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Catalysis by Chelates of Transition Elements of the Liquid Phase Oxidation of Propylene

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Several azo-compound chelates of MoO_2^{2+}, WO_2^{2+}, Co^{2+}, Cr^{3+}, and Cu^{2+} were used as catalysts in the oxidation of propylene by molecular oxygen. The propylene was dissolved in benzene at 150°C, kept under a total pressure of 45 atm, and its conversion was limited to 7.5%. The MoO_2^{2+} and WO_2^{2+} chelates lead to 70% selectivities in epoxypropane when the concentration of the transition element is 3.10^{-4} cation g/kg of the benzene–propylene mixture. The specificity of the catalyst activity toward the formation of epoxypropane depends at the same time on the kind of heavy cation and on the structure of ligand. A parallelism can be noted between the results obtained here and those observed with the enzymatic oxidases.

INTRODUCTION

At a temperature ranging between 130 to 200°C, about 30 to 40% yields in epoxypropane are obtained in the noncatalized oxidation of propylene by molecular oxygen. Peroxidic compounds react in the liquid phase with olefins, and produce epoxides. Hydrogen peroxide epoxidizes acrolein and methacrolein in an alkaline medium (*2*). The epoxy compounds being greatly hydrolyzed, the selectivities obtained are low (*3*). Similar difficulties arise with the peracids, the main secondary reaction being the esterification of the epoxy (*4*). Better selectivities in epoxy compounds are however obtained with organic hydroperoxides (*5*). The transition element salts, molybdenum, tungsten, and vanadium especially, increase the yield in epoxide (*6*).

The present paper reports the results registered in the catalized oxidation of propylene in the liquid phase by molecular oxygen. The aim was to study how the nature of the heavy cation, and of its ligand, influence the catalytic activity. Heavy ligands, like the coenzymes, are used to chelate the cations of transition elements.

EXPERIMENTAL METHODS

Catalyst Preparation

Several azo-compound chelates of transition elements were used as catalysts. The cobalt, chromium, and copper chelates, as well as the nonmetallic azo compounds were supplied by the Carbochimique, S.A. (Tertre, Belgium). These substances were first synthesized by diazotization. The compounds were then condensed and metallized. Table 1 gives their structures. MoO_2Cl_2 and WO_2Cl_2 derive from a 500°C fusion of MoO_3 and WO_3 with NaCl (*7*). As to the oxychlorides, they were extracted with ether. The ethereal solution was then added to the nonmetallic azo compound alcoholic solution, with stoichiometric ratios molybdenum or tungsten/azo compound of 1:1 or 1:2. The mixture so obtained was boiled and its volume was reduced by distillation. The crystallized chelate was filtered and then crystallized again in alcohol. The chelates were destroyed by aqua regia, and the molybdenum and tungsten were analyzed colorimetrically as the thiocyanate after reduction according to (*8*). The fol-

TABLE 1
STRUCTURE OF THE CATALYSTS

Primary compounds	Transition element	Cation/azo compound atom g/mole	Abbrev.
4-[*N*-methyl-*N*(β-cyanoethyl)] sulfamido-2-aminophenol (*1*) + *o*-chloroacetoacetanilide	Mo	1/1	A 1 Mo
	W	1/1	A 1 W
	Co	1/2	A 1 Co
	Cr	1/2	A 1 Cr
	Cu	1/2	A 1 Cu
4-[*N*-methyl-*N*(β-cyanoethyl)] sulfamido-2-aminophenol (*1*) + 1-phenyl-3-methyl-pyrazolone (*5*)	Mo	1/1	A 3 Mo
	W	1/1	A 3 W
	Co	1/2	A 3 Co
	Cr	1/2	A 3 Cr
	Cu	1/2	A 3 Cu
2-Anisidine-4-sulfonediethylamine + 6,8-disulfonaphthol (*2*) acid	Mo	1/2	A 11 Mo
	W	1/2	A 11 W
	Co	1/2	A 11 Co
	Cr	1/2	A 11 Cr
	Cu	1/2	A 11 Cu

lowing chelates were obtained in this way: (Azo 1)MoO_2, (Azo 3)MoO_2, (Azo 11)$_2$ MoO_2; (Azo 1)WO_2; (Azo 3)WO_2; and (Azo 11)$_2WO_2$. The structures of the other chelates were (Azo i)$_2$Co, (Azo i)$_2$Cr and (Azo i)$_2$Cu. The structures were confirmed by elementary analysis (C, H, O, and transition element). The catalysts were completely soluble in the reaction medium.

Oxidation Process

The oxidations were carried out in a Pyrex glass vessel enclosed in a 304 stainless steel autoclave (500 ml) equipped with a magnetic stirrer (*9*). A normal charge consisted of 80 g of benzene (Merck, analytical grade), 51 g of propylene (Air Liquide, 99%) and the soluble catalyst. The reactor was charged at room temperature, except for propylene. It was closed, cooled to 0°C, filled with propylene, and stabilized at a steady temperature of 150°C. The temperature inside the reactor was measured by a thermocouple. Oxygen was introduced into the autoclave to a partial pressure of 12 atm, which corresponded to a total pressure of 45 atm. The magnetic stirrer was switched on, while the reactor pressure was maintained constant during the oxidation by steady addition of oxygen coming from a small reservoir kept under high pressure. The fall in pressure of the reservoir indicated the amount of oxygen consumed. In every reaction, the conversion of propylene was limited to 7.5%. Induction times went from 10 to 30 min, and the oxidation rates amounted to about 15 to 20%/hr of propylene consumption for both the noncatalyzed and the catalyzed reactions. When the oxidation was completed, the reactor was cooled to −20°C and the gases which were gradually liberated were slowly let out (12 hr) through traps cooled by an acetone–Dry Ice mixture.

Analyses of Products

The product cooled to 0°C was analyzed by gas chromatography (Wilkens Aerograph 1520B; detection by flame ionization). The light products (epoxypropane, methylformate, methanol, and acetone) were separated using a 6-m column filled with 100–120 mesh Chromosorb P impregnated with 15 wt % dinonylphthalate. The internal standard was isopropanol. The temperature of the column was programmed from 40 to 60°C. The heavy products (propylene glycol, mono- and diformates; propylene glycol, mono- and diacetates) were separated with a column 2-m long filled with 100–120 mesh Chromosorb P impregnated with 15 wt % Carbowax 20 M. The

TABLE 2

Products from the Catalyzed Oxidation of Propylene Dissolved in Benzene

Propylene/benzene = 0.63 g/g; 150°C; total pressure = 45 atm; partial oxygen pressure = 12 atm; conversion: 7.5%; acetaldehyde: 0.87 × 10^{-2} mole/kg of the propylene–benzene mixture; catalyst: 2.7 × 10^{-4} cation g/kg of the propylene–benzene mixture.

	Products (moles/100 moles of propylene oxidized)					
Catalyst	Methyl formate	Methanol	Epoxypropane	Acetone	Mono- and diglycol formates	Mono- and diglycol acetates
None	1.9	14	35	5.3	14.8	11.2
A 1 Mo	2.6	17	53	6.3	8.0	6.0
A 3 Mo	1.9	12	55	7.6	6.9	5.2
A 11 Mo	2.5	15	70	7.8	2.0	1.5
A 1 W	2.5	16	61	7.6	4.5	3.3
A 3 W	2.2	17	65	5.8	4.4	3.3
A 11 W	2.2	14	71	7.3	2.5	1.7
A 1 Co	2.5	11	40	5.8	13.5	9.8
A 3 Co	2.4	10	32	5.9	16.0	12.0
A 11 Co	2.4	11	46	6.9	11.0	8.2
A 1 Cr	2.5	12	35	5.8	14.5	10.5
A 3 Cr	2.5	13	39	6.0	12.4	8.5
A 11 Cr	2.0	11	45	5.8	11.4	8.4
A 1 Cu	2.5	16	31	5.8	16.0	12.0
A 3 Cu	2.5	11	39	6.0	13.3	10.5
A 11 Cu	2.5	10	47	6.8	10.2	7.2

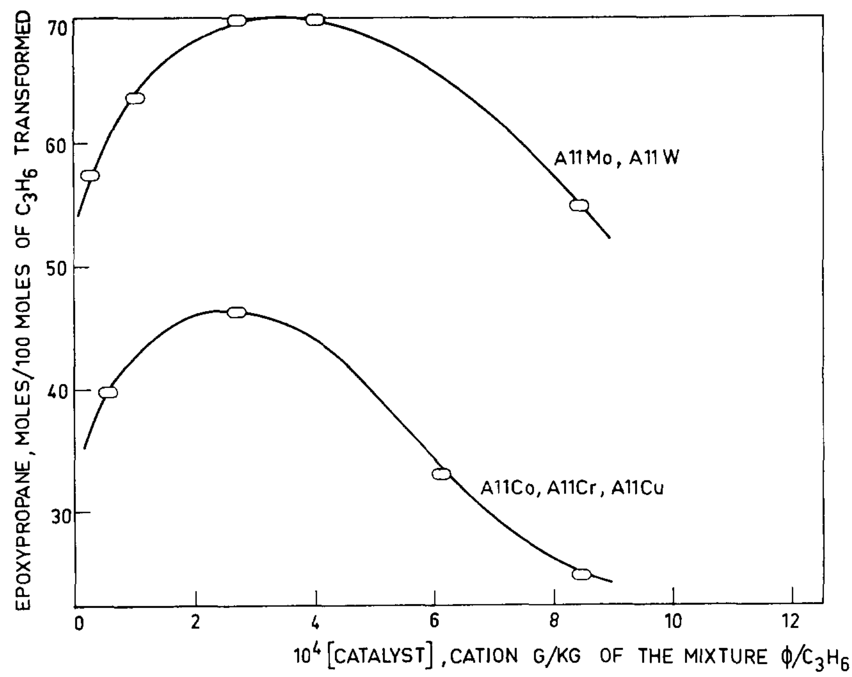


Fig. 1. Influence of catalyst concentration on the selectivity in epoxypropane. Epoxypropane is produced by the oxygen oxidation of propylene dissolved in benzene (propylene/benzene = 0.63 g/g) at 150°C, under a total pressure of 45 atm and a partial pressure of oxygen equal to 12 atm. Conversion: 7.5%. Acetaldehyde: 0.87 × 10^{-2} mole/kg of the propylene–benzene mixture.

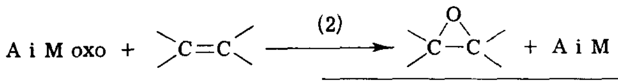
temperature in the second column was programmed from 75 to 130°C and the substance used as the internal standard was *para*-xylene. Propylene glycol; ethanol and its esters; formic, acetic, and acrylic acids were not detected; amounts of acrolein lower than 2 mole % of the total products were detected.

RESULTS AND DISCUSSION

Table 2 records the distribution of products from the noncatalized and the catalized oxidation by oxygen of propylene dissolved in benzene. An optimum catalyst concentration is noted. The catalyst concentration amounts to about 3×10^{-4} cation g/kg of benzene–propylene mixture (Fig. 1). A 11 Mo and A 11 W give selectivities in epoxypropane as high as 70%.

The formation of the peroxo derivatives of the transition elements is considered the cause of the selective catalysis toward the epoxies formation in the stoichiometric reaction of hydroperoxides with olefins. The peroxo compounds are thus considered as the effective epoxidizing agents of the olefins (*10*). We have observed that hydroperoxides decompose completely in the presence of transition elements: 1 g % *t*-butyl hydroperoxide in the presence of cobalt naphthenate (4×10^{-4} cation g/liter) leads to a violent explosion under the reaction conditions. An even higher instability must be expected from the hydroperoxides of propylene. The peroxidic radicals would thus be taking part to the peroxidation of the catalyst. The following diagram represents the catalytic cycle:

$$RO_2\cdot + \text{A i M} \xrightarrow{(1)} R' + \text{A i M oxo}$$



The second step is realized in water as well as in benzene (*6, 10*). One cannot conclude whether the process is an ionic or a radical one. The EPR spectra of the metallic oxidase enzymes suggests however the participation of a radical mechanism (*11*). Different chelates of the same cation give different selectivities in epoxypropane. A parallelism is noted between the influence of the ligand observed here and the specificities and selectivities of the enzymatic oxidases. The molybdyl and tungstyl chelates give higher selectivities in epoxypropane than the cobalt, copper, and chromium chelates do. The hydroxylation power of the molybdenum xanthine oxidase is well known.

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