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# Characteristics of cationic phase-transfer catalysts in the oxidation of hydrocarbons by O<sub>2</sub>

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The oxidation of tetralin and cyclohexene by  $O_2$  was investigated in the presence of cationic phase-transfer catalysts (PTCs). It was found that the oxidation takes place analogously to the recently investigated catalysed decompositions of hydroperoxide initiator molecules. The natures of both the onium cation and the counteranion are determining factors. The catalytic activity of the onium salt is determined by the effective charge on the onium ion and by the size and polarizability of the anion. For both hydrocarbons, the primary product of oxidation is the corresponding hydroperoxide, which may undergo further oxidation. For tetralin, tetrally hydroperoxide underwent disproportionation into  $O_2$  and tetralol, and reuse of the  $O_2$  thus produced resulted in a considerable "overoxidation" in the closed reactor. Tetralone was formed in a smaller amount. The main products in the oxidation of cyclohexene were its hydroperoxide, cyclohexene oxide and 2-cyclohexen-1-ol. In contrast to the oxidation of tetralin, "overoxidation" did not occur here, and the formation of 2-cyclohexen-1-one was never observed. The oxidations of these hydrocarbons in the presence of cationic PTCs proved to be strongly influenced by the concentration of homogeneously dissolved water. The oxidation products of these hydrocarbons also exerted considerable influence on the progress of the oxidation.

#### Introduction

It was recently reported<sup>1</sup> that cationic PTCs interact with the nucleophilic inner O atom of *tert*-butyl hydroperoxide (t-BHP), or other hydroperoxide initiator molecules. This results in the decomposition into radicals when water is also present in the system, and the latter simultaneously attacks the outer O atom of the hydroperoxide by H-bond formation. The yield of radicals depends on the nature of the quaternary centre of the cationic PTC, the charge density of which is always controlled by the given counteranion. The present paper discusses how the oxidation of tetralin (T) and cyclohexene (Ch) takes place in the presence of either different cationic PTCs with a common anion, or a common onium ion with different anions. It is also demonstrated how the progress of oxidation is influenced by the oxidation products of these substances and by the presence of water.

### **Experimental**

Materials: The PTC reagents and t-BHP were Fluka products and were used without any purification. Cyclohexene and 1,2,3,4-tetrahydronaphthalene (T) were also Fluka products; for removal of their peroxidic impurities, they were passed over an activated  $Al_2O_3$  column, then distilled twice under a N<sub>2</sub> blanket and stored in the dark, in a refrigerator. Chlorobenzene was applied as non-polar solvent. Its purification is described in ref. 2. Cyclohexene oxide (Ch-O), 2-cyclohexen-1-ol (Ch-ol) and 2-cyclohexen-1-one (Ch-one) were Fluka products; and purified by distillation. Fluka 3,4-dihydro-1(2H)-naphthalenone (T-one) was distilled at 138 °C, at 15 mm Hg. 1,2,3,4-Tetrahydro-1-naphthol (T-ol) was recrystallized four times from petroleum ether (30–60 °C).

For many experiments (Tables 1–3), stock solutions of the given PTCs were prepared in chlorobenzene and stored at room temperature in the dark. In others (Tables 5 and 6), aliquots of these catalyst stock solutions were mixed with an equal volume of water adjusted to the given pH, and the mixture was stirred efficiently at 3000 rpm for at least 10 min. Then, after separation of the phases, the organic phase was filtered on a Whatman 1PS silicone-treated phase separator and stored similarly at room temperature and in the dark. These catalyst solutions differ in their homogeneously dissolved water contents. Analogous data can be found in Table 1 in ref. 3.

The oxidation was carried out in the dark in a thermostatted, magnetically well-stirred batch reactor (fitted with a reflux condenser cooled with water to 10 °C). A reaction mixture containing 2.00 or 3.00 cm<sup>3</sup> hydrocarbon and an appropriate volume of catalyst solution was made up to 8.00  $cm^3$  with chlorobenzene, and saturated with dried  $O_2$  for 3 min at room temperature. The reaction vessel was next connected to the thermostat preheated to 70 °C and, after a warming up period, of exactly 3 min, the reactor was attached to a gas burette of syringe type filled with  $O_2$ , fitted with a temperature control, and recording of the O<sub>2</sub> uptake was simultaneously started. The gas measuring device automatically regulates the inside pressure at the atmospheric level. After a net conversion time of 120 min (without the time lag), the reaction products were estimated by iodometry  $(O_{act}, the$ hydroperoxide content) and by gas chromatograpy (the -ol, -one and -epoxide contents). The column for Ch was  $2 \text{ m} \times 4$ mm id filled with Chromosorb W-AW-DMCS coated with Carbowax 20 M; carrier gas:  $N_2$  at 40 cm<sup>3</sup> min<sup>-1</sup>, detector: FID. The column for T was  $1 \text{ m} \times 4 \text{ mm}$  id filled with Chromosorb W coated with 20% LAC IR 296; carrier gas:  $N_2$  at 40 cm<sup>3</sup> min<sup>-1</sup>; detector: FID. Reaction products were

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identified with the aid of authentic samples in both cases. The time lag was defined as the period that elapsed from the time of switching on the heating until the uptake of the first 0.03 cm<sup>3</sup>  $O_2$ .

### **Results and discussion**

### (i) Catalytic efficiencies of different quaternary ammonium salts with chloride as anion

The following sequences of efficiency (expressed as O<sub>2</sub> uptake:  $\Delta$ [O<sub>2</sub>]/mmol 120 min<sup>-1</sup>, given in parentheses) for different quaternary ammonium salts with chloride as anion were found. For the oxidation of Ch (see Table 1): Me<sub>4</sub>N (0.174) < Hex<sub>4</sub>N (1.859) < BnEt<sub>3</sub>N (2.036) < BnBu<sub>3</sub>N (2.282) < MeOct<sub>3</sub>N (2.606) < Bu<sub>4</sub>N · H<sub>2</sub>O (2.855), and for the oxidation of T (see Table 2): Bu<sub>4</sub>N · H<sub>2</sub>O (0.031) < Me<sub>4</sub>N (0.349) < MeOct<sub>3</sub>N (1.010) < Hex<sub>4</sub>N (1.587) < BnBu<sub>3</sub>N (3.771) < BnEt<sub>3</sub>N (4.330).

The sequence of efficiency for quaternary ammonium chloride salts in the catalysed decomposition of the initiator t-BHP was:<sup>1</sup> Me<sub>4</sub>N (0.060) < MeOct<sub>3</sub>N (0.077) < BnEt<sub>3</sub>N (0.147) < Bu<sub>4</sub>N · H<sub>2</sub>O (0.151) < BnBu<sub>3</sub>N (0.249) < Hex<sub>4</sub>N (0.257).

It is seen that for both hydrocarbons the conversions determined during the oxidations do not follow the sequence of the catalysed disappearance of t-BHP. This is understandable, because the  $O_2$  uptake is produced by the chain oxidation of the hydrocarbon present initiated by radicals formed in the PTC-catalysed decomposition of t-BHP. The latter radicals, however, undergo radical-exchange reactions with the hydroperoxide formed in the oxidation of the given hydrocarbon, even in the very early stage of oxidation.

The salt  $Bu_4NCl \cdot H_2O$  must be considered as an exception: this salt hydrolyses in chlorobenzene solutions of both hydrocarbons and produces HCl. (In such solutions, slips of Merck universal pH indicator paper turned red within a few minutes.) In separate experiments, it was checked that the Hex<sub>4</sub>NCland ALCl<sup>†</sup>-(Aliquat<sup>®</sup> 336, MeOct<sub>3</sub>NCl) catalysed oxidations of both substances were strongly inhibited by the addition of 0.120 mmol HCl, which was equivalent to the quantity of Bu<sub>4</sub>NCl·H<sub>2</sub>O used in each run.

For the halide salts, it was observed that onium ions containing shorter alkyl chains (*e.g.* the  $Me_4N^+$  ion) are less active catalysts than the ions bearing longer organophilizing alkyl or aryl chains.

The onium chloride-catalysed oxidations revealed their lower activities not only in the slower formation of the given hydroperoxide, but also in the slower further oxidation steps of the primary products.

### (ii) Dependence of the catalytic activity on the nature of the cationic centre of the onium ion

The catalytic efficiencies of cationic PTCs further depend on the nature of the cationic centre of the onium ion. The consecutive data in parentheses below relate to the O<sub>2</sub> uptakes in the oxidations of tetralin and cyclohexene: BnBu<sub>3</sub>NCl (3.771, 2.282) > HdBu<sub>3</sub>PBr (2.076, 1.420) > HdPyCl (0.842, 1.682). Similar behaviour was earlier described by Ohkubo and Yamabe<sup>4</sup> for the oxidation of cumene.

## (iii) Dependence of the catalytic activities on the nature of the counteranions

The nature of the anion is another factor determining the rate of oxidation of hydrocarbons. In the case of Ch oxidation (see Table 1), the catalytic efficiencies of anions with  $Bu_4N^+$  as cation were as follows:  $I^-(4.039) > Cl^- \cdot H_2O$  (2.855) >

 Table 1
 Oxidation of cyclohexene in the presence of onium salt catalysts<sup>a</sup>

Onium salt catalyst	$\Delta[O_2]/mmol$	$\Delta[O_{act}]^{corr}/mmol$	$\Delta$ [Ch–O]/ mmol	Δ[Ch–ol]/mmol	$\Delta$ [products]- $\Delta$ [O <sub>2</sub> ]/mmol
None	0.061	0.059	0.000	0.001	-0.001
Me <sub>4</sub> NCl	0.174	0.178	0.000	0.000	0.004
(HdPyCl)	1.682	1.213	0.062	0.408	0.001
Hex <sub>4</sub> NCl	1.859	1.492	0.082	0.288	0.003
BnEt <sub>3</sub> NCl	2.036	1.412	0.078	0.533	-0.013
BnBu <sub>3</sub> NCl	2.282	1.571	0.093	0.616	-0.002
MeOct <sub>3</sub> Cl	2.606	1.571	0.105	0.916	-0.014
$Bu_4NCl \cdot H_2O$	2.855	1.929	0.116	0.806	-0.004
Me <sub>4</sub> NBr	0.322	0.317	0.000	0.002	-0.003
Bu <sub>4</sub> NBr	1.118	1.014	0.000	0.090	-0.014
(NaBr)	1.216	0.930	0.074	0.211	-0.001
Hex <sub>4</sub> NBr	1.432	1.173	0.072	0.184	-0.003
BnBu <sub>3</sub> NBr	1.782	1.173	0.094	0.513	-0.002
Me <sub>4</sub> NI	0.158	0.158	0.000	0.000	0.000
$(NaI \cdot 2 H_2O)$	2.134	1.094	0.115	0.917	-0.008
MeDd <sub>3</sub> NI	2.576	-0.001	0.154	2.425	0.002
BnBu <sub>3</sub> NI	3.158	0.218	0.184	2.754	-0.002
Hex <sub>4</sub> NI	3.568	0.178	0.202	3.184	-0.004
Bu <sub>4</sub> NI	4.039	0.318	0.342	3.361	-0.018
Bu <sub>4</sub> NF	0.235	0.019	0.043	0.170	-0.003
Bu <sub>4</sub> NNO <sub>3</sub>	0.936	0.894	0.026	0.018	0.002
Bu <sub>4</sub> SCN	1.031	0.497	0.051	0.480	-0.003
Bu <sub>4</sub> NClO <sub>4</sub>	1.522	1.213	0.099	0.205	-0.005
Hex <sub>4</sub> NOH	0.518	0.497	0.000	0.019	-0.002
Hex <sub>4</sub> HSO <sub>4</sub>	1.530	1.253	0.000	0.278	0.001
MeOct <sub>3</sub> NHSO <sub>4</sub>	0.060	0.059	0.000	0.001	0.000
HdPyCl	1.682	1.213	0.062	0.408	0.001
HdBu <sub>3</sub> PBr	1.420	1.153	0.065	0.194	-0.011

<sup>a</sup> Conditions: A mixture of 19.744 mmol Ch, 0.100 mmol t-BHP initiator and 0.120 mmol onium salt was made up to 8.00 cm<sup>3</sup> with chlorobenzene; in the dark, at 343 K, reaction time: 120 min. Abbreviations: Ch: cyclohexene, Ch–O: cyclohexene oxide, Ch–ol: 2-cyclohexen-1-ol, Hex: hexyl, Bu: butyl, Et: ethyl, Bn: benzyl, Me: methyl, Oct: Octyl, Hd: hexadecyl, Dd: dodecyl and Py: pyridinium.

 $<sup>\</sup>dagger$  It should be mentioned here, that, although ALCl is an efficient PTC, it is not a homogeneous product; it contains C<sub>8</sub> and C<sub>10</sub> chains, with C<sub>8</sub> predominating.

 Table 2
 Oxidation of tetralin in the presence of onium salt catalysts<sup>a</sup>

Onium salt catalyst	$\Delta[O_2]/mmol$	$\Delta[O_{act}]^{corr}/mmol$	$\Delta$ [T-one]/ mmol	$\Delta[T-ol]/mmol$	$\Delta$ [products]– $\Delta$ [O <sub>2</sub> ]/mmol
None	0.252	0.258	0.000	0.000	-0.006
$Bu_4NCl \cdot H_2O$	0.031	0.011	0.000	0.020	0.000
Me <sub>4</sub> NCl	0.349	0.298	0.000	0.051	0.000
(HdPyCl)	0.842	0.736	0.000	0.104	-0.002
MeOct <sub>3</sub> Cl	1.010	0.358	0.258	0.775	0.381
Hex <sub>4</sub> NCl	1.587	0.696	0.770	0.241	0.120
BnBu <sub>3</sub> NCl	3.771	2.248	0.501	2.068	1.046
BnEt <sub>3</sub> NCl	4.330	2.605	0.502	2.412	1.189
(NaBr)	0.378	0.338	0.000	0.077	0.037
BnBu <sub>3</sub> NBr	1.529	0.934	0.206	0.782	0.393
Me₄NBr	1.609	1.293	0.179	0.278	0.141
Hex <sub>4</sub> NBr	1.637	1.074	0.431	0.244	0.112
Bu₄ŇBr	1.813	1.312	0.238	0.488	0.225
HdBu <sub>3</sub> PBr	2.076	1.611	0.195	0.524	0.254
(NaI · Ž H <sub>2</sub> O)	0.810	0.755	0.000	0.096	0.041
Me <sub>4</sub> NI	0.888	0.815	0.000	0.069	-0.004
Hex <sub>4</sub> NI	1.163	-0.100	0.412	1.701	0.850
Bu <sub>4</sub> NI	2.519	-0.100	0.544	4.149	2.074
BnBu <sub>3</sub> NI	2.879	-0.100	1.066	3.838	1.925
MeDd <sub>3</sub> NI	2.957	-0.100	1.124	3.867	1.934
Bu <sub>4</sub> NNO <sub>3</sub>	0.179	0.178	0.000	0.000	-0.001
Bu <sub>4</sub> NF	0.654	-0.001	0.174	0.981	0.500
Bu <sub>4</sub> SCN	0.924	0.377	0.235	0.690	0.378
$Bu_{4}NClO_{4}$	1.849	1.292	0.160	0.844	0.477
Hex <sub>4</sub> NHSO <sub>4</sub>	1.016	0.895	0.094	0.103	0.076
Hex <sub>4</sub> NOH	2.964	2.128	0.298	1.044	0.506
MeOct <sub>3</sub> NHSO <sub>4</sub>	0.094	0.079	0.000	0.021	0.006
HdPyČl	0.842	0.736	0.000	0.104	-0.002
HdBu <sub>3</sub> PBr	2.076	1.611	0.195	0.524	0.254

<sup>*a*</sup> Conditions: A mixture of 22.077 mmol T, 0.100 mmol t-BHP initiator and 0.120 mmol onium salt was made up to 8.00 cm<sup>3</sup> with chlorobenzene; reaction time: 120 min, in the dark, at 343 K. Abbreviations: T: tetralin, T-one: 3,4-dihydro-1-(2*H*)-naphthalenone, T-ol: 1,2,3,4tetrahydro-1-naphthol, Hex: hexyl, Bu: butyl, Et: ethyl, Bn: benzyl, Me: methyl, Oct: octyl, Hd: hexadecyl, Dd: dodecyl, Py: pyridinium.

 $\begin{array}{ll} ClO_4^- & (1.522) > Br^- & (1.118) > SCN^- & (1.031) > NO_3^- \\ (0.936) > F^- & (0.235) & \text{or with } Hex_4N^+ & \text{as cation: } I^- \\ (3.568) > Cl^- & (1.859) > HSO_4^- & (1.530) > Br^- & (1.432) > OH^- \\ (0.518). \end{array}$ 

Bromide salts, and even more so iodides, are in general more effective catalysts than chlorides for hydrocarbon oxidation by  $O_2$ . The replacement of chloride by bromide with  $Hex_4N^+$  cation resulted in a 3% increase in  $O_2$  uptake, as T-OOH; the T-one formation was somewhat hindered, while the concentration of T-ol remained at the same level. From this finding, it may be tentatively concluded that the rate of disproportionation of T-OOH is not influenced (or to only the same slight extent as for chloride) by the bromide salt.

In the presence of iodide, hydroperoxide was not found, but there was a larger increase in the T-ol yield, together with an increase in the "overoxidation", as mentioned earlier. This indicates that the disproportionation of T-OOH into  $O_2$  and T-ol is probably promoted by the iodide salt alone. BnEt<sub>3</sub>N<sup>+</sup>, BnBu<sub>3</sub>N<sup>+</sup> and Bu<sub>4</sub>N<sup>+</sup> halides behaved similarly. In contrast, such behaviour was not observed for Me<sub>4</sub>N<sup>+</sup> iodide, which is barely soluble in chlorobenzene, the oxidation stopped at the formation of T-OOH, and no formation of iodine was observed, which is a characteristic of the more soluble quaternary ammonium iodide salts containing longer organophilizing chains. Interestingly, sodium iodide, which is similarly soluble in non-polar solvents, cannot be regarded as an oxidation catalyst.

Bromide salts proved to be more active than the chlorides with respect to both the primary and the subsequent steps of the Ch oxidation. The iodide salts were even better oxidation catalysts, promoting the formation of Ch-O and Ch-ol at the expense of the primary product Ch-OOH.

The following may be stated as concerns the influence of other anions. The exchange of chloride for  $HSO_4^-$  resulted in an approximately 90% decrease in the rate of oxidation of T

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in the case of  $MeOct_3N^+$  (see Table 2). The consumed  $O_2$  was converted to T-OOH, which was hardly transformed further into T-ol and T-one. In the case of  $Hex_4N^+$ , the same anion exchange caused only a 36% drop in the rate of oxidation, though the formation of higher oxidation products was similarly suppressed here.

As concerns the catalysed oxidation of Ch, the replacement of chloride by HSO<sub>4</sub><sup>-</sup> resulted in a large drop in the oxidation rate for  $MeOct_3N^+$ , but a much lower decrease was found for Hex<sub>4</sub>N<sup>+</sup>. As common behavior, it can be emphasized that Ch-O was not formed in either case. We have not been able to check yet whether or not such an (epoxide-formation hindering) influence of HSO<sub>4</sub><sup>-</sup> ion is manifested for other onium ions too. However, it was recently reported by Sato et al.5 that the use of onium hydrogensulfates rather than conventional chlorides as PTCs was crucial for high reactivity in the epoxidation of terminal olefins in a system analogous to described by Venturello *et al.*:<sup>6,7</sup> that  $H_{2}O_{2} Na_2WO_4$ -MeBu<sub>3</sub>NHSO<sub>4</sub>-NH<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>. They further found that the addition of NaCl significantly retarded the epoxidation.

It is worth noting, that the harder fluoride ion has a much lower catalytic activity than that of chloride.  $NO_3^-$  and the more easily polarizable SCN<sup>-</sup> exhibit medium catalytic efficiencies, whereas the scarcely polarizable large  $ClO_4^-$  exerts a considerably higher activity. This points to the size and the polarizability of the anion being factors contributing to the catalytic efficiency of the onium salts in the oxidation of these hydrocarbons.

# (iv) Influence of iodine on the catalytic efficiency of the onium halides

Table 3 presents data obtained during the oxidation of T and Ch catalysed by onium halides in the presence of iodine in

 Table 3
 Influence of iodine on catalytic activities of tetrahexylammonium halides in the oxidation of hydrocarbons<sup>a</sup>

Onium salt	Iodine/ mmol	$\Delta[O_2]/mmol$	$\Delta[O_{act}]^{corr}/mmol$	$\Delta$ [T-one]/ mmol	$\Delta[T- ol]/mmol$	$\Delta$ [products]– $\Delta$ [O <sub>2</sub> ]/mmol
22.077 mmol	tetralin					
None	none	0.252	0.258	0.000	0.000	-0.006
Hex <sub>4</sub> NCl	none	1.587	0.696	0.770	0.241	0.120
Hex <sub>4</sub> NCl	0.0197	3.307	1.193	1.106	2.006	0.996
Hex <sub>4</sub> NCl	0.118	3.946	-0.100	1.461	5.168	2.583
Hex <sub>4</sub> NBr	none	1.637	1.074	0.431	0.244	0.112
Hex <sub>4</sub> NBr	0.0197	2.112	-0.100	0.802	2.821	1.411
Hex <sub>4</sub> NBr	0.118	4.719	-0.100	2.136	5.406	2.723
Hex <sub>4</sub> NI	none	3.452	-0.100	1.426	4.291	2.165
Hex <sub>4</sub> NI	0.0197	4.657	-0.100	2.177	5.142	2.562
Hex <sub>4</sub> NI	0.118	2.174	-0.100	0.687	3.184	1.597
19.744 mmol	cyclohexene					
none	none	0.061	0.059	0.000	0.001	-0.001
Hex <sub>4</sub> NCl	none	1.859	1.492	0.082	0.288	0.003
Hex <sub>4</sub> NCl	0.0197	1.944	-0.001	0.130	1.805	-0.010
Hex <sub>4</sub> NCl	0.118	4.034	-0.020	0.246	3.787	-0.021
Hex <sub>4</sub> NBr	none	1.432	1.173	0.072	0.184	-0.003
Hex <sub>4</sub> NBr	0.0197	2.818	0.179	0.152	2.484	-0.003
Hex <sub>4</sub> NBr	0.118	4.475	-0.100	0.165	4.408	-0.002
Hex <sub>4</sub> NI	none	3.568	0.178	0.202	3.184	-0.004
Hex <sub>4</sub> NI	0.0197	2.724	-0.001	0.165	2.551	-0.009
Hex <sub>4</sub> NI	0.118	2.622	-0.100	0.137	2.588	0.003

<sup>*a*</sup> Conditions: A mixture of the given quantity of hydrocarbon, 0.100 mmol t-BHP initiator and 0.120 mmol onium salt was made up to 8.00 cm<sup>3</sup> with chlorobenzene; in the dark, reaction time: 120 min, at 343 K.

different quantities. This investigation was necessary because the use of onium iodides as catalysts always involves the formation of some iodine in the oxidation system, and the appearance of iodine strongly influences the decomposition of the initiating hydroperoxide.

The addition of iodine caused increases in the oxidation rates for both the chlorides and the bromides, while rate decreases were observed for the iodides, presumably as a consequence of the transformation of the halides into the corresponding trihalide (or mixed trihalide) anions,<sup>1</sup> especially when the concentrations of halide and iodine were commensurable.

For T, in the presence of the most easily oxidizable onium iodide (except for  $Me_4NI$ , which is inert in this respect) as catalyst, when only a small quantity of iodine was applied, no T-OOH could be detected, since it is decomposed into T-ol and  $O_2$  immediately after its formation. This tendency was not modified on further increase of the iodine concentration in the reaction mixture.

In the case of the moderately oxidizable bromide salt, the disproportionation of T-OOH proved to be much slower; consequently, in the absence of iodine, a considerable quantity of  $O_{act}$  was detected. When a small quantity of iodine was also applied, the rate of  $O_2$  uptake was increased. Nevertheless, no formation of T-OOH was observed; instead, there were considerable increases in the concentrations of T-one and T-ol together with the "overoxidation" *i.e.*  $(\Delta[O_2])^{exc}(= \Delta[\text{products}] - \Delta[O_2])$ . In the presence of an equivalent quantity of iodine, the oxidation rate was further increased, together with the higher oxidation of T, but hydroperoxide was entirely absent. This points to the fact that even a minute amount of iodine is able to promote the disproportionation of T-OOH, probably by a route involving radicals similarly to the steps proposed earlier by Sheldon and van Doorn.<sup>8</sup>

For the onium chloride, which is most resistant to oxidation, the rate of T oxidation was again increased on addition of iodine, but all the hydroperoxide formed was removed only when an equivalent quantity (*i.e.* equivalent to the chloride) of iodine was applied.

In the case of the Ch oxidation, different results were obtained. This was due to the fact that Ch-OOH does not

disproportionate into  $O_2$  and Ch-ol, even in the presence of iodine or some other catalyst (see the final columns of Tables 1 and 3). The catalysed oxidations of Ch reveal the following sequence of efficiency for the Hex<sub>4</sub>N<sup>+</sup> halides: I<sup>-</sup> (3.568) > Cl<sup>-</sup> (1.859) > Br<sup>-</sup> (1.432). When some iodine was also applied, the overall rates of oxidation were increased for the chloride and bromide salts, together with the formation of further products of oxidation: Ch-O and Ch-ol. In contrast, for the iodide salt, the O<sub>2</sub> uptake was somewhat decreased when iodine was simultaneously applied, and the extent of formation of Ch-OOH, Ch-O and Ch-ol was also reduced, especially when a larger quantity of iodine was introduced (see Table 3), due to the formation of the bulky and easily polarizable I<sub>3</sub><sup>-</sup> ion.<sup>1</sup>

# (v) Role of water in the oxidation of hydrocarbons catalysed by cationic PTCs

According to the report of Fendler,<sup>9</sup> the most important difference between aqueous and reversed micelles is that substrates do not penetrate appreciably into the former, but, if polar, they are localized in the hydrophilic cavities of the reversed micelles. The kinetic effects observed are consequences of substrate solubilization in the micellar pseudophase. These effects can be attributed to electrostatic, hydrophobic, nucleophilic, and/or electrophilic interactions, accompanied by alterations in the free energy of activation for the overall process. Micelles can bind substrates fairly strongly in specific orientations and configurations in their polar region. It is known further that water can promote the formation of larger and more stable inverted (reversed) micelles.

On the other hand, it was earlier observed<sup>10</sup> that the rates of uncatalysed oxidation of hydrocarbons by  $O_2$  are influenced according to a maximum curve by water homogeneously dissolved in the non-polar solvents. In the presence of traces, or a much higher amount of water (when the water forms a separate phase), the oxidation takes place at a very low rate; at intermediate water contents, as the concentration of water is increased, the oxidation is first promoted then inhibited. Accordingly, it was to be expected that the oxidation of hydrocarbons catalysed by cationic PTCs would cer-

 Table 4
 The influence of water on the oxidation of hydrocarbons catalysed by cationic PTCs<sup>a</sup>

PTC	H <sub>2</sub> O/ mmol	$\Delta[O_2]/mmol$	Δ[O <sub>act</sub> ] <sup>corr</sup> mmol	Δ[T-one] /mmol	Δ[T-ol] /mmol	$\Delta [O_2]^{exc}$ /mmol	Δ[Ch-O] /mmol	$\Delta$ [Ch-ol] /mmol
ALC1*	0.390	3.506	2.287	0.855	0.717	0.356	_	_
ALC1	0.334	1.332	0.696	0.266	0.743	0.373	_	_
Hex₄NCl*	0.281	1.425	0.417	0.468	1.079	0.539	_	_
Hex <sub>4</sub> NCl	0.273	1.606	0.616	0.296	1.396	0.702	_	—
ALCl*	0.301	2.547	1.650		_	0.001	0.075	0.823
ALC1	0.282	3.272	2.983	_	_	-0.036	0.117	0.136
Hex₄NCl*	0.305	3.154	1.690	_	_	0.003	0.147	1.320
Hex <sub>4</sub> NCl	0.258	1.303	0.544	—	—	0.001	0.110	0.650
ALCl Hex <sub>4</sub> NCl* Hex <sub>4</sub> NCl	0.282 0.305 0.258	3.272 3.154 1.303	2.983 1.690 0.544		 	$-0.036 \\ 0.003 \\ 0.001$	0.117 0.147 0.110	0.136 1.320 0.650

<sup>*a*</sup> Conditions: A mixture of 22.077 mmol tetralin or 19.744 mmol cyclohexene + 0.100 mmol t-BHP + 0.048 mmol of the given PTC (either saturated with water adjusted to pH 4.5, denoted by \*, or without water saturation) was made up to 8.00 cm<sup>3</sup> with chlorobenzene; at 343 K, in the dark, reaction time 120 min. The water content was determined in separate samples with a Metrohm 684 KF Coulometer, using Riedel de Haen No. 34836 Hydromat-Coulomat reagent solution.

tainly be influenced by water. The data in Table 4 show that the activities of onium salt catalysts depend strongly on the quantity of homogeneously dissolved water. The rate of oxidation of T catalysed by ALCl was considerably higher when the catalyst solution was previously saturated with water. However, just the opposite was true when  $\text{Hex}_4\text{NCl}$  was used instead of ALCl as catalyst.

In the oxidation of Ch ALCl proved to be a better catalyst when it was not saturated with water. In contrast, in the catalysis with  $Hex_4NCl$ , the efficiency was increased when the catalyst solution was saturated with water. These observations point to the fact that the individual behavior of hydrocarbons with respect to oxidation can be modified by the water content of the reaction mixture. It is likely that aggregates containing restricted number of monomers associate to form lamellar micelles, with the polar and hydrophobic groups being placed end to end and tail to tail, with water, organic solvents, and substrates between them. The presence of water causes the micelles to swell and to assume different shapes and hence their kinetic behavior is altered. In the absence of traces of water it is possible that the surfactant does not aggregate at all.

### (vi) Influence of the products of oxidation on the oxidation of hydrocarbons

The aim of this investigation was to acquire information on the reasons for termination of the oxidation reactions of hydrocarbons by  $O_2$ . To this end, the influences of the -ol, -one and epoxide products of the oxidations of T and Ch, were examined. (The influence of Ch-one was also studied, in spite of the fact that it was never observed to be formed under the experimental conditions used here. This finding is in contrast with the observations of Van Sickle *et al.*,<sup>11</sup> who detected minute quantities of -one products during the uncatalysed oxidations of cyclic olefins (cyclopentene, Ch and cycloheptene) under milder conditions (at 60 °C), but only after a prolonged reaction time (811 min).) The data obtained in the presence of ALCl and Hex<sub>4</sub>NCl as PTCs are presented in Tables 5 and 6.

### General comments

The data in Tables 1–6 convincingly demonstrate that the effects of PTCs on the oxidation of hydrocarbons are rather individual and depend considerably on the nature of the hydrocarbon to be oxidized. This occurs in spite of the fact that the primary role of the cationic PTCs is always the same: the activation of  $O_2$  in its triplet spin state. The activation of  $O_2$  is attained by the oxidation of the hydrocarbon present, during which insertion of the triplet  $O_2$  molecule in one of the (usually activated for different reasons) C–H bond(s) of the given hydrocarbon results in the corresponding hydro-

peroxide in the singlet spin state. The O–O bond of the hydroperoxide thus formed breaks to furnish chain-carrying radicals by interaction with the cationic PTCs. This interaction, however, is not the sole role of the onium salts in the catalysed oxidation because considerable changes were observed in the rates and in the extents of product formation when the oxidation was catalysed by another cationic PTC, *e.g.* when Hex<sub>4</sub>NCl was applied instead of ALCl. From a comparison of

**Table 5** Oxidation of hydrocarbons with  $O_2$  catalysed by 0.006 M ALCl at pH 4.5<sup>*a*,*b*</sup>

Tetralin	Cyclohexene
Additive: none $\Delta[O_2]$ 3.506 $\Delta[O_{ac}]^{cort}$ 2.287 $\Delta[T-one]$ 0.855 $\Delta[T-ol]$ 0.717 $\Delta[O_2]^{exe}$ 0.356	$\begin{array}{l} \Delta[O_2] \ 2.547 \\ \Delta[O_{ac}]^{corr} \ 1.650 \\ \Delta[O_2]^{exc} \ 0.001 \\ \Delta[Ch-O] \ 0.075 \\ \Delta[Ch-ol] \ 0.823 \end{array}$
T-ol 3.000 $\Delta$ [O <sub>2</sub> ]: 0.408 $\Delta$ [O <sub>acl</sub> ] <sup>corr</sup> : -0.159 $\Delta$ [T-one]: 0.702 $\Delta$ [T-ol]: -0.234 $\Delta$ [O <sub>2</sub> ] <sup>core</sup> : -0.102 After reaction: ΣΔ[T-ol]: 3.483	$\Delta$ [O <sub>2</sub> ]: -0.464 $\Delta$ [O <sub>acl</sub> ] <sup>corr</sup> : -0.556 Δ[Ch-O]: -0.015 Δ[Ch-ol]: 0.115 After reaction: ΣΔ[T-ol]: 3.000
T-one 3.000 $\Delta$ [O <sub>2</sub> ]: -0.490 $\Delta$ [O <sub>acl</sub> ] <sup>eorr</sup> : -0.756 $\Delta$ [T-one]: -0.837 $\Delta$ [T-ol]: 2.238 $\Delta$ [O <sub>2</sub> ] <sup>exc</sup> : 1.118 After reaction: ΣΔ[T-one]: 3.018	$\Delta$ [O <sub>2</sub> ]: 0.254 $\Delta$ [O <sub>ac]</sub> <sup>corr</sup> : 0.160 $\Delta$ [Ch-O]: 0.091 $\Delta$ [Ch-ol]: 0.027 After reaction: ΣΔ[T-one]: 3.004
Ch-O 1.978 $\Delta$ [O <sub>2</sub> ]: -2.123 $\Delta$ [O <sub>act</sub> ] <sup>eorr</sup> : -1.389 $\Delta$ [T-one]: -0.698 $\Delta$ [T-ol]: 0.011 $\Delta$ [O <sub>2</sub> ] <sup>exe</sup> : 0.024 After reaction: ΣΔ[Ch-O]: 1.979	$\begin{split} &\Delta[O_2]: -1.622 \\ &\Delta[O_{ac}]^{\text{corr}}: -0.935 \\ &\Delta[\text{Ch-O}]: -0.023 \\ &\Delta[\text{Ch-o}]: -0.552 \end{split}$ After reaction: $\Sigma\Delta[\text{Ch-O}]: 2.009$
Ch-ol 3.056 $\Delta[O_2]$ : -1.544 $\Delta[O_{act}]^{corr}$ : -1.034 $\Delta[T-one]$ : -0.673 $\Delta[T-ol]$ : 0.333 $\Delta[O_2]^{ex}$ : 0.166 After reaction: $\Sigma\Delta[Ch-ol]$ : 3.057	$\Delta$ [O <sub>2</sub> ]: -1.287 $\Delta$ [O <sub>acl</sub> ] <sup>corr</sup> : -0.875 Δ[Ch-O]: -0.042 Δ[Ch-ol]: -0.436 After reaction: ΣΔ[Ch-ol]: 3.450
Ch-one 3.108 $\Delta[O_2]: -0.029$ $\Delta[O_{act}]^{orr}: -0.199$ $\Delta[T-one]: -0.321$ $\Delta[T-0]: 1.012$ $\Delta[O_2]^{exc}: 0.518$ After reaction: $\Sigma\Delta[Ch-one]: 3.108$	$\Delta$ [O <sub>2</sub> ]: 0.128 $\Delta$ [O <sub>acl</sub> ] <sup>orr</sup> : 0.000 Δ[Ch-O]: 0.095 Δ[Ch-ol]: 0.021 After reaction: ΣΔ[Ch-one]: 3.450

<sup>*a*</sup> Composition: A mixture of 22.077 mmol tetralin or 19.744 mmol cyclohexene, -0.100 mmol t-BHP + 0.048 mmol catalyst + a given quantity of additive was made up to 8.00 cm<sup>3</sup> with chlorobenzene. <sup>*b*</sup> All concentrations in mmol. Table 6 Oxidation of hydrocarbons with  $\rm O_2$  catalysed by 0.006 M  $\rm Hex_4NCl$  at pH  $4.5^{a,b}$ 

Tetralin	Cyclohexene
Additive: none $\Delta[O_2]$ 1.425 $\Delta[O_{ac1}]^{corr}$ 0.417 $\Delta[T-one]$ 0.468 $\Delta[T-ol]$ 1.079 $\Delta[O_2]^{exc}$ 0.539	$\begin{array}{l} \Delta[{\rm O}_2] \ 3.154 \\ \Delta[{\rm O}_{acl}]^{\rm corr} \ 1.690 \\ \Delta[{\rm Ch-ol}] \ 0.147 \\ \Delta[{\rm Ch-ol}] \ 1.320 \end{array}$
T-ol 3.000 $\Delta$ [O <sub>2</sub> ]: 2.050 $\Delta$ [O <sub>ac1</sub> ] <sup>corr</sup> : 0.995 $\Delta$ [T-one]: 0.671 $\Delta$ [T-ol]: 0.777 $\Delta$ [O <sub>2</sub> ] <sup>esc</sup> : 0.393 After reaction: ΣΔ[T-ol]: 4.856	$\begin{split} \Delta[O_2]: & -1.211 \\ \Delta[O_{acl}]^{corr}: & -0.796 \\ \Delta[Ch-O]: & -0.055 \\ \Delta[Ch-ol]: & -0.353 \end{split}$ After reaction: $\Sigma\Delta[T-ol]: 3.022$
T-one 3.000 $\Delta[O_2]$ : 0.672 $\Delta[O_{ac}]^{corr}$ : 0.199 $\Delta[T-one]$ : -0.405 $\Delta[T-o1]$ : 1.800 $\Delta[O_2]^{ex}$ : 0.922 After reaction: ΣΔ[T-one]: 3.063	$\begin{split} \Delta[O_2]: & -0.710 \\ \Delta[O_{acl}]^{corr}: & -0.358 \\ \Delta[Ch-O]: & -0.010 \\ \Delta[Ch-ol]: & -0.354 \end{split}$ After reaction: $\Sigma\Delta[T\text{-one}]: 3.001$
Ch-O 1.978 $\Delta$ [O <sub>2</sub> ]: -0.056 $\Delta$ [O <sub>ac]</sub> ] <sup>corr</sup> : 0.478 $\Delta$ [T-one]: -0.204 $\Delta$ [T-ol]: -0.667 $\Delta$ [O <sub>2</sub> ] <sup>ex</sup> : -0.337 After reaction: ΣΔ[Ch-O]: 1.982	$\begin{array}{l} \Delta[O_2]: -2.453 \\ \Delta[O_{acl}]^{corr}: -1.193 \\ \Delta[Ch-O]: -0.104 \\ \Delta[Ch-ol]: -1.145 \end{array}$ After reaction: $\Sigma\Delta[Ch-O]: 2.022$
Ch-ol 3.056 $\Delta[O_2]$ : 1.679 $\Delta[O_{acl}]^{corr}$ : 1.274 $\Delta[T-one]$ : 0.123 $\Delta[T-ol]$ : 0.589 $\Delta[O_2]^{exc}$ : 0.307 After reaction: $\Sigma\Delta[Ch-ol]$ : 3.060	$\Delta$ [O <sub>2</sub> ]: -1.814 $\Delta$ [O <sub>act</sub> ] <sup>corr</sup> : -1.074 $\Delta$ [Ch-O]: -0.029 $\Delta$ [Ch-ol]: -0.772 After reaction: ΣΔ[Ch-ol]: 3.604
Ch-one 3.108 $\Delta[O_2]$ : 0.171 $\Delta[O_{ac}]^{corr}$ : 0.279 $\Delta[\text{T-one}]$ : -0.029 $\Delta[\text{T-ol}]$ : -0.116 $\Delta[O_2]^{exc}$ : -0.037 After reaction: $\Sigma\Delta[\text{Ch-one}]$ : 3.114	$\begin{array}{l} \Delta[O_2]: -2.212 \\ \Delta[O_{acl}^{orr:} -1.213 \\ \Delta[Ch-O]: 0.040 \\ \Delta[Ch-ol]: -1.038 \end{array}$ After reaction: $\Sigma\Delta[Ch-one]: 3.111 -$

<sup>*a*</sup> Composition: A mixture of 22.077 mmol tetralin or 19.744 mmol cyclohexene + 0.100 mmol t-BHP + 0.048 mmol catalyst + a given quantity of additive was made up to 8.00 cm<sup>3</sup> with chlorobenzene. <sup>*b*</sup> All concentrations in mmol.

the data in Tables 5 and 6, it appears that ALCl was a more effective catalyst than the homogeneous and uniform  $Hex_4NCl$  in the oxidation of T. Just the opposite was true for the oxidation of Ch. The individuality of the different PTCs can be clearly observed when the influences of the oxidation products on the oxidations of T and Ch are compared. This can readily be seen in Table 7 where the O<sub>2</sub> uptakes are given for each case, and the symbols + and - illustrate an increase or a decrease in the O<sub>2</sub> uptake after the initial introduction of the oxidation products of these hydrocarbons. These findings indicate that the cationic PTCs participate not only in the O<sub>2</sub>

Table 7Comparison of the activities of ALCl and  $Hex_4NCl$  as catalysts at pH 4.5 in the oxidation of hydrocarbons

Catalyst	ALCI	ALCI	Hex <sub>4</sub> NCl	Hex <sub>4</sub> NCl
Additive	Т	Ch	Т	Ch
None α-Tetralol α-Tetralone Cyclohexene oxide 2-Cyclohexen-1-ol 2-Cyclohexen-1-one	3.506 + - - -	2.547  +  +	1.425 + + + + + + +	3.154

activation step, but also in the subsequent events in the oxidation of hydrocarbons.

As concerns the termination of the oxidation of hydrocarbons by  $O_2$ , after a prolonged (15 h) oxidation, besides those already mentioned we could not detect any other reaction product which could be regarded as an inhibitor, in spite of the fact that the reaction rate was slowed considerably.

#### Some additional comments on the influences of certain additives

In the oxidation of T, the addition of T-ol exerted a promoting effect: the  $O_2$  uptake was increased by about 12%, while the yield of T-OOH was somewhat suppressed and the time lag remained unchanged. The concentration of T-one was almost doubled, but at the same time the concentration of T-ol was reduced to 67%; in parallel with this, the "overoxidation" also decreased, by about the same extent. This observation indicates that the disproportionation of T-OOH is an equilibrium process, the extent of which is reduced when the T-ol concentration is initially increased. As regards the increase in the T-one concentration, this finding seems to be in harmony with the observation of Lavabre et al.12 that in the self-initiated and uncatalysed oxidation of T by O<sub>2</sub> the rate of formation of T-one is enhanced by the addition of 0.02 M T-ol initially. We consider that the increased T-one formation in response to T-ol addition is due to enhancement of the radical isomerization step: <sup>12</sup> HRO'  $\rightarrow$  'R-OH. This is probably promoted by tetralol through the formation of a double H-bond interaction complex between HRO' and T-ol, which then undergoes a fast exothermic decomposition into 'R-OH and T-ol. T-one is produced in a subsequent H-abstracting step by one of the radicals present.

The influence of the addition of  $\alpha$ -tetralone (3,4-dihydro-1(2*H*)-naphthalenone) suggests that the disproportionation of T-OOH can be promoted by T-one, probably by H-bond interaction. Further, it is assumed that the decrease in the  $\alpha$ -tetralone concentration is due to a Bayer–Villiger<sup>13,14</sup> oxidation reaction between T-one and some of the hydroperoxide present, resulting in an alkyl(aryl)-4-(hydroxyphenyl) butyrate or its lactone derivative. According to Schroeter,<sup>15</sup>  $\alpha$ -tetralone was transformed into 4-hydroxy-4-(o-hydroxyphenyl)butyric acid lactone when the oxidation was carried out by peroxymonosulfuric acid. In our view, the hydroxylated derivative described by Schroeter is due to the presence of hydrogen peroxide produced during the preparation of peroxymonosulfuric acid used in this patent.

#### Conclusions

The oxidations of T and Ch by O2 can be catalysed by cationic PTCs, but to rather different extents. The rates of these oxidations generally follow the rates of decomposition of the corresponding hydroperoxide, which is the primary product of oxidation. T-OOH disproportionates into  $O_2$  and T-ol. The reuse of  $O_2$  results in a considerable "overoxidation" in a closed reactor. The disproportionation is probably an equilibrium process, which can be suppressed by the addition of T-ol at the start of the reaction. Such a reaction cannot be observed in the case of Ch-OOH. The catalytic efficiencies of PTCs were determined. The activity of the onium salt catalyst depends on the nature of the positive central atom, the actual charge density of which is determined by the nature of the cation and the size and polarizability of the anion. The activities of the onium halides can therefore be strongly influenced by the addition of iodine, as a consequence of the formation of  $I_3^-$  or mixed trihalide anions. The structures and catalytic activities of inverse micelles can be altered considerably by the solubilized water content of the reaction mixtures. The oxidation products of the investigated hydrocarbons exert a strong influence on the rates of their oxidation by  $O_2$ .

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### References

 L. J. Csányi, K. Jáky, I. Pálinkó, A. Rockenbauer and L. Korecz, Phys. Chem. Chem. Phys., 2000, 2, 3801.

- 2 L. J. Csányi, K. Jáky and K. Hollósi, Oxid. Commun., 1984, 6, 199.
- 3 L. J. Csányi, K. Jáky and G. Galbács, J. Mol. Catal. A, 2000, 164, 109.
- 4 K. Ohkubo and T. Yamabe, Bull. Jpn. Petroleum Inst., 1970, 12, 130.
- 5 K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, J. Org. Chem., 1996, 61, 8310.
- 6 C. Venturello, R. D'Aloiso, J. C. J. Bart and M. Ricci, J. Mol. Catal., 1985, **32**, 107.
- 7 C. Venturello, E. Alneri and M. Ricci, J. Org. Chem., 1983, 48, 3831.
- 8 R. A. Sheldon and and J. A. van Doorn, J. Catal., 1973, 31, 427.
- 9 J. H. Fendler, Acc. Chem. Res., 1976, 9, 153.
- 10 L. J. Csányi and K. Jáky, J. Catal., 1993, 141, 721.
- 11 D. E. Van Sicle, F. R. Mayo and R. M. Arluck, J. Am. Chem. Soc., 1965, 87, 4824.
- 12 D. Lavabre, J. C. Micheau, T. Buhse and W. Thiemann, Int. J. Chem. Kinet., 1995, 28, 333.
- 13 G. R. Krow, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon Press, New York, 1991, p. 671.
- 14 A. Bayer and V. Villiger, Berichte, 1899, 32, 3625.
- 15 G. Schroeter, German Pat. 562,827, 1932.