

A STUDY OF RADICALS ARISING IN THE LOW-TEMPERATURE RADIOLYSIS OF THIOPHENE AND SOME OF ITS DERIVATIVES

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EPR was used to investigate the radicals formed by radiolysis of furan, thiophene, and some of their substitution products having the general formula C_4H_3RS , where $R = Cl, Br, COOH, C(CH_3)_3$, and of di-*tert*-butylthiophene. By analyzing the EPR spectra it is shown that radicals formed by radiolysis of furan, thiophene, their alkyl substitution products, and 2-thiophene carboxylic acid arise in primary radiation-chemical events with splitting of the C-H bond in both ring and side chain. Characteristic of the radiolysis of these compounds is formation of secondary radicals by addition of hydrogen atoms at the double bond of the heteroaromatic ring. The values of the hyperfine splittings in the spectra of the secondary radicals are, for protons of methylene group 32 e [positions 2(5)] or 40 e [positions 3(4)], and 13 e for protons of the thiophene ring. In radiolysis of 2-chlorothiophene and 3-bromothiophene the main products are radicals with the unpaired electron localized on the sulfur atom.

It is of great interest to ascertain the nature of the radicals formed by radiolysis of heteroaromatic sulfur-containing compounds. Up to the present only a small amount of research [1-4] has been done on the subject. In the papers cited it was shown that, as in the radiolysis of aromatic hydrocarbons [5], the main secondary reaction is addition of a hydrogen atom to the heterocyclic ring with opening of a double bond. The present work aims to use EPR to study in greater detail the nature of the secondary radicals in furan, thiophene, and some of their derivatives.

EXPERIMENTAL

The work was done with an EPR-2 IKhf instrument, set up under a beam of fast, 1.6 MeV electrons. The experimental procedure and treatment of the results have been described previously [6]. The doses received by the specimens were within the limits 5-50 Mrad. The compounds used in the work were cp for spectroscopic analysis. The degree of splitting was determined by means of a solution of 1,1-diphenyl-2-picrylhydrazine (DPPH) in benzene. The error in determining the splitting did not exceed 2 e.

All the compounds were irradiated at -130° to -160° ; to aid interpretation of the EPR spectra, irradiated specimens were heated to higher temperatures. This cut the intensity of the central component of the spectrum because of recombination of primary radicals, and improved the hyperfine structure (HS). No new lines were found in the spectra.

EXPERIMENTAL RESULTS

Figure 1 gives the EPR spectra of furan and thiophene at $T = -160^\circ$ and warmed to $T = -100^\circ$ to -120° . Analysis shows them to be identical, and to consist of a triplet of triplets with a hyperfine splitting $\Delta H_1 = 32$ e, $\Delta H_2 = 13$ e.

The EPR spectrum of irradiated 2-thiophene carboxylic acid (see Fig. 2a) is the result of superposition of at least two spectra. One is a triplet of doublets with splitting $\Delta H_{tr} = 33$ e, and $\Delta H_d = 13$ e, the second is a doublet of triplets for which the splitting is $\Delta H_d = 33$ e, $\Delta H_{tr} = 13$ e. Figure 2b gives the EPR spectrum of irradiated 2-*tert*butylphenol, which is a superposition of a triplet of doublets having $\Delta H_{tr} = 32$ e, $\Delta H_d = 13$ e and a triplet of doublets having $\Delta H_{tr} = 40$ e and $\Delta H_d = 13$ e. At low temperature a triplet spectrum is also observed having $\Delta H = 20$ e.

The EPR spectrum given in Fig. 3 for 2,5-di-*tert*-butylthiophene consists of 12 lines. Analysis shows that components *a* form a 7-line spectrum having $\Delta H \approx 19$ e, while components *c* form a triplet spectrum with $\Delta H \approx 44$ e. At low temperature a triplet with $\Delta H \approx 20$ e is also observed, as in the case of 2-*tert*-butylthiophene.

As is evident from Fig. 4a, the EPR spectrum of irradiated 3-bromo-thiophene is a single line with a weak hyperfine structure. The distance between the points of maximum slope is $\Delta H \approx 50$ e. The Fig. 4b spectrum of irradiated 2-chlorothiophene is an asymmetric triplet, splitting $\Delta H_1 \approx 20$ e and $\Delta H_2 \approx 10$ e. All components exhibit a weakly resolved hyperfine splitting.

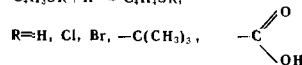
The EPR spectrum of carbon disulfide irradiated at $T = -170^\circ$ is an asymmetric triplet with $H_1 = 46$ e and $H_2 = 27$ e, with weak hyperfine splitting.

ASSESSMENT OF THE RESULTS

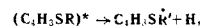
The EPR spectra of irradiated furan, thiophene, and their derivatives described above (see Figs. 1-4) cannot be explained by low temperature radiolysis of them giving only radicals formed by cleavage of a hydrogen atom from 5-membered rings, since the EPR spectra of those radicals should, by analogy with aromatic hydrocarbons [7], be a narrow single line. The low yield of hydrogen ($G_{H_2} = 0.03$ and 0.11 mole/100 eV) from liquid phase radiolysis of thiophene and furan [8], and study of the end products in the radiolysis of aqueous solutions of thiophene [1] make it possible to assume by analogy with aromatic hydrocarbons, that in the solid phase, too, the hydrogen atoms formed in the primary event add at double bonds.

Actually, it has been shown by a number of authors [3, 4], who used EPR as the means of study of the γ -radiolysis of single crystals of 2-thiophene and 2-furan carboxylic acids, that formation of secondary radicals is due to addition of a H atom, mainly at position 5, and often at position 2.


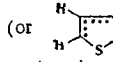
The results that we have obtained make it possible to conclude that formation of radicals by radiolysis of this group of compounds takes place according to the equations



where in reaction 3 a H atom adds at position 2(5). In addition, in the case of alkyl-substituted thiophenes, there is the reaction



i. e. detachment of a hydrogen atom from the side chain.

Actually, the 9-line EPR spectra observed in the radiolysis of thiophene and furan (see Fig. 1) can be ascribed to the radical  (or  when the splitting $\Delta H_1 = 32$ e, as is shown by juxtaposing the spectra of thiophene and its derivatives, is due to interaction of the unpaired electron with two protons of the $>CH_2$ group, while the splitting $\Delta H_2 = 13$ e is due to the interaction with two α -protons at positions 3 and 5.

The authors of paper [2] explain the EPR spectra obtained when thiophene and furan are irradiated by formation of the radical

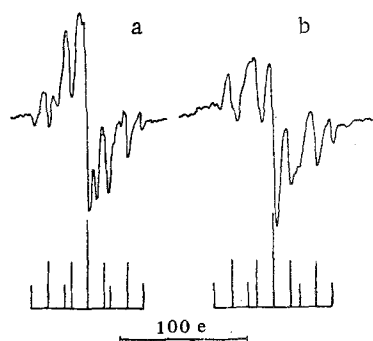


Fig. 1. EPR spectra of materials given a dose of 30 Mrad at $T = -160^\circ$; a) furan after warming up to -120° ; b) thiophene after warming up to -105° .

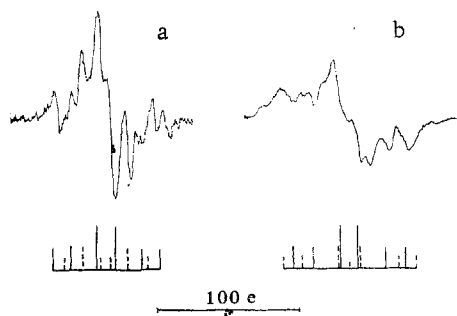
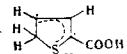
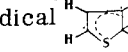
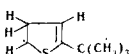
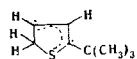


Fig. 2. EPR spectra of irradiated materials: a) 2-thiophene carboxylic acid at $T = +20^\circ$; dotted line is

for radical  continuous line for radical 

b) 2-tert-butylthiophene ($T_{\text{IRR}} = -160^\circ$) after warming to $T = -70^\circ$; the

dotted line is for radical  continuous line for radical



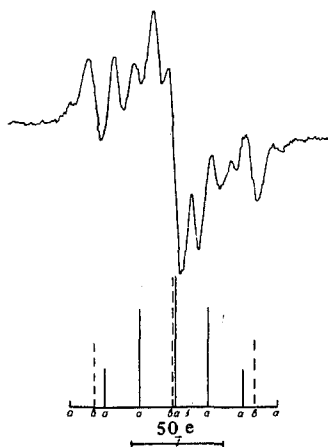


Fig. 3. EPR spectra of 2,5-di-tert-butylthiophene irradiated at $T = -160^\circ$, after warming to $T = -30^\circ$: the dotted line

is for radical Cc1c(C)sc(C)c1
 continuous line for radical

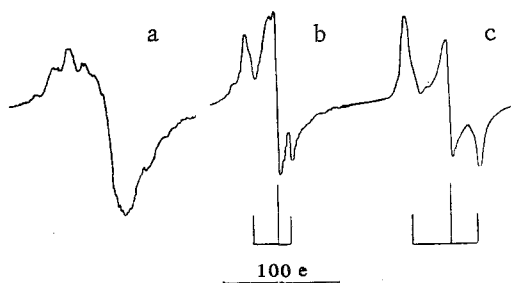
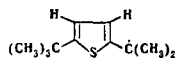
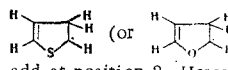


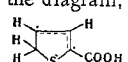
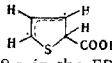
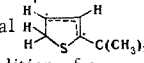


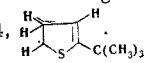
Fig. 4. EPR spectra of compounds irradiated at -160° : a) 3-bromothiophene; b) 2-chlorothiophene after warming up to $T = -110^\circ$; c) carbon disulfide.

 (or , i.e. on the assumption that the H atoms add at position 3. However the spectrum of such a radical should be a triplet (due to interaction between the unpaired electron and protons of the >CH₂ group) of doublets (interaction with α-protons at position 2), and not a triplet of triplets.

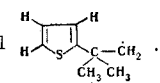
Since in 2-thiophene carboxylic acid the H atom at position 2 is replaced by the  group, which does not give hyperfine splitting, the EPR spectrum of the secondary radical must appear as a triplet of doublets, and the values of the splittings should not differ substantially from those observed for thiophene. On the basis of an analysis of the spectra of 2-thiophene carboxylic acid (see Fig. 2a) we postulate that the dotted lines shown in the diagram, which form a triplet of doublets, belong to the radical , when the

splitting values for triplet and doublet are 33 and 13 e respectively.* The further observed doublet of triplets with splittings 33 and 13 e,

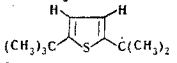
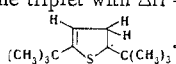
obviously belongs to radical . The triplet of doublets, having $\Delta H_{TT} = 33$ e, $\Delta H_d = 13$ e in the EPR spectrum of irradiated 2-tert-butylthiophene carboxylic acid belongs to the radical . There is evidently formed along with this radical, by addition of a

H atom at position 4,  whose lines (triplet with splitting $\Delta H = 40$ e, each component of which is split into a doublet with $\Delta H = 13$ e) are also found in the spectrum.

The triplet at low temperature, having $\Delta H = 20$ e, is due to interaction of the unpaired electron with two α-protons of the group -CH₂,

and indicates formation of the radical .

The 7-line spectrum with splitting $\Delta H = 19$ e (see Fig. 3) arising when 2,5-di-tert-butylthiophene is irradiated, is due to interaction of the unpaired electron with the 6 equivalent protons of the radical


 the triplet with $\Delta H = 40$ e, also found, obviously belongs to the radical .

A H atom can add at position 3(4), because position 2(5) is protected by the tert-butyl groups. It is to be noted that the hyperfine splitting at the >CH₂ groups at position 3(4) ($\Delta H = 40$ e) is somewhat greater than for position 2(5) ($\Delta H = 32$ e).

It is known [9] that the EPR spectrum of radicals having an unpaired electron localized at the sulfure atom, and obtained by irradiating proteins, shows a symmetric triplet. To get information about the spectrum, of the simplest sulfur radical, in the absence of functional groups with which the unpaired electron might interact, we obtained the EPR spectra of radicals formed by irradiation of solid H₂S. As Fig. 4c shows, the resultant spectrum is, like that of the sulfur radical previously described [9], an asymmetric triplet. Its resemblance to the spectra of the sulfur radical in irradiated proteins, carbon disulfide, and 2-chlorothiophene (see Fig. 4) makes it possible to conclude that the radiolysis of 2-chlorothiophene also gives radicals with a certain

unpaired electron density at the sulfur atom. Decrease in the value of the splittings in the sulfur radical of irradiated 2-chlorothiophene obviously indicates delocalization of an unpaired electron over the 5-membered ring. Analysis of possible structures of the sulfur radical in irradiated 2-chlorothiophene showed that the observed spectrum is due to a secondary radical, formed by addition of a H atom to a S atom, and having a structure.



In the radiolysis of 3-bromothiophene there is obviously also addition of a H atom to the sulfur atom to give the radical , whose asymmetric triplet is present in the EPR spectrum of irradiated 3-bromothiophene (see Fig. 4a); the poor resolution of the spectra makes it impossible to determine the nature of radicals of other types arising during radiolysis.

Results of analyzing the EPR spectra of irradiated furan, thiophene and their derivatives show that the mechanisms for the formation of radicals in the low-temperature radiolysis of heteroaromatic compounds and aromatic hydrocarbons are similar.

It is of interest to note that the hyperfine interaction constant (HIC) of the unpaired electron with the protons of the group >CH₂ in the case of benzene derivatives is practically independent of the position of the >CH₂ group and substituent with respect to one another. As is evident from the data given for heteroaromatic compounds, the HIC depends on the position of the >CH₂ group relative to the sulfur atom.

Conspicuous is the fact that replacement of ring hydrogen atoms by halogen changes the direction of the secondary reactions, the hydrogen atoms not adding at positions 2(5) or 3(4), but to the sulfur atom.

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*For the spectrum of this same radical, [4] obtains the following splitting values: $\Delta H_1 = 25$ and 30 e for protons of the >CH₂ group, $\Delta H_2 = 6.6$ e for protons at ring positions 2 and 5, and a weak splitting $\Delta H_3 = 2$ e due to negative spin density for the proton at ring position 3.