

The role of vanadium(V) in the catalysed oxidation of hydrocarbons

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Abstract

Monomeric and oligomeric vanadium(V) species (the latter obtained by acid-induced aggregation) are mostly anionic, and can be solubilized in non-polar solvents by cationic phase-transfer catalysts. Monomeric and cyclic tetra- and pentavanadate form 1:1 ion-pair complexes with Aliquat 336 (ALCl). The ion-pairs of decavanadates have the compositions $[\text{ALCl}]/[\text{V(V)}]_{\text{org}}$ 1:0.3–0.5, due to the formation of differently protonated species at lower pHs. Both ALCl and the ion-pair complex $\text{AL}-\text{V(V)}$ influence the rate of decomposition of *t*-butylhydroperoxide and the rates of oxidation of hydrocarbons by O_2 . Pure ALCl is more active at $\text{pH} > 7$ than at $\text{pH} < 7$, in consequence of the transformation of ALCl into ALOH in alkaline medium. In contrast, the ion-pair complex $\text{AL}-\text{V(V)}$ is hardly active at $\text{pH} > 7$, due to the low or zero activity of monomeric V(V). The activities of ion-pairs containing oligomeric V(V) species exceed that of ALCl alone. It was observed that the activities of both ALCl and the ion-pair complex $\text{AL}-\text{V(V)}$ depend almost linearly on their concentration, but when an upper limit (about 0.1 M) is exceeded, the catalytic activity suddenly drops to a low value. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The chemistry of V(V) aroused wide-ranging interest when it turned out that vanadium is an essential element. Vanadium is an efficient inhibitor or activator of a number of enzymes. Like most of the high-valency transition metal ions, V(V) undergoes aggregation on the action of acid and different oligomers are formed. It was recently observed that V(V) oligomers ex-

ert different activities during the oxidation of hydrocarbons and that most of the oligomers exhibit biochemical activities (see the relevant citations in Ref. [1]). The present paper deals with the organophilization of oligomers of V(V) (obtained by acidification) through the use of phase-transfer reagents, and the application of ion-pair complexes of oligomers as catalysts in the oxidation of hydrocarbons by molecular O_2 in non-polar organic solvents.

The acid-promoted aggregation of V(V) was investigated earlier by different methods among them potentiometry, NMR, IR, UV and visible

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spectrophotometry, solvent extraction, light scattering and salt cryoscopy. The various results (sometimes contradictory) have led to the following generally accepted views, summarized on the basis of the papers of Tracey et al. [1] and Pettersson et al. [2].

In the pH range 1–5, $\text{VO}_2^+ \cdot \text{aq}$ (existing in relatively highly acidic medium) is transformed into differently protonated decavanadate ions, $\text{H}_n\text{V}_{10}\text{O}_{28}^{(6-n)-}$.

At about pH 6.5, in the ‘metavanadate range’, four ions exist: $\text{V}_5\text{O}_{15}^{5-}$, $\text{V}_4\text{O}_{12}^{4-}$ and in smaller quantities $\text{H}_2\text{V}_2\text{O}_7^{2-}$ and H_2VO_4^- .

At increasing basicities, HVO_4^{2-} , VO_4^{3-} , $\text{HV}_2\text{O}_7^{3-}$ and $\text{V}_2\text{O}_7^{4-}$ have been found.

The formation constants of different oligomers were also estimated by Tracey et al. [1], who established that the pH-dependent formation constant of the dimer increases by a factor of 3 when the pH is reduced from 9.1 to 8.5. In the same pH range, the stability constant of the trimer increases by about 6-fold, that of the tetramer 76-fold and that of the cyclic pentamer 225-fold.

2. Experimental

2.1. Materials

$\text{NaVO}_3 \cdot \text{H}_2\text{O}$ and NH_4VO_3 were used after two recrystallizations from water. The vanadium contents of solutions were estimated by the spectrophotometric method of Budevská and Johnová [3]. Aldrich Aliquat 336 (methyltriocetylammmonium chloride), tetrahexylammmonium chloride (THACl), and Fluka Aerosol OT ((bis(2-ethylhexyl)-sulphosuccinate-Na, AOT) were used as phase-transfer catalysts (PTCs) without any purification. Chlorobenzene was applied as non-polar solvent; its purification is described in Ref. [4].

pH-Titrations were performed with a Metrohm Potentiograph E 436, using an EA 121 combined glass electrode. About 0.7 M HCl reagent was used in a 2.00 cm³ syringe burette

with a slow delivery rate (0.03 cm³ min⁻¹) to promote the setting-in of the oligomerization equilibria. Electrical conductivity was measured with a Radelkis Conductivity Meter OK 102/1, using bright Pt-plate electrodes with areas of 6 × 9 mm². The recorder output of the Meter was connected to the Potentiograph, whereby the conductance vs. acid consumption curve could be recorded on the same sheet of recording paper.

2.2. Extraction of vanadium oligomers

V(V) solutions were adjusted to the desired pH, allowed to stand for at least one day in the dark, and then extracted with cationic PTCs dissolved in chlorobenzene. 0.001 M PTC solution in a quantity of 0.5–6.00 cm³ was added to 6.00 cm³ aqueous V(V) sample and the organic phase was made up to 6.00 cm³ with chlorobenzene. The mixture was then effectively stirred (3000 rpm) for 10 min to extract the anionic species into the organic phase. After separation of the phases, the organic phase was filtered on a Whatman 1PS silicone-treated phase separator to remove the adhering traces of water. Next, the vanadium content of the organic phase was estimated by measuring the optical density at 300 nm. The plot of the absorbance values obtained vs. the actual concentrations of PTC resulted in an almost linearly rising curve, which levelled off when a sufficient quantity of PTC had been introduced. The PTC concentration relating to the point of intersection of the rising and the nearly horizontal sections of the curve was regarded as the ‘neutralization point’, where the V(V) oligomer anions are just ‘neutralised’ by the surfactant cations, forming uncharged (neutral) ion-pair complexes dissolved in the non-polar solvents.

2.3. Oxidation of hydrocarbons

Cyclohexene, tetralin and cumene were used as model substances for the investigation of catalytic oxidation. Into a thermostatted and

magnetically stirred batch reactor of about 30 cm³ (fitted with a reflux condenser, cooled with water at 10°C), 2.00 or 3.00 cm³ hydrocarbon, 0.1 mmol *t*-butylhydroperoxide (*t*-BHP) and catalyst solution were introduced, and the volume was made up to 8.00 cm³ with chlorobenzene. Thoroughly dried O₂ was then bubbled through the solution for 3 min at room temperature. The reaction vessel was next switched on to the thermostat preheated to 70°C and simultaneously connected to the automatic syringe gas burette filled with O₂ and fitted with a temperature control. After a net conversion time of 120 min, the reaction products were determined by iodometry and gas-chromatography: for cyclohexene on a 2 m long 4 mm i.d. column filled with Chromosorb WAW/DMCS coated with 10% Carbowax 20 M, carrier gas N₂ at 40 cm³ min⁻¹; FID detector; for tetralin: 1 m long 4 mm i.d. column filled with Chromosorb W coated with 20% LAC IR 296, carrier gas N₂ at 40 cm³ min⁻¹; FID detector.

3. Results and discussion

3.1. Oligomerization of V(V) ions

An aqueous 0.1 M solution of NaVO₃ is slightly alkaline, with pH ~ 9. When such a solution is titrated with hydrochloric acid, a two-step titration curve is obtained. Step I (between pH 6 and 9) gives a non-regular sigmoid curve (see Fig. 1, curve a). Initially, the pH change is small, as the solution is well buffered. Inflexion point I is found at about pH 7.1. On further acid addition, step II occurs, which also furnishes a complex curve: it is steeper up to the inflexion point (at about pH 3.4) than after it. During steps I and II, only small conductance increases of 2.7% and about 7% were observed. After step II, the conductance increased considerably more steeply (see Fig. 1, curve a').

On titration of a solution of ammonium vanadate (initial pH 6.8), step I observed during the titration of the sodium salt did not appear at all,

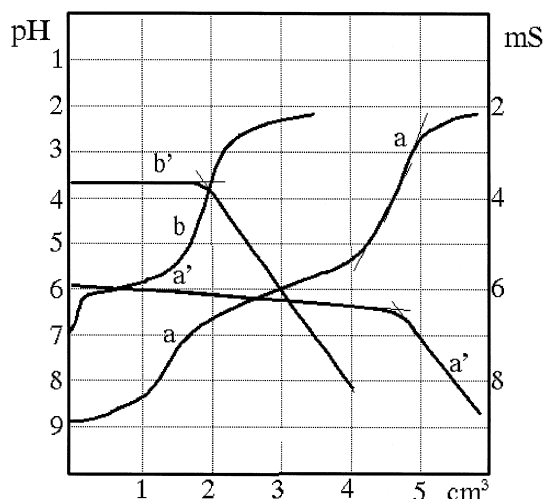


Fig. 1. Potentiometric and conductometric titrations with 0.7288 M HCl; compositions at curves a and a': 10.00 cm³ 0.09444 M NaVO₃ + 5.00 cm³ water at curves b and b': 14.907 cm³ 0.045139 M NH₄VO₃.

whereas step II was formed similarly. The conductance remained constant during step II, but it increased considerably when step II was over (Fig. 1, curves b and b').

Data on such acid titrations are listed in Table 1. The average consumption of acid for step I corresponds to $[H^+]/[V(V)] = 0.242$. The difference between the equivalence points (II–I)/[V(V)] is 0.541. The ratio of (II)/(I) is 3.27 and the value of (II–I)/(I) = 2.272. These results are in harmony with the conclusions of previous investigators, summarized in Section 1. The data indicate that the monomeric alkali metal vanadate is transformed into cyclic tetra- and pentavanadate at pH 7.1 (inflexion I) and into decavanadate at about pH 3.4 (inflexion II). For ammonium salt solutions (pH 6.8), only the second step (inflexion II) is observed.

3.2. Transfer of anionic V(V) species into non-polar solvents

Results on the extraction of V(V) ions, as a function of the pH of the aqueous phase, are reported in Table 2. In weakly alkaline medium, monomeric vanadate ions exist. They can be

Table 1
Titration of vanadium(V) salts with acid

V(V)/mmol	HCl/M	Inflexion I at pH = 7.1/mil H ⁺	I/[V(V)]	Inflexion II at pH = 4.2/mmol H ⁺	II/[V(V)]	(II-I)/ [V(V)]	II/I	(II-I)/I	Delivery rate
<i>NaVO₃</i>									
0.5493	0.2788	0.1438	0.2618	0.4739	0.8627	0.6009	3.295	2.295	B
0.5493	0.2788	0.1291	0.2349	0.4728	0.8607	0.6257	3.660	2.662	B
0.5493	0.1930	0.1481	0.2696	0.4391	0.7993	0.5297	2.965	1.965	A
0.5493	0.1930	0.1532	0.2789	0.4350	0.7924	0.5130	2.840	1.840	B
0.6592	0.1930	0.1723	0.2614	0.5233	0.7938	0.5320	3.037	2.035	A
0.8789	0.2788	0.2471	0.2811	0.7560	0.8601	0.5790	3.059	2.059	A
0.9944	0.7288	0.1818	0.1828	0.6869	0.6907	0.5069	3.770	2.757	A
0.9944	0.7288	0.1717	0.1746	0.6616	0.6728	0.4943	3.835	2.835	A
0.9777	0.7263	0.2516	0.2574	0.7499	0.7671	0.5096	2.980	1.980	A
0.9777	0.7263	0.2268	0.2320	0.7483	0.7653	0.5333	3.300	2.290	A
0.9777	0.7263	0.2262	0.2316	0.7424	0.7592	0.5276	3.270	2.280	A
0.9833	0.7288	0.2259	0.2297	0.6741	0.6855	0.4558	2.984	1.984	B
1.0216	0.7288	0.2186	0.2186	0.6923	0.4636	0.4636	3.235	2.166	B
<i>NH₄VO₃</i>									
0.6582	0.2788	–	–	0.3761	0.5714	–	–	–	A
0.6729	0.7263	–	–	0.3148	0.4678	–	–	–	A
0.6729	0.7263	–	–	0.3249	0.4828	–	–	–	A
0.8899	0.7263	–	–	0.5151	0.5788	–	–	–	A
0.8999	0.7263	–	–	0.5151	0.5788	–	–	–	A

Delivery rate: (A): 0.0348 cm³/min, (B): 0.0869 cm³/min.

Table 2

Extraction of V(V) ions with cationic phase-transfer reagents into chlorobenzene as a function of the pH of the aqueous phase

Extracted Compound	/mmol	pH	Q ⁺ X ⁻	/mmol	[V(V)] _{org} /mmol	QX/[V(V)] _{org}	Intercept
NH ₄ VO ₃	0.102	6.70	CH ₃ (Oct) ₃ NCl	0.096	0.100	0.960	0
NaVO ₃	3.093	8.10	CH ₃ (Oct) ₃ NCl	3.250	3.093	1.050	0
NaVO ₃	0.506	7.00	CH ₃ (Oct) ₃ NCl	0.501	0.503	0.996	0
NaVO ₃	9.788	5.38	CH ₃ (Oct) ₃ NCl	4.430	9.590	0.461	> 0
NaVO ₃	9.788	5.15	CH ₃ (Oct) ₃ NCl	4.560	9.520	0.478	> 0
NaVO ₃	9.550	5.00	CH ₃ (Oct) ₃ NCl	4.560	9.270	0.491	> 0
NaVO ₃	9.708	4.02	CH ₃ (Oct) ₃ NCl	4.000	9.560	0.418	0
NaVO ₃	9.630	3.65	(Hex) ₄ NCl	2.790	9.430	0.295	0
NaVO ₃	9.670	3.65	CH ₃ (Oct) ₃ NCl	3.730	9.500	0.392	0
NaVO ₃	9.470	3.56	CH ₃ (Oct) _A NCl	3.670	8.990	0.408	0
NaVO ₃	0.286	3.50	CH ₃ (Oct) ₃ NCl	0.127	0.286	0.444	< 0
NaVO ₃	9.395	2.95	CH ₃ (Oct) ₃ NCl	3.580	9.160	0.390	< 0
NaVO ₃	8.650	2.96	CH ₃ (Oct) ₃ NCl	3.500	8.140	0.429	> 0
NaVO ₃	7.950	2.00	CH ₃ (Oct) ₃ NCl	3.150	6.620	0.475	> 0
NaVO ₃	7.970	2.00	CH ₃ (Oct) ₃ NCl	3.120	6.620	0.471	> 0

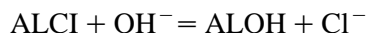
extracted quantitatively with equimolar cationic PTCs. For ammonium vanadate solution (pH 6.8), which presumably contains cyclic tetra- or pentavanadate or both, the molar ratio 1:1 remain unaltered. This points to the fact that the numbers of negative charges on the cyclic tetra- and pentavanadate ions are equal to the numbers of vanadium atoms in these oligomers. In contrast, in the pH range between 6 and 2, the molar ratio [PTC]/[V(V)] decreases to 0.3–0.5, due to the formation of differently protonated decavanadates. It is worth mentioning that at pH 2, where VO₂⁺·aq starts to appear, the extraction of vanadium does not remain quantitative because the cations cannot be extracted by cationic PTCs.

3.3. Catalysis of oxidation of hydrocarbons by O₂ with PTC and the ion-pair complex PTC–V(V)

The catalytic effects of V(V) ion-pair complexes should be compared with the effect of the given PTC used for solubilization, because the cationic PTCs themselves exert an oxidation-promoting effect.

First, the catalysed decomposition of *t*-BHP (applied as initiator) was investigated (see Table

3; the reaction mixtures were prepared as described in the footnote). In the presence of AlCl₃ alone, *t*-BHP undergoes considerable decomposition at pH > 7; at lower pH, the reaction is slower. During the decomposition, O₂ is evolved at close to 2:1 stoichiometry. The high activity at pH > 7 can be attributed to an exchange reaction in alkaline medium, resulting in the more active ALOH:



In contrast, the catalysed decomposition of *t*-BHP was slow at pH > 7 in the presence of the ion-pair complex AL–V(V); it increased considerably at pH 5.5, and then decreased slightly in the pH range 2–4. In alkaline medium, monomeric vanadate ions exist; their ion-pair complexes are stable and have low or no catalytic activity. At lower pHs, oligomeric V(V) species appear, resulting in an increase in the rate of decomposition. At higher acidities, differently protonated decavanadates are formed, with somewhat lower catalytic activities.

The pH-dependence of the catalysed oxidation of hydrocarbons by O₂ can be seen in Table 4. The data in Table 4 reveal changes with a course analogous to that for the decomposition of *t*-BHP. At pH 9.15, AlCl₃ resulted in the fastest oxidation for all three hydrocar-

Table 3

Decomposition of *t*-BHP initiator catalysed by AlCl₃ and the ion-pair complex AL–V(V) prepared at different pHs

pH	[<i>t</i> -BHP] _{0 min} mmol	[<i>t</i> -BHP] _{60 min} mmol	Δ[<i>t</i> -BHP] mmol	ΔO ₂ mmol	Conversion %
<i>ALCl</i>					
9.15	0.437	0.118	0.318	0.191	72.7
9.15	0.437	0.114	0.323	0.194	73.9
7.50	0.437	0.109	0.328	0.195	75.0
5.60	0.437	0.148	0.289	0.160	66.1
4.20	0.437	0.196	0.241	0.146	55.1
3.10	0.437	0.198	0.239	0.149	54.6
2.60	0.437	0.247	0.190	0.111	43.4
2.60	0.437	0.240	0.196	0.106	44.8
2.00	0.437	0.198	0.239	0.147	54.6
<i>AL–V(V)</i>					
9.15	0.509	0.505	0.004	–	0.70
6.38	0.509	0.451	0.058	–	11.3
5.46	0.509	0.107	0.402	–	78.9
5.43	0.509	0.106	0.403	–	79.2
4.20	0.509	0.112	0.397	–	77.9
3.29	0.509	0.217	0.292	–	57.3
2.66	0.509	0.169	0.340	–	66.8
2.41	0.509	0.326	0.183	–	35.9
1.85	0.509	0.359	0.150	–	29.4

Composition: ALCl: 9.962–04 M AlCl₃ + 5.491–0.2 M *t*-BHP in 8.00 cm³ chlorobenzene, AL–V(V): 1.00–03 M AlCl₃ + 9.44–04 M V(V) + 5.092–02 M *t*-BHP in 10.00 cm³ chlorobenzene.

bons, due to the exchange reaction mentioned previously. The oxidation decreased somewhat at lower pHs. In the presence of the ion-pair complex catalyst, the oxidation was slow at pH > 7, but increased immediately when the oligomerization set in at pH ≤ 7, and reached its maximum between pH 3 and 4. At lower pH, the rate of the catalysed oxidation was lower. It should be mentioned that the catalytic activities of both AlCl₃ and AL–V(V) depend on their concentrations according to a maximum curve.

It is a characteristic feature of the dependence on the concentration of the catalysts that at concentrations lower than 0.001 M the catalytic efficiency of AlCl₃ always exceeds the catalytic activity of the ion-pair complex AL–V(V), while in the concentration range 0.001–0.1 M the efficiency of the ion-pair complex becomes more than double that of AlCl₃, though at concentrations of about 0.1 M the activities of both catalysts drop to low values. This behaviour can probably be attributed to the change in structure

Table 4

Dependence of catalysed oxidation of hydrocarbons by O₂ on the pH adjusted in the preparation of the catalyst

Catalyst	Hydrocarbon 2.468 M	(ΔO ₂) _{120 min} in mmol measured with catalyst prepared at pH								
		9.15	7.08	6.59	6.01	5.54	4.86	4.40	3.88	3.40
AlCl ₃	Cyclohexene	3.281	–	3.064	–	3.097	–	3.069	–	3.143
AL–V(V)	Cyclohexene	1.544	3.429	4.239	4.432	4.522	4.620	4.660	4.722	4.810
AlCl ₃	Tetralin	3.129	–	2.545	–	2.490	–	2.449	–	2.371
AL–V(V)	Tetralin	0.216	1.273	1.849	2.927	3.638	4.292	4.624	4.874	4.814
AlCl ₃	Cumene	1.448	–	1.323	–	1.348	–	1.330	–	1.315
AL–V(V)	Cumene	0.228	0.586	0.891	1.146	1.457	1.512	1.508	1.706	1.696

[AlCl₃]: 6.110–03 M, [AL–V(V)]: 6.070–03 M.

of the micelles. The details of this explanation will be discussed elsewhere.

Acknowledgements

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