Investigation of the catalytic behavior of ion-pair complexes of vanadium(V) in the liquid-phase oxidation of hydrocarbons with molecular O_2

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Abstract

Ion-pair complexes of decavanadate were prepared with different cationic phase-transfer catalysts (PTCs) and their catalytic behavior was investigated in the oxidations of tetralin and cyclohexene with molecular O_2. It was found that both the PTCs themselves and their ion-pair complexes enhanced the rate of oxidation. The catalytic activities of both the PTCs and their ion-pair complexes depend strongly on their concentrations. At low concentrations ($<10^{-3}$ M), the PTCs themselves (in the form of spherical inverse micelles) proved to be the more active but at higher concentrations where the growing micelles are transformed into a more open layer structure, the ion-pair complexes exerted the higher catalytic activities. At concentrations near 0.1 M the efficiencies of both types of catalysts decreased because the layers start to transform into a more closed micellar structure. The structure of the micelles is also influenced by the pH of the aqueous phase used during the preparation of the catalyst solutions. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It was first reported by Brederec et al. [1] that the autoxidations of oleic acid and tetralin are accelerated by quaternary ammonium salts. This effect was at that time called 'halide catalysis'. Some years later, the oxidations of tetralin, cumene and *p*-xylene were investigated by Fukui et al. [2] in the presence of other onium ions, such as sulphonium, phosphonium, selenonium and arsonium salts. They attributed the catalysis to the activation of O_2 by an interaction with the vacant d-orbitals of the central S, P, Se and As atoms.

Later, Ohkubo et al. [3–5] advanced the proposition, that the homolysis of hydroperoxide present into radicals is promoted by onium ion catalysts. This idea was accepted by van Tilborg [6] when he rejected the O_2 activation concept as arising from an experimental artifact. Hronec et al. [7,8] recently returned to the 'halide catalysis' concept.

During the past decade, PTCs have been widely used in the liquid-phase oxidation of hydrocarbons. For example, the autoxidations of cyclohexene, tetralin and cumene were investigated in the presence of non-ionic, anionic and cationic surfactants [9] and it was found that all three types of phase-transfer reagents are able to influence the rate of oxidation. If their hydrophile-lipophile balance (HLB), with a scale of 1–20 values [10,11] are not too low or not

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too high ($3 < HLB < 15$), all the non-ionic surfactants increase the rate of oxidation, otherwise they exert a slight inhibitory effect. If present in acid form, anionic surfactants all increase the rate of oxidation while their Na-salts slightly inhibit the oxidation. Cationic surfactants all increase the autoxidation rate but their catalytic efficiencies depend strongly on the experimental conditions. In biphasic systems, the catalytic activities of cationic surfactants are strongly reduced by the presence of water [12–14] as a separate phase. The oxidation rate is strongly reduced when non-ionizing but strongly solvating solvents are simultaneously applied in the reaction mixture. The rate-diminishing effect seems to correlate with the sequence of solvating ability of the solvents [9].

A recent paper [15] reported that in non-polar solvents anionic vanadium(V) species can be solubilized in the form of ion-pair complexes by cationic phase-transfer reagents. Monomeric and cyclic tetravanadate and pentavanadate formed 1:1 ion-pair complexes with Aliquat 336 (ALCl). In the range $2 < pH < 5$ because of the formation of differently protonated species, the ion-pairs had the composition 0.3–0.5. Our experiments indicated that monovanadate derivatives were catalytically inactive whereas ion-pairs of oligomeric vanadium(V) species catalyzed the oxidation of hydrocarbons by O_2 and enhanced the rate of decomposition of t-butylhydroperoxide (t-BHP). The present paper describes the catalytic behavior of ion-pair complexes of vanadium(V) with cationic phase-transfer reagents and an attempt is made to elucidate the characteristic features of this new type of catalyst.

2. Experimental

$NaVO_3 \cdot H_2O$ was used after two recrystallizations from water. Aliquat 336 (methyltrioctylammonium chloride) and the other phase-transfer reagents were Fluka products and were used without any purification. Chlorobenzene was applied as a non-polar solvent, its purification is described in [16]. To prepare an ion-pair complex, an aqueous sodium vanadate solution was adjusted to the desired pH, an equal volume of phase-transfer reagent dissolved in chlorobenzene was then added and the ion-pair complex was extracted by stirring for 10–30 min at 3000 rpm. When

the phases were separated, the organic phase was filtered on a Whatman 1PS silicone-treated phase separator.

Cyclohexene and tetralin were used as oxidation substrates. Their hydroperoxide contents (if any) were removed by passage through an activated (4 h at 400°C) Al_2O_3 column. The oxidation was carried out in a thermostated, magnetically stirred batch reactor of about $30 \, cm^3$ (fitted with a reflux condenser cooled with water to 10°C). A reaction mixture containing 2 or $3 \, cm^3$ hydrocarbon and an appropriate volume of catalyst solution was made up to $8 \, cm^3$ with chlorobenzene and was then 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 simultaneously to an automatic syringe gas buret filled with O_2 and fitted with a temperature control. The O_2 uptake versus time data were registered. After a net conversion time of 120 min (without the duration of the time lag), the reaction mixture was cooled down to about 10°C and the reaction products were estimated by iodometry (O_{act}, the content of hydroperoxide) and gas-chromatography (-ol, -one and -epoxide). The time lag is defined as the period elapsed from the time of switching on the heating until the uptake of $0.03 \, cm^3 \, O_2$.

3. Results and discussion

3.1. Oxidation of hydrocarbons in the absence of catalysts and influence of water on the oxidation

For the two hydrocarbons (freed from their hydroperoxides and freshly distilled), ΔO_2 versus time curves of an autocatalytic nature were obtained. During a net observation time of 120 min, the average rates of O_2 consumption were 0.37 and $0.23 \, \mu mol \, min^{-1}$ and the time lags amounted to 76 and 75 min for tetralin and cyclohexene, respectively. The micromol scale of the O_2 uptake should be noted because the catalyzed oxidations (discussed below) take place a 1000 times faster. Subsequently, to shorten or eliminate the time lag, in most of the experiments 0.1 mmol t-BHP initiator was applied.

It was earlier found [12–14] that the catalytic activities of phase-transfer reagent solutions depend strongly on the quantity of water present in the re-

Table 1
Concentrations of water in different solvents and catalyst solutions[a]

Solvent or catalyst solution[b]	Drier	pH of aqueous phase	Content of water (mg dm^{-3})	Concentration of water in the organic phase (M)
Benzene	P_4O_{10}	No	88.8	4.745×10^{-3}
Benzene	No	No	196.4	10.902×10^{-3}
Benzene	No	3.04	268.0	14.876×10^{-3}
Chlorobenzene	P_4O_{10}	No	20.4	1.132×10^{-3}
Chlorobenzene	No	No	212.6	11.804×10^{-3}
Chlorobenzene	No	9.04	153.5	8.523×10^{-3}
Chlorobenzene	No	3.00	244.7	13.583×10^{-3}
0.001 M ALCl	No	9.04	442.5	24.563×10^{-3}
0.001 M ALCl	No	7.15	461.0	25.589×10^{-3}
0.001 M ALCl	No	4.54	284.5	15.792×10^{-3}
0.001 M ALCl	No	3.04	197.2	10.947×10^{-3}
0.010 M ALCl	No	3.04	699.2	38.812×10^{-3}
0.01 M AL–V(V)	No	3.00	399.4	22.171×10^{-3c}

[a] The water content was measured with a Metrohm 684 KF Coulometer, using Riedel de Haen No. 34836 Hydromat-Coulomat reagent solution.

[b] Catalyst solutions were prepared in chlorobenzene.

[c] It was checked separately that vanadium(V) does not interfere with the Karl Fischer determination.

action mixtures. Table 1 provides information on the concentrations of water in the catalyst solutions and in the pure solvent. It should be borne in mind that the solubility of water depends on the pH of the aqueous solution applied during the preparation of the catalysts. It was found that the hydration of the quaternary salt AL^+–Cl^- was decreased when protonated water clusters were present instead of individual water molecules in the aqueous phase. The ion-pair complex AL–V(V) takes up fewer water molecules than the pure ALCl solution at similar concentration.

3.2. Dependence of the catalyzed oxidation on the phase-transfer reagent concentration

Figs. 1 and 2 depict the O_2 uptake curves for the catalyzed oxidations of tetralin and cyclohexene as a function of log[ALCl]. As the phase-transfer reagents themselves exert catalytic activity, for easier comparison the curves obtained for ALCl and for the ion-pair complex AL–V(V) are plotted together. The oxidations of both hydrocarbons vary according to a maximum curve as a function of the ALCl concentration. At low concentrations, ALCl proved more active than the ion-pair complex AL–V(V), at increasing catalyst concentration, the activity of the ion-pair complex AL–V(V) exceeds that of ALCl. A common feature of these catalysts is that above a certain concentra-

tion, about 0.1 M, the activity starts to decrease; the decrease is steeper for AL–V(V) than for pure ALCl. It should be observed, that the drop in rate of oxidation occurs at higher concentration in the presence of AL–V(V) as catalyst. For more detailed information concerning the measurements shown in Figs. 1 and 2, the numerical data, together with product analyses for each of the individual measurements, are compiled in Tables 4–19 in the Appendix. It should be emphasized that the drop in catalytic efficiency found here does not resemble the critical catalyst concentration (CCC) catalysis-inhibition phenomenon observed earlier in the metal oxide-catalyzed autoxidation of hydrocarbons [17]. In the CCC phenomenon, the oxidation suddenly stops when only a minute further amount of catalyst is applied which is enough to destroy the precursors of the chain-carrying radicals at once.

It was also checked that the activities of other cationic PTCs such as tetrahexylammonium chloride, benzyltributylammonium chloride, benzyltriethylammonium chloride, cetyltributyl-phosphonium bromide, etc. behave similarly when their concentrations are altered.

3.3. Other characteristics of cationic phase-transfer reagents

The oxidations of hydrocarbons can be catalyzed by all cationic surfactants, although their activities may
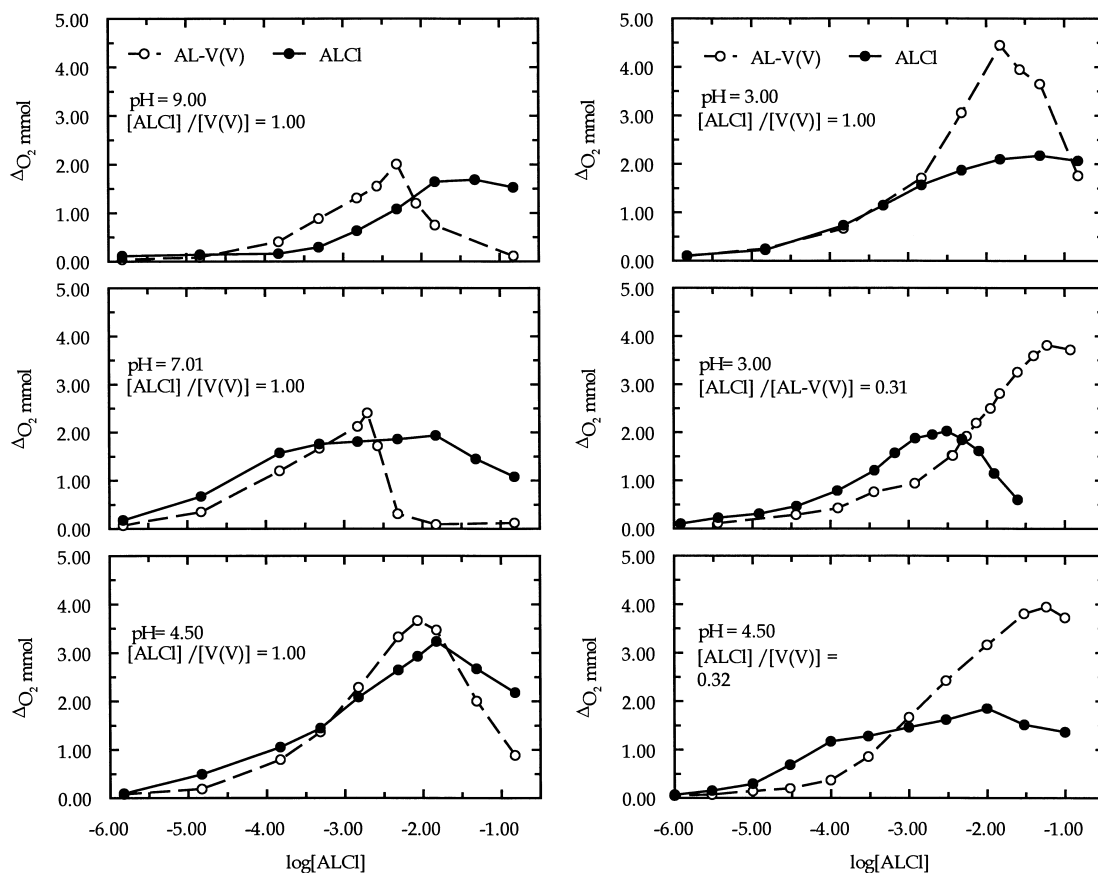
Fig. 1. Dependence of catalyzed oxidation of tetralin on the catalyst concentration at different pHs 22.078 mmol tetralin, 0.1 mmol *t*-BHP and the given concentration of catalyst were dissolved in 8 cm^3 chlorobenzene.

differ considerably [9]. The oxidations may occur with shorter or longer time lags, even when the hydrocarbon is freed from hydroperoxide immediately prior to the addition of the PTC. The oxidation of tetralin occurs faster and the time lag is shorter when the different surfactant is applied in lower concentration (0.001 M) than at higher concentration (0.01 M) in those cases when the surfactants involve a chloride counteranion. Surfactants with bromide or iodide as counteranions behave in the opposite way: a higher quantity of phase-transfer reagent (0.01 M) results in faster oxidation (Table 2). The reason for this is probably that bromide and iodide ions are oxidized more easily and the free halogens exert an additional catalytic effect. Some deviation from the above rule was observed for PTCs in which one of the alkyl groups was re-

placed by a benzyl group. With these catalyts, the higher concentration (0.01 M) results in a somewhat higher conversion. Cyclohexene behaves similarly (see Table 2).

3.4. Changes in physical properties of the catalysts as a function of their concentrations

From a kinetic point of view, the cationic surfactants behave analogously, disregarding the slight modifying effect of their counteranions. On increase of their concentrations, the rate of oxidation first increases linearly, then reaches a maximum and eventually decreases. For the ion-pair complex, the decrease in activity is usually greater. To understand this behavior, the different physical properties of ALCl and
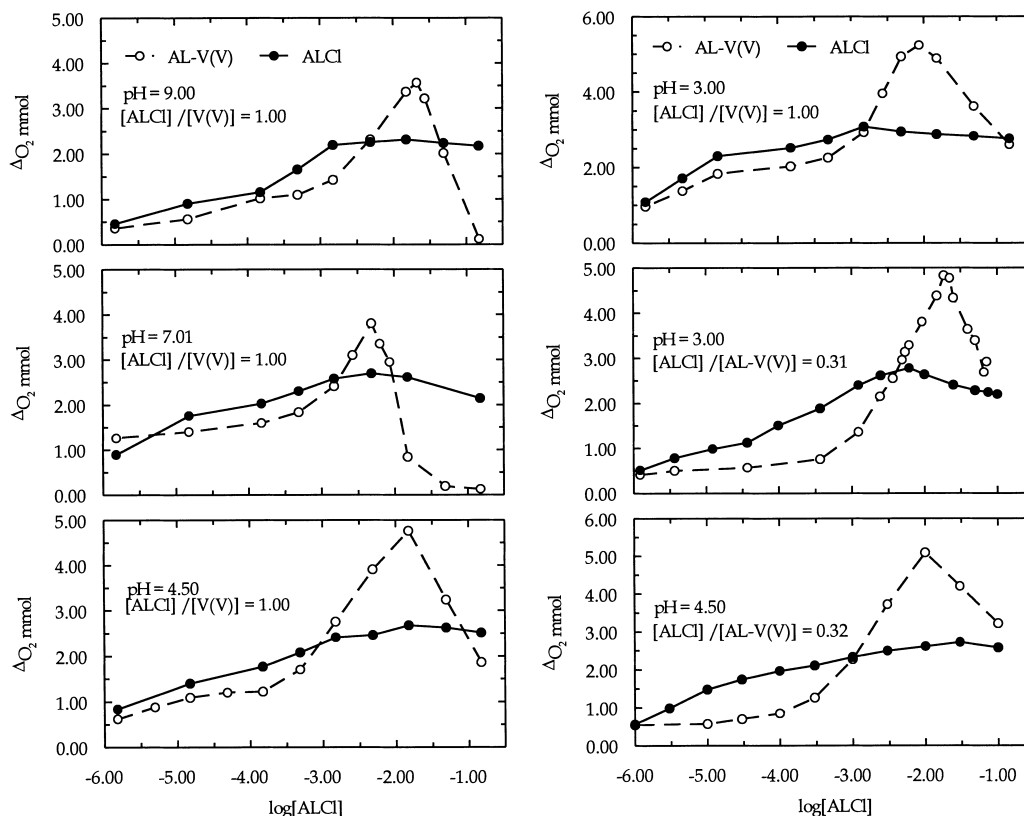
Fig. 2. Dependence of catalyzed oxidation of cyclohexene on the catalyst concentration at different pHs 19.744 mmol cyclohexene, 0.1 mmol *t*-BHP and the given concentration of catalyst were dissolved in $8\,cm^3$ chlorobenzene.

the ion-pair AL–V(V) catalysts were investigated in the concentration range 0.001 and 0.10 M in the presence of tetralin or cyclohexene. In the presence of either hydrocarbon, the viscosity of the catalyst solution first increased slowly and then ever faster between 0.01–0.1 M. The densities of these solutions displayed a similar but inverse change. The decrease in density indicates a loosening of the structure of the micelles with increasing concentration. The electrical conductivities of ALCl and the ion-pair AL–V(V) solutions underwent changes similar to those in the viscosity when their concentrations were altered. The light absorption and light scattering increased very slowly up to about 0.02 M and then accelerated with concentration.

The molar excess volumes (V_{exc}) of these solutions too were calculated. V_{exc} was defined for such complex systems on analogy to binary mixtures as follows

$$V_{exc} = \frac{x_1 M_1 + x_2 M_2 + \ldots + x_n M_n}{d_{mixt}} - \left(\frac{x_1 M_1}{d_1} + \frac{x_2 M_2}{d_2} + \ldots + \frac{x_n M_n}{d_n} \right)$$

where x_i and M_i are the concentrations and the molar weights of the species, respectively, $x_i M_i$ ($i = 1, 2 \ldots n$) is the molar quantity of component i (including the solvent) and d_{mixt} and d_i are the densities of the mixture and of pure component i, respectively. For the density of the ion-pair complex AL–V(V) an arbitrary value of 2 was chosen and the values of V_{exc} were then calculated. The V_{exc} values obtained for different reaction mixtures displayed a course analogous to that for the viscosity versus [ALCl] curve. These observations lend credence to the idea that the characteristic change in the oxidation rate as a func-

Table 2
Catalyzed oxidations of hydroperoxide-free tetralin and cyclohexene with O_2 in the presence of cationic phase-transfer catalysts $(Q^+–X^-)^a$

$Q^+–X^-$ (mmol)	2.759 M tetralin			2.468 M cyclohexene		
	ΔO_2 (mmol)	$\Delta O_{act}{}^{corr}$ (mmol)	Time lag (min)	ΔO_2 (mmol)	$\Delta O_{act}{}^{corr}$ (mmol)	Time lag (min)
– (0.000)	0.055	0.057	71	0.028	0.028	75
ALCl (0.001)	3.628	2.208	4	2.643	1.572	15
ALCl (0.010)	1.429	1.154	18	1.851	1.313	34
CPyCl (0.001)	2.833	2.348	0	1.738	1.353	8
CPyCl (0.010)	0.422	0.418	7	0.093	0.092	31
CBPBr (0.001)	1.608	1.432	0	0.943	0.736	8
CBPBr (0.010)	1.869	1.432	2	0.814	0.676	19
TBNCl (0.001)	2.615	1.552	1	1.893	0.895	33
TBNCl (0.010)	0.356	0.358	14	0.019	0.007	86
TBNBr (0.001)	0.921	0.875	0	0.528	0.358	6
TBNBr (0.010)	1.097	0.875	0	0.723	0.398	1
TBNI (0.001)	1.810	1.015	0	1.639	0.995	0
TBNI (0.010)	4.280	0.318	0	3.803	0.637	0
BBNCl (0.001)	2.630	1.711	0	2.025	1.413	6
BBNCl (0.010)	2.804	1.552	0	1.768	1.035	14
BENCl (0.001)	2.238	1.154	0	2.147	1.333	5
BENCl (0.010)	3.182	1.731	0	2.101	1.174	8

[a] Conditions: T+ $Q^+–X^-$ were dissolved in 8 cm³ chlorobenzene, abbreviations for $Q^+–X^-$: CBPBr, cetyltributylphosphonium bromide; CPyCl, cetylpyridinium chloride; TBNX⁻, tetrabutylammonium-X⁻ where X⁻ is chloride, bromide or iodide; BBNCl, benzyltributylammonium chloride; BENCl, benzyltriethylammonium chloride.

tion of the catalyst concentration is connected with the change in the structure of the micelles. At low concentrations (below 0.001 M), ALCl proved to be more active than the same quantity of the ion-pair AL–V(V) as catalyst. This can be understood because the polar V(V)-oligomer ion-pair is situated in the interior of the spherical inverse micelles and consequently the substrate molecules are hindered in their approach to the active centers, at the same time, the activity of ALCl is also reduced by the formation of an ion-pair complex. The onium ion itself displays catalytic activity because it can interact with hydroperoxide, if present, and produce chain-carrying radicals [9]. At concentrations higher than 0.001 M the catalytic activities of both catalysing species are increased considerably, presumably because the micelles are growing and transforming into larger but at the same time more open layer structures [18]. At higher concentrations (near 0.1 M), however these layers start to fold back on themselves and form a hollow spherical structure in which the interaqueous compartment is isolated from

the surroundings, resulting thereby in a fall in catalytic activity for both types of catalyst.

In order to acquire further evidence to confirm the structural changes in the inverse micelles when the concentration of the catalysts are altered, ESCA and small-angle neutron scattering (SANS) measurements are foreseen.

It should be stressed again that oxidation of these hydrocarbons may also occur but with longer time lags when the hydroperoxide is removed immediately before the start of the oxidation. In that case, the time lag is necessary for new production of a small quantity of the primary product of oxidation, the hydroperoxide of the given hydrocarbon, the (thermal or catalytic) decomposition of which is responsible for the further oxidation which is usually of an autocatalytic nature. If the substrate is a readily oxidizable substance, the oxidation starts immediately after addition of the PTC or the ion-pair complex catalyst, if not, the oxidation sets in after a considerable shorter induction period than without PTC (see data in Table 2).

If an O_2 activation mechanism had been operative, the oxidation should have started without any time lag because O_2 is present in the reaction mixture from the very beginning. It should be emphasized that we have tried to confirm the direct activation of molecular O_2 by cationic phase-transfer reagents by means of ESR, IR and Raman spectroscopy but these efforts have failed.

3.5. Products of catalyzed oxidation and the pH-dependence

The reaction mixtures were analyzed by iodometry and gas-chromatography. The iodometric estimation of O_{act}, however, is not a selective method for determination of the hydroperoxide content, as hydrogen peroxide (if formed at all) is likewise measured by this method. In order to obtain more reliable information,

an aliquot of the reaction mixture was extracted with water in a volume ratio of 1:2 under intensive stirring for 2 min. This time is sufficient for the quantitative extraction of hydrogen peroxide while only a small percentage of the hydroperoxide is transferred to the aqueous phase. It was checked that the presence of different hydroperoxides in low quantity in a weak sulfuric acid medium does not interfere with the spectrophotometric determination of hydrogen peroxide with Ti(IV) reagent. For example, in the presence of 0.0015 M ALCl (pH 4.5) as catalyst, the oxidation of 2.4 M cyclohexene resulted in 60.9% hydroperoxide, 0.6% hydrogen peroxide, 1.4% epoxide and 37.8% cyclohexenol. Cyclohexenone could not be observed at all, even on exhaustive oxidation. When the oxidation was carried out in the presence of 0.0015 M AL–V(V) (pH 4.5), the oxidation of 2.4 M cyclohexene furnished 1.27% hydroperoxide, 0.0% hydrogen

Table 3
Products of catalyzed oxidation of hydrocarbons, expressed as percentages of ΔO_2 uptake

pH	Tetralin at 1.499×10^{-3} M ALCl					Tetralin at 1.499×10^{-3} M ALCl + 1.499×10^{-3} M V(V)				
	O_{act}^{corr} (%)	[T-one] (%)[a]	[T-ol] (%)[b]	$(\Delta O_2)_{exc}$ (%)	[T-ol]/ $(\Delta O_2)_{exc}$[b]	O_{act}^{corr} (%)	[T-one] (%)[a]	[T-ol] (%)[b]	$(\Delta O_2)_{exc}$ (%)	[T-ol]/ $(\Delta O_2)_{exc}$[b]
9.00	84.7	0.0	30.0	14.7	2.04	27.3	59.4	28.7	15.4	1.86
7.00	62.7	20.1	34.1	16.9	2.01	21.5	48.9	56.7	27.2	2.08
6.38	66.7	21.1	23.4	11.5	2.03	12.6	84.2	5.6	2.5	2.24
4.50	57.3	27.6	30.1	15.0	2.00	16.9	61.9	42.8	21.7	1.97
3.00	76.1	17.1	12.9	6.0	2.15	31.3	52.7	34.9	18.9	1.85
4.50[c]	55.2	25.1	42.1	22.5	1.87	10.6	59.2	62.0	31.9	1.94
3.62[c]	63.2	25.3	24.1	12.6	1.91	20.0	75.2	2.5	0.0	–
3.00[c]	69.2	31.2	0.4	0.8	0.5	24.4	74.7	1.8	0.9	2.00

|	Cyclohexene at 1.499×10^{-3} M ALCl				Cyclohexene at 1.499×10^{-3} M ALCl + 1.499×10^{-3} M V(V)			
	O_{act}^{corr} (%)	[Ch-E] (%)[d]	[Ch-ol] (%)[e]	Σ (%)	O_{act}^{corr} (%)	[Ch-E] (%)[d]	[Ch-ol] (%)[e]	Σ (%)
9.00	77.1	2.5	20.4	100	6.9	26.3	66.7	99.9
7.00	63.6	3.5	32.8	99.9	1.6	19.2	78.9	99.7
6.38	67.6	4.0	28.5	100.1	1.6	19.2	78.8	99.6
4.50	60.9	1.4	37.8	100.1	2.2	16.2	78.4	96.8
3.00	63.9	4.3	32.0	100.2	1.3	12.0	85.6	98.9
4.50[f]	58.1	2.7	38.2	99.0	0.0	109.8	81.9	101.7
3.62[f]	76.2	3.1	21.1	100.4	0.0	12.0	87.9	99.9
3.00[f]	67.6	3.4	29.2	100.2	0.0	14.7	82.6	97.3

[a] T-one, tetralone.

[b] T-ol, tetralol.

[c] For these samples, the concentration ratio [ALCl]/[V(V)] = 0.32 was applied.

[d] Ch-E, cyclohexene epoxide.

[e] Ch-ol, 2-cyclohexen-1-ol.

[f] For these samples, the concentration ratio [ALCl]/[V(V)] = 0.32 was applied.

peroxide, 16.2% epoxide and 78.4% cyclohexenol. For both catalysts, the sum of the oxidation products was always equal to the O_2 uptake. Further data obtained at different pHs can be seen in Table 3. With the ALCl catalysts, the oxidation of 2.7 M tetralin produced 57.3% hydroperoxide, 0.4% hydrogen peroxide, 30.1% tetralol and 27.6% tetralone. Under similar conditions, the oxidation of tetralin catalyzed by the ion-pair complex resulted in 16.9% hydroperoxide, 0.0% hydrogen peroxide, 61.9% tetralone and 42.8% tetralol. In contrast with the oxidation of cyclohexene, the sum of the oxidation products here usually exceeded the level expected from the O_2 uptake. An indication of the source of this 'excess oxidation' is the ratio [tetralol]/(Σ[products] $-\Delta O_2$). As may be seen in Table 3, this ratio has a value of 2 (within experimental error). Accordingly, it may be concluded that the 'excess O_2' arises from the disproportionation of tetralyl hydroperoxide

$$2HR–OOH \rightarrow O_2 + 2HR–OH$$
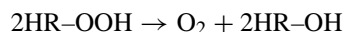
the dioxygen formed during this decomposition is used for further oxidation in the closed system.

It should be added that the disproportionation of tetralylperoxo radicals proposed by Russell [19] can not be considered here because of the following stoichiometry

$$2HR–OO^\bullet \rightarrow O_2 + RO + HR–OH$$
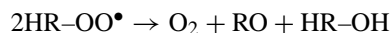
i.e. [excess O_2] $\cong$ [tetralone] was never observed.

Figs. 1 and 2 and the data in Table 2 reveal that the oxidations of the hydrocarbons depend not only on the concentrations of the catalysts but also on the pH of the aqueous phase applied for the preparation of the catalysts. The reason for this is that the water concentration of the organic phase depends on the pH of the aqueous phase. The water content is similarly a determining factor for the micelle structure.

4. Conclusions

Cationic PTCs were succesfully applied for quantitative solubilization of oligomeric vanadium(V) anions in non-polar organic solvents. The ion-pair complexes formed proved to be effective catalysts for the oxidation of hydrocarbons by O_2. The ion-pair complexes and also the PTCs themselves, undergo characteristic changes in catalytic activity when their concentrations are altered. This behavior was explained in terms of the structural changes in the inverse micelles formed.

Acknowledgements

Appendix A

Numerical data, together with product analyses for each individual measurements plotted in Figs. 1 and 2 are compiled In Tables 4–19 below:

Table 4
Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion–pair AL–V(V), respectively (pH: 9.00)[a]

log [ALC1]	log [AL–V(V)]	ΔO_2/ mmol	ΔO_{act}^{corr}/ mmol	Δ[T-one]/ mmol	Δ [T-ol]/ mmol	Σ [products] $-\Delta O_2$
−5.824	–	0.115	0.059	0.000	0.054	−0.002
−4.824	–	0.140	0.099	0.000	0.084	0.043
−3.824	–	0.161	0.138	0.000	0.046	0.023
−3.312	–	0.295	0.238	0.000	0.115	0.058
−2.824	–	0.633	0.536	0.000	0.190	0.093
−2.312	–	1.081	0.616	0.195	0.557	0.287
−1.824	–	1.642	0.736	0.347	1.129	0.570
−1.312	–	1.687	0.855	0.252	1.115	0.535
−0.824	–	1.528	1.133	0.298	0.186	0.089
−5.824	−5.824	0.037	0.019	0.000	0.018	0.000
−4.824	−4.824	0.084	0.059	0.000	0.050	0.025
−3.824	−3.824	0.408	0.298	0.031	0.135	0.056
−3.312	−3.312	0.883	0.516	0.090	0.553	0.276
−2.824	−2.824	1.309	0.357	0.778	0.376	0.202
−2.312	−2.312	2.005	0.059	1.507	0.899	0.460
−1.824	−1.824	0.748	0.099	0.654	0.034	0.038
−0.824	−0.824	0.113	−0.100	0.213	0.000	0.000

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 5
Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion–pair AL-V(V), respectively (pH: 7.01)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[T-one]/mmol	Δ[T-ol]/mmol	Σ [products] $-\Delta O_2$
−5.824	–	0.178	0.178	0.000	0.055	0.055
−4.824	–	0.666	0.516	0.012	0.270	0.132
−3.824	–	1.573	1.054	0.465	0.128	0.074
−3.312	–	1.758	1.153	0.332	0.517	0.244
−2.824	–	1.808	1.134	0.364	0.617	0.307
−2.312	–	1.861	1.213	0.288	0.706	0.346
−1.824	–	1.935	1.332	0.224	0.733	0.354
−1.312	–	1.448	0.847	0.125	0.746	0.270
−0.824	–	1.078	0.716	0.186	0.284	0.108
−5.824	−5.824	0.068	0.059	0.000	0.009	0.000
−4.824	−4.824	0.348	0.206	0.097	0.120	0.075
−3.824	−3.824	1.200	0.437	0.475	0.582	0.289
−3.312	−3.312	1.668	0.537	0.933	0.423	0.225
−2.824	−2.824	2.125	0.457	1.040	1.206	0.578
−2.312	−2.312	0.310	−0.001	0.166	0.263	0.119
−1.824	−1.824	0.088	−0.028	0.000	0.177	0.001
−0.824	−0.824	0.123	−0.100	0.000	0.222	−0.001

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 6
Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 6.38)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[T-one]/mmol	Δ[T-ol]/mmol	Σ [products] $-\Delta O_2$
−5.204	–	0.302	0.281	0.000	0.017	−0.004
−4.204	–	0.867	0.676	0.043	0.283	0.135
−3.903	–	0.950	0.636	0.112	0.344	0.138
−3.505	–	1.217	0.815	0.222	0.356	0.176
−3.204	–	1.540	1.412	0.149	0.001	0.022
−2.903	–	1.818	1.213	0.383	0.426	0.209
−2.505	–	2.175	1.451	0.326	0.739	0.341
−2.204	–	2.682	1.651	0.623	0.799	0.391
−1.903	–	2.035	1.293	0.553	0.351	0.162
−1.602	–	1.678	0.616	0.679	0.768	0.385
−5.204	−5.248	0.114	0.079	0.035	0.002	0.002
−4.509	−4.549	0.435	0.298	0.116	0.043	0.022
−4.204	−4.248	0.741	0.377	0.309	0.704	0.649
−3.903	−3.947	1.034	0.377	0.466	0.397	0.206
−3.505	−3.549	1.384	0.377	0.658	0.750	0.401
−2.903	−2.947	2.037	0.258	1.716	0.115	0.052
−2.505	−2.549	1.099	0.178	0.841	0.160	0.080
−2.204	−2.248	0.170	−0.028	0.274	0.000	0.076
−1.903	−1.947	0.098	−0.100	0.165	0.000	−0.033

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 7
Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 4.50)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[T-one]/mmol	Δ[T-ol]/mmol	Σ [products] $-\Delta O_2$
−5.824	–	0.093	0.087	0.000	0.013	0.007
−4.824	–	0.494	0.461	0.000	0.067	0.034
−3.824	–	1.056	0.895	0.063	0.198	0.100
−3.312	–	1.449	0.915	0.184	0.676	0.326
−2.824	–	2.087	1.197	0.576	0.628	0.314
−2.312	–	2.649	1.169	0.903	1.192	0.615
−1.824	–	3.233	1.929	1.256	0.086	0.038
−1.312	–	2.671	1.248	0.693	1.452	0.722
−0.824	–	2.183	1.531	0.411	0.502	0.261
−5.824	−5.824	0.077	0.059	0.000	0.039	0.021
−4.824	−4.824	0.189	0.138	0.000	0.096	0.045
−3.824	−3.824	0.795	0.457	0.111	0.453	0.226
−3.312	−3.312	1.370	0.457	0.490	0.852	0.429
−2.824	−2.824	2.290	0.387	1.419	0.981	0.497
−2.312	−2.312	3.327	0.417	2.187	1.468	0.745
−1.824	−1.824	3.470	−0.100	3.566	0.000	−0.004
−1.312	−1.312	2.008	−0.100	2.108	0.000	0.000
−0.824	−0.824	0.887	−0.100	0.987	0.000	0.000

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm³ chlorobenzene.

Table 8
Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 3.00)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[T-one]/mmol	Δ[T-ol]/mmol	Σ [products] $-\Delta O_2$
−5.824	–	0.111	0.099	0.000	0.024	0.012
−4.824	–	0.226	0.178	0.000	0.095	0.047
−3.824	–	0.732	0.616	0.000	0.229	0.113
−3.312	–	1.149	0.855	0.100	0.409	0.215
−2.824	–	1.568	1.193	0.268	0.202	0.095
−2.312	–	1.873	1.173	0.471	0.439	0.210
−1.824	–	2.098	1.551	0.459	0.173	0.085
−1.312	–	2.176	1.492	0.560	0.145	0.021
−0.824	–	2.069	1.153	0.742	0.349	0.175
−5.824	−5.824	0.100	0.091	0.000	0.0090	0.000
−4.824	−4.824	0.252	0.258	0.000	0.000	0.006
−3.824	−3.824	0.670	0.537	0.036	0.218	0.121
−2.824	−2.824	1.712	0.537	0.902	0.598	0.325
−2.312	−2.312	3.056	0.557	2.377	0.241	0.119
−1.184	−1.184	4.445	−0.100	3.960	1.139	0.554
−1.568	−1.568	3.948	−0.100	4.032	0.000	−0.016
−1.312	−1.312	3.651	−0.100	3.378	0.000	−0.013
−0.824	−0.824	1.760	−0.100	1.854	0.000	−0.006

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm³ chlorobenzene.

Table 9

Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 4.50)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[T-one]/mmol	Δ[T-ol]/mmol	Σ [products] $-\Delta O_2$
−5.522	–	0.154	0.139	0.000	0.015	0.000
−5.000	–	0.295	0.258	0.000	0.079	0.039
−4.522	–	0.689	0.497	0.199	0.002	0.009
−4.000	–	1.172	0.974	0.198	0.003	0.003
−3.522	–	1.283	0.935	0.371	0.007	0.030
−3.000	–	1.469	1.094	0.381	0.000	0.006
−2.522	–	1.619	0.895	0.407	0.682	0.365
−2.000	–	1.857	1.213	0.552	0.178	0.086
−1.520	–	1.520	1.332	0.201	0.004	0.017
−1.000	–	1.367	0.895	0.466	0.010	0.004
−6.000	−5.504	0.043	0.035	0.000	0.009	0.001
−5.522	−5.027	0.069	0.051	0.000	0.018	0.000
−5.000	−4.504	0.141	0.099	0.034	0.006	−0.002
−4.522	−4.027	0.204	0.138	0.000	0.057	−0.009
−4.000	−3.504	0.368	0.258	0.133	0.000	0.003
−3.522	−3.027	0.859	0.317	0.429	0.224	0.111
−2.522	−2.027	2.426	0.258	1.437	1.505	0.774
−2.000	−1.504	3.168	0.059	2.527	1.190	0.608
−1.522	−1.027	3.808	−0.001	2.481	2.578	1.250
−1.240	−0.744	3.946	−0.068	2.945	2.091	1.022
−1.000	−0.504	3.725	−0.100	2.963	1.698	0.836

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 10

Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 3.62)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[T-one]/mmol	Δ[T-ol]/mmol	Σ [products] $-\Delta O_2$
−5.522	–	0.329	0.298	0.027	0.003	−0.001
−5.000	–	0.519	0.417	0.036	0.077	0.011
−4.522	–	0.639	0.616	0.023	0.019	0.019
−4.000	–	0.811	0696	0.065	0.061	0.011
−3.488	–	1.320	0.895	0.209	0.436	0.220
−3.000	–	1.945	1.332	0.586	0.053	0.026
−2.698	–	2.392	1.512	0.606	0.576	0.302
−2.000	–	1.642	1.253	0.386	0.000	−0.003
−1.488	–	1.379	0.656	0.630	0.197	0.104
−1.000	–	1.119	0.616	0.499	0.003	−0.001
−5.509	−4.995	0.103	0.103	0.000	0.007	0.007
−4.509	−3.995	0.279	0.274	0.067	0.000	0.062
−3.509	−2.995	0.768	0.470	0.334	0.000	0.036
−2.986	−2.472	1.405	0.429	0.980	0.040	0.105
−2.509	−1.995	2.238	0.449	1.684	0.057	−0.048
−2.204	−1.705	2.810	0.298	2.505	0.002	−0.005
−1.903	−1.404	3.288	0.218	3.068	0.002	0.000
−1.426	−0.927	4.011	−0.100	4.116	0.000	0.005
−1.225	−0.726	3.824	−0.100	3.885	0.000	−0.039
−0.924	−0.407	3.493	−0.100	3.600	0.000	0.007

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 11
Dependence of the oxidation of tetralin with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 3.00)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[T-one]/mmol	Δ[T-ol]/mmol	Σ [products] $-\Delta O_2$
−5.435	–	0.223	0.206	0.020	0.003	0.006
−4.912	–	0.310	0.206	0.008	0.076	−0.020
−4.435	–	0.466	0.410	0.050	0.005	−0.001
−3.912	–	0.789	0.756	0.042	0.000	0.009
−3.435	–	1.210	0.879	0.308	0.007	−0.016
−2.912	–	1.875	1.368	0.467	0.067	0.027
−2.690	–	1.950	1.572	0.349	0.011	−0.018
−2.312	–	1.859	1.286	0.580	0.008	0.015
−2.096	–	1.609	1.368	0.197	0.023	−0.021
−1.903	–	1.145	0.858	0.253	0.020	−0.014
−1.602	–	0.599	0.470	0.098	0.029	−0.002
−5.440	−4.923	0.112	0.144	0.000	0.000	0.032
−4.440	−3.923	0.291	0.286	0.027	0.008	0.030
−3.903	−3.403	0.426	0.258	0.163	0.000	−0.005
−3.440	−2.923	0.762	0.516	0.100	0.084	−0.062
−2.917	−2.400	0.942	0.510	0.221	0.445	0.234
−2.315	−1.798	1.842	0.449	1.376	0.033	0.016
−1.950	−1.440	2.499	0.532	1.980	0.000	0.013
−1.602	−1.102	3.253	0.178	2.116	1.732	0.767
−1.397	−0.808	3.590	0.079	2.510	1.939	0.938
−1.225	−0.730	3.812	−0.100	3.918	0.000	0.006
−0.924	−0.424	3.717	−0.100	3.822	0.000	0.005

[a] Conditions: 2.759 M tetralin + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm³ chlorobenzene.

Table 12
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 9.00)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−5.824	–	0.461	0.457	0.010	0.000	0.006
−4.824	–	0.901	0.895	0.044	0.000	0.038
−3.824	–	1.154	0.994	0.035	0.118	−0.007
−3.312	–	1.657	1.412	0.035	0.204	−0.006
−2.824	–	2.194	1.691	0.055	0.447	−0.001
−2.312	–	2.257	1.571	0.162	0.518	−0.006
−1.824	–	2.314	1.392	0.055	0.876	0.009
−1.312	–	2.235	1.571	0.059	0.589	−0.016
−0.824	–	2.172	1.133	0.038	1.002	0.001
−5.824	−5.824	0.360	0.337	0.019	0.020	0.016
−4.824	−4.824	0.562	0.516	0.061	0.030	0.045
−3.824	−3.824	1.017	0.417	0.171	0.458	0.029
−3.312	−3.312	1.097	0.147	0.315	0.612	−0.023
−2.824	−2.824	1.424	0.099	0.361	0.942	−0.022
−2.312	−2.312	2.317	0.059	0.461	1.810	−0.032
−1.824	−1.824	3.365	0.019	0.371	2.910	−0.065
−1.678	−1.678	3.566	−0.001	0.282	3.290	0.005
−1.569	−1.569	3.220	−0.020	0.231	3.005	−0.004
−1.312	−1.312	2.013	−0.060	0.383	1.675	−0.015
−0.824	−0.824	0.121	−0.100	0.010	0.216	0.005

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm³ chlorobenzene.

Table 13
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 7.01)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−5.824	–	0.895	0.815	0.032	0.085	0.037
−4.824	–	1.756	1.492	0.065	0.215	0.016
−3.824	–	2.025	1.432	0.114	0.489	0.010
−3.312	–	2.304	1.452	0.102	0.767	0.017
−2.824	–	2.578	1.630	0.090	0.846	−0.012
−2.312	–	2.697	1.531	0.096	1.132	0.062
−1.824	–	2.614	1.690	0.080	0.817	−0.027
−0.824	–	2.142	1.332	0.056	0.800	0.046
−5.824	−5.824	1.261	1.094	0.242	0.000	0.075
−4.824	−4.824	1.400	0.895	0.274	0.221	−0.010
−3.824	−3.824	1.596	0.218	0.402	0.966	−0.010
−3.312	−3.312	1.838	0.059	0.404	1.358	−0.017
−2.824	−2.824	2.409	0.099	0.516	1.794	0.000
−2.568	−2.568	3.100	0.051	0.347	2.709	0.007
−2.312	−2.312	3.807	−0.021	0.238	3.636	0.046
−2.195	−2.195	3.356	−0.032	0.240	3.170	0.022
−2.064	−2.064	2.948	−0.061	0.238	2.741	0.001
−1.824	−1.824	0.841	−0.020	0.133	0.726	−0.002
−1.312	−1.312	0.195	−0.100	0.014	0.283	0.002
−0.824	−0.824	0.131	−0.100	0.023	0.225	0.017

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 14
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 6.38)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−5.505	–	0.599	0.556	0.022	0.029	0.008
−5.204	–	0.935	0.934	0.043	0.000	0.042
−4.509	–	1.774	1.691	0.067	0.046	0.030
−4.204	–	2.257	1.850	0.095	0.328	0.016
−3.903	–	2.533	1.929	0.121	0.485	0.002
−3.204	–	2.814	1.770	0.254	0.783	−0.007
−2.903	–	2.847	1.909	0.114	0.810	−0.014
−2.204	–	3.002	1.810	0.102	1.080	−0.010
−1.903	–	3.035	1.730	0.176	1.123	−0.006
−1.602	–	2.712	1.531	0.108	1.053	−0.020
−0.999	–	2.059	1.531	0.099	0.428	−0.001
−5.505	−5.549	0.677	0.668	0.052	0.000	0.043
−4.509	−4.549	0.953	0.537	0.238	0.156	−0.022
−4.204	−4.248	0.969	0.198	0.319	0.435	−0.017
−3.903	−3.947	1.051	0.138	0.300	0.608	−0.005
−3.505	−3.549	1.482	0.059	0.507	0.811	−0.105
−3.204	−3.248	1.827	0.051	0.362	1.407	−0.007
−2.903	−2.947	2.444	0.039	0.470	1.927	−0.008
−2.505	−2.549	3.400	0.011	0.271	3.128	0.010
−2.204	−2.248	2.816	−0.068	0.157	2.720	−0.007
−2.028	−2.072	2.373	−0.076	0.245	2.190	−0.014
−1.903	−1.947	0.489	−0.068	0.042	0.544	0.029

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 15
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 4.50)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−5.824	–	0.839	0.815	0.005	0.013	−0.006
−4.824	–	1.402	1.372	0.047	0.000	0.017
−3.824	–	1.770	1.472	0.024	0.205	−0.069
−3.312	–	2.079	2.048	0.064	0.000	0.033
−2.824	–	2.409	1.466	0.032	0.912	0.001
−2.312	–	2.461	1.730	0.085	0.640	−0.006
−1.824	–	2.675	1.466	0.034	0.116	−0.059
−1.312	–	2.624	1.691	0.066	0.848	−0.019
−0.824	–	2.511	1.691	0.030	0.779	−0.011
−5.824	−5.824	0.623	0.616	0.024	0.000	0.017
−5.312	−5.312	0.880	0.815	0.042	0.027	0.004
−4.824	−4.824	1.094	0.895	0.067	0.127	0.005
−4.312	−4.312	1.203	0.815	0.122	0.268	0.002
−3.824	−3.824	1.223	0.338	0.325	0.552	−0.008
−3.312	−3.312	1.705	0.118	0.520	1.052	−0.015
−2.824	−2.824	2.755	0.059	0.446	2.151	−0.099
−2.312	−2.312	3.908	−0.061	0.397	3.581	0.009
−1.824	−1.824	4.760	−0.001	0.214	4.641	−0.005
−1.312	−1.312	3.240	−0.100	0.071	3.267	−0.002
−0.824	−0.824	1.864	−0.100	0.045	1.918	−0.001

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 16
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 3.00)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−5.824	–	1.086	0.994	0.015	0.091	0.014
−5.312	–	1.717	1.472	0.005	0.224	−0.016
−4.824	–	2.303	1.491	0.059	0.779	0.016
−3.824	–	2.522	1.507	0.060	0.940	−0.15
−3.312	–	2.739	2.248	0.072	0.422	0.003
−2.824	–	3.081	1.969	0.134	0.985	0.007
−2.312	–	2.948	2.566	0.046	0.327	−0.009
−1.824	–	2.880	1.663	0.068	1.157	0.008
−1.312	–	2.833	1.790	0.039	1.005	0.001
−0.824	–	2.767	1.468	0.050	1.248	−0.001
−5.824	−5.824	0.968	0.755	0.044	0.190	0.021
−5.312	−5.312	1.379	0.994	0.234	0.150	−0.001
−4.824	−4.824	1.834	1.094	0.189	0.543	−0.008
−3.824	−3.824	2.032	0.576	0.399	1.061	0.004
−3.312	−3.312	2.259	0.218	0.514	1.513	−0.014
−2.824	−2.824	2.935	0.039	0.351	2.514	−0.031
−2.569	−2.569	3.956	−0.040	0.546	3.400	−0.050
−2.312	−2.312	4.937	−0.060	0.605	4.359	−0.033
−2.064	−2.064	5.240	−0.060	0.421	4.863	−0.016
−1.824	−1.824	4.890	−0.080	0.231	4.672	−0.067
−1.312	−1.312	3.623	−0.100	0.149	3.542	−0.032
−0.824	−0.824	2.605	−0.100	0.071	2.599	−0.035

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 17
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 4.50)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−6.000	–	0.567	0.454	0.015	0.093	−0.005
−5.522	–	0.989	0.974	0.017	0.000	0.002
−5.000	–	1.480	1.352	0.023	0.111	0.006
−4.522	–	1.746	1.332	0.029	0.380	−0.005
−4.000	–	1.969	1.531	0.069	0.357	−0.012
−3.522	–	2.109	1.492	0.050	0.600	0.033
−3.000	–	2.330	1.452	0.068	0.782	−0.028
−2.522	–	2.498	1.452	0.067	0.930	−0.049
−2.000	–	2.616	1.490	0.069	1.055	−0.002
−1.522	–	2.725	1.531	0.072	1.102	−0.20
−1.000	–	2.583	1.293	0.063	1.231	0.004
−6.000	−5.504	0.546	0.496	0.054	0.000	0.004
−5.000	−4.504	0.580	0.377	0.096	0.111	0.004
−4.522	−4.026	0.705	0.179	0.243	0.78	−0.005
−4.000	−3.504	0.849	0.417	0.255	0.192	0.015
−3.522	−3.027	1.266	0.059	0.391	0.773	−0.043
−3.000	−2.504	2.277	−0.029	0.582	1.689	−0.035
−2.522	−2.027	3.724	−0.084	0.738	3.051	−0.019
−2.000	−1.504	5.091	−0.100	0.499	4.666	−0.026
−1.522	−1.027	4.203	−0.100	0.216	4.016	−0.071
−1.000	−0.504	3.214	−0.100	0.130	3.156	−0.028

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalyst dissolved in 8.00 cm^3 chlorobenzene.

Table 18
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 3.62)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−6.000	–	0.500	0.497	0.020	0.000	0.017
−5.698	–	0.682	0.676	0.030	0.000	0.024
−5.301	–	1.088	1.011	0.045	0.033	0.001
−5.000	–	1.397	1.332	0.049	0.015	−0.001
−4.602	–	1.742	1.492	0.066	0.172	−0.012
−4.124	–	1.800	1.492	0.059	0.234	−0.015
−3.602	–	1.856	1.452	0.083	0.330	0.009
−2.999	–	2.060	1.551	0.061	0.443	−0.005
−2.602	–	2.218	1.691	0.070	0.467	0.010
−2.301	–	2.388	1.810	0.098	0.476	−0.004
−1.903	–	2.550	1.890	0.086	0.564	−0.010
−1.602	–	2.674	1.850	0.070	0.746	−0.008
−1.301	–	1.620	1.173	0.027	0.430	−0.010
−1.125	–	1.110	1.014	0.022	0.055	−0.019
−0.999	–	0.907	0.795	0.017	0.107	0.012
−5.810	−5.296	0.598	0.388	0.077	0.113	−0.020
−5.644	−5.130	0.575	0.437	0.066	0.0620	−0.010
−5.509	−4.995	0.570	0.347	0.081	0.150	0.008
−4.986	−4.472	0.285	0.164	0.083	0.036	−0.002
−4.509	−3.995	0.465	0.185	0.094	0.207	0.021
−3.945	−3.431	0.754	0.042	0.357	0.506	0.151
−3.509	−2.995	1.057	−0.019	0.249	0.820	−0.007
−2.986	−2.473	2.021	0.022	0.377	1.667	0.045
−2.685	−2.172	2.913	−0.019	0.349	2.560	−0.023
−2.301	−1.802	4.039	−0.068	0.318	3.784	−0.005
−1.903	−1.404	4.557	−0.100	0.304	4.338	−0.015
−1.602	−1.103	4.812	−0.100	0.301	4.564	0.047
−1.301	−0.802	3.880	−0.100	0.152	3.784	−0.044
−1.145	−0.647	3.517	−0.100	0.155	3.446	−0.016

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalysts dissolved in 8.00 cm^3 chlorobenzene.

Table 19
Dependence of the oxidation of cyclohexene with O_2 on the concentration of catalysts ALC1 and ion-pair AL–V(V), respectively (pH: 3.00)[a]

log[ALC1]	log[AL–V(V)]	ΔO_2/mmol	ΔO_{act}^{corr}/mmol	Δ[Ch-E]/mmol	Δ[Ch-ol]/mmol	Σ [products] $-\Delta O_2$
−5.912	–	0.513	0.511	0.017	0.000	0.015
−5.435	–	0.782	0.695	0.033	0.058	0.004
−4.913	–	0.989	0.980	0.026	0.000	0.017
−4.435	–	1.129	1.009	0.031	0.111	0.022
−4.009	–	1.508	1.327	0.031	0.102	−0.048
−3.435	–	1.883	1.613	0.053	0.224	0.007
−2.912	–	2.399	1.816	0.090	0.501	0.008
−2.602	–	2.619	1.770	0.089	0.766	0.006
−2.213	–	2.777	1.939	0.134	0.732	0.028
−1.999	–	2.638	1.878	0.085	0.662	−0.013
−1.602	–	2.404	1.770	0.065	0.567	−0.002
−1.301	–	2.286	1.810	0.076	0.390	−0.010
−1.125	–	2.243	1.690	0.064	0.478	−0.011
−1.000	–	2.198	1.472	0.061	0.655	−0.010
−5.912	−5.399	0.414	0.316	0.061	0.023	−0.014
−5.435	−4.923	0.506	0.287	0.079	0.129	−0.011
−4.435	−3.923	0.571	0.075	0.088	0.380	−0.028
−3.435	−2.923	0.759	−0.018	0.195	0.561	−0.021
−2.912	−2.399	1.364	0.002	0.291	1.045	−0.026
−2.612	−2.098	2.152	−0.003	0.316	1.713	−0.126
−2.310	−1.798	2.964	−0.051	0.506	2.506	−0.003
−2.033	−1.521	3.809	−0.072	0.436	3.405	−0.040
−1.732	−1.220	4.836	−0.060	0.342	4.512	−0.042
−1.404	−1.059	3.643	−0.100	0.256	3.446	−0.041
−1.301	−0.806	3.396	−0.100	0.131	3.318	−0.047
−1.146	−0.651	2.920	−0.100	0.130	2.921	0.031

[a] Conditions: 2.468 M cyclohexene + 0.0125 M t-BHP + the corresponding catalysts dissolved in 8.00 cm^3 chlorobenzene.

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