OXIDATION OF ALLYL ALCOHOL BY HYDROGEN PEROXIDE IN THE PRESENCE OF PHOSPHOTUNGSTIC HETEROPOLY ACID

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The compounds of molybdenum(VI) and tungsten(VI) catalyze the epoxidation of olefins by hydrogen peroxide through the intermediate formation of peroxo complexes [1]. It was suggested [2, 3] that the epoxidation of olefins by organic peroxides in the presence of molybdenum compounds can also take place through the intermediate formation of peroxo complexes of Mo(VI). The heteropoly acid (HPA) $H_3PW_{12}O_{40}$ is not decomposed by hydrogen peroxide complexes [4]. It seemed of interest to study these complexes as epoxidizing agents.

EXPERIMENTAL

Solutions of the peroxide complexes were obtained by the addition of hydrogen peroxide (0.15-1.0 M) to a solution of $H_3PW_{12}O_{40}$ (0.05-0.25 M). We used reagents of chemically pure grade. The reaction with allyl alcohol was carried out 30 min after the solutions had been prepared in a thermostated reactor at 50-90°C in an atmosphere of argon. To study the kinetics of the reaction we took samples of the solution, cooled them rapidly, and decomposed them with 30% sodium hydroxide solution. The glycerol was determined by spectrophotometry from the formation of a complex with $CuCl_2$ [5]. To detect the glycidol the reaction solutions were rapidly cooled and treated three times with ether. The ether extracts were analyzed by the method in [6] with pyridine chloride. tert-Butyl hydroperoxide was synthesized by the method in [7]. The ^{31}P and $^{13}C-\{^1H\}$ NMR spectra were recorded on a Bruker CXP-300 spectrometer at 121.47 and 75.46 MHz, respectively.

DISCUSSION OF RESULTS

During the oxidation of allyl alcohol (AA) with hydrogen peroxide in the presence of W(VI) compounds [8-10] glycidol is formed, and it is hydrolyzed in the acidic medium with the formation of glycerol (I).

$$CH_2{=}CHCH_2OH \xrightarrow[\text{Cat.}]{H_2O_2} CH_2{-}CHCH_2OH \xrightarrow[\text{Cat.}]{H_2O} \underset{OH\ OH\ OH}{CH_2CHCH_2}$$

The peroxo complexes of the phosphotungstic HPA react rapidly with AA at 50-90°C, as can be judged from the decrease in the intensity of their yellow color. To identify the obtained products in the reaction process we recorded the ^{13}C NMR spectra of the solutions at 30°C; [HPA] = 0.15; $[H_2O_2] = 0.8—1.8$, $[C_3H_5OH] = 2.0—6.0$ M, pH 0.7-1.1. Compound (I) is formed as a result of the reaction (δ 71.7 and 62.3 ppm from TMS). The intermediate product (glycidol) does not accumulate in the investigated system; it was not detected by chemical analysis with pyridine chloride and was not observed in the ^{13}C NMR spectra recorded during the reaction. The glycidol is evidently converted rapidly into (I) on account of catalysis by H^+ ions and, possibly, heteropoly anions.

The yield of (I) (Table 1) after the hydrogen peroxide has been completely used (1-2 h, when the solutions had been fully decolorized) amounted to 100-64%, depending on the conditions (according to chemical analysis). The decrease in the yield of (I) calculated on the reacted hydrogen peroxide with increase in the temperature and in the $[H_2O_2]/[HPA]$ ratio is explained by the decomposition of the hydrogen peroxide under the reaction conditions, which is observed at $[H_2O]/[HPA] \geq 4$, as can be judged from measurement of the volume of oxygen released. With $[H_2O_2] = 0.6$, [HPA] = 0.15 M, at 70°C, and at pH_0 1.6-0.7 between 3 and 10% of the hydrogen peroxide is decomposed in 60 min. With large $[H_2O_2]/[HPA]$ ratios, when free

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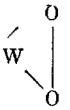
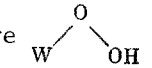
TABLE 1. The Yield of Glycerol as a Function of the Reaction Conditions (calculated on the reacted H_2O_2)

pH_0	T, °C	$[H_2O_2]/[HPA]$	[HPA], M	$[H_2O_2]$, M	$[C_3H_5OH]$, M	Yield of $C_3H_8O_3$, %
0,7	70	4	0,15	0,6	2,0	96
0,7	80	4	0,15	0,6	2,0	100
0,7	90	4	0,15	0,6	2,0	78
0,85	70	4	0,15	0,6	2,0	98
1,0	70	4	0,15	0,6	2,0	89
1,8	70	4	0,15	0,6	2,0	83
0,7	70	6	0,15	0,9	6,0	89
0,75	70	6	0,05	0,3	6,0	84
0,75	70	12	0,05	0,6	6,0	74
0,75	70	24	0,05	1,2	6,0	64

hydrogen peroxide is present in the solution [4], the yield of (I) calculated on the reacted hydrogen peroxide decreases (Table 1) on account of the more intense decomposition of the peroxide not combined into the complex; with $[H_2O_2]$ = 0.6, [HPA] = 0.05 M, at 70°C, and at pH_0 0.95 up to 40% of the hydrogen peroxide decomposes in 60 min.

With hydrogen peroxide at 20°C $H_3PW_{12}O_{40}$ a series of complexes, which contain between one and four peroxide groups and differ in their ^{31}P NMR spectra (δ 14.0; −13.5; −13.0; −12.2 ppm from H_3PO_4 respectively) [4]. As follows from these spectra (Fig. 1a, curve 1 and Fig. 1b, curve 1), when the solutions are heated to 60°C in the absence of AA, the complexes containing less than four O_2^{2-} groups disproportionate into complexes with four O_2^{2-} groups and free HPA (δ −12.2 and −15.0 ppm, respectively). With a large hydrogen peroxide content ($[H_2O_2]/[HPA] > 4$), according to the ^{31}P NMR spectrum, at 20 and 60°C there are complexes with two, three, and four peroxide groups and two complexes of unknown composition with δ −19.5 and −20.8 ppm (Fig. 1c, curve 1), which may be heteropoly anions coordinating more than four O_2^{2-} groups.

Unlike hydrogen peroxide, tert-butyl hydroperoxide (TBHP) does not form complexes with $H_3PW_{12}O_{40}$ under these conditions. With the addition of TBHP (0.6 M) the signal of $H_3PW_{12}O_{40}$ remains unchanged, and new lines do not appear. The absence of any appreciable complex formation between TBHP and the HPA also favors a cyclic structure for the peroxide complexes HPA  formed under analogous conditions, since the complex formation constants of the HPA with hydrogen peroxide and TBHP for the complex with the linear structure  were similar [1]. In the presence of $H_3PW_{12}O_{40}$ TBHP does not oxidize AA to an appreciable degree.

To compare the reactivities of the various peroxide complexes of the HPA we investigated the composition of the solution during the reaction with AA by means of the ^{31}P NMR spectrum. With $[H_2O_2]/[HPA]$ = 1 the signal of the initial solution at 60°C contains signals of $H_3PW_{12}O_{40}$ and a tetraperoxo complex, but the addition of AA does not lead to the appearance of new signals. The intensity of the line for the tetraperoxo complex decreases during the reaction, while that of the $H_3PW_{12}O_{40}$ lines increases, and at the end of the reaction the $H_3PW_{12}O_{40}$ is fully regenerated (Fig. 1a, curves 2 and 3). With $[H_2O_2]/[HPA]$ = 4 at 70°C with the addition of AA the lines of the di- and triperoxo complexes, present in small amounts in the initial solution, and also the weak line with δ −21 ppm disappear first (Fig. 1b, curve 2). At the same time, three new lines appear during the reaction and then disappear (δ 6.1, 2.3, and −0.4 ppm), and they are not observed at any hydrogen peroxide in the absence of AA [4]. At the end of the reaction only the $H_3PW_{12}O_{40}$ line remains (Fig. 1b, curve 3). The reactivity of the peroxo complexes and the formation of the intermediate compounds can be followed most clearly with $[H_2O_2]/[HPA]$ = 12 at 30°C, when they are observed in commensurable concentrations (Fig. 1c). With the addition of AA the line of the triperoxo complex (δ −13.6 ppm), which was present at a significant concentration in the initial solution, disappears first. The lines with δ −19.5 and −20.8 ppm also decrease in intensity, and at the same time the line of $H_3PW_{12}O_{40}$ appears and increases in intensity (Fig. 1c, curves 2-4). At the same time, the same three more intense lines of the intermediate compounds of the peroxo complexes

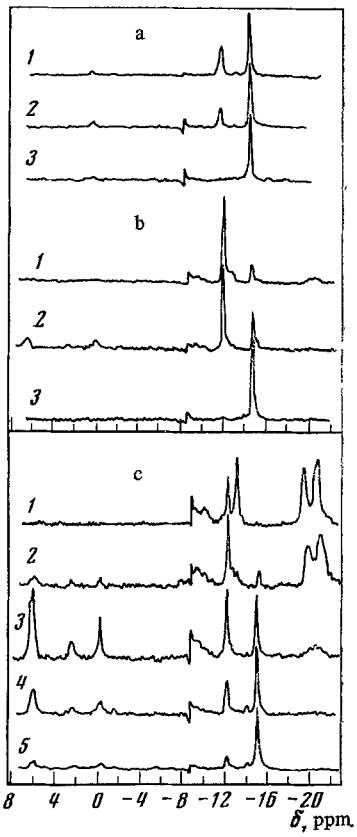


Fig. 1. The ^{31}P NMR spectra of solutions of the HPA, recorded during the reaction. a) [HPA] = 0.15, $[H_2O_2]_0$ = 0.15 M, pH_0 0.7, 60°C: 1) $[C_3H_5OH]$ = 0; 2) $[C_3H_5OH]_0$ = 6.0 M, τ 13 min; 3) the same, 22 min. b) [HPA] = 0.15; $[H_2O_2]_0$ = 0.6 M, pH_0 0.7, 70°C: 1) $[C_3H_5OH]$ = 0; 2) $[C_3H_5OH]_0$ = 6.0 M, τ 7 min; 3) the same, 12 min. c) [HPA] = 0.15, $[H_2O_2]_0$ = 1.8 M, pH_0 0.7, 30°C: 1) $[C_3H_5OH]$ = 0; 2) $[C_3H_5OH]_0$ = 6.0 M, τ 1 min; 3) the same, 6 min; 4) the same, 12 min; 5) the same, 28 min.

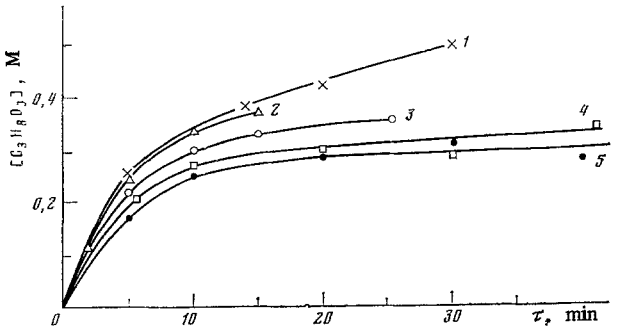


Fig. 2. The dependence of the amount of glycerol formed on time at various initial pH values: 1) 0.70; 2) 0.73; 3) 0.98; 4) 1.1; 5) 1.3. [HPA] = 0.15, $[H_2O_2]_0$ = 0.6, $[C_3H_5OH]$ = 1.5 M, 70°C.

with AA reappear (δ 6.1, 2.3, and −0.4 ppm). At the end of the reaction only the line of $H_3PW_{12}O_{40}$ and the weak lines of the unreacted particles are observed (Fig. 1c, curve 5).

Thus, with all the investigated $[H_2O]/[HPA]$ ratios one complex $H_3PW_{12}O_{40}$ remains in the solution after the end of the reaction, i.e., the initial HPA is fully regenerated. Since the di- and triperoxo complexes disappear first with the addition of alcohol and are not

TABLE 2. The Dependence of the Half-Conversion Time of the Hydrogen Peroxide (to glycerol) on the Concentrations of $H_3PW_{12}O_{40}$ and H_2O_2

$[H_2O_2]_0$	[HPA]	$[H_2O_2]_0/[HPA]$	$\tau_{1/2}$, min	Conditions
M				
0,92	0,23	4	7	$[C_3H_5OH]_0$=7,5 M, pH_0=0,7, 60°
0,60	0,15	4	6,5	
0,40	0,10	4	6	
0,20	0,05	4	5	
0,15	0,15	1	9	$[C_3H_5OH]_0$=7,5 M, pH_0=0,7, 70°
0,30	0,15	2	6	
0,45	0,15	3	4	
0,60	0,15	4	3,5	
0,90	0,15	6	2	
0,30	0,05	6	1,6	
0,60	0,05	12	1,6	

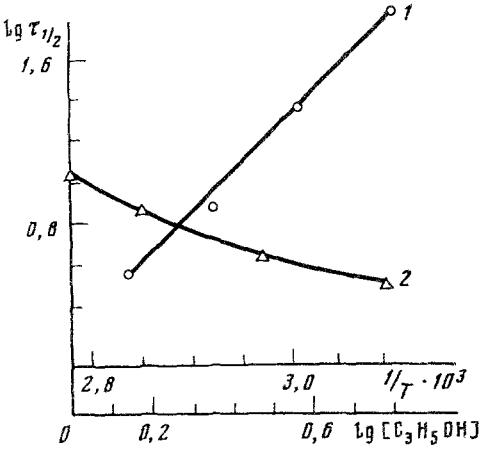


Fig. 3. The dependence of log $\tau_1/_2$ on 1/T (1) and log $[C_3H_5OH]$ (2): 1) $[C_3H_5OH]_0$ = 1.5 M, pH_0 0.7; 2) 70°C, pH_0 0.7. [HPA] = 0.15, $[H_2O_2]_0$ = 0.6 M.

observed during the reaction, it can be concluded that they are more reactive than the tetraperoxo complex, which has enhanced stability. Subsequently the reaction takes place either with the participation of the tetracomplex or through the formation of the more reactive di- and triperoxo complexes, but their concentration during the reaction is small. The complexes with δ −19.5 and −20.8 ppm, formed with large $[H_2O_2]/[HPA]$ ratios, exhibit enhanced activity.

The ^{31}P NMR spectra shed some light on the nature of these complexes. Their formation is evidently not due to the destruction of the HPA, since H_3PO_4 is not observed in the PMR spectra (Fig. 1c, curve 1) and unsaturated heteropoly acids ($PW_{11}O_{39}^{7-}$, $PW_9O_{34}H_6^{3-}$), the chemical shifts of which are always less than −15 ppm, are also not observed [11]. The fact that the HPA is not destroyed in the reaction with hydrogen peroxide under AA is confirmed by the total regeneration of the initial form of $PW_{12}O_{40}^{3-}$ under mild conditions and in a short time, whereas $PW_{12}O_{40}^{3-}$ is distinguished by a very low formation rate and by the rearrangement of the HPA [12]. The addition of the first four O_2^{2-} groups, associated with their entry into the HPA structure, gives rise to a successive change in the chemical shift [4], and δ changes in the direction expected with decrease in the interaction between the coordination sphere of the HPA and the PO_4 tetrahedron [11]. With the entry of a larger number of peroxide groups a further change in this direction could be expected. In fact, with large concentrations of hydrogen peroxide a change in the opposite direction is observed in the chemical shift of the peroxo complexes, and the lines of these complexes are significantly broader (see Fig. 1c). It is possible that the protonated form of the peroxide is coordinated at larger concentrations of hydrogen peroxide, and the broadening of the lines of such complexes is due

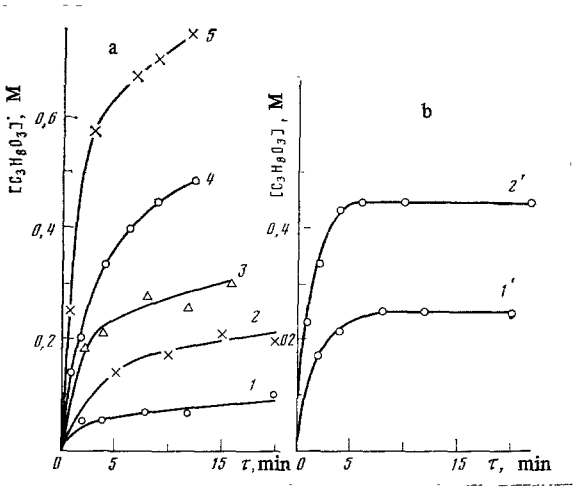
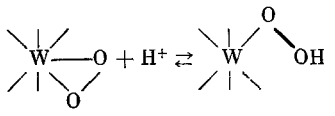


Fig. 4. The dependence of the amount of glycerol formed on time for various concentrations of H_2O_2. a) [HPA] = 0.15 M; 1) $[H_2O_2]_0$ = 0.15 M; 2) the same 0.3; 3) the same, 0.45; 4) the same, 0.6; 5) the same, 0.9. b) [HPA] = 0.15 M: 1) $[H_2O_2]_0$ = 0.3 M; 2) the same, 0.6, $[C_3H_5OH]_0$ = 6.0 M, pH_0 0.7, 70°C.

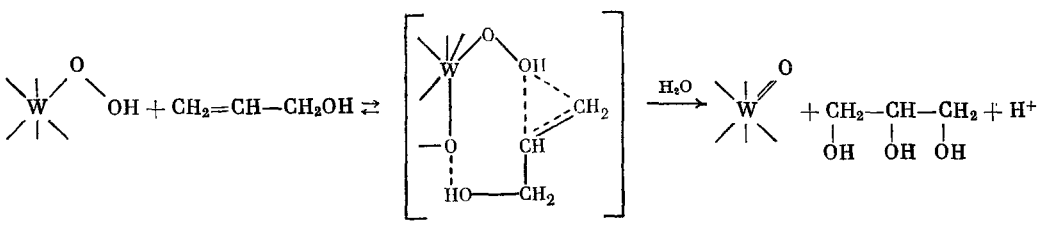
to their lability. At the present time the structure of the complexes observed in the ^{31}P NMR spectra is being investigated.

The kinetic relationships governing the reaction were studied from the accumulation of (I) with $[H_2O_2]/[HPA]$= 4, when the tetraperoxo complex is formed preferentially. The reaction rate decreases with increase in the initial pH values of the solution (Fig. 2). Under pseudozero-order conditions in AA (with $[C_3H_5OH]$ = 6.0 M) the half-conversion time of the hydrogen peroxide is practically independent of the concentration of the peroxo complex (Table 2), and the reaction can be described by a first-order equation: $W = k_{eff}[HPA(O_2)_4]$, where $k_{eff} \sim 1/\tau_{1/2}$. The temperature coefficient of the reaction in the range of 50-80°C, calculated from the dependence of $\log \tau_{1/2}$ on 1/T, is 22 kcal/mole (Fig. 3, curve 1). The reaction order in the concentration of AA, determined in the range of $[C_3H_5OH]$ = 1.0-6.0 M, is less than 1 and decreases with increase in the concentration of the alcohol (Fig. 3, curve 2). From Fig. 4 and Table 2 it is seen that the half-conversion time of the hydrogen peroxide decreases with increase in the $[H_2O_2]/[HPA]$ ratio from 1 to 12, indicating the formation of more active complexes in the system.

On the basis of the obtained results the mechanism of the oxidation of AA by the peroxide complexes of the HPA can be represented by the following scheme:



(1)



(2)

The acceleration of the reaction with increase in the acidity of the solution in the range of pH 1.3-0.7, if the peroxo complexes of the HPA $H_3PW_{12}O_{40}$ are not decomposed [4], shows that the peroxo group is protonated reversibly at the first stage of the reaction. At the next stage a triple complex of HPA with the peroxide and AA is formed. This stage can be an equilibrium stage, since the order with respect to the concentration of AA is less than unity.

It can be supposed that the signals in the ^{31}P NMR spectra observed during the reaction (δ 6.1, 2.3, and −0.4 ppm) belong to intermediate complexes containing HPA, peroxide groups, and AA. The formation of the complex of AA with the peroxo complexes of the HPA can be promoted by coordination of the OH group of the alcohol at the W atoms in the structure of the HPA. This interaction facilitates electrophilic transfer of the oxygen of the peroxo group to the olefin in the controlling stage of the reaction.

CONCLUSIONS

1. Peroxo complexes of phosphotungstic heteroply acid catalyze the epoxidation of allyl alcohol.

2. The composition of the solution during the process of the reaction is studied by the method of ^{13}C and ^{31}P NMR, the reaction kinetics is studied according to the accumulation of glycerol, and a scheme of the mechanism is suggested.

LITERATURE CITED

1. Fuloio Di Furia and Giorgio Modena, Pure Appl. Chem., 54, 1853 (1982).
2. V. M. Belousov, K. B. Yatsimirskii, A. P. Filippov, and S. B. Grinenko, Kinet. Katal., 18, 554 (1977).
3. G. A. Konishevskaya, A. P. Filippov, Yu. Sobchak, Yu. Yu. Zyulkovskii, K. B. Yatsimirskii, and V. M. Belousov, Kinet. Katal., 21, 933 (1980).
4. L. I. Kuznetsova, R. I. Maksimovskaya, M. A. Fedotova, and K. I. Matveev, Izv. Akad. Nauk SSSR, Ser. Khim., 1983, 733.
5. S. H. Bertram and R. Rutgers, Rec. Trav. Chim., 57, 681 (1938).
6. J. Mitchel, I. M. Kolthof, E. S. Proskauer, and A. Weissberger, Organic Analysis, Vol. 1, Interscience (1953), p. 136.
7. N. A. Micholas, A. Milas, and D. Sugenor, J. Am. Chem. Soc., 68, 205 (1946).
8. P. G. Sergeev and L. M. Bukreeva, Zh. Obshch. Khim., 28, 101 (1958).
9. Z. Raciszewski, J. Am. Chem. Soc., 82, 1267 (1960).
10. T. Mazonski, D. Gasztych, and W. Zielinski, Przem. Chem., 41, 251 (1962).
11. R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, and M. Fournier, Inorg. Chem., 16, 2916 (1977).
12. M. A. Fedotov, R. I. Maksimovskaya, D. U. Begalieva, and A. K. Il'yasova, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 1477.

DEPENDENCE OF THE MULTIDIPOLE EFFECT ON THE ACTIVITY OF THE ATTACKING PARTICLE IN RADICAL ADDITION REACTIONS

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In our previous studies on the multidipole effect in radical reactions of the π-bond of polyol esters of methacrylic and acrylic acids, it has been mentioned that the lower the activity of the particle attacking the double bond of a polyfunctional compound [1-3], the greater the magnitude of the effect. For example, the rate constants of the addition of cumene peroxy radicals to the π-bond of methyl acrylate and pentaerythritol tetramethacrylate calculated on one double bond are equal to 1.8 and 0.8 liter/mole·sec at 323°K, respectively [1]. At the same time, on passing from the monoester to tetraester, the rate constant of the reaction of the π-bond with oxygen decreases by an order of magnitude [2]. An analogous picture was also observed for the acrylic esters: Cumeme hydroperoxide reacts more slowly with pentaerythritol tetraacrylate by almost an order of magnitude as compared with butyl acrylate [3], while in the reaction of cumene peroxy radical with the double bond only an insignificant decrease of the rate constant was noted (0.5 and 0.3 liter/mole·sec at 323°K for the mono- and tetraester, respectively [1]).

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