

MECHANISM OF THE METAL-PHTHALOCYANINE-CATALYSED OXIDATION OF CUMENE IN THE LIQUID PHASE

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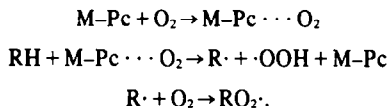
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Abstract—It is shown that the catalysis of the autoxidation of cumene by metal-phthalocyanines is not due to some type of oxygen activation, but is caused by a catalysed homolytic cleavage of hydroperoxides.

INTRODUCTION

Activation of molecular oxygen has often been proposed to explain the catalytic effect of certain transition-metal compounds (and of sulfonium compounds) on the oxidation of organic substrates. However, in all cases examined critically, it was shown that the catalytic effect is due to a catalysed homolysis of hydroperoxide.¹ Nevertheless, the unambiguous demonstration of the occurrence of oxygen activation would be of great interest with respect to its mechanistic implications in biochemistry as well as its technical applications in liquid-phase oxidation. Concerning the biochemical implications, Baldwin² and Traylor³ have demonstrated the existence of iron-porphyrin-type complexes which, like haemoglobin, are capable of reversibly binding molecular oxygen. Similarly, it has been suggested that certain metal-phthalocyanine and related compounds⁴ form complexes with oxygen, sometimes in a reversible manner.⁵

In these cases it is evident that a direct metal-oxygen interaction does exist but, except for metal-phthalocyanines, it is not known whether the oxygen molecule in such complexes is sufficiently activated to react with a C-H bond. The oxidation catalysis observed for metal-phthalocyanines⁷⁻¹⁹ has been ascribed to oxygen activation by several authors^{4,8,19} who used the proposed metal-oxygen complexes as a basis for their mechanistic model. Although Min'kov *et al.*²⁰ and Norton²¹ doubted the occurrence of oxygen activation at temperatures above 120°C, Kropf *et al.*^{10,12,16} claimed that below 100°C oxygen activation is the main process responsible for the catalysis of cumene oxidation by metal-phthalocyanines. Kropf's mechanism, based on the theoretical possibility that bonding to metal-phthalocyanines enhances the radical character of oxygen, enabling it to abstract aliphatic hydrogen, can be depicted as follows:¹⁶



Thus, the oxygen-activation reaction provides for the initiation of the radical chain autoxidation. Since we felt that Kropf's mechanism was open to doubt and in view of the high theoretical as well as practical importance of any oxygen-activation mechanism we have reinvestigated the mechanism of oxidation catalysis by metal-phthalocyanines.

RESULTS

Some explicit conditions have to be fulfilled in order to establish any oxygen-activation mechanism: (1) the

hydrocarbon used (cumene) should be completely free of hydroperoxide, (2) one must be able to measure very low rates of oxygen uptake and (3) the catalyst should preferably be homogeneous to simplify the kinetics. The second condition derives from the consideration that initiation via oxygen activation can easily be obscured by the simultaneous occurrence of the "normal" initiation via hydroperoxide homolysis.

For our studies we used highly purified cumene (see Experimental) and metal-4,4',4'',4'''-tetra-*t*-butylphthalocyanines (M-TB Pc) as the soluble catalysts. Oxygen uptake was measured by a bubble counter device which enabled us to measure the rate of oxygen uptake with an accuracy of 6×10^{-10} mol. s⁻¹. Under these conditions, without added catalyst, we observed for cumene at 60° an induction period of 120 min. This long induction period was not caused by the presence of an inhibitor as the oxidation started immediately at an initial rate of about 10^{-8} mol O₂ . s⁻¹ per 10 ml of cumene when initiated with 6×10^{-5} M 2,2'-azoisobutyronitrile.

In the presence of 1.25×10^{-3} M Cu-TB Pc the induction period was 45 min, during which time the oxygen uptake was below our detection limit. We also studied the kinetics of the oxidation of cumene in the presence of our soluble catalysts as well as in the presence of partly soluble unsubstituted metal-phthalocyanines (Table 1). Although the activity of both types of catalyst (expressed as rates of initiation, R_i) varies strongly with the metal, the soluble catalysts were found to be at least a hundred times more active than the unsubstituted metal-phthalocyanines. The rate of initiation caused by a given catalyst proved to be independent of the concentration of ROOH, i.e. apart from the induction period and a short period thereafter, straight lines were obtained when the oxygen uptake (dO₂/dt) was plotted against time. As is to be expected for radical-chain-type oxidations, we observed a square-root relationship between the rate of initiation (R_i) and the oxidation rate (Exp. 2-5), the former being proportional to the catalyst concentration (Exp. 3-5).

The selectivity towards hydroperoxide (S, Table 1) depends not only on the catalyst used, but also on the rate of the oxidation. As at higher rates the chain lengths are shorter and, consequently, more hydroperoxide is used for the initiation, selectivities are lower. The "non-hydroperoxide" products arising from chain termination are found as by-products.

The efficiency factor α (Table 1), which denotes the number of moles of initiating radicals formed per mole of hydroperoxide decomposed, can be calculated from the measured rate of oxygen uptake, the rate of initiation and the selectivity towards hydroperoxide by the expression

Table 1. Metal-phthalocyanine-catalysed oxidations of cumene (10 ml) at 1 bar O₂

Exp. No.	Phthalocyanine ^a	Concentr. M. 10 ³	Temp., °C	R _i × 10 ⁶ , M.s ⁻¹	($\frac{dO_2}{dt}$) ² /R _i ^b × 10 ⁴	Chain ^c length	S ^d	α ^e
1	no metal ^f		80				98	
2	Cu-TB Pc ^g	12.5	60	130	5.3	2.0	36	0.70
3	Cu-TB Pc	3.1	60	93	5.3	2.8	40	0.70
4	Cu-TB Pc	1.3	60	36	4.0	3.3	52	0.62
5	Cu-TB Pc	0.6	60	19	4.5	4.9	70	0.68
6	Zn-TB Pc	1.3	80	0.6	20	58	96	0.60
7	VO-TB Pc	1.3	80	4.0	21	23	95	0.80
8	Cu-Pc ^h	18	60	1.0	5.8	24	90	0.40
9	Cu-Pc ^h	18	80	1.8	19	33	86	0.25
10	Zn-Pc ^h	18	80	0.12	22	135	98	0.20
11	VO-Pc ^h	18	80	0.8	15	43	95	0.47
12	Mg-Pc ^h	19	80	0.9	25	53	93	0.26
13	Bi-Pc ^h	18	80	8.2	18	15	85	0.44
14	Co-Pc ^{g,h}	18	80				7	

a) -TB Pc: 4,4',4'',4'''-tetra-tert-butylphthalocyanine.

b) In the radical chain oxidation of cumene this value must be constant: 5×10^{-3} and 18×10^{-4} M.s⁻¹ at 60 and 80 °C, respectively^{23,24}.

c) Calculated from $\frac{dO_2}{dt}/S$.

d) Selectivity (S) to ROOH, calculated on oxygen consumed.

e) Moles of initiating radicals formed per mole of hydroperoxide decomposed.

f) The reaction stopped after the uptake of 0.33 moles of oxygen.

g) Catalyst only partly dissolved (solubility of Cu-TB Pc at 60 °C in cumene is about 5×10^{-3} M).

h) The reaction stopped after the uptake of 1.0 mole of oxygen.

(for derivation, see Experimental):

$$\alpha = \frac{R_i}{dO_2/dt(1-S)}$$

For the soluble catalysts α was found to be 0.6–0.8. The—only partly soluble—unsubstituted metal-phthalocyanines have efficiencies only half as large. (For comparison, α has a value of about one in the thermal, i.e. uncatalysed, autoxidation of cumene at temperatures above 120°.)

DISCUSSION

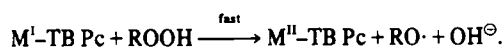
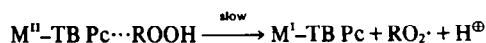
During the later stages of an oxidation hydroperoxide is present in fairly high concentrations. Since both oxygen activation and hydroperoxide homolysis constitute possible initiation processes, the interpretation of experimental data is rather complicated. In the initial stages of an oxidation, especially during the induction period, very little hydroperoxide is formed and initiation via oxygen activation is less apt to be obscured by that due to hydroperoxide homolysis.

We first consider the induction period measurements. In Kropf's¹⁰ study, the copper-phthalocyanine ([Cu-Pc] = 7×10^{-3} M)-catalysed oxidation of cumene at 76–7°C showed an initial oxidation rate, ascribed to oxygen activation,¹⁰ of 1.1 mmol O₂/mol of cumene.h. with an energy of activation¹⁰ of 37.7 kJ . mol⁻¹ (9.0 kcal . mol⁻¹). This extrapolates to a rate $v = 1.2 \times 10^6$ M.s⁻¹ at 60°C. By means of the oxidation-rate relationship²² $v = dO_2/dt = k_p[RH](R_i/kt)^{1/2}$, in which dO₂ is expressed in mol O₂ per litre of cumene and, for cumene²³ at 60°, $k_p/k_t^{1/2} = 3.2 \times 10^{-3}$ M^{-1/2} . s^{-1/2} and [RH] = 7.3 M, we calculate a rate of initiation of 2.7×10^{-9} M . s⁻¹. However, for our pure cumene in the presence of 1.3×10^{-3} M Cu-TB Pc we observed an induction period of 45 min, during which oxygen uptake was less than 6×10^{-10} M . s⁻¹. Thus, the

average rate of initiation \bar{R}_i was lower than 6×10^{-12} M . s⁻¹, i.e. one thousandth of the rate of initiation ascribed by Kropf to oxygen activation. Using the rate of the Cu-TB Pc-catalysed decomposition of cumene hydroperoxide (vide infra) we find that the average rate of initiation during the induction period can be accounted for by the initial presence of less than 10^{-10} M hydroperoxide in our cumene sample. We therefore conclude that even during the induction period oxygen activation, if occurring, is only of minor importance.†

These results are supported by the behaviour of cumene, in the presence of these catalysts, at higher oxidation rates, i.e. at high hydroperoxide concentrations. As required for a radical-chain autoxidation of hydrocarbons we found that the oxidation rate of cumene in the presence of the homogeneous as well as of the heterogeneous catalysts is proportional to the square root of the rate of initiation, i.e. $(dO_2/dt)^2/R_i$ is constant‡ (5.2×10^{-4} and 18×10^{-4} M . s⁻¹ at 60 and 80°C, respectively^{23,24} Table 1, 6th column).

In contrast to the "uncatalysed" (thermally initiated) autoxidation of cumene, we observed that in the presence of the homogeneous as well as of the heterogeneous catalysts, the rate of initiation (R_i) was independent of the hydroperoxide concentration. This implies that the decomposition of hydroperoxides by these catalysts is preceded by a very effective complex formation between hydroperoxide and catalyst. Thus, the concentration of the complex is identical to that of the added catalyst and by plotting R_i vs [Cu-TB Pc] the pseudo-first-order decomposition rate of the complex Cu^{II}-TB Pc...ROOH) is found to be 2.9×10^{-2} s⁻¹. Analogous to the cobalt stearate catalysis²⁶ we propose the following mechanism for the metal-phthalocyanine-catalysed decomposition of hydroperoxides:



†The extreme care that has to be taken in removing hydroperoxide contaminants when studying oxygen activation is best illustrated by the fact that the rate of initiation, ascribed by Kropf¹⁰ to oxygen activation, can be brought about by as little as 10^{-7} M hydroperoxide.

‡This observation also precludes another type of oxygen activation, viz. insertion of oxygen into a C-H bond.^{23,25}

According to this mechanism, one initiating radical is produced per molecule of hydroperoxide decomposed, i.e. $\alpha \leq 1$. If oxygen activation would have been operative we should have found values for α much greater than one (cf Table 1), since the generation of chain-initiating radicals via oxygen activation does not consume hydroperoxide.

Our data of the induction period and of the efficiency factors (Table 1) clearly preclude oxygen activation as an important process during either the induction period or the later stages of the metal-phthalocyanine-catalysed oxidation of cumene.

EXPERIMENTAL

(1) *Materials.* Cumene was washed with H_2SO_4 until no colouration occurred (6–8 times), with water, NaOHaq and water, dried over $MgSO_4$ and distilled under N_2 from Na. The purified cumene was stored under N_2 at -20° and percolated over basic alumina immediately before use. The latter treatment is essential²⁷ in order to obtain hydroperoxide-free cumene: without this treatment the induction period is less than 10 min as compared to more than 90 min after chromatography.

2,2'-Azo-isobutyronitrile and 2,6-di-*t*-butyl-4-methylphenol were recrystallized from ether and ethanol, respectively.

The metal-4,4',4'',4'''-tetra-*t*-butylphthalocyanines were prepared²⁸ from 4-*t*-butylphthalocyanitrile.

(2) *Measurements.* The oxidations were carried out with 10 ml of cumene in a thermostatted 50-ml. flat-bottomed Pyrex flask, provided with a side arm and a magnetic stirrer. The flask was cleaned after each experiment by rinsing with ethanolic KOH, water, 5% HF, water and acetone p.a. After the flask had been charged with 10 ml of cumene (and catalyst) under nitrogen, it was placed in the thermostatted bath and allowed to equilibrate (60 or 80°) for 5 min. Then the N_2 atmosphere was replaced by O_2 and the system closed. The oxidations were carried out at atmospheric pressure. The rate of oxygen uptake was measured with the aid of a thermostatted (30°) bubble counter with a printing device.

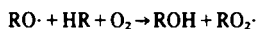
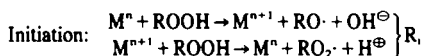
Calibrations repeated at regular intervals gave a volume of 0.0050 ± 0.0002 ml for one bubble of O_2 . Detection limit for O_2 uptake was one bubble per 6 min. Initiation rates were measured using the non-approximative inhibitor method of Berger.²⁹ Selectivities (S) to hydroperoxides were calculated, on the basis of total oxygen uptake, from the yield of hydroperoxide determined iodometrically.

The formula to calculate the efficiency factor α is derived as follows:

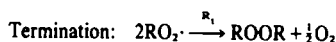
The selectivity to hydroperoxide is limited by initiation losses; therefore:

$$S = \frac{(d\text{ROOH}/dt)_{\text{total}} - (d\text{ROOH}/dt)_{\text{initiation}}}{(d\text{ROOH}/dt)_{\text{total}}} \quad (1)$$

The rate of hydroperoxide formation, with neglect of initiation losses, $(d\text{ROOH}/dt)_{\text{total}}$, equals the rate of oxygen consumed (dO_2/dt) , corrected for the oxygen used in the initiation process (not producing ROOH) and for oxygen produced by termination.



rate of oxygen consumption for initiation: $\frac{1}{2} R_i$



rate of oxygen production by termination $\frac{1}{2} R_t$

therefore:

$$(d\text{ROOH}/dt)_{\text{total}} = \frac{dO_2}{dt} - \frac{1}{2} R_i + \frac{1}{2} R_t = \frac{dO_2}{dt} \quad (2)$$

(the latter two cancel as in the steady state $R_i = R_t$).

$$\text{Rate of initiation } R_i = \alpha \left(\frac{d\text{ROOH}}{dt} \right)_{\text{initiation}} \quad (3)$$

Substitution of (2) and (3) into (1) results in

$$S = \frac{dO_2/dt - R_i/\alpha}{dO_2/dt}$$

from which α can be derived.

REFERENCES

- A. D. Vreugdenhil, *J. Catalysis* **28**, 493 (1973); R. A. Sheldon, *Chem. Comm.* 788 (1971); V. P. Kurkov, J. Z. Pasky and J. B. Lavigne, *J. Am. Chem. Soc.* **90**, 4743 (1968) and A. Fusi, R. Ugo, F. Fox, A. Pasini and S. Cenini, *J. Organometal. Chem.* **26**, 417 (1971).
- J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.* **95**, 5757 (1973).
- C. K. Chang and T. G. Taylor, *Ibid.* **95**, 8475, 8477 (1973).
- O. Vonderschmitt, K. Bernauer and S. Fallab, *Helv. Chim. Acta* **48**, 951 (1965).
- P. Donatsch, K. H. Gerber, A. Zuberbühler and S. Fallab, *Ibid.* **53**, 262 (1970).
- C. J. Pederson, *J. Org. Chem.* **22**, 127 (1957); see also J. H. Fuhrhop and D. Mauzerall, *J. Am. Chem. Soc.* **91**, 4174 (1969).
- H. Kropf and K. Knaack, *Liebigs Ann.* **757**, 121 (1972).
- M. Rougee, D. Prince, V. Favaudon and M. Momenteau, *Colloques Internat. Centre Nation. Rech. Scient.* **191**, 335 (1970).
- H. Hock and H. Kropf, *Angew Chem* **69**, 313 (1957).
- H. Kropf, *Liebigs Ann.* **637**, 73 (1960).
- H. Kropf, *Ibid.* **637**, 93 (1960).
- H. Hock and H. Kropf, *J. Prak. Chim.* **13**, 20 (1961).
- H. Kropf, *Tetrahedron Letters* 577 (1962).
- H. Kropf, *Chem. Ing. Tech.* **36**, 759 (1964).
- H. Kropf and Hd. Hoffmann, *Tetrahedron Letters* 659 (1967).
- H. Kropf and W. Knabjohann, *Liebigs Ann.* **739**, 95 (1970).
- H. Kropf and K. Knaack, *Ibid.* **757**, 109 (1972).
- H. Kropf and K. Knaack, *Tetrahedron* **28**, 1143 (1972).
- Y. Kamiya, *Tetrahedron Letters* 4965 (1968).
- A. I. Min'kov and N. P. Keier, *Kinetics and Catalysis* **8**, 133 (1967).
- R. V. Norton, *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.* Vol. 15, No. 3, B18 (1970).
- N. M. Emanuel, E. T. Denisov and Z. K. Maizus, *Liquid Phase Oxidation of Hydrocarbons*, pp. 10, 175. Plenum Press, New York (1967).
- A. D. Vreugdenhil, *J. Catal.* **28**, 493 (1973).
- I. Sérée de Roch, *Ind. Chim. Belge* **33**, 994 (1968).
- N. H. A. van Ham, B. E. Nieuwenhuys and W. M. H. Sachtler, *J. Catal.* **20**, 408 (1971).
- N. M. Emanuel, Z. K. Maizus and I. P. Skibida, *Angew Chem.* **81**, 93 (1969).
- R. A. Sheldon, *Chem. Comm.* 788 (1971).
- F. H. Moser, A. L. Thomas, *Phthalocyanine Compounds* p. 128. Reinhold, New York (1963).
- H. Berger, *Abstracts 1st Annual Meeting New. Chemical Society*, No. 2.4a. Manchester 10–14 April (1972).