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Abstract

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On the Radiation-Chemical Stability of Some Heterocyclic Compounds

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The radiation-chemical stability of compounds is determined by the structure of the molecule and by its associated reactivity with respect to the primary products of radiolysis. Thus, it is known that molecules with conjugated double bonds, for example aromatic compounds, possess the greatest resistance to the action of ionizing radiation. In these compounds, because of the high mobility of the π-electrons, the energy absorbed by the molecule does not have time to become localized on any particular bond and is mainly dissipated before its rupture can occur.

In the present work an attempt was made to trace the radiation stability of molecules as a function of their structure, using as examples certain compounds of the heterocyclic series: furan, pyrrole, thiophene, and pyridine. The sharp change in reactivity on going from one compound to another, caused by the presence of a heteroatom, together with the preservation of aromatic properties, predetermined their choice for investigation. As a method for observing changes in the radiation-chemical properties of the systems studied, we used the method of electron paramagnetic resonance (EPR), which makes it possible to record the formation and accumulation of radical products that, as was found, appear during irradiation of these compounds at low temperatures. The work employed an EPR-2IKhF spectrometer combined with an EG-2.5 electron accelerator. Irradiation of the samples was carried out at temperatures of $-170 \div -160$°C by the method described in (^{1}), in ampoules made of glass that gives no EPR signal upon irradiation. The sensitivity of the setup made it possible to reliably record radical concentrations no lower than $5 \cdot 10^{16}$ spins per 1 g. The signal intensity was determined by double integration of the derivative of the absorption line. To determine the absolute concentration of radicals, a single crystal of $CuCl_2 \cdot 2H_2O$ with a known content of paramagnetic ions was used. The dose absorbed by the sample was determined from the current. The accuracy of determining the yield of radical accumulation did not exceed 30%.

Figure 1 gives the results of experiments on the kinetics of accumulation of intermediate radical products formed during irradiation of five-membered heterocycles. From the plots in Fig. 1 it is seen that the curves of radical accumulation as a function of dose have the character typical of saturation curves. At the same time, saturation in radical concentration is reached in the case of furan and pyrrole at lower doses than in the case of thiophene. The initial yield of radical

Fig. 1

Figure 1: Fig. 1

accumulation increases in the series thiophene $<$ pyrrole $<$ furan and is equal, respectively, to 0.1, 0.5, and 1.1. It is seen that in the case of furan the initial yield of radicals is very close to the yield of radical products from the aliphatic ring tetrahydrofuran (1,5). Such a sequence in the degree of radiation stability of heterocyclic compounds may be related to changes in their structure, if one takes into account that the strength of these compounds, expressed in terms of resonance energy, is characterized by an analogous sequence: $30 > 24.7 >$

>20.4 kcal/mole (2,3). The closeness of the values of G_R upon irradiation of furan and tetrahydrofuran is apparently explained by the strong influence of the electron pair of the heteroatom on the density distribution of the π cloud around the ring, which leads to a considerable weakening of the aromatic properties. It is known, for example, from the chemistry of furan that the free electron pair at the heteroatom creates an increased density of the π-electron cloud at the α-carbon atoms, as compared with the density at the β-atoms. As a result of this, the reactivity of furan, in comparison with pyrrole and thiophene, increases to such an extent that it becomes capable of diene-synthesis reactions.

Fig. 1. Dependence of the accumulation of radicals on dose during irradiation of heterocyclic compounds: **1**—thiophene, **2**—pyrrole, **3**—furan, **4**—tetrahydrofuran.

The influence of the heteroatom on the radiation stability of a molecule with conjugated bonds is also, in our opinion, well illustrated by the radiation-chemical properties of pyridine. It was found that the initial yield of radical products formed upon irradiation of pyridine considerably exceeds the yield of radicals from benzene under the same irradiation conditions and reaches a value of 0.7 (Fig. 2). It should be noted here that with increasing irradiation dose, G_R from pyridine increases.

Thus, despite the increase in the strength of the aromatic ring in going from benzene to pyridine (according to calculations, the resonance energy of benzene is 40 (2), and that of pyridine 43 (3) kcal/mole), more significant for the radiation stability of pyridine is the occurrence of a nonuniform distribution of electron density around the ring (because of the heteroatom). This explanation seems acceptable to us, since it is known from the chemistry of pyridine that the nonuniformity of the density of the π cloud around the ring is the cause of the sharp change in the reactivity of the aromatic ring in going from benzene to pyridine. Along with the study of the kinetics of accumulation of radical products during radiolysis of the heterocyclic compounds under consideration, an investigation was carried out of the EPR spectra of these compounds. The EPR spectra of the irradiated samples are presented in Fig. 3. Analyzing these data, one may point, first, to the similarity of the basic structure of the spectra

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

of the heterocycles, evidently associated with an analogy in the mechanism of formation of the radical products. Second, it may be concluded that the EPR spectra of the irradiated heterocycles are the result of superposition of the spectra of two types of radicals: one of them is formed as a result of abstraction of an H atom from the heterocycle molecule, and the other upon addition of H to the neutral molecule.* Obviously, the spectrum of the first radical is a doublet line with a splitting of ~ 30 oersted, the center of which coincides with the g-factor of the free electron. The spectrum of the second type of radicals is characterized by a multiplet hyperfine structure (h.f.s.) caused by the interaction of the unpaired electron with four protons. The spin density of the electron at the sites of the protons is not the same: for most of the time the unpaired electron is located at the carbon atom bound to two hydrogen atoms.

Fig. 2. Dependence of the accumulation of radical products on dose during irradiation of benzene (1), pyridine (2)

The total splitting at these protons, as can be concluded from the spectra, is approximately 70 oersted, which greatly exceeds the splitting in the aromatic ring. The components of the line of this radical, apparently having a triplet h.f.s. with an intensity ratio of $1:2:1$, are in turn split by other protons located one at each carbon atom. This leads to a complication of the appearance of the spectrum. Analysis of the spectrum indicates that heteroatoms strongly influence the degree of delocalization of the unpaired electron over the ring. As the analysis shows, the spin density of the electron at carbon atoms with one H, compared with the density of the unpaired electron at the carbon atom with two protons, increases in the order pyrrole $<$ thiophene $<$ furan; moreover, according to the estimate, in quantitative terms the increase in spin density is consistent with the increase in electron affinity energy at the heteroatoms $(0.48, 71$ kcal/mol$)^*$.

Fig. 3. E.p.r. spectra of irradiated heterocycles: furan (a), pyrrole (b), thiophene (c); A –absorption intensity

On the basis of the available data it was possible to conclude that addition of

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* Indirect confirmation of the formation of H during radiolysis of the systems studied could be provided by the results of experiments on analysis of gases formed during radiolysis of liquid thiophene, the most resistant in the series of heterocycles studied to the action of radiation. Evolution of hydrogen was detected, although with a small yield (0.06).

Fig. 4. EPR spectrum of irradiated pyridine

Figure 4: Fig. 4. EPR spectrum of irradiated pyridine

H atoms formed during radiolysis of heterocycles

* Analyzing data on the electron-affinity energy of the atom, Syrkin and Dyatkina come to the conclusion that in atoms with three lone p-electrons the electron-affinity energy is close to 0 (4).

goes to the carbon atom located in the β-position relative to the heteroatom.

Upon irradiation of frozen pyridine, the mechanism of formation of the radical radiolysis products is apparently analogous to that set forth above and thus coincides with the mechanism described in the literature for the case of benzene radiolysis (5). This conclusion can be reached on the basis of analysis of the EPR spectrum of irradiated pyridine. This spectrum (Fig. 4) is a triplet with a component-intensity ratio of $1:2:1$ and a splitting between the outer components of approximately 60 Oe. The main structure of the spectrum is evidently manifested through the interaction of the spin of the unpaired electron with the magnetic moments of two protons located at the same carbon atom. It may be assumed that atomic hydrogen adds to the γ-carbon of the pyridine ring. Each line of the triplet, as is seen from the figure, is split into three components. This could be explained by interaction of the spin of the unpaired electron with the nitrogen nucleus ($I_N = 1$) or with two protons of the ring [$I_H = \frac{1}{2}$]*. In our opinion, the first assumption appears more probable. If one takes into account that in the pyridine ring the distribution of electron density is nonuniform ($\rho_N > \rho_{C_\gamma} > \rho_{C_\alpha} > \rho_{C_\beta}$, where ρ is the density of the π-electron cloud at the corresponding atoms), then addition of atomic hydrogen to C_γ, with subsequent preferential localization of the unpaired electron in the ortho and para positions (already with respect to C_γ), as in the case of the C_6H_7 radical (5), leads to an even greater increase in the electron-cloud density at the nitrogen atom.

Fig. 4. EPR spectrum of irradiated pyridine

It should be emphasized, however, that the question of the site of addition of H atoms to the molecules of the heterocycles considered should by no means be regarded as settled. The specific properties of the H atom (as an oxidizing agent or a reducing agent, depending on the nature of the compound reacting with H), which in the present case apparently may be manifested in the ability of the H atom to act as a donor or acceptor of an electron pair, do not give an unambiguous answer to the question of the direction of attack by the H atom.

In conclusion, we note that the study of the radiolytic behavior, as well as of the EPR spectra, of the compounds described made it possible to reveal the interaction of two factors affecting the radiation stability of compounds in opposite directions and to different degrees: the presence of conjugated bonds (

"aromaticity") and the nonuniformity of the distribution of electron density in the heterocyclic ring, caused by the properties of the heteroatom.

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REFERENCES

1. Yu. N. Molin, A. T. Koritskii et al., *Pribory i tekhn. eksp.*, **6**, 73 (1960).
2. H. C. Longuet-Higgins, *Trans. Farad. Soc.*, **45**, 173 (1949).
3. M. Simonetta, *J. Chim. Phys.*, **49**, No. 2, 68 (1952).
4. Ya. K. Syrkin, M. E. Dyatkina, *Chemical Bond and the Structure of Molecules*, Moscow—Leningrad, 1946, p. 54.
5. V. A. Tolkachev, Yu. N. Molin et al., *DAN*, **141**, 911 (1961).
6. D. A. Brown, M. J. S. Dewar, *J. Chem. Soc.*, 1953, 2406.

* The line width of the spectrum ($\Delta H_{1/2} \sim 25$ Oe) suggests that all protons of the ring apparently participate in the splitting of the components of the main triplet. However, splitting due to these protons was not observed, probably because of the limited capabilities of the EPR spectrometer.

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