

Nature of the Radical Intermediates in the Decomposition of Peroxovanadium Species in Protic and Aprotic Media[†]

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Received October 6, 1993*

The decomposition reaction of peroxovanadium species, either formed *in situ* by addition of H₂O₂ to vanadium compounds or added as the isolated complex VO(O₂)(Pic)(H₂O)₂ (Pic = picolinic acid anion), has been studied both in aqueous acid solutions and in CH₃CN. In all cases, evidence for a radical chain mechanism has been obtained, initiated by the reaction between two molecules of peroxide, either H₂O₂ or a monoperoxovanadate. The occurrence of vanadium and other intermediate with unpaired electrons have been observed by indirect but rather convincing kinetic evidence.

Introduction

The finding that vanadium peroxo complexes, under very mild conditions, can hydroxylate aromatic compounds to the corresponding phenols^{1,2} has both chemical and biochemical implications. Aside from the obvious scope of vanadium in preparative organic chemistry³ its physiological role is increasingly recognized.^{4,5} Vanadium-containing enzymes, such as haloperoxidases, play an important role in biochemical oxidations.⁵ In addition, vanadium can substitute for copper in dopamine β-monooxygenase⁶ that catalyzes the hydroxylation of dopamine to norepinephrine. Moreover, vanadium binds to glycopeptides such as bleomycins, thus activating DNA cleavage by dioxygen.⁷ In these biochemical oxidations, the intermediacy of peroxovanadium species is postulated though not unambiguously proved.^{4,5} It may be anticipated, however, that chemistry more complex than that of Fenton-like systems⁸ should take place in the reactions between vanadium species and dioxygen or its reduced forms, i.e. superoxide ion and hydrogen peroxide. The lack of detailed information of such a chemistry prompted us to reinvestigate^{2,9–14} the simplest model system, i.e. the decomposition of peroxo-

vanadium species, both in aqueous and in organic solvents, with a view toward establishing the nature of the species occurring in solution. In fact, despite extensive work on these systems,^{9–14} particularly on the aqueous ones, the intermediates formed during the decomposition reaction remain somewhat elusive. Nevertheless our results indicate that radicals dominate the scene in peroxovanadium decompositions. On the other hand, the nature and the chemistry of such radical species, deduced from kinetic and spectroscopic data, are clearly different from those of hydroxyl radical.⁸

Experimental Section

EPR spectra have been recorded on a Bruker ER-220D instrument, equipped with a Bruker ER-4111 temperature control unit and a Systron-Donner 6246 A microwave frequency counter. Electronic spectra have been obtained by using a Lambda 5 Perkin-Elmer instrument with a temperature control better than ±0.05 °C.

The stoichiometry of the decomposition reaction has been determined by measuring the amount of dioxygen evolved at the end of the reaction by means of a standard gas buret thermostated at the desired temperature. The mathematical treatment leading to the calculated curve of Figure 9 involves the simultaneous integration of the equations of Scheme 3 with the Bulirsch–Stoer method.¹⁵ The mean square difference between the calculated and the experimental data has been minimized with the Simplex procedure.¹⁶

Materials. Milli-Q grade water and HPLC grade acetonitrile were used. VOSO₄, NH₄VO₃ and hydrogen peroxide (35% w/v solution) were commercially available products used as received. Complex I has been synthesized according to published procedures.^{1,2}

Kinetic Measurements. In the vanadium-catalyzed decomposition of H₂O₂ the decrease of the peroxide content with the time has been determined by iodometry. In a typical experiment, to a 25 mL of aqueous solution of H₂O₂ of known concentration, adjusted at the desired pH value by addition of HClO₄, was added 1 mL of an aqueous solution of the vanadium catalyst to start the decomposition.

In the decomposition of I in CH₃CN the course of the reaction was monitored by measuring the decrease of the absorbance at 450 nm (ε = 444) typical of the peroxo complex.

[†] Work taken in part from the Ph.D. Thesis of M. Bonchio.

* Abstract published in *Advance ACS Abstracts*, March 15, 1994.

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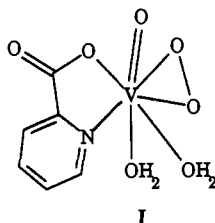
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Results

In the family of peroxovanadium compounds, the self-decomposition reaction and the oxidation of certain organic substrates appear to be two closely related processes.^{1,2,17-21} In particular, in protic solvents, peroxovanadium complexes, formed *in situ* by addition of H₂O₂ to a vanadium precursor, are usually fairly stable. Accordingly, in such media, nucleophilic substrates, e.g. thioethers, sulfoxides, and allylic alcohols can be conveniently oxidized, providing quantitative yields of the corresponding products sulfoxides, sulfones, and epoxy alcohols, respectively.^{20,21} Particularly in the case of allylic alcohol epoxidation, the chemoselectivity observed indicates that the oxidation proceeds through a polar mechanism.²² It should be noted that in such processes the concentration of peroxovanadium species is always rather small, e.g. 10⁻⁵ mol L⁻¹. This, as we shall see later in this paper, has important mechanistic consequences because, under these conditions, radical decomposition processes triggered by the bimolecular reaction of the vanadium species with the peroxide are minimized.²³

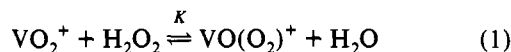
In aprotic solvents, such as CH₃CN, some peroxovanadium complexes containing heteroligands such as picolinic acid e.g. VO(O₂)(Pic)(H₂O)₂ (I), whose solid-state structure is



undergo a relatively fast self-decomposition whose radical nature is suggested by the autocatalytic behavior observed, typical of chain reactions.^{1,2}

When, in such media, together with I, aliphatic or aromatic hydrocarbons are present, a parallel hydroxylation reaction takes place, yielding alcohols and phenols respectively.^{1,2} Again, this suggests the occurrence of oxidizing radicals. Therefore, a careful examination of the decomposition reaction of peroxovanadium species under different conditions is a necessary requisite for the understanding of the oxidation chemistry of such compounds, particularly the radical one.

Decomposition of the V(V)/H₂O₂ System in Acidic Aqueous Solution. In typical experiments 2 × 10⁻³ mol NH₄VO₃ in the presence of a 30-fold excess of H₂O₂ at pH = 0 (HClO₄) was dissolved in water at 25 °C. Under these acidity conditions the predominant vanadium species present is the red monoperoxo derivative [VO(O₂)⁺](aq) (λ_{max} = 455 nm, ε = 278) formed in a very fast equilibrium reaction largely shifted to the right, as in eq 1.⁹⁻¹⁴



At the same time, a smooth decomposition of hydrogen peroxide takes place which can be conveniently monitored by measuring the decrease of the active oxygen content by iodometry. It is worthy of note that, in the absence of added V(V), the

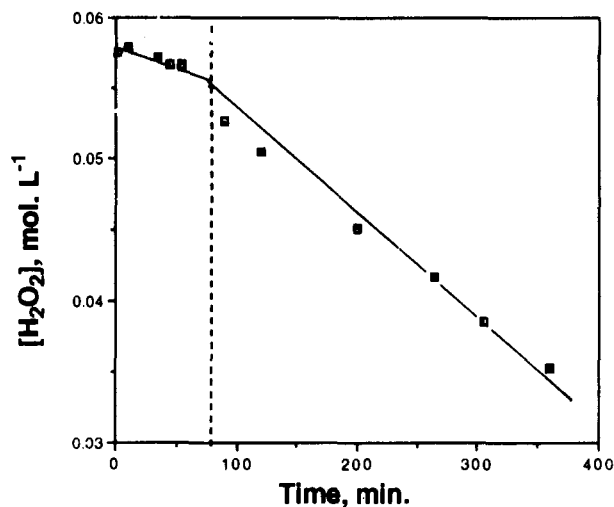


Figure 1. Reaction profile in the V(V)-catalyzed decomposition of H₂O₂ in water (pH = 0) at 25 °C, [NH₄VO₃]₀ = 2 × 10⁻³ mol L⁻¹, and [H₂O₂]₀ = 0.057 mol L⁻¹.

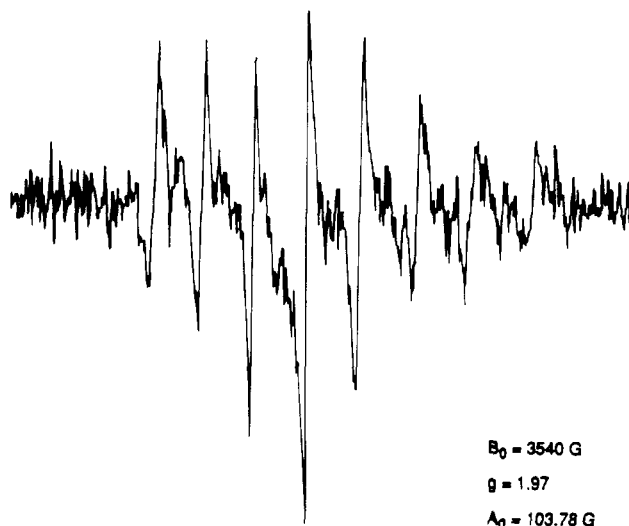


Figure 2. EPR spectrum registered in the V(V)-catalyzed decomposition of H₂O₂ in water (pH = 0) at 25 °C, [NH₄VO₃]₀ = 2 × 10⁻³ mol L⁻¹, and [H₂O₂]₀ = 0.057 mol L⁻¹.

decomposition of H₂O₂ in the same time interval is almost negligible, as confirmed by control experiments. The variation of the hydrogen peroxide concentration as a function of time is shown in Figure 1.

Two distinct parts of the decomposition reaction can be observed. In particular, after a relatively slow decrease of the active oxygen content, a faster process takes place, eventually leading to the complete disappearance of hydrogen peroxide. Under the assumption that the initial slow part is the induction step of an autocatalytic process whereas the second part is the corresponding full chain process, the occurrence of a radical chain mechanism may be proposed.

To support such a proposal, the reaction has been carried out in the cavity of an EPR instrument. A signal was detected, whose fine structure, shown in Figure 2, is attributed, by comparison with literature data,¹¹ to a vanadium(IV) species. Furthermore, plotting the intensity of the EPR signal as a function of time allows the behavior shown in Figure 3 to be observed. The EPR signal increases with the beginnings of the decomposition, reaching its maximum intensity when the full chain reaction starts, and then it forms a plateau. The identification of paramagnetic species in a reaction mixture does not necessarily indicate that the reaction mechanism is a radical one. In fact owing to the difficulty in determining the concentration of radicals in solution, the EPR signals could result from a parallel side reaction. However the

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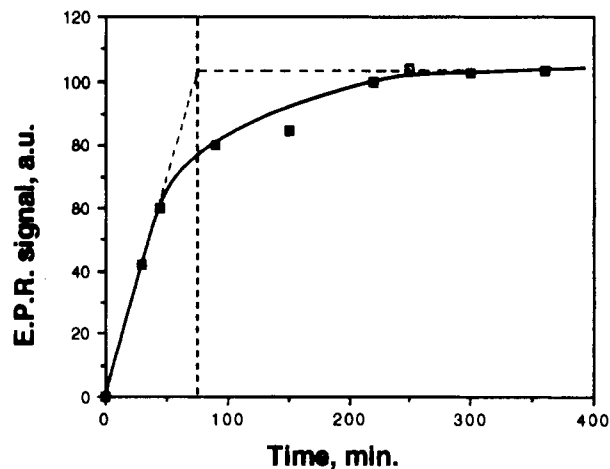


Figure 3. Variation of the signal intensity (arbitrary units) with time in the V(V)-catalyzed decomposition of H_2O_2 in water ($\text{pH} = 0$) at 25°C , $[\text{NH}_4\text{VO}_3]_0 = 2 \times 10^{-3} \text{ mol L}^{-1}$, and $[\text{H}_2\text{O}_2]_0 = 0.057 \text{ mol L}^{-1}$.

Table 1. Rate of the Full Chain Part as a Function of the Initial Concentration of Reactants in the V(V)-Catalyzed Decomposition of H_2O_2 in Aqueous Acidic ($\text{pH} = 0$) Solution at 25°C

run no.	$[\text{VO}_3\text{NH}_4]_0$, $\text{mol L}^{-1} \times 10^3$	$[\text{H}_2\text{O}_2]_0$, $\text{mol L}^{-1} \times 10^3$	R_{prop} , $\text{mol L}^{-1} \text{ s}^{-1} \times 10^6$
1	1.0	57	0.73
2	2.0	57	1.10
3	4.0	57	2.80
4	2.0	28	0.51
5	2.0	115	2.60

fact that in the present system such an EPR signal reaches a plateau when the steep part of the decomposition begins must have mechanistic significance.

Further evidence that during the induction period there is the buildup of a vanadium(IV) species, which then acts as a chain carrier in the subsequent propagation steps, is provided by the observation that the addition of vanadium(IV) ($2 \times 10^{-4} \text{ mol L}^{-1} \text{ VOSO}_4$) from the beginning to the system under investigation causes the disappearance of the induction period and, also, accelerates the rate of hydrogen peroxide consumption.

A kinetic analysis of the system was carried out, aimed at establishing the rate laws of the two parts of the reaction. Such an analysis is rather straightforward for the chain-established part, since it simply involves the determination of the slopes, as a function of the initial concentrations of hydrogen peroxide and NH_4VO_3 , respectively, of the part which is a straight line. By contrast, such a method cannot be applied to the initiation step of the process because of the very small decrease of hydrogen peroxide observed that would lead to large errors in the estimation of the slopes. On the other hand, such a difficulty may be overcome by taking into account the fact that the length of the induction period, which can be measured with an acceptable degree of accuracy, is necessarily related to the initiation rate. In particular, an inverse proportionality between the two parameters is expected as a result of the fact that a fast initiation corresponds to a short induction time.²⁴ Therefore, by plotting the reciprocal of such induction time as a function of the initial concentration of the two reagents, H_2O_2 and $\text{VO}(\text{O}_2)^+$ (see eq 1) respectively, their apparent kinetic orders may be determined. The linearity of such plots leads to the conclusion that the kinetic order of both reactants is one, which leads to the simple rate law

$$R_{\text{init}} = k_{\text{init}}[\text{H}_2\text{O}_2][\text{NH}_4\text{VO}_3] \equiv k_{\text{init}}[\text{H}_2\text{O}_2][\text{VO}(\text{O}_2)^+] \quad (2)$$

From the data reported in Table 1, referring to the full chain part of the process, it may be also observed that for this reaction

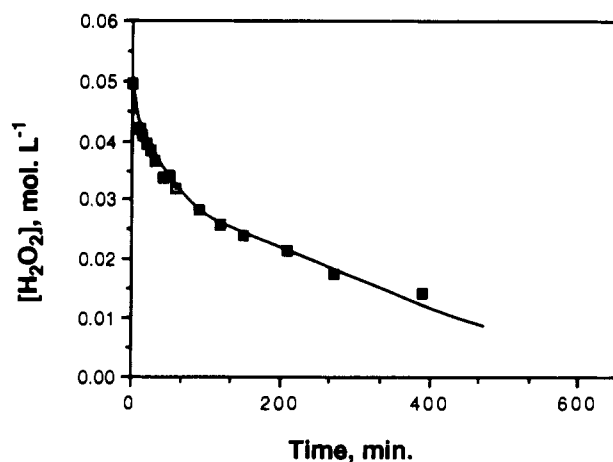


Figure 4. Reaction profile in the V(IV)-catalyzed decomposition of H_2O_2 in water ($\text{pH} = 0$) at 25°C , $[\text{VOSO}_4]_0 = 2 \times 10^{-3} \text{ mol L}^{-1}$, and $[\text{H}_2\text{O}_2]_0 = 0.05 \text{ mol L}^{-1}$.

a linear dependence of the slopes on the concentration of both reactants is observed. Thus, the rate law of the full chain process is again overall second order and first order in each reagent, as in eq 3 where the subscript "prop" denotes the full chain portion of the reaction.

$$R_{\text{prop}} = k_{\text{prop}}[\text{H}_2\text{O}_2][\text{VO}(\text{O}_2)^+] \quad (3)$$

It should be noted that the two rate constants k_{init} and k_{prop} and, in particular, the latter one are, very likely, complex constants including the elementary rate constants are the various steps of the chain reaction.

Decomposition of V(IV)/ H_2O_2 System in Acidic Aqueous Solution. The role of vanadium(IV) in the vanadium(V)-catalyzed decomposition of hydrogen peroxide, suggested by the evidence reported in the preceding paragraph, has been investigated in some detail.

Also in this case a very simple system has been considered involving $2 \times 10^{-3} \text{ mol L}^{-1} \text{ VOSO}_4$ in the presence of a 25-fold excess of hydrogen peroxide at $\text{pH} = 0$ (HClO_4) dissolved in water at 25°C . Under these conditions, two subsequent processes may be predicted on the basis of literature data. These should be the fast oxidation of V(IV) to V(V) by hydrogen peroxide⁹⁻¹⁴ followed by the rapid addition of hydrogen peroxide to V(V), as in eq 1, to form the $\text{VO}(\text{O}_2)^+$ monoperoxo derivative. At this point the system should become identical to the one where vanadium(V) is added from the beginning. The prediction is only partially fulfilled as indicated by the behavior of hydrogen peroxide consumption shown in Figure 4. Again two parts are observed but the first part of the reaction is the faster one. Moreover, in the course of this first part, almost 50% of the active oxygen content is consumed. Clearly such a consumption cannot be due to the stoichiometric oxidation of V(IV) to V(V), due to the large excess of H_2O_2 employed. Rather, it is plausible that such a reaction proceeds through a radical chain mechanism which causes also a decomposition of H_2O_2 .

As before a kinetic analysis of the system was carried out by measuring the variation of the slopes of the straight lines corresponding to the disappearance of the active oxygen in the first part of the reaction as a function of the initial concentration of both reactants. The pertinent results are collected in Table 2 and these are in agreement with the EPR results of Brooks and Sicilio.¹⁰

Such slopes are independent of the initial concentration of hydrogen peroxide whereas they do depend on vanadium(IV) initial concentration. From the slope of a $\log R_{\text{init}}$ vs $\log [\text{VOSO}_4]_0$ plot, it has been found that the kinetic order of vanadium in the rate law of the process, which accounts for ca. 50% disappearance of the active oxygen, is two. It is worth noting that the quadratic

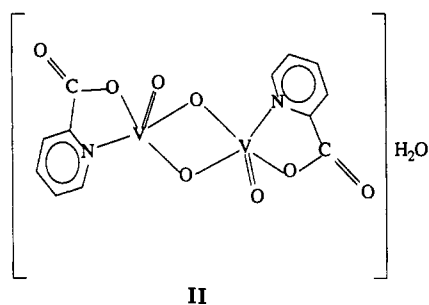
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Table 2. Rate of the Initiation Part as a Function of the Initial Concentration of Reactants in the V(IV)-Catalyzed Decomposition of H₂O₂ in Aqueous Acidic (pH = 0) Solution at 25 °C

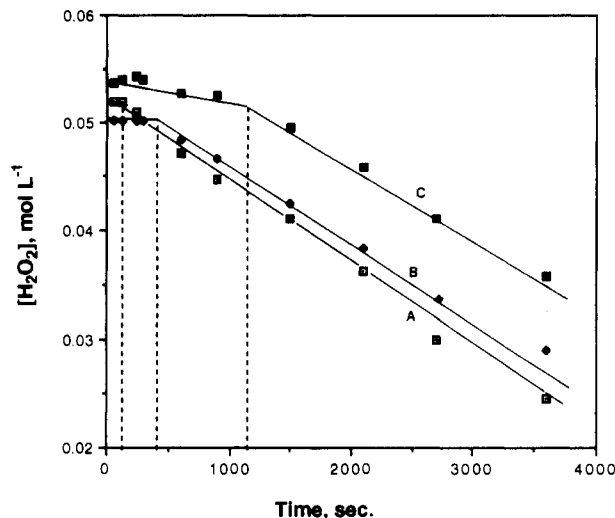
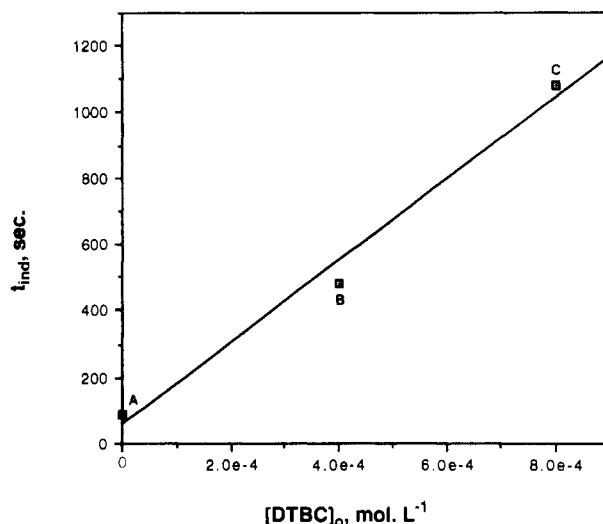
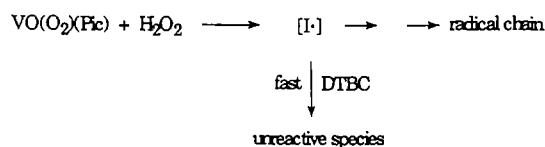
run no.	[VOSO ₄] ₀ , mol L ⁻¹ × 10 ²	[H ₂ O ₂] ₀ , mol L ⁻¹ × 10 ²	R _{inits} , mol L ⁻¹ s ⁻¹ × 10 ⁵
1	0.20	0	0
2	0	5.0	0
3	0.10	5.0	0.36
4	0.15	5.0	0.76
5	0.20	5.0	1.45
6	0.25	5.0	2.20
7	0.30	5.0	3.40
8	0.20	1.6	1.28
9	0.20	2.7	1.40
10	0.20	3.4	1.45
11	0.20	7.0	1.41

dependence of decomposition rates on vanadium(IV) fits with the observation, reported in the previous paragraph, that V(IV) acts as a catalyst of hydrogen peroxide decomposition in the absence of NH₄VO₃.

Decomposition of the Complex I/H₂O₂ System in CH₃CN. The experiments reported in this section have been carried out with a view toward establishing the role of the solvent in the V(V)-catalyzed decomposition of hydrogen peroxide. To this aim, a comparison of the behavior observed in water with that in CH₃CN may provide useful clues. The vanadium(V) species employed is the soluble peroxocomplex I mentioned above. Such a complex, as already discussed, undergoes a relatively fast decomposition in CH₃CN¹ yielding a V(V) species, e.g. II, from which I is rapidly restored by addition of hydrogen peroxide.^{2,25}



Therefore, also in the present system, where a 25-fold excess of hydrogen peroxide over vanadium is used, the predominant vanadium species is a monoperoxo derivative ($\lambda_{\text{max}} = 450 \text{ nm}$, $\epsilon_{\text{max}} = 444$).⁹⁻¹⁴ A typical decomposition reaction is shown in Figure 5, curve A. A strict analogy with the system operating in aqueous solution is observed. In fact, although the overall process is markedly faster in CH₃CN than in water, the occurrence of an initial slow decomposition followed by a more rapid decrease of the active oxygen content are common features likely corresponding to an induction period followed by the full chain steps. To put this analogy on a more quantitative basis, a kinetic analysis was carried out in order to obtain the rate laws of the two parts of the reaction. Again, as far as the second part is concerned, no major difficulties are encountered since the slopes of the straight lines can be easily measured. By contrast, the determination of the kinetic orders of the reactants in the first part is even more complicated than in water. In fact, not only is the active oxygen decrease too small to allow accurate measurements but also the induction times are too short, thus making troublesome their estimate. To overcome such a difficulty a different approach has been used, based on the addition of increasing amount of a species capable of acting as a radical trap, i.e. di-*tert*-butyl-*p*-cresol (DTBC).² The rationale behind such a procedure may be explained as follows. Let us assume that the

**Figure 5.** Reaction profile in the decomposition of H₂O₂ catalyzed by I in CH₃CN at 25 °C, [I]₀ = 2 × 10⁻³ mol L⁻¹, and [H₂O₂]₀ = 0.05 mol L⁻¹. Key: curve A, [DTBC]₀ = 0; curve B, [DTBC]₀ = 4 × 10⁻⁴ mol L⁻¹; curve C, [DTBC]₀ = 8 × 10⁻⁴ mol L⁻¹.**Figure 6.** Dependence of the induction time from the [DTBC]₀ in the decomposition of H₂O₂ catalyzed by I in CH₃CN at 25 °C, [I]₀ = 2 × 10⁻³ mol L⁻¹, [H₂O₂]₀ = 0.05 mol L⁻¹ (see Figure 8).**Scheme 1**

trap reacts very rapidly with the radical species whose concentrations are building up in the induction period. If this is the case, the net result will be an increase in the induction time since the radical carrier is deactivated by the radical trap. Therefore, if the role played by DTBC is simply in decreasing the concentration of the radical carrier, as exemplified in Scheme 1, a proportionality between the concentration of DTBC and the induction time should be observed.

As shown by the results of Figures 5 and 6, the assumptions made are fulfilled. In particular, it is observed that increasing amounts of DTBC cause an increase of the induction times, Figure 5, curves B and C, without affecting the slopes of the second part of the reaction. Moreover, if such induction times, which are easily measured, are plotted, as a function of DTBC concentration, a linear correlation is observed, Figure 6. It should be noted that, according to Scheme 1, there must be a correlation between the

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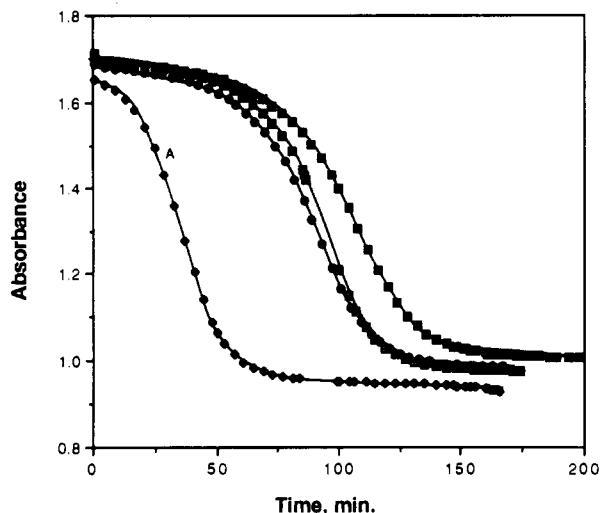


Figure 7. Reaction profiles in the decomposition of I in CH₃CN at 20 °C and [I]₀ = 4 × 10⁻³ mol L⁻¹, in the presence of various concentrations of DTBC: (◇) [DTBC]₀ = 0; (●) [DTBC]₀ = 8.4 × 10⁻⁵ mol L⁻¹; (□) [DTBC]₀ = 1 × 10⁻⁴ mol L⁻¹; (Δ) [DTBC]₀ = 1.7 × 10⁻⁴ mol L⁻¹.

Table 3. Rate of the Initiation and Full Chain Parts as a Function of the Initial Concentration of Reactants in the Decomposition of H₂O₂ Catalyzed by I in CH₃CN at 25 °C

run no.	[I] ₀ , mol L ⁻¹ × 10 ²	[H ₂ O ₂] ₀ , mol L ⁻¹ × 10 ²	R _{init} , mol L ⁻¹ s ⁻¹ × 10 ⁷	R _{prop} , mol L ⁻¹ s ⁻¹ × 10 ⁶
1	0.0	5.0	0	0
2	0.2	0.0	0	0
3	0.2	5.0	8.0	6.3
4	0.2	10.0	14.8	10.3
5	0.4	5.0	14.7	10.5
6	0.4	10.0	24.0	16.0

rate of formation of the radical carrier, i.e. the initiation rate, R_{init}, and the rate of disappearance of DTBC. In particular, it may be argued²⁴ that the following equation holds:

$$\frac{[\text{DTBC}]_0}{\Delta t_{\text{ind}}} = R_{\text{init}} \quad (4)$$

Therefore, the R_{init} values may be obtained simply by measuring the induction times at the various DTBC concentrations. Table 3 collects such R_{init} values at different reactant concentrations as well as the slopes of the full chain part of the reaction again at various reactant concentrations. Such data allow to evaluate the rate laws of the two parts of the reaction. These are both overall second-order, first order in H₂O₂ and first order in I, as was found in water.

Therefore, it is likely that the same general mechanism of decomposition holds both in aqueous solution and in CH₃CN.

Decomposition of Complex I in CH₃CN. Preliminary data on the decomposition of I in CH₃CN have been presented in a previous data.² A typical decomposition profile is shown in Figure 7, curve A, where the decrease of the absorbance of I at 450 nm is plotted against the time. It is worthy of note that the general behavior of the decomposition reaction appears very similar to those observed for the V(V)/H₂O₂ systems both in water and CH₃CN.

Thus, also in the present case, a radical chain mechanism should operate, characterized by a rather short induction period followed by the full chain reaction. A further similarity with the previous systems is the linearity of the second part of the decomposition maintained up to 65% disappearance of the active oxygen. This makes rather easy the determination of the corresponding rate law by measuring the value of the slopes at differential initial concentrations of I. By contrast, and again similar to the systems previously presented, the determination of the rate law of the initiation step is not at all straightforward. The difficulties are

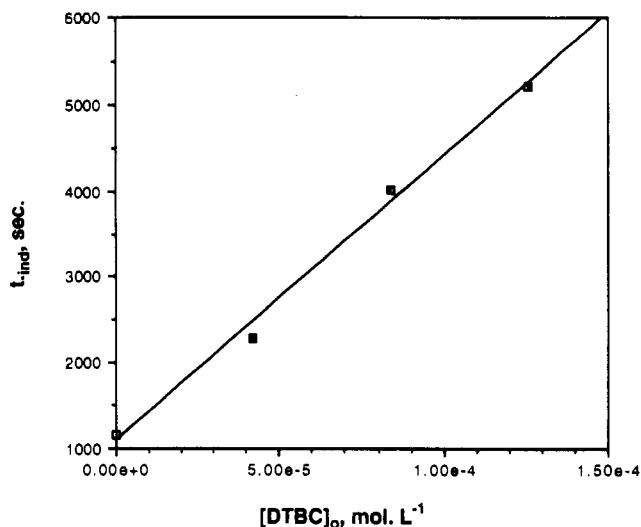


Figure 8. Dependence of the induction time on the [DTBC]₀ in the decomposition of I in CH₃CN at 20 °C and [I]₀ = 4 × 10⁻³ mol L⁻¹.

Table 4. Rates of the Initiation and Full Chain Parts as a Function of the Initial Concentration of Reactant in the Decomposition of I in CH₃CN at 20 °C

run no.	[I] ₀ , mol L ⁻¹ × 10 ³	R _{init} , mol L ⁻¹ s ⁻¹ × 10 ⁸	R _{prop} , mol L ⁻¹ s ⁻¹ × 10 ⁸
1	1.7	0.6	15.0
2	2.0	0.7	21.3
3	2.5	1.1	26.0
4	3.0	2.0	37.0
5	3.7	2.8	64.8
6	4.3	3.4	75.6

due to the facts that the induction time is too short to be measured with reasonable accuracy and also that the decrease of the concentration of I before the full chain part is very small. Fortunately, the method of adding a radical trap described above proved to be very helpful also in this case. Figure 7 shows the effect of increasing amounts of the DTBC on the reaction, resulting in an increase of the induction times without affecting the slope of the full chain part while, in Figure 8, the occurrence of a linear correlation between such induction times and the DTBC concentration is displayed.

Such a correlation indicates that the R_{init} values can be obtained also in this case by employing eq 4. Table 4 collects the R_{init} values thus calculated together with the R_{prop} values simply measured from the slopes of the straight lines corresponding to the full chain part of the decomposition reaction. From the log-log plots of R_{init} and R_{prop} against [I], slopes of 2.0 and 1.8 were obtained, respectively. The latter value is presumed to indicate second order.

Interestingly, it is found that a second-order rate law, eqs 5 and 6, holds for both parts of the decomposition reaction.

$$R_{\text{init}} = k_{\text{init}}[\text{I}]^2 \quad (5)$$

$$R_{\text{prop}} = k_{\text{prop}}[\text{I}]^2 \quad (6)$$

Such a result is less unexpected than it could appear at first glance. Rather, it confirms the similarity among the various systems. In fact, in all the three systems where a peroxovanadium is present, either formed *in situ* or added as an isolated species, the rate laws of both parts of the decomposition reactions involve two peroxidic species, either the peroxovanadium complex and hydrogen peroxide or two peroxovanadium complexes. As anticipated, this may account for the duality of mechanisms found for peroxovanadium complexes. In particular, since the initiation of radical decomposition is a second-order process, it may be inferred that such a process becomes a significant one at relatively

large vanadium concentrations. Accordingly, polar reactions should prevail at lower vanadium concentrations.

Discussion

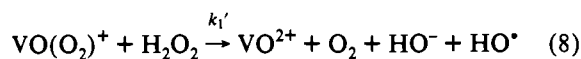
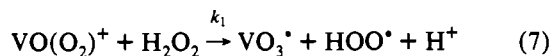
The information provided by the results presented above can be summarized as follows:

i. The decomposition of and by peroxovanadium complexes, either formed *in situ* by addition of an excess of hydrogen peroxide to a vanadium(V) precursor or added as the isolated complex I, both in water and in CH₃CN, is a radical chain reaction characterized by an induction time followed by a full chain reaction where dioxygen is produced.

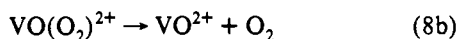
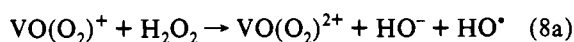
ii. In the three reactions examined, the initiation is a second-order reaction whose rate law includes two molecules of peroxide, either the peroxy complex and hydrogen peroxide or two molecules of the peroxy complex I when it is allowed to decompose in CH₃CN in the absence of hydrogen peroxide.

iii. The induction time is remarkably reduced by addition of species which can act as one-electron donors. This is the case of vanadium(IV) presented above and also, as reported earlier,² of Co(II). Furthermore, clear EPR evidence (Figures 2 and 3) has been collected that vanadium(IV) is formed in the induction part of the V(V)-catalyzed decomposition of H₂O₂ and that its concentration remains significant during the full chain part of the reaction. Also the length of the induction period can be extended by addition of radical scavenger DTBC.

On this basis, the most likely formulation of the initiation step is the reaction of two molecules of peroxidic materials one acting as one-electron donor and the other one as one-electron acceptor. In the case of I, it might be inferred that the peroxovanadium complex should be able to play both roles. We shall see later that this is not completely true and that a more complex mechanism operates. As far as the decompositions in water are concerned, two alternatives may be considered, which are schematically shown in eqs 7 and 8.



The latter equation may be a combination of two steps:

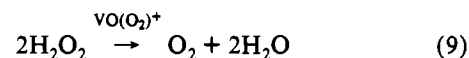


Thompson⁹ and Brooks and Sicilio¹⁰ gave evidence for eq 8b; Czapski¹¹ reviewed the chemistry of superoxocomplexes of which class VO(O₂)²⁺ is a member.

In eq 7 the peroxy complex acts as the oxidant whereas in eq 8 it may be considered a one-electron donor. A distinction between the two possibilities, based on the kinetic data available here, is not possible. Indeed it can be shown that, with both initiations, a mechanistic scheme in agreement with the stoichiometry of the process and with its radical chain nature can be easily written. Here we take the view of favoring an initiation where the peroxy complex is the oxidant. Such a choice is based on the well known fact that peroxovanadium complexes are considerably stronger (i.e. more reactive) oxidants than H₂O₂ under identical experimental conditions²¹ even though this comparison can only be made for oxidation of nucleophilic substrates in polar reactions.

The observation that a V(IV) species is formed during the decomposition fits with the hypothesis that the peroxocomplex is a one-electron acceptor, however that is not conclusive as indicated by the sum of eqs 8a and 8b.

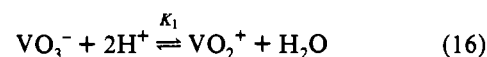
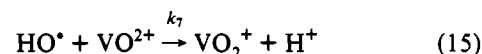
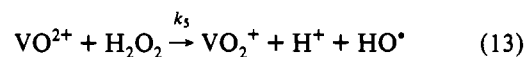
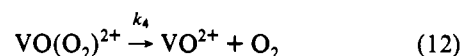
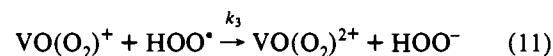
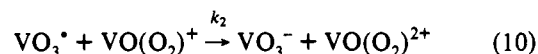
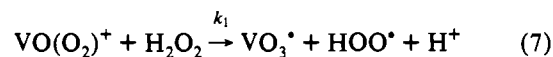
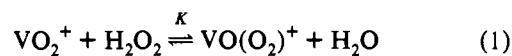
As long as H₂O₂ is in excess over vanadium(V), the stoichiometry of the decomposition is shown to be



through measurements of dioxygen evolution (see Experimental Section). Small deviations due to V(V) reduction, V(IV) oxidation, and loss of active oxygen from VO(O₂)⁺ are to be expected.

A mechanism with a number of steps is postulated here:

Scheme 2



From this mechanism (using steady state and chain approximations), the rate law

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = \left(k_1 + \left(\frac{2k_1k_5k_6}{k_7} \right)^{1/2} \right) [\text{H}_2\text{O}_2][\text{VO}(\text{O}_2)^+] \quad (17)$$

can be derived, and this agrees with the observed laws of eqs 2 and 3.

There are six intermediates written in the mechanism steps. The cation VO²⁺ is, of course, a normal V(IV) species and has been detected in this work by EPR spectroscopy. The superoxovanadium cation here written VO(O₂)²⁺ has been established.⁹⁻¹¹ The radicals HOO^{*} and HO^{*} are often reported in reactions of H₂O₂ and O₂.

The species VO₃^{*}, whose structure is unknown, should have an unpaired electron on oxygen; it is postulated to be formed by addition of an electron to VO(O₂)⁺, presumably resulting in cleavage of the peroxide bond. The intermediate VO₃⁻ should be a vanadium(V) species with no unpaired electrons; on protonation it should form the stable cation which will, when H₂O₂ is in excess, form VO(O₂)⁺ rapidly.¹²

Equations 1 and 16 represent conversions in the coordination sphere of vanadium(V) and should be very rapid. Equations 14-15 are known steps.^{9,10,14} When VO²⁺ is added to a reaction mixture, the very fast reactions^{10,14} of eqs 14 and 15 result in the large initial drop in peroxide concentrations shown in Figure 6, and the vanadium(IV) concentration decreases to a steady-state concentration akin to that of mixtures of VO(O₂)⁺ and H₂O₂.

A sequence of steps almost identical to that shown in Scheme 2 may be written also for the decomposition of H₂O₂ catalyzed by complex I in CH₃CN. In fact, it should be remembered that

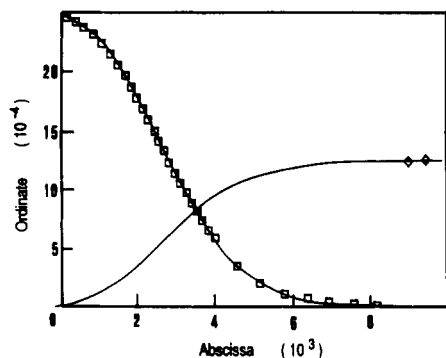
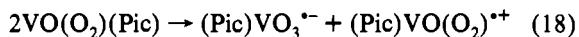


Figure 9. Experimental points and calculated curves describing the decomposition of I in CH₃CN at 20 °C and [I]₀ = 2.5 × 10⁻³ mol L⁻¹. The values obtained for the rate constants are $k_1 = 0.015 \text{ mol}^{-1} \text{ L s}^{-1}$, $k_{-1} = 1.6 \times 10^{-6} \text{ s}^{-1}$, $k_2 = 2.5 \times 10^{-3} \text{ s}^{-1}$, $k_4 = 31 \text{ mol}^{-1} \text{ L s}^{-1}$, $k_5 = 19 \text{ mol}^{-1} \text{ L s}^{-1}$, and $k_7 = 3 \text{ mol}^{-1} \text{ L s}^{-1}$.

both the behavior of H₂O₂ disappearance and the overall rate law are very similar for the two systems considered. In addition, it has been previously shown that complex I is rapidly restored by addition of H₂O₂ to its reduced form,^{2,25} complex II, which, in CH₃CN, has been formulated as a dimeric derivative of V(V).¹

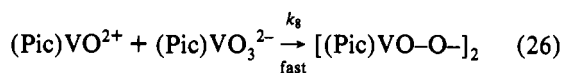
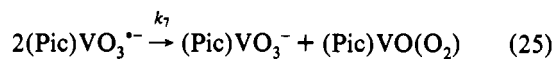
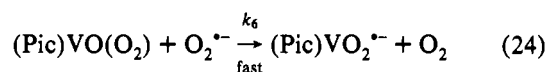
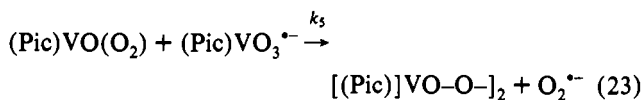
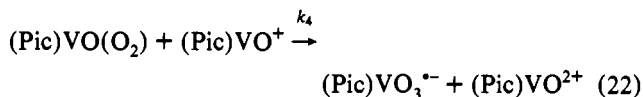
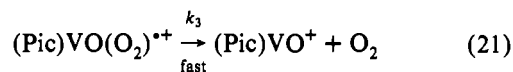
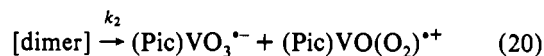
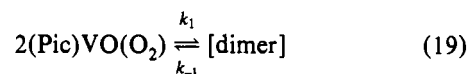
In the case of the decomposition of I alone in CH₃CN, again the shape of the active oxygen disappearance and the second-order rate law observed could be taken as an indication that the decomposition mechanism involves a series of steps similar to those proposed for the other systems discussed above. Here, of course, the peroxospecies cannot be restored by addition of H₂O₂, so that eq 1 of Scheme 2 is not operating. A second important difference could be in the initiation step. Although the second order in I indicates that two molecules of I are reacting in an initiation step, a simple bimolecular outer sphere electron transfer such as



is conceivable but not likely. The extent to which (Pic)VO₃^{•-} is comparable to VO₃^{•-} and to which (Pic)VO(O₂)^{•+} is comparable to VO(O₂)₂^{•+} is not known, but it seems fair to assume considerable chemical similarity.

On the basis of these considerations the sequence of reactions which accommodate the experimental findings is given in Scheme 3. Instead of a bimolecular initiation, a two-step process is considered where a dimeric intermediate is formed. The nature of such an intermediate, resulting from the association of two molecules of I, is at present completely unknown. Such an intermediate then undergoes an intramolecular electron transfer. The validity of Scheme 3 is supported by the results shown in Figure 9, where the rate behavior of the decomposition of I has been calculated by a mathematical method, see Experimental Section, on the basis of Scheme 3. Very good agreement between the calculated curve and the experimental one is observed. Interestingly, the same mathematical treatment applied to a reaction scheme where the formation of the dimeric intermediate is not considered and the simple bimolecular reactions of eq 18 is taken as the initiation does not fit the experimental points.

Scheme 3



Conclusions

As mentioned in the Introduction, the main purpose of the study presented here was to obtain information on the nature on the unpaired electron species which may be formed in solution, particularly in CH₃CN. The kinetic investigation carried out do provide such an information, though an indirect one. In particular, there appears to be confirmed the role played by the formal radical anion resulting from the one-electron transfer to the peroxovanadium complex I. It may be noticed that such a radical anion is formed in water as well as in CH₃CN together with other radical species, e.g. HOO[•] and HO[•] and O₂^{•-}, which might have oxidative ability toward organic substrates. However, in CH₃CN, the only alternative to the hypothesis that (Pic)VO₃^{•-} is the oxidant of benzene and substituted benzenes is O₂^{•-} whose oxidation chemistry is sufficiently known to exclude its involvement.²⁶

Therefore, further studies on radical oxidations by peroxovanadium complexes should be centered on the identification, on the properties of the species resulting from the one-electron reduction of the peroxovanadium complexes themselves, and on the evaluation of the rate constants.

Acknowledgment. We thank Prof. P. H. Rieger, Brown University, Providence, RI, for helpful assistance in the EPR experiments and Prof. V. Lucchini, University of Venezia, Venezia, Italy, for having made available the mathematical treatment of the data. Financial support from MURST, Italy, and Solvay Interox is gratefully acknowledged.

(26) Fridovich, I. *Acc. Chem. Res.* 1972, 5, 321.