Onium-decavanadate ion-pair complexes as catalysts in the oxidation of hydrocarbons by O_2

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Abstract

The catalysed oxidations of hydrocarbons were found to involve radicals and to be inhibited effectively by phenolic scavengers. The dependences of the activities of the catalysts on their concentrations are explained by the structural changes in the inverse micelles, from the first small spherical associates through an open-layered more active structure, which finally folds back by forming a hollow spherical closed structure, with a fall in the rate. The ^{51}V NMR spectral behaviour of the ion-pair catalysts and the colour changes in the solutions are discussed. The decavanadate structure is not destroyed entirely during the catalysed oxidation, in spite of the partial reduction of the V(V) centres and some structural deformations. The essential role of water and the influence of the products of oxidation by O_2 on the courses of the reactions are also discussed.
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1. Introduction

The acid-induced aggregation of alkali metal vanadate(V) in aqueous solution in the pH range 3–6 is known to result in differently protonated decavanadate oligomers [1]. In non-polar solvents, these anionic species can be solubilised by appropriate quaternary onium salts which are insoluble or only slightly soluble in water, e.g. Hex_4NCl or $MeOct_3NCl$ (Aliquat 336, in brief ALCl). The resulting ion-pair complexes may serve as efficient catalysts in the

oxidation of hydrocarbons by O_2. It has been observed that the activities of these inverse micelles follow maximum curves as functions of their concentrations [2]. The primary role of the onium salts as catalysts in the oxidation of hydrocarbons by O_2 is to generate radicals by interacting with hydroperoxides present in the oxidation mixtures and with water homogeneously dissolved in the non-polar solvents [3]. The characteristics of cationic phase-transfer catalysts in general have recently been discussed; it has been established that the catalytic activity of an onium salt is determined by the effective charge on the onium ion and by the size and polarisability of its anion [4]. In the present paper, an attempt is made to clarify the role of onium-decavanadate ion-pair

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complexes in the catalysed oxidation of hydrocarbons by O_2.

2. Experimental

The materials used, the methods applied for their purification, the procedures for the kinetic investigations of the catalysed oxidations of the hydrocarbons cyclohexene (Ch) and tetralin (T) by O_2, and the techniques for the analysis of these systems are detailed elsewhere [4]. The onium-decavanadate ion-pair catalyst solutions were prepared by the extraction of aqueous vanadium(V) solutions (adjusted to the desired pH with HCl, sufficient time always being allowed for the aggregation equilibria to be established) with an equal volume of the appropriate onium salt dissolved in chlorobenzene under efficient stirring (at 3000 rpm) for 30 min. After separation of the phases, the organic phase was filtered on a Whatman 1PS silicone-treated phase separator and stored at room temperature in the dark. It follows from this mode of preparation that the organic phase always contained a certain amount of homogeneously dissolved (dragged) water.

The NMR and ESR investigations were carried out with Bruker Avance DRX 500, JEOL JES FE3X and Bruker ECS 106 spectrometers. The chemical shifts of ^{51}V at 131.5 MHz are referred to an external reference of $VOCl_3$, assigned to 0.0 ppm.

3. Results and discussion

3.1. Structure of decavanadate(V)

The structure of decavanadate(V) is well established ([5], and [1–7] therein). Wang et al. [6] determined the structure of $[n\text{-}Bu_4N]_4[H_2V_{10}O_{28}]$, the composition of which is closely analogous to those of the ion-pair complexes we used as catalysts. According to these authors [6] in the onium-decavanadate(V) salts, all the V^{5+} are hexacoordinated by O^{2-} (see Fig. 1). If regular octahedral geometry is assumed to a first approximation, all the central vanadium(V) may exert an attractive force (partial charge) of $+5/6 = +0.833$ towards each O^{2-}. Consequently, four types of O^{2-} can be distinguished in this aggregate: (a) eight non-bridging outer O^{2-}, each bearing a formal

partial charge of -1.166 ($= -2 + 0.833$), the surplus electrons being back-donated to the empty d orbitals of the vanadium(V); (b) 14 O^{2-} bridging two vanadium(V) centres, each with a partial charge of -0.333 ($= -2 + 2 \times 0.833$); (c) four O^{2-} bridging three vanadium(V) centres, with a partial charge of $+0.499$ ($= -2 + 3 \times 0.833$); and (d) two O^{2-} bridging six vanadium(V) centres, each with a partial charge of $+3.00$ ($= -2 + 6 \times 0.833$). The overall charge of the $V_{10}O_{28}$ unit is -6.

The vanadium(V) centres are also not equivalent: there are two short V(1)–O(4) and V(1)–O(5) bonds of 166.8 and 167.9 pm in a *cis* configuration, this can be regarded as a dioxovanadium(V) ion, VO_2^+, and the bonds V(2)–O(11), V(4)–O(13), and V(3)–O(12), V(5)–O(14) are similarly short: 160.7, 160.4 and 158.5, 157.9 pm, respectively, these are oxovanadium(V) species, VO^{3+} (see Fig. 1).

The bond orders of the O atoms were calculated [6] with the aid of the formula: $s = (R/1.791)^{-5.1}$ used earlier by Evans and Pope [7], in which s is the bond order, and R is the V–O distance. These calculations (Table 1, last column) indicate that the triple bridging O(2) and double bridging O(6) have the lowest bond orders, 1.34 and 1.30, respectively, while the other O atoms have bond orders in the range 1.74–2.04. From this, it was concluded that the four protons are located on the latter O atoms, and the elongations of the V–O distances involving these O atoms may be a consequence of the protonation. The pH-dependence of oxidation catalysed by onium-decavanadate complex is due to the protonation of anion.

3.2. Experimental evidence for the chain character of catalysed oxidations

It was reported earlier [1] that aqueous anionic vanadium(V) species can readily be extracted into non-polar organic solvents with the aid of water-insoluble phase-transfer catalysts (QX). With the exception of the monomeric vanadium(V) onium salts, all the oligomeric ion-pair complexes, and especially the onium-decavanadate complexes, are active catalysts in the oxidation of hydrocarbons by O_2. ESR measurements [3] have revealed that radicals are formed in the homolytic decomposition of hydroperoxides catalysed by either onium salts or ion-pair complexes. To confirm this, further catalysed oxidations
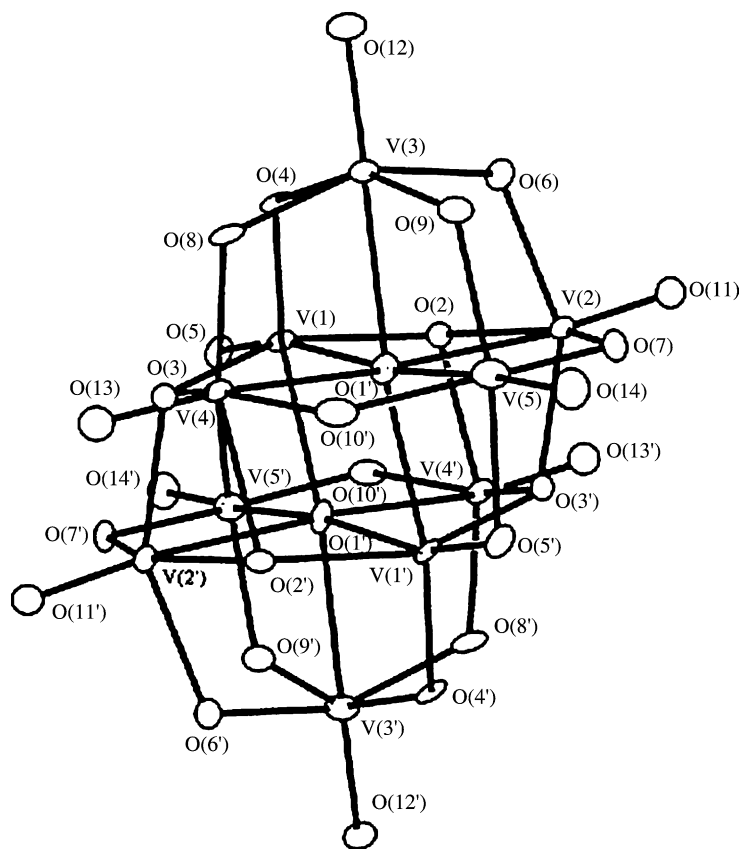
Fig. 1. Crystal structure of tetra-*n*-butyl ammonium decavanadate according to Wang et al. [6].

were carried out in the presence of the widely used scavenger 2,6-di-*t*-butyl-4-methylphenol (a hindered phenol; in brief, ionol). Results of these investigations are listed in Table 2. The O_2 uptake versus ionol concentration data indicate that the catalysed oxidations of both hydrocarbons are strongly inhibited by ionol. It is noteworthy that, when the ionol concentration used was only about one-tenth of the initiator *t*-butyl hydroperoxide (*t*-BHP) concentration, the O_2 uptake was somewhat higher than in the absence of the scavenger. Analogous behaviour was observed earlier when the initial concentrations of different hydroperoxide initiators were altered: for instance, higher values of O_2 uptake were always obtained when 0.0025 M hydroperoxide was used than at 0.0125 M. The explanation of this observation is simple if it is considered that the decomposition of hydroperoxide

catalysed by a pure onium salt or by an ion-pair complex is a fast process and results in a high concentration of radicals virtually at once. If the rate of reaction between the radical formed and the substrate molecule is lower than that of the (usually bimolecular) recombination of radicals, then at a lower concentration of initiator a greater conversion of substrate should be expected, and this was indeed found in the presence of ionol. The data in Table 2 prove that the oxidation catalysed by ion-pair complex is a radical process involving decomposition of the initiator *t*-BHP, and of the hydroperoxides of the given hydrocarbons as primary products of oxidations into the radicals OH, RO and RO_2, with both oxidising and reducing abilities. Molecular products are also formed, such as T-ol, T-one, Ch-ol and Ch–O. In the presence of a pure onium salt catalyst, besides the corresponding

Table 1

Oxidation of hydrocarbons by O_2 catalysed by ion-pair complex $Hex_4N–V(V)$ (0.4:1, pH 4.5)

log[catalyst]	$\Delta[O_2]$	$\Delta[O_{act}^{corr}]$	$\Delta[T\text{-one}]$	$\Delta[T\text{-ol}]$	$\Delta[O_2]^{exc}$
Tetralin
−4.648	0.410	0.298	0.061	0.104	0.053
−3.994	0.656	0.298	0.251	0.213	0.106
−3.693	1.737	1.093	0.352	0.583	0.293
−3.404	1.722	0.318	0.923	0.982	0.501
−3.103	2.000	0.118	1.016	1.732	0.866
−2.818	1.874	0.039	1.349	1.047	0.561
−2.517	1.584	−0.020	1.210	0.785	0.391
−2.220	1.052	−0.040	0.838	0.506	0.252
−1.919	1.817	−0.020	1.444	0.785	0.392
−1.743	1.476	−0.060	1.050	0.970	0.484

log[catalyst]	$\Delta[O_2]$	$\Delta[O_{act}^{corr}]$	$\Delta[Ch\text{–O}]$	$\Delta[Ch\text{-ol}]$	$\Delta[O_2]^{exc}$
Cyclohexene
−4.648	0.292	0.158	0.019	0.113	–
−4.295	0.424	0.298	0.033	0.096	–
−3.994	0.622	0.417	0.029	0.178	–
−3.693	1.558	0.377	0.458	0.723	–
−3.404	1.327	−0.001	0.349	0.964	–
−3.103	1.477	−0.040	0.486	1.034	–
−2.517	1.044	−0.060	0.215	0.891	–
−2.220	1.923	−0.068	0.290	1.701	–
−1.919	1.672	−0.060	0.300	1.425	–
−1.743	1.687	−0.060	0.256	1.488	–

Conditions: 22.077 mmol T or 19.744 mmol Ch + 0.100 mmol t-BHP + 0.324 mmol catalyst was made up to 8.00 cm^3 with chlorobenzene; in the dark, at 343 K.

Table 2

Effects of ionol on catalysed oxidation of hydrocarbons

[Ionol] (mmol)	Ion-pair catalyst	Substrate	[O_2 uptake]$_{120\,min}$ (mmol)	Time lag (min)
0.000	A	T	2.102	0
0.008	A	T	2.729	0
0.016	A	T	0.044	45
0.024	A	T	0.035	47
0.032	A	T	0.404	51
0.040	A	T	0.019	70
0.080	A	T	0.033	47
0.000	A	Ch	2.262	0
0.008	A	Ch	2.422	46
0.016	A	Ch	0.012	84
0.024	A	Ch	0.002	105
0.032	A	Ch	0.000	124
0.040	A	Ch	0.001	119
0.080	A	Ch	0.017	65
0.000	B	T	2.102	0
0.008	B	T	2.286	0
0.016	B	T	1.264	1
0.024	B	T	1.295	29
0.032	B	T	0.041	38
0.040	B	T	0.018	83
0.080	B	T	0.031	49
0.000	B	Ch	2.320	0
0.008	B	Ch	1.941	37
0.016	B	Ch	0.330	67
0.024	B	Ch	0.041	51
0.032	B	Ch	0.029	63
0.040	B	Ch	0.010	98
0.080	B	Ch	0.023	77

Conditions: 22.077 mmol T or 19.744 mmol Ch + 0.100 mmol t-BHP + catalyst A: 0.01908 mmol ALCl + 0.004291 mmol decavanadate, pH 4.5; or catalyst B: 0.01908 mmol Hex$_4$NCl + 0.004306 mmol decavanadate, pH 4.5 + the given mmol ionol was made up to 8.00 cm^3 with chlorobenzene; in the dark, at 343 K.

hydroperoxides, the formation of some H_2O_2 was observed [2], but H_2O_2 was never found in the presence of vanadium(V)-containing ion-pair complexes.

3.3. Oxidation of hydrocarbons as a function of catalyst concentration

The data in Table 1 reveal that the rates of oxidation of both hydrocarbons initially increased nearly linearly with increase of the concentration of the catalyst; then, after a short constant section, the rate started to decrease at about 0.1 M. At concentrations $<10^{-4}$ M, the catalytic activity of the ion-pair complex was somewhat lower than that of the pure onium salt because the oligomer anion is situated in the interior of the spherical inverse micelles, and the approach of the substrate molecules to the vanadium(V) centres is therefore hindered. With increasing concentration of the complex catalyst, the micelles grow and are transformed into a more open-layer structure. It is believed that at higher concentrations (at about 0.1 M), the growing layers start to fold back and form a hollow spherical structure in which the inter-aqueous compartments are again isolated from the surroundings and the activity starts to fall [2]. At lower catalyst concentrations, the hydroperoxides primarily formed underwent slow transformation. From $\sim 3 \times 10^{-3}$ M catalyst in the oxidation of T, and from $\sim 4 \times 10^{-4}$ M in that of Ch, all the hydroperoxides quickly disappeared and were transformed into higher oxidation products. It should be mentioned, however, that these threshold concentrations depend on the nature and on

the concentration of free onium salt, on whether it was used in excess during the preparation, and on the pH of the extracted aqueous vanadium(V) solution. Beyond the threshold concentrations, the yields of T-one, T-ol, Ch–O and Ch-ol increase considerably.

3.4. ^{51}V NMR spectral behaviour of ion-pair catalysts

The NMR spectral behaviour of vanadium(V) in aqueous solution has been thoroughly investigated ([8,9] and related references therein). We observed three peaks (A, B and C) for aqueous decavanadate (at 0.0116 M), with chemical shifts similar to the literature data [8]: −422 to −425, −502 to −505 and −517 to −524 ppm (see spectra (a) in Figs. 2 and 3), but with somewhat different area ratios: 1:2.30:2.40, instead of the published 1:2:2. The decavanadate peaks start to appear just below pH 7, together with the peaks of differently protonated mono-(VO_4^{3-}), di-($V_2O_7^{4-}$), cyclic tetra-($V_4O_{13}^{6-}$) and cyclic pentavanadates ($V_5O_{15}^{5-}$). In the range $3 < pH < 5$, decavanadate is the only species present; below pH 3, the peak of the hexacoordinated VO_2^+ can also be observed, at −545 ppm.

The NMR spectrum of aqueous decavanadate, however, is altered considerably at room temperature when it is extracted into chlorobenzene by ALCl or Hex$_4$NCl in the form of a neutral ion-pair complex. At equivalent phase-transfer concentrations (where the concentration ratio [QX]/[V(V)] is about 0.4:1, i.e. the composition of the ion-pair complex is probably $Q_4^+[H_2V_{10}O_{28}^{4-}]$ [1]) at room temperature and in a N$_2$ atmosphere, peak A was broadened and shifted to −414 ppm in both cases of PTCs. Peak B appeared only as a shoulder at −488 ppm for ALCl, and as a peak at −489 ppm for Hex$_4$NCl. Peak C appeared at −508 ppm in both cases (see spectra (b) in Figs. 2 and 3). This broadening and shifting of the peaks, together with the changes in the area ratios, may be due to strong interactions between the decavanadate anion and the cations, resulting in considerable structural deformation of the decavanadate oligomer. However, it should also be considered that aqueous and organic ^{51}V NMR shifts seldom correlate well [10] which is especially valid for non-polar solvents.

When the temperature of the solutions containing the ion-pair complexes was raised to 343 K and

the solutions were kept under a N$_2$ atmosphere for 120 min, the NMR spectra changed considerably (see spectra (c) in Figs. 2 and 3), but formation of vanadium(IV) could not be detected by ESR. The spectra changed similarly when these hydrocarbons were subjected to oxidation in the presence of ion-pair complexes (see spectra (d) and (e) in Figs. 2 and 3).

The appearance of new peaks and the alterations in the peak areas can be attributed in part to hydrolytic (e.g. the hydrolytic cleavage of O bridges binding two or three V atoms in decavanadate) and in part to redox processes (e.g. one-electron reduction of vanadium(V) in the vanadium oligomer by radicals formed). It should be mentioned that, after maintenance of the ion-pair catalyst solutions at 343 K under either a N$_2$ or an O$_2$ atmosphere, these solutions remained perfectly clear for many days, and no turbidity or precipitation could be observed with the naked eye. This allows the conclusion that neither the hydrolytic nor the redox processes caused any severe disintegration or destruction of the decavanadate structure. If disaggregation had occurred, it would have resulted in smaller ions with more negative charges. Consequently, a larger quantity of positive onium ion would then be needed to neutralise the increased number of negative charges (see the formulae mentioned in the introduction of this section), as otherwise some of the vanadium species would be precipitated. Similarly, no turbidity or precipitation was observed when the ion-pair catalyst was prepared with phase-transfer catalyst in excess.

The changes in the NMR spectra were usually accompanied by changes in colour of the reaction mixtures. During the oxidation of hydrocarbons catalysed by the onium-decavanadate ion-pair complexes, the initially yellowish solutions turned greenish-yellow, yellowish-brown, brown, etc., depending on the conditions and the extent of O$_2$ uptake. In such cases, the NMR investigations of oxidised solutions revealed new lines at $−550 → −630$ ppm, besides the decavanadate peaks. Particularly in the oxidation of T, at greater conversions, and especially when the reaction mixture was rather dark, the solution sometimes became NMR-silent, presumably because the vanadium(V) centres were reduced quantitatively.

The one-electron reduction of some vanadium(V) centres was also indicated by the ESR measurements. In the oxidation reaction mixtures of both
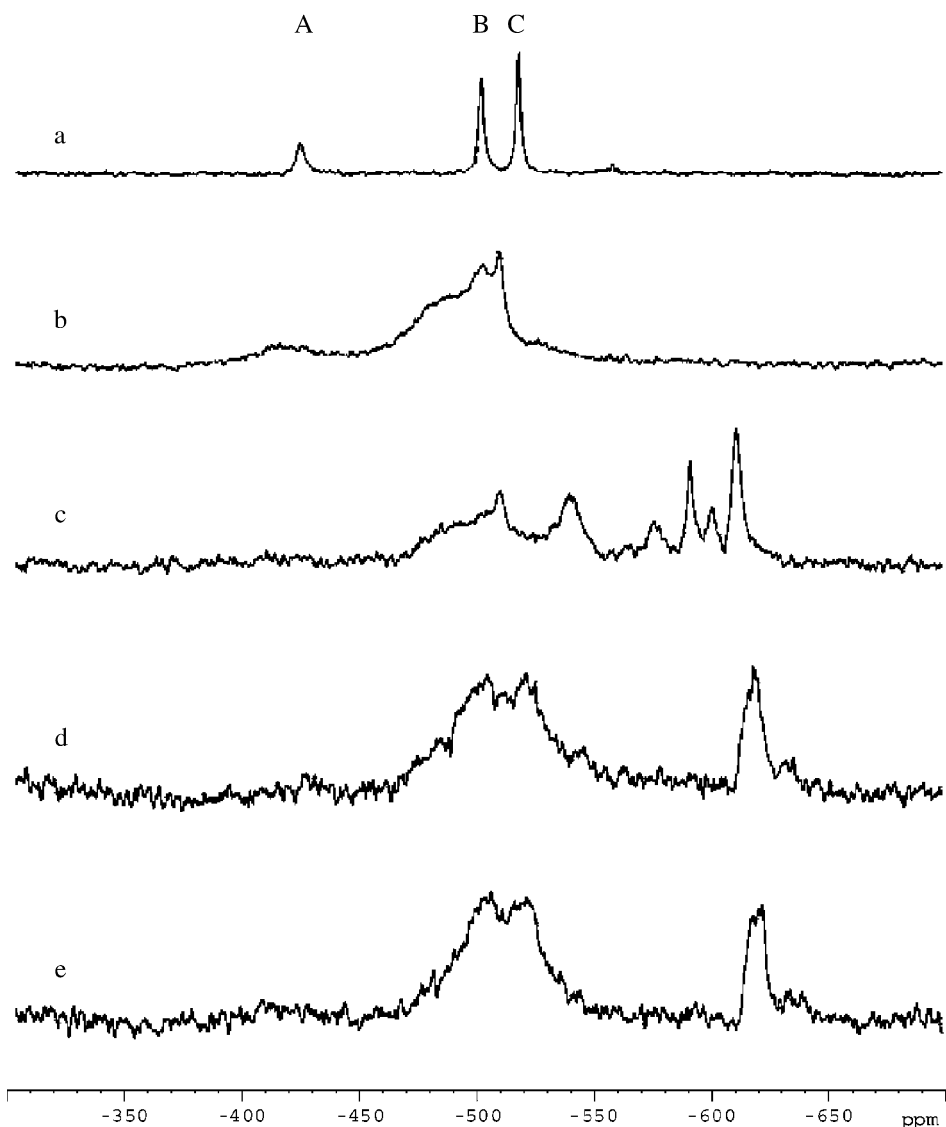
Fig. 2. NMR spectra of decavanadate in water and in chlorobenzene. Conditions: (a) 0.01156 M aqueous NaVO₃ adjusted to pH 4.50, at 298 K, in N₂ atmosphere, (b) 0.0884 mmol AL–V(V), 0.4:1, pH 4.50 ion-pair complex dissolved in 8.00 cm³ chlorobenzene, at 298 K, in N₂ atmosphere, (c) as (b), but after heating at 343 K for 120 min in N₂ atmosphere, (d) 0.0884 mmol AL–V(V), 0.4:1, pH 4.50 ion-pair complex + 0.1 mmol t-BHP + 19.744 mmol Ch filled up to 8.00 cm³ with chlorobenzene, after oxidation at 343 K for 120 min, (e) 0.0884 mmol AL–V(V) 0.4:1, pH 4.50 ion-pair complex + 0.1 mmol t-BHP + 22.072 mmol T filled up to 8.00 cm³ with chlorobenzene, after oxidation at 343 K for 120 min.

hydrocarbons, the well-known eight-peak vanadium(IV) spectrum was observed; a 15 hyperfine-peak spectrum characteristic of the mixed-valence vanadium(IV, V) complexes was never obtained.

3.5. Influence of water on the catalyst activity

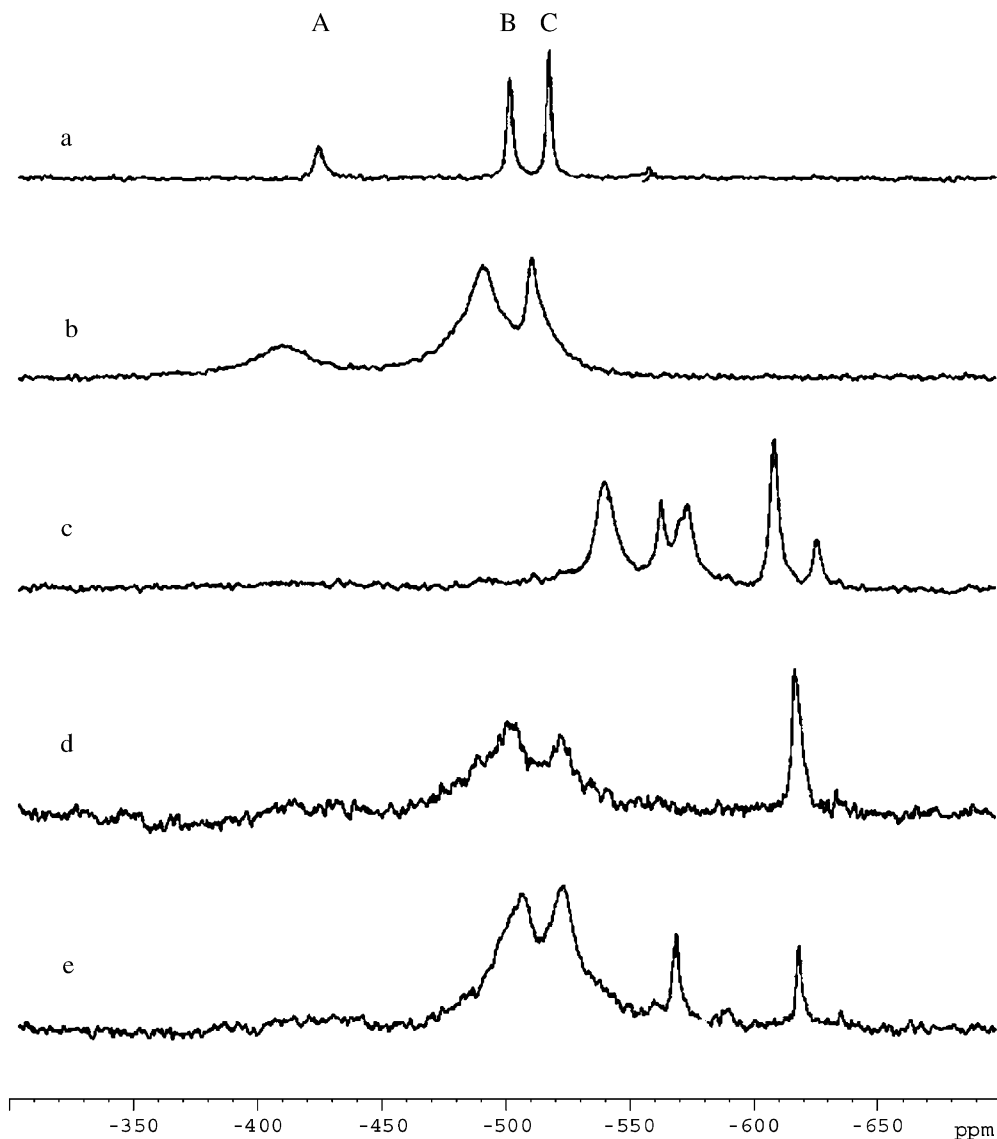In connection with the use of an onium-decavanadate ion-pair catalyst for the oxidation of hydrocarbons

Fig. 3. NMR spectra of decavanadate in water and in chlorobenzene (below the spectra). Conditions: (a) 0.01143 M aqueous $NaVO_3$ adjusted to pH 3.50, at 298 K, in N_2 atmosphere, (b) 0.09025 mmol Hex_4N–V(V), 0.4:1, pH 3.50 ion-pair complex dissolved in 8.00 cm^3 chlorobenzene, at 298 K, in N_2 atmosphere, (c) as (b), but after heating at 343 K for 120 min in N_2 atmosphere, (d) 0.09025 mmol Hex_4N–V(V) 0.4:1, pH 3.50, ion-pair complex + 0.1 mmol t-BHP + 19.744 mmol Ch filled up to 8.00 cm^3 chlorobenzene, after oxidation at 343 K for 120 min, (e) 0.09025 mmol Hex_4N–V(V) 0.4:1, pH 3.50 ion-pair complex + 0.1 mmol t-BHP + 22.072 mmol T filled up to 8.00 cm^3 with chlorobenzene, after oxidation at 343 K for 120 min.

by O_2, the role of water should be considered. It was mentioned above that water is always present in the catalyst solutions as an unavoidable concomitant of the extraction of the aqueous catalyst solutions into a non-polar solvent. Additionally, some water

is always formed during the oxidation of the hydro-carbons. However, removal of the water from the organic phase with a usually effective drying agent (e.g. Na-A zeolite, $Mg(ClO_4)_2$ or P_4O_{10}) proved un-successful because drying for several days led to a

fall in the efficiency of the ion-pair catalyst, together with transformation or partial disaggregation of the decavanadate species.

When the water content was removed with Na-A from a freshly prepared catalyst solution in chlorobenzene, and the solution was kept over the zeolite at least for 2 days, the original yellow colour became orange-yellow and the activity of the catalyst diminished considerably. The activity could not be restored by replacing the water removed in this way ($\sim$20 μl H_2O/sample). The colour change can be attributed to a slow hydrolysis of Na-A by the water-saturated chlorobenzene solution, Na-A being the salt of a very weak acid and a strong base. Part of the onium-decavanadate ion-pair started to disaggregate in response to the alkali formed in situ in chlorobenzene, and lower aggregates appeared with their orange-yellow colour. In the presence of $Mg(ClO_4)_2$ as drying agent in a chlorobenzene solution of the ion-pair complex, a fall in catalytic activity was similarly observed. The NMR spectrum of such a dried solution was very noisy, probably because of the colloidal (unfilterable) onium-ClO_4 particles present.

When P_4O_{10} was used as drying agent, the NMR spectrum of such an onium-decavanadate solution changed fundamentally: instead of the usual peaks

A, B and C, only a single sharp peak appeared, at −361 ppm, and the originally faint orange-yellowish solution was an unripe lemon-yellow, probably due to the formation of some heteropolyphosphate derivative of vanadium(V).

3.6. Influence of the reaction products on the oxidation of hydrocarbons by O_2

The aim of this investigation was to acquire information on the reasons for the early termination of the catalysed oxidations of hydrocarbons by O_2. To this end, the effects of the -ol, -one and epoxide products of the oxidations of T and Ch were examined. The influence of Ch-one was not studied in detail, because this product was never observed under the experimental conditions applied. (Our latter finding is in contrast with the observation [11] of minute quantities of -one products during the uncatalysed oxidation of cyclic olefins (cyclopentene, Ch and cycloheptene) by O_2 under somewhat milder conditions (at 333 K), but only after a prolonged reaction time (811 min).) Data obtained in the presence of the ion-pair complexes of decavanadate with ALCl and Hex$_4$NCl are presented in Tables 3 and 4. For easier orientation, the alterations caused by the initial addition of the oxidation

Table 3

Oxidation of tetralin by O_2 catalysed by ion-pair complexes $Q^+_{(6-n)}[H_nV_{10}O_{28}^{(6-n)-}]$ (Q^+: $AL^+(MeOct_3N^+)$, Hex_4N^+)

	$AL^+(MeOct_3N^+)$					Hex_4N^+				
	$\Delta[O_2]$	$\Delta[O^{corr}_{act}]$	Δ[T-one]	Δ[T-ol]	$\Delta[O_2]_{exc}$	$\Delta[O_2]$	$\Delta[O^{corr}_{act}]$	Δ[T-one]	Δ[T-ol]	$\Delta[O_2]_{exc}$
Additive: none										
	4.082	0.357	2.138	3.173	1.586	3.990	0.328	2.223	2.878	1.439
Additive: 3.000 mmol T-ol										
	1.066	0.098	0.784	3.368[a]	0.184	0.330	−0.060	0.330	3.120[a]	0.060
Difference	−3.016	−0.259	−1.354	−2.805	−1.402	−3.660	−0.388	−1.893	−2.758	−1.379
Additive: 3.000 mmol T-one										
	4.750	0.138	5.151[a]	4.921	2.460	4.332	0.218	5.236[a]	3.775	1.897
Difference	+0.668	−0.217	+0.013	+1.748	+0.874	+0.342	−0.120	+0.013	+0.897	+0.458
Additive: 1.978 mmol Ch–O										
	3.327	0.417	2.087	1.645	0.822	0.547	0.099	0.362	0.170	0.084
Difference	−0.755	+0.060	−0.051	−1.528	−0.764	−3.443	−0.239	−1.861	−2.708	−1.355
Additive: 3.056 mmol Ch-ol										
	0.589	−0.060	0.413	0.463	0.227	0.181	−0.060	0.067	0.347	0.173
Difference	−3.493	−0.417	−1.725	−2.710	−1.359	−3.809	−0.398	−2.156	−1.876	−1.266

Composition: 22.077 mmol tetralin + 0.1 mmol t-BHP + 0.048 mmol catalyst (pH 4.50, 1:1) dissolved in 8.00 cm^3 chlorobenzene.

[a] The total quantities of the given species. At the end of each run, the applied quantities of additives were recovered quantitatively.

Table 4

Oxidation of cyclohexene by O_2 catalysed by ion-pair complexes $Q^+_{(6-n)}[H_n V_{10} O_{28}^{(6-n)-}]$ (Q^+: $AL^+(MeOct_3N^+)$, Hex_4N^+)

	$AL^+(MeOct_3N^+)$				Hex_4N^+			
	$\Delta[O_2]$	$\Delta[O_{act}^{corr}]$	$\Delta[Ch-O]$	$\Delta[Ch-ol]$	$\Delta[O_2]$	$\Delta[O_{act}^{corr}]$	$\Delta[Ch-O]$	$\Delta[Ch-ol]$
	Additive: none							
	5.266	−0.020	0.402	4.871	3.932	0.059	0.186	3.687
	Additive: 3.000 mmol T-ol							
	2.437	0.059	0.276	2.103	0.491	−0.060	0.060	0.493
Difference	−2.829	+0.079	−0.126	−2.768	−3.441	−0.119	−0.126	−3.194
	Additive: 3.000 mmol T-one							
	5.116	−0.020	0.515	4.621	3.508	0.119	0.379	3.011
Difference	−0.150	0.000	+0.113	−0.250	−0.424	+0.060	+0.193	−0.676
	Additive: 1.978 mmol Ch–O							
	4.493	−0.040	1.978[a]	4.532	2.370	0.158	1.978[a]	2.212
Difference	−0.773	+0.020	−0.402	−0.339	−1.562	+0.099	−0.186	−1.475
	Additive: 3.056 mmol Ch-ol							
	0.327	−0.060	0.026	3.416[a]	0.115	−0.068	0.036	3.205[a]
Difference	−4.939	−0.040	−0.376	−4.511	−3.817	−0.127	−0.150	−3.538

Composition: 19.650 mmol cyclohexene + 0.1 mmol *t*-BHP + 0.048 mmol catalyst (pH 4.50, 1:1) dissolved in 8.00 cm^3 chlorobenzene.

[a] The total quantities of the given species. At the end of each run, the applied quantities of additives were recovered quantitatively.

products, expressed in term of the conversion ratios, are provided separately in Table 5.

The data in Table 5 show that the O_2 uptake was hindered (with the exception of T-one) by all the reaction products of both hydrocarbons and for both ion-pair complex catalysts. In the meanwhile, however, the nature of the oxidation products was not altered at all. This observation allowed the conclusion that the early termination of the catalysed oxidation of hydrocarbons by O_2 is mostly due to inhibition by products of oxidation. Nevertheless, the available kinetic information (relating to the changes in the O_2 uptake in time, and the estimation of the reaction products after a given

conversion) and the knowledge that radicals can be detected do not appear to be sufficient. It would be desirable to collect further information on the nature and the fate of intermediates involved before a final conclusion can be reached. Until then, the available information will be summarised as follows.

ALCl has been reported [2] to be a more effective onium salt catalyst than Hex_4NCl for the oxidation of T, whereas just the opposite was found during the catalysed oxidation of Ch. However, this behaviour was somewhat altered when the appropriate ion-pair complexes of decavanadate were used as catalysts instead of simple onium ions: the catalysed oxidations

Table 5

Influence of products on the catalysed oxidations of hydrocarbons by O_2 (expressed in term of conversion ratio $[\Delta O_2]^{product}/(\Delta O_2)_{none}$)

Catalyst	AL–V(V)	Hex_4N–V(V)	AL–V(V)	Hex_4N–V(V)
Substrate	T	T	Ch	Ch
ΔO_2 (mmol)	4.082	3.990	5.266	3.932
Additive: conversion ratio				
α-Tetralol (3.0 mmol)	0.261	0.083	0.463	0.125
α-Tetralone (3.0 mmol)	1.163	1.085	0.971	0.892
Cyclohexene oxide (1.978 mmol)	0.815	0.137	0.853	0.603
2-Cyclohexen-1-ol (3.056 mmol)	0.144	0.045	0.062	0.029

Conditions: as in Tables 3 and 4.

of both hydrocarbons were faster in the presence of Al–V(V) than in the presence of Hex$_4$N–V(V). The deviations in the catalytic activities can probably be explained by the differences in the water contents of the catalyst solutions: although hygroscopic, commercial Hex$_4$NCl contains much less water than does ALCl. It is noteworthy, that the quantity of water is reduced during extraction into the organic phase, when decavanadate is also present in the aqueous phase (see Table 1 in [3]). Further, it should also be considered that the symmetries of these onium ions are different: CH$_3$(Oct)$_3$N$^+$ is not as symmetric as (Hex)$_4$N$^+$, and consequently their polarising abilities differ.

The oxidations of both hydrocarbons were strongly suppressed when T-ol was initially added to the reaction mixtures. In the oxidation of T, this behaviour may be explained by assuming a reversible disproportionation of T–OOH resulting in O$_2$ and T-ol. According to another view, it may be assumed that the decomposition of T–OOH involves radicals: e.g. HR–OOH $\rightarrow$ HR–O$^\bullet$ + $^\bullet$OH, HR–OOH + $^\bullet$O–RH $\rightarrow$ HR–OO$^\bullet$ + HR–OH, HR–OO$^\bullet$ + $^\bullet$OH $\rightarrow$ O$_2$ + HR–OH, that this route could similarly be inhibited by T-ol acting as a phenolic inhibitor. Unfortunately, because of the lack of a pure preparation, the decomposition of T–OOH has not been investigated so far, and a decision between these alternatives should therefore be postponed.

It was also observed that the formation of T-one was considerably diminished when T-ol was introduced initially into the reaction mixture; the added T-ol was recovered at end of oxidation. This latter observation may be an indication that T-one is formed in another way, and not via a subsequent oxidation of T-ol.

In the catalysed oxidation of Ch, the rates of Ch-ol formation were also reduced in response to the initial addition of T-ol, in spite of the fact that an analogous disproportionation or decomposition of Ch–OOH producing O$_2$, has never been observed here. It seems that T-ol exerts some phenol-like inhibitory effect in this case.

It was observed that the rate of oxidation of T for both ion-pair complex catalysts were promoted by T-one applied initially: an enhanced O$_2$ uptake and T-ol formation (together with an increase of $(\Delta O_2)_{exc}$ according to 2:1 stoichiometry) were found. In contrast, similar behaviour was not detected during the catalysed oxidation of Ch. Therefore, the observed acceleration of T oxidation by T-one cannot simply be ascribed to impurities in the T-one preparation used. It should be mentioned that the commercial brown liquid T-one gave a colourless fraction during vacuum distillation (at 15 mmHg and 411 K), and its HPLC control indicated the presence of only a single component. As an explanation of this finding, an equilibrium interaction of T-one with tetralyl hydroperoxide is proposed, resulting in tetralyl-(1-hydroxyl-tetralyl)peroxide, similarly to the analogous reaction observed between cyclohexanone and *t*-BHP by Denisov [12]. New kinetic data [13] likewise indicated that the interactions of some hydroperoxide with ketones may contribute to the labilising of the O–O bond in such adducts. The easier homolysis of the tetralyl hydroperoxide-α-tetralone derivative may serve as a faster parallel route for the formation of radicals and result in an increased overall rate of oxidation. It must be emphasised again that such an activation of cyclohexenyl hydroperoxide by T-one was not observed at all.

The oxidations of both hydrocarbons were inhibited by the initial addition of Ch–O. Although sufficient homogeneously dissolved water is available in the reaction mixture, the hydrolysis of epoxide into diol (which could act as deactivating ligands towards vanadium(V) centres or as radical scavenger) can be excluded because Ch–O was always recovered quantitatively at the end of the oxidation. In the catalysed oxidation of Ch, surplus epoxide was not formed at all, when Ch–O was initially applied to the reaction mixture.

2-Cyclohexen-1-ol behaved as an effective inhibitor during the oxidations of both hydrocarbons: the O$_2$ uptake and the formation of other products of oxidation were similarly reduced in the presence of either ion-pair catalyst.

4. Conclusions

The oxidation of hydrocarbons by O$_2$ can be catalysed by onium-decavanadate ion-pair complexes. Free radicals are involved and the reactions can be stopped effectively with the radical scavenger ionol. The oxidations depend on the concentrations of ion-pair complexes according to maximum curves probably because of the structural changes in the inverse micelles

in response to concentration changes. The ^{51}V NMR spectrum of aqueous decavanadate ion is altered when it is transformed into ion-pair complexes and dissolved in non-polar solvent. The original peaks are shifted and new lines appear at -550 to -630 ppm when the solution is heated up to 343 K in a N_2 atmosphere. During the oxidations of these hydrocarbons, the initial yellowish colour of the catalysts is deepened and becomes greenish-yellow, yellowish-brown or brown. The changes can be attributed to both redox and hydrolytic processes, during which the decavanadate structure is probably retained. The removal of water from the catalyst solutions with effective drying agents (Na-A zeolite and $Mg(ClO_4)_2$) resulted in a decreased catalytic efficiency, and in the case of P_4O_{10} transformation of decavanadate into heteropoly derivative was observed. The rates of the catalysed oxidations of Ch and T by O_2 are strongly influenced by the -ol, -one and epoxide reaction products of these hydrocarbons.

Acknowledgements

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