LITERATURE CITED

1. A. A. Isirikyan, S. S. Mikhailova, I. A. Polunina, and S. N. Tolstaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2452 (1981).
2. A. V. Kiselev and A. V. Uvarov, Surf. Sci., 6, 4, 399 (1967).
3. S. N. Tolstaya, S. S. Mikhailova, A. B. Taubman, and A. V. Uvarov, Lakokras. Mater. Ikh Primen., 6, 8 (1967).
4. D. M. Griffiths and C. H. Rochester, J. Chem. Soc. Faraday Trans., 1, 1977, 73(12), 1988.
5. M. Primet, P. Pichat, and M.-V. Mathien, J. Phys. Chem., 75, 1221 (1971).
6. A. A. Isirikyan, S. S. Mikhailova, S. N. Tolstaya, and A. B. Taubman, Izv. Akad. Nauk SSSR, Ser. Khim., 1253 (1975).
7. A. A. Isirikyan, S. S. Mikhailova, I. A. Polunina, and S. N. Tolstaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1197 (1978).

LIQUID-PHASE OXIDATION OF CYCLOHEXENE UNDER CATALYSIS BY LAMELLAR COMPOUNDS OF GRAPHITE AND TRANSITION-METAL CHLORIDES

N. I. Kovtyukhova, V. M. Belousov,
S. V. Mikhalovskii, L. D. Kvacheva,
Yu. N. Novikov, and M. E. Vol'pin

UDC 542.943.7:547.592.2

The liquid-phase oxidation of cumene and ethylbenzene by molecular oxygen can be catalyzed by lamellar compounds of graphite (LCG) with transition-metal chlorides, reaction proceeding according to a heterogeneous-homogeneous mechanism with the formation of hydroperoxides [1]. It is, moreover, known that hydroperoxides are capable of epoxylating olefins in the presence of compounds of the metals of Groups V and VI of the periodic table [2].

It seemed of interest to develop a process in which the epoxylating hydroperoxides might be directly formed in the reacting system rather than introduced into the latter from without. Cyclohexene (CH) suggested itself for such a study since it is readily epoxylated by hydroperoxides, and selectively oxidized by molecular oxygen in the presence of cyclohexenyl hydroperoxides (CHHP) [3].

The present work was a study of the oxidation of CH, and the decomposition of CHHP, in the presence of LCG with Cu, Co, Mn, Fe, Ni, Zn, and Mo chlorides. For comparison, study was also made of the catalytic activity of the free chlorides of these same metals.

EXPERIMENTAL

The lamellar compounds of graphite with metal chlorides (Table 1) were prepared by the methods of [4-7]; their structures were determined by x-ray diffractometry using a Dron-1 diffractometer (CuK_α radiation, Ni filter). The LCG were used in powder form, the powders having approximately the same granular composition with specific surface areas falling in the 0.5-0.8 m^2/g range.

The cyclohexane was prepared by the method of [8] and distilled over metallic sodium. The CHHP content of the olefin was $2 \cdot 10^{-3}$ mole/liter. Catalytic activities were determined from the O_2 uptake as measured in a gasometric system at 60°C and 1 atm pressure. The volume of the liquid phase was 3 ml in every case.

Experiments of CHHP breakdown used its solution in cyclohexene, prepared by CH oxidation [9], and containing 0.10-0.12 mole/liter of CHHP.

The products obtained from CH oxidation and CHHP breakdown were analyzed by LG chromatography (30% PEG-1500 on NAW-HMDS Chromaton, 120°C). The concentration of active oxygen in the oxidate was determined iodometrically [10].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukranian SSR, Kiev.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 25-30, January, 1983. Original article submitted April 13, 1982.

TABLE 1. Rates of Oxygen Uptake (W_{O_2}), and Product Distributions, in the Oxidation of Cyclohexene on Transition Metal Compounds at 60°C

Catalyst	Salt content of LCG, %	LCG echelon[a]	Salt concentration[b], q·10³, mole/liter	$W_{O_2}\cdot 10^5$, mole/l[c]	Time, min	Selectivity, % CHHP	CHO	CHOL + CHONE
Without catalyst	—	—	—	0,4	130	100	0	0
Graphite	—	—	12,7[d]	0,7	120	86	8	6
			0,4	0,3	120	100	0	0
LCG – $CuCl_2$	49,0	I	57,2	10,6	24	50	5	45
LCG – $CuCl_2$	49,0	I	1,2	4,3	90	61	3	36
$CuCl_2$		—	1,0	9,0	73	66	7	27
LCG – $CoCl_2$	62,0	I	58,8	11,9	27	51	8	41
LCG – $CoCl_2$	62,0	I	1,0	3,5	131	62	2	36
$CoCl_2$		—	1,2	5,5	38	84	5	11
LCG – $MnCl_2$	46,0	I	57,4	9,5	62	76	9	15
LCG – $MnCl_2$	46,0	I	1,2	2,4	185	83	6	11
$MnCl_2$		—	1,1	2,0	148	84	16	Weak
LCG – $FeCl_3$	46,6	I	58,2	3,7	135	93	5	2
LCG – $FeCl_3$	46,6	I	1,1	0,7	121	100	0	0
$FeCl_3$[e]		—	1,0	1,8	33	90	4	6
LCG – $FeCl_2$	38,6	II	59,0	2,4	171	75	4	21
LCG – $NiCl_2$	44,0	II	58,9	3,8	182	77	5	18
LCG – $NiCl_2$	44,0	II	1,0	0,4	140	100	0	0
$NiCl_2$[e]		—	1,0	0,5	154	100	Weak	0
LCG – $MoCl_5$	38,0	III	0,9	3,1	133	19	40	41
$MoCl_5$[e]		—	1,0	0,3	195	4	45	51
LCG – $ZnCl_2$	27,7	III	58,7	1,2	30	90	5	5

---

a. The number of graphitic carbon sheets between successive layers of compound.

b. The value of q was calculated from the salt content of the LCG compound.

c. The rates given here and in Table 3 are maximum values.

d. Graphite content in g/liter.

e. Salts of limited solubility in the reaction mixture.

DISCUSSION OF RESULTS

The rate of oxygen uptake (W_{O_2}) in the presence of LCG with metal chlorides was considerably higher than the rate of either thermal CH oxidation or the oxidation of CH in the presence of graphite alone (see Table 1). Comparison showed that, with the exception of LCG-$MoCl_5$, the order of decrease of the catalytic activity of the LCG in the CH oxidation was exactly the same as the order of decrease of the activities of the free chlorides, namely, $CuCl_2 > CoCl_2 > MoCl_5 > MnCl_2 > FeCl_3 > NiCl_2$ for the former and $CuCl_2 > CoCl_2 > MnCl_2 > FeCl_3 > NiCl_2 \approx MoCl_5$ for the latter. Similar relations were observed in the compositions of the reaction products (see Table 1). The indication here was that the catalytic activity of the LCG is determined by the nature of the salt embedded in the graphite, the chloride molecules located between the graphite sheets and on the faces of the graphite crystals functioning as catalytically active centers. The specific catalytic activity of the LCG (per g-atom of salt) could be expressed relative to the face molecules, or relative to the entire amount of salt embedded in the graphite. In the first case, the activity of the LCG was several orders higher than the activity of the free chloride, while in the second case the two activities were of the same order of magnitude.

The fact that the rate of oxidation of the oxidate after removal of the LCG was still 20-30% of the oxidation rate in the presence of the catalyst suggested that a small amount of the salt must have passed out of the graphite in the course of reaction. It would seem, however, that it was only those molecules which were weakly bound between the graphite sheets which passed into solution since changes in the LCG activity and selectivity were not observed with samples in which chloride leaching had been brought to an end by a *preliminary* 4-h treatment in a cyclohexene CHHP solution at 60°C.

It seems likely that the mechanism of the catalytic action of the LCG with a given metal chloride is similar in many respects to the mechanism of the catalytic action of the chloride itself. The fact, however, that the Fe, Ni, and Mo chlorides were less active in oxidation, and more active in CHHP decomposition, than their LCG counterparts suggested that nonradical hydroperoxide breakdown must occur in their presence (see Tables 1 and 2).

Cyclohexene hydroperoxide, cyclohexene oxide (CHO), cyclohex-2-ene-1-ol (CHOL), and cyclohex-2-ene-1-one (CHONE) were the principal products obtained from CH oxidation, on both the free metal chlorides and

TABLE 2. Rate of Breakdown of Cyclohexene Hydroperoxide (W_{CHHP}), and the Distribution of Products from the CHHP Breakdown, on Transition Metal Compounds, at 60°C

Catalyst	$W_{CHHP} \cdot 10^3$, mole/(liter·sec)[a]	Initial CHHP concentration, mole/l	$q_{Ct} \cdot 10^3$, mole/liter	Time, min	Product concentrations, mole/liter		
					CHHP	CHO	CHOL + CHONE
without catalyst	0,02	0,10	–	93	0,099	–	Trace
LCG–$CuCl_2$	1,0	0,10	59,7	91	0,063	Trace	0,040
$CuCl_2$	1,4	0,12	1,1	40	0,111	–	0,012
LCG–$CoCl_2$	1,5	0,10	58,3	94	0,046	Trace	0,057
$CoCl_2$	1,0	0,12	1,1	41	0,110	0,001	0,005
LCG–$MnCl_2$	0,7	0,10	57,7	97	0,074	Trace	0,027
$MnCl_2$	0,6	0,12	1,1	41	0,111	–	0,001
LCG–$FeCl_3$	0,5	0,12	59,6	63	0,116	–	0,003
$FeCl_3$[b]	2,0	0,12	0,9	42	0,118	–	Trace
LCG–$FeCl_2$	2,3	0,10	58,7	105	0,087	–	0,020
LCG–$NiCl_2$	0,1	0,10	59,0	92	0,096	Trace	Trace
$NiCl_2$[b]	1,0	0,12	1,1	43	0,114	–	–
LCG–$MoCl_5$	4,3	0,05	1,0	80	0,004	0,040	0,042
$MoCl_5$[b]	20,0	0,05	1,0	80	0,001	0,047	0,050

---

a. Initial rates of CHHP breakdown; over 15-20 min in the case of LCG with transition metal compounds, and over 3-5 min in the case of free chlorides.

b. Salt of limited solubility in the reaction mixture.

the LCG. The compositions of the products obtained under the two types of catalysis were approximately the same, and were characteristic of those met in radical-chain olefin oxidation processes [3].

In the case of the LCG-$CuCl_2$, LCG-$CoCl_2$, LCG-$MnCl_2$, LCG-$MoCl_5$ catalysts, the rate of CH oxidation increased with an increase in q, the amount of catalyst present in the system, eventually reaching a limiting value characteristic of the catalyst itself (Fig. 1). At low LCG concentrations, the reaction order was 0.5. This particular reaction order is characteristic of those heterogeneous-homogeneous hydrocarbon oxidation mechanisms in which the catalyst serves only to initiate the reaction. In the case of oxidation in the presence of the LCG with $MoCl_5$, the reaction rate rose, reached a maximum value, and then fell off sharply, showing that critical effect which is characteristic of catalysts for radical-chain oxidation processes [11].

On the basis of the data obtained here it was assumed that the LCG initiated the oxidation process by promoting radical breakdown of the CHHP formed as intermediate oxidation products. This assumption was supported by the following facts: 1) with exception of LCG-$MoCl_5$ and LCG-$FeCl_2$, the catalytic activities of the LCG in CHHP breakdown can be correlated with their catalytic activities in CH oxidation; 2) the oxidation of CH is an autocatalytic process, possibly because of CHHP buildup; 3) the initial rate of oxygen uptake increases with an increase in the initial CHHP concentration in the cyclohexene. The catalytic action of the LCG was not, however, limited to promoting peroxide breakdown since the relative amounts of the CH oxidation products depended on the nature of the catalyst and varied over wide limits (see Table 1). Buildup of CHO in the radical-chain CH oxidation could occur as the result of cyclohexylperoxy radical addition at the cyclohexene double bond [12]. It seems likely that this would be the mechanism of CHO formation in the presence of compounds of Cu, Co, Mn, Fe, Ni, and Zn since epoxides are almost completely lacking in the products resulting from CHHP breakdown on these catalysts (see Tables 1 and 2). On the other hand, CHO formation on LCG-$MoCl_5$, and on free $MoCl_5$, proceeds largely through CH epoxidation by CHHP, the intermediate oxidation products as evidenced by the fact that CHO did not appear among the products obtained from CHHP breakdown on these catalysts (see Table 2). The results of the experiments covered by Fig. 2 point to the direct involvement of the CHHP in CHO formation. There LCG-$MoCl_5$ was introduced into CH which was undergoing oxidation on LCG-$CoCl_2$. The fact that there was an abrupt drop in the CHHP concentration, and an equally abrupt increase in the CHO concentration, in the first 5 min after this addition was taken as indication of epoxidation by the hydroperoxides.

In the presence of Mo compounds, the CHHP can break down through either a radical or a molecular mechanism (CH epoxidation). It is possible that the high activity of $MoCl_5$ in epoxidation of the CHHP could account for the fact that the rate of oxygen uptake was low, and the induction period long (40 min), for CH oxidation on this compound. In the case of the LCG with $MoCl_5$, an increase of the amount of catalyst present in the system led to an increase in the rate of CHHP breakdown through the molecular mechanism, and a reduction in the rate of free radical formation, the net effect being to reduce the rate of oxidation in the presence of large amounts of the catalyst. It is, however, possible that this critical effect resulted from participation of the LCG-$MoCl_5$ catalyst in the chain rupture process [8].

TABLE 3. Rate of Oxygen Uptake (W_{O_2}), and CHO Formation (W_{CHO}), and the Composition of the Reaction Products Resulting from CH Oxidation on CatA and CatB Catalysts

CatA	$q\cdot10^3$, mole/liter		$W_{O_2}\cdot10^5$	$W_{CHO}\cdot10^3$	Time, min	Composition of products, %		
	CatA	CatB	mole/(liter·sec)			CHHP	CHO	CHOL + CHONE
—	—	0,9	3,1	2,5	240	15	42	43
LGC-$CuCl_2$	1,1	0,9	7,0	3,8	100	22	34	44
LCG-$CuCl_2$	7,4	0,9	7,0	3,3	30	37	28	35
LCG-($CuCl_2$+$MoCl_5$)^a	6,9^b 1,0^a	—	3,9	2,4	165	28	32	40
LCG-$CoCl_2$	1,1	1,0	4,5	3,1	140	15	38	47
LCG-$CoCl_2$	7,0	1,0	7,1	3,8	127	33	31	36
LCG-($CoCl_2$+$MoCl_5$)^a	7,2^d 1,0^a	—	2,4	1,9	228	22	38	40
LCG-$MnCl_2$	1,1	1,0	3,8	3,3	180	11	43	46

---

a. Without CatB

b. $CuCl_2$ content.

c. $MoCl_5$ content.

d. $CoCl_2$ content.

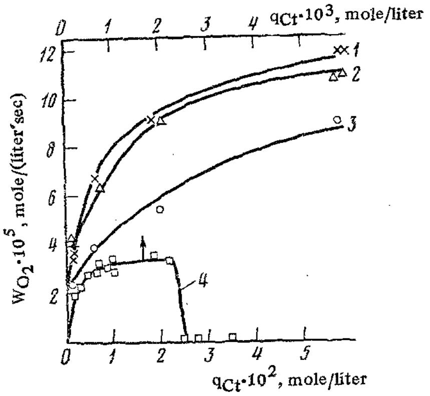

Fig. 1

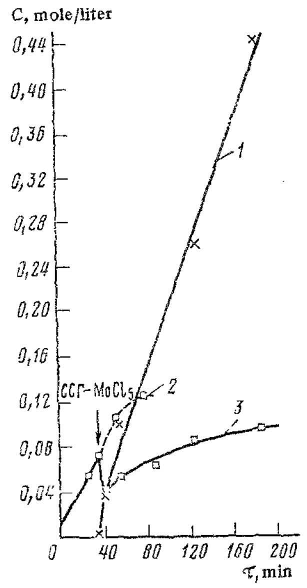

Fig. 2

Fig. 1. Variation of the maximum rate of cyclohexene oxidation with the amount of catalyst present in the system: 1) LCG-$CoCl_2$; 2) LCG-$CuCl_2$; 3) LCG-$MnCl_2$; 4) LCG-$MoCl_5$.

Fig. 2. Build-up of reaction products after the introduction of LCG-$MoCl_5$ into cyclohexene undergoing oxidation on LCG-$CoCl_2$: 1) Cyclohexene oxide; 2) cyclohexene hydroperoxide, formed during oxidation of LCG-$CoCl_2$; 3) cyclohexene hydroperoxide, after introduction of LCG-$MoCl_5$.

Cyclohexene oxidation was also carried out on catalytic pairs with a view to promoting epoxide formation. Here catalyst A was responsible for CHHP formation and catalyst B for epoxidation by the CH hydroperoxides. Lamellar graphite compounds with high activity in CH oxidation and high selectivity in CHHP formation were chosen as component A, while LCG-$MoCl_5$ served as component B. Study was also made of two-component LCG, one containing $CuCl_2$ and $MoCl_5$, and the other $CoCl_2$ and $MoCl_5$ (Table 3).

The rate of O_2 uptake and the rate of CHO formation, were higher for CH oxidation on the catalyst pairs than for oxidation on catalysts A and B alone. Increasing the activity of catalyst A for CH oxidation reduced both the selectivity for CHO formation and the duration of catalytic activity in the system. These same effects were found to accompany an increase in the A/B mole ratio. An increase in the A/B mole ratio did not, however, lead to an increase in the activity, in either oxidation or CHO formation, in the case of LCG-$CuCl_2$. This was in line with the results of earlier experiments on CH oxidation on mixed homogeneous catalysts [13]. The highest CHO yields were obtained in the LCG-$MnCl_2$ and LCG-$MoCl_2$ systems. In the last case, the high CHO yield may result from the low activity of the catalyst in radical CHHP breakdown. The catalytic activities of the two-component LCG, i.e., of compounds containing two chlorides embedded in the same graphite, proved to be lower than the activities of mixtures of the individual LCG's.

CONCLUSIONS

1. Lamellar compounds of graphite with Cu, Co, Mn, Fe, Ni, Mo, and Zn chlorides are catalytically active in the liquid-phase oxidation of cyclohexene by molecular oxygen and in the breakdown of cyclohexyl hydroperoxides. Appreciable quantities of cyclohexene oxide are formed in these reactions on LCG-$MoCl_5$.

2. On the basis of the determined product compositions, and our knowledge of the kinetics of heterogeneously catalyzed liquid-phase oxidation reactions, oxidation in the presence of the LCG must proceed through a radical-chain heterogeneous-homogeneous mechanism.

LITERATURE CITED

1. V. M. Belousov, N. I. Kovtyukhova, S. V. Mikhalovskii, Yu. N. Novikov, and M. E. Vol'pin, Dokl. Akad. Nauk SSSR, 253, 346 (1980).
2. G. A. Tolstikov, Reactions of Hydroperoxide Oxidation [in Russian], Nauka, Moscow (1976), p. 11.29.
3. D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, J. Am. Chem. Soc., 87, 4824 (1965).
4. Yu. N. Novikov, V. A. Semion, Yu. T. Struchkov, and M. E. Vol'pin, Zh. Struk. Khim., 11, 1039 (1970).
5. Yu. N. Novikov, V. A. Semion, Yu. T. Struchkov, and M. E. Vol'pin, Zh. Strukt. Khim., 11, 880 (1970).
6. Yu. N. Novikov, N. D. Lapkina, Yu. T. Struchkov, and M. E. Vol'pin, Zh. Strukt. Khim., 17, 756 (1976).
7. M. E. Volpin (Vol'pin), Yu. N. Novikov, et al., J. Am. Chem. Soc., 97, 3366 (1975).
8. Weigand, Experimental Methods in Organic Chemistry [Russian translation], IL, Moscow (1950), vol. 2, p. 345.
9. E. S. Lould, M. Rado, and E. D. Peters, J. Catal., 13, 238 (1969).
10. C. D. Wagner, R. H. Smith, and E. D. Peters, Anal. Chem., 19, 976 (1947).
11. N. M. Émanuél', E. T. Denisov, and Z. K. Maizus, Chain Reactions in the Liquid Phase Oxidations of Hydrocarbons [in Russian], Nauka, Moscow (1965), p. 218.
12. C. D. Brill, J. Am. Chem. Soc., 85, 141 (1963).
13. A. Fusi, R. Ugo, and C. M. Zanderighi, J. Catal., 34, 175 (1974).