

Oxidation of hydrocarbons by O₂ in the presence of VO(acac)₂ as catalyst

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Abstract

The reactions of cyclohexene (Ch) and tetralin (T) in the pure liquid state and in their solutions in chlorobenzene were found to exhibit a strong dependence on the concentration of the catalyst VO(acac)₂: a double maximum curve was observed in consequence of the presence of the catalyst in various forms as a result of its tendency to undergo aggregation. The monomer form of the catalyst below 10⁻⁴ M proved more active than the dimer (or oligomer) at higher concentrations. However, only a single maximum was observed when toluene was applied as solvent in place of chlorobenzene. In a closed reactor system, the oxidation of Ch produced Ch-OOH, Ch-O (epoxide) and Ch-ol, but Ch-one was never found. In the oxidation of T, T-OOH, T-ol and T-one were obtained. In some cases, the sum of the oxidation products was greater than might be expected from the measured O₂ uptake, because of the disproportionation of T-OOH into O₂ and T-ol. It was observed that the catalyst is able to interact with and is thereby activated by T. Consequently, the oxidation of T can start in the absence of a hydroperoxide initiator; this was not the case, however, in the oxidation of Ch. The ion-pair VO²⁺-aerosol-OT also exerted a catalytic effect, but with lower activity, and a double maximum was not produced on increase of the ion-pair concentration. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The acetylacetonate complex of the vanadyl ion, VO(acac)₂, was first prepared and described by Morgan and Moss [1] in 1914. Problems later arose concerning the composition and behaviour of this compound. These problems were clarified by Jones [2], and the recipes given by Rowe and Jones [3] have subsequently been generally applied by the users of this reagent. The compound can now be obtained commercially in crude form.

Graddon [4] determined the molecular weight of VO(acac)₂ dissolved in molten solvents: 523 (dimer) in triphenylmethane, 546 in diphenyl, 510 in diphenylamine, and 247 (monomer) in camphor (the melting point of camphor is 179–181 °C, whereas those of the other three compounds are well below 100 °C). Graddon considered that the dimerization involves double –O– bridges incorporating the O atoms of the VO group. Graddon also observed that the solutions of VO(acac)₂ in molten hydrocarbons were at first homogeneous, but slowly deposited a blue solid (we have found it to be dark-grey or black), which is possibly a polymeric six-coordinated species containing –O– bridges. Atherton et al. [5] called attention to the air-sensitivity of VO(acac)₂ solutions (in mixtures of

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ethanol and carbon tetrachloride): it was observed that solutions prepared on the open bench had ESR spectra which changed with time, the hyperfine coupling becoming greater than that for either of the pure solvents used; at the same time, the solutions turned orange.

In the past 40 years, a number of communications have dealt with the application of VO(acac)₂ as oxygen-transfer catalyst in the oxidation of Ch in the presence of the widely-used *t*-butyl hydroperoxide (*t*-BHP) [6–12] or of dioxygen [13–17] as oxidizing agent. Although these papers contain many important and still acceptable findings and conclusions concerning the oxidation mechanism, almost all the authors ignored the fact that this catalyst is prone to association with itself, and with the solvent molecules. Further, discrepancies emerged concerning the products of oxidation of Ch. Some authors [7,13–16] stated that the catalysed oxidation of Ch leads to the formation of cyclohexene oxide (CH-O), 2-cyclohexen-1-ol (Ch-ol) and 2-cyclohexen-1-one (Ch-one) besides the hydroperoxide (Ch-OOH), but the formation of Ch-one was not confirmed by other authors [6,8,17]. Additionally, most of the authors did not take into consideration the fact that catalyst solutions prepared on the open bench may easily deteriorate during longer use. Accordingly, we report here results obtained during a reinvestigation of the oxidations of cyclohexene and tetralin by O₂ in the presence of VO(acac)₂ and another vanadium(IV) catalyst.

2. Experimental

2.1. Materials

Aldrich 95% VO(acac)₂, was recrystallized four times from chloroform (refluxed on P₄O₁₀ for 30 min then distilled). The purified preparation can be stored for many months in a N₂-filled desiccator (P₄O₁₀) in the dark, without any deterioration. Ch, T (1,2,3,4-tetrahydronaphthalene), *t*-BHP, and Aerosol OT (AOT, bis(2-ethylhexyl)sulfosuccinate-Na), an anionic phase-transfer reagent, were Fluka products. The hydrocarbons were passed over an activated (at 450 °C for 5 h) basic Al₂O₃ column for removal of their peroxidic impurities, then distilled twice under a N₂ blanket and stored in the dark, in a refrigerator.

Chlorobenzene, purified as described in [18], was applied as non-polar solvent. The oxidation was carried out in a thermostated, magnetically well-stirred batch reactor (fitted with a reflux condenser cooled with water to 10 °C). In some experiments, the given hydrocarbon was used as both substrate and solvent. In other measurements, a reaction mixture containing 2 or 3 cm³ hydrocarbon and an appropriate volume of catalyst solution (in chlorobenzene) was made up to 8 cm³ with chlorobenzene, and saturated with dried O₂ for 3 min at room temperature. The reaction vessel was next connected to the thermostat preheated to 70 °C, after a warming-up period of exactly 3 min the reactor was attached to the gas burette of syringe type filled with O₂ (with a temperature control) and the recording of the O₂ uptake was started simultaneously. The gas-measuring device automatically regulates the inside pressure at the atmospheric level. After a net conversion time of 120 min (always without the time lag), the reaction products were estimated by iodometry (O_{act}, the hydroperoxide content) and by gas chromatography (for Ch, the Ch-O and the Ch-ol; and for T, the T-ol and T-one contents). The column for Ch: 2 m × 4 mm i.d. 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: 1 m × 4 mm i.d. filled with Chromosorb W coated with 20% LAC IR 296; carrier gas N₂ at 40 cm³ min⁻¹; detector: FID. The reaction products were identified with the aid of authentic samples in both cases. The time lag was defined as the period that elapsed from the time of switching on the heating until the uptake of the first 0.03 cm³ of O₂.

Catalyst and other solutions were made up in a moderately illuminated room and were kept in the dark. Measurements were made with a Hewlett-Packard HP 8452A spectrophotometer, and the optical cell was removed from the light path during the waiting period.

3. Results and discussion

In connection with the oxidation of Ch, Gould et al. [6] assumed that the first step involved the activation of the catalyst: the vanadyl ion is oxidized by *t*-BHP to vanadium(V), which immediately interacts with *t*-BHP in a fast and reversible step, resulting in a kinetically active vanadium(V)–hydroperoxo

complex. This assumption was supported by Sams and Jørgensen [11], who investigated this rapid reaction by means of ESR and spectrophotometry; they found a rate constant of $12.9 \text{ M}^{-1} \text{ s}^{-1}$. In the initiating step, alkyl- or aryl-oxy radicals are formed. The interaction of $\text{VO}(\text{acac})_2$ with *t*-BHP (or some other hydroperoxide) is indicated by a transient red coloration [6,8]. Heterolysis of the vanadium(V)-hydroperoxo complex resulted in Ch-O and Ch-ol. However, Ch-ol was not formed in equivalent quantity in each case, because of the formation of by-products in side-reactions involving radicals (see later).

The tendency of the catalyst to undergo aggregation is supported by the data in Table 1. In differently solvating solvents, the molar absorbance of $\text{VO}(\text{acac})_2$ was found to depend on the concentration. In benzene and chlorobenzene at concentrations below

$5 \times 10^{-5} \text{ M}$, the ϵ_λ values were well in excess of 20000, whereas roughly the half of this value was found above this concentration. In toluene, only the lower value was observed, even at the lower concentrations.

The above observations led us to investigate the catalysed oxidations of Ch and T by O_2 as a function of the concentration of catalyst. Figs. 1 and 2 convincingly reveal that the O_2 uptake depends on the actual catalyst concentration. In the oxidations by O_2 of these hydrocarbons in the pure liquid state and in their solutions in chlorobenzene, two conversion maxima are observed. At the first maximum, the catalyst (at concentrations lower than 10^{-4} M), is probably present in monomer form, which is the more active form kinetically. At the second (lower) maximum, the catalyst exists as a dimer (or oligomer). In the oxidation

Table 1
Molar absorbancy of $\text{VO}(\text{acac})_2$ at different concentrations in different solvents

$[\text{VO}(\text{acac})_2]$ (M)	Solvent	λ_{max} (nm)	l (cm)	Absorbance	ϵ_λ ($\text{M}^{-1} \text{ cm}^{-1}$)
75.426×10^{-5}	Carbon tetrachloride	300	0.10	1.9321	25615.8
37.713×10^{-5}	Carbon tetrachloride	300	0.20	1.9104	25328.1
15.085×10^{-5}	Carbon tetrachloride	300	0.20	0.7856	26039.1
7.546×10^{-5}	Carbon tetrachloride	300	1.00	1.6856	22337.6
2.127×10^{-5}	Carbon tetrachloride	300	1.00	0.5249	24677.9
75.426×10^{-5}	Benzene	300	0.10	1.8181	24104.4
37.713×10^{-5}	Benzene	300	0.20	1.7710	23479.9
15.085×10^{-5}	Benzene	300	0.20	0.7249	24027.1
7.546×10^{-5}	Benzene	300	1.00	1.6182	21444.4
2.696×10^{-5}	Benzene	302	1.00	0.6069	22511.1
^a 2.696×10^{-5}	Benzene	282	1.00	0.4567	16939.9
539.297×10^{-5}	Chlorobenzene	302	0.01	1.3242	24554.2
414.843×10^{-5}	Chlorobenzene	302	0.01	1.0111	24373.1
79.432×10^{-5}	Chlorobenzene	302	0.10	1.8744	23597.5
39.716×10^{-5}	Chlorobenzene	302	0.10	0.8856	22298.3
15.085×10^{-5}	Chlorobenzene	302	0.20	0.6254	20729.2
8.296×10^{-5}	Chlorobenzene	302	1.00	1.9096	23018.3
4.148×10^{-5}	Chlorobenzene	302	1.00	0.5599	13498.0
^a 3.971×10^{-5}	Chlorobenzene	286	0.50	0.2783	14016.6
3.771×10^{-5}	Chlorobenzene	300	1.00	0.4803	12736.6
3.771×10^{-5}	Chlorobenzene	292	1.00	0.4901	12996.5
^a 2.696×10^{-5}	Chlorobenzene	288	1.00	0.3730	13835.3
539.297×10^{-5}	Acetonitrile	302	0.01	1.1500	21324.0
2.696×10^{-5}	Acetonitrile	272	1.00	0.3470	12870.9
2.694×10^{-5}	Acetonitrile	274	1.00	0.3297	12230.3
75.426×10^{-5}	Toluene	286	0.10	0.9736	12909.0
37.713×10^{-5}	Toluene	286	0.20	1.0766	14273.6
15.085×10^{-5}	Toluene	286	0.20	0.4932	16347.3
7.546×10^{-5}	Toluene	286	1.00	1.1838	15687.7
3.771×10^{-5}	Toluene	286	1.00	0.6120	16229.1

^a After 2 h.

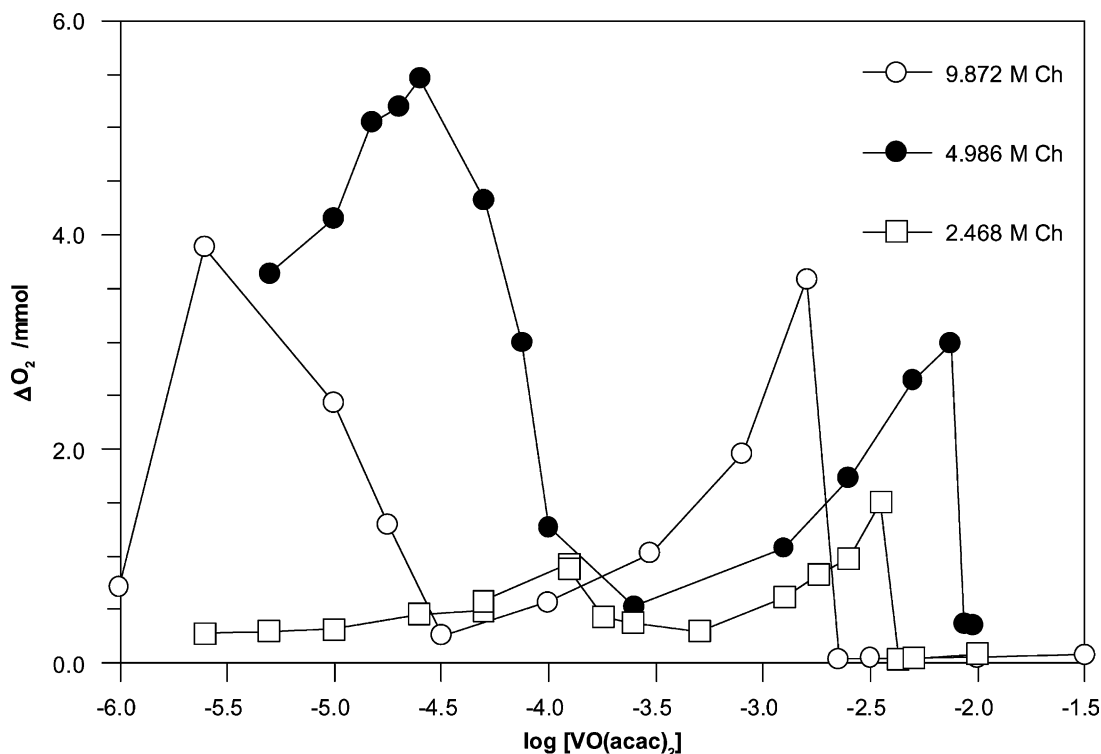


Fig. 1. Oxidation of cyclohexene by O₂ as a function of the concentration of the catalyst VO(acac)₂. Conditions: (○), Ch alone; (●), 39.488 mmol Ch + 0.100 mmol *t*-BHP; (□), 19.744 mmol Ch + 0.100 mmol *t*-BHP made up to 8.00 cm³ with chlorobenzene.

of T, the second rate maximum can sometimes barely be observed. However, in solutions of Ch and T in toluene, only a single maximum was recorded at catalyst concentrations below 10⁻⁴ M. This is in good harmony with the results of light absorbance measurement.

The products of oxidation of Ch are listed in Table 2. Following removal of the initial hydroperoxide content of the Ch, the oxidation started only after a long time lag. The oxidation of Ch produces Ch-OOH, Ch-O and Ch-ol. The sum of these products was always equivalent to the O₂ uptake. This can be seen by comparing the data in column six of Table 2 with the values of [Ch-ol]_{found}: the agreement is convincingly good in a wide range. It should be emphasized that, in accordance with the earlier findings of Gould et al. [6], Su et al. [8] and Farmer and Sundralingam [17], but in contrast with the reports of other authors [13–16], we were never able to detect any formation of Ch-one.

In the oxidation of T, tetraol hydroperoxide (T-OOH), T-ol and T-one are formed (see Table 3). In spite of the initial removal of the hydroperoxide content of the T, the oxidation here started without any time lag. It seems, that T is able to interact with the catalyst and this interaction immediately starts and then accelerates the O₂ uptake. It may be conditionally assumed that T contains oxidizing impurities which quickly produce vanadium(V). The formation of vanadium(V) acetylacetonate, however, does not result in formation of the hydroperoxide derivative, as no hydroperoxide is present which could induce prompt O₂ uptake. Consequently, we have to continue to assume that the catalyst is activated by T.

The data in column six of Table 3 indicate that the quantities of oxidation products obtained were sometimes more than that equivalent to the measured O₂ uptake. This phenomenon is referred to as “overoxidation”, expressed as $\sum \Delta[\text{products}] - \Delta\text{O}_2$. Comparison of these figures with the values of

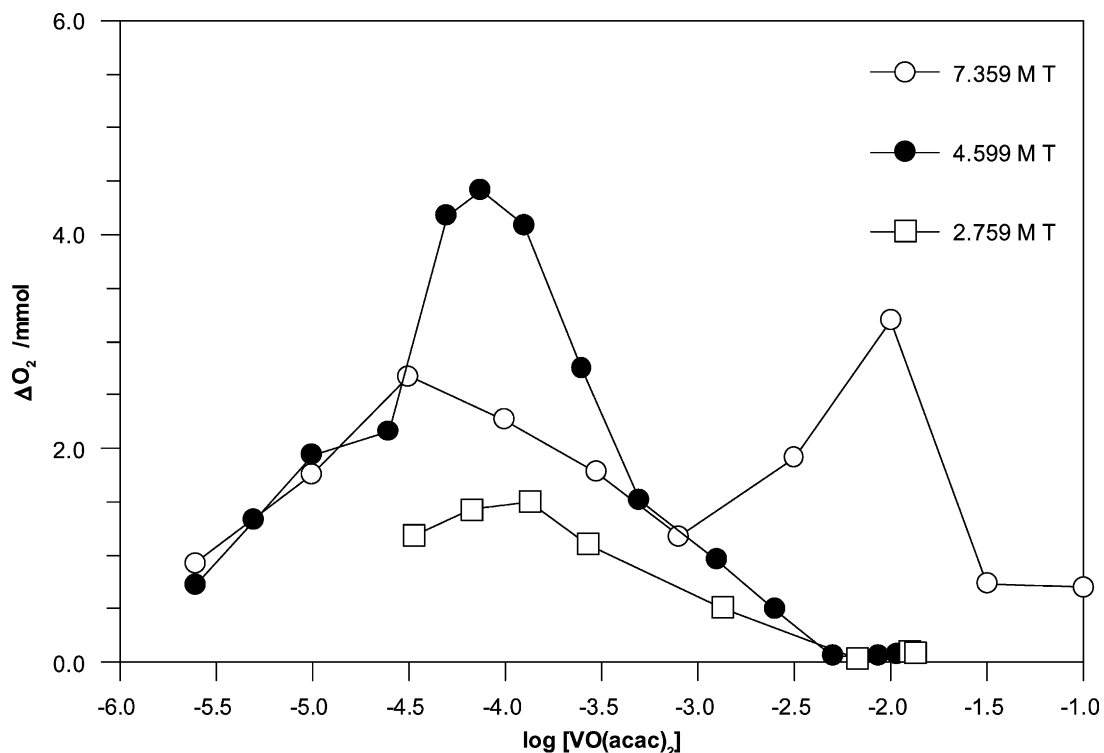


Fig. 2. Oxidation of tetralin by O_2 as a function of the concentration of the catalyst $VO(acac)_2$ Conditions: (○), T alone; (●), 36.795 mmol T + 0.100 mmol *t*-BHP; (□), 22.077 mmol T + 0.100 mmol *t*-BHP made up to 8.00 cm³ with chlorobenzene.

Table 2
Oxidation of cyclohexene by O_2 in the presence of $VO(acac)_2$ as catalyst^a

[VO(acac) ₂]/log M	ΔO_2	ΔO_{act}^{corr}	$\Delta [Ch-O]$	$\Delta [Ch-ol]$ (mmol)	$\Delta [O_2] - (\Delta O_{act}^{corr} + \Delta [Ch-O])$	Time lag (min)
-6.0040	0.717	0.597	0.074	0.046	0.046	9
-5.6060	3.887	2.188	1.521	0.158	0.178	39
-5.6060	3.882	2.188	1.528	0.161	0.166	38
-5.0040	2.435	1.353	1.084	0.000	0.002	13
-4.7490	1.291	0.338	0.167	0.790	0.786	20
-4.4990	0.257	0.039	0.102	0.116	0.116	25
-4.0040	0.572	0.049	0.330	0.203	0.193	16
-3.5270	1.028	0.052	0.440	0.587	0.536	7
-3.0970	1.960	0.040	0.505	1.410	1.415	6
-2.7950	3.584	0.048	1.591	1.940	1.945	0
-2.6450	0.041	0.000	0.021	0.019	0.020	49
-2.5000	0.045	0.000	0.017	0.027	0.028	62
-2.0000	0.095	0.008	0.032	0.055	0.055	24
-2.0000	0.057	0.000	0.014	0.044	0.043	54
-2.0000	0.194	0.000	0.102	0.093	0.092	36
-1.5000	0.081	0.000	0.035	0.046	0.046	32

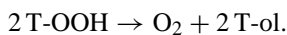
^a Conditions: a mixture of 0.100 mmol *t*-BHP initiator, and the given mmol catalyst was dissolved in 8.00 cm³ cyclohexene; in the dark, at 343 K, reaction time: 120 min. Abbreviations: Ch-O, cyclohexene oxide; Ch-ol, 2-cyclohexen-1-ol.

Table 3
Oxidation of tetralin by O₂ in the presence of VO(acac)₂ as catalyst^a

[VO(acac) ₂]/log M	ΔO ₂	ΔO _{act} ^{SOFF}	Δ[T-one]	Δ[T-ol] (mmol)	∑ Δ[products] – ΔO ₂	Time lag (min)
-5.6060	0.925	0.915	0.010	0.010	0.010	0
-5.0040	1.757	1.671	0.084	0.007	0.005	0
-5.0040	2.171	2.149	0.022	0.000	0.000	0
-4.5050	2.455	2.069	0.394	0.001	0.009	0
-4.4992	2.674	2.128	0.553	0.000	0.007	0
-4.0040	2.033	1.990	0.044	0.010	0.011	0
-4.0040	2.269	0.756	1.214	0.598	0.299	0
-3.5270	2.960	2.606	0.354	0.000	0.000	0
-3.5270	1.779	0.517	1.237	0.037	0.012	0
-3.0970	1.178	0.756	0.275	0.288	0.141	0
-2.5000	1.911	0.080	1.280	1.083	0.532	0
-2.0000	3.196	0.000	2.885	0.611	0.300	0
-2.0000	3.199	0.000	1.817	2.796	1.414	0
-1.4990	0.733	0.000	0.445	0.571	0.283	0
-1.0000	0.707	0.000	0.408	0.597	0.298	0

^a Conditions: a mixture of 0.100 mmol *t*-BHP initiator, and the given mmol catalyst was dissolved in 8.00 cm³ tetralin; in the dark, at 343 K, reaction time: 120 min. Abbreviations: T-ol, α-tetralol; T-one, α-tetralone.

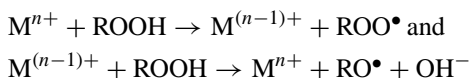
Δ[T-ol] reveals that the source of the [ΔO₂]_{excess} must be the catalysed disproportionation of T-OOH



To explain the formation of the by-products by the subsequent reactions of alkoxy and alkylperoxy radicals occurring during the metal-catalysed oxidation of olefins, the reformation of O₂ was assumed by Sheldon and van Doorn [7]:



The radicals RO[•] and ROO[•] are formed in the well-known reactions between alkyl hydroperoxide and metal ions in different oxidation states:



The formation of ROO[•] in this system was proved by Talsi et al. [12] with the aid of ESR measurements. However, the disproportionation assumed above could never be observed by the procedure used in [6], because the consumption of O₂ was not measured at all. To the best of our knowledge, the oxidation of T furnished the first experimental support for the correct-

ness of the findings of Sheldon and van Doorn [7] given earlier in connection with the metal-catalysed epoxidation of olefins with organic hydroperoxides.

In an attempt to explain the difference in kinetic behaviour of Ch and T, we investigated the absorption spectrum of catalyst VO(acac)₂ in the absence and in the presence of these hydrocarbons freed from their hydroperoxides, with the maximum possible exclusion of air or O₂. In the presence of Ch, the spectrum of catalyst did not exhibit any appreciable changes, either in chloroform or in chlorobenzene solution (Table 4). As there is no effective interaction between the catalyst and Ch, therefore, the hydrocarbon oxidation can start only after a long time lag, when a certain amount of Ch-OOH has accumulated in consequence of the slow oxidation with O₂. In the presence of T, however, the interaction led to a considerable decrease in absorbance in both solvents. The change in absorbance is instantaneous in chloroform, but a period of several minutes is necessary for stable absorbances to be obtained in chlorobenzene. The sharp peak of VO(acac)₂ at 302 nm is shifted to 304 nm and reduced, while the much lower peaks at 392, 592 and 662 nm remain practically uninfluenced. The absorption spectrum of vanadium(IV) acetylacetonate was investigated by Selbin and Ortolano [19] in the range 800–350 nm in different pure solvents. The fall in absorbance was found to be depend on the concentration

Table 4
Optical interactions between VO(acac)₂ and hydrocarbons

Solvent	Hydrocarbon	VO(acac) ₂ (M)	[Hydrocarbon] [VO(acac) ₂]	Duration (min)	λ _{max} (nm)	ε _λ (M ⁻¹ cm ⁻¹)
Chloroform	None	5.0 × 10 ⁻⁴	–	–	302	23921
Chloroform	Ch	5.0 × 10 ⁻⁴	4936	12	300	23194
Chloroform	Ch	5.0 × 10 ⁻⁴	4936	40	300	23293
Chlorobenzene	None	5.0 × 10 ⁻⁴	–	–	301	24843
Chlorobenzene	Ch	5.0 × 10 ⁻⁴	4936	12	302	24832
Chlorobenzene	Ch	5.0 × 10 ⁻⁴	4936	40	302	24769
Chloroform	None	5.0 × 10 ⁻⁴	–	–	302	23969
Chloroform	T	5.0 × 10 ⁻⁴	3679	12	304	17588
Chloroform	T	5.0 × 10 ⁻⁴	3679	40	304	17403
Chlorobenzene	None	5.0 × 10 ⁻⁴	–	–	302	23917
Chlorobenzene	T	5.0 × 10 ⁻⁴	3679	12	304	18610
Chlorobenzene	T	5.0 × 10 ⁻⁴	3679	40	304	18263
Chlorobenzene	None	5.0 × 10 ⁻⁴	–	–	302	25012
Chlorobenzene	T	5.0 × 10 ⁻⁴	5519	15	304	15372
Chlorobenzene	T	5.0 × 10 ⁻⁴	5519	40	304	15210
Chlorobenzene	None	2.5 × 10 ⁻³	–	–	302	24941
Chlorobenzene	T	2.5 × 10 ⁻³	1104	15	302	21095
Chlorobenzene	T	2.5 × 10 ⁻³	1104	40	302	21096
Chlorobenzene	None	5.0 × 10 ⁻³	–	–	302	25100
Chlorobenzene	T	5.0 × 10 ⁻³	552	15	302	22901
Chlorobenzene	T	5.0 × 10 ⁻³	552	40	302	22109

Table 5
Oxidation of tetralin and cyclohexene by O₂ in the presence of VO²⁺(AOT⁻)₂ as catalyst^a

[Catalyst]/log M	ΔO ₂	ΔO _{act} ^{soff}	Δ[T-one]	Δ[T-ol] (mmol)	∑ Δ[products] – ΔO ₂	Time lag (min)
-5.487	0.042	0.019	0.000	0.023	0.000	34
-4.487	0.089	0.019	0.000	0.084	0.014	4
-3.487	0.390	-0.100	0.232	0.515	0.257	1
-3.010	1.804	-0.100	0.929	1.894	0.919	0
-2.487	4.854	-0.100	2.974	4.060	2.080	0
-2.186	5.231	-0.100	2.749	5.062	2.480	0
-1.788	5.457	-0.100	2.329	6.462	3.234	0
-1.487	4.597	-0.100	2.092	5.201	2.596	0
-1.311	1.621	-0.100	1.002	1.436	0.717	0
-1.698 ^b	0.091	0.079	0.000	0.010	-0.002	6
-0.823 ^b	0.176	0.099	0.000	0.076	-0.001	8
[Catalyst]/log M	ΔO ₂	ΔO _{act} ^{soff}	Δ[Ch-O]	Δ[Ch-ol]	∑ Δ[products] – ΔO ₂	Time lag(min)
-4.487	0.153	0.158	0.005	0.000	0.000	6
-4.010	0.328	0.337	0.031	0.000	0.040	1
-3.487	0.387	-0.020	0.296	0.082	-0.029	0
-2.766	0.642	-0.075	0.408	0.320	0.011	0
-2.487	0.522	-0.060	0.298	0.326	0.042	0
-2.465	1.666	-0.019	1.475	0.309	0.099	0
-2.311	1.302	-0.061	0.326	1.040	0.003	0
-2.125	2.186	0.099	0.436	1.641	-0.010	0
-3.000 ^b	0.409	0.397	0.020	0.000	0.008	0
-2.766 ^b	0.642	-0.075	0.408	0.320	0.011	0

^a Conditions: a mixture of 22.077 mmol T or 19.744 mmol Ch+0.100 mmol *t*-BHP initiator, and the given concentration of VO²⁺(AOT⁻)₂.

^b Only AOT as catalyst was dissolved in 8.00 cm³ chlorobenzene; in the dark, at 343 K, reaction time: 120 min. Abbreviations: T-ol, α-tetralol; T-one, α-tetralone; Ch-O, cyclohexene oxide; Ch-ol, 2-cyclohexene-1-ol.

ratio $[T]/[VO(acac)_2]$. Hence, it can be concluded that T interacts with the catalyst and thereby promotes the oxidation without a time lag even in the absence of any hydroperoxide.

The catalytic effect of vanadyl ion was also investigated in the absence of the ligand acac by using AOT for its solubilization. In spite of the fact that anionic phase-transfer catalysts, in salt form, slightly inhibit the oxidations of the hydrocarbons by O_2 [20], the ion-pair $VO^{2+}-(AOT^-)_2$ moderately catalysed the oxidations of both T and Ch. Similar oxidation products were formed as in the case of the acac complex (see Table 5). When the concentration of catalyst was increased, however, the ΔO_2 uptake versus $\log[VO^{2+}-(AOT^-)_2]$ curve displayed the usual limiting shape. Since the oxidation started without a time lag in most cases, it can be concluded that the access of the catalytically active VO^{2+} is not appreciably hindered by the presence of the bulky counteranion. The “overoxidation” phenomenon due to the disproportionation of T-OOH was observed in the $VO^{2+}-(AOT^-)_2$ ion-pair-catalyzed oxidation of T. Similar effects were demonstrated recently [21] when different ion-pair complexes $Q^+-V_{10}O_{28}^{6-}$ were applied (where Q^+ represents the surfactant cation of the cationic phase-transfer reagent) as catalysts for the oxidation of T. It seems that vanadium(IV) or vanadium(V) ions are able to influence the above disproportionation.

4. Conclusions

The present investigation has called attention to the fact that the activity of a catalyst susceptible to aggregation can alter with the change in its concentration. This was observed in the case of $VO(acac)_2$ during the oxidations of Ch and T by O_2 . In both cases, the ΔO_2 uptake versus $\log[VO(acac)_2]$ curves displayed double maxima of different heights corresponding to the different activities of the differently aggregated species: the monomer is more active than the dimer (oligomer). In contrast, the ion-pair complex $VO^{2+}-(AOT^-)_2$, which is not prone to aggregation, gives the usual limiting curve when its concentration is increased. The above hydrocarbons behave differently when freed them from their hydroperoxides immediately before the oxidation: for T, the O_2

uptake starts at once; for Ch, it starts only after a long time lag. This is so because the catalyst is activated by interaction with T, whereas Ch is not.

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