New data on the mechanism of hydrogen peroxide decomposition in acetic acid in the presence of vanadyl and cobalt(II) acetylacetonates

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The process of catalytic hydrogen peroxide decomposition in acetic acid in the presence of vanadyl and cobalt(II) acetylacetonates was studied using modern spectroscopic and kinetic techniques. The formation of intermediates during the catalytic decomposition of hydrogen peroxide in the presence of $VO(acac)_2$ was observed using UV—Vis and ESR spectroscopy. The decomposition of H_2O_2 occurs both catalytically and *via* the radical route.

Key words: hydrogen peroxide, catalytic decomposition, acetic acid, intermediates.

Interest in studying the kinetics and mechanism of the homogeneous catalytic decomposition of hydrogen peroxide by d-element compounds is due, on the one hand, to the necessity to specify the role of the catalyst in chemical and biological processes.[1,2] On the other hand, the development of these studies was encouraged by the works on the replacement of molecular oxygen in oxidative processes by hydrogen peroxide. This trend is explained by incombustibility, nontoxicity, environmental purity, convenience in use, and relative cheapness of hydrogen peroxide.[3] Ions of the iron family are traditionally used as catalysts for processes of this type.[1—3]

The works on studying hydrocarbon oxidation with hydrogen peroxide catalyzed by the vanadium compounds are known.[4] It was shown that the adducts $VO^{2+}—H_2O_2$ can be transformed into peroxo particles,[4,5] which rapidly decompose to form active species, such as $^{\bullet}OH$ and $^1O_2$.[5,6] The high activity of the $VO^{2+}—H_2O_2—AcOH$ system in the oxidation of nonreactive hydrocarbons is related to the presence of similar particles.[4,5]

However, the mechanism of the catalyst—hydroperoxide interaction is far from being understood. It is especially important to obtain the experimental confirmation of the existence of highly reactive metal-containing peroxo/oxo particles. The present work is focused on the experimental observation of the formation of such intermediates during the catalytic decomposition of H_2O_2 in acetic acid under the action of $VO(acac)_2$ and $Co(acac)_2$ and to the refinement of the mechanism of this process.

Experimental

Perhydrol (35%, Aldrich) was used to prepare 70% H_2O_2 by a known procedure.[7a] Glacial acetic acid, $VO(acac)_2$, and $Co(acac)_2$ (Merck) were used as received. Benzoquinone was synthesized from hydroquinone and purified by recrystallization.[7b]

The UV—Vis spectra of solutions of $VO(acac)_2$ and $Co(acac)_2$ in AcOH before and after the addition of H_2O_2 were recorded on a Hewlett Packard 8453 spectrometer in the wavelength range from 190 to 1000 nm (1-cm quartz cells).

For ESR recording, H_2O_2 was added to solutions of the catalyst. After 10 and 40 min, the samples were freezed with liquid nitrogen and analyzed on a Bruker ELEXSYS E-500-10/12 spectrometer at 40 K.

The kinetics of hydrogen peroxide was studied in temperature-controlled (35 °C) glass round-bottom flasks (25 mL) with a reflux condenser with rigorous magnetic stirring. The consumption of hydrogen peroxide during the reaction was determined by iodometric titration with sodium thiosulfate (0.01 mol L^{-1}). The rate of hydrogen peroxide decomposition was determined from the slope ratio of the tangent to the kinetic curve of hydrogen peroxide consumption in the initial time period.

Results and Discussion

The addition of hydrogen peroxide to a solution of $VO(acac)_2$ induces a very fast (1—2 s) change in the initial

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green-blue color to yellow. During the next 7—10 min the color of the mixture first turns yellow-brown and then green-blue as the initial solution. These color transitions reflect the UV spectra of a vanadyl solution obtained before and after the addition of H_2O_2 (Fig. 1).

The curves corresponding to the electronic absorption spectra recorded at different time moments after the addition of H_2O_2 meet at one point (see Fig. 1). The time dependences of the absorption intensity (see Fig. 1, inset) show that when H_2O_2 is added the absorbance of the solution at 400 nm increases sharply during next several seconds. Then the absorbance remains constant for the transmission of the light of this wavelength during ~3 min. After this period, the absorption at 400 nm also decreases sharply (5—10 s) simultaneously with the same fast increase in the absorption at 350 nm. The isosbestic point in the spectra in the visible and UV regions and the similar shape of the curves of the time dependences of the absorption for the two characteristic wavelengths (350 and 400 nm) indicate the formation and subsequent decomposition of intermediates of at least two types. According to the literature data,[4] the structure of such species can correspond to the peroxo and oxo complexes of vanadyl. This assumption is confirmed by the changes in the ESR spectra of the initial green-blue solution of $VO(acac)_2$ (Fig. 2, *a*) and the intensive yellow solution (Fig. 2, *b*) formed immediately after the addition of H_2O_2.

The comparison of these spectra suggests that we deal with species of different nature, since the shape of the signal changes, the signal intensity decreases (see Fig. 2, *a*, *b*), the ESR line is splitted, and the widths of peaks in this line increase by ~10 G compared to that in the initial and final solutions. Finally, both the color of the solution

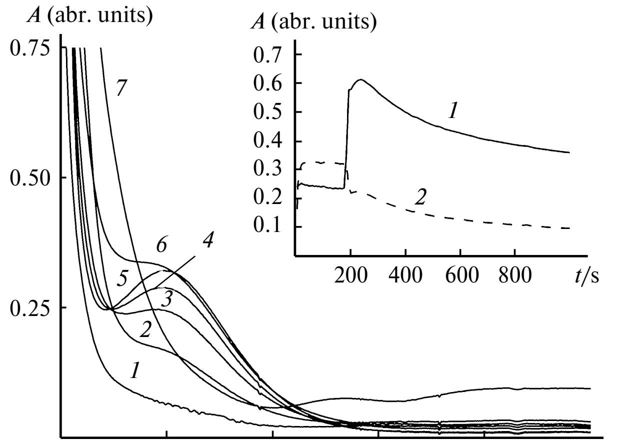

Fig. 1. Electronic absorption spectra of the initial 1 m*M* solution of $VO(acac)_2$ in AcOH at 20 °C (*1*) and the same solution 5 (*2*), 10 (*3*), 15 (*4*), 20 (*5*), 25 (*6*), and 400 s (*7*) after addition of 50 m*M* H_2O_2. Inset: the change in the absorbance at $\lambda = 350$ (*1*) and 400 nm (*2*) in time.

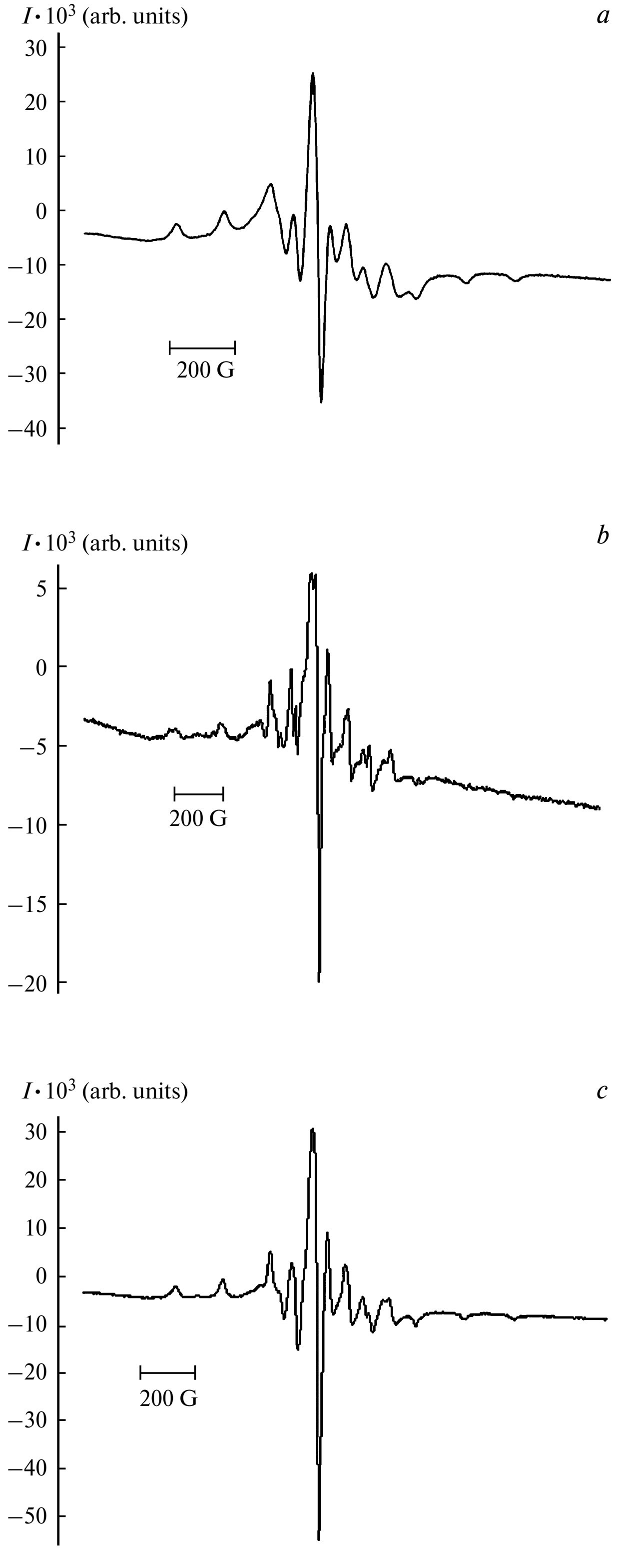

Fig. 2. ESR spectra of the initial 2.5 m*M* solution of $VO(acac)_2$ in AcOH (*a*) ($g = 2.012$, gree-blue color of the mixture) and the same solution 10 ($g = 2.011$, orange-yellow color of the mixture) (*b*) and 40 min ($g = 2.011$, green color of the mixture) after addition of 25 m*M* H_2O_2 (*c*), 40 K.

and the shape and intensity of its electronic spectra (see Fig. 1, curves *1* and *7*) and the ESR spectra (see Fig. 2, *a* and *c*) become close to the initial values (registered before the addition of H_2O_2). Thus, the data presented confirm that cyclic processes can proceed through the formation of the peroxo and oxo complexes of vanadium.[4b,c] The latter are strong oxidants and can be reduced by hydrogen peroxide *via* the Haber—Weiss mechanism.[5b,8]

When H_2O_2 was added to $Co(acac)_2$, an initial pale pink color of the solution remained almost unchanged during several hours. After 20 h the solution gained a dirty green color characteristic of a mixture of cobalt ions in the lowest and highest oxidation states (a similar color was observed for an artificial mixture of a solution of Co^{2+}/Co^{3+} ions in AcOH). The slow change in the color of the solution under the action of H_2O_2 is explained by the weak dissociation of ionic compounds (in our case, Co^{2+} salt) and their good solvation in solvents with low dielectric constant (acetic acid).[9a,b] The spectra in the visible and UV regions were recorded to represent graphically the processes that occur in acetic acid solutions of $Co(acac)_2$ under the action of H_2O_2 (Fig. 3).

When H_2O_2 was added to this solution, the change in time of the intensity of the absorption of the light with the wavelength 520 (Co^{2+}) and 600 nm (Co^{3+}) occurred very slowly (see Fig. 2, inset). No formation of unstable intermediates during the transformation of Co^{2+} into Co^{3+} was detected: the absorption maximum was bathochromically shifted (see Fig. 3) without the intersection of the spectral curves at the isosbestic point. However, it can be assumed that the oxidized and reduced forms of cobalt ions are simultaneously present in the reaction mixture until the reaction is completed. The confirmation can be found in the shape of the spectrum of an artificial mixture of Co^{2+}/Co^{3+} (see Fig. 3, curve *am*).

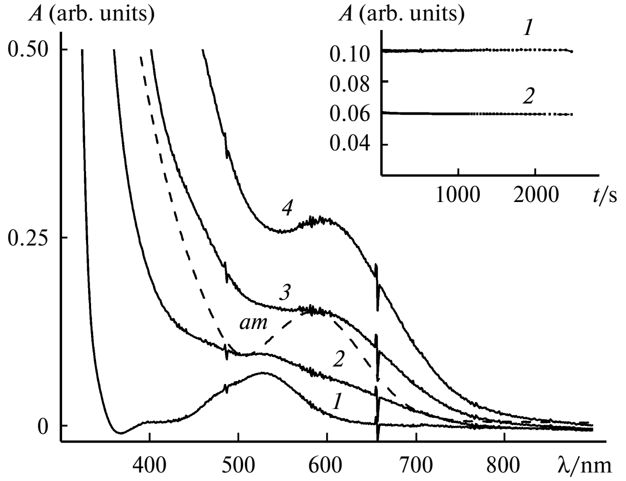

Fig. 3. Electronic absorption spectra of the initial 5 m*M* solution of $Co(acac)_2$ in AcOH at 20 °C (*1*) and the same solution 2 (*2*), 4 (*3*), and 6 h (*4*) after addition of 100 m*M* H_2O_2; *am* is the spectrum of an artificial mixture 4 m*M* $Co(acac)_2$ + 1 m*M* $Co(acac)_3$. Inset: the change in the absorbance at λ = 520 (*1*) and 600 (*2*) nm in time.

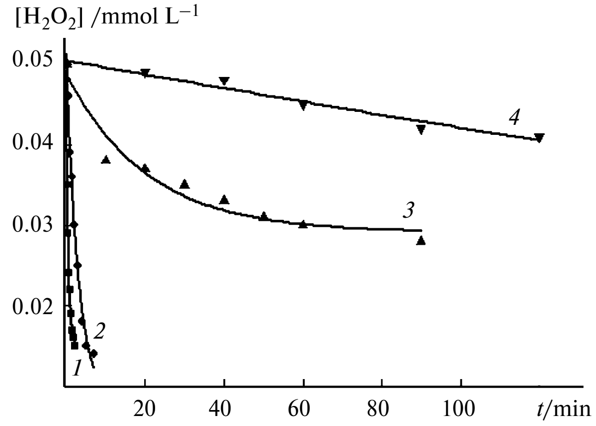

Fig. 4. Kinetics of the noninhibited (*1*, *2*) and inhibited (*3*, *4*) decomposition H_2O_2 in AcOH at 35 °C in the presence of 2.5 m*M* $VO(acac)_2$ (*1*, *3*) and 2.5 m*M* $Co(acac)_2$ (*2*, *4*); $[H_2O_2]_0$ = = 50 mmol L^{-1}, $[Q]_0$ = 10 mmol L^{-1} (Q is quinone).

The results of studying the kinetics of H_2O_2 decomposition in the presence of the catalysts are shown in Fig. 4. It is seen that the rate of hydrogen peroxide decomposition catalyzed by $VO(acac)_2$ is considerably higher than that in the case of $Co(acac)_2$. The kinetic curves of H_2O_2 consumption obey the first-order rate equation (see Fig. 4), and the linear dependences of the rates (*W*) on the concentrations of metal ions (M^{n+}) (Fig. 5) indicate the formation of the catalyst—peroxide complexes. The method of inhibitors was used for the quantitative estimation of the route of H_2O_2 decomposition induced by free radicals. The presence of quinone inhibits the decomposition of H_2O_2 when the both catalysts are used (Figs 6 and 7), which can be a consequence of both the chain termination

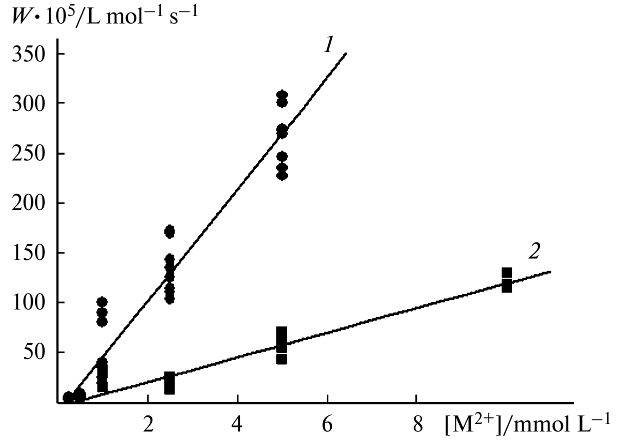

Fig. 5. Rate of H_2O_2 decomposition as a function of the catalyst nature and its concentration: $VO(acac)_2$ (*1*); $Co(acac)_2$ (*2*); $[H_2O_2]_0$ = 50 mmol L^{-1}, AcOH, 35 °C.

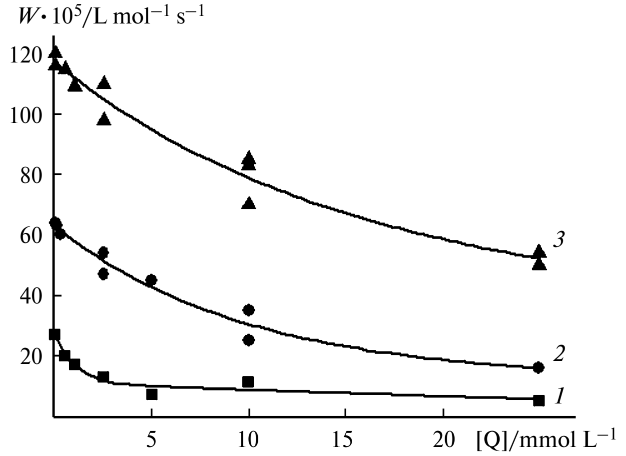

Fig. 6. Rate of H_2O_2 decomposition as a function of the concentration of quinone (Q) and $Co(acac)_2$ in the reaction mixture at $[Co(acac)_2]_0$ = 2.5 (*1*), 5 (*2*) and 10 mmol L^{-1} (*3*); $[H_2O_2]_0$ = = 50 mmol L^{-1}, AcOH, 35 °C.

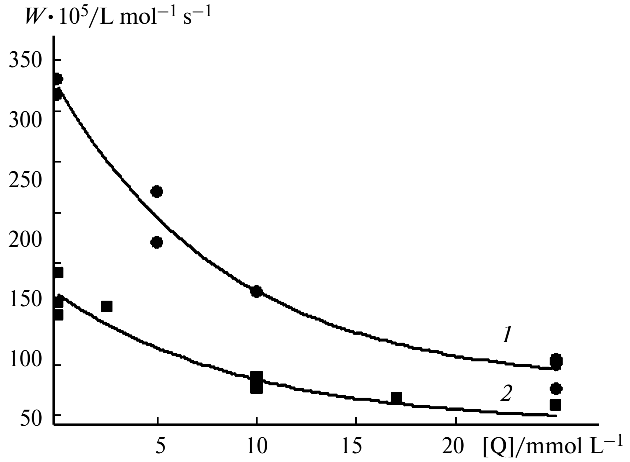

Fig. 7. Rate of H_2O_2 decomposition as a function of the concentration of quinone and $VO(acac)_2$ in the reaction mixture at $[VO(acac)_2]_0$ = 5 (*1*) and 2.5 mmol L^{-1} (*2*); $[H_2O_2]_0$ = = 50 mmol L^{-1}, AcOH, 35 °C.

on the inhibitor molecules and the chelation of the catalyst molecules by the inhibitor.[10] The kinetics of H_2O_2 decomposition in the presence of the inhibitor is described by the first-order rate equation (see Figs 6 and 7), which assumes that one radical and one quinone molecule are involved in the chain termination.

Thus, it can be concluded that under ambient conditions the decomposition of H_2O_2 in the presence of $VO(acac)_2$ proceeds through the formation of intermediate species (presumably the vanadium peroxo and oxo complexes) and includes both the homolytic and induced routes. It is most likely that a lower temperature of experiments is needed for the detection of intermediates in the process with the cobalt catalyst.

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