Epoxidation of cyclohexene by iron and cobalt phthalocyanines, study of the side reactions

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Abstract

This paper investigates the existence of side reactions involving oxygen donors in the epoxidation of cyclohexene in the presence of iron and cobalt phthalocyanines. An evaluation of the catalytic role of fragments coming from the degradation of phthalocyanines in the overall reactions has been undertaken. It is shown that neither tert-butyl-hydroperoxide (t-BHP) nor iodosylbenzene (PhIO), two commonly used donors, are convenient for evaluating the catalytic performances of phthalocyanines in the epoxidation of olefins. With t-BHP, the oxidation reaction is, at least partially, violently triggered by fragments from phthalocyanine decomposition; the reaction involves homogeneous radical pathways, and mainly leads to oxidized derivatives different than the epoxide. Its use necessitates precautions to preclude this decomposition. In the case of PhIO, the oxygen donor oxidizes the substrate even in the absence of catalyst. By contrast, hydrogen peroxide does not give way to major side reaction; it is efficient and selective for the heterogeneously catalyzed epoxidation of cyclohexene. It is therefore suitable, without special procedure, for studying the activity of phthalocyanines. Due to some spontaneous decomposition of H_2O_2, some precautions are nevertheless necessary to evaluate correctly the kinetics of the reaction.

Keywords: Olefins; Epoxidation; Phthalocyanine; Side reaction

1. Introduction

Due to their similitude with the active center of oxidation enzymes, like cytochrome P-450, porphyrin and phthalocyanine complexes of transition metals have been the object of several recent publications. Investigations were carried out to improve their performances as catalysts, namely their selectivity and resistance to deacti-

vation, for partial oxidation of hydrocarbons in mild conditions (room temperature and atmospheric pressure) [1–26]. These reactions are generally performed in organic solvents, and require the presence of an oxygen donor like iodosylbenzene (PhIO) [1,2,5,7,12,13], tert-butyl-hydroperoxide (t-BHP) [5,7,11,12] or hydrogen peroxide (H_2O_2) [21,27], although this reactant has been used more rarely than the others.

However there are strong indications that phthalocyanines have a very poor stability and are rapidly deactivated when used as catalysts in hydrocarbon oxidation

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[1,2,6,7,11,13,17,20,21,25]. This phenomenon has been discussed in the literature and different hypotheses have been put forward to explain it. Nevertheless some authors agree that phthalocyanine deactivation is due to their degradation in small soluble fragments [17], a fact which was confirmed by some of our results [27].

In this context, we have recently initiated a series of investigations on the deactivation of metal phthalocyanines in the epoxidation of cyclohexene, and the effect of their encapsulation in Y-zeolite [27]. The present paper constitutes the first of the series.

The objective of the present paper is to detect the various side reactions which can take place in the reacting medium, involving oxygen donors and the other constituents. A first selection of the oxygen donor suitable for the investigation of the catalytic performances of phthalocyanines, namely those triggering the minor side reactions, is operated in that respect. The second purpose is to investigate whether the previously selected oxygen donor is able to epoxidize efficiently the substrate by a truly heterogeneous catalytic reaction over phthalocyanines. Particular attention is paid to the evaluation of the role of the soluble fragments coming from the degradation of the phthalocyanines. A second selection of the oxygen donor is achieved. Finally precautions to be taken in the set-up of procedures for the correct evaluation of the performance of the catalysts are proposed.

Three series of catalytic tests were performed. The first one deals with the stability of the available oxygen donors in the conditions of reaction. This includes the evaluation of their capability to react spontaneously with one or several species present in the reacting medium. The second series checks, in a classical test procedure, whether the so-selected stable donors are efficient and selective in the catalyzed epoxidation of cyclohexene. Finally, the third series of tests was carried out to check whether the activity observed in the previous tests, conversion of the olefin and production of the epoxide derivative, was heterogeneously catalyzed by

phthalocyanines or whether the reaction was triggered by soluble fragments (as opposed to the unaltered phthalocyanines) in the homogeneous phase.

2. Experimental

All the catalytic tests were performed in batches, under an efficient magnetic stirring, at 25°C and under atmospheric pressure. Each test required 20 ml of dichloromethane (Aldrich, HPLC grade 99.9%) as solvent. Iron (FePc) or cobalt (CoPc) phthalocyanines (Aldrich, 95%) (100 mg) were used without any further purification. The standard feed (called substrate in this paper in accord with the terminology often used in similar works) of the test was 0.3 ml of cyclohexene (Fluka, 99% GC grade, commercially stabilized with traces of 2,6-di-tert-butyl-p-cresol). Three different oxygen donors were used. PhIO (iodosylbenzene) was prepared in the laboratory by basifying a mixture of appropriate quantities of iodobenzene diacetate (Aldrich, 98%), sodium carbonate (Janssen Chemica, p.a.) and ice. After ageing, the solid obtained was filtered, washed with distilled water and chloroform (Aldrich, HPLC grade), and dried at room temperature in air. 600 mg of PhIO were used when needed in the test. When required, 2 ml of an aqueous solution of H_2O_2 (Aldrich, 30 wt.-%) or of t-BHP (tert-butyl-hydroperoxide) (Aldrich, 70 wt.-%) were used.

Samples of the organic liquid phase were taken after different times of reaction. The products were identified by gas chromatography with a mass spectrometer detector (GC–MS), and their quantities in the system measured with a gas chromatograph equipped with a flame ionisation detector (FID).

2.1. Stability and spontaneous reactions of the oxygen donors

Table 1 shows the series of tests performed to evaluate the stability of the different oxygen

Table 1
Tests performed to evaluate the stability and to detect the side reactions of the oxygen donors

Test no.	Catalyst	Oxygen donor	Substrate	Analysis after
S1	–	–	✔	30 h
S2	–	PhIO	–	24 h
S3	–	t-BHP	–	30 min
S4	–	H_2O_2	✔	2, 45 h
S5	–	PhIO	✔	1, 4, 30 h
S6	–	t-BHP	✔	30 min
S7	FePc	H_2O_2	–	1, 4 h
S8	CoPc	H_2O_2	–	20 h
S9	CoPc	PhIO	–	1, 4, 30 h
S10	FePc	t-BHP	–	5 min
S11	CoPc	t-BHP	–	10 min

Table 2
Tests performed to evaluate the efficiency of the stable oxygen donors in the epoxidation of cyclohexene

Test no.	Catalyst	Oxygen donor	Substrate	Analysis after
C1	FePc	H_2O_2	✔	60 min
C2	CoPc	H_2O_2	✔	100 h
C3	FePc	t-BHP	✔	80 min
C4	CoPc	t-BHP	✔	2 h

donors when contacted with other parts of the catalytic system.

Test S1 is the blank experiment which checks the stability of the substrate with respect to the solvent.

Evaluation of the spontaneous conversion of hydrogen peroxide was not possible since a FID gas chromatograph is not suitable for its detection. Nevertheless a qualitative observation of its stability was undertaken on a mixture comprised of a dose of H_2O_2 in the solvent (test S12): attention was paid to detecting phenomena such as gaseous emission, changes in the temperature of the system, etc.

2.2. Efficiency of the oxygen donors in the epoxidation of cyclohexene

The oxygen donors selected for their stability and their low tendency to trigger side reactions with other constituents of the reacting medium (see Section 2.1. and Section 3.1.) have been tested in the oxidation of cyclohexene following

a classical procedure in the presence of FePc and CoPc. Table 2 presents the tests achieved with t-BHP and H_2O_2 as oxygen donors.

The objective of these tests is to evaluate the efficiency of the stable oxygen donors in the oxidation of cyclohexene and, in particular, their capability to produce the epoxide derivative.

2.3. Detection of homogeneous reactions

Some experiments were performed to test whether the activity observed in the tests 'C' was not triggered in the homogeneous phase by soluble fragments coming from the degradation of phthalocyanines in the reaction, rather than by the intact catalysts.

2.3.1. Influence of liquid residues

Tests in two steps were performed to determine whether the reactions observed in tests 'C' took place, at least partially, in homogeneous phase or were catalyzed by the phthalocyanines in a completely heterogeneous way. Catalysts were first contacted in a standard batch of solvent with the tested oxygen donor. After a given contact time, the catalytic system was filtered so that any traces of phthalocyanines in suspension were removed from the liquid phase. A new

Table 3
Tests performed in order to determine the influence of the liquid residues

Test no.	Catalyst	Oxygen donor	Time of contact	Analysis after
L1	FePc	H_2O_2	30 min	15, 30 min, 1, 3, 10, 70 h
L2	CoPc	H_2O_2	24 h	15, 30 min, 1, 4, 40 h
L3	FePc	t-BHP	5 min	5, 20, 60 min
L4	CoPc	t-BHP	10 min	5, 10, 30 min, 1, 3, 18 h

Table 4
Tests with metal salts

Test no.	Catalyst	Oxygen donor	Analysis after
O1	Fe salt	H_2O_2	30 min
O2	Co salt	H_2O_2	30 h
O3	Fe salt	t-BHP	30 min
O4	Co salt	t-BHP	30 h

load of oxygen donor, as well as a standard dose of substrate, were thereafter added to the obtained liquid residue. Chromatographic analyses were carried out after different times of reaction as indicated in Table 3.

2.3.2. Influence of metal salts

In further investigations, tests were performed in which phthalocyanines were replaced by salts of the corresponding complexed metals as catalysts: $FeSO_4 \cdot 7H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (see Table 4). The quantities of salts used in the tests were taken so that the quantity of metal equivalents used was equal to that employed in tests 'C' performed with phthalocyanines ($1.75 \cdot 10^{-4}$ equiv.).

3. Results and discussion

3.1. Stability and spontaneous reactions of the oxygen donors

Cyclohexene does not suffer from spontaneous conversion when contacted with the solvent during 30 h (test S1). Any disappearance of this substrate observed in other tests must thus be attributed to one or more constituents of the catalytic system besides the solvent.

3.1.1. Iodosylbenzene (PhIO)

Large quantities of iodobenzene (PhI), the product obtained from deoxygenation of PhIO, are detected in the test S2 after times as short as 1 h. This shows that this oxygen donor decomposes even in the absence of any catalyst. This conversion is accelerated in the presence of a

metal phthalocyanine, as shown in the test S9. The amount of activated oxygen formed in the system is probably partially recombined to molecular oxygen which leaves the system. Another explanation of the conversion of PhIO in S2 and S9 would be the disproportionation of two PhIO molecules forming, on one hand, PhI, and on the other, the highly stable iodoxybenzene ($PhIO_2$) [1,2,12,13]. We did not attempt to confirm this part, nor did we investigate the oxidative properties of $PhIO_2$.

Test S5 shows that the spontaneously released oxygen is sufficiently active for oxidizing the olefinic substrate. A 19% conversion of cyclohexene is observed while cyclohexene oxide, cyclohexenol and cyclohexenone are detected (respective yields: 1.2%, 2% and 3.6%). Moreover the mass balance calculated with respect to the cyclohexene is not equilibrated: only 31% of the converted cyclohexene was found in the oxidized products.

A conclusion for this series of experiments is that the amount of PhI produced (and any expression whose calculation is based on it) does not provide a correct evaluation of the capability of phthalocyanine to catalytically decompose PhIO since this decomposition occurs spontaneously. Moreover, iodosylbenzene is significantly able to trigger, without catalyst, the oxidation of the substrate, and probably other unidentified reactions. The results are consistent with similar experiments performed by Yang et al. [28]. Thus it is unsuitable for the testing of the performance of catalysts in the epoxidation of olefins under conditions similar to those mentioned above.

3.1.2. Hydrogen peroxide (H_2O_2)

No conversion of cyclohexene is measured when contacted only with the solvent and hydrogen peroxide (S4), in addition, no oxidized derivatives are detected. On the other hand, a slight gaseous emission is noted in the presence of the FePc (S7). No similar phenomenon is observed when hydrogen peroxide is used alone

(S12), or in the presence of CoPc (S8). The conclusion is that this emission is due to the catalytic decomposition of H_2O_2, forming water and molecular oxygen. FePc, being sufficiently active, exhibits some catalytic activity in this reaction, but CoPc does not.

Knowing this, hydrogen peroxide is consequently acceptable for testing the catalytic performance of phthalocyanines in the epoxidation of olefins. Nevertheless the oxygen released catalytically may not be totally incorporated into the oxidation products. Some activated oxygen may form molecular oxygen, and thus may leave the system without reaction with the substrate. Consequently, when the conversion of hydrogen peroxide is measured, this cannot be used for the calculation of the selective oxidation activity of the catalyst.

3.1.3. tert-Butyl-hydroperoxide (t-BHP)

t-BHP does not decompose when used alone (S3), but it does in the presence of the substrate (S6). In this case, a slight conversion of cyclohexene is noted and traces of tert-butyl-cyclohexene are detected. However, no oxidized derivative of cyclohexene is observed. In the presence of phthalocyanine, FePc (S10) or CoPc (S11), a violent gaseous emission and an increase of the temperature of the system are noted. Several unidentified products are detected, including some isoindole. An explanation of this phenomenon would be that the catalyst rapidly releases oxygen from t-BHP. The released oxygen is consumed, at least partially, for the oxidation of the metallic sites of the phthalocyanine. The metal in a high oxida-

tion state thus obtained would trigger the degradation of the phthalocyanine in small fragments through a mechanism similar to that described elsewhere [17,27]. The small soluble fragments obtained from the corresponding process would explain the formation of the isoindole, as well as that of some of the other detected products. The observed gaseous emission and the exothermicity have to be attributed to this succession of transformations or to some of their side reactions.

At this stage of the investigation, t-BHP is still suitable for the evaluation of the catalytic performance of phthalocyanines in the epoxidation of cyclohexene. Indeed t-BHP does not oxidize the substrate in the absence of catalyst. Nevertheless it can be admitted that the conversion of t-BHP cannot be taken into account for the calculation of the activity since it decomposes spontaneously. The same precaution must be taken with cyclohexene which is converted without any catalyst in the presence of t-BHP, but without being oxidized.

3.2. Efficiency of the oxygen donors in the epoxidation of cyclohexene

Table 5 presents the yields for the different detected oxidized derivatives of cyclohexene obtained in the tests of the series 'C'. It is found that, with hydrogen peroxide as oxygen donor, the main product is the cyclohexene oxide. Cyclohexenol and cyclohexenone are formed in smaller quantities. In addition, the distribution of the products remains the same when the catalyst is changed; nevertheless FePc appears to be much more active than CoPc, as already observed in the series of 'S' tests (S7, S8).

With t-BHP as oxygen donor and with both catalysts, cyclohexenone is largely the main product of the reaction, with a significant quantity of cyclohexenol. Cyclohexene oxide only appears as a minor derivative of the reaction. In this case the activity of CoPc is higher than that of FePc.

Table 5
Yields (%) measured in the tests of the series 'C'

Test no.	Cyclohexene oxide	Cyclohexenol	Cyclohexenone
C1 after 60 min	6.4%	0.8%	1.05%
C2 after 100 h	0.5%	–	–
C3 after 80 min	0.4%	7.4%	15.9%
C4 after 2 h	0.4%	21.1%	54.1%

Table 6
Yields (%) measured in tests L3 and L4

Test no.	cyclohexene oxide	cyclohexenol	cyclohexenone
L3 after 20 min	1.5%	10.1%	22%
L4 after 18 h	0.7%	10.1%	38.5%

3.3. Detection of homogeneous reactions

3.3.1. Influence of the liquid residues

The tests listed in Table 3 were designed to investigate the role of the liquid residues obtained by filtration after contact with phthalocyanines, namely, products coming from the degradation of the phthalocyanines. In the tests performed with hydrogen peroxide (tests L1 and L2, Table 3), traces of cyclohexene oxide are observed after 40 h contact with the liquid residue obtained from CoPc. A 0.2% yield of cyclohexene oxide is measured after 70 h with the liquid residue obtained from FePc. Nevertheless this activity can be neglected when compared with the activities observed in our standard catalytic tests: a 6.4% yield after only 60 min with FePc (Table 5, C1).

Table 6 shows the yields measured in the tests with liquid residues obtained after contact of the phthalocyanines with t-BHP (tests L3 and L4, Table 2).

The nature of the detected products, as well as the yields and the ratios in their respective yields, are similar to those obtained in standard catalytic tests with phthalocyanines and t-BHP (Table 5, C3, C4).

3.3.2. Influence of metal salts

With hydrogen peroxide as oxygen donor (tests O1 and O2, Table 4), metal salts only trigger a gaseous emission. No conversion of cyclohexene is measured.

In the tests with t-BHP (O3 and O4), the same products as those detected in C3 and C4, as well as in L3 and L4, are produced in traces with a comparable distribution: cyclohexenone > cyclohexenol ≫ cyclohexene oxide.

The tests L1, L2, O1 and O2 (performed with hydrogen peroxide) show that small soluble fragments, particularly free metal ions, formed from the destruction of phthalocyanines, are not able to convert the substrate in the presence of hydrogen peroxide. The reactions taking place in the homogeneous phase are only representative of a very small part of the observed activity in the conventional tests 'C'.

On the contrary, fragments liberated in the liquid due to the phthalocyanine deactivation, and metal ions, are able to trigger the oxidation of cyclohexene in the presence of t-BHP. The similitude in the yields in oxidation products obtained with liquids without phthalocyanines and with phthalocyanines even suggests that the homogeneous phase reactions represent the main part of the activity observed in the conventional tests frequently reported in the literature.

Another result is that the distribution of the oxidation derivatives in the conventional tests 'C' is very different with H_2O_2 and t-BHP. Only cyclohexene oxide is mainly obtained with H_2O_2; with t-BHP, the products are: cyclohexenone > cyclohexenol ≫ cyclohexene oxide. Moreover the most active catalyst is different with the two oxygen donors: FePc in the case of H_2O_2, CoPc in the case of t-BHP. We therefore come to the conclusion that totally different catalytic mechanisms are involved with the two oxygen donors. In the case of hydrogen peroxide, intact phthalocyanines are the active catalysts. This is not the case with tert-butyl-hydroperoxide. In addition, taking into account the violence of the reactions observed in the series of 'S' tests performed with t-BHP, as well as the formation of tert-butyl-cyclohexene, it is highly probable that a radical mechanism operates in that last case, namely a mechanism different from the catalytic reaction due to the action of phthalocyanines.

The consequence for the study of the catalytic performance of phthalocyanines in the epoxidation of cyclohexene is that t-BHP is unsuitable. Only reactions with H_2O_2 may give meaningful results.

It is nevertheless necessary to mention that t-BHP as oxygen donor can be used in investigations of the hydrocarbon oxidation of phthalocyanine, if some precautions are taken. The side reactions detected with t-BHP essentially come from the soluble fragments formed by the degradation of the catalysts during the first moments of the reaction. It is known that this is a bimolecular process involving two molecules of phthalocyanine. A way to avoid the deactivation of the catalysts, and so the side reactions, would be to work in conditions in which the contact between phthalocyanines is precluded or at least minimized: substitution of the rings of the complexes with bulky groups or encapsulation in zeolite cages. This has been particularly applied with good results by Parton et al. [11]. However, it remains necessary to check by careful characterizations whether the catalysts have not, at least partially, been disturbed during the test to validate the results. Also precautions still have to be taken when the conversion of t-BHP and of the substrate is used for the calculation of the activity, as already mentioned previously.

4. Conclusions

Three oxygen donors were tested: PhIO, t-BHP, H_2O_2.

Iodosylbenzene (PhIO) decomposes spontaneously in the reaction mixture. Its decomposition triggers the oxidation of cyclohexene even in the absence of catalyst.

When working on conventional (non-substituted and non-encapsulated) catalysts, *tert-butyl-hydroperoxide* (t-BHP) rapidly destroys the phthalocyanine; it triggers very violent radical reactions in the homogeneous phase.

With *hydrogen peroxide*, precautions must be taken when expressing the performance of the catalysts. The consumption of the oxygen donor is not representative of the progress of the catalytic reaction since it decomposes spontaneously and the released oxygen is not incorporated integrally into the oxidized derivatives of

the substrate. Consequently, all the quantities characterizing the catalytic performance: turnover number, yield or selectivity based on the initial amount of donor in the system, and/or on its consumption should be used with caution. Nevertheless, hydrogen peroxide is the only suitable tested oxygen donor for the study, without any special procedures, of the epoxidation of cyclohexene catalyzed by phthalocyanines. In this case, the homogeneous phase reactions are very slow compared to the heterogeneously catalyzed one.

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