion in solution or in a sheath of ligands has much in common with the same metal ion in an oxide lattice, that the catalytic action of the ion should significantly resemble that of the oxide, and that similarities in behavior tend to be overlooked because reactions employing heterogeneous catalysts are generally carried out under very different conditions from homogeneous reactions.

In the present study, the catalytic actions of oxides of the first row of transition metals are compared with those of the corresponding metal ions, as the oil-soluble acetylacetonates (acac derivatives), for a single reaction, the autoxidation of cyclohexene; this reaction, with metal catalysts absent, has been studied in detail in one of these laboratories (*2*). In earlier studies, Chalk and Smith found that this reaction, when catalyzed by transition metal ions (*3*a), and chelates (*3*b), in homogeneous systems, exhibits free-radical chain character; although their work indicated the mechanism of chain initiation, detailed product analyses, aside from hydroperoxide yields, were not reported. Subsequently, it was demonstrated that transition metal oxides also initiate the radical chain oxidation of cyclohexene under mild conditions (*4*). Of interest also is the report (*5*), that the products formed in the V_2O_5-catalyzed oxidations of olefins correspond to those formed when an olefin and a hydroperoxide react in the presence of soluble vanadium species (*6–8*).

In our experiments, reaction conditions for the heterogeneous and homogeneous catalyzed oxidations were kept as nearly alike as possible. In general, strong similarities were noted between the oxide-catalyzed and the homogeneous acetylacetonate-catalyzed reactions, but there were differences in detail.

EXPERIMENTAL

a. Oxidation experiments. Reaction mixtures contained 20.0 ml of cyclohexene (prepurified by passing over activated

TABLE 1

OXIDATIONS OF CYCLOHEXENE CATALYZED BY METAL OXIDES AND ACETYLACETONATES (ACAC) AT 70°[a]

Catalyst	Induction period (min)	Time[b] (min)	Rate (M hr^{-1})		O_2 abs. (mmole)	% Conv.	Products (mmole)				
			After induction period	Before stopping			Hydroperoxide	Alc.	Ket.	Epox.	Res.[c]
ABN, 0.072 M	0	52	0.48	—	11.2	5.65	8.55	0	0.62	0.23	0.55
$Cu(acac)_2$	3.8	24	1.6	1.6	5.95	6.00[d]	2.02	1.87	0.92	0.12	0.30
CuO	0	15	4.2	1.2	12.40	6.25	7.25	1.75	2.05	0.16	0.84
$Cr(acac)_3$	18	36	2.2	2.2	12.8	6.46	4.25	1.15	4.30	0.41	0.98
Cr_2O_3[e]	1.5	30	1.0	0.7	9.8	4.98	5.20	0.38	3.46	0.13	—[f]
Cr_2O_3[g]	85	98	2.8	1.1	11.6	5.86	5.55	1.45	3.14	0.45	0.73
$Co(acac)_2$	55	66	8.8	1.7	10.6	5.37	3.67	3.87	3.93	0.34	0.83
$Co(acac)_3$	17.5	31	2.2	2.2	10.4	5.27	5.55	1.55	2.09	0.20	1.14
CoO	122	164	1.2	0.7	12.3	6.21	5.33	2.7	2.25	0.19	0.96
$Mn(acac)_3$	0	13	6.0	1.1	10.5	5.28	4.94	2.81	3.63	0.23	0.85
Mn_3O_4	0	77	0.8	0	16.3	8.24	9.73	0.12	3.98	0.39	1.60
MnO_2	3	91	0.3	0.2	8.7	4.50	5.92	1.05	1.39	0.15	0.97
$MoO_2(acac)_2$	2.0	88	0.4	0	6.4	3.23	0.17	3.71	3.90	4.11	1.55
MoO_3	0	102	0.08		3.1	1.57	0.08	1.95	0.84	1.86	—[f]
$Fe(acac)_3$	4.0	66	0.1	0.7	10.2	5.15	5.38	0.93	1.68	0.35	0.35
Fe_2O_3	0	97	0.23	0.17	7.26	3.30	4.21	0.71	0.60	0	0.80
$VO(acac)_2$	175	206	0.91	0.91	11.85	5.99	0.33	4.11	2.49	4.20	—[f]
V_2O_5	3.0	41	0.6	0.5	8.2	4.11	0.33	2.32	1.82	2.44	0.73

[a] MnO, $Mn(acac)_2$, and ZnO showed no catalytic action.

[b] Reaction time, including induction.

[c] Assumed to be dimeric peroxide containing one dialkyl peroxide and one hydroperoxide group, (see ref. *2*).

[d] Experiment using 10 ml of cyclohexene.

[e] Oxidation at 70°, catalyst preheated *in vacuo*.

[f] Mixtures analyzed without distillation; hydroperoxide includes both volatile and nonvolatile.

[g] Oxidation at 85°, catalyst preheated in air.

alumina until it gave a negative test for dissolved hydroperoxide), and 2.00 ml of chlorobenzene (as an internal standard for the glc analyses); in the acetylacetonate experiments, solutions were 0.001 *M* in metal chelate. In experiments using metal oxides, 1.0 g of oxide was added. The metal oxides used, except for MnO_2, were prepared by thermal decompositions: CuO and CoO from the corresponding carbonates, MnO from the carbonate under nitrogen, Mn_3O_4 from $MnCO_3$ in air, Cr_2O_3 from $(NH_4)_2Cr_2O_7$, MoO_3 from $(NH_4)_2MoO_4$, and V_2O_5 from NH_4VO_3. Crystalline acetylacetonates, obtained from the MacKenzie Chemical Co., Central Islip, New York, were used as received. Oxidations were carried out at 70° with initial oxygen pressures of 95 psi and were halted after pressure had dropped to about 55 psi (corresponding to approximately 5% olefin conversion).

After oxidation, the reaction mixture was analyzed iodometrically for total hydroperoxide, then, after vacuum transfer, for volatile (monomeric) hydroperoxide. Remaining components were determined by glc after treatment with sufficient triphenylphosphine to reduce the hydroperoxide (*2*). All volatile components were cyclohexene derivatives; aside from the epoxide and the added chlorobenzene, there was no evidence for any saturated or aromatic product, nor for any volatile dimer.

Three oxidation experiments, in which analyses were less nearly complete, were carried out. In these, the undistilled oxidation mixture was titrated for total hydroperoxide, treated with Ph_3P, then analyzed by glc: no estimate was made of the residues.

In a separate experiment involving CuO catalysis, the possibility that reaction was catalyzed by a soluble copper species was ruled out by filtering off the solid oxide from a partially oxidized solution, then reoxidizing the filtrate immediately under the same conditions. In this experiment, which employed only 331 mg of CuO and 20 cc of olefin, the oxidation rate fell from 1.56 moles l^{-1} hr^{-1} in the presence of the oxide to 0.13 mole l^{-1} hr^{-1} after its removal.

In still another pair of experiments with CuO, it was found that a threefold decrease in the catalyst/olefin ratio resulted in a 2.7-fold decrease in the initial rate of oxidation.

In a number of cases, very short induction periods, or none at all, were detected; in others, induction periods greater than 1 hr, followed by a striking onset of reaction, were observed. Induction periods for the Cr_2O_3-catalyzed oxidation were markedly dependent on the nature of the catalyst pretreatment. When the catalyst, prepared from decomposition of $(NH_4)_2Cr_2O_7$, was preheated in air for 1 hr, induction periods of 1.0–2.5 hr were observed. If the Cr_2O_3 was preheated *in vacuo* at 500° for 90 min, induction periods fell to 1.5 min with a slight decrease in the initial rate. Although the predominant mode of decomposition of the dichromate is to Cr_2O_3 and N_2, some decomposes to NH_3 (the odor of which is detectable during the decomposition) and, necessarily, to a higher oxide of chromium.

b. Metal-catalyzed decompositions of cyclohexenyl hydroperoxide. A solution of of cyclohexenyl hydroperoxide in cyclohexene was prepared by autoxidation of a solution of 50 cc of cyclohexene, 5 cc of chlorobenzene, and 1.06 g of azo(bis)isobutyronitrile (ABN) at 70°; for this preparation 1.86 g of O_2 was absorbed in 101 min. The volatile components of the reaction mixture were separated from the nonvolatile by vacuum transfer. The mixture of volatiles, a cyclohexene solution 0.7 *M* in hydroperoxide, which contained smaller quantities of cyclohexenone and cyclohexene oxide as well, was separated into 3.0-ml aliquots, and these were treated with the appropriate metal catalysts as indicates in Table 2. Catalyst quantities were chosen to simulate the catalyst/olefin ratios in the oxidation experiments, and reactions times likewise corresponded to those in the oxidation experiments (total times minus induction periods). Heating the hydroperoxide solution for 30 min with 130 mg of finely ground Pyrex glass resulted in negligible hydroperoxide decomposition.

RESULTS AND DISCUSSION

Times, rates, induction periods, and product analyses for the oxidation experi-

TABLE 2

DECOMPOSITIONS OF CYCLOHEXENYL HYDROPEROXIDE IN CYCLOHEXENE, CATALYZED BY METAL OXIDES AND ACETYLACETONATES (ACAC) AT 70° [a]

Catalyst, mg	Reaction time (min)	Oxidized compounds (mmole)			
		Hydroperoxide	Alc.	Ket.	Epox.
None[a]	—	2.23	0	0.16	0.06
$Cu(acac)_2$, 3.6	25	0.13	0.91	1.00	0.05
CuO, 119	14	0.08	0.88	1.11	0.19
$Cr(acac)_3$, 3.6	20	1.34	0.02	1.09	0.10
Cr_2O_3, 111	16	1.20	0.01	1.16	0.08
Cr_2O_3, 124	105	1.40	0.14	1.25	0.08[b]
$Co(acac)_2$, 6.0	20	0.67	0.60	0.91	0.03
	60	0.40	1.01	0.95	0.04[b]
$Co(acac)_3$, 4.6	16	1.10	0.84	0.71	0.10[b]
CoO, 121	45	1.49	0.24	0.70	0.06
$Mn(acac)_3$, 7.7	40	0.74	0.73	0.78	0.07
$Fe(acac)_3$, 7.1	61	1.55	0.21	0.64	0.07
$MoO_2(acac)_2$, 4.8	60	0.03	1.36	0.21	1.79
V_2O_5, 96.8	50	0.02	1.26	0.84	1.04

[a] 3.00-ml samples (2.51 g) heated in closed bulbs with the catalysts listed. First entry is unheated starting mixture.

[b] Increase in content of oxidized product indicates that additional cyclohexene was oxidized during the decompositions of hydroperoxide or in the subsequent analysis.

ments are summarized in Table 1, and the distributions of products are compared with that resulting from the ABN-catalyzed autoxidation in the absence of metal derivatives. With both ABN and metal compounds absent, oxidation at 70° was negligible in 4 hr.

Most of the transition metal derivatives exhibited catalytic action, and in some cases catalysis was striking. For example, the initial rate with 1 g of CuO corresponds to the value calculated for a solution 5 *M* in the initiator ABN at the same temperature, and rates with $Co(acac)_2$ (after the induction period) and with $Mn(acac)_3$ were still higher.

Those reactions exhibiting very short or negligible induction periods were those catalyzed by soluble derivatives of metals in their higher oxidation states or by the corresponding oxides. If, as our evidence indicates, such oxidations are chain processes, they appear to proceed without initial accumulation of hydroperoxide. It then may be inferred that the catalyst is reacting either with oxygen or with the hydrocarbon yielding a chain carrier; we suggest reaction with the hydrocarbon to be the more likely, e.g.,

$$CuO(s) + RH \rightarrow CuO(H)(s) + R\cdot$$

after which the chain proceeds homogeneously in the usual manner. Those oxidations showing marked induction periods very probably require initiation by homolysis of hydroperoxide, and this is almost certainly metal-catalyzed, for the oxidation rates are far greater than would be observed in the absence of metal compounds. Those metal oxides whose catalytic action decreases as the oxidation proceeds may be assumed to be deactivated by absorption of one or more of the oxidation products, most probably the ketone (*4*). Decrease of catalytic activity at low conversions is less usual with the soluble metal catalysts. With $Co(acac)_2$ it appears to be due, at least in part, to precipitation of an oxide of cobalt; with $Mn(acac)_3$, some conversion to the retardant $Mn(acac)_2$ may be occurring. The induction period observed for the Cr_2O_3-catalyzed oxidation is greatly shortened when the oxide is preheated at 500° *in vacuo*, suggesting that NH_3, formed during preparation of the oxide, is a retarder at some stage in the reaction but that it may be removed by intense heating.

The mixtures of products resulting from the metal chelate- and metal oxide-catalyzed oxidation contain proportionately much less hydroperoxide than is formed in the ABN-catalyzed oxidation, but much more ketone and, in most cases, a greater fraction of cyclohexenol. Moreover, the oxidations catalyzed by the vanadium and molybdenum compounds give substantial yields of epoxide. An important question concerning these differences is whether they arise from a modification of the propagating species by the metal compound, or whether they may be attributed to metal-catalyzed decomposition of cyclohexenyl hydroperoxide (which is the dominant product in the usual radical-chain oxidation under these conditions).

Our experiments on the decomposition of

the hydroperoxide in the presence of the metal derivatives strongly support the latter alternative. The products from the decomposition reactions are summarized in Table 2. In all cases, the decrease in hydroperoxide content accompanies a marked increase in ketone content and a (sometimes less striking) increase in alcohol content. High yields of epoxide observed only for decompositions in the presence of $MoO_2(acac)_2$ and V_2O_5; *these are the same catalysts that favor epoxide formation in the oxidation experiments.* Moreover, this finding is in accord with the known effectiveness of vanadium and molybdenum compounds in catalyzing the nonchain epoxidation of olefins with hydroperoxides (*6–8*). The autoxidations catalyzed by $VO(acac)_2$, V_2O_5, and $MoO_2(acac)_2$ yield very nearly equal quantities of epoxide and alcohol, suggesting that the two products are formed together from a common source, i.e., the hydroperoxide. Contrary to an earlier report (*6*), we do not find $Cr(acac)_3$ to be a good epoxidation catalyst; in our experiments, this chelate greatly favors formation of the ketone, as does its oxide counterpart, Cr_2O_3.

The remaining hydroperoxide decompositions appear to fall into two groups—those yielding principally ketone, and those giving nearly equal quantities of alcohol and ketone. Decompositions of the latter type are generally observed with metals having two accessible oxidation states differing by a single unit (Cu, Co, Mn) and presumably proceed by a continuous process in which the metal is alternately oxidized and reduced (*9*). In decompositions yielding predominately ketone, the metal ion or oxide may function as a Lewis acid, initiating heterolysis of the O–O bond.

Irrespective of the detailed explanation, the trend here again appears to be clear; those catalysts which give principally ketone in the hydroperoxide decomposition [e.g., $Cr(acac)_3$, and $Fe(acac)_3$] also yield high ketone/alcohol ratios in the autoxidations. On the other hand, those catalysts giving nearly equal quantities of alcohol and ketone in the decomposition experiments do so also in the autoxidations. (Hydroperoxide yields tend to be higher in the autoxidations than in the decompositions, for in the autoxidations hydroperoxide is being formed as well as being destroyed.) Thus, the qualitative correlation between the two sets of experiments strongly supports the notion that the distribution of autoxidation products is determined in large part by the metal-catalyzed decomposition of cyclohexenyl hydroperoxide.

A striking parallelism is evident between the product distributions in the heterogeneous oxidations and those in the homogeneous oxidations with the corresponding metals. Vanadium and molybdenum compounds, both soluble and insoluble, give much higher epoxide yields than do any of the other metal catalysts. Copper, cobalt, and manganese compounds (both soluble and insoluble) give high hydroperoxide yields and, except for Mn_3O_4, comparable amounts of alcohol and ketone. Finally chromium and iron(III) compounds, both soluble and insoluble, give high yields of hydroperoxide, along with alcohol-ketone mixtures containing considerably more ketone than alcohol. The yields of hydroperoxide and ketone resulting from the various autoxidations are plotted as functions of atomic number of the transition metal in Fig. 1; again, the curves for the heterogeneous and the homogeneous catalysts are remarkably similar.

The experiments here are preliminary and, since they obviously leave unanswered a number of questions concerning the detailed role of the active metal species in both types of systems, it would be well to interpret our results with some caution. In particular, it might be argued that the heterogeneous reactions we describe are really reactions catalyzed by soluble metal speices to which the oxide catalysts have been, in part, converted. For CuO, one of the most effective catalysts used, we have demonstrated that this is not the case by showing that catalytic action in the CuO-catalyzed oxidation virtually disappears when the oxide is filtered out. Moreover, in none of our oxide systems do we find visual evidence (colored solutions or colored residues on evaporation) that the oxide has dissolved significantly in the reaction mixture.

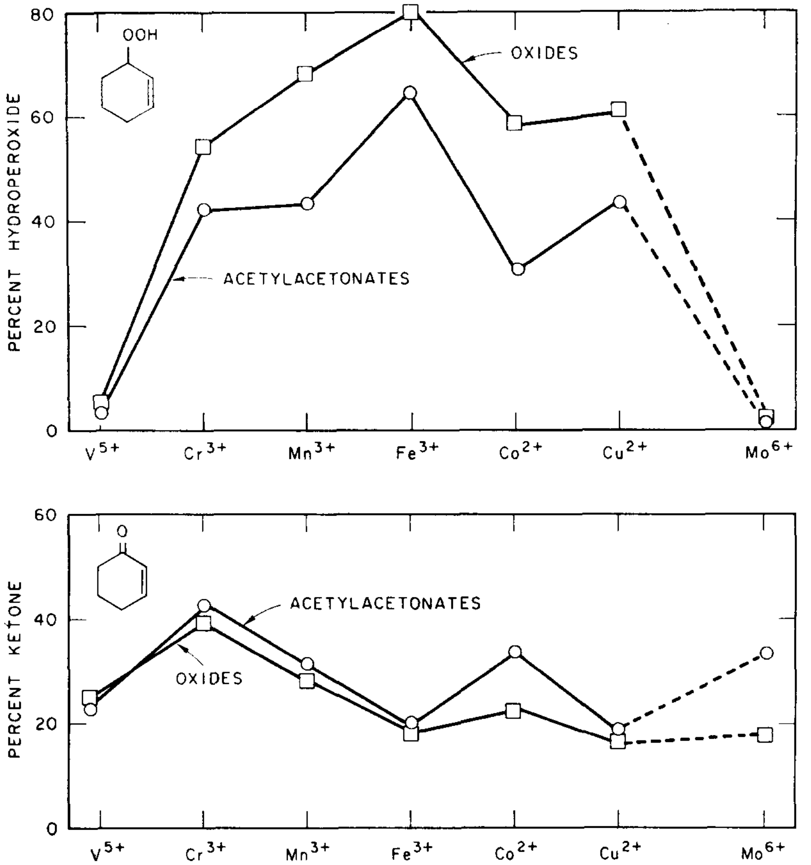

FIG. 1. Hydroperoxide and ketone contents of mixtures of products resulting from autoxidation of cyclohexene, catalyzed by oxides and acetylacetonates of transition metals, 70° (residues excluded).

Soluble metal species, if present at all in the oxide-catalyzed reactions, are many orders of magnitude less concentrated than in the chelate-catalyzed reactions, although, as seen, catalytic activity in the two types of situations may be quite comparable. For the oxide-catalyzed reactions, it is thus difficult to escape the conclusion that the greater part, if not all, of the catalytic action observed is derived from the solid phase, rather than from dissolved species. On this basis, the strong parallelism between results for the oxide- and chelate-catalyzed oxidations indicates that for these systems the atomic number and oxidation state of the transition metal in the catalyst is much more important than the detailed catalyst structure in determining both the course of the reaction and the relative yields of products.

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