

Oxidation of hydrocarbons by O₂ in the presence of onium salts and onium ion-pair complexes as catalysts

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Abstract

The oxidations of cyclohexene (Ch) and tetralin (T) are induced by insertion of O₂ into their activated –C–H groups and primarily hydroperoxides are formed. The onium salts promote the homolysis of the hydroperoxides formed. The efficiency of the catalysts depend on the polarizing power (partial charge) of the onium cations, the polarizability of the counteranions and the concentration of the catalyst. During the catalysed oxidation of substrates and during the catalysed decompositions of their hydroperoxides radical formation was detected by means of a spin trap, and some singlet O₂ was also evolved. The catalysed cooxidations demonstrated that the oxidation products mutually influence the transformations of these hydrocarbons. The onium-decavanadate ion-pair complexes are more effective catalysts than the pure onium salts. The Arrhenius parameters of the oxidations were determined and a possible mechanism is outlined.

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1. Introduction

It was earlier established [1] that the different onium salts promote the decomposition of *tert*-butyl hydroperoxide (*t*-BHP, an initiator widely used in oxidation reactions) into O₂ and *tert*-butanol as main products, together with a few per cent of di-*tert*-butyl peroxide. This decomposition is accompanied by the formation of two types of free radicals. In contrast, no data have been reported concerning the onium-catalysed decompositions of cyclohexenyl (Ch–OOH) and tetralyl hydroperoxides (T–OOH). Such data will be presented in this paper, and the factors determining the catalytic efficiencies of different onium salts will be discussed. The products of oxidation of Ch and T are the corresponding hydroperoxides plus cyclohexene oxide (Ch–O) and 2-cyclohexen-1-ol (Ch–ol), or 1,2,3,4-tetrahydro-1-naphthol (T–ol) and 3,4-dihydro-1(2H)-naphthalenone (T–one); some water has also been found [2]. The results on the catalysed cooxidations of Ch and T will demonstrate how the conversions

are mutually influenced by the reaction products. Further, the Arrhenius parameters and a probable mechanism of the oxidation will be presented.

2. Experimental

The materials used, the methods applied for their purification, and the preparations of the ion-pair catalysts are detailed elsewhere [3]. The hydroperoxide stock solutions were obtained by prolonged oxidation of the pure hydrocarbons by O₂ at room temperature. The Ch–OOH solution was used without any separation. It contained 0.497 M Ch–OOH, 0.352 M Ch–O, 1.437 M Ch–ol and 7.586 M Ch. In the case of T, the oxidate was cooled down to –20 °C, when T–OOH separated out [4]. It was filtered off and subjected to thorough suction, and the crystals were then dissolved in chlorobenzene. The composition of the solution was 0.517 M T–OOH, 0.049 M T–one, 0.468 M T–ol and 0.27 M T. Stock solutions were stored in a refrigerator at about 4 °C.

The oxidation reactions were carried out in the dark, in a thermostated, magnetically well-stirred (about 850 rpm) batch reactor (fitted with a reflux condenser cooled with

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water to 10 °C). The rate of oxidation was found to become independent of the stirring rate when the latter exceeded 200 rpm. The reaction mixtures contained 2.00 cm³ Ch or 3.00 cm³ T and the given quantity of catalyst, made up to 8.00 cm³ with chlorobenzene, and saturated with dried O₂ for 3 min at room temperature. The reaction vessel (ca. 35 cm³) was connected to a 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 O₂, fitted with a temperature control, and the recording of the O₂ uptake was started simultaneously. The gas measuring device automatically regulated the inside pressure to the atmospheric level. After a net conversion time of 120 min (the time lag was not included), the reaction products were estimated by iodometry (O_{act}, the hydroperoxide content) and by gas chromatography (the epoxide, -ol and -one contents). The time lag was defined as the period that elapsed from the start until the uptake of the first 0.03 cm³ O₂.

It should be mentioned that the individual hydroperoxide contents could not be determined iodometrically in the mixed solutions of the hydrocarbons; instead, their sums were given. The -epoxide, -ol and -one products were measured by gas chromatography on separate columns after the quantitative transformation of the corresponding hydroperoxides into -ols by triphenylphosphine. Accordingly, the sum of the total -ol values obtained had to be corrected by the measured (ΔO_{act})_{Ch,T} values, which yielded the required $\Delta[-ol]_{Ch,T} = \{\Delta[Ch-ol]_{Ch,T} + \Delta[T-ol]_{Ch,T}\} - (\Delta O_{act})_{Ch,T}$ values. These data are given in Tables 3 and 4.

The column for Ch measured 2 m × 4 mm i.d.; it was filled with Chromosorb W-AW-DMCS coated with Carbowax 20 M; carrier gas: N₂ at 40 cm³ min⁻¹; detector: FID. The column for T measured 1 m × 4 mm i.d.; it was filled with Chromosorb W coated with 20% LAC IR 296; carrier gas: N₂ at 40 cm³ min⁻¹; detector: FID. Reaction products were identified with the aid of authentic samples.

The ESR spectra were taken with a Bruker ECS 106 spectrometer. The chemiluminescence was detected with a Perkin-Elmer MPF-44A spectrofluorimeter, using the highest voltage for the photomultiplier, with the highest amplification in dc mode; in most cases, the monochromator was uncoupled to enhance the sensitivity.

3. Results and discussion

3.1. Efficiency of onium salt catalysis, influence of the counteranions

The data in Table 1 afford information on the catalytic efficiencies of the onium salts with different counteranions in different concentrations in the oxidations of Ch and T. In these measurements, no initiator was used at all, and the corresponding hydroperoxide (if any) was removed from the stock hydrocarbons by passage through an activated alumina column and distillation. The catalytic efficiency is charac-

terized by the value of ΔO_2 uptake/120 min measured after the time lag. The formula of the onium salt is followed by two numbers in parentheses, the first the catalytic efficiency observed at 0.001 M, and the second that at 0.01 M catalyst concentration.

On the basis of these data, the sequence of catalytic efficiency in the oxidation of Ch is ALCl (2.686, 1.856) > Hex₄NCl (2.449, 1.573) > BnEt₃NCl (2.147, 2.101) > BnBu₃NCl (2.025, 1.768) > Bu₄NCl (1.893, 0.019) > CetPyCl (1.738, 0.093) > Bu₄Ni (1.639, 3.803) > CetBu₃PBr (0.943, 0.814) > Hex₄NHSO₄ (0.631, 0.469) > Bu₄NBr (0.528, 0.723) (where ALCl: Aliquat 336 (MeOct₃Cl), Bn: benzyl, Cet: cetyl = hexadecyl).

That in the oxidation of tetralin is: ALCl (3.679, 1.429) > Hex₄NCl (3.163, 2.710) > CetPyCl (2.833, 0.422) > BnBu₃NCl (2.700, 2.789) > Bu₄NCl (2.615, 1.097) > BnEt₃NCl (2.238, 3.182) > Bu₄Ni (1.810, 4.280) > CetBu₃PBr (1.608, 1.869) > Bu₄NBr (0.921, 1.097) > Hex₄H₂SO₄ (0.217, 0.142).

Table 1 lists the data relating to the full analyses of the investigated systems and the time lags. These data permit the following conclusions.

- (i) Catalysts with chloride as counteranion generally result in higher conversions when used in lower than in higher concentration. The reason for this behaviour is probably that at lower catalyst concentrations less radicals are released during the promoted decomposition of the freshly formed hydroperoxides and these contribute mostly to the chain propagation instead of their (usually bimolecular) termination reactions. At higher catalyst concentrations, however, more radicals will be released at once, and hence their recombinations tend to dominate, the O₂ uptake thereby being diminished. The catalysts containing a benzyl substituent behave somewhat differently because the polarizing ability of an onium cation is moderately altered by the presence of a benzyl radical.
- (ii) The onium salts with bromide and especially with iodide as counteranion are more active than those with chloride, probably because the formers can be oxidized to the given halogens, which are transformed immediately into the corresponding trihalides. In the presence of these more bulky counteranions, the polarizing power of the onium cation is increased and hence the rate of oxidation will be enhanced. It should be mentioned that the addition of free halogen (formed transiently) to double bonds was never observed.
- (iii) In a 'chloride-free' medium (e.g. when Q-Cl was replaced by Q-HSO₄), the oxidations of the hydrocarbons were reduced considerably, whereas an increase would be expected on the basis of the observations of Noyori and coworkers [5]. This contradiction is only apparent, however, for in the present systems the catalytic efficiency of the onium cation is determined by the polarizability of its counteranion and not by the

Table 1
Oxidation of hydrocarbons by O₂ in the presence of onium salt catalysts in the absence of initiator (in mmol unit)

Hydrocarbon	Catalyst		Time lag (min)	O ₂ uptake	$\Delta[\text{O}_{\text{act}}]_{\text{CH}}^{\text{corr}}$	$\Delta[\text{Ch-O}]$	$\Delta[\text{Ch-ol}]$	$\Delta[\text{T-one}]$	$\Delta[\text{T-ol}]$	$\Sigma(\text{O-atom})^{\text{exc}}$
Ch	ALCl	0.008	18	2.686	1.592	0.078	1.019	–	–	2.683
Ch	ALCl	0.080	37	1.856	1.313	0.046	0.490	–	–	1.863
T	ALCl	0.008	4	3.679	2.228	–	–	1.167	0.529	2.267
T	ALCl	0.080	19	1.429	1.154	–	–	0.274	0.005	1.151
Ch	Hex ₄ NCl	0.008	1	2.449	2.447	0.000	0.002	–	–	2.449
Ch	Hex ₄ NCl	0.080	4	1.573	1.571	0.000	0.002	–	–	1.573
T	Hex ₄ NCl	0.008	1	3.163	2.666	–	–	0.200	0.594	2.666
T	Hex ₄ NCl	0.080	2	2.710	1.989	–	–	0.325	0.790	1.991
Ch	Hex ₄ NHSO ₄	0.008	5	0.631	0.621	0.000	0.010	–	–	0.631
Ch	Hex ₄ NHSO ₄	0.080	3	0.469	0.457	0.000	0.012	–	–	0.469
T	Hex ₄ NHSO ₄	0.008	13	0.217	0.218	–	–	0.000	0.000	0.216
T	Hex ₄ NHSO ₄	0.080	21	0.142	0.139	–	–	0.000	0.005	0.140
Ch	Bu ₄ NCl	0.008	34	1.893	0.895	0.037	0.960	–	–	1.894
Ch	Bu ₄ NCl	0.080	87	0.019	0.012	0.007	0.000	–	–	0.019
T	Bu ₄ NCl	0.008	2	2.615	1.552	–	–	0.635	0.875	1.533
T	Bu ₄ NCl	0.080	14	0.356	0.358	–	–	0.000	0.000	0.354
Ch	Bu ₄ NBr	0.008	7	0.528	0.358	0.000	0.170	–	–	0.528
Ch	Bu ₄ NBr	0.080	2	0.723	0.398	0.032	0.326	–	–	0.690
T	Bu ₄ NBr	0.008	1	0.921	0.875	–	–	0.048	0.000	0.871
T	Bu ₄ NBr	0.080	1	1.097	0.875	–	–	0.122	0.192	0.883
Ch	Bu ₄ NI	0.008	0	1.639	0.995	0.095	0.550	–	–	1.638
Ch	Bu ₄ NI	0.080	0	3.803	0.637	0.181	2.992	–	–	3.796
T	Bu ₄ NI	0.008	0	1.810	1.015	–	–	0.348	0.932	0.977
T	Bu ₄ NI	0.080	0	4.280	0.318	–	–	1.961	4.082	0.238
Ch	BnBu ₃ NCl	0.008	7	2.025	1.413	0.056	0.548	–	–	2.033
Ch	BnBu ₃ NCl	0.080	15	1.768	1.035	0.048	0.690	–	–	1.763
T	BnBu ₃ NCl	0.008	1	2.700	2.168	–	–	0.526	0.000	2.180
T	BnBu ₃ NCl	0.080	2	2.789	2.009	–	–	0.741	0.000	2.087
Ch	BnEt ₃ NCl	0.008	6	2.147	1.333	0.040	0.775	–	–	2.146
Ch	BnEt ₃ NCl	0.080	8	2.101	1.174	0.040	0.874	–	–	2.114
T	BnEt ₃ NCl	0.008	1	2.238	1.154	–	–	0.745	0.675	1.157
T	BnEt ₃ NCl	0.080	0	3.182	1.731	–	–	1.113	0.637	1.770
Ch	CetPyCl	0.008	9	1.738	1.353	0.044	0.340	–	–	1.735
Ch	CetPyCl	0.080	32	0.093	0.092	0.000	0.000	–	–	0.094
T	CetPyCl	0.008	1	2.833	2.348	–	–	0.492	0.000	2.334
T	CetPyCl	0.080	8	0.422	0.418	–	–	0.010	0.011	0.395
Ch	Cet Bu ₃ PBr	0.008	9	0.943	0.736	0.044	0.146	–	–	0.942
Ch	Cet Bu ₃ PBr	0.080	20	0.814	0.676	0.032	0.110	–	–	0.810
T	Cet Bu ₃ PBr	0.008	1	1.608	1.432	–	–	0.177	0.004	1.426
T	Cet Bu ₃ PBr	0.080	3	1.869	1.432	–	–	0.417	0.000	1.472

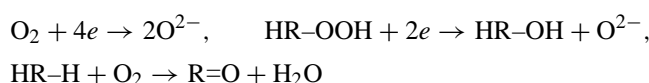
Conditions: 19.744 mmol Ch or 22.077 mmol T (previously freed from its hydroperoxide) + onium salt catalyst solution was made up to 8.00 cm³ with chlorobenzene; reaction time: 120 min; oxidation at 343 K, in the dark.

chloride-free environment as for heteropolytungstate catalysts.

The last column of Table 1 presents the values of $\Sigma(\text{O-atom})^{\text{exc}}$ are which provide information on the sum of other (but not hydrocarbon derivatives) O-atom-containing species (e.g. water) formed during the catalysed oxidation. $\Sigma(\text{O-atom})^{\text{exc}}$ is defined as

$$\Sigma(\text{O-atom})^{\text{exc}} = \{2 \times (\text{O}_2 \text{ uptake})_{\text{CH}}\} - \{\Delta[\text{O}_{\text{act}}]_{\text{CH}}^{\text{corr}} + \Delta[\text{Ch-O}] + \Delta[\text{Ch-ol}] + 2 \times \Delta[\text{T-one}]\}$$

where CH refers to the hydrocarbon molecules in general, and represents Ch and/or T, or both in the mixed oxidations. The redox processes during the oxidation are



It should be emphasized that the reaction mixtures were initially always perfectly clear and transparent; they remained similarly clear and homogeneous for many days, even when the samples were stored in a refrigerator at about 4 °C. This is due to the powerful solubilization of

Table 2
Onium salt-catalysed decompositions of hydroperoxides (in mmol units)

Hydroperoxide	Catalyst	Temperature (K)	$\Delta[\text{O}_2]$ evolved	$\Delta[\text{O}_{\text{act}}]$, $[\text{O}_{\text{act}}]$	$\Delta[\text{Ch-O}]$, $[\text{Ch-O}]$	$\Delta[\text{Ch-ol}]$, $[\text{Ch-ol}]$	$\Delta[\text{T-one}]$, $[\text{T-one}]$	$\Delta[\text{T-ol}]$, $[\text{T-ol}]$	$\Sigma(\text{O-deriv.})_{\text{CH}}$
Ch-OOH (0.994)	None	295	0.000	0.000 (0.994)	0.000 (0.702)	0.000 (2.873)	–	–	(4.569)
T-OOH (1.034)	None	295	0.000	0.000 (1.034)	–	–	0.000 (0.098)	0.000 (0.937)	(2.069)
Ch-OOH (0.994)	None	343	0.018	–0.039 (0.955)	0.003 (0.705)	0.002 (2.875)	–	–	(4.571)
T-OOH (1.034)	None	343	0.000	0.000 (1.034)	–	–	0.000 (0.098)	0.000 (0.937)	(2.069)
Ch-OOH (0.994)	Hex ₄ NCl (0.050)	343	0.089	–0.182 (0.812)	0.007	0.038	–	–	(4.615)
Ch-OOH (0.994)	Hex ₄ NCl (0.050)	343	0.089	–0.179 (0.815)	0.007	0.041	–	–	(4.621)
Ch-OOH (0.994)	ALCl (0.050)	343	0.059	–0.119 (0.875)	0.007	0.007	–	–	(4.585)
T-OOH (1.034)	Hex ₄ NCl (0.050)	343	0.131	–0.262 (0.772)	–	–	0.056 (0.154)	–0.055 (0.882)	(2.070)
T-OOH (1.034)	ALCl (0.050)	343	0.145	–0.294 (0.740)	–	–	0.029 (0.127)	–0.029 (0.908)	(2.065)
T-OOH (1.034)	ALCl (0.050)	343	0.144	–0.290 (0.744)	–	–	0.031 (0.129)	–0.031 (0.906)	(2.067)

Conditions: 2.00 cm³ of stock solution + 2.00 cm³ catalyst solution were measured into the reaction vessel, the volume was made up to 8.00 cm³ with chlorobenzene, and the solution was freed from O₂ by bubbling N₂ through it. The gas evolved at 343 K, during 120 min was collected in an automatic gas burette at atmospheric pressure.

the onium salts, and the relatively high solubility of water (1.13×10^{-2} M) in chlorobenzene.

3.2. Catalysed decompositions of cyclohexenyl and tetralyl hydroperoxides

The data in Table 2 reveal that Ch–OOH underwent a slight decomposition when it was heated up to 343 K for 120 min in the absence of catalyst and O₂, with Ch–O and Ch–ol being formed in traces; in contrast, T–OOH remained unchanged under such circumstances.

In the presence of onium salt catalysts, both reaction mixtures underwent slow decomposition. For the Ch system, Hex₄NCl proved to be a somewhat more active catalyst than AlCl₃, while just the opposite was observed for the T system. The losses in O_{act} occurred in the form of O₂ according to the stoichiometry $2\text{HR-OOH} \rightarrow \text{O}_2$ (2:1) for both hydroperoxides. The loss in T–ol was found to be equal to the increase in the T–one concentration: $2\text{HR-OH} \xrightarrow{\text{O}_2} \text{R=O} + \text{H}_2\text{O} + \text{HR-H}$. The sum of the O-derivatives of T, $\Sigma(\text{O-deriv.})_{\text{T}} = 2 \times \Delta[\text{O}_2] + [\text{O}_{\text{act}}] + [\text{T-one}] + [\text{T-ol}]$, proved to be constant within the error of analysis for each run. For the Ch system, an analogous reaction could be assumed for the evolution

of O₂ and the production of Ch–O according to the equation: $\text{Ch} + \text{Ch-OO}^\bullet \rightarrow \text{Ch-O} + \text{Ch-O}^\bullet$, though the values of $\Sigma(\text{O-deriv.})_{\text{Ch}} = 2 \times \Delta[\text{O}_2] + [\text{O}_{\text{act}}] + [\text{Ch-O}] + [\text{Ch-ol}]$ exhibited somewhat higher fluctuations than those in T system.

3.3. Catalysed oxidations of hydrocarbons alone or in mixed solutions; mutual effects of the oxidation products

It was earlier observed that the onium salt-catalysed oxidations of these hydrocarbons were influenced by the products when these were added as individual additives in higher concentrations to the reaction mixtures before the start of the oxidations [2,3]. The oxidations of Ch and T were now carried out in mixed solutions (cooxidation) in the presence of different catalysts. The results are summarized in Tables 3 and 4. For easier comparison, the data on the individual oxidations are also presented. The measurement data revealed that the rates of oxidations are mutually moderated in mixed solutions as compared to those for the separate samples. It was a general experience that T was oxidized somewhat more effectively than Ch when onium salt catalysts were used, but the opposite was observed

Table 3

Oxidations of Ch and T by O₂ in separate or mixed solutions in the presence of differently prepared onium salt catalysts; data in mmol units

Catalyst	pH	O ₂ uptake for			$\Delta[\text{O}_{\text{act}}]^{\text{corr}}$ for			$\Delta[\text{Ch-O}]$	$\Delta[\text{T-one}]$	$\Delta[\text{Ch-ol}]$	$\Delta[\text{T-ol}]$	$\Sigma(\Delta[\text{-ol}]_{\text{Ch,T}})$	$\Sigma[\text{O-atom}]^{\text{exc}}$
		Ch	T	Ch, T	Ch	T	Ch, T						
Q _x : Hex ₄ NCl													
A	4.5	2.596	–	–	1.770	–	–	0.109	–	0.718	–	–	2.595
	4.5	–	3.072	–	–	2.008	–	–	0.752	–	0.479	–	2.073
	4.5	–	–	5.415	–	–	2.796	0.291	0.632	–	–	2.490	3.989
A	3.5	2.841	–	–	2.009	–	–	0.140	–	0.693	–	–	2.840
	3.5	–	3.082	–	–	2.367	–	–	0.599	–	0.232	–	2.367
	3.5	–	–	5.949	–	–	3.481	0.227	0.708	–	–	2.137	4.637
B	4.5	3.142	–	–	2.009	–	–	0.148	–	0.988	–	–	3.139
	4.5	–	4.083	–	–	2.844	–	–	0.870	–	0.737	–	2.845
	4.5	–	–	6.354	–	–	3.202	0.272	0.931	–	–	2.741	4.631
B	3.5	2.985	–	–	1.969	–	–	0.096	–	0.921	–	–	2.984
	3.5	–	3.823	–	–	2.784	–	–	0.883	–	0.324	–	2.772
	3.5	–	–	5.702	–	–	4.110	0.168	0.535	–	–	1.150	4.906
Q _x : MeOctNCl													
A	4.5	2.598	–	–	1.963	–	–	0.105	–	0.532	–	–	2.596
	4.5	–	2.999	–	–	1.969	–	–	0.486	–	1.090	–	1.967
	4.5	–	–	5.538	–	–	3.799	0.106	0.348	–	–	2.000	4.475
A	3.5	2.541	–	–	1.969	–	–	0.128	–	0.445	–	–	2.540
	3.5	–	3.574	–	–	2.705	–	–	0.475	–	0.777	–	2.716
	3.5	–	–	5.309	–	–	4.110	0.184	0.620	–	–	0.513	4.571
B	4.5	2.788	–	–	1.890	–	–	0.092	–	0.801	–	–	2.793
	4.5	–	4.244	–	–	2.446	–	–	0.822	–	1.954	–	2.444
	4.5	–	–	5.549	–	–	2.446	0.125	0.691	–	–	3.570	3.575
B	3.5	2.763	–	–	1.929	–	–	0.191	–	0.643	–	–	2.763
	3.5	–	4.725	–	–	2.924	–	–	0.898	–	1.809	–	2.921
	3.5	–	–	5.584	–	–	3.560	0.145	0.520	–	–	2.230	4.193

Conditions: 19.744 mmol Ch or 22.077 mmol T alone or together + 0.100 mmol *t*-BHP + (A): 0.0192 mmol Q_x, or (B): 0.048 mmol Q_x catalyst was made up to 8.00 cm³ with chlorobenzene; reaction time: 120 min, in the dark, at 343 K.

Table 4

Oxidations of Ch and T by O₂ in separate or mixed solutions in the presence of differently prepared onium-decavanadate ion-pair catalysts; data in mmol units

Q _x V ₁₀ O ₂₈	pH	O ₂ uptake for			Δ[O _{act}] ^{corr}	Δ[Ch–O]	Δ[Ch–ol]	Δ[T–one]	Δ[T–ol]	Σ[O-atom] ^{exc}
		Ch	T	Ch, T						
Q: Hex ₄ N ⁺										
x = 4	4.5	4.389	–	–	–0.020	0.798	3.612	–	–	4.388
x = 4	4.5	–	3.293	–	0.178	–	–	1.550	3.128	0.180
x = 4	4.5	–	–	6.331	–0.013	0.782	2.873	0.829	3.719	3.643
x = 4	3.5	4.245	–	–	–0.020	0.453	3.805	–	–	4.252
x = 4	3.5	–	3.164	–	0.337	–	–	1.185	3.290	0.331
x = 4	3.5	–	–	4.832	–0.020	0.687	2.128	1.148	1.749	2.824
x = 10	4.5	4.202	–	–	0.059	0.697	3.450	–	–	4.198
x = 10	4.5	–	5.029	–	0.178	–	–	2.631	4.438	0.180
x = 10	4.5	–	–	5.704	–0.013	0.358	2.252	1.889	2.436	2.597
x = 10	3.5	4.390	–	–	–0.041	0.655	3.843	–	–	4.323
x = 10	3.5	–	4.713	–	0.178	–	–	2.777	3.516	0.178
x = 10	3.5	–	–	4.486	–0.040	0.294	1.859	0.930	2.849	2.150
Q: MeOct ₃ N ⁺										
x = 4	4.5	4.284	–	–	–0.001	0.681	3.602	–	–	4.286
x = 4	4.5	–	3.992	–	0.258	–	–	2.295	2.877	0.259
x = 4	4.5	–	–	5.794	–0.020	0.515	2.518	1.178	3.219	3.000
x = 4	3.5	4.078	–	–	0.019	0.882	3.177	–	–	4.078
x = 4	3.5	–	2.844	–	0.397	–	–	1.086	2.722	0.397
x = 4	3.5	–	–	5.715	0.039	1.037	2.363	0.827	2.896	3.441
x = 10	4.5	4.717	–	–	–0.020	0.487	4.250	–	–	4.717
x = 10	4.5	–	4.228	–	0.059	–	–	2.136	4.069	0.056
x = 10	4.5	–	–	4.504	–0.020	0.407	1.993	0.936	2.390	2.366
x = 10	3.5	4.817	–	–	–0.020	0.485	4.352	–	–	4.817
x = 10	3.5	–	3.850	–	0.337	–	–	1.860	3.305	0.338
x = 10	3.5	–	–	3.985	0.019	0.784	1.561	0.537	2.124	2.408

Conditions: 19.744 mmol Ch or 22.077 mmol T alone or together + 0.100 mmol *t*-BHP + 0.0048 mmol Q_xV₁₀O₂₈ catalyst solution was made up to 8.00 cm³ with chlorobenzene; reaction time: 120 min, in the dark, at 343 K.

when onium-decavanadate ion-pair complexes were applied. It was established that the values of both O₂ uptake and Δ[O_{act}]_{CH}^{corr} were lower for the mixed solutions than the sum of the corresponding data for the individual solutions. For onium salt catalysts, the higher Ch–O values for the mixed solutions were probably due to the fact that both hydroperoxides (Ch–OOH and T–OOH) may contribute to the formation of Ch–O. The ‘pH change’ of the onium salt catalysts (the onium salts were dissolved in chlorobenzene and then saturated with an equal volume of water adjusted to the same pH as used in the preparation of decavanadate, and the separated organic phases were applied) exerted hardly any influence on the catalytic efficiency. On the other hand, the activities of the onium-decavanadate ion-pair complexes displayed a pH dependence. The decavanadate ions became more protonated at pH 3.5 and were then probably transformed into a somewhat loosened structure, with lower activity, whereby the overall O₂ uptake was decreased. With increase of the catalyst concentrations, the rate of oxidation increased, though not linearly, due to the structural changes in the inverse micelles [2,6,7].

3.4. Dependence of the progress of hydrocarbon oxidations by O₂ on the concentration of the onium salt catalyst and on the initial quantity of initiator

The oxidations of Ch and T were investigated with different initiator hydroperoxides (cyclohexenyl, tetralyl, cumyl and *tert*-butyl hydroperoxides) in different initial concentrations at increasing concentrations of onium salt catalysts. In these cases, the stock hydrocarbons were freshly freed from their hydroperoxide contents before use. It was observed that the rates of oxidation first increased linearly up to onium salt catalyst concentrations of about 10^{–3} M. Above this, the rates started to decrease and reached a limiting value between 10^{–2} and 10^{–1} M. From then on, the oxidation rates started to drop, sometimes rather suddenly. This behaviour proved to be general; only small quantitative deviations were observed for the different hydroperoxides. It may be attributed to the structural changes in the inverse micelles [7] with increasing concentrations. As the concentration of catalyst was increased, the initially small spherical micelles grew and were transformed into more open layer structures. The activity of the catalyst began to diminish during further

growth, and the structure then started to fold back and form a hollow spherical, more closed and less active form at about 0.1 M.

However, it was also observed that the rates of oxidation were always considerably lower when the initially applied hydroperoxide concentration was 0.0125 M than when it was only 0.0025 M, and this did not depend on the nature of the hydroperoxide used. This latter behaviour can similarly be explained by the influence of the initial hydroperoxide concentration on the propagation/termination rate ratios.

3.5. Onium salts as radical-producing catalysts

The oxidations of hydrocarbons by O_2 were carried out in situ in the cavity of the ESR spectrometer, but no signal was observed at 343 K. In the presence of the spin trap *N-tert-butyl- α -phenylnitrone* (PBN), however, formation of radicals could be detected at 343 K for both hydrocarbons (Fig. 1, spectra A and B).

Further, an attempt was made to detect radicals by direct ESR spectrometry in the hydroperoxide stock solutions by using onium salt catalysts. The formation of radicals could not be observed either at room temperature or at 343 K. However, in the presence of the spin trap PBN, radicals could be detected at 343 K (Fig. 1, spectra C and D).

The PBN spin trap was chosen for these investigations because it is a stable compound, quickly soluble in chlorobenzene, it can be used in the presence of O_2 and their spin adducts are usually stable. The trapped radical is attached to the β -C atom relative to the nitroxyl O-atom of the spin trap. According to Janzen [8] the spectrum of the trapped

radical generally consists of a triplet of doublets due to the N and β -H coupling of the spin adduct. This can be characterized by a_N and a_H hyperfine coupling values. In our measurements, spectra A, B and D exhibited only broad triplets, with values of $a_N = 13.88$ G for spectra A and B, and $a_N = 13.97$ G for spectrum D; the doublets were not resolved at all. The better resolved spectrum C presented the usual triplet of doublets, with $a_N = 13.88$ G and $a_H = 2.20$ G. These findings can be interpreted as follows. The negative results of direct ESR measurements probably indicate that short-lived radicals are formed in the onium salt-catalysed oxidation reactions of hydrocarbons and in the catalysed decompositions of their hydroperoxides. The application of PBN provided evidence that radicals really are involved in these systems. As regards the nature and structures of the radicals trapped, the obtained spectra offer only meagre information. The magnitude of a_H is known to decrease with increasing bulk of the attached groups. From the facts that a_H was small in the case of spectrum C, while in spectra A, B and D the β -H coupling could not be resolved at all, it may be concluded that bulky radicals are formed in these systems, perhaps oxy or peroxy radicals of parent hydrocarbons.

The levels of chemiluminescence of the hydroperoxide stock solutions (see Section 2) were investigated in the presence of either $AlCl_3$ or Hex_4NCl as catalyst (samples: 2.00 cm^3 stock solutions + 2.00 cm^3 0.006 M onium salt dissolved in chlorobenzene). The emission was observed with a spectrofluorimeter in a 1.00 cm silica cell heated to 343 K. The weak photon emissions of all such samples indicated that the O_2 formed during the onium salt-catalysed decompositions of both hydroperoxides was (at least partly)

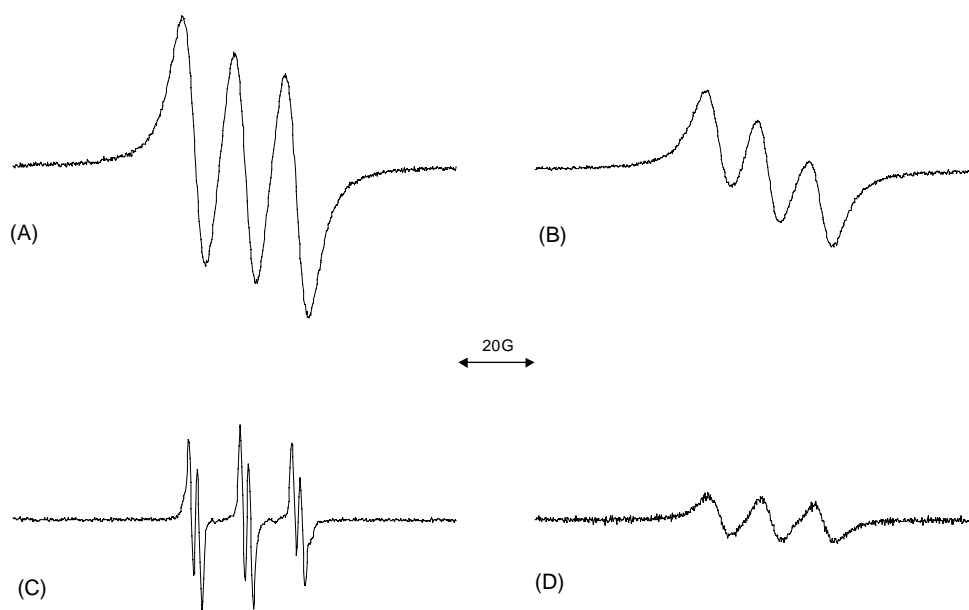


Fig. 1. ESR spectra obtained in the oxidation of T and Ch by O_2 and in the decomposition of their hydroperoxides by onium salt catalysts. Compositions: (curve A) 22.077 mmol T + 0.100 mmol *t*-BHP + 0.024 mmol Hex_4NCl ; (curve B) 19.744 mmol Ch + 0.100 mmol *t*-BHP + 0.024 mmol $AlCl_3$, each made up to 8.00 cm^3 with chlorobenzene; (curve C) 2.00 cm^3 T-OOH stock solution + 2.00 cm^3 0.006 M Hex_4NCl ; (curve D) 2.00 cm^3 Ch-OOH stock solution + 2.00 cm^3 0.006 M $AlCl_3$.

in the singlet spin state. In the presence of AlCl_3 as catalyst, the T–OOH sample emitted about twice as many photons as the Ch–OOH solution, although their concentrations were almost equal. The recorded spectrum was too noisy; the emission exhibited only a tendency to increase from 400 towards 700 nm.

3.6. Arrhenius parameters of the catalysed oxidations of hydrocarbons by O_2

The temperature dependence of the oxidations was investigated at 5 K intervals in the range 328–348 K in the presence of onium salts or of their onium-decavanadate ion-pair complexes. The ion-pair complexes obtained at pH 4.5 were investigated either with an equivalent quantity of onium salt (which was just sufficient for the quantitative extraction of aqueous decavanadate ions into the aprotic chlorobenzene phase ($Q^+ : V(V) = 4:10$) or with a 2.5-fold excess of quaternary salt (10:10). The resulting data are presented in Table 5. The oxidations of the two hydrocarbons took place at comparable rates for both onium salt catalysts; the lower energy of activation was compensated by a more negative entropy of activation for Hex_4NCl , while the opposite situation was observed for the less symmetrical AlCl_3 . In the presence of onium-decavanadate ion-pairs, nearly the same Arrhenius parameters were found when only an equivalent quantity of Hex_4NCl was used, whereas there was a greater difference when AlCl_3 was applied in a 2.5-fold excess. The difference can probably be explained by the increased quantity of water which was dragged with the increased concentration of the more hygroscopic AlCl_3 .

3.7. Possible mechanism of hydrocarbon oxidation

It should be mentioned in advance that the substrates Ch and T are symmetrical molecules, and consequently it

should be expected that they dispose of symmetrically activated H-atoms (due to the effects of their allyl and benzyl group, respectively): on C atoms 2 and 6 in Ch, on C atoms 1 and 4 in T. Earlier ^1H and ^{13}C NMR investigations revealed [9] that prolonged oxidation of unsubstituted Ch (972 min) and T (1500 min) resulted in not only mono-, but also dihydroperoxide derivatives, the latter in considerably lower quantities. The ratios of monohydroperoxide to dihydroperoxide were 100:7 for Ch, and 100:2.5 for T. It was not checked, however, what would occur in the presence of onium salts. In our opinion, the negligible formation of dihydroperoxide (which could be measured together with the mono derivatives) during a much shorter conversion time (120 min) will not seriously influence the conclusions.

As concerns the mechanism of the catalysed oxidations of these hydrocarbons (the substrates are symbolized by HR–H, to emphasize the presence of activated H atoms), we proceed from the observation that, in the absence of any initiator, the oxidation always starts after a shorter or longer time lag, during which some hydroperoxide is formed as primary product:



The insertion of $^3\text{O}_2$ into the activated –C–H bond induces considerable transformations: the bond length of –O–O– is 145 pm in comparison with 121 pm in O_2 , the multiple bond is transformed into a single bond, and the O_2 will be reduced to hydroperoxide by $2e$, i.e. the oxidation number of O changes from 0 to –1. In the hydroperoxides, the spin state of O is presumed to be singlet, like as in hydrogen peroxide. The spontaneous decomposition and the oxidation of hydrogen peroxide by hypohalites resulted in $^1\text{O}_2$ on spin-conservation grounds [10–12].

The spontaneous homolytic decomposition of the hydroperoxide formed is very slow:



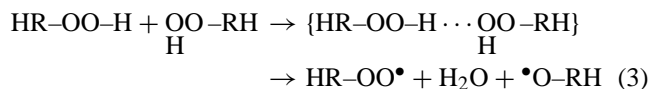
Table 5

Arrhenius parameters of the oxidations of Ch and T by O_2 in the presence of onium salts and their onium-decavanadate ion-pair catalysts

Catalyst	$Q^+ : V(V)$	Energy of activation (kcal mol^{-1})		Entropy of activation ($\text{J deg}^{-1} \text{mol}^{-1}$)	
		Ch	T	Ch	T
MeOct_3NCl (pH 4.5)	10:0	16.50 ± 1.4 0.9854	14.94 ± 1.3 0.9836	-127.08 ± 9.4	-142.47 ± 9.2
$(\text{MeOct}_3\text{N})_4\text{H}_2\text{V}_{10}\text{O}_{28}$ (pH 4.5)	4:10	17.41 ± 0.82 0.9955	17.17 ± 0.95 0.9938	-112.27 ± 6.5	-116.66 ± 7.3
$(\text{MeOct}_3\text{N})_4\text{H}_2\text{V}_{10}\text{O}_{28} + 0.0288 \text{ mmol MeOct}_3\text{NCl}$ (pH 4.5)	10:10	13.84 ± 0.24 0.9906	16.70 ± 0.79 0.9965	-155.32 ± 2.5	-120.73 ± 6.5
Hex_4NCl (pH 4.5)	10:0	13.23 ± 1.0 0.9832	12.76 ± 0.8 0.9905	-165.80 ± 8.0	-169.18 ± 6.4
$(\text{Hex}_4\text{N})_4\text{H}_2\text{V}_{10}\text{O}_{28}$ (pH 4.5)	4:10	17.42 ± 0.5 0.9989	18.07 ± 0.8 0.9960	-112.90 ± 4.3	-106.14 ± 6.5
$(\text{Hex}_4\text{N})_4\text{H}_2\text{V}_{10}\text{O}_{28} + 0.0288 \text{ mmol Hex}_4\text{NCl}$ (pH 4.5)	10:10	16.97 ± 0.7 0.9972	15.14 ± 1.3 0.9798	-117.95 ± 6.1	-141.51 ± 9.2

Conditions: 19.744 mmol Ch and/or 22.077 mmol T + 0.100 mmol *t*-BHP + 0.048 mmol catalyst (onium salt or deca-vanadate ion-pair complex) was made up to 8.00 cm^3 with chlorobenzene; oxidations were carried at 5 K intervals in the temperature range 328–348 K; reaction time: 120 min, in the dark.

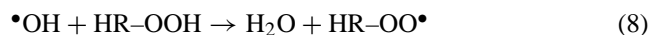
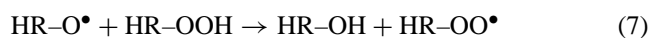
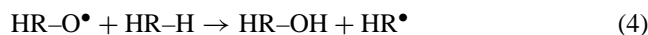
and very few radicals are formed. When hydroperoxide accumulates in time, the oxidation starts to undergo self-acceleration in a bimolecular initiation step:



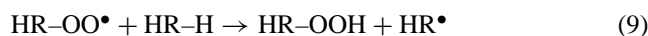
which results in branching of the oxidation chain.

A further and more effective acceleration of the oxidation can be attained when an onium salt catalyst is applied. The cation of the onium salt then attacks at the more nucleophilic O atom (the inside one, near the organic radical) of the hydroperoxide and enhances the homolysis, co-operation being provided by water molecules present via H-bond interactions at the outer O atom of the hydroperoxide [1]. The formation of hydrogen peroxide in traces (by recombination of OH radicals) can be regarded as experimental proof of the occurrence of the homolytic decomposition of hydroperoxides. It was reported earlier [7] that, during the oxidations of both hydrocarbons catalysed by AlCl_3 , H_2O_2 was detected with Ti(IV) reagent. The analogous investigations with Hex_4NCl as catalyst have now confirmed the appearance of H_2O_2 among the reaction products, in a quantity of somewhat less than 0.5%.

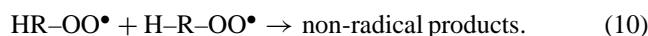
The radicals thus formed are involved in the oxidation chain:



The peroxy radicals formed in this way either react with substrate molecules again:



or terminate the chain:

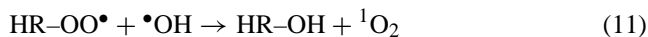


It was proposed by Russell [13] that the secondary peroxy radicals may reversibly and rapidly form a tetroxide intermediate, which is slowly decomposed in an irreversible manner into O_2 , ketone and alcohol, the latter in 1:1 stoichiometry. It was later proved by Bartlett and Guaraldi [14] that the analogous di-*tert*-butyl tetroxide is a stable species below 190 K.

However, the assumption made by Russell was not fulfilled in the present systems. In the oxidation of Ch, Ch-OOH plus Ch-O and Ch-ol were obtained, but Ch-one was not observed at all. Ch-O is probably formed according to step (9). It must be mentioned that Van Sickle et al. [15] detected the formation of cyclohexenone (in an amount of less than 5%) during the uncatalyzed oxidation of Ch at

60 °C, but only after a prolonged reaction time (810 min), but we were not able to reproduce this observation.

Further, in the oxidation of T, the concentration of T-one was never found to be equal to that of T-ol, which is required by Russell's assumption. Accordingly, it was presumed that O_2 was formed via step (11). This latter reaction may be the source of singlet oxygen:



The vibrational transitions of ${}^1\text{O}_2$ were in fact detected, as mentioned before, by measurement of a slight emission accompanying the catalysed decompositions of the hydroperoxides.

The O_2 molecules formed in step (11) may be reused via step (6). If this reaction occurs, then somewhat lower O_2 uptake values and more oxidation products could be found in closed reactor. However, we were not able to confirm the production and reuse of O_2 because only the O-containing derivatives of hydrocarbons were estimated, other derivatives of oxidation, e.g. water, not being measured in these reaction mixtures by the Karl Fischer method. Instead, the O-balance values, $\Sigma(\text{O-atom})^{\text{exc}}$ (see last columns of Tables 1–4), were calculated. These proved to be positive in all runs, and no extra production of O-derivatives was indicated. In this question, a decision could be expected only if reliable estimations of contents of water and other (but not hydrocarbon) O-derivatives were available.

Our substrates contain almost equally activated H atoms; nevertheless, there is a great difference between the two substances: T is a diatropic compound (able to sustain an induced ring current [16]), while Ch contains only one localized pi-bond. This may result in considerable differences in the rates of both the propagation and the termination steps and may explain why cyclohexenone could not be observed during the oxidation of Ch.

The formation of T-one was promoted by the initial addition of T-ol when an onium salt was used as catalyst. It was assumed [3] that the ketone is formed by isomerization of the radical HR-O^\bullet , which may be enhanced by a double H-bond interaction between HR-O^\bullet and T-ol, followed immediately by an exothermic decomposition of this complex into $\bullet\text{R-OH}$ and T-ol. T-one is produced in the subsequent H-abstracting steps by radicals present.

The *Q-V(V)* ion-pair catalysts behaved differently: in these cases, the T-one concentration was lowered considerably when T-ol was applied initially. In that case, however, the O_2 uptake was also appreciably diminished, as was the T-OOH concentration.

It should be noted that, when the concentration is higher (0.05–0.1 M), hydroperoxides may form another type of H-bond interaction than that outlined in step (3): a six-membered cyclic associate [17,18]. This latter is thermodynamically more stable and consequently kinetically less active [19] than the simple H-bonded linear associate. In consequence of such cyclic associations, more than half of the total O_2 uptake really occurs in this form of

hydroperoxide during the oxidation of the hydrocarbon catalysed by an onium salt. Moreover, the rather slow catalysed decompositions of the hydroperoxides (see Table 2) are due to the existence of the cyclic hydroperoxide associates. However, for the onium-decavanadate ion-pair complex catalysts, such an accumulation of hydroperoxides can not be observed because the vanadium (V) centres participate more actively in chain propagation.

4. Conclusions

During the catalysed oxidations of Ch and T by O₂, initially hydroperoxides are formed. The onium cations promote the homolysis of the hydroperoxides with the cooperation of water present by means of H-bond interactions. The polarizing power of an onium cation is strongly influenced by the nature (polarizability) of the counteranions, and the concentration of the onium salt is also a factor determining the catalytic efficiency. During the onium salt-catalysed oxidations of Ch and T, and during the catalysed decompositions of their hydroperoxides, radicals were detected with the aid of a PBN spin trap. The formation of a little singlet oxygen was also observed. The onium-decavanadate ion-pair complexes are more effective catalysts for oxidation. Their activities scarcely depended on the onium salt concentration (either in equivalent quantity or in excess). The catalysed cooxidations of Ch and T demonstrated that the oxidation products mutually influenced the catalysed oxidations of these hydrocarbons. The Arrhenius parameters did not differ considerably when only onium salts or onium-decavanadate ion-pair complexes were used as catalysts. The proposed mechanism is in harmony with the experimental observations; termination reactions of peroxy radicals via a tetroxide intermediate could not be confirmed in the investigated systems.

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