Decomposition of hydrogen peroxide catalyzed by vanadium(v) compounds: the pathways for the formation of ozone

A. E. Gekhman,[a]★ *N. I. Moiseeva,*[b] *and I. I. Moiseev*[a]

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 117907 Moscow, Russian Federation.
Fax: +7 (095) 952 1279
[b]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

Reactions of H_2O_2 in trifluoroacetic acid catalyzed by vanadium(v) compounds were studied. The system under study exhibits unusual behavior: along with oxygen, large quantitaties (10—15 %) of ozone are found in the products of hydrogen peroxide decomposition; difficultly oxidizable compounds (alkanes, arenes, and perfluoroalkenes) are oxidized under mild conditions. The rates of the oxidation of individual substrates are commensurable. However, when two compounds are simultaneously present in the reaction mixture, cyclohexane stops the oxidation of all of the other substrates, arenes suppress the oxidation of perfluoroolefins, and perfluoro-1-octene stops the consumption of internal perfluoroolefins. The effect of the oxidizable substrates on the amount of ozone evolved was studied. Based on the kinetic data obtained, a mechanism that involves the consecutive formation of several active complexes of vanadium(v) responsible for the oxidation of substrates and for the formation of ozone is suggested. In terms of the scheme suggested, the inner-sphere oxidation of the peroxo ligand by the coordinated peroxotrifluoroacetic acid affords a complex incorporating O_3^{2-} as a ligand. The latter acts as the precursor of the ozone. A mathematical model that adequately describes the experimental data is proposed.

Key words: hydrogen peroxide, vanadium(v) complexes, ozone, catalysis, oxidation, alkanes, arenes, perfluoroolefins.

1. Introduction

Decomposition of hydrogen peroxide to give triplet dioxygen and water (ΔG^0_{298} = −56 kcal mol^{-1}, ΔH^0_{298} = −47 kcal mol^{-1}) is accelerated by compounds of some metals.[1] When the formation of triplet oxygen in the elementary event responsible for the evolution of O_2 is spin-forbidden, dioxygen in the singlet state is produced.[2] This reaction is less thermodynamically favorable, but is still quite beneficial (ΔH^0_{298} = −24 kcal mol^{-1}). Some catalytic systems containing transition metal compounds are known to catalyze decomposition of hydroperoxides to give active species that generate $^1O_2$ or transfer it to substrates.[3,4] For example, in the oxidation of anthracene and its derivatives in the $V^V/H_2O_2/CH_3COOH$ system, singlet oxygen is transferred from the V^V complex to the substrate, rather than evolving into the bulk.[3]

Thermodynamics does not forbid the formation of another allotropic modification of oxygen, ozone, in the decomposition of H_2O_2 (ΔG^0_{298} = −45 kcal mol^{-1}). In fact, the $V^V/H_2O_2/CF_3COOH$ system catalyzes decomposition of H_2O_2 to produce substantial amounts of ozone (10—15 %).[4]

The formation of small quantities of ozone in the stoichiometric decomposition of peroxides by concentrated H_2SO_4 has been known for about 100 years. For example, peroxide compounds of uranium, molybdenum, and titanium and peroxoboric, peroxosulfuric, peroxocarbonic, and pyrovanadic acids and their salts decompose through the action of concentrated sulfuric acid to give oxygen containing traces of ozone.[5]

The present study has been undertaken in order to identify the main elements of the mechanism of the ozone formation in the $V^V/H_2O_2/CF_3COOH$ system. For this purpose, we considered the behavior of a number of substrates that are hard to oxidize, such as arenes, perfluoroarenes, and their derivatives, in this catalytic system. The chemical transformations of these compounds and the mechanism of their oxidation are also of interest by themselves.

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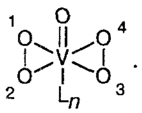
2. The reactions of hydrogen peroxide in a V^V/RCOOH system

2.1. Complex formation in the V^V/H_2O_2/RCOOH system

Vanadium(v) compounds react with hydrogen peroxide to yield complexes that incorporate one to four peroxide ligands depending on the reaction conditions,* for example, complexes of the type $[VO(O{-}O)(pic)]$,[6] $K_3[VO(O{-}O)_2(C_2O_4)]\cdot H_2O$,[7] $NH_4[VO(O{-}O)_2(bipy)]\cdot 4H_2O$,[8] $K_2[VO(O{-}O)_2F]$,[9] $M_2[V(O{-}O)_3Cl]$,[10] $(NH_4)_3V(O{-}O)_4$.[11] These peroxo compounds, which are stable in aqueous solutions, have been isolated and characterized by physicochemical methods (IR, Raman, and NMR spectroscopy), and in some cases, also by X-ray diffraction analysis.[12] The coordination of hydrogen peroxide to a V^V atom increases the tendency of this ligand to abstract a proton to the extent that in the vast majority of cases, it affords complexes containing coordinated peroxo groups, rather than H_2O_2 molecules or HO_2^- ions. Both oxygen atoms of each peroxo ligand are located at identical distances from the vanadium atom, thus forming metal-containing rings of the type



X-ray structural studies of these complexes have shown that both peroxo ligands and the vanadium atom lie practically in the same plane. For example in the complex where L_n = (bipy)[13], the $[VO(O{-}O)_2(bipy)]^-$ anion is a slightly distorted bipyramid with the oxygen atom of the vanadyl group located in one vertex and one of the bipyridyl nitrogen atoms located in the other vertex (the other nitrogen atom lies in the plane of the peroxo groups). The interatomic distances are the following $d_{(O(1)-V)}$ = 1.911; $d_{(O(2)-V)}$ = 1.883; $d_{(O(3)-V)}$ = 1.909, and $d_{(O(4)-V)}$ = 1.880 Å.

^{51}V NMR studies of these compounds have shown that an increase in the number of peroxo groups at the vanadium atom results in a downfield shift of the resonance signal.[14,15]

The interaction of hydrogen peroxide with V^V in water is restricted to the formation of peroxo complexes; no decomposition of H_2O_2 is observed. However, vanadium(v) complexes dissolved in carboxylic acids (CH_3COOH[3,15] or CF_3COOH[16,17]) or pyridine[18] efficiently catalyze the decomposition of hydrogen peroxide and the corresponding peroxo acid. The ESR and ^{51}V NMR data indicate that V^V complexes catalyzing the decomposition of hydrogen peroxide predominate in the reaction solutions irrespective of the starting compound (KVO_3 or $V(acac)_2$) and the oxidation state of vanadium in it. As the experiment implies, the oxidation state of vanadium has no effect on the composition of the products of the decomposition of hydrogen peroxide and the oxidation of substrates, or on the main regularities of the oxidation.

A study of the $H_2O_2/V^V/CH_3COOH$ catalytic system led the authors to the conclusion[3,15] that decomposition of H_2O_2 involves the intermediate formation of vanadium mono-, di-, and triperoxo complexes according to the following scheme.

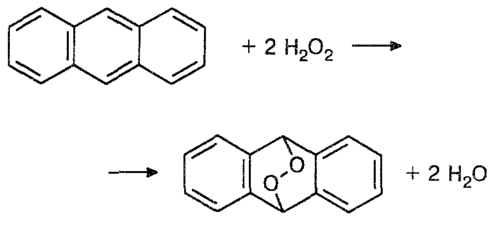
$$[V^V(O_2)]^+ + H_2O_2 \rightleftharpoons [V^VO(O{-}O)]^+ + H_2O$$

$$[V^VO(O{-}O)]^+ + H_2O_2 \rightleftharpoons [V^VO(O{-}O)_2]^- + 2H^+$$

$$[V^VO(O{-}O)_2]^- + H_2O_2 \rightleftharpoons [V^VO(O{-}O)_3]^- + H_2O$$

In principle, all of these complexes can yield the dioxygen observed. However, kinetic studies in the $H_2O_2/V^V/CH_3COOH$ system have shown[15] that the dioxygen results predominantly from the transformations of the complex that incorporates three peroxo groups, $[V^V(O{-}O)_3]^-$.

Oxidation of anthracene with H_2O_2 in a CH_3COOH solution in the presence of V^V affords[3,15] anthraquinone in a nearly 100 % yield. The presence of anthracene in this system almost completely suppresses evolution of oxygen into the bulk. Using ^1H NMR spectroscopy and GC-MS it has been found that under these conditions an endoperoxide, *viz.*, 9,10-dihydro-9,10-epidioxyanthracene, is the primary product of the oxidation.



The formation of endoperoxides is one of the tests that may indicate that oxidation involves singlet oxygen. However, kinetic data are at variance with the suggestion that free dissolved singlet oxygen participates in the reaction under consideration. In fact the rate constant of quenching of $^1O_2$ in AcOH is $2.5\cdot 10^5$ M^{-1} s^{-1}. The rate constant of the reaction of $^1O_2$ with anthracene is of the same order ($2\cdot 10^5$ $M^{-1}\cdot s^{-1}$). If anthracene reacted with the dissolved singlet oxygen, then at an anthracene concentration of 0.05 *M*, the yield of gaseous oxygen would decrease by only 5 %. However, the experimental data indicate that at the above-mentioned concentration

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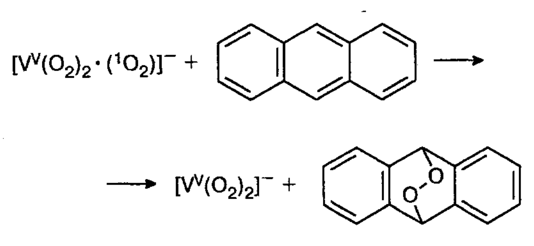
* The following abbreviations have been used: pic is 2-methylpyridine (α-picoline), bipy is bipyridyl, acac is acetylacetone.

of anthracene, the amount of gaseous O_2 decreases by more than 95 %.

These facts imply that anthracene is converted into endoperoxide by the reaction with a vanadium(v) complex containing singlet oxygen as a ligand, rather than with free $^1O_2$



Moreover, if singlet oxygen is formed in the decomposition of vanadium peroxo derivatives, for example, according to the reaction

$$[V^V(O_2)_3]^- \rightarrow [V^V(O_2)_2\cdot(^1O_2)]^- \rightarrow [V^V(O_2)_2]^- + {}^1O_2,$$

it is rapidly converted into triplet oxygen, which is inert under the reaction conditions, with a probability close to 100 %, before it has a chance to react with anthracene.

2.2. Decomposition of peroxides in the V^V/CF_3COOH system

Decomposition of hydrogen peroxide to give ozone[16,17]

A peculiarity of the V^V-catalyzed decomposition of H_2O_2 in a CF_3COOH solution is that this reaction yields a substantial amount of ozone (no less than 10—15 % (v/v) of the total gaseous products), *i.e.*, the amount of H_2O_2 that decomposes according to reaction (1) to give ozone (~15 %) is comparable to the amount that decomposes to give oxygen (reaction (2)) (~85 %).

$$3\ H_2O_2 \rightarrow 3\ H_2O + O_3 \qquad (1)$$

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad (2)$$

The formation of ozone has also been observed in the decomposition of H_2O_2 in acetic acid solutions containing V^V. However, under these conditions, the yield of ozone was no more than 1 % (v/v) of the total gaseous products.

The literature data that indicate that ozone is evolved through the action of strong acids on peroxides[4] or in the presence of sources of free radicals[19,20] suggest two pathways for the formation of ozone from peroxide compounds: a route involving species of the type HO^+ and a route involving free radicals.

It may seem that the comparison of the yields of ozone in the decomposition of H_2O_2 in acetic and trifluoroacetic acids in the presence of 10^{-5}—10^{-3} M V^V supports the hypothesis that O_3 is formed with the participation of HO^+. For example, the increase in the yield of O_3 on going from CH_3COOH to CF_3COOH could be explained by the fact that CF_3COOH is a strong acid (unlike CH_3COOH) and can protonate H_2O_2 or the peroxide group coordinated to vanadium to give free or coordinated ions like HO^+ (see Ref. 21). In this case, ozone would actually result from the reaction of these species with H_2O_2 or with the oxygen liberated. Contrary to this suggestion, the presence of 2 M H_2SO_4 or 0.7 M $HClO_4$ in acetic acid completely arrests the evolution of O_3 (Table 1), and this rules out the possibility of the above-discussed mechanism for the formation of O_3. In the presence of 0.2—2 M CF_3COONa in acetic acid, the yield of O_3 does not considerably change. These data imply that the formation of ozone is not associated with protonation of H_2O_2 or vanadium complexes or with the participation of HO^+ type species.

A thermodynamically favorable disproportionation of $RO_2^{\cdot}$ to yield $^1O_2$ and R_2O_2 is known.[22,23] In the case of $HO_2^{\cdot}$*, *i.e.*, when R = H, we obtain

$$2HO_2^{\cdot} \rightarrow H_2O_2 + {}^1O_2 \quad \Delta G^0_{298} \approx -11 \text{ kcal mol}^{-1}. \qquad (3)$$

Disproportionation of $HO_2^{\cdot}$ radicals with the liberation of ozone is also thermodynamically possible:

$$2HO_2^{\cdot} \rightarrow H_2O + O_3 \quad \Delta G^0_{298} \approx -23 \text{ kcal mol}^{-1}. \qquad (4)$$

There are data indicating that ozone can arise in catalytic systems from the decomposition of hydroperoxides that are able to generate free radicals. For example, evolution of large quantities of ozone was reported in a patent[19] in which a system consisting of an aqueous solution of a Fe^{II} salt, an ammonium or alkali metal salt of heptamolybdenic acid, and concentrated H_2O_2 is described.** In addition, a small amount of

Table 1. The formation of ozone in the $H_2O_2/V^V/RCOOH$ system (10 °C, [V] = 10^{-3} M)

Run	RCOOH	Compound added (C/M)	The yield of O_3 (%)
1	CH_3COOH	—	~1
2	CH_3COOH	$HClO_3$ (0.7)	~0
3	CH_3COOH	H_2SO_4 (2)	~0
4	CF_3COOH	—	~15
5	CF_3COOH	CF_3COONa (1)	~15

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* The ΔG^0_{298} values for reactions (3) and (4) were evaluated using the literature data[24] assuming that $\Delta S^0_{298}(^1O_2) \approx \Delta S^0_{298}(^3O_2)$.

** The absence of any quantitative data (concentrations of the starting compounds, the yield of O_3, the reaction temperature, *etc.*) makes a comparison of this system with the system studied in the present work impossible.

ozone (0.4—0.8 %) has also been produced[20] in the decomposition of peroxyacetic acid initiated by Co^{II} compounds. The formation of ozone in these catalytic systems may be due to disproportionation of peroxide radicals, for example, according to the square termination reaction (4).

In principle, this mechanism could occur in the system under consideration containing V^V compounds, which is supported[16,17] by the existence of the $V^V(O_2^{-\bullet})$ complex radical in the solutions. However, the absence of V^{IV} signals in the ESR spectra recorded during decomposition of H_2O_2 in CF_3COOH casts some doubt on the free-radical mechanism of the formation of ozone in the $H_2O_2/V^V/CF_3COOH$ system.

Though the occurrence of reaction (4) under the conditions of catalysis by vanadium complexes cannot be ruled out completely, all of the facts and considerations outlined suggest that the vanadium(v) complexes resulting from the reaction of hydrogen peroxide with the catalyst are responsible for the formation of ozone during the decomposition of H_2O_2 in CF_3COOH.

Decomposition of peroxytrifluoroacetic acid in the presence of V^V complexes [16,17]

Peroxytrifluoroacetic acid quickly forms in the H_2O_2/CF_3COOH system and is almost universally present, since its formation is catalyzed by the trifluoroacetic acid itself, which is a good donor of protons.

$$CF_3COOH + H_2O_2 \xrightarrow{H^+} CF_3COOOH + H_2O$$

A study of the decomposition of CF_3COOOH in CF_3COOH in the presence of V^V allowed the authors[16,17] to conclude that, along with the normal decomposition of the peroxy acid to give O_2 (O_2 and O_3, in the given case), catalytic decarboxylation of CF_3COOOH also occurs to yield CO_2, HF, and COF_2.

$$CF_3COOOH \longrightarrow CO_2 + COF_2 + HF$$

$$COF_2 + H_2O \longrightarrow CO_2 + 2HF$$

Decarboxylation of CF_3COOOH yields 3 moles of HF per 1 mole of the superacid reacted. As shown by ^{51}V NMR spectroscopy, the reaction of HF with vanadium(v) gives stable oxofluoride complexes of the VOF_4^- type. As this takes place, decomposition of CF_3COOOH stops. However, in the presence of H_2O_2 (or H_2O), both hydroperoxides (H_2O_2 and CF_3COOOH) are consumed almost entirely, probably due to the fact that H_2O_2, unlike CF_3COOOH, can replace the well-coordinating F^- ligand in the oxofluoride complexes of V^V. Thus, the retardation of the decomposition of CF_3COOOH by readily coordinating ligands, for example F^-, may be regarded as an indication of the fact that decomposition of peroxytrifluoroacetic acid is preceded by its coordination to V^V.

3. Oxidation of individual substrates in the $H_2O_2/V^V/CF_3COOH$ system

To obtain additional information on the catalytic possibilities of the $H_2O_2/V^V/CF_3COOH$ system, we studied the oxidation of substrates of various natures. The formation of ozone in the decomposition of hydrogen peroxide in CF_3COOH in the presence of V^V suggests that this system can exhibit high oxidation activity. Therefore, we chose compounds difficult to oxidize, *viz.*, cyclohexane, arenes, perfluoroarenes, and perfluoroolefins, as objects of the study. The experiments showed that the reactions with these compounds occur rather efficiently and are complete, when all of the hydrogen peroxide is consumed, within 2—5 min after mixing the reactants.

Decomposition of H_2O_2 in trifluoroacetic acid[16,17] is completed over a period of several (2—5) minutes even when $[V^V] = 10^{-4}$—10^{-3} *M*. Therefore, conventional methods for determining rates of chemical reactions cannot be applied to the $H_2O_2/V^V/CF_3COOH$ catalytic system.

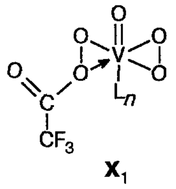
Oxidation of cyclohexane[16,17,25]

Oxidation of cyclohexane (CH) in the system in question affords cyclohexanol and cyclohexyl trifluoroacetate in a yield of up to 100 % based on the reacted CH. Neither cyclohexanone, which is the main product of the oxidation of CH involving free radicals,[28] nor products of its transformation have been detected in the reaction mixture. This fact and also the fact that inhibitors have no effect[16,25] on the reactions occurring in the $H_2O_2/V^V/CF_3COOH$ system allow one to infer that in this system, CH is not oxidized according to a free-radical mechanism and that neither oxyl nor peroxyl radicals are involved in this process.

In the presence of CH, the amount of CO_2 in the gaseous reaction products[16,25] is lower than in the decomposition of CF_3COOOH in CF_3COOH without any admixtures. The amount of HF formed also decreases, as follows from the ^{51}V NMR spectra of the reaction solutions recorded after decomposition of hydrogen peroxide in the presence of cyclohexane:[16,17] the intensity of the signal of the vanadium(v) oxofluoride complex decreases, and a signal corresponding to the V^V oxo complex that contains no F^- ligands appears. All of these facts indicate that CH decreases the rate of decarboxylation of CF_3COOOH. Since CH does not form any complexes with V^V compounds, it is reasonable to assume that the phenomena observed result from a decrease in the steady-state concentration of the complex responsible for the decarboxylation of the peracid, for example, due to a reaction of this complex with CH. Obviously, this complex incorporates a molecule of peroxytrifluoroacetic acid (or its anion).

HF evolution in the absence of H_2O_2 retards decomposition of CF_3COOOH (see above), and its consumption is again initiated by the addition of H_2O_2 or H_2O. However, in the case of decomposition of hydrogen peroxide, HF has no effect on the consumption of H_2O_2 or on the yield of ozone. The fact that neither oxidation of CH nor decomposition of peroxides are retarded by the hydrogen fluoride liberated indicates that the formation of the active complex oxidizing CH involves hydrogen peroxide (along with CF_3COOOH).

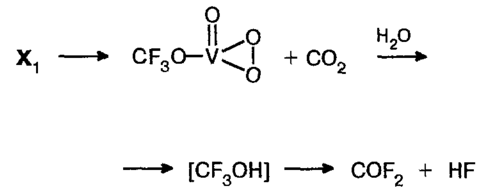
The assumption that CH is oxidized by the reaction with a vanadium(v) complex (for example, $\mathbf{X}_1$) that contains a peroxide group and CF_3COOOH or its anion as ligands is consistent with all of the above-stated facts.



$\mathbf{X}_1$

L = CF_3COOH, H_2O_2

Decomposition of this type of complex to give CO_2 may be the key step of the catalytic decarboxylation of peroxytrifluoroacetic acid.



Oxidation of CH opens a new channel for the consumption of complex $\mathbf{X}_1$ and thus decreases its steady-state concentration and, consequently, decreases the yields of CO_2 and HF.

It should be noted that in the presence of CH, the evolution of ozone stops. Since it has been found that CH practically does not react with ozone under the conditions employed, this fact implies that the formation of ozone is also preceded by complex $\mathbf{X}_1$.

Oxidation of arenes[16,17,26]

Oxidation of benzene (PhH), hexafluorobenzene (HFB), octafluorotoluene, and substituted arenes with electron-releasing (Me or Me_2) or electron-withdrawing (F, CF_3, or $(CF_3)_2$) substituents[26] were studied by the method of competing reactions.[29] As one should expect, electron-releasing substituents accelerate the reaction and electron-withdrawing substituents decelerate it. However, contrary to the expectations, all of the reaction rates are commensurable in their order of magnitude. The results obtained allowed the following conclusions to be drawn:

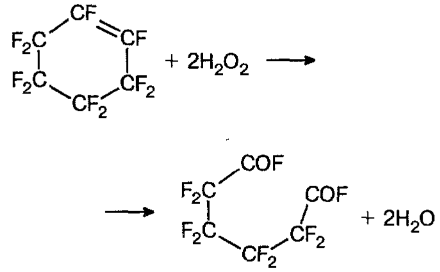
1. The applicability of the method of competing reactions to this system indicates that the same species is responsible for the oxidation of all of these substrates;

2. The low sensitivity of the reaction to the nature of the substituent (k_{HFB}/k_{PhH} ~ 0,5), the satisfactory correlation of $\log(k_{ArH}/k_{PhH})$ with σ_m Hammett constants (and not with σ^+), and also the low absolute value of ρ (−0.99) imply that the degree of the transfer of the electron density from the aromatic ring to the electrophilic species in the activated complex of the rate-determining step is small. Therefore, the probability that HO^+ or HO_2^+ type species participate in the oxidation of arenes is low.

Oxidation of perfluoroolefins[16,17,27]

The yield of epoxide in the oxidation of perfluoro-1-octene (PFO-1) in the system under study does not exceed 10 %, and in the case of perfluoro-2-octene (PFO-2) or perfluorocyclohexene (PFCH), no epoxides are formed. For all of these perfluoroolefins, the corresponding perfluoroacyl fluorides are the primary reaction products.

$$R^1CF{=}CFR^2 + 2H_2O_2 \longrightarrow$$
$$\longrightarrow R^1COF + R^2COF + 2H_2O \qquad (5)$$



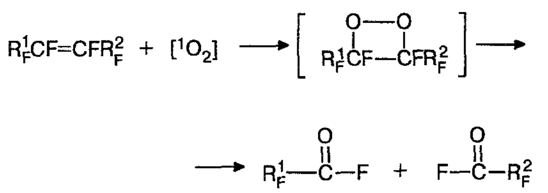
(6)

Epoxides of perfluoroolefins are known to isomerize through the action of fluoride ions to give perfluorinated ketones or perfluoroacyl fluorides with the same molecular weights. However, the products observed call into question the intermediate formation of epoxy compounds in reactions (5) and (6) for the following reasons:

1) if this mechanism had been realized in the system under study, PFO-1 would have yielded perfluorooctanoyl fluoride (rather than perfluoroheptanoyl fluoride), and PFO-2 would have given perfluoromethylhexylketone, which was not detected in the reaction mixture;

2) the experiments with perfluoro-1-octene oxide introduced into the reaction system for the oxidation of PFO-1 have shown that this epoxide is completely stable even when the degree of conversion of the olefin is ~100 %.

However, all of the results can be interpreted in the context of a scheme that involves the transfer of a singlet oxygen molecule from the active oxidant to the substrate as the key step of the process (reaction (7)).



$$R_F^1CF{=}CFR_F^2 + [^1O_2] \longrightarrow \left[R_F^1\overset{O-O}{CF-CFR_F^2} \right] \longrightarrow R_F^1{-}\overset{O}{\overset{\|}{C}}{-}F + F{-}\overset{O}{\overset{\|}{C}}{-}R_F^2 \qquad (7)$$

4. The nature of the active oxidant in the $H_2O_2/V^V/CF_3COOH$ system

Decomposition of hydroperoxides can yield $O_2(^1\Delta_g)$[1–3] and $O_2(^3\Sigma_u)$.[29] In addition, in the $V^V/H_2O_2/CF_3COOH$ system, ozone is formed and the complex radical, $V^V(O_2^{-\cdot})$,[16,17] has also been detected. These compounds could participate in the oxidation of the substrate. However, none of the forms of free oxygen, $^1O_2$, $^3O_2$, and O_3, or the coordinated superoxide anion act as the active oxidant in the system under consideration, which is indicated by the facts listed below.

1. The rate of the interaction of $^1O_2$ with electron-deficient olefins is several orders of magnitude lower than the rate of its deactivation in the condensed phase.[31,32] Therefore, the complete consumption of the substrate would require at least a 100-fold excess of H_2O_2, which is inconsistent with the experimental data (Fig. 1).

2. Under the conditions of initiated free-radical oxidation, dioxygen ($^3\Sigma_u$) selectively (~100 %) and slowly epoxidizes only terminal perfluoroolefins.[33] However, in the system considered, not only internal, but also cyclic perfluoroolefins (PFO-2, PFCH) are oxidized, and epoxides form as side products or do not form at all. Under the conditions of the free-radical oxidation of terminal perfluoroolefins, an increase in the yield of perfluoroacyl fluorides is observed when the steady-state concentration of the organofluorine peroxyl radicals, which are chain transfer agents, is increased.[33] However, no ESR signals of these species were detected in our experiments. This casts doubt on both the participation of $O_2(^3\Sigma_u)$ in the oxidation of substrates and the occurrence of free-radical reactions in the $H_2O_2/V^V/CF_3COOH$ system.

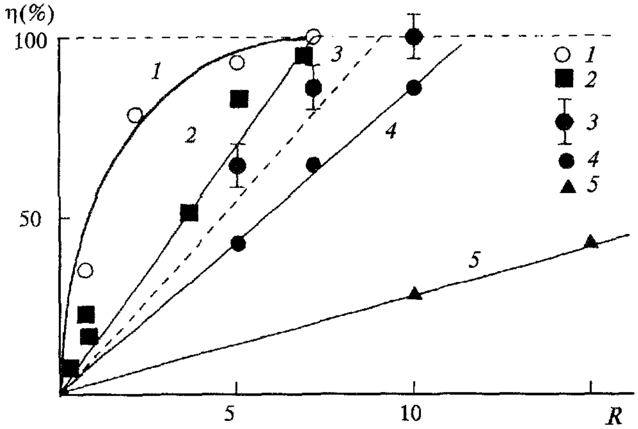


Fig. 1. Dependences of the degree of conversion (η) of PFO-1 (*1*), CH (*2*), HFB (*3*), PFO-2 (*4*), PFCH (*5*) on the $R = [H_2O_2]_0/[S]_0$ ratio in CF_3COOH, $[S]_0 = 0.1$ *M*, $[V] = 10^{-3}$ *M*, 15 °C.

3. It has been demonstrated that free radicals do not participate in the oxidation of CH in the system studied[25] (see above).

4. It is known that molecular oxygen in the triplet or the singlet state does not react with benzene or with hexafluorobenzene under mild conditions.[29,32] However, arenes are efficiently oxidized in the system under study.[26]

5. Species like HO^+ and HO^+_2 cannot be responsible for the oxidation of electron-deficient perfluoroolefins, since under the conditions of our experiments, these species do not participate even in the oxidation of arenes, which are richer in electrons.[26]

The ozone formed in the system in question could in principle be responsible for the consumption of some of the substrates studied, since it is a strong oxidizing agent. Taking into account that at $[PFO\text{-}1]_0 = 0.1$ *M*, 7 moles of H_2O_2 per 1 mole of perfluoroolefin is needed for the complete conversion of the latter (see Fig. 1) and that the yield of ozone in the decomposition of H_2O_2 is 10—15 %, one can see that a 7-fold excess of hydrogen peroxide would suffice for the formation of ~1 mole of ozone per 1 mole of PFO-1: $(0.1 \text{ to } 0.15)\times 7 = (0.7 \text{ to } 1.05)$. Since the oxidation of 1 mole of PFO-1 requires 1 mole of O_3 (as the normal oxidation of olefins[34]), then the quantity of ozone liberated would be sufficient for the virtually complete conversion of the substrate.

However, a comparison of the rates of ozonation of CH, HFB, PFO-1 and PFO-2, and PFCH in trifluoroacetic acid[35] has shown that the rates of their consumption decrease in the order*

$$\text{PFO-2}>\text{PFO-1}>\text{HFB}>>>\text{PFCH} . \qquad \text{(I)}$$

When these substrates are oxidized in the $V^V/H_2O_2/CF_3COOH$ system, the activity series is different (see Fig. 1):

$$\text{PFO-1}>\text{CH}>\text{HFB}>\text{PFO-2}>\text{PFCH} . \qquad \text{(II)}$$

This eliminates ozone as a species responsible for the conversion of substrates in the system studied.[16,17,35]

Thus, none of the species considered ($^1O_2$, $^3O_2$, O_3, free peroxyl radicals, HO^+, HO_2^+) is responsible for the transformations of substrates observed. The only sugges-

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* It should be noted that the nonbranched internal olefin (PFO-2) reacts with ozone ~1.5 times more rapidly than the terminal olefin (PFO-1), which is usually much more active. As far as we know, this is the only example of the inversion of reactivity in organofluorine chemistry. The cyclic perfluoroolefin, PFCH, practically does not react with free O_3.

Table 2. The competing oxidation of perfluoro-1-octene, perfluoro-2-octene, hexafluorobenzene, and perfluorocyclohexene in the $H_2O_2/V^V/CF_3COOH$ catalytic system (0 °C, $[V^V]$ = 10 *M*)

Entry	The substrate being oxidized (*C*/*M*)		$[S_1]/[S_2]$	$[H_2O_2]_0/\Sigma[S]_0$	The degree of conversion (%)		k_1/k_2
	S_1	S_2			η_1	η_2	
1	HFB (0.1)	PFO-1 (0.1)	1.0	5.0	62.9	3	32.6
2	HFB (0.1)	PFO-2 (0.3)	0.3	2.5	86.3	6	32.1
3	HFB (0.1)	PFO-2 (1.0)	0.1	1.1	95.0	2	148.3
4	PFO-1 (0.1)	PFO-2 (0.1)	1.0	3.0	86.3	9	21.1
5	PFO-1 (0.06)	PFCH (0.22)	0.27	2.3	100	0	—
6	PFCH (0.15)	PFO-2 (0.11)	~1	2.3	9.0	27	0.3
7	PFCH (0.1)	PFO-2 (0.1)	1.0	7.0	32.8	74	0.3

tion consistent with the experimental data is that the intermediate oxygenyl complexes of vanadium(v) are responsible for the oxidation and the formation of ozone in this system.

5. Comparison of the rates of oxidation of substrates

The high rates of the decomposition of H_2O_2 and the consumption of all of the difficult-to-oxidize substrates studied in the $H_2O_2/V^V/CF_3COOH$ system do not allow the direct determination of these values by the conventional methods of chemical kinetics and indicate that the process involves "superactive" species.

None of the compounds studied is able to form stable complexes with V^V or to induce or inhibit decomposition of H_2O_2, therefore, the rate of the consumption of hydrogen peroxide should not change in the presence of substrates. For the transformations under consideration, the reaction times are limited by the time required for the complete decomposition of H_2O_2. Therefore, one may assume that decomposition of H_2O_2 is limited by one of the steps of its interaction with the catalyst and that substrates react with the complexes formed either in the limiting step or in subsequent steps.

These facts allow the following assumption: the degree of conversion* η of each substrate can be used as a function for comparing the reactivities of various compounds, and η_{HFB} = 57 %, $\eta_{PFO\text{-}2}$ = 48 %, η_{PFCH} = 15 % (interpolation of the experimental data, Fig. 1), *i.e.*, the rates of consumption of the substrates used are commensurable with both the rate of H_2O_2 decomposition and with each other.

An attempt to use the method of competing reactions[29] for calculating the ratio between the rate constants of the oxidation of substrates of various natures gave unexpected results.[16,17] It turned out that in the case of simultaneous oxidation of any pair of these substrates, CH, arenes, PFO-1, and PFO-2, the degree of conversion of one of them is at least an order of magnitude lower than that of the other substrate. For example, the presence of CH practically completely suppresses the oxidation of HFB and benzene (Table 2, runs *1* and *2*), HFB stops the oxidation of PFO-1 and PFO-2 (see Table 2, runs *3*—*5*), PFO-1 stops the consumption of PFO-2 and PFCH (see Table 2, runs *6* and *7*). Formally, this could allow one to conclude that the reactivity of the substrates decreases in the order

$$\text{CH} \gg \text{HFB} \gg \text{PFO-1} \gg \text{PFO-2} > \text{PFCH}. \quad \text{(III)}$$

According to the results of the experiments on the simultaneous oxidation (see Table 2, runs *2*, *3*, and *6*), the lower limit* of the ratio between the rate constant of the reaction of CH with the active oxidant and the corresponding constant for PFO-2 calculated from the equation

$$k_{CH}/k_{PFO\text{-}2} = (k_{CH}/k_{HFB})(k_{HFB}/k_{PFO\text{-}1})(k_{PFO\text{-}1}/k_{PFO\text{-}2}), \quad (8)$$

is $\sim 5 \cdot 10^5$, which does not agree with the inference that the reactivities of the substrates are commensurable (see above) based on the results of the oxidation of the individual substrates, and not their mixtures.

It is also noteworthy that the ratio between the rate constants of the consumption of the substrates calculated in terms of the scheme of parallel competing oxidation varies as the initial concentrations of the compounds being oxidized vary (see Table 2, runs *4* and *5*).

These results imply that the method of competing reactions in inapplicable to the system in question. This fact cannot be accounted for by the formation of a stable inactive complex between the oxidation product of one of the substrates and the catalyst. For example, the termination of the oxidation of PFO-2 in the presence of PFO-1 is not due to the products of the oxidation of PFO-1, *viz.*, perfluoroacyl fluorides (or perfluoro-

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* Hereafter, by the degree of conversion we mean the degree of conversion of a substrate achieved when the H_2O_2 added is entirely exhausted.

* Since the degrees of conversion of the substrates being simultaneously oxidized in the reaction system are incommensurable (see Table 2), only the lower limits of the ratios between the rate constants of the oxidation of various types of substrate can be evaluated.

carboxylic acids) and PFO-1 oxide, since none of these products can form stable adducts with V^V, and HF, as experiments have shown, has no effect on the degrees of conversion of both perfluoroolefins. The inapplicability of the method of competing reactions to the study of the processes occurring in the $H_2O_2/V^V/CF_3COOH$ system is more likely explained by the fact that the oxidation in this system occurs *via* several, rather than one, active species resulting from the interaction of the oxidant with the catalyst, and one of these species is the direct source of ozone.

6. The minimum scheme of the decomposition of hydrogen peroxide

An explanation for the suppression of oxidation of the substrates

In terms of the order in which the oxidation is suppressed (reactivity series (III)), all of the substrates can be divided into 4 groups: 1) alkanes (in this case, cyclohexane); 2) arenes (fluorinated and non-fluorinated and substituted); 3) terminal perfluoroolefins (in this case, PFO-1); 4) internal perfluoroolefins (linear PFO-2 and cyclic PFCH).

The presence of any compound from a preceding group suppresses the oxidation of any representative of a subsequent group.

All of these data can be explained by assuming that at least four types of active intermediate, $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{X}_3$, and $\mathbf{X}_4$,* arise in the $H_2O_2/V^V/CF_3COOH$ system, and each of these is responsible for the oxidation of substrates of a particular nature: alkanes ($\mathbf{X}_1$), aromatic compounds ($\mathbf{X}_2$),** terminal perfluoroolefins ($\mathbf{X}_3$), and internal perfluoroolefins ($\mathbf{X}_4$).** Interconversions of the active oxidants and their reactions with substrates ($\mathbf{S}_i$) can be represented as Scheme 1, in which the following designations are used: k_i is the rate constant for the transformation of active intermediate $\mathbf{X}_i$ into $\mathbf{X}_{i+1}$; k'_i is the rate constant for deactivation of the active intermediate $\mathbf{X}_i$ to give O_2 or O_3; k''_i is the second-order rate constant for the interaction of active species $\mathbf{X}_i$ with the corresponding substrate; S_1 is CH, S_2 is HFB (or another arene), S_3 is PFO-1, S_4 is PFO-2 (or PFCH).

This mechanism accounts for the suppression of the oxidation of some substrates in the presence of other substrates. For example, CH reacts with $\mathbf{X}_1$ and completely arrests the consumption of other substrates, arenes or perfluoroolefins (see Table 2). In terms of the scheme being discussed, this requires that the steady-state concentrations of the $\mathbf{X}_2$, $\mathbf{X}_3$, and $\mathbf{X}_4$ species responsible for the oxidation of the other substrates dramatically decrease. This can occur if $\mathbf{X}_1$ is "intercepted" by CH before it has time to be converted into complex $\mathbf{X}_2$, *i.e.*, provided that the rate of the reaction of $\mathbf{X}_1$ with CH is much higher than the rate of the transformation of $\mathbf{X}_1$ into $\mathbf{X}_2$: $k_1''[\mathrm{CH}] >> k_1$.

Similarly, since the presence of HFB, which reacts with intermediate $\mathbf{X}_2$, almost suppresses the consumption of other (nonaromatic) substrates, the rate of the reaction of $\mathbf{X}_2$ with HFB should be much higher than the rate of its conversion into $\mathbf{X}_3$: $k_2''[\mathrm{HFB}] >> k_2$. The fact that oxidation of PFO-2 is stopped by the addition of PFO-1 can be explained by assuming that $\mathbf{X}_3$ reacts with PFO-1 much more rapidly than it is converted into $\mathbf{X}_4$: $k_3''[\mathrm{PFO\text{-}1}] >> k_3$. In other words, in the context of this scheme, the rate of conversion of any intermediate $\mathbf{X}_n$ into $\mathbf{X}_{n+1}$ is much lower than the rate of the reaction of intermediate $\mathbf{X}_n$ with the corresponding substrate $\mathbf{S}_n$.

$$w_n << w''_n \qquad (9)$$

The direct source of ozone

In order to identify which of the active intermediates formed in the $H_2O_2/V^V/CF_3COOH$ system is responsible for the ozone formation, evolution of ozone in the presence of all of the substrates under consideration has been studied. The following regularities were established (see Fig. 2, Ref. 16):

1) the presence of HFB, benzene, and CH in the reaction mixture completely stops the liberation of ozone;

2) the yield of O_3 during the oxidation of PFO-1 is ~5 times lower than that during decomposition of H_2O_2 in the same system without a substrate;

3) the presence of perfluorooctene-2 and perfluorocyclohexene has no effect on the quantity of ozone in the gaseous reaction products.

Thus, the formation of ozone is entirely suppressed in the presence of those substrates that react with active species $\mathbf{X}_1$ and $\mathbf{X}_2$, according to the scheme suggested. At the same time, substrates that react with $\mathbf{X}_4$ (PFO-2 and PFCH) do not affect the quantity of ozone evolved. These data indicate that only complex $\mathbf{X}_3$ can act as the direct source of ozone.

A possible chemical composition of the active complexes

Several considerations can be stated regarding the chemical composition of these complexes.

Complex $\mathbf{X}_0$ probably results from the reaction of the dissolved vanadium(v) compound with either H_2O_2 or

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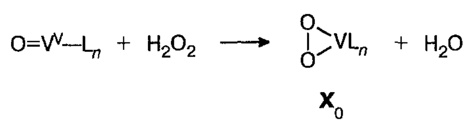
* In the present paper, we consider the minimum possible scheme for the reactions occurring in the $H_2O_2/V^V/CF_3COOH$ system, which contains no more than four active intermediates.

** The same active species is responsible for the consumption of all of the fluorinated and nonfluorinated arenes, since the rates of their separate oxidation are comparable and no mutual suppression of the oxidation is observed.[26] A similar conclusion can be drawn concerning both internal olefins, perfluoro-2-octene and perfluorocyclohexene, which is indicated by a comparison of the data for their simultaneous and separate oxidation.[16,17]

Scheme 1

$$\begin{tikzcd}
{} & {} & {} & {} & {} & \\
X_0 \arrow[u, "k_0'\text{, }H_2O_2"] \arrow[r, "k_0\text{, }CF_3COOOH"] & X_1 \arrow[u, "k_1'"] \arrow[r, "k_1"] \arrow[d, "k_1''S_1"] & X_2 \arrow[u, "k_2'"] \arrow[r, "k_2"] \arrow[d, "k_2''S_2"] & X_3 \arrow[u, "k_3'"] \arrow[r, "k_3"] \arrow[d, "k_3''S_3"] & X_4 \arrow[u, "k_4'"] \arrow[r, "k_4"] \arrow[d, "k_4''S_4"] & {} \\
 & {} & {} & {} & {} &
\end{tikzcd}$$

CF_3COOOH. Since the peroxo dianion, O_2^{2-}, forms rather stable complexes with vanadium(v) and is considered to be one of the strongest nucleophilic groups in the coordination chemistry of d^0 central atoms, the vanadium compound most likely reacts initially with H_2O_2, rather than with CF_3COOOH. This fact justifies the assumption that X_0 is a monoperoxo compound.



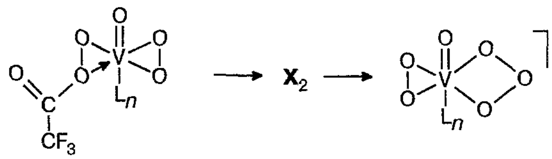
X_0

Symbol X_0 in Scheme 1 actually corresponds to a group of complexes containing one peroxo group per vanadium(v) atom and differing from one another in the number and arrangement of other possible ligands (carboxylate, fluoride, hydroxo, or aqua ligands) denoted by the symbol L. Complex X_1 responsible for the oxidation of CH contains one peroxo group and one coordinated CF_3COOOH molecule (or its anion), as has been suggested above.[16,17,25]

Peroxytrifluoroacetic acid (or its anion) is a much weaker nucleophile than hydrogen peroxide, due to the effect of the strong acceptor of electrons, the perfluoroacyl group. No complexes of vanadium(v) with this ligand have been reported. It is not improbable that the insertion of CF_3COOOH or the corresponding anion into the monoperoxo complex X_0 to give X_1 is the slowest step in the scheme under consideration and is the rate-determining step of all of the transformations leading to the liberation of ozone.

The fact that hydrogen peroxide forms more stable complexes with V^V than CF_3COOOH (see Refs. 17, 25) compels us to include the addition of H_2O_2 to complex X_0 (k_0' is the rate constant) to give diperoxo complexes in our consideration. This step is most likely the first one in the reaction pathway that leads to intermediates that are inactive toward ozone formation and oxidation of the substrates studied.

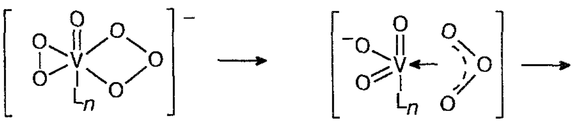
Complex X_3. In our opinion, the structure of complex X_3 should be considered before we discuss the structure of complex X_2. The fact is that the kinetic data obtained by us unambiguously indicate that in the context of the mechanism suggested, it is complex X_3 that acts as the direct source of ozone and, therefore, some considerations concerning its structure can be stated. Only after that, using the known data on the compositions of complexes X_1 and X_3, we will be able to make some assumptions concerning complex X_2, which is formed from X_1 and is converted into X_3.



X_1 X_3

A probable minimum composition of the coordination sphere of complex X_3 liberating ozone should include a group that is able to eliminate ozone in an elementary event. We believe that this group should contain at least three O atoms. The O_3^{2-} ligand, which is a kind of intermediate for ozone, complies with this requirement. No mentions of stable complexes of this ligand with metals are known to us, but, for example, phosphorus ozonides containing a O_3^{2-}group are well known and have been extensively studied.[36] To give free O_3, this ligand must lose two electrons. It is most likely that in complex X_3, the coordinated peroxo group, O_2^{2-}, would act as the acceptor of the electrons (Scheme 2).

Scheme 2



X_3

$\longrightarrow VO_3L_n + O_3$

$$O_2^{2-} + O_3^{2-} \longrightarrow 2O^{2-} + O_3$$

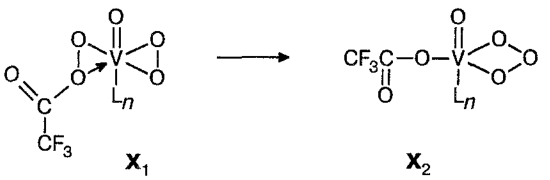
Complex X_2. One can easily see that the formation of ozone, according to stoichiometry, requires three molecules of hydroperoxide, whereas complex X_1 involves only two peroxide molecules. Therefore, in considering the kinetic model one should take into account the possibility of the addition of a third hydroperoxide molecule to one of the active intermediates.

Two possible ways for the addition of the third hydrogen peroxide molecule exist.

1. H_2O_2 adds to complex X_1 to give a triperoxo complex, which then isomerizes into complex X_3. Intermediate X_1 can be formally considered to be a diperoxo complex. The addition of the third peroxide molecule to this type of complex is known to occur at least an order of magnitude more slowly than the addition of the first two molecules.[37] Since in the context of Scheme 1, the formation of complex X_1 is the limiting step in the oxidation of the substrates studied and in the liberation of ozone, the next step, *viz.*, the formation of X_2 from X_1, should be rapid. Therefore, the probability that the third H_2O_2 molecule adds to intermediate X_1 is low.

2. Hence, it is more likely that complex X_1 isomerizes into complex X_2, which then reacts with the third H_2O_2 molecule. In this case, a probable minimum composition of the coordination sphere of complex X_2, like that for complex X_3, should include an O_3^{2-} ligand. The formation of X_2 from X_1 can be represented as inner-sphere oxidation of the O_2^{2-} ligand by the coordinated anion of peroxytrifluoroacetic acid (Scheme 3).

Scheme 3

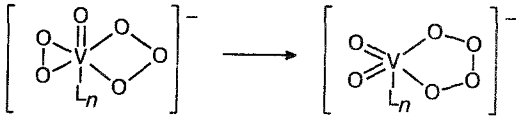


X_1 X_2

$$O_2^{2-} + CF_3COOO^- \longrightarrow O_3^{2-} + CF_3COO^-$$

Notice that during the transformation of X_2 into X_3, the replacement of the poorly coordinating ligand, the anion of trifluoroacetic acid, occurs rapidly. Therefore, in the context of the scheme suggested, the possibility of rapid addition of the third hydroperoxide molecule to complex X_2 really exists.

Complex X_4. At present, no experimental data are available that would allow us to make justified conclusions concerning the composition of the coordination sphere of complex X_4. This complex may result from isomerization of X_3 with the formation of a vanadyl group and an O_4^{2-} ligand.



X_3 X_4

To the best of our knowledge, no metal complexes with these ligands have been reported in the literature.

To sum up the discussion of the experimental data, we suggest a kinetic scheme (Scheme 4) for the reactions occurring in the $H_2O_2/V^V/CF_3COOH$ system that involves participation of both peroxytrifluoroacetic acid and hydrogen peroxide in the transformations observed (*viz.*, oxidation of the substrates and the formation of O_3).

The vanadium(v) compound reacts with hydrogen peroxide to give monoperoxy complex X_0. The reaction of this complex with H_2O_2 (lim′) later results in the evolution of oxygen.

The reaction of complex X_0 with peroxytrifluoroacetic acid to give complex X_1 containing the coordinated CF_3COOOH should be the limiting step of the whole process (lim) resulting in the liberation of ozone. The third molecule of peroxide (H_2O_2) adds to complex X_2 more rapidly, than CF_3COOOH adds in the limiting step, or at a rate comparable to the addition of CF_3COOOH. In terms of this mechanism, the limiting step is followed by a series of consecutive reactions in which catalytically active complexes responsible for the oxidation of substrates and the liberation of O_3 are produced. Each of these complexes reacts with a particular type of substrate more rapidly than it is converted into the next complex, which accounts for the observed suppression of the oxidation of some substrates in the presence of other compounds. The ozone that results from the decomposition of complex X_3 is responsible for the oxidation of PFO-1.

7. A mathematical model for the oxidation of substrates and decomposition of hydrogen peroxide in the $H_2O_2/V^V/CF_3COOH$ system

Oxidation of substrates

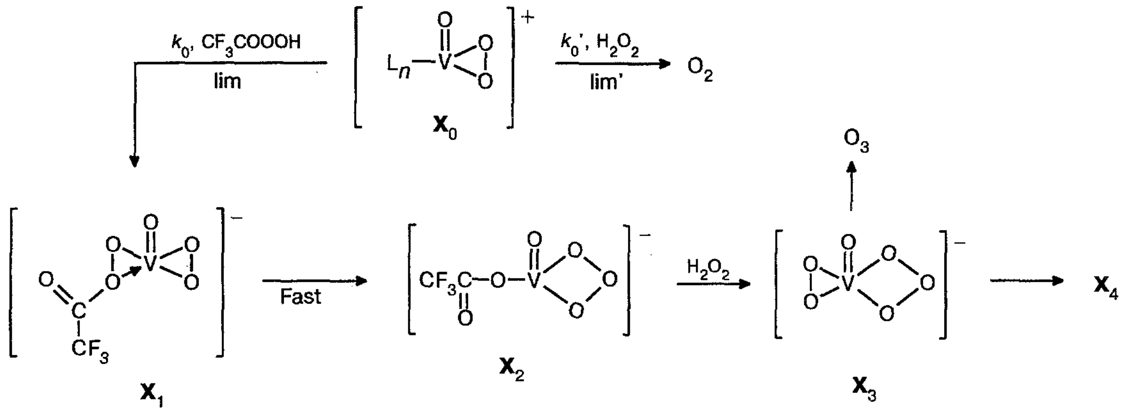
The kinetic model for the set of reactions considered (see Schemes 1 and 4) assumes the following.

1. Active species X_1, X_2, X_3, and X_4 are produced in consecutive steps and their concentrations are steady-state:

$$\frac{dX_i}{d\tau} = 0 . \tag{10}$$

2. Each of the active species, X_i, can decompose to give compounds that are inactive in this system, for example, O_2 or O_3, *i.e.*, be deactivated at the rate w'_i.

Scheme 4



3. A substrate S_i stops oxidation of S_j in the case when $i < j$:

$w_i'' >> w_j''$,

specifically, for neighboring intermediates, taking into account item 1, one can write:

$$k_n[S_n][X_n] >> k_{n+1}[S_{n+1}][X_{n+1}] \ . \quad (11)$$

4. Active species with numbers smaller than i (*i.e.*, those preceding X_i) do not react with substrate S_i.

It is known that in a solution of H_2O_2 in CF_3COOH, an equilibrium between H_2O_2 and CF_3COOOH is rapidly established (reaction (12)).

$$CF_3COOH + H_2O_2 \overset{k_0}{\rightleftharpoons} CF_3COOOH + H_2O \quad (12)$$

Taking into account that H_2O_2 ultimately completely decomposes to give water, the material balance with respect to H_2O_2 can be written in the following way:

$$[H_2O_2]_0 = [H_2O_2] + [CF_3COOOH] + [H_2O] -$$
$$- [CF_3COOOH] = [H_2O_2] + [H_2O].$$

Then by substituting $[H_2O] = [H_2O_2]_0 - [H_2O_2]$ into the expression for the equilibrium constant, we obtain

$$K_0 = \frac{[CF_3COOH]([H_2O_2]_0 - [H_2O_2])}{[H_2O_2]} \ , \quad (13)$$

from which we have

$$[CF_3COOH] = K_0 \frac{[H_2O_2]}{([H_2O_2]_0 - [H_2O_2])} \ .$$

If $K_0 >> 1$, then $[H_2O_2]_0 >> [H_2O_2]$, and one may write

$$[CF_3COOOH] = K[H_2O_2] \ , \quad (13')$$

where $K = K_0/[H_2O_2]_0$.

Let us assume that intermediate X_n is formed by a transformation of the preceding complex X_{n-1} without participation of H_2O_2 and X_{n+1} results from the addition of H_2O_2 to X_n.

In the framework of Scheme 1, the steady state condition for the active intermediates has the following form

$$k_0[X_0][CF_3COOOH] = (k_1+k_1' + k_1''S_1)[X_1]$$
$$k_1[X_1] = (k_2+k_2' + k_2''S_2)[X_2]$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$k_{n-1}[X_{n-1}] = (k_n[H_2O_2]+k_n' + k_n''[S_n])[X_n]$$
$$k_n[X_n][H_2O_2] = (k_{n+1}+k'_{n+1}+k''_{n+1}S_{n+1})[X_{n+1}]k''_n$$

Let us assume that the system contains only substrates S_n and S_{n+1}. By solving the set of equations for $[X_n]$, *i.e.*, the species with which the third peroxide molecule reacts, we obtain

$$[X_n] = \frac{k_0X_0[CF_3COOOH]A_{n-1}}{k_n[H_2O_2] + k_n' + k_n''[S_n]} \ , \quad (14)$$

where $A_{n-1} = \prod_{i=1}^{n-1} \frac{k_i}{k_i + k_i'}$.

The rate of consumption of substrate S_n can be described by the differential equation

$$-\frac{d[S_n]}{d\tau} = \frac{k_0X_0[CF_3COOOH]A_{n-1}k_n''[S_n]}{k_n[H_2O_2] + k_n' + k_n''[S_n]} \ . \quad (15)$$

The steady state condition for $[X_{n+1}]$, which is produced by the addition of the third peroxide molecule to the V^V complex and is responsible for the oxidation of substrate S_{n+1}, takes the form

$$k_n[X_n][H_2O_2] = (k_{n+1}+k'_{n+1}+k''_{n+1}[S_{n+1}])[X_{n+1}], \quad (16)$$

from which $$[X_{n+1}] = \frac{k_n[X_n][H_2O_2]}{(k_{n+1} + k'_{n+1} + k''_{n+1}[S_{n+1}])} \ . \quad (16')$$

The consumption of hydrogen peroxide

In conformity with the suggested Scheme 4, the rate of the consumption of H_2O_2 would be described by the following equation

$$-\frac{d[H_2O_2]}{d\tau} = (k_0[CF_3COOOH] + k'_0[H_2O_2])X_0 \ . \quad (17)$$

However, this equation is valid only for the reactions of perfluoroolefins, the primary oxidation products of which are resistant toward oxidizing agents.

Oxidation of cyclohexane and arenes does not stop when the primary products of the interaction of the active intermediate with the substrate are formed, but proceeds to deeper steps (for example, in the case of the oxidation of HFB, CO_2 and oxalyl fluoride were detected and there were no other intermediate oxidation products). Therefore, one cannot rule out that oxidation of these substrates requires a larger amount of hydroperoxide than that taken into account by Schemes 1 or 4, since the primary products of the oxidation of the substrate can rapidly react with the species produced in the steps that precede the limiting step.

This additional consumption of hydrogen peroxide during the oixidation of CH and HFB is also indicated by the fact that the order in which the reactivity of the substrates evaluated in the experiments on their separate oxidation varies (see Fig. 1)

PFO-1 > CH > HFB > PFO-2

does not coincide with the activity series

CH >> HFB >> PFO-1 >> PFO-2 > PFCH, (IV)

obtained from the results of the simultaneous oxidation of the same substrates.

The fact that the reaction mixture contains no primary products of the oxidation of substrates may attest that these are rapidly consumed. In this case, the equation for the consumption of hydrogen peroxide assumes the form:

$$-\frac{d[H_2O_2]}{d\tau} = (k_0[CF_3COOOH] + k'_0[H_2O_2])X_0 + \alpha_n\left(-\frac{dS_n}{d\tau}\right) , \quad (17')$$

where α_n is a coefficient depending on the nature of the substrate.

For perfluoroolefins, α is equal to zero, since the corresponding acyl fluorides are the primary and actually the final products of the oxidation of perfluoroolefins in the $H_2O_2/V^V/CF_3COOH$ system, and PFO-1 oxide is stable under the experimental conditions.[27]

The simultaneous oxidation of substrates

Let us assume that a reaction solution contains two substrates, S_n and S_{n+1}, and the concentrations of other substrates are equal to zero. It can be demonstrated that in the simultaneous presence of S_n and S_{n+1}, substrate S_n will suppress the oxidation of S_{n+1} provided that $w_n << w''_n$ (see Eq. (9)), *i.e.*,

$$k_n[H_2O_2] << k''_n[S_n].$$

In fact, the condition for the termination of the consumption of a substrate in the presence of another substrate is expressed by the following equation

$k''_n[S_n][X_n] >> k''_{n+1}S_{n+1}[X_{n+1}]$ or

$$\frac{[X_{n+1}]}{[X_n]} << \frac{k''_n[S_n]}{k''_{n+1}[S_{n+1}]} \ . \quad (18)$$

By substituting the value for $[X_{n+1}]$ from Eq. (16') into inequality (18) we obtain the inequality

$$\frac{k_n[H_2O_2]}{(k_{n+1} + k'_{n+1} + k''_{n+1}[S_{n+1}])} << \frac{k''_n[S_n]}{k''_{n+1}[S_{n+1}]} \ . \quad (19)$$

Since the consumption of hydrogen peroxide during the oxidation of any of the substrates is comparable to its stoichiometric amount, one may conclude that the rate of the nonproductive consumption of the oxidant (the sum of the rate of decomposition of the active complex and the rate of its conversion into the next complex, $k'_{n+1}+k_{n+1}$) is comparable to the rate of the oxidation of the substrate, $k''_{n+1}[S_{n+1}]$ (*i.e.*, the denominator of the fraction on the right-hand side of the inequality cannot exceed the denominator on the left-hand side by a factor of more than ~2). From this, it follows that

$$k_n[H_2O_2] << k''_n[S_n], \quad (20)$$

i.e., substrate S_n can actually suppress the oxidation of substrate S_{n+1} provided that the rate of the reaction of S_n with complex X_n is much higher than the rate of the conversion of this complex into the next one (see Schemes 1 and 4).

Oxidation of substrate S_n (the intermediate X_n is formed from complex X_{n-1} without participation of H_2O_2)

Taking into account relationship (20), we may neglect the term depending on $[H_2O_2]$ in the denominator on the right-hand side of Eq. (15). Then the equation for determining the rate of the consumption of substrate S_n assumes the form

$$-\frac{d[\mathbf{S}_n]}{d\tau}=\frac{k_0\mathbf{X}_0[\mathrm{CF_3COOOH}]A_{n-1}k_n''[\mathbf{S}_n]}{k_n'+k_n''[\mathbf{S}_n]}\ . \qquad (15')$$

After division of (15′) by (17′) and separation of variables, by substituting the expression for [CF_3COOOH] from (13′), we have

$$\frac{1+k_0'/k_0K}{A_{n-1}}\left(\frac{k_n'}{k_n''}\frac{1}{[\mathbf{S}_n]}+1\right)d[\mathbf{S}_n]+\alpha_n d\mathbf{S}_n=d[\mathrm{H_2O_2}]\ . \qquad (21)$$

By integrating the left-hand side from $[\mathbf{S}_n]_0$ to $[\mathbf{S}_n]$ and the right-hand side from $[H_2O_2]_0$ to 0 taking into account that $([\mathbf{S}_n]_0 - [\mathbf{S}_n])/[\mathbf{S}_n]_0 = \eta_n$ (where η_n is the degree of conversion of substrate $\mathbf{S}_n$), we obtain the expression for η_n:

$$\left(\alpha_n+\frac{1+k_0'/k_0K}{A_{n-1}}\right)\eta-\frac{1+k_0'/k_0K}{A_{n-1}}\frac{k_n'}{k_n''[\mathbf{S}_n]_0}\ln(1-\eta)=$$

$$=\frac{[\mathrm{H_2O_2}]_0}{[\mathbf{S}_n]_0} \qquad (22)$$

Oxidation of substrate S_{n+1} *(intermediate* X_{n+1} *is formed from complex* X_n *with participation of* $\mathrm{H_2O_2}$*)*

In the absence of other substrates, the steady-state condition with respect to $[\mathbf{X}_{n+1}]$ takes the form

$$k_n[\mathrm{X}_n][\mathrm{H_2O_2}] = (k_{n+1}+k'_{n+1}+k''_{n+1}[\mathrm{S}_{n+1}])[\mathrm{X}_{n+1}]\ . \qquad (23)$$

By solving Eq. (23) for $[\mathbf{X}_{n+1}]$ and substituting the expression for $[\mathbf{X}_n]$ obtained from (14), we may write the kinetic equation for the consumption of $\mathbf{S}_{n+1}$ in the following way:

$$-\frac{d[\mathbf{S}_{n+1}]}{d\tau}=$$

$$=\frac{k_0\mathbf{X}_0[\mathrm{CF_3COOOH}]A_{n-1}k_n[\mathrm{H_2O_2}]k''_{n+1}[\mathbf{S}_{n+1}]}{(k_n[\mathrm{H_2O_2}]+k_n')(k_{n+1}+k'_{n+1}+k''_{n+1}[\mathbf{S}_{n+1}])}\ . \qquad (24)$$

If we divide (24) by (17′) and separate the variables, and then substitute the expression for [CF_3COOOH] from (13'), we will obtain

$$\frac{1+k_0'/k_0K}{A_{n-1}}\left(\frac{k_{n+1}+k'_{n+1}}{k''_{n+1}[\mathbf{S}_{n+1}]}+1\right)d[\mathbf{S}_{n+1}]+\alpha_{n+1}d\mathbf{S}_{n+1}=$$

$$=\frac{k_n[\mathrm{H_2O_2}]}{k_n[\mathrm{H_2O_2}]+k_n'}d[\mathrm{H_2O_2}] \qquad (25)$$

or, in the integral form,

$$\left(\alpha_{n+1}+\frac{1+k_0'/k_0K}{A_{n-1}}\right)\eta_{n+1}-$$

$$-\frac{1+k_0'/k_0K}{A_{n-1}}\frac{k_{n+1}+k'_{n+1}}{k''_{n+1}[\mathbf{S}_{n+1}]_0}\ln(1-\eta_{n+1})=$$

$$=\frac{[\mathrm{H_2O_2}]_0}{[\mathbf{S}_{n+1}]_0}\left(1-\frac{\ln(k_n[\mathrm{H_2O_2}]_0/k_n'+1)}{k_n[\mathrm{H_2O_2}]/k_n'}\right)\ . \qquad (26)$$

According to Eq. (26), the dependence of the limiting degree of conversion on the initial concentration of hydrogen peroxide should be described by an S-shaped curve. The absence of inflection points on the experimental plots of η *vs* $R = [H_2O_2]_0/[\mathbf{S}_{n+1}]_0$ (or *vs* $[H_2O_2]_0$, since in the case when $[\mathbf{S}_{n+1}]_0$ = const, $R = [H_2O_2]_0$) for all of the substrates studied (see Fig. 1) indicates that the term on the right-hand side of Eq. (26) that is nonlinear with respect to $[H_2O_2]_0$ is much smaller than $[H_2O_2]_0$, *i.e.*,

$$\frac{\ln(k_n[\mathrm{H_2O_2}]_0/k_n'+1)}{k_n[\mathrm{H_2O_2}]/k_n'}<<1 \qquad (27)$$

or $k'_n << k_n[H_2O_2]_0$.

Thus, in the context of the scheme being analyzed, the rate of deactivation of $\mathbf{X}_n$ should be much lower than the rate of its interaction with the third molecule of the peroxide.

Then Eq. (26) transforms in the following way:

$$\left(\alpha_{n+1}+\frac{1+k_0'/k_0K}{A_{n-1}}\right)\eta_{n+1}-$$

$$-\frac{1+k_0'/k_0K}{A_{n-1}}\frac{k_{n+1}+k'_{n+1}}{k''_{n+1}[\mathbf{S}_{n+1}]}\ln(1-\eta_{n+1})=\frac{[\mathrm{H_2O_2}]_0}{[\mathbf{S}_{n+1}]_0}\ . \qquad (28)$$

It can be easily seen that the form of Eq. (28) is precisely (within the coefficients) identical to that of Eq. (22). It can be shown that the equation for the degree of conversion of the substrate that reacts with species $\mathbf{X}_{n-1}$, which forms before the third peroxide molecule is introduced into the active complex, will also coincide in form with Eqs. (22) and (28). That is, if we accept this scheme for the reaction, we conclude that the addition of the third peroxide molecule has no effect on the kinetics of the oxidation of the substrates.

Thus, it can be said with confidence that:

1) in terms of the scheme suggested, hydrogen peroxide can in principle add to each of the active species,

2) hydrogen peroxide adds to species $\mathbf{X}_n$ more rapidly

than this species is deactivated to give O_2 (inequality (27)).

The processing of the results of the separate oxidation of CH, HFB, PFO-1, PFO-2, and PFCH in the context of equations of the form (22) or (28) shows that the whole set of experimental data is adequately described by the scheme suggested, which is indicated by the satisfactory correlation coefficient and the absence of systematic deviations of the calculated curves from the experimental plots (Table 3).*

The intermediate that reacts with the third peroxide molecule

The data of Table 3 and Fig. 1 indicates that in the oxidation of all of the substrates except for PFO-1, the degree of conversion of a substrate is directly proportional to $[H_2O_2]_0$.

From relationships $k_n[H_2O_2] << k''_n[S_n]$ and (27), it follows that $k_n << k''_n[S_n]$, *i.e.*, the nonlinear term on the left-hand side of Eq. (22) that describes the oxidation of substrate $\mathbf{S}_n$, which reacts with the third molecule of H_2O_2, can be neglected. Thus, if H_2O_2 reacts with $\mathbf{X}_n$ and participates in the formation of active intermediate $\mathbf{X}_{n+1}$, the dependence of η_n on $[H_2O_2]_0$ should degenerate into a linear dependence, and the degree of conversion of substrate $\mathbf{S}_n$ reacting with $\mathbf{X}_n$ should be directly proportional to $[H_2O_2]_0$.

A nearly linear dependence of η on $[H_2O_2]_0$ is observed for the separate oxidation of CH and HFB (see Fig. 1). Therefore, H_2O_2 can add either to $\mathbf{X}_1$ or to $\mathbf{X}_2$, which does not contradict the above-stated suggestion that the third hydrogen peroxide molecule adds to complex $\mathbf{X}_2$.

The formation of ozone

The α coefficient for PFO-1 may be set equal to zero (see above), which allows one to calculate the $(k_3+k'_3)/k''_3[S_3]_0$ value, where k'_3 is the rate constant of the formation of ozone and k''_3 is the rate constant of the oxidation of PFO-1, from the parameters of the regression equation (Eq. (28), Table 3), to be 0.48. This value, together with the fact that liberation of ozone is incompletely suppressed in the presence of PFO-1 (Fig. 2), indicate that the rates of the formation of ozone and the oxidation of PFO-1 are comparable.

The parameters obtained using this kinetic model allow one to calculate the yield of ozone in the decomposition of hydrogen peroxide in the V^V/CF_3COOH system.

The accumulation of ozone is described by the following differential equation

$$\frac{d[O_3]}{d\tau} = k'_3[X_3] \quad (29)$$

Table 3. The parameters of Eq. (28)

Substrate $\mathbf{S}_n$	A_{n-1}	$\dfrac{k_n+k'_n}{k''_n}$ /mol L^{-1}	The adequacy variance σ^2 (the number of points)
CH	0.16±0.01	$(9.5\pm1)\cdot10^{-4}$	0.20 (6)
HFB	0.13±0.01	$(6\pm0.5)\cdot10^{-3}$	0.25 (4)
PFO-1	0.51±0.02	$(5.7\pm0.3)\cdot10^{-2}$	0.213 (5)
PFO-2	0.0095±0.002	$(2.4\pm0.2)\cdot10^{-2}$	0.157 (5)

Taking into account relationships (16′) and (17), we may write

$$-\frac{d[O_3]}{d[H_2O_2]} = \frac{k'_3}{k_3+k'_3}\,\frac{A_2k_0K}{k'_0+k_0K}\,. \quad (30)$$

Since $A_3 = A_2[k_3/(k_3+k'_3)]$, expression (30) assumes the form

$$-\frac{d[O_3]}{d[H_2O_2]} = \frac{A_2-A_3}{1+k'_0/k_0K}\,. \quad (31)$$

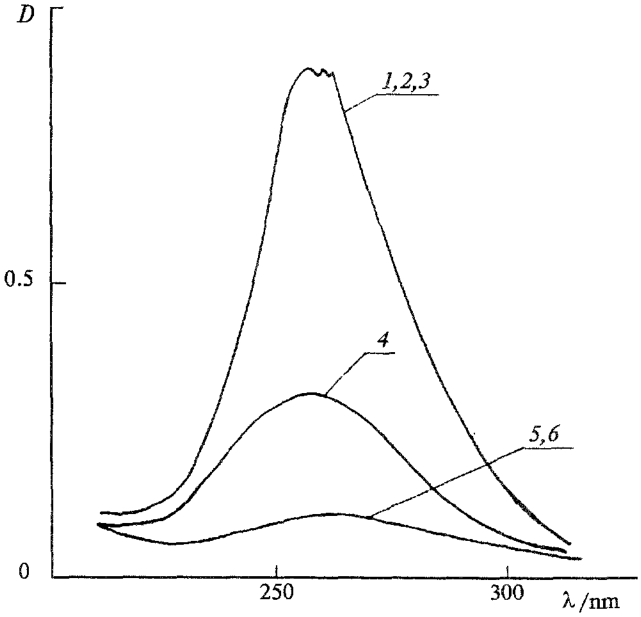


Fig. 2. The UV spectra of gaseous products of the decomposition of H_2O_2 in CF_3COOH in the presence of vanadium(v) compounds: in the absence of substrates (*1*), in the presence of perfluoro-2-octene (*2*) and perfluorocyclohexene (*3*), in the oxidation of perfluoro-1-octene (*4*), in the presence of arenes (*5*) and cyclohexane (*6*).

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* For the processing the experimental data according to Eq. (22), the method of linear regression analysis was used.

Integration and substitution of the magnitudes of the parameters from Table 3 gives for the yield of ozone:

$$\eta_{O_3} = \frac{1/2.26 - 1/11.2}{3} 100~\% = 11.7~\% ,$$

which is close to the experimental value, 10—15 %. The similarity of the calculated and experimental values for η_{O_3} is evidence for the adequacy of the model suggested.

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