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Metal Phthalocyanines Used as Catalysts in Gas Phase Reactions

IV. Oxidation of 2-Propanol Catalyzed by Monomeric β-Cu-Phthalocyanine in the Presence of Sulfur Compounds

FRIEDRICH STEINBACH AND HERBERT H. SCHMIDT

Institut für Physikalische Chemie der Universität Hamburg,
Laufgraben 24, 2 Hamburg 13, Germany

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The stability of monomeric β-Cu-phthalocyanine (CuPc) against poisoning by sulfur compounds has been shown with respect to catalytic oxidation at 350°C of 2-propanol to acetone and water in the presence of 2-propanthiol in threefold excess to 2-propanol.

H_2S, generated by decomposition of 2-propanthiol, blocks the active sites (the central Cu ions) of the CuPc. In the presence of O_2, H_2S is oxidized to SO_2 and H_2O.

The steady state activity of CuPc in the presence of 2-propanthiol is 45% of the activity in the absence of sulfur compounds. When O_2 is absent, as in the study of the decomposition of 2-propanthiol, CuPc is poisoned to 8% of the initial activity.

By titration of the adsorbed H_2S with pulses of O_2 it is shown that H_2S is not only adsorbed at the active sites on the outer (010) faces of the CuPc crystals but penetrates into the interior. The ability of small molecules such as O_2 or H_2S to penetrate into the CuPc lattice is further shown by comparison of the amount of adsorbed O_2, titrated by pulses of 2-propanol, and the amount of adsorbed 2-propanol, titrated by pulses of O_2.

INTRODUCTION

Metal phthalocyanines (MePc) are very stable organic complex compounds (*1*). Like other organic dyestuffs they may be used as catalysts in a number of reactions (*2–6*); especially, oxidation reactions in the liquid phase have been investigated in detail (*7–21*). Because of their good thermal stability, MePc are also suitable as catalysts in gas phase reactions (*22–29*).

Monomeric MePc form plane quadratic molecules (symmetry D_{4h}) of an area of 123 Å^2 (*30,31*), the metal ion being held in the center of the molecule. The catalytic activity in oxidation reactions is due to an activated adsorption of oxygen at the central metal ion (*7,22–25,32–39*). Upon sublimation, crystalline powders of β-MePc are produced (*1*); the crystals form monoclinic needles generated by stacks of the disc shaped molecules, the distance between the discs being about 3.3 Å (*30*). The growing face of the crystal needles (010-face) exposes the central metal ions to the reactant molecules. These catalytic centers are present in large number; all centers of the catalyst have identical surroundings and their catalytic activity is high (*22–25*).

A model of the interaction of O_2 with the orbitals of the central metal ion in the complex has been proposed on the basis of a comparison of the catalytic activity in oxidation reactions of MePc with Me ions of differing d-electron number (*22*).

Catalysts with metals or metal oxides as active components are poisoned by mercaptans (*40–42*). Poisoning results from formation of a strong adsorption bond or even a stable surface compound of the poisoning substance. Frequently, poisons are selective with respect to the catalytic reaction or to the kind of catalyst used (*43*). The amount of poisoning is determined by the relative strengths of adsorption of the poison and the reactant. Frequently, not only the sulfur compound present in the reactant mixture but one of its reaction products is the toxic substance (*40*). Since the central metal ions which are the active sites of MePc catalysts are bound strongly in a catalytically inactive environment, formation of sulfur compounds with the active sites is less likely than on the surface of oxide or metal catalysts. Furthermore, a study of poisoning is particularly convenient when all active sites of the catalyst have the same ligand field.

The catalytic properties of MePc in a gas phase reaction have been investigated in a study of the oxidation of 2-propanol to acetone and water (*22–25*); at temperatures above 300°C the reaction occurs with a number of MePc catalysts showing high degrees of conversion and good selectivity. Since the activation energy has the lowest value (9 kcal/mol) with CuPc as catalyst, the investigation of poisoning was carried out with β-CuPc. For a convenient comparison of the reactions, analogous reactants, viz, 2-propanol and 2-propanthiol, were used.

EXPERIMENTAL METHODS

The gas chromatographic pulse technique was used. Oxygen at atmospheric pressure was passed at 22°C through either 2-propanol, 2-propanthiol, or mixtures of both. Pulses of 0.62 ml containing either (a) oxygen and 40 Torr (1.4×10^{-6} mol) 2-propanol, (b) oxygen and 120 to 240 Torr (4.4 to 8.8×10^{-6} mol) 2-propanthiol, or (c) oxygen and 40 Torr 2-propanol and 120 to 240 Torr 2-propanthiol were passed in a helium flow (99.999%, Linde) of 40 ml/min velocity over 100 to 200 mg (2 to 4×10^{-4} mol) of the catalyst kept at 350°C in a Duran reaction vessel (*24*). Reaction products were analyzed by a Varian 1720 gas chromatograph (5-ft columns of Carbowax 1500 or molecular sieve 5 A, both Perkin-Elmer; column temperature 105°C, tungsten hot wire detector, 175 mA). Single reactants were injected by means of Hamilton microliter syringes.

Monomeric β-CuPc (Bayer or BASF) was purified by sublimation at 10^{-4} Torr and 450°C. After 12 hr heating in flowing helium at 300°C the β-CuPc had a BET area of 2.5 m^2/g. By means of X-ray analysis (Philips, PW 1050 + PW 1352, $K\alpha$ line of Cu) no impurities and no change of the structure of CuPc due to its use as catalyst were detected.

RESULTS AND DISCUSSION

The Catalytic Reactions

1. 2-Propanol underwent three reactions (*23–25,28*):

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

$$CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + H_2, \quad (2)$$

$$CH_3CHOHCH_3 \rightarrow CH_2{=}CHCH_3 + H_2O. \quad (3)$$

Per 100 mg CuPc the degree of conversion according to reaction (1) was between 4 and 25 molar% of 2-propanol; it was constant even after long runs. The degree of conversion depended on the sublimation conditions used to prepare the CuPc; only on CuPc samples taken from the same sublimation batch were equal degrees of conversion per unit mass of the catalyst observed. The side reactions (2) and (3) were investigated in the absence of oxygen by injecting pulses of 2-propanol or pulses of 2-propanol and N$_2$. The degree of conversion according to reaction (2) was 0.3 to 2 molar%/100 mg CuPc; the maximum degree of conversion according to reaction (3) was 1%. The sum of the degrees of conversion according to reactions (2) and (3) was 5 to 15% of the degree of conversion of reaction (1).

2. In the presence of 2-propanthiol the following reactions occurred:

$$CH_3CHSHCH_3 \rightarrow CH_2{=}CHCH_3 + H_2S, \tag{4}$$

$$2\,CH_3CHSHCH_3 + \tfrac{1}{2}O_2 \rightarrow (CH_3)_2CH{-}SS{-}CH(CH_3)_2 + H_2O, \tag{5}$$

$$CH_3CHSHCH_3 + H_2O \rightarrow CH_3CHOHCH_3 + H_2S, \tag{6}$$

$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O. \tag{7}$$

Reaction (4) was investigated by injecting pulses of 10^{-5} to 10^{-6} mole 2-propanthiol. The amount of H_2S observed in the chromatogram was essentially smaller than the amount of propene, i.e., H_2S was strongly adsorbed on CuPc. When several pulses of 2-propanthiol were injected successively, the amount of propene generated during each pulse decreased rapidly. Already in the third pulse a steady state degree of conversion of only 5 to 8% of the degree of conversion in the first pulse was reached.

When pulses of 2-propanthiol were passed over the catalyst after it had been saturated with H_2S by previously injecting several pulses of H_2S, decomposition according to reaction (4) was inhibited immediately in the first pulse of 2-propanthiol (Table 1). In pulses of 2-propanthiol and O_2, there was not only decomposition but also oxidation of 2-propanthiol, forming diisopropyldisulfide and H_2O. This latter reaction is known already from liquid phase investigations (*10–19*). Water, generated in reaction (5) or adsorbed during previous pulses, caused saponification of 2-propanthiol according to reaction (6), forming 2-propanol and H_2S; 2-propanol

TABLE 1

DEGREE OF CONVERSION OF 2-PROPANTHIOL FORMING PROPENE AND H_2S AFTER VARIOUS PRETREATMENTS OF CuPc[a]

No. of pulse	Pulse	Peak height (cm)		Degree of conversion according to reaction (4)	
		Propene	H_2S	mol	%
1–3	3 × 0.5 ml O_2				
4	1 μl 2-propanthiol	68.8	0	3.6×10^{-6}	33
5	1 μl 2-propanthiol	9.4	0	0.5×10^{-6}	4.5
6	1 μl 2-propanthiol	3.2	0	0.2×10^{-6}	1.5
7	1 μl 2-propanthiol	3.0	0	0.2×10^{-6}	1.5
8–10	3 × 0.5 ml H_2S				
11	1 μl 2-propanthiol	2.3	6.4	1.2×10^{-7}	1.1
12	1 μl 2-propanthiol	2.1	3.2	1.0×10^{-7}	1.0
13–15	3 × 0.5 ml O_2				
16	1 μl 2-propanthiol	78.4		4.1×10^{-6}	38
17–19	3 × 0.5 ml H_2S				
20	1 μl 2-propanthiol	6.6	12.1	3.5×10^{-7}	3.2
21	1 μl 2-propanthiol	3.9	6.7	2.1×10^{-7}	1.9
22	1 μl 2-propanthiol	3.1	6.3	1.6×10^{-7}	1.5
23	1 μl 2-propanthiol	2.3	5.5	1.2×10^{-7}	1.1

[a] Time between pulses: 10 min.

then underwent oxidation according to reaction (1). H_2S was oxidized forming SO_2 and H_2O.

The degree of conversion of 2-propanthiol during passage of subsequent pulses of 2-propanthiol and O_2 decreased from pulse to pulse, until after about 10 pulses a steady state activity of the CuPc was reached (Fig. 1). Simultaneously, the degree of conversion to di-isopropyldisulfide decreased, and the degree of conversion to SO_2 (via H_2S) increased to steady state values. Oxidation of 2-propanthiol was inhibited; however, inhibition was not as strong as with respect to reaction (4) in the absence of O_2, since H_2S was oxidized to SO_2. During steady state conditions, formation of disulfide per pulse was 40 to 44% of the formation in the first pulse. Saponification forming 2-propanol as well as conversion to acetone in the sequence of reactions (6) and (1) were rather high in the first pulse. However, during the second pulse, degrees of conversion were decreased to only 1/5 of the conversion in the first pulse. During subsequent pulses, in the steady state, the degree of saponification was about 3%. Certain additional side reactions with degrees of conversion below 1% were not further investigated.

Experiments with H_2Pc

In order to confirm the role of the Cu ion as the active site, the various reactions were studied with H_2Pc as catalyst under the same experimental conditions as with CuPc. The conversion to acetone in pulses of O_2 and 2-propanol started only at temperatures above 430°C [200°C on MePc (*23–25*)].

No reaction products were detected in pulses of O_2 and 2-propanthiol up to temperatures of 365°C. Only at temperatures above 400°C were SO_2, acetone and 2-propanol detected, and no disulfide was formed. The results show that the catalytic reactions (1) to (7) occur only when the central ion is present as an active site.

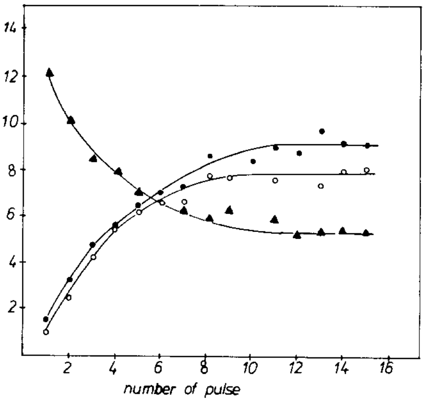

FIG. 1. Degree of conversion to SO_2 (○) and di-isopropyldisulfide (▲) during oxidation of 2-propanthiol (●) in 15 subsequent pulses injected at intervals of 30 min containing 240 Torr 2-propanthiol and 520 Torr O_2. (●) 1 unit = 10 cm; (○) 1 unit = 5 cm; (▲) 1 unit = 1 cm.

Adsorption on CuPc

H_2S

When pulses of 50 μl H_2S were passed over CuPc, no peaks of H_2S were initially observed in the chromatogram due to complete adsorption. The amount of H_2S adsorbed was determined directly as well as by titration with pulses of O_2, the amount of SO_2 being a measure for the adsorbed H_2S (Table 2). Under the conditions used, about 2.5×10^{-6} mol H_2S were adsorbed by 259 mg catalyst. With 4.5×10^{-4} mol CuPc (259 mg) of a specific surface area of 2.5 m^2/g, the implication is that a surface area of 40 Å^2 is available for one adsorbed H_2S molecule, assuming that the total surface of the crystals is used to an equal extent in adsorption. However, adsorption of H_2S should take place on (010) surfaces only, since only there are Cu ions situated in the surface. The area of the CuPc molecule amounts to 123 Å^2, i.e., one Cu ion is present per 123 Å^2 (*30,31*). Assuming equal distribution of (001), (010) and (100) surfaces in the CuPc crystal powder, this means that one Cu ion is situated in the surface per 369 Å^2 of crystal surface. At 40 Å^2/H_2S molecule overall, this implies

TABLE 2

CONVERSION TO SO_2 IN PULSES OF O_2 PASSED OVER CuPc SATURATED BY PREVIOUS PULSES OF H_2S[a]

No. of pulse	Pulse	Conversion to SO_2: Peak height (cm)	Conversion to SO_2: Total SO_2 formed (equals H_2S adsorbed) (mol)
1-3	3 × 0.5 ml H_2S		
4	0.5 ml O_2	37.2	2.5 × 10^{-6}
5	0.5 ml O_2	3.5	
6	0.5 ml O_2	0.5	
7	0.5 ml O_2	0.3	
8	0.5 ml O_2	0.2	
9-11	3 × 0.5 ml H_2S		
12	0.05 ml O_2	13.0	2.6 × 10^{-6}
13	0.05 ml O_2	11.6	
14	0.5 ml O_2	17.6	
15	0.05 ml O_2	1.5	
16	0.5 ml O_2	0.8	
17	0.5 ml O_2	0.3	

[a] Time between pulses: 10 min.

that 9 H_2S molecules should be adsorbed on this Cu ion! Certainly, in real crystals the area of (010) faces is even smaller; therefore, the excess of H_2S molecules over the Cu ions in the surface is even higher.

Considering the long adsorption time of H_2S, it may be assumed that in the (001) and (100) faces H_2S penetrates between the layers formed by the disc-shaped CuPc molecules into the interior of the crystal to be sorbed there. At present, one cannot distinguish whether this adsorption (sorption) in the interior is achieved by interaction with the Cu ions of the CuPc or whether a condensation-like physisorption process occurs in the channels and gaps between the stacks of CuPc molecules. The distance between two CuPc molecules being 3.3 Å (*30*) and the diameter of the H_2S being about 2.6 Å, both ways of adsorption seem to be possible.

The H_2S molecules held in the interior by either way are apt to diffuse to the outer surface of the crystal. Consequently, H_2S adsorbed on the (010) surfaces is rapidly removed by titration with pulses of O_2; H_2S held in the interior of the CuPc crystal reacts slowly either because O_2 has to penetrate between the CuPc molecules or H_2S has to migrate to the outer surface (Table 2).

O_2

The occurrence of a fast and a slow process was shown further by pretreatment of CuPc with pulses of O_2 and subsequent titration of the adsorbed O_2 by pulses of H_2S (Table 3). Again, SO_2 and H_2O were formed with degrees of conversion decreasing rapidly during a succession of H_2S pulses. However, even after 10 min comparatively large amounts of O_2 were present on the CuPc, as was shown by the amounts of SO_2 formed. The total amount of O_2 adsorbed on CuPc was found to be about one third of the total amount of H_2S adsorbed by the same catalyst (Tables 2 and 3). Apparently, the adsorption bond of H_2S is stronger than that of O_2. Adsorption of O_2 at the central metal ion has been discussed considering the MO system of MePc (*22*). Uptake of oxygen into the interior of MePc crystals has been as-

TABLE 3

CONVERSION TO SO_2 IN PULSES OF H_2S PASSED OVER CuPc SATURATED BY PREVIOUS PULSES OF O_2[a]

No. of pulse	Pulse	Conversion to SO_2	
		Peak height (cm)	Total SO_2 formed (equals O_2 adsorbed) (mol)
1-3	3×0.5 ml O_2		
4	0.5 ml H_2S	13.1	8×10^{-7}
5	0.5 ml H_2S	0.3	
6	0.5 ml H_2S	0.1	
7-11	5×0.5 ml O_2		
12	0.5 ml H_2S	14.2	8.5×10^{-7}
13	0.5 ml H_2S	0.3	
14	0.5 ml H_2S	0.1	

[a] Time between pulses: 10 min.

sumed also for FePc (*44,45*) as well as for electroreduction on MePc (*38*). In addition, similar results, observed in a study on formation of H_2O during pulses of H_2 on CuPc pretreated with O_2 (*46*), as well as the slow desorption of products during decomposition of N_2H_4 on CuPc (*29*), point to the ability of small molecules to penetrate into the MePc lattice.

2-Propanol

By pretreatment of CuPc with O_2 and subsequent titration with pulses of 0.4 μl 2-propanol, injected 4 to 20 sec after the last O_2 pulse, the rate of desorption of O_2 was determined from the amounts of acetone formed (Fig. 2). After a few seconds only small amounts of O_2 were present on the CuPc surface. However, after 10 min or an even longer time, acetone was still being formed in about the same amount as after 20 sec. When the catalyst was pretreated with 2-propanol and titrated with pulses of O_2 injected after the same intervals of time, the desorption rate of 2-propanol was obtained. The decay was similar to O_2 desorption; however, after 10 min, 2-propanol was no longer being adsorbed on the catalyst.

These results further support the conclusion that small molecules such as O_2 and H_2S may penetrate between the CuPc molecules and may be adsorbed in the interior of the crystal, whereas the voluminous 2-propanol is incapable of such an adsorption.

2-Propanthiol, Di-isopropyldisulfide

A long adsorption of 2-propanthiol leading to inhibition of its own reactions was not found at the temperature used in this investigation (350°C). No disulfide was generated in pulses of O_2, passed over

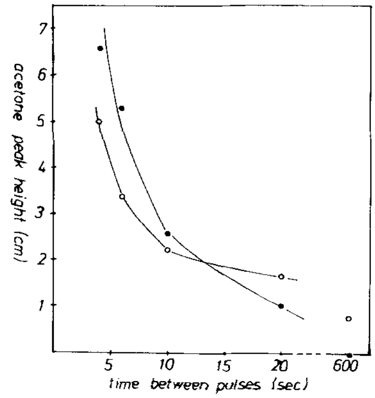

FIG. 2. Desorption of O_2 and 2-propanol. (●) formation of acetone during titration with pulses of 0.5 ml O_2 after pretreatment of CuPc with 2-propanol; (○) formation of acetone during titration with pulses of 1 μl 2-propanol after pretreatment of CuPc with O_2.

CuPc after pretreatment with pulses of 2-propanthiol. Possibly, the thiol molecule undergoes only a short interaction with the active site being decomposed rapidly into propene and H_2S.

Disulfides are known to be strong poisons in catalysis (*42*). However, diisopropyldisulfide is desorbed very quickly from CuPc; possibly, due to steric hindrance by the bulky C_3H_7 group, the two S atoms cannot interact with the Cu ion.

Influence of Adsorption on Activity

H_2S generated by decomposition of 2-propanthiol, being adsorbed strongly by CuPc, constitutes the poisoning compound. The influence of poisoning upon oxidation of 2-propanol was measured in pulses of 0.62 ml containing 40 Torr 2-propanol, 120 Torr 2-propanthiol and 600 Torr O_2. A comparison was made between the degree of conversion in these three-component pulses with the degree of conversion in pulses without 2-propanthiol under consideration of the amount of acetone formed by saponification and oxidation of 2-propanthiol. Such a comparison showed a decrease of the degree of oxidation of 2-propanol to acetone to about 45% of the value found in the absence of 2-propanthiol. This is equivalent to a decrease of the oxidation of 2-propanthiol to 40 to 44% (Fig. 1).

CuPc was reactivated either by oxidation of the adsorbed H_2S according to reaction (7) or by desorption of H_2S in flowing helium. Reactivation by oxidation was fast and complete. CuPc pretreated with pulses of H_2S or pulses of thiol and O_2 was regenerated during the first subsequent pulse of 2-propanol and O_2. The degree of conversion after repeated cycles of poisoning and reactivation was found to be equal to the degree of conversion on fresh catalysts.

Desorption of H_2S in flowing helium was very slow. After 12 hr at 350°C in a flow of 10 ml/min, only about 75% of the initially adsorbed H_2S were desorbed. Even after 72 hr of helium flow, SO_2 was generated in pulses of O_2; the reactivation by desorption remained incomplete.

CONCLUSIONS

CuPc is a selective catalyst with respect to oxidation of 2-propanol forming acetone. Dehydration and dehydrogenation are side reactions with degrees of conversion less than 4%.

2-Propanthiol is decomposed forming propene and H_2S; it is oxidized forming diisopropyldisulfide and H_2O. Saponification to 2-propanol occurs as a side reaction. Due to poisoning by H_2S, a steady state activity—lower than the activity found in the absence of S-compounds—is generated. In the steady state the strong adsorption of H_2S is balanced by oxidation of the adsorbed H_2S forming SO_2, the latter being desorbed rapidly.

In the absence of O_2 (decomposition reactions), the CuPc catalyst is poisoned severely by H_2S to about 8% of the original activity; in the presence of O_2 (oxidation reactions), about 45% of the original activity remains with the catalyst. Even CuPc strongly poisoned may be reactivated by oxidation or by desorption of H_2S.

The number of adsorbed H_2S molecules is at least one order of magnitude higher than the number of Cu ions in the surface of CuPc (010 faces). It is assumed that small molecules like H_2S and O_2 are able to penetrate between the CuPc molecules and are adsorbed (sorbed) in the interior of the CuPc crystals.

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