

The role of onium salts in the oxidation of hydrocarbons by O₂ catalysed by cationic phase-transfer reagents

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Experimental and theoretical evidence is presented that cationic phase-transfer catalysts promote the homolytic decomposition of hydroperoxide initiators into radicals, this being a fundamental step in the catalysis of the oxidation of hydrocarbons by O₂. Such decomposition of the model substance *tert*-butyl hydroperoxide (t-BHP) results in O₂, *tert*-butanol (90–95%) di-*tert*-butyl peroxide (5–10%) and traces of CO₂. The stoichiometric ratio Δ[t-BHP]/ΔO₂ was found to have a value of 2, independently of the nature of the counteranion present. It is assumed that the interaction between hydroperoxide and onium cation is mainly electrostatic in nature and that its effectivity depends on the positive charge density on the onium cation, which is controlled by the nature and dimensions of the counteranion. The role of water in the decomposition of t-BHP is also elucidated.

Introduction

Appropriate phase-transfer catalysts¹ (PTCs) are currently widely used for the solubilization of water-soluble inorganic reagents in non-polar organic solvents, since the ion-pair complexes formed during the dissolution may serve as excellent catalysts for the oxidation of hydrocarbons by O₂. It was recognized first by Bredereck *et al.*² that the autoxidation of certain organic materials can be accelerated by quaternary ammonium salts. Some years later, systematic investigations by Fukui *et al.*³ led to the conclusion that the oxidation of hydrocarbons (*p*-xylene, cumene, *etc.*) can be accelerated not only by ammonium salts, but also by other onium salts, such as sulfonium, phosphonium, selenonium, arsonium and telluronium salts. They attributed such catalysis to the activation of O₂ by an interaction with the vacant d-orbitals of the central sulfur, phosphorus, selenium, *etc.*, atoms. Ohkubo *et al.*⁴ later proposed that the oxidation of hydrocarbons may also be induced by radicals produced during the onium ion-promoted decomposition of hydroperoxide present. The idea of hydroperoxide decomposition was embraced by van Tilborg⁵ when he rejected the O₂ activation concept as being inadequately supported by spectral observations.

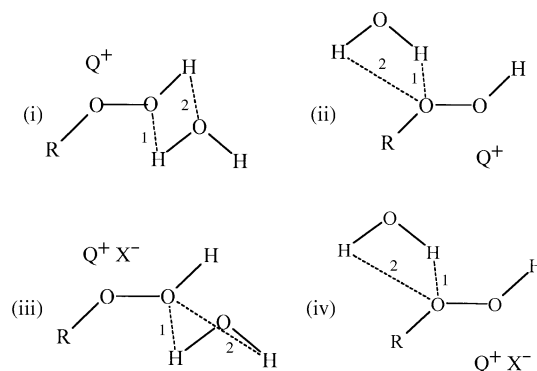
We have also advocated the latter idea (although, similarly to earlier authors, without presenting experimental evidence) by emphasizing⁶ that the O atoms of the peroxy group in the hydroperoxides (unlike those in hydrogen peroxide) are not equivalent: the inner O atom (attached to the hydrocarbon radical) is nucleophilic, whereas the outer one (attached to H) is electrophilic. It is therefore to be expected that the positively charged onium ion (Q⁺) will probably attack at the nucleophilic inner O atom, while the outer O atom interacts with water [see Scheme 1(iii)]: it has been observed that the oxidation of hydrocarbons is influenced by the presence of water. This postulate, however, has not been checked experimentally to date. In this work, an attempt was made to

support this working hypothesis with experimental findings and theoretical considerations. Further, an explanation is sought for the long-observed fact that the catalytic activities of cationic PTCs depend on the nature of the counteranions in the onium salts.

Experimental

The phase-transfer reagents and t-BHP were Fluka products and were used without any purification. Chlorobenzene was applied as a non-polar solvent. Its purification has been described.⁷

The investigation of the effects of the counteranions on the decomposition of the initiator t-BHP was carried out in the dark in a thermostated magnetically stirred batch reactor (fitted with a reflux condenser cooled with water to 10 °C)⁸ supplied with a septum and with a Young stopcock. Appropriate quantities of t-BHP and onium salt as catalyst were dissolved in 8.00 cm³ of chlorobenzene and added to the reactor. After removal of traces of O₂ by bubbling N₂, the reaction vessel was connected to a thermostat pre-heated to



Scheme 1

70 °C. After a warm-up period of exactly 3 min, recording of the gaseous product evolved was started with the aid of a syringe gas buret. The gas measuring device automatically maintained the inside pressure at the atmospheric value. After a reaction time of 120 min, the stopcock was closed and the reaction vessel was cooled first to 6–8 °C and then to liquid nitrogen temperature. When the reaction mixture was frozen, a 5.00 cm³ gas sample was taken with a pressure-lok syringe; after thawing, the concentration of t-BHP remaining in the solution was determined by iodimetry.

The quantity of O₂ evolved was estimated by a modified Winkler method.⁹ After O₂ traces has been removed by thorough flushing with N₂, 3.0 cm³ of concentrated NaOH (20 mmol) and 8.0 cm³ of manganese(II) chloride (9 mmol) solutions (both previously freed from O₂ by an N₂ stream) were introduced into the reaction vessel whilst the O₂-free environment was secured with a stream of N₂. A white precipitate of Mn(OH)₂ was formed in the reaction vessel. The inside pressure was next reduced to 5–10 Torr, the previously taken 5.00 cm³ gas sample was introduced through the septum and O₂ was absorbed quantitatively by thorough stirring and agitation for 30 min. A 15 cm³ volume of 20% hydrochloric acid was then added to dissolve the hydroxide precipitate, about 1 g of KI was added and the liberated iodine was titrated with thiosulfate reagent solution.

The other products of decomposition were analysed by gas chromatography on a column (2 m × 4 mm id) filled with Chromosorb W-AW-DMCS coated with Carbowax 20M with N₂ as carrier gas at 40 cm³ min⁻¹, flame ionization detection and identification with the aid of authentic samples. For control, MS-10 and QMS 200 mass spectrometers were applied.

Results and discussion

Effect of water

It was observed earlier^{6,8} that water exerts a catalytic influence on the oxidation of hydrocarbons in the presence of onium salts. It seemed reasonable, therefore, to investigate whether the decomposition of t-BHP catalysed by onium salts is similarly influenced by the presence of water. The data in Table 1 show that the decomposition of t-BHP in the presence of a cationic phase-transfer reagent is enhanced by the addition of water up to a given quantity; but at higher water concentrations the rate of the decomposition decreases. This observation allows the conclusion that water contributes to the catalyzed decomposition of the initiator.

Effects of counteranions on the decomposition of t-BHP

Table 2 presents data relating to the decomposition of t-BHP. In the absence of onium salts, only a very slight decomposition can be observed at 70 °C during 120 min, and a small amount of gaseous product (gp) is formed with the stoichiometry $\Delta[\text{t-BHP}]/\Delta[\text{gp}] = 2$. The same stoichiometry was found when different cationic phase-transfer reagents were applied with different counteranions, with the exception of iodide. The catalytic activities of the onium salts differed and depended on the nature of the counteranion. For tetrabutylammonium cation, for instance, the sequence of efficiency was $\text{Br}^- > \text{SCN}^- > \text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^- > \text{F}^-$, whereas for the tetrahexylammonium cation it was $\text{Br}^- > \text{Cl}^- > \text{HSO}_4^- > \text{OH}^-$. The sequence of catalytic efficiencies of different quaternary ammonium ions, all with chloride counteranion, was $\text{Hex}_4\text{N}^+ > \text{BzBu}_3\text{N}^+ > \text{BzEt}_3\text{N}^+ > \text{MeOct}_3\text{N}^+ > \text{Me}_4\text{N}^+ > (\text{CetPy})^+$.

The gaseous product of the catalyzed decomposition of t-BHP overwhelmingly contained O₂ in each case, independently of the nature of the counteranion. The decomposition

products which remained dissolved in the chlorobenzene solution were determined by gas chromatography.

In the presence of 0.120 mmol of Hex₄NCl during 280 min, the decomposition of 2.108 mmol of t-BHP in 8.00 cm³ of chlorobenzene produced 0.687 mmol of O₂, which corresponds to 1.374 mmol of t-BHP; $\Delta[\text{t-BHP}]$ was found to be 1.376 mmol. Additionally, 1.329 mmol of *tert*-butanol (96.6%) and 0.0406 mmol di-*tert*-butyl peroxide (5.9%) were found by gas chromatography. These data indicate that only O₂, *tert*-butanol and some di-*tert*-butyl peroxide are formed during the decomposition.

In the case of Hex₄NBr as catalyst under similar conditions, 0.851 mmol of t-BHP was decomposed and produced 0.424 mmol of O₂ (which is equivalent to 0.848 mmol of t-BHP). Moreover, 0.795 mmol of *tert*-butanol (93.4%) and 0.0275 mmol of di-*tert*-butyl peroxide (6.4%) were found, which is in good harmony with the stoichiometric factors given in Table 2.

Effects of onium iodides

When the decomposition of t-BHP was carried out as described in the Experimental section with Hex₄NI as catalyst, different results were obtained (Table 3). Rapid decomposition was observed, but only a little gaseous product was obtained, and the value of the stoichiometric factor was consequently well in excess of 2. The reason for this can be understood by considering the data from those measurements in which the quantity of catalyst was altered. These indicate that the decomposition is too fast relative to the resolving ability of the gas measuring device used. When the catalyst was added to the closed reactor without waiting 3 min for warming up, during which the stopcock of the reactor was open to the atmosphere, the decomposition took place with a stoichiometric factor of 2. The volume increments caused by the temperature increase were taken into consideration.

In the presence of 0.120 mmol of Hex₄NI as catalyst during 120 min, 2.045 mmol of t-BHP were decomposed (out of 2.108 mmol) and this furnished 1.022 mmol of O₂ (equivalent to 2.044 mmol of t-BHP, 99.9%) and 1.831 mmol of *tert*-butanol (89.5%) and 0.108 mmol of di-*tert*-butyl peroxide (10.6%). It may therefore be concluded that the decomposition of t-BHP is catalyzed analogously by all cationic PTCs, independently of the nature of the counteranions, although the decomposition rates differ considerably. All these interactions produce O₂, *tert*-butanol and some di-*tert*-butyl peroxide as the main products. Mass spectrometry furnished similar results, but also indicated the formation of traces of CO₂.

Limited decomposition of t-BHP can be induced by the presence of NaI as well as by Me₄NI, again with a stoichiometric factor of 2. Interestingly, Me₄NI proved to be a very poor catalyst in comparison with the other quaternary ammonium ions containing longer aliphatic chains.

Since a small quantity of iodine was formed on mixing during the application of onium iodides (except for the sparingly soluble Me₄NI!), the influence of iodine was also investigated separately. In the lower half of Table 3, in addition to 0.120 mmol of Hex₄NX (X = Cl⁻, Br⁻ or I⁻), 0.019 or 0.118 mmol of iodine was also applied in the samples. The iodine was homogeneously dissolved with a reddish violet color in chlorobenzene. In the presence of iodine, the rate of t-BHP decomposition catalyzed by chloride and bromide salts was enhanced, and larger amounts of gaseous products were formed, but the ratio $\Delta[\text{t-BHP}]/\Delta[\text{gaseous product}]$ remained unchanged at 2.

In the presence of the iodide salt, however, different behavior was observed. At 0.008 mmol Hex₄NI, the decomposition of t-BHP took place almost quantitatively in 10–15 min, with a stoichiometric factor of 2. When both iodide salt and iodine were applied, the rate of decomposition of t-BHP was reduced

Table 1 Influence of water on the decomposition of t-BHP catalysed by Aliquat 336^a

[H ₂ O]/mmol	Δ[gp ^b]/mmol	Δ[t-BHP]/mmol	Δ[t-BHP]/Δ[gp ^b]
0.062	0.067	0.141	2.10
0.186	0.275	0.582	2.11
0.242	0.326	0.657	2.01
0.298	0.334	0.670	2.00
0.298	0.371	0.746	2.01
0.414	0.305	0.618	2.02

^a Conditions: 1.318 mmol t-BHP and 0.120 mmol Aliquat 336 (methyltrioctylammonium chloride) were dissolved in 8.00 cm³ of chlorobenzene at 70 °C for 120 min in the dark. ^b gp = gaseous product.

considerably, presumably because of the transformation of iodide ion into triiodide. The presence of iodine alone has no influence on the decomposition of t-BHP (see the data in Table 3). This situation is just the opposite to that found for onium chloride and bromide. The rate-increasing effect of iodine in the cases of the chloride and bromide salts, however, cannot be explained by the formation of the corresponding trihalides, since there are great differences between the formation constants: the values¹⁰ for I₂Cl⁻, I₂Br⁻ and I₃⁻ in aqueous solution are 1.66, 10.5 and 710 M⁻¹, respectively. Hence, only in the transformation of I⁻ into I₃⁻ would some observable change in decomposition rate be expected. The situation may well be more involved, since iodine is present together with t-BHP oxidant, which makes possible the transformation of the I₂ first into ICl and IBr, and subsequently into the corresponding mixed trihalide ions, IClI⁻ and IBrI⁻. The corresponding formation constants [similarly in aqueous medium, defined, for example, as ICl(aq) + I⁻(aq) = I₂Cl⁻(aq)] are 3 × 10⁸ and 2.6 × 10⁶ M⁻¹.¹⁰ These consider-

Table 2 Influence of counteranions in onium salts on decomposition of t-BHP^a

PTC	Δ[gp]/mmol	Δ[t-BHP]/mmol	Δ[t-BHP]/Δ[gp]
—	0.038	0.077	2.026
MeOct ₃ NCl	0.077	0.156	2.025
MeOct ₃ NHSO ₄	0.023	0.049	2.130
Hex ₄ NHSO ₄	0.064	0.133	2.078
Hex ₄ NOH	0.110	0.224	2.036
Hex ₄ NCl	0.257	0.515	2.004
Hex ₄ NBr	0.460	0.920	2.000
Bu ₄ NF	0.024	0.053	2.208
Bu ₄ NClO ₄	0.050	0.105	2.100
Bu ₄ NNO ₃	0.145	0.292	2.013
Bu ₄ NCl · H ₂ O	0.151	0.304	2.013
Bu ₄ NSCN	0.286	0.574	2.007
Bu ₄ NBr	0.390	0.781	2.002
Me ₄ NCl	0.060	0.124	2.066
Me ₄ NBr	0.054	0.109	2.018
HdBu ₃ PBr	0.508	1.020	2.007
BzBu ₃ NCl	0.249	0.503	2.020
BzBu ₃ NBr	0.186	0.375	2.016
BzEt ₃ NCl	0.147	0.304	2.068
CetPyCl	0.025	0.053	2.120

^a Conditions: 1.318 mmol t-BHP and 0.120 mmol PTC were dissolved in 8.00 cm³ of chlorobenzene at 70 °C in the dark. Abbreviations: Me, methyl; Oct, octyl; Hex, hexyl; Bu, butyl; Hd, hexadecyl; Bz, benzyl; Et, ethyl; Cet, hexadecyl; Py, pyridinium ion.

ably higher values may serve as the basis of the explanation of the rate increase observed in the cases of the onium chloride and bromide. Because of the lack of the necessary information, earlier explanations made use of data determined in aqueous media, although it is well known that the transition from water to a non-aqueous solvent is commonly attended by an increase of several orders of magnitude in the stability constants of polyhalide ions. The stability constants in chlorobenzene as solvent are not yet available, and it must be

Table 3 Influence of iodide counteranion in onium salts and/or of iodine on decomposition of t-BHP^a

PTC [PTC]/mmol	Δ[gaseous product]	Δ[t-BHP]/mmol	Δ[t-BHP] ^b /mmol	Δ[t-BHP]/Δ[gaseous product]
Hex ₄ NI 0.120	0.092	1.290	1.106	14.02
Hex ₄ NI 0.008	0.370	1.199	0.459	3.24
Hex ₄ NI 0.030	0.158	1.290	0.974	8.16
Hex ₄ NI 0.120	0.073	1.310	1.164	17.94
Hex ₄ NI 0.800	0.047	1.278	1.184	27.19
Hex ₄ NI 0.008	0.625	1.259	0.009	2.014
Hex ₄ NI 0.030	0.653	1.306	0.000	2.000
Bu ₄ NI 0.120	0.097	1.290	1.096	13.29
BzBu ₃ NI 0.120	0.035	1.299	1.229	37.11
MeDd ₃ NI 0.120	0.033	1.306	1.240	39.57
Me ₄ NI 0.120	0.147	0.303	0.000	2.061
NaI · 2H ₂ O 0.120	0.215	0.443	0.013	2.060
Hex ₄ NCl 0.120	0.253	0.515	0.009	2.035
Hex ₄ NCl 0.120 + I ₂ ^c	0.644	1.286	-0.002	1.996
Hex ₄ NCl 0.120 + I ₂ ^d	0.471	0.944	0.002	2.004
Hex ₄ NBr 0.120	0.344	0.693	0.002	2.014
Hex ₄ NBr 0.120 + I ₂ ^c	0.551	1.103	0.001	2.002
Hex ₄ NBr 0.120 + I ₂ ^d	0.596	1.191	-0.001	1.998
Hex ₄ NI 0.008	0.625	1.259	0.009	2.014
Hex ₄ NI 0.008 + I ₂ ^c	0.117	0.236	0.002	2.017
Hex ₄ NI 0.008 + I ₂ ^d	0.066	0.133	0.001	2.015
— —	0.038	0.077	0.001	2.026
— I ₂ ^c	0.034	0.073	0.005	2.147
— I ₂ ^d	0.029	0.061	0.003	2.103

^a Conditions: 1.318 mmol of t-BHP and the given amount of PTC are dissolved in 8.00 cm³ of chlorobenzene, at 70 °C for 120 min in the dark. Abbreviations: Me, methyl; Oct, octyl; Hex, hexyl; Bu, butyl; Bz, benzyl; Dd, dodecyl. ^b Δ[t-BHP]^{*} = Δ[t-BHP] - 2 × Δ[gaseous product], this proportion of the decomposition does not produce O₂. ^c 0.019 mmol I₂. ^d 0.118 mmol I₂.

Table 4 Computed bond distances (pm) in the assumed arrangements (Scheme 1)

Arrangement	O–O	O–H	HOH···O(R)O(H)	HOH···O(H)–O(R)	H···Cl [−]
(i)	146	1 165 2 102	—	203	—
(ii)	151	1 270 2 293	309	—	—
(iii)	157	1 276 2 307	—	336	128
(iv)	143	1 270 2 484	434	—	140
Isolated t-BHP	152	—	—	—	—

emphasized, therefore, that the above explanations may indicate only the tendency of the changes.

As concerns the role of onium salts containing counteranions other than halides, all of them result in decomposition of the hydroperoxide initiator with different degrees of efficiency, but always with the same stoichiometric factor of 2. We therefore believe that the interaction between the hydroperoxide and the onium cation is electrostatic in nature and that the rate of decomposition depends on the effective charge density on the quaternary cation, which is controlled by the nature (electronegativity) and the size and polarizability of the counteranion. For orientation, the ionic radius, polarizability and dimension data¹⁰ are 181 pm and 3.475 Å³ for Cl[−], 196 pm and 4.821 Å³ for Br[−] and 219 pm and 7.216 Å³ for I[−], with dimensions of ~270 pm for I₂Cl[−], ~280 pm for I₂Br[−] and 290 pm for I₃[−].

The pyrolysis of t-BHP was long ago investigated by Milas and Surgenor,¹¹ who found that it is decomposed into O₂ and *tert*-butyl alcohol at 95–100 °C, while methanol, acetone, *tert*-butyl alcohol, formaldehyde and water are formed at 250 °C. The pyrolysis of di-*tert*-butyl peroxide produces only acetone and ethane at 200, 250 and 300 °C. A free radical mechanism was proposed by those authors to explain the thermal decompositions of both t-BHP and di-*tert*-butyl peroxide.

Since a free radical mechanism was earlier assumed to explain the pyrolysis of t-BHP, an EPR method was now used to collect information on the possible mechanism of the decomposition of t-BHP catalysed by onium salts. With the aid of an *N-tert*-butyl- α -phenylnitron spin trap, we were able to detect the formation of two types of free radicals at room temperature in the reaction mixtures containing about 0.8 mmol of t-BHP and 0.06 mmol of Hex₄NX (where X = Cl[−], Br[−] and I[−]) in 2 cm³ of chlorobenzene.

Theoretical considerations

For modeling of the assumed activation process, the PM3 routine¹² included in the Hyperchem package¹³ was used. The

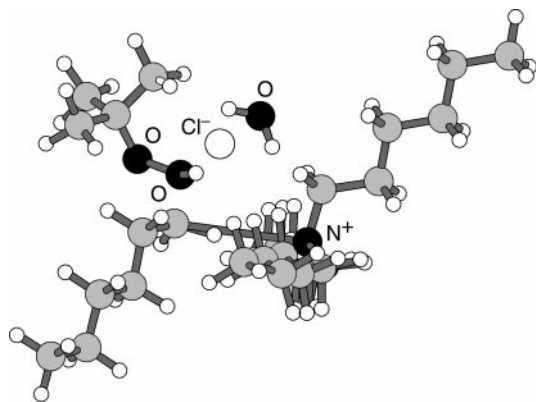


Fig. 1 The minimum structure for arrangement (iii). The larger unmarked atom is carbon and the smaller one is hydrogen.

compounds assumed to participate in the radical-producing processes, such as the onium ion, t-BHP and water, were placed in the vicinity of each other, enforcing close contact. Four arrangements were investigated [see (i)–(iv) in Scheme 1] as the basis of comparison: (i) the onium ion is positioned in the vicinity of the inner, nucleophilic O atom and the water molecule is close to the outer O atom of the hydroperoxide molecule, (ii) the positions are just the opposite of those in (i), *i.e.*, the water molecule is close to the inner O atom, while the onium ion is in the vicinity of the outer O atom. Arrangements (iii) and (iv) were analogous to those in (i) and (ii), except that in these cases the counteranion was also placed in the vicinity of the onium ion. After the initial geometries had been prepared, the compounds were optimized together. At convergence, the gradient norms were always less than 0.1 and the force matrices were found to be positive definites, verifying that minima were found. After minimization, the distances between certain non-hydrogen atoms were determined. They were taken as hydrogen bonds when the distance between the heavy atoms fell within the sum of their van der Waals radii compiled by Bondi¹⁴ and the angle defined by the two heavy atoms and hydrogen (donor atom–H-acceptor atom) was additionally larger than 90°. This double criterion was suggested recently.¹⁵ In the final, minimum arrangements, the O–O bond length in the peroxide was also measured.

In considering the experimentally studied systems, the t-BHP, Hex₄N⁺Cl[−] and H₂O system will be described. After optimization of these components together, with (i) and (ii) taken as the initial arrangements, the minimum structures possessed the following geometric properties. The HOH···O(H)–O(R) distance was 209 pm in arrangement (i) and the HOH···O(R)–O(H) distance was 309 pm [obtained from initial arrangement (ii)]. The former is well within the sum of the van der Waals radii of the oxygens (304 pm), and the second is just outside this limit. The relevant angles in both cases were larger than 90°. It is therefore, safe to say that the water is attached to t-BHP through short (strong) hydrogen bonds (165 pm, 102 pm) in the minimum structure corresponding to arrangement (i), while only weak contacts exist in arrangement (ii) (HOH···O(R)–OH distances of 270 and 293 pm). In these structures, the O–O bond distances in the peroxide were 146 pm [arrangement (i)] and 151 pm [arrangement (ii)]. The O–O bond distance in isolated t-BHP was 152 pm after full geometry optimization. A comparison of these data reveals that stabilization of the O–O bond rather than its activation took place in the optimized agglomerates.

When the chloride counteranion was included in the optimization, the situation changed considerably. Minimum structures corresponding to arrangements (iii) and (iv) were also computed. It emerged that the H₂O molecule was no longer H-bonded to either of the peroxide O atoms in either of these structures. The O–O bond in the peroxide became longer (149 pm) in the agglomerate corresponding to arrangement (iv) than in the structure corresponding to arrangement (ii). However, it was still shorter than that in isolated t-BHP (152 pm). Although this elongation of the O–O bond was prom-

ising, it was still not sufficient to allow the claim that the activated intermediate had been found. However, when chloride was included in the structure corresponding to arrangement (i), the length of the O–O bond increased considerably (iii). It became 157 pm, which is significantly longer than that in the isolated molecule. The results of the optimizations are compiled in Table 4, and the minimum structure for (iii) is depicted in Fig. 1.

Since optimization was performed within the same framework (the same molecules and ions, and the same method), the observed difference is much larger than it should be owing to the unambiguity of the semiempirical method. Accordingly, it may be claimed that the minimum structure (iii), in which the O–O bond was found to be longer than that in the isolated molecule, can be regarded as a possible activated complex in the catalyzed decomposition of the initiator hydroperoxide.

Conclusions

Although there were considerable differences in the rates of the catalysed decomposition of the initiator t-BHP, it was found that the investigated cationic PTCs all accelerate the oxidation of hydrocarbons by O₂. This could serve as further evidence that the decompositions of t-BHP catalyzed by different onium salts are indeed radical processes. It seems probable that homolysis of the hydroperoxide is promoted by the interaction with the onium salt and with a water molecule, the radicals thus formed initiating the oxidation of hydrocarbon present. We consider the interaction between the hydroperoxide and the onium cation to be electrostatic in nature and to depend on the effective charge density on the quaternary cation, which is controlled by the nature and size of the counteranion.

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