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Metal Phthalocyanines Used as Catalysts in Gas Phase Reactions

IX. Oxidation and Decomposition of 2-Propanthiol Vapor Catalyzed by Crystalline Monomeric β-Metal Phthalocyanines of the First Transition Period

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Monomeric β-metal phthalocyanines (MPc's) have been shown to be good catalysts for decomposition and oxidation of 2-propanthiol vapor at 250–350°C. From the heats of activation and the degrees of conversion the following sequences of catalytic activity have been derived: FePc > CuPc > MnPc > CoPc > ZnPc > NiPc for the oxidation and CoPc > CuPc > FePc > ZnPc > MnPc, NiPc for the decomposition. Low heats of activation correspond to high degrees of conversion (FePc, CoPc) and vice versa (NiPc). Metal-free phthalocyanine is found to be inactive. H_2S, formed by decomposition of 2-propanthiol, is strongly adsorbed; therefore, the steady-state degree of conversion of decomposition of 2-propanthiol is low. However, in the presence of O_2, adsorbed H_2S is oxidized readily forming SO_2; the original catalytic activity of MPc's for decomposition of 2-propanthiol is thereby restored. For the same reason, the catalytic activity in oxidation of 2-propanthiol is influenced only to a moderate extent by H_2S inhibition. Heats of activation are independent of the amount of H_2S adsorbed; i.e., H_2S reduces only the number of active centers involved in the reaction.

INTRODUCTION

Solid metal phthalocyanines (MPc) of the first transition period (M = Mn, Fe, Co, Ni, Cu, and Zn) catalyze various reactions in the liquid (*1–4*) and gas phase (*5–10*); in particular, oxidation reactions have been investigated (*1–3, 5–8*). Oxidation of thiols in the liquid phase is well known (*11–15*); the gas phase reaction catalyzed by monomeric β-CuPc has been studied only recently (*5, 6*).

According to reaction (1) 2-propanthiol vapor is decomposed forming H_2S and propene. H_2S is adsorbed and poisons the active sites; adsorption of propene is not observed (*6, 16*). In mixtures of oxygen and 2-propanthiol vapor reaction (2) is observed with various degrees of conversion and apparent heats of activation, both depending on the central metal ion. Decomposition of 2-propanthiol and small amounts of saponification forming 2-propanol according to reaction (3) are observed as side reactions. 2-Propanol is oxidized to acetone (*8*) according to reaction (4).

Because of the presence of H_2S, generated by decomposition and saponification, the degree of conversion of the oxidation is reduced (*6*). By oxidation of the poisoning H_2S to SO_2 and H_2O [reaction (5)], both readily desorbing from the MPc catalyst, a stable steady-state activity of the MPc catalysts with respect to oxidation of 2-propanthiol is generated. The other sulfur

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compounds, 2-propanthiol and diisopropyldisulfide, involved in the process of catalytic oxidation, do not act as blocking agents (*5, 6, 16*).

$$CH_3CHSHCH_3 \rightarrow H_2S + CH_3CH{=}CH_2 \quad (1)$$

$$2\ CH_3CHSHCH_3 + \tfrac{1}{2}\ O_2 \rightarrow H_2O + (CH_3)_2CHSSCH(CH_3)_2 \quad (2)$$

$$CH_3CHSHCH_3 + H_2O \rightarrow H_2S + CH_3CHOHCH_3 \quad (3)$$

$$CH_3CHOHCH_3 + \tfrac{1}{2}\ O_2 \rightarrow H_2O + CH_3COCH_3 \quad (4)$$

$$H_2S_{ads} + \tfrac{3}{2}\ O_2 \rightarrow H_2O + SO_2 \quad (5)$$

The crystal structures of the β-polymorphs of the bivalent Mn, Fe, Co, Ni, Cu, and Zn phthalocyanine complexes used as catalysts are isomorphous (*17–20*). The monoclinic crystals are formed by stacks of parallel square planar MPc molecules, having nearly D_{4h} symmetry, the stacks ending in the (010) faces. With the planes of molecules of neighboring stacks being inclined against the crystal axis at constant angles throughout the crystal, the distance between the molecules of one stack is about 3.3 Å (*20*). The central metal ions have identical surroundings and are separated from one another by the extended phthalocyanine ligand which has an area of about 124 Å^2.

The interaction between the phthalocyanine π system and the metal orbitals allows electron transfer from the metal to the Pc ligand and vice versa. This favors oxidation and reduction of the complex (*21*), addition of axial ligands (*1*), and adsorption on the central ion.

MO calculations on the first row transition metal and metal-free phthalocyanines have been published (*21–24*). The orbital patterns of the MPc's used as catalysts in this study are similar. They differ in population and energy of the MOs which are predominantly localized on the metal. The ligand field order has been established by experiment (*1, 25*) and calculation (*21–24*): $d_{xy} < d_{xz}, d_{yz} < d_{z^2} \ll d_{x^2-y^2}$. Because of the close resemblance of crystal structure and orbital pattern, it should be possible to come to a uniform treatment of gas solid catalysis by MPc's making use of the concepts of complex chemistry.

EXPERIMENTAL

A gas chromatographic pulse technique as well as a steady-state flow reactor with gas chromatographic analysis were used. A mass constant gas flow of oxygen or nitrogen was passed through thermostated 2-propanthiol at about atmospheric pressure. The gas vapor mixture, containing 15 to 30 mol% of 2-propanthiol, was introduced into a helium flow (99.999%, Linde) of 40- to 60-ml/min velocity. The pulse (1.3 to 2.5×10^{-6} mol of 2-propanthiol) was passed through 1.5 to 5.0×10^{-4} mol of β-MPc crystal powder in a Duran reaction tube (*8*), the surface area of the catalyst being 0.2 to 0.7 m^2. Equal reaction tubes were used in flow experiments.

Gas chromatographic analysis was carried out by a Varian Model 1720 with tungsten hot-wire detector, 2-m columns of Carbowax 1500, Marlophen 87, and Porapak QS (all from Perkin–Elmer). Single reactants were injected by means of Hamilton microliter syringes. MPc's and H_2Pc (BASF or Bayer) were purified by twofold sublimation in a high vacuum at about 450°C (*1*). After several hours of heating in a helium flow at 300°C, the stable β-polymorph was formed, crystal modification being controlled by ir spectroscopy (Beckmann IR 20 A). BET surface area was determined gravimetrically by means of a Sartorius Gravimat. By field electron microscopy (Kontron), shape, surface structure, and size distribution of the MPc crystals were controlled before and after use in catalytic experiments. The main surface area of the catalysts is formed by the (100) and (001) faces of the monoclinic single crystals (*20*). The thin long needles are broken parallel to the (010) faces.

In an inert gas atmosphere, the MPc's are stable up to 400°C (*2*). In the presence of oxygen oxidation of the MPc catalysts is observed starting at temperatures lower than 400°C depending on the central ion and pretreatment of the catalyst (*26*). In order to obtain the upper temperature limit for use in catalytic experiments, the stability of each freshly sublimed MPc was tested by passing pulses of oxygen through the catalyst in the reaction vessel at various temperatures. Oxidation products CO_2 and water were analyzed by gas chromatography; the solid was investigated by ir spectroscopy, the intensity and position of the MPc bands being a reliable indication of the degree of oxidative destruction of the MPc. Both methods are very sensitive with respect to detection of small amounts of MPc destroyed by oxidation (*16*, *26*).

RESULTS

Metal-free phthalocyanine. Metal-free phthalocyanine is catalytically inactive and gives results the same as those obtained in experiments carried out with an empty reaction vessel. In both cases the decomposition of 2-propanthiol starts at 360°C; at 400°C the degree of conversion is smaller than 1%. No adsorption of H_2S and oxygen on H_2Pc is observed.

The uncatalyzed reaction in pulses containing a mixture of oxygen and 2-propanthiol, starting at 350°C, yields propene, sulfur dioxide, water, and acetone; diisopropyldisulfide is not formed below 430°C. The heats of activation of these homogeneous reactions are higher than 220 kJ/mol.

Kinetic measurements. The kinetic results comprise reaction order at constant reaction time and apparent heat of activation data. The decomposition reaction was found to be first order at low pressures of 2-propanthiol (pulses of 1.3×10^{-6} mol of 2-propanthiol) and decreased with increasing partial pressure (larger pulses) to zero. Apparent heats of activation (E_a) have been determined from Arrhenius plots using a zero-order reaction-velocity function, which is allowable because of the small degrees of conversion ($<5\%$).

TABLE 1

Apparent Heat of Activation (E_a), Degree of Conversion (C_s) at Three Temperatures, and Relative Preexponential Factor (k_0t_1) of Oxidation of 2-Propanthiol on MPc's

	FePc	CuPc	MnPc	CoPc	ZnPc	NiPc
E_a (kJ/mol)	54	63	71	76	92	—
C_s (%)						
275°C	34	24	6.6	3.4	0	0
325°C	—	53	—	10.0	2.0	0
350°C	—	—	—	—	5.8	2.2
$k_0t_1 \cdot 10^4$	5.8	27	40	60	643	—

2-Propanthiol was oxidized according to reaction (2) by the use of a 10- to 20-fold excess of oxygen. Under these conditions, the reaction was found to be first order in 2-propanthiol. The reaction order is smaller than 0.8 in oxygen and decreases to zero at higher oxygen pressure. A Rideal–Eley mechanism (*27*) appears to be evident. Heats of activation have been established by plotting Arrhenius diagrams obtained by use of a reaction-velocity function which is first order in 2-propanthiol and zero order in oxygen.

From Tables 1 and 2 it is seen that the apparent heats of activation of both reactions depend on the central metal ion. The values shown are averaged from a great number of experiments with catalysts of various batches of sublimation, using catalysts which have been pretreated by pulses of either O_2, H_2S, or 2-propanthiol, applying either pulse technique or steady-state flow method in various reaction vessels. Hence, the resulting error was about 10% in total but only 4% in one experiment.

TABLE 2

Apparent Heat of Activation (E_a), Degree of Conversion (C_s), at 350°C and Different Pretreatments of MPc's (See Text), Relative Preexponential Factor $(k_0t_1)_{Fl}$ Obtained in Flow Experiments, and Ratio of Preexponential Factors (Flow Experiments and after Pretreatment with Oxygen Pulses) of Decomposition of 2-Propanthiol on MPc's.

	CoPc	CuPc	FePc	ZnPc	MnPc	NiPc
E_a (kJ/mol)	52	67	98	106	>110	>110
C_s (%), T_r = 350°C						
(O_2)	5.2	28	7.1	0.21	0.17	0.05
(Th)	1.8	1.3	1.3	0.08	—	—
(Fl)	1.1	0.94	0.42	0.13	—	—
log $(k_0t_1)_{Fl}$	0.40	1.59	3.84	4.00	—	—
$(k_0t_1)_{Fl}/(k_0t_1)_{O_2}$	0.21	0.029	0.057	0.62	—	—

Influence of oxygen and H_2S adsorption on activity. Oxygen and H_2S are adsorbed tightly by the MPc's used as catalysts in this study (*16*). The central metal ion is assumed to be the adsorption site as well as the active center of the catalyst. In oxidation reactions catalytic activity of MPc's is regarded as due to the activation of adsorbed oxygen by interaction with the central metal ion (*7–10, 28–30*). H_2S adsorption blocks the active centers at the surface of the solid.

H_2S, formed by decomposition in pulses of 2-propanthiol, is adsorbed completely, whereas adsorption of propene is not observed. The degree of conversion C_s according to reaction (1) decreases drastically because of H_2S adsorption (Table 2). At constant reaction temperature and reaction time, maximum amounts of propene formation are found in pulses of 2-propanthiol passed over MPc after treatment with pulses of oxygen [marked (O_2) in Table 2]. Periodic pulses of 2-propanthiol without intermittent pulses of oxygen give rise to a constant small degree of conversion [marked (Th) in Table 2]. This is due to the fact that H_2S desorbing between pulses is replaced in the consecutive pulse. The minimum degree of conversion is observed in steady flow experiments [marked (Fl) in Table 2]. The heats of activation, however, are independent of the pretreatment; adsorption of H_2S only reduces the number of active centers involved in the reaction. By oxygen treatment the MPc's can be completely reactivated according to reaction (5).

When MPc has been covered with oxygen by several successive pulses, formation of diisopropyldisulfide in the following pulse of 2-propanthiol is observed. This is due to the reaction of adsorbed activated oxygen with 2-propanthiol during the pulse. After pretreatment of MPc with 2-propanthiol, no oxidation products in a subsequent oxygen pulse are observed, because 2-propanthiol is not adsorbed long enough (time between pulses, 5 to 10 min).

The degree of conversion in the oxidation according to reaction (2) is increased by oxygen pretreatment, whereas adsorption of H_2S poisons the catalyst. Periodically alternating pulses of oxygen and of 2-propanthiol generate a constant degree of conversion, at constant reaction temperature and reaction time, independent of the preliminary treatment of the MPc's. The data given in Table 1 refer to this steady-state activity.

Degrees of conversion and relative preexponential factors. The preexponential factor k_0 of the Arrhenius equation cannot be obtained, because the exact reaction time t_1 is unknown. Hence, a relative preexponential factor is calculated for a first-order reaction from Eq. (6).

$$k_0 t_1 = \frac{\ln[1/(1 - C_s)]}{\exp(-E_a/RT_r)}, \qquad (6)$$

where C_s is the degree of conversion as a percentage at standard conditions; T_r is the reaction temperature at which C_s is obtained, and E_a is the apparent heat of activation.

To compare results between various catalyst beds of different MPc's obtained in various reaction vessels, it is necessary to convert measured degrees of conversion C_m into standard values C_s. They are evaluated for a standard reaction time and referred to unit surface area of the catalyst (*16*). The results are shown in Tables 1 and 2.

Comparison of activities. The C_s and E_a data in Tables 1 and 2 are used to compare the catalytic activities of the different MPc's. With regard to the decomposition of 2-propanthiol the MPc's can be classified into two groups: CoPc, CuPc, and FePc which are active, and ZnPc, MnPc, and NiPc which in spite of high reaction temperatures, effect very small degrees of conversion even in the unpoisoned state ($<0.3\%$). Apparent heats of activation lead to a sequence of decreasing activity with increasing energy values: CoPc > CuPc > FePc > ZnPc > MnPc, NiPc. An equal sequence of C_s values is found in flow experiments (Table 2). Degrees of conversion in pulse experiments depend on the velocity of adsorption and desorption of H_2S and on the initial activity of the unpoisoned catalyst; therefore, the sequence within the active group of MPc's differs in some cases from the sequence given by activation energies.

From the results of catalytic oxidation of 2-propanthiol a clear sequence of activity of MPc's is derived (Table 1). Apparent heats of activation increase and, without exception in the complete temperature range studies, C_s values decrease in the following sequence of activity: FePc > CuPc > MnPc > CoPc > ZnPc >NiPc, with FePc being the most active and NiPc being the most inactive catalyst in oxidation of 2-propanthiol.

From the data given in Table 1 there results a linear correlation between apparent heats of activation and preexponential factors of oxidation of 2-propanthiol, while from the data given in Table 2, there results an exponential correlation between the respective kinetic parameters of decomposition of 2-propanthiol.

DISCUSSION

Two qualitative theoretical considerations, based either on MO calculations or on crystal field theory (*35*), respectively, applied to a number of reactions catalyzed by a series of first row transition MPc's, have been shown to be of great utility in understanding the catalytic activity of complexed metal ions in MPc's (*7*, *10*). In these models the approaching reactant is considered to act for a short time as an additional ligand of the central ion. Catalytic activity is effected by the overlap of metal and reactant orbitals, which enables charge transfer from the metal ion to the reacting molecule and vice versa. The inactivity of metal-free phthalocyanine clearly indicates that the central metal ion is the active site of the catalyst.

Decomposition of 2-Propanthiol

A short-lived interaction between the 2-propanthiol molecule and the metal ion is the basic requirement to enable catalytic decomposition. The reaction order, decreasing from one to zero when the pressure of 2-propanthiol is increased, shows that 2-propanthiol decomposes in the adsorbed state (*27*). Interaction between the central ion and 2-propanthiol is prevented by adsorption of H_2S, whereas adsorbed oxygen is removed by reaction with 2-propanthiol to form diisopropyldisulfide and water.

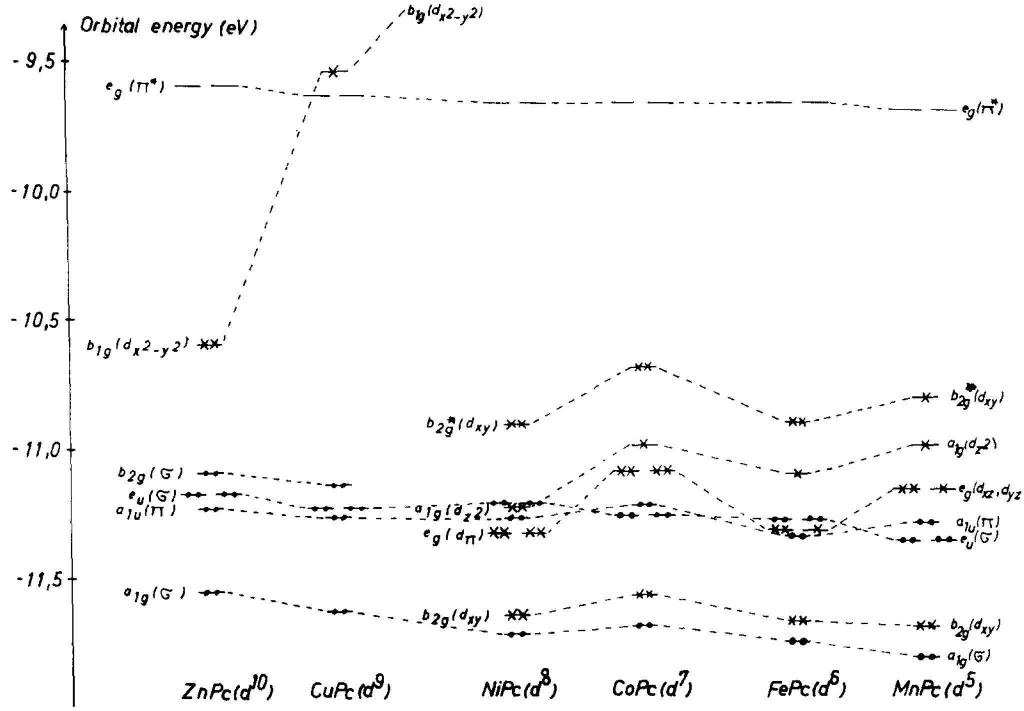

FIG. 1. MO diagrams of the investigated MPc's (*22*). ×, electrons in metal MOs; ●, electrons in ligand MOs. Equal orbitals of different MPc's are connected by dashed lines. In ZnPc and CuPc the energy of b^*_{2g}, a_{1g}, e_g, and b_{2g} is lowered below the energy range given in the figure (compare lowering of b_{1g} which, except for ZnPc and CuPc, is of higher energy than the energy range shown in the figure).

From the crystal as well as molecular structure of MPc it is seen that (i), one H_2S molecule blocks one active site and (ii) one metal ion interacts with only one thiol molecule. To induce catalytic decomposition of thiols the C–S bond has to be weakened by interaction with the active site in order to abstract H_2S.

Figure 1 shows the MO diagram of the investigated MPc's as published by Schaffer *et al.* (*22*). The MO energy levels of orbitals having predominantly metallic character are considered to be responsible for the catalytic properties of the central metal ion. They differ from one another in electron population and orbital energy, whereas the ligand field order is the same in the MPc's considered. The diamagnetic NiPc and ZnPc (*31*) are nearly inactive; with both catalysts the reaction exhibits high activation energies. Except for MnPc, the paramagnetic MPc's (*31*) belong to the active group consisting of CoPc, CuPc, and FePc.

As is seen by comparison of decomposition of 2-propanthiol with adsorption of H_2S, different kinds of interaction between MPc and reactant seem to be present. Adsorption of H_2S may be understood quite well by a model assuming that H_2S acts as a σ-donor requiring empty $a_{1g}(d_{z^2})$ orbitals of the central ions (*10*, *32*). However, in decomposition of 2-propanthiol CoPc is the most active catalyst, whereas FePc, showing the strongest interaction with H_2S, is only a moderate catalyst, ranging even behind CuPc. On the other hand, good agreement is found under the assumption that 2-propanthiol might act as an electron acceptor; this, however, is not observed in adsorption studies of similar molecules, e.g., CS_2 and aldehydes (*32*).

Understanding the rather high activity

of CuPc, generally observed in a number of quite different reactions (*6–8, 10*), is difficult because the respective Cu orbitals are filled. The interaction obviously taking place might be seen in connection with the strong contraction of the metal orbitals in the Cu ion.

Oxidation of 2-Propanthiol

Molecular adsorption of oxygen on MPc's has been proved by various methods (*16, 36–38*). Adsorption occurs on the central metal ion as the active center (*5–8, 28–30*). In solution, even reversible adducts of oxygen with derivatives of CoPc and FePc are formed (*39–43*). The kinetics of oxidation and the experiments with oxygen pretreatment of MPc's show that adsorbed activated oxygen reacts with the thiol molecule (Eley–Rideal mechanism). This mechanism is also confirmed by the sequences of catalytic activity found for the oxidation of 2-propanol (*8*) and the reaction of adsorbed oxygen with pulses of H_2S (*10, 16*), both sequences of activity being equal to the sequence of activity for the oxidation of 2-propanthiol.

It is reasonable to assume the dissociation of activated oxygen, induced by the interaction with 2-propanthiol, as the rate-determining step. By transfer of electron density from the metal to the oxygen orbital, the O–O bond is weakened. The dissociation energy of the oxygen molecule in the adsorbed state is the lower; the higher is the extent of charge transfer from metal to oxygen; this is in fact the activation.

A qualitative model of activated adsorption of oxygen by MPc's based on the orbital diagrams (Fig. 1) has been proposed and discussed by analogy with oxygen binding at room temperature (*7, 10*). Though it correctly describes the sequence of activity observed in this work, it must be pointed out that it contains several assumptions and severe simplifications which must be examined by further studies.

CONCLUSION

MPc's of the first transition period are active and selective catalysts with respect to oxidation and decomposition of 2-propanthiol. Catalytic oxidation of hydrocarbons, if simultaneously present, is not observed; therefore, a selective oxidation of sulfur compounds in hydrocarbons is possible. H_2S, formed by decomposition of 2-propanthiol and being strongly adsorbed, reduces the steady-state degree of conversion in both reactions. In the presence of O_2, adsorbed H_2S is oxidized forming SO_2 and H_2O, both desorbing readily. Therefore, the steady-state catalytic activity in the oxidation of 2-propanthiol is influenced to a lesser extent than in decomposition. The heats of activation are independent of the amount of H_2S adsorbed; i.e., H_2S reduces only the number of active centers involved in the reaction.

The inactivity of metal-free phthalocyanine clearly indicates that the central metal ions are the active sites of the catalysts. From the heats of activation, as well as the degrees of conversion, a sequence of catalytic activity is derived for either reaction: FePc > CuPc > MnPc > CoPc > ZnPc > NiPc for the oxidation, and CoPc > CuPc > FePc > ZnPc > MnPc, NiPc for the decomposition of 2-propanthiol.

Because of the isomorphous crystal structure of MPc's, a series of closely related catalysts is provided, i.e., catalysts with active sites which are complexed metal ions differing in the energy of the metal orbitals and in the number of *d* electrons.

For the short time of the reaction, the reacting molecule may be considered to be an additional ligand of the central ion. The interaction between central ions and reactant molecules leading to activation can be discussed in terms of overlap of metal and reactant orbitals leading to electron transfer from the metal ion to the activated molecule and vice versa.

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