Postirradiation changes in the solutions of acetylacetone

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On the irradiation of aqueous solutions of acetylacetone the reactions of acetylacetone with the products of the radiolysis of water take place and give carboxylic acids. The proposed mechanism assumes the formation of an unstable cyclic peroxide and its successive decomposition into carboxylic acids. In the irradiated methanolic solutions of acetylacetone such reactions do not take place because the products of the radiolysis of methanol do not form peroxide with acetylacetone.

The study of the chemical changes produced by the effect of ionizing radiation in the solutions of acetylacetone enables us to find the pathway of the radiolysis of this important chelating agent. The findings obtained in the radiolysis of reagent solutions may be used for the interpretation of the radiation reactions of chelates which give valuable information on the reactivity of complex ions in solutions [1]. *Rao et al.* [2] studied the radiation chemistry of tris(acetylacetonato)cobalt(III) chelate. They found that besides the main products of the radiolysis of aqueous solutions free acetylacetone and Co(II) formed, a part of which was bound in the form of bis(acetylacetonato)cobalt(II) chelate. *Koga* and *Hara* [3] investigated the oxidation of acetylacetone in the presence of Co(II). The radiolysis of pure acetylacetone or its solutions has not been investigated up to now.

The changes typical for the irradiated aqueous solutions of acetylacetone take place several days after irradiation. These changes have not been observed in the irradiated methanolic solutions of acetylacetone. The aim of this study is to explain the course of some reactions for which these postirradiation effects are responsible.

Experimental

Water used for the preparation of the aqueous solutions of acetylacetone was purified by two-step distillation in a quarz apparatus. Anal. grade methanol was distilled before use. The solvents were deprived of air by bubbling through nitrogen. The aqueous and methanolic 10^{-3} M, 5×10^{-4} M, 10^{-4} M, and 5×10^{-5} M solutions of acetylacetone (product of UCB, Belgium) were prepared. During irradiation and in the period after irradiation till the measurements the samples were kept in a nitrogen atmosphere. They were irradiated with gamma ^{60}Co radiation with the dose of 50 krad at the dosage rate 300 rad s^{-1}. The changes produced by irradiation were investigated spectrophotometrically on a recording Specord UV-VIS (GDR) spectrophotometer. Simultaneously with irradiated samples the changes were also followed in non-irradiated solutions and in an aqueous solution of acetylacetone containing an admixture of H_2O_2 (10^{-3} M acetylacetone and 10^{-1} M-H_2O_2 in water).

Results and discussion

Immediately after irradiation the u.v. spectra of the irradiated and non-irradiated solutions of acetylacetone showed some differences in absorbance at 273 nm. The absorbance of aqueous solution decreased more appreciably than that of methanolic solution (Fig. 1). In the course of four days after irradiation the absorbance of irradiated aqueous solution of acetylacetone increased in the region between 200 and 210 nm. This change was most marked in the sample with 10^{-3} M concentration of acetylacetone (Fig. 2). No increase in absorbance in the region 200—210 nm was observed in methanolic solutions. In neither of solutions the absorbance at 273 nm changed with time.

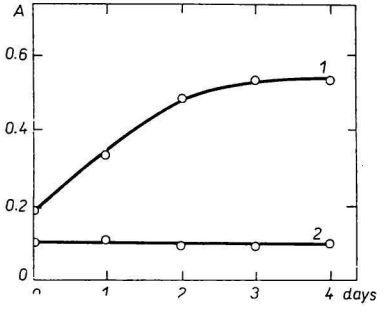


Fig. 1. Change in the absorbance of u.v. spectrum of the solution of acetylacetone (10^{-3} M) for $\lambda = 205$ nm after irradiation.
1. aqueous solution; *2.* methanolic solution.

No changes in the u.v. spectra of the non-irradiated solutions of acetylacetone appeared during 5 days. In the spectrum of the non-irradiated aqueous solution of acetylacetone containing an admixture of H_2O_2 the change of absorbance at 200—210 and 273 nm showed a trend resembling that of irradiated aqueous solution.

The region of increased absorbance is characteristic of the absorbance of a carboxylic group. It may be assumed that the increase in absorbance is due to the concentration increase of carboxylic acids in the irradiated aqueous solutions. This assumption is also supported by the increased acidity of irradiated solutions. The pH of non-irradiated solution was 6.3 and four days after irradiation it made 4.62. The fact that carboxylic

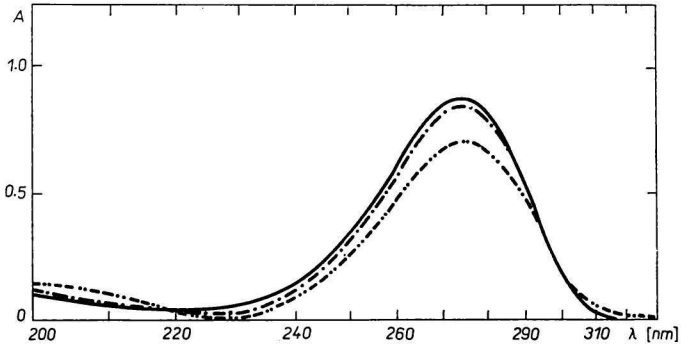
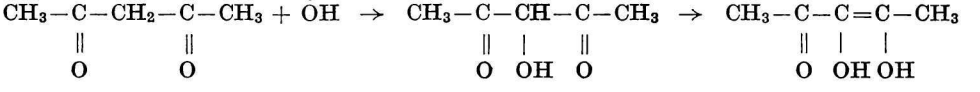


Fig. 2. Ultraviolet spectra of the solutions of acetylacetone (5×10^{-4} M).
———— aqueous solution before irradiation; —..—..— aqueous solution after irradiation ($D = 50$ krad); —.—.— methanolic solution after irradiation ($D = 50$ krad).

acids raise the absorbance of investigated solutions was corroborated by the addition of acetic acid into the solution measured which resulted in a considerable increase in the absorbance in the region of 205—210 nm.

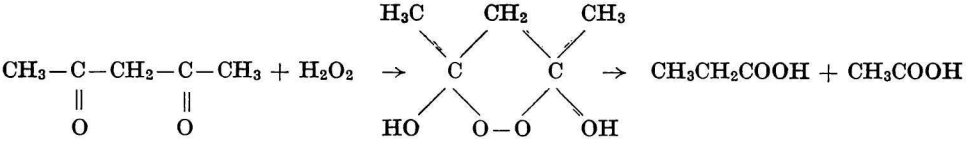
The molar extinction coefficients of carboxylic acids in this region of spectrum vary from 50 to 70 mol^{-1} cm^{-1}. From the found difference in absorbances and averaged molar extinction coefficient the yield of acids in irradiated solutions was calculated. Thus the value G (R—COOH) = 15 molecules/100 eV was found. The yield of the radiolytic decomposition of acetylacetone cannot be calculated on the basis of the change in absorbance at 273 nm. There are several carbonyl compounds that absorb in the region of 270—280 nm; this fact manifests itself by a lower apparent yield of the radiolytic decomposition of acetylacetone. Thus a smaller decrease in the absorbance of the methanolic solution of acetylacetone at 273 nm (Fig. 1) as compared with its aqueous solution may be explained since the radiolysis of methanol gives formaldehyde which absorbs in that region.

In the aqueous solution acetylacetone reacts with $\dot{O}H$ radicals which are formed in the radiolysis of water. Their substitution in acetylacetone affords hydroxyacetylacetone or its tautomeric form diacetylcarbinol. The region of maximum absorbance of these compounds is at 278—280 nm.



Such mechanism of ligand destruction in an aqueous solution of Co(III) chelate is also assumed by *Rao et al.* [2].

Carboxylic acids are formed in aqueous solutions of acetylacetone by the reaction with hydrogen peroxide which is also a radiolytic product of water. Hydrogen peroxide forms in acid medium with acetylacetone a cyclic peroxide which is unstable and decomposes into carboxylic acids.



Such mechanism was established by *Payne* [4] for the reaction of H_2O_2 with dimethylacetylacetone.

In our experiments we examined the effect of hydrogen peroxide on the aqueous solution of acetylacetone and it was found that the presence of H_2O_2 had a similar effect as the irradiation of solution.

No peroxides which could react with acetylacetone in a similar manner are produced by the radiolysis in methanolic solutions and therefore no carboxylic acids have been found in these solutions.

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