

# ESR study of low-temperature radiolysis and photolysis of substituted *N'*-furfurylidenebenzhydrazides

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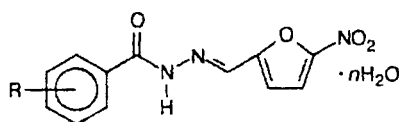
Low-temperature (77 K)  $\gamma$ - and UV irradiation of substituted *N'*-furfurylidenebenzhydrazides produces paramagnetic particles in radiation-chemical yields of (0.05–0.5)/100 eV and quantum yields of  $4 \cdot 10^{-5}$ – $10^{-3}$ , respectively. ESR study showed that hydrazyl radicals and  $\text{HC}\cdot\text{O}$  and  $\text{N}\cdot\text{O}_2$  are the main products of radiolysis and photolysis, and the latter decay upon heating of the sample to 190 K, whereas the hydrazyl radicals survive up to 423 K. Further heating results in thermodestruction of the hydrazides, and the ESR spectrum exhibits only a singlet with splitting at 1 mT, which is characteristic of polyconjugated compounds.

**Key words:** substituted *N'*-furfurylidenebenzhydrazides, ESR spectra, radiolysis, photolysis, kinetics of radical accumulation and recombination.

Substituted *N'*-furfurylidenebenzhydrazides are photosensitive compounds: photochemical transformations occur in their crystals under UV irradiation.<sup>1–3</sup> Both crystal hydrates and anhydrous forms are photosensitive. The photosensitivity of the latter decreases as the density of crystal packing increases.<sup>3</sup> Based on spectral and X-ray diffraction studies, we assumed that UV irradiation of substituted *N'*-furfurylidenebenzhydrazides results in the intermolecular  $\text{N} \rightarrow \text{O}$  transfer of an amide proton along the chain of H bonds in the crystals.

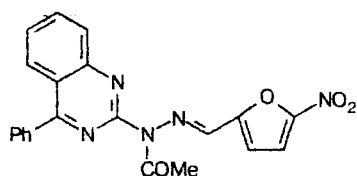
This work is devoted to the ESR study of radicals that formed during low-temperature radiolysis and photolysis of substituted *N'*-furfurylidenebenzhydrazides and establishment of a correlation between the data obtained and results of optical and X-ray diffraction studies.

Compounds 1–5 were studied:



1–4

1: R = 3,5-( $\text{NO}_2$ )<sub>2</sub>,  $n = 1$ ; 2: R = *p*-Br,  $n = 2$ ;  
3: R = *p*- $\text{SO}_2\text{CHF}_2$ ,  $n = 1$ ; 4: R = H,  $n = 1$



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## Experimental

Compounds 1–5 were synthesized by the previously described procedures.<sup>4–8</sup> The physicochemical parameters of these compounds coincide with those available in the literature.

$\gamma$ -Irradiation was carried out on a K-150000  $^{60}\text{Co}$  setup. UV irradiation was carried out both with the full light of a DRSh-1000 mercury lamp and using light filters. A BUV-30P lamp was used for UV irradiation with  $\lambda = 253.7$  nm. ESR spectra were recorded at 77 K on an EPR-21 radiospectrometer (in a wavelength interval of  $\sim 3$  cm) with a power of the microwave field of  $10^{-4}$  W. The error of determination of absolute concentrations of paramagnetic particles was 40%, and that of relative concentrations was 5–10%. Optical spectra were recorded on a Specord M-40 spectrophotometer in the UV and visible wavelength ranges. For the determination of quantum yields of radicals, we took samples with such a thickness all that the incident UV light remained in the sample. To monitor the optical density in the sample, a reference sample was placed behind the sample under study, and the formation of radicals in this sample was checked by ESR spectra.

## Results and Discussion

The ESR spectra of compound 1 subjected to  $\gamma$ -irradiation at 77 K ( $D = 7000$  kGy) and further heating to 473 K are presented in Fig. 1. It can be seen that the temperature increase results in the disappearance of lateral signals, the distances between which being 12.4 and 16.6 mT. It is most probable that these are the components of the spectrum of the  $\text{N}\cdot\text{O}_2$  and  $\text{HC}\cdot\text{O}$  radicals. It is known that the spectra of the  $\text{N}\cdot\text{O}_2$  radical represent a triplet which is anisotropic with respect to  $g$  factor and hyperfine coupling (HFC) with splitting from 4.0 to 6.7 mT, depending on the matrix used for their

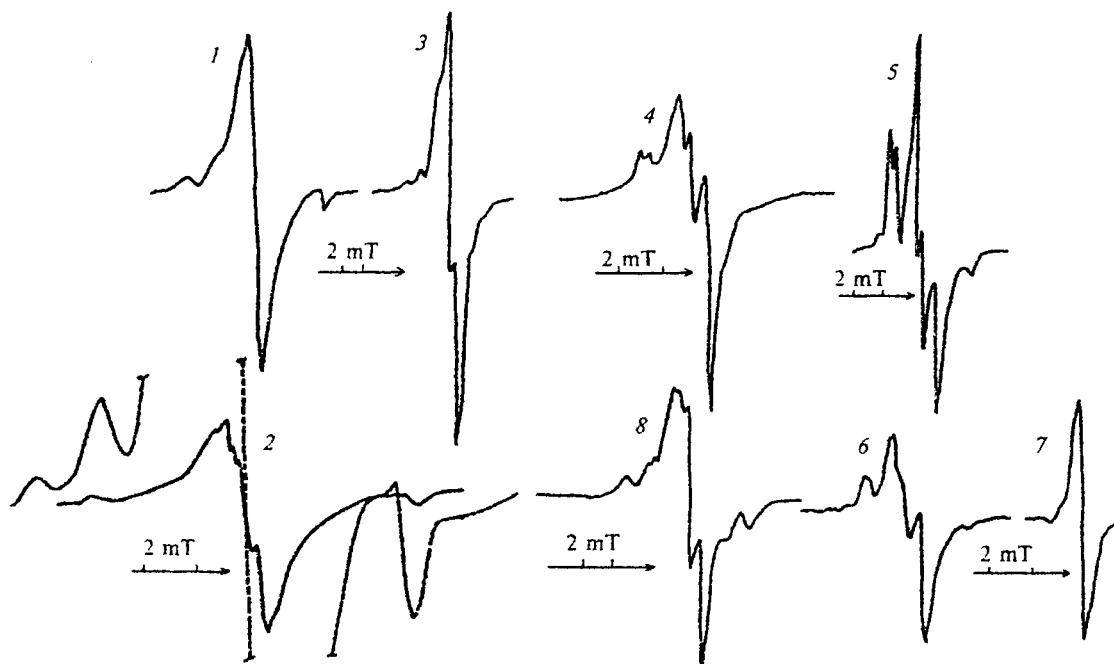
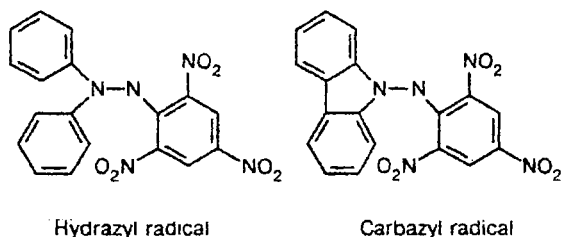


Fig. 1. ESR spectra of compound **1**  $\gamma$ -irradiated at 77 K (1, 2) and then heated to 190 (3), 333 (4), 373 (5), 423 (6), and 473 K (7) and a solid solution of carbazyl in methyl methacrylate (8). Irradiation dose is 7000 kGy. Temperature of recording the spectra is 77 K.

isolation, and the distance between the extreme components of the triplet in  $\gamma$ - and UV irradiated cellulose nitrate is 12.2 mT.<sup>9,10</sup> The  $\text{HC}^\bullet\text{O}$  radical gives an asymmetrical doublet spectrum with a very large (about 18 mT) hyperfine splitting in the ESR spectrum.<sup>11,12</sup> When the sample irradiated at 77 K is heated to 190 K, signals of the  $\text{N}^\bullet\text{O}_2$  and  $\text{HC}^\bullet\text{O}$  radicals completely disappear, and the spectrum exhibits seven lines with a distance between the extreme components of  $\sim 7$  mT, which is characteristic of the carbazyl radical.<sup>13</sup>



The ESR spectrum of the hydrazyl in the solution consists of five equivalent lines. An unpaired electron interacts, approximately to equal extents, with both nitrogen atoms of the hydrazide group, and the HFC constants are equal to 0.935 and 0.785 mT. As the viscosity of the solution increases, the components of the spectrum are broadened, and the resolution worsens. The spectrum of the solid solution of the carbazyl in methyl methacrylate consists of seven asymmetrical lines

with a distance of 7.2 mT between the extreme components (see Fig. 1, spectrum 8) and is almost identical to the spectrum of compound **1** irradiated at 77 K and then heated to 333 K (Fig. 1, spectrum 4). Spectrum 2 shows that the hydrazyl radicals are formed along with the  $\text{N}^\bullet\text{O}_2$  and  $\text{HC}^\bullet\text{O}$  radicals when the sample is irradiated at 77 K. The  $\text{N}^\bullet\text{O}_2$  and  $\text{HC}^\bullet\text{O}$  radicals disappear when the sample is heated to 190 K, and the hydrazyl radicals are retained up to 443 K. Further heating to 473 K results in the transformation of the multicomponent spectrum of the hydrazyl radical into a singlet with splitting  $\Delta H = 1$  mT, and the starting light-yellow sample becomes dark-brown. It is most likely that at these temperatures the substance undergoes thermodestruction to form a radical containing conjugated bonds.

The ESR spectra of  $\gamma$ -irradiated compounds 2–5 are identical to that of compound **1**  $\gamma$ -irradiated at 77 K (Fig. 2). The extreme components of the anisotropic triplet with a distance between them of 12.4 mT, as in the case of compound **1**, disappear when the samples are heated to 190 K (Fig. 2, spectra 7 and 8). The spectrum of compound **5** (Fig. 2, spectrum 4) somewhat differs from those by the presence of additional signals with a distance between them of 11 mT. Probably, these are the extreme components of the triplet of the cyclohexadienyl radical that is formed due to the addition of hydrogen to the benzene ring.

UV irradiation of compound **1** (Fig. 2, spectrum 6) and its further heating result in the same transforma-

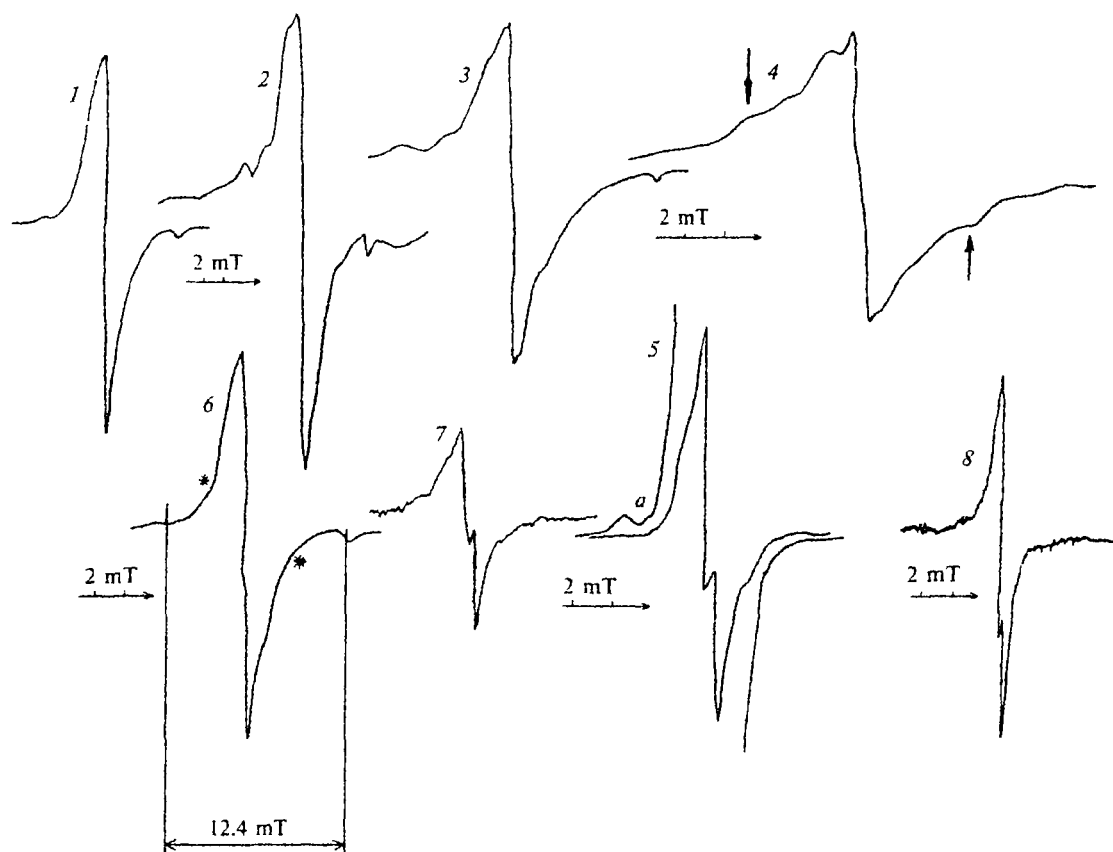


Fig. 2. ESR spectra of compounds 2–5  $\gamma$ -irradiated at 77 K (1–4), compound 2  $\gamma$ -irradiated at 77 K and then heated to 333 K (5), and compound 1 UV irradiated at 77 K (6) and then heated to 373 (7) and 473 K (8). Spectrum 5a is spectrum 5 recorded with a tenfold amplification. Irradiation doses: 7000 kGy (1); 500 kGy (2–4) ( $I_0 = 6 \cdot 10^{18}$  quantum  $\text{cm}^{-2} \text{s}^{-1}$  (6)). Temperature of recording the spectra was 77 K.

tions in the sample as  $\gamma$ -irradiation. However, in the latter case, the ESR spectra are obtained with a worse resolution. This is most likely related to the fact that high local concentrations of the radicals are formed during UV irradiation due to high absorption coefficients, which results in dipole broadening of the line.

Thus,  $\gamma$ - and UV irradiation of substituted *N'*-furfurylidenebenzhydrazides results in the formation of hydrazyl radicals, and the eliminated hydrogen atom can add to both the oxygen atom of the adjacent molecules to form the formyl  $\text{HC}\cdot\text{O}$  radical and the benzene ring to form the cyclohexadienyl radical. In addition, the energy absorption also leads to the elimination of the  $\text{NO}_2$  group to form the  $\text{N}\cdot\text{O}_2$  radicals.

The optical absorption spectra of the compounds under study exhibit several common bands (at 230, 275, and 375 nm) and bands characteristic only of the compound under study. For example, compound 3 is characterized by the following absorption bands: 235, 275, 374, 392, and 430 nm. Under UV irradiation a very weak band at 450 nm appears in the optical absorption spectrum and decreases during further irradiation. This

indicates that this band does not belong to the radicals formed under irradiation, because they are stable and their yield increases with the irradiation dose.

The kinetics of accumulation of the radicals is characteristic of solid state reactions (Fig. 3). The quantum yields amounted to  $1.4 \cdot 10^{-4}$  for compound 1,  $4 \cdot 10^{-5}$  for compound 2,  $0.7 \cdot 10^{-3}$  for compound 3, and  $1 \cdot 10^{-3}$  for compound 5. For the evacuated sample of 3, the yield of radicals was  $1.1 \cdot 10^{-3}$ , which exceeds by 1.5 times that of the radicals in the non-evacuated sample. The radiation-chemical yields are  $\sim 0.05/100$  eV for compounds 1 and 2 and  $0.5/100$  eV for compound 5.

The photo- and  $\gamma$ -irradiated samples differ by the kinetics of decay of the radicals (Fig. 4). In the temperature region above 200 K, the  $\gamma$ -irradiated samples are characterized by a smooth decrease in the concentration of the hydrazyl radicals, whereas a step is observed on the curves of decay of the radicals in the photoirradiated samples. It is most likely that during photolysis a considerable portion of the radicals is stabilized in more rigid regions of the matrix (in deeper "traps") than during radiolysis. The kinetics of decay of

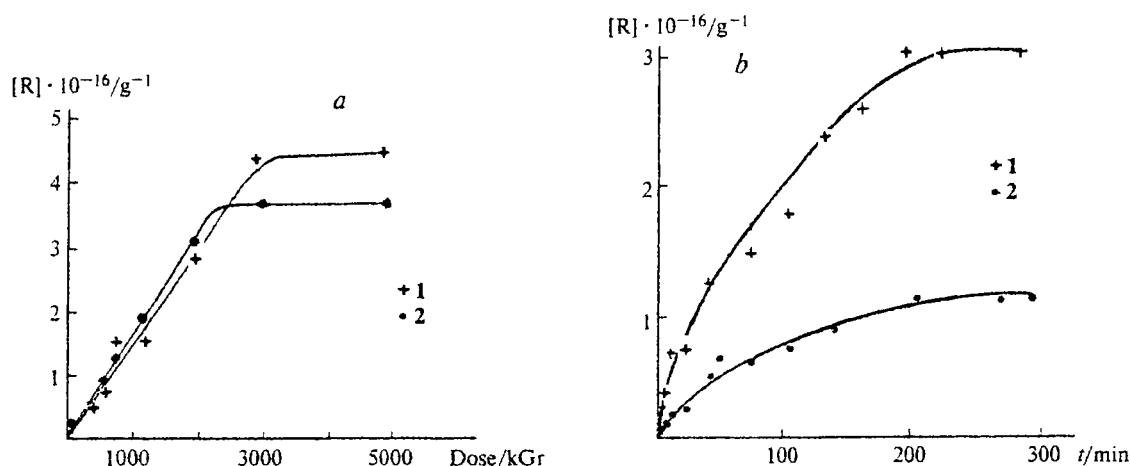


Fig. 3. Kinetics of accumulation of radicals in compounds 1 and 2 during  $\gamma$ - (a) and UV irradiation (b) at 77 K.

the radicals in samples 1 and 2 also differ. In sample 1 after heating to 373 K, only 4–5% of the radicals remain of the primary concentration, which was the highest and amounted to  $1.7 \cdot 10^{19}$  particles/g, whereas in sample 2 only 10–12% remain of the primary con-

centration, which was also the highest and amounted to  $1.3 \cdot 10^{19}$  particles/g. The difference between the thermostabilities of the radicals for compounds 1 and 2 is more pronounced in the case of photolysis than for radiolysis. On heating to 373 K, the number of radicals that remain in sample 2 is 2.5 times higher than that for sample 1. This is most likely related to the fact that compound 2 has a more rigid crystalline lattice than compound 1. Taking into account that compound 2 is the last in the series of photosensitivity among the compounds under study,<sup>1–3</sup> we suggest that the packing density affects the photosensitivity of anhydrous forms of these compounds and their crystal hydrates as well.

Thus, radiolysis and photolysis of substituted *N'*-furfurylidenebenzhydrazides result mainly in the elimination of the H atom or the substituent, as in the case of compound 5, from the N(1) atom of the hydrazide group to form hydrazyl radicals. These results are well consistent with the X-ray diffraction and optical data, which suggest that the transfer of a proton from the nitrogen atom of the hydrazide groups along the chain of H bonds in the crystal to the carbonyl group of the adjacent molecule is the main reaction responsible for the photosensitivity of substituted *N'*-furfurylidenebenzhydrazides. Kinetic information on the recombination of the radicals formed in crystals of substituted *N'*-furfurylidenebenzhydrazides under UV irradiation can be a criterion for the density of crystal packing.

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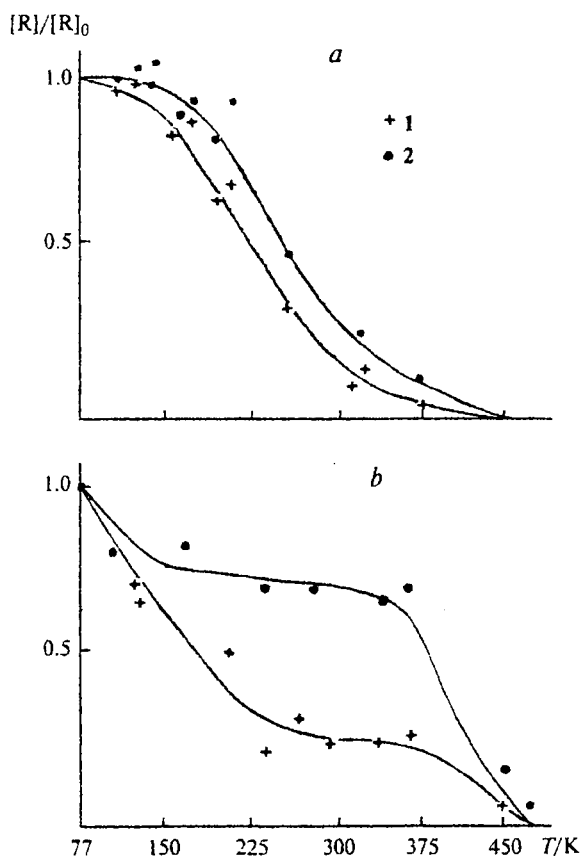


Fig. 4. Kinetics of decay of radicals during heating of  $\gamma$ - (a) and UV irradiated (b) at 77 K compounds 1 and 2.

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