

## The Catalysis of Propylene Oxidation by Silver Chelates

J. ROUCHAUD AND M. DE PAUW

*From the Department of Physical Organic Chemistry, University of Lovanium, Kinshasa XI, Leopoldville, Congo*

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Propylene dissolved in benzene is oxidized by oxygen. Silver chelates are used as insoluble catalysts. Only the oxo complexes of silver, obtained by treatment of the silver chelates with hydrogen peroxide, are able to induce high selectivities in epoxypropane.

### INTRODUCTION

The soluble salts of chromium, vanadium, and molybdenum catalyze the epoxidation of olefins with hydroperoxides (1). No report has been made on the catalytic activity of the silver compounds in the liquid-phase epoxidation of olefins by hydroperoxides or oxygen.

In the reaction of oxygen with propylene using benzene solvent we have investigated the influence of catalytic amounts of soluble silver chelates on the yield in epoxypropane.

### EXPERIMENTAL

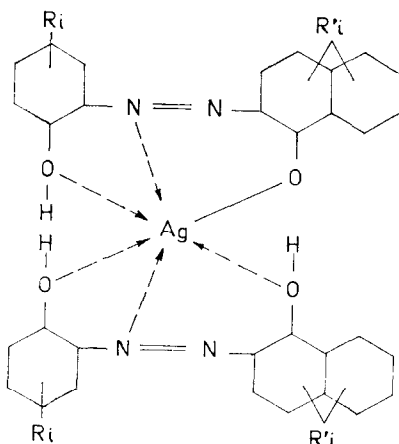
**Oxidation process.** The oxidations were carried out in a Pyrex glass vessel enclosed in a 304 stainless steel autoclave (500 ml) equipped with a magnetic stirrer (2). A normal charge consisted of 80 g of benzene (Merck, analytical grade), 51 g of propylene (Air Liquide, 99%), and the soluble catalyst. The reactor was charged at room temperature, except for propylene. It was closed, cooled down 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% per hour of propylene consumption for both the noncatalyzed and the catalyzed reactions. When the oxidation was completed, the reactor was cooled down 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 down to 0°C was analyzed by gas chromatography (Wilkins Aerograph 1520 B; detection by flame ionization). The light products (epoxypropane, methyl formate, methanol, and acetone) were separated using a 6-m column filled with 100-120 mesh Chromosorb P impregnated with 15 wt% dinonyl phthalate. 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 temperature in the second column was programmed from 75° to 130°C and the substance used as the internal standard was *p*-xylene. Propylene glycol, ethanol and its esters, and formic, acetic, and acrylic acids were not detected; amounts of acrolein lower than 2 mole% of the total products were detected.

**Catalyst preparation.** Three azo compounds were used as ligands. They were

provided by the Carbochimique, S. A. (Tertre, Belgium). The first azo compound (Z1) resulted from the diazotization and condensation of the system: picramic acid + 1-acetylamino-7-naphthol. The second azo compound (Z2), from the system: 4-diethylaminesulfonyl-2-anisidine + 6-8-disulfonic acid-2-naphthol. The third one (Z3), from the system: 2-amino-4-nitro-1-phenol + 1-acetylamino-7-naphthol. The aqueous solution of the azo compound and of silver nitrate (following the stoichiometric ratio silver:azo compound = 1:2 atoms g/mole) were mixed, then boiled, and concentrated. The chelate (ZiAg) was filtered, and crystallized in ethanol. The stoichiometric formula of the chelates, [Azo compound]<sub>2</sub>Ag was confirmed by elemental analysis (C, H, O, Ag). The dry powder was treated with an excess of 30% hydrogen peroxide; the solution was evaporated at 100°C, yielding the peroxy derivatives of the chelates (ZiAg oxo). The results of iodometric titration of active oxygen gave (equivalent of active oxygen/mole of chelate): 0.4 for Z1Ag oxo, 0.5 for Z2Ag oxo, and 0.3 for Z3Ag oxo. The magnetic susceptibilities of the ligands and chelates were measured by the Gouy method with the Alpha 7500 electromagnet. The probable structural formula of the Ag(I) chelates before the treatment with hydrogen peroxide is



The dotted lines represent the possible nonionic bonds. There are a great variety

of silver complexes. The coordination number depends on the nature of the ligand and a variety of types can occur because of the possibilities of *sp*, *sp*<sup>2</sup>, and *sp*<sup>3</sup> bonding of Ag<sup>+</sup>. As for the ligands with *dπ* bonding potential, the three- and four-coordinate species can predominate (3). The structure of the ligands suggests here that silver is most probably tetracoordinated. Quite a number of Ag(II) tetracoordinated complexes are known (4). The solubility of silver(I) in concentrated H<sub>2</sub>O<sub>2</sub> has been measured and is used to calculate a solubility product for silver hydroperoxide. This compound may be an intermediate in the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> by silver ions, but the solid material has not been isolated (5). A peroxidic compound of silver would be the effective epoxidizing agent in the vapor-phase oxidation of ethylene toward the formation of ethylene oxide (6). Whereas the exact structure of the peroxy catalyst is not known here, its specific catalytic activity toward the formation of propylene oxide suggests that the peroxy derivative of silver is the effective epoxidizing agent.

## RESULTS AND DISCUSSION

The catalysts Z1Ag, Z2Ag, and Z3Ag did not influence the selectivity to epoxypropane (Table 1). Z1Ag oxo, Z2Ag oxo, and Z3Ag

TABLE 1  
 PRODUCTS FROM THE OXIDATION  
 OF PROPYLENE DISSOLVED IN BENZENE  
 (PROPYLENE/BENZENE = 0.63 G/G) AT 150°C<sup>a</sup>

Catalyst	Products (moles/100 moles of propylene oxidized)					
	Epoxy- propane	Methyl for- mate	Meth- anol	Acet- one	Pro- pylene glycol mono- and difor- mates	Pro- pylene glycol mono- and diacet- ates
No catalyst	35	2	14	5	15	11
Z1Ag	32	2	13	6	16	12
Z2Ag	33	3	14	7	15	12
Z3Ag	37	2	12	6	14	10
Z1Ag oxo	65	2	13	6	4	2
Z2Ag oxo	60	2	10	7	5	2
Z3Ag oxo	57	2	10	8	7	6

<sup>a</sup> Total pressure, 45 atm; partial pressure of oxygen, 12 atm; conversion, 7.5%;  $2 \times 10^{-4}$  cation g of silver/kg of the propylene-benzene mixture.

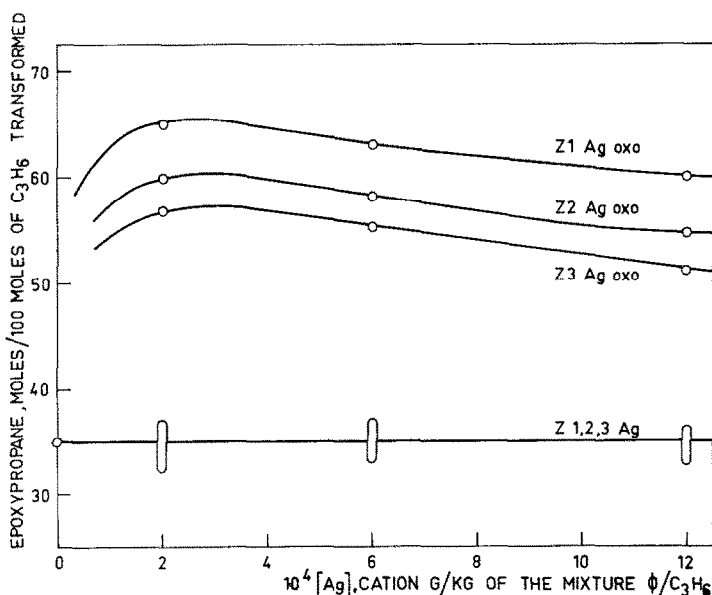


Fig. 1. Influence of catalyst concentration on the selectivity in epoxypropane. Propylene/benzene = 0.63 g/g;  $T = 150^{\circ}\text{C}$ ; total pressure, 45 atm; partial pressure of oxygen, 12 atm; conversion, 7.5%.

oxo catalyzed the oxidation to give high yields of epoxypropane. The catalyst concentration, between  $10^{-4}$  and  $10^{-3}$  g ions of silver per kg of the benzene-propylene mixture, has no strong effect on the selectivity (Fig. 1).

The diamagnetism of Z1Ag, Z2Ag, and Z3Ag shows that the silver cation is in the oxidation state one (Table 2). In Z1Ag oxo,

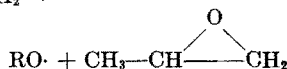
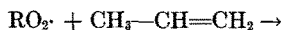
TABLE 2  
MOLAR MAGNETIC SUSCEPTIBILITIES ( $\chi_M$ )  
OF THE LIGANDS AND THE CHELATES AT  $25^{\circ}\text{C}$

Ligands and chelates	$\chi_M \times 10^6$ (em cgs)
Z1	-280
Z2	-320
Z3	-340
Z1Ag	-520
Z2Ag	-500
Z3Ag	-650
Z1Ag oxo	810
Z2Ag oxo	620
Z3Ag oxo	550

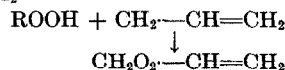
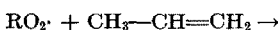
Z2Ag oxo, and Z3Ag oxo the silver complexes have magnetic susceptibilities of about  $+6 \times 10^{-4}$  em cgs (electromotive cgs units). Considering the diamagnetism of the ligand,

the silver cation has the  $d^9$  configuration and is in the valency state two, with one unpaired electron.

The reaction products are formed following two competitive oxidation mechanisms: (1) the addition of the peroxidic radicals to the olefinic bond with formation of the epoxy group (?);



(2) the hydrogen atom abstraction from propylene, followed by the isomerization of the peroxidic radicals and the rupture of the hydrocarbon chain, yielding methanol, formic, and acetic acids.



No free acids are detected, showing that esterification is nonkinetically determinative of the selectivity in epoxypropane.

The selective catalysis by some transition element compounds in the epoxidation of olefins by peroxidic compounds is explained by the formation of peroxy derivatives of the

catalyst; these constitute the selective epoxidizing agent of the olefinic bond (8). In the catalyzed oxidation, the products result from the simultaneous mechanisms of the noncatalyzed and the catalyzed reactions; the last mechanism corresponds to the selective epoxidation by the peroxy derivative of the catalyst. The chelates of  $\text{Ag}^{2+}$ , unlike those of  $\text{Ag}^{1+}$ , are able to realize the catalytic cycle toward the formation of epoxypropane.

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