TRANSFORMATIONS OF FUROYL PEROXIDE AND HYDROPEROXIDE IN THE PRESENCE OF WATER AND HYDROGEN PEROXIDE

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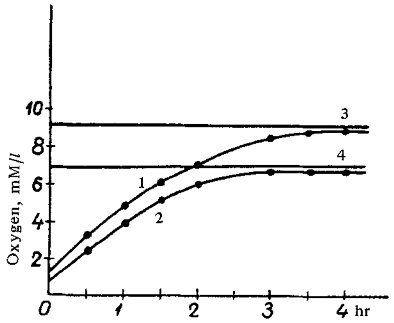
In the presence of water, furoyl peroxide and hydroperoxide are hydrolyzed to pyromucic acid and hydrogen peroxide, between which there is a partial reaction.

The oxidation of furan compounds forms an accessible source for the production of a large number of valuable chemical products. Extremely promising in this respect is the use of hydrogen peroxide as oxidizing agent.



Accumulation of H_2O_2 in the decomposition in 96% ethanol of: 1) furoyl hydroperoxide; 2) furoyl peroxide; 3 and 4) total content of organic peroxides and H_2O_2 (iodometric method).

According to current ideas, oxidation with molecular oxygen has the nature of a chain process taking place through the formation of peroxide compounds [1–4]. There is no information relating to peroxides as intermediates in the oxidation of furfural with H_2O_2 [5–7].

In the oxidation of furfural with H_2O_2, we detected peroxide compounds of undetermined nature. In view of this, information on the behavior of furoyl peroxide and hydroperoxide, the formation of which is possible in the oxidation of furfural [8, 9], is of interest.

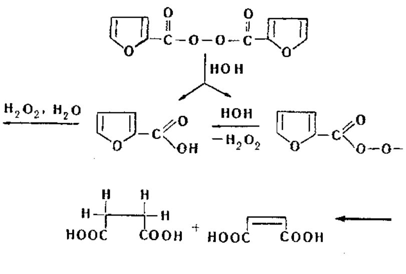
Since, in hydrogen peroxide oxidation, the reaction takes place in an aqueous medium, the conversions of furoyl peroxide (FP) and furoyl hydroperoxide (FHP) were considered in water and, to elucidate the influence of the water, in absolute ethanol. During the experiments, the accumulation of H_2O_2 and the consumption of FP and FHP were followed and the UV spectra of the reaction products were recorded at various stages of the reaction. The final products, mixtures of acids, were subjected to chromatography.

It was found that in water both peroxides at a concentration of 6.77×10^{-4} mole/l are very rapidly hydrolyzed to pyromucic acid; in ethanol containing 2.45 mole/l of water the hydrolysis takes place more slowly but again yields pyromucic acid. This was observed by the displacement of the absorption in the UV spectra of the products of the conversion of the peroxides. In the UV spectra of solutions of pure FP and FHP in absolute ethanol the absorption maximum is at λ 262 nm (ε = 31 800) for FP and at λ 240 nm (ε = 10 000) for FHP. The maximum of the absorption curve of pyromucic acid in ethanol is at 243 nm [10]. In our study of the transformations of FP and FHP both in water and in ethanol a shift in λ_{max} to 243 nm was observed. In water the complete shift of the maximum took place instantaneously, and in 96% ethanol it took 24 hr. Ultraviolet irradiation of solutions of FP and FHP in 96% ethanol accelerated the hydrolysis process (the shift of the maximum took place completely in 3 hr).

The content of organic peroxides was determined iodometrically and the content of H_2O_2 cerimetrically [11]. It was found that hydrogen peroxide is formed in the hydrolysis of FP and FHP. The increase in the amount of H_2O_2 takes place up to a definite limit, after which its amount remains constant, which corresponds to the complete decomposition of the organic peroxide undergoing analysis (figure). The chromatographic analysis of the final products of the conversion of FP and FHP showed, in addition to pyromucic acid, the presence of very small amounts of fumaric, maleic, and succinic acids. We ascribe their formation to the partial oxidation of the pyromucic acid by the H_2O_2 liberated. As is well known, this process is quite possible [12].

To confirm these conclusions, we carried out experiments with solutions of FP and FHP in ethanol (33.9×10^{-6} and 13×10^{-6} M, respectively) with the addition of 0.5 ml of 27% H_2O_2 (4.4×10^{-3} mole). It was established by chromatography and spectroscopy that under these conditions the initial peroxides were converted into mixtures of pyromucic, dibasic, and volatile acids.

On the basis of these results, the scheme of the transformations of furoyl peroxide and hydroperoxide in the presence of water and H_2O_2 can be represented in the following way:



EXPERIMENTAL

The experiments were carried out with furoyl peroxide and hydroperoxide synthesized by known methods [13]. The purity of the samples, checked by iodometry, was 99% and the mp of the FP was 85° C (decomp.) and that of the FHP 59° C (decomp.). According to the literature [13], mp of FP 86° C, mp of FHP 60° C.

The determination of the hydrogen peroxide in the presence of the organic peroxides was carried out cerimetically by a method that we have developed. The sum of the organic peroxides and H_2O_2 was determined iodometrically. The spectra of the conversion products of the FP and FHP at various stages of the reaction were recorded on an SF-4 instrument. The mixtures of acids in the final products were separated by descending paper chromatography [14] and column adsorption chromatography on silica gel [15].

REFERENCES

1. N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity [in Russian], Izd-vo AN SSSR, Moscow, p. 614, 1958.
2. K. I. Ivanov, Intermediate Products and Intermediate Reactions in the Autoxidation of Hydrocarbons [in Russian], Gostoptekhizdat, Moscow-Leningrad, pp. 43, 51, 493, 1949.
3. A. V. Karyakin, V. A. Nikitin, and A. N. Sidorov, ZhFKH, 29, 1624, 1955.
4. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, Chain Reactions of the Oxidation of Hydrocarbons in the Liquid Phase [in Russian], Nauka, Moscow, 1965.
5. A. P. Salchinkin and A. P. Arestenko, ZhPKh, 36, 2290, 1963.
6. M. P. Pyatintskii and L. B. Lapkova, ZhPKh, 36, 678, 1963.
7. F, Kallay, Acta Chim. Acad. Sci. Hung., 10, 157, 1956.
8. Yu. I. Khol'kin, Candidate's thesis [in Russian], Krasnoyarsk, 1961.
9. V. G. Kul'nevich and T. E. Goldovskaya, Izv. VUZ, Pishchev, tekhnol., 6, 74, 1962.
10. R. Andrisano and G. Paperalardo, Gazz. Chim. Ital., 83, 340, 1953.
11. M. M. Buzlanova, V. F. Stepanovskaya, and V. L. Antonovskii, ZhAKh, 20, 271, 1965.
12. L. B. Lapkova, Candidate's thesis [in Russian], Krasnodar 1963.
13. N. A. Milas and A. McAllvy, J. Am. Chem. Soc., 56, 1219, 1934.
14. K. M. Ol'shanova, M. A. Potapova, V. D. Kopylova, and N. M. Morozova, Handbook on Ion-exchange, Partition, and Sedimentation Chromatography [in Russian], Khimiya, Moscow, pp. 126, 152, 1965.
15. M. P. Pyatnitskii and L. I. Kiprach, Uch. zap. Krasnodarsk. gos. ped. inst., 24, 258, 1959.

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LETTERS TO THE EDITOR

REACTION OF sym-OCTAHYDROTHIOXANTHYLIUM PERCHLORATES WITH A GRIGNARD REAGENT

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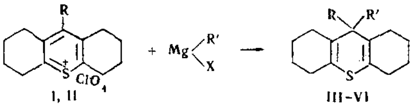
We have established for the first time that sym-octahydrothioxanthylium perchlorate and its 9-alkyl derivatives smoothly react with a Grignard reagent forming 9-alkyl(aralkyl)-sym-octahydrothioxanthenes with yields of 80–85%;



I, II

I R = H;

II R = CH_3

X = Cl, Br

III–VI

III R = H, R′ = CH_3;

IV R = H, R′ = C_2H_5;

V R = H, R′ = $CH_2C_6H_5$;

VI R = CH_3, R′ = $CH_2C_6H_5$

This reaction is of scientific and practical interest, since it opens up the possibility of the synthesis of hydrothioxanthenes of new homologous series. The structures of III and IV are confirmed by the absence of a depression in mixtures of them with authentic 9-methyl- and 9-ethyl-sym-octahydrothioxanthenes, which have been obtained by independent syntheses. [1]. The structures of V and VI are confirmed by the results of elementary and spectral analyses and also by the analysis of their sulfones.

9-Ethyl-sym-octahydrothioxanthene (IV).– colorless crystals mp 23°–25° C (from a mixture of ethanol and ether, 2 : 1), yield 88%. Main frequencies in the IR spectrum: 675, 768, 820, 845, 1008, 1075, 1342, 1350 (shoulder), 1380, 1455, 1650, 1675 and a strong broad band at 2830–2980 with peaks at 2840, 2860, 2935, and 2970 (shoulder) cm^{-1} (the UV spectra were taken on a UR-10 instrument in paraffin oil). Sulfone—mp 126°–127° C (from petroleum ether). Found, %: C 67.70, 67.63; H 8.13, 8.29; S 11.70. Calculated for $C_{15}H_{22}SO_2$, %: C 67.67; H 8.27; S 12.03.

9-Benzyl-sym-octahydrothioxanthene (V). Yield 95.2%. Colorless crystals, mp 108°–110° C (from ethanol). Found, %: C 81.52, 81.46; H 7.80, 8.19; S 10.38, 10.74. Calculated for $C_{20}H_{24}S$, %: C 81.11; H 8.11; S 10.81. Main frequencies in the IR spectrum; 611, 671, 695, 747, 955, 1002, 1070, 1132, 1240, 1261, 1271, 1305, 1317, 1331, 1345, 1375, 1440, 1453, 1492, 1548, 1581, 1600, 1632, 1654 cm^{-1}.