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Abstract

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ON THE ACTION OF GAMMA RADIATION ON AQUEOUS SOLUTIONS OF THIOPHENE

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At present, reactions involving the interaction of organic substances with the products of water radiolysis are attracting very great interest. However, the number of systems investigated is still very limited. In particular, no one has studied the possibility of radiolytic oxidation, in the presence of water, of heterocyclic compounds, for example, of the thiophene series. These processes are of great interest because oxy derivatives of the thiophene series cannot be obtained by the usual oxidation method. Therefore, their direct synthesis by a radiation-chemical route has practical prospects.

The authors of the present communication studied the action of radiation on solutions of thiophene in water saturated with oxygen, in order to determine the direction of the oxidation process and the possibility of formation of oxythiophene—thienol. In doing so, the influence on this process of a number of factors was studied: the concentration of dissolved products, the pH of the medium, and some others.

For irradiation, a source equivalent to 50 g Ra was used. The dose rate was varied from 0.5 to $1.1 \cdot 10^{15}$ eV/ml • sec. Irradiation was carried out in glass ampoules. When working with elevated oxygen pressure, steel ampoules having a glass insert were used. A mixture of thiophene with water was prepared by mixing 0.1 ml of thiophene with 100 ml of water saturated with oxygen. The concentration of thiophene in such a mixture corresponds to $1.265 \cdot 10^{-2}$ M/l. Solutions containing thiophene at lower concentration were prepared by dilution.

For identification of the products formed, colorimetric and spectrophotometric methods were used. The colorimetric method is based on the coupling of thienol, whose formation was assumed, with *p*-nitroaniline or with sulfanilic acid. Both couplings showed the presence in the irradiated solutions of a compound giving with these substances a coloration characteristic of phenolic compounds ($\lambda_{\max} =$ 520 mμ) (^{1}). The spectrophotometric method used in the work is based on recording absorption spectra in the ultraviolet region. For this purpose an SF-4 spectrophotometer was used.

Figure 1 shows the absorption spectra of the initial (1) and irradiated (2) aqueous solution of thiophene. It is seen that in the irradiated solution there appears a product absorbing ultraviolet rays of longer wavelength than thiophene. It should be noted here that the position of the absorption maximum depends on the pH of the irradiated solution and shifts from 256 mμ in acidic solutions to 268 mμ in alkaline solutions. Also shown there is the dependence of the absorption of α-oxythiophene in water on the wavelength of light, Fig. 1, 3, constructed on the basis of literature data (^{2}). Obviously, it makes sense to compare only the right-hand parts of the spectrum (curves 2 and 3), since at wavelengths below 258 mμ the remaining thiophene in the irradiated solution absorbs.

Comparison and qualitative reactions give grounds to consider that one of the main products of oxidation of thiophene is thienol. The obtaining of more

the blurred peak upon irradiation can be explained by the existence of thienol in two tautomeric forms.

Figure 2 gives the dependences of the optical density of the irradiated solution at 260 mμ on the irradiation dose for solutions with different initial concentrations of thiophene. As the dose increases, the optical density of the solution increases; however, the radiation-chemical yield of thienol formation falls rather rapidly. Experiments carried out at increased oxygen pressure (up to 25 atm) showed that the decrease in yield is not connected with depletion of dissolved oxygen (see Fig. 2, 1), but is apparently connected with reactions of transformation of the product formed, proceeding at an appreciable rate in acidified solutions. When experiments are carried out in a neutral medium, the yield begins to fall at considerably higher doses. In this case the oxygen pressure significantly increases the linear portion.

Fig. 1. Absorption spectra of aqueous thiophene solutions. 1 —before irradiation, 2 —after irradiation, 3 —dependence of the extinction coefficient of α-oxythiophene on wavelength

Fig. 2. Increase in the optical density of a thiophene solution in 0.8 N H_2SO_4 at $\lambda = 260$ mμ as a function of irradiation dose: 1, filled points $-1.2 \cdot 10^{-2} M$ thiophene; open points —the same under an oxygen pressure of 25 atm. 2 — $1.26 \cdot 10^{-4} M$; 3 $-0.52 \cdot 10^{-5} M$ thiophene solution in 0.8 N H_2SO_4

Fig. 3. Dependence of the yield of thienol on the concentration of thiophene in the irradiated solution, 0.8 N H_2SO_4. $1'$ $-E$ (mol/cm) $= 2.83 \cdot 10^3$; $2'$ — superposition of 1 with the theoretical curve (shown by a dashed line)

It has been established that the initial value of the yield of thienol formation depends on the initial concentration of thiophene in the solution (see, for example, curves 2 and 3 in Fig. 2 and curve 1 in Fig. 3).

Fig. 4. Dependence of the oxidation yield of thiophene on the pH of the irradiated solution

Figure 1: Fig. 4. Dependence of the oxidation yield of thiophene on the pH of the irradiated solution

For calculating the radiation-chemical yields* of thiophene oxidation, the molar extinction of α-oxythiophene was used. As is seen from Fig. 3, curve 1, constructed as a result of such an estimate, has the typical form of the concentration dependence of the yield of transformation of a dissolved substance (^{3}) (see the dashed line in Fig. 3), but is located higher. On introducing the corresponding correction, the curves are readily superposed. For this purpose it was sufficient to reduce all values of the thienol yields obtained by the first method by a factor of 1.55; such a check of the results obtained gives grounds to consider that the yield of thienol formation was estimated fairly accurately, with only a slight overestimate relative to the true value. On considering curves 2 and 3 (Fig. 2), it is easy to calculate that the percentage conversion of thiophene to hydroxythiophene is substantial: it corresponds to 50% by the first method of estimation and 30% by the second.

With regard to the mechanism of thiophene oxidation in its aqueous solution, it may be assumed that thienol, like the product of benzene oxidation (^{4,5}), is formed through the interaction of thiophene with hydroxyl radicals according to the overall reaction:

$$\text{thiophene} + 2\text{OH} \rightsquigarrow \text{hydroxythiophene} + H_2O.$$

Fig. 4. Dependence of the oxidation yield of thiophene on the pH of the irradiated solution

The dependence we obtained for the magnitude of the oxidation yield of thiophene on the pH of the medium (see Fig. 4) corresponds to the same dependence for benzene (^{6}), which confirms the similarity of the oxidation mechanisms in both cases. The nature of the effect of competing acceptors of OH radicals also argues in favor of this mechanism. It was established, for example, that introducing glycerin into a thiophene solution at a concentration of 0.5 N leads to the complete cessation of thienol formation.

The figures for the yields, obtained with the aid of the above-described methods for estimating the concentration of the thienol formed, reach, under favorable conditions, 8 equiv/100 eV. They evidently correspond to a high degree of participation of radiolyzed water molecules in oxidation processes by a chain mechanism.

* The yield was calculated from the initial section of the curve of thienol accumulation as a function of dose (in the range from 1-10000 r).

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Note: Figure translations are in progress. See original paper for figures.