Synthesis and properties of photosensitive derivatives of cellulose

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Some photosensitive derivatives were synthesized by introducing the o-nitroaryl chromophore into polymer chain of acetylated hydroxyethylcellulose (HEC). The products were characterized viscosimetrically and by u.v., i.r. as well as ¹³C-n.m.r. spectroscopy. The phototransformation reactions of the synthesized products were investigated. By the effect of ultraviolet radiation acetylated HEC is subjected to photodestructive and photooxidative transformations. The presence of the o-nitroaryl chromophore enhances the photosensitivity of the cellulose derivative.

Были синтезированы светочувствительные производные· введением о-нитроарильного хромофора в полимерную цепь ацетилированной гидроксиэтилцеллюлозы (ГЭЦ). Продукты были характеризованы вискозиметрически и при помощи УФ, ИК и ¹³С-ЯМР спектроскопий. Изучены реакции фотопревращений синтезированных продуктов. Ацетилированная ГЭЦ подвержена действию ультрафиолетового облучения, что ведет к фоторазложению и фотоокислению. Наличие о-нитроарильного хромофора повышает светочувствительность целлюлозного производного.

The photosensitive polymer systems were very intensively studied recently and their application in different lines continues to increase. These systems have been used in polygraphic reproduction, microelectronics, production of lacquers and dyestuffs, *etc.* [1, 2]. The record of light information is based on the change in physicochemical properties, especially solubility after the effect of ultraviolet radiation.

In this paper, we describe the synthesis and properties of some new photosensitive derivatives of cellulose on the base of acetylated hydroxyethylcellulose the photosensitivity of which has been enhanced by introducing the o-nitroaryl chromophores into polymer chain. Some photodestructive reactions take place in this system by the effect of ultraviolet radiation owing to which the cellulose derivative originally soluble in organic solvents is transformed into a water-soluble one. In order to raise the sensitivity, the reaction consisting in intramolecular abstraction of hydrogen atom by the excited nitro group in the triplet state in aromatic ring [3, 4] is used. The reaction mechanism of intramolecular reduction was investigated for low-molecular substances with 2-nitrobenzaldehyde and different substituted derivatives of 2-nitrotoluene [3]. In this case, the nitro group is reduced to a nitroso group which may be subjected to deeper photochemical transformations, while the oxygen atom is bonded to the carbon atom in the *ortho* position with respect to the nitro group. In a simplified way, this reaction may be expressed as follows (Scheme 1)
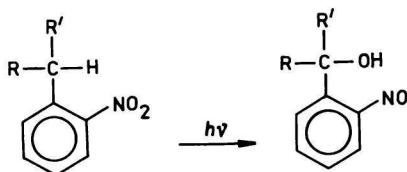
Scheme 1

According to the substituents R and R' and the reaction medium, 2-nitrosobenzaldehyde, 2-nitrosobenzoic acid and its esters were identified as final products of the photochemical reaction. These substances can undergo consecutive condensation and addition reactions and give different azoxy and azo products [3]. *Petropoulos* [5] used this type of photosensitive system for the synthesis of photosensitive poly(2-nitrobenzaldehyde acetals) which are degraded by the effect of ultraviolet radiation to give 2-nitrosobenzoates and alcohol rests. Polymers of this type were proposed for the use in photomechanical reproduction as positive photoresists.

Experimental

Water-soluble hydroxyethylcellulose (average viscosimetric polymerization degree $(DP_v) = 397$, content of ethoxy groups = 21.6 mass %, degree of substitution $(DS) = 0.70$, module of substitution $(MS) = 1.02$, lenght of side chain $n = 1.45$) was used for synthesis of the photosensitive derivatives.

274

Acetyl-hydroxyethylcellulose (I)

22.3 g of purified water-soluble hydroxyethylcellulose were added under intensive stirring into 700 cm³ of acetylation mixture consisting of benzene and acetanhydride in the volume ratio 4:6. This mixture contained an admixture of perchloric acid working as catalyst in the amount of 0.1 volume % of acetylation mixture. The acetylation proceeded for 3 h under constant stirring at 30 °C. When the reaction was finished, the product was precipitated and washed with ethanol and dried. The yield was 17.85 g (49.33 mass % C, 6.04 mass % H; 49.9 mass % CH_3COO; $DS_{CH_3CO} = 2.240$, $M_{m\,subst.gl.u.} = 303.0$ g mol⁻¹).

2-Nitrobenzaldehyde acetyl-hydroxyethylcellulose acetal (II)

We added 2-nitrobenzaldehyde (4 g) and 4-toluenesulfonic acid (0.084 g) functioning as catalyst into acetylated HEC (4 g) in toluene (10 cm³). The reaction proceeded in nitrogen atmosphere for 10 h at 140 °C and 2 h at 180 °C under reflux on an oil bath under intensive stirring. When the reaction was completed, the resinous dark-brown product was dissolved in 1,2-dichloroethane and precipitated three times into ether. After drying in vacuum drier we obtained 3.9 g of the product (48.94 mass % C, 5.97 mass % H, 0.37 mass % N; 46.22 mass % CH_3COO; $DS_{CH_3CO} = 2.139$).

2-Nitrobenzyl-acetyl-hydroxyethylcellulose (III)

Saturated aqueous solution of sodium carbonate (30 cm³) and 2-nitrobenzyl chloride (9 g) were added to acetylated HEC (3 g) under intensive stirring. The reaction mixture was heated for 30 min under reflux on a water bath. The reaction finished, the product was precipitated with methanol. The white precipitate was filtered off, washed with methanol and dried in a vacuum drier at 50 °C. Thus we obtained 3.6 g of the product (48.85 mass % C, 5.43 mass % H, 2.13 mass % N; 37.43 mass % CH_3COO; $DS_{CH_3CO} = 2.093$).

2-Nitrobenzoyl-acetyl-hydroxyethylcellulose (IV)

Acetylated HEC (3.6 g) and triethylamine (4 cm³) were put into 1,2-dichloroethane (50 cm³). The reaction mixture was cooled to 0 °C, stirred for 1 h until the acetylated HEC completely dissolved. Then 2-nitrobenzoyl chloride (3 g) dissolved in 1,2-dichloroethane (10 cm³) was slowly added into the reaction mixture. After adding the total quantity of that solution, the reaction proceeded for 13 h at 19—22 °C. Triethylammonium chloride was filtered off and the product present in filtrate was precipitated with methanol, washed with methanol, and dried in vacuo at 50 °C. Yield 2.8 g (49.98 mass % C, 5.89 mass % H, 0.19 mass % N).

The films consisting of individual polymer substances I—IV were prepared by pouring 1 % solution of the derivative in chloroform on NaCl plates. These samples were irradiated with a medium-pressure mercury lamp RVK-125 Tesla. The intensity of luminous flux was

1.88×10^{-9} e cm^{-2} s^{-1}. The exposed film was cooled by circulation of neighbouring air. The temperature in the level of impinging radiation was 22—23 °C. The photochemical transformations of photosensitive polymer systems were investigated by means of ultraviolet spectra (Specord UV VIS, Zeiss, Jena) and infrared spectra (method of interrupted test) (Specord IR-71, Zeiss, Jena).

The ^{13}C-n.m.r. spectra (δ_r/ppm) were measured with a instrument FX-60 (Jeol). The working frequency of the intrument for ^{13}C was 15 MHz. The width of the recorded spectra was 4000 Hz (≈ 280 ppm). The spectra were measured with the number of 4024 points in a time domain. Deuteriochloroform with 1 % of TMS serving for internal standard was used as solvent. The measurements were carried out with a saturated solution of cellulose derivative.

The e.s.r. spectra were taken with an instrument Varian E-3, the modulation being 100 kHz in zone X. The measurements were performed with irradiated samples dissolved in chloroform immediately after exposure at laboratory temperature. The spectra were simulated with a spectral computer Varian SS 100.

The change in distribution of molecular mass due to the effect of ultraviolet radiation was investigated by gel permeation chromatography of solutions of the individual samples dissolved in tetrahydrofuran with an instrument ALC-GPC 501 (Waters). The index of refraction was recorded by means of a differential refractometer. The fractionation system consisted of a system of eight columns packed with Styragel (4×10^{-5} m, 2×10^{-6} m, and 2×10^{-7} m). The overall length of gel bed was 480 cm while the flow rate of eluting agent was 1 cm^3 min^{-1}. The solutions of samples of 0.2 mass % concentration were dosed by means of a 2 cm^3 loop. The system of columns was calibrated by the use of polystyrene standards (Waters).

Results and discussion

Acetylated hydroxyethylcellulose (AcHEC) was used as starting substance for the preparation of photosensitive nitro derivatives on the base of cellulose. The acetylation of HEC was performed in a benzene—acetanhydride mixture containing perchloric acid as catalyst under conditions making possible the synthesis of a derivative (DS$_{ethoxy}$ = 0.70, DS$_{CH_3CO}$ = 2.24) fairly soluble in acetone, chloroform, and 1,2-dichloroethane. Acetyl-hydroxyethylcellulose forms hard, flexible, and transparent films.

The introduction of the nitroaryl chromophore into cellulose chain was carried out by means of the reaction of AcHEC with 2-nitrobenzaldehyde, 2-nitrobenzyl chloride or 2-nitrobenzoyl chloride under particular reaction conditions. The physicochemical properties of the synthesized substances are presented in Table 1. The differences between the values of the measured limiting viscosity numbers may be due to different reaction conditions used for the preparation of derivatives *II*, *III*, and *IV*. The extreme decrease in [η] of product *II* may be attributed to considerable degradation of the main polymer chain of cellulose owing to extreme

Table 1

Characterization of the synthesized products *I—IV*

Product	DS_{CH_3CO}	$DS_{nitroaryl}{}^a$	C/O^a	$[\eta]^b/(100\ cm^3\ g^{-1})$	λ_{max}/nm	$\tilde{v}_{as}(NO_2)/cm$
I	2.240	—	1.105	0.898	204	—
II	2.139	0.083	1.094	0.268	223	1540
III	2.093	0.579	1.123	0.724	212	1525
					267	
IV		0.042	1.137	0.998	211	1530

a) Calculated according to elemental analysis; *b*) limiting viscosity number measured in 1,2-di-chloroethane.

reaction conditions and acid medium. This view is also confirmed by the shift in maximum of the elution curve of the high-molecular portion of acetylated HEC into the region of lower molecular mass (from $V_e = 120\ cm^3$ to $V_e = 135\ cm^3$) (Fig. 1). However, a more significant decrease in content of the acetyl groups appeared only under conditions of nitrobenzylation.

A comparison of the values of λ_{max} shows clearly that the aromatic chromophore affects the absorption region according to character of the chemical bond aromatic ring—polymer. The linkage of nitroaryl chromophore extended the absorption
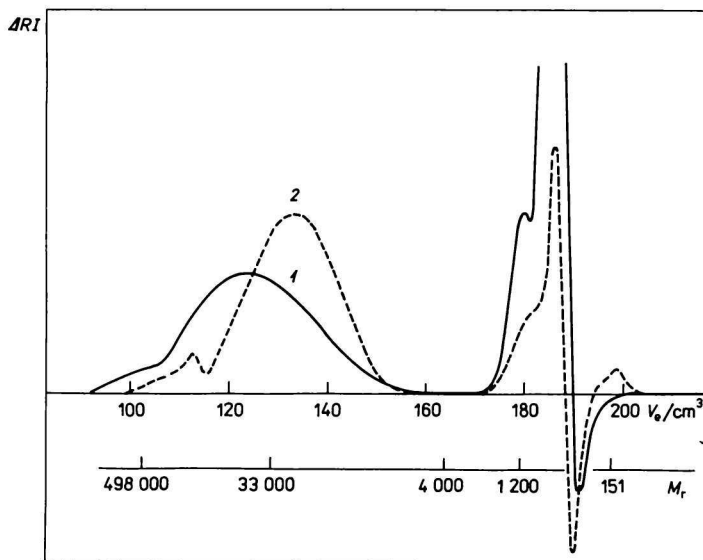

Fig. 1. G.p.c. elution curves: *1.* original acetylated HEC; *2.* after reaction with 2-nitrobenzaldehyde.

region in the spectrum of AcHEC towards higher wavelengths and this fact manifested itself by a remarkable maximum only with product *III* ($\lambda_{max\ II} = 267$ nm) which has the highest degree of substitution ($DS_{nitroaryl} = 0.579$). In the infrared spectra some shifts in $\tilde{\nu}_{as}(NO_2)$ of individual products are to be observed.

The study of structure of synthesized products *II* and *III* by ^{13}C-n.m.r. spectroscopy confirmed the linkage of nitroaryl chromophore to the polymer chain of cellulose. Table 2 contains the ^{13}C-n.m.r. data of products *I* and *III* which were

Table 2

^{13}C-NMR spectra of products *I* and *III*

Product	Chemical shift (δ_r/ppm)							
	CH_3-	$-COO$	C-1	C-2—C-6	C-6	$-CH_2-CH_2-$	C_6H_4-	$C_6H_4-CH_2-$
I	20.8	169—172	100—103	69—79	60—65	60—65	—	—
III	20.8	169—172	100—103	69—79	60—65	60—65	120—140	43.27

interpreted on the basis of the spectrum of α-D-glucose known from literature [6]. In the region of resonance of anomeric carbon atoms the position of a band with a few maxima (δ_r/ppm = 100.44, 100.84, and 102.40) unambiguously reveals the β-anomeric character of glucopyranose rests. These maxima are due to the effect of substituents on different carbon atoms of a glucopyranose unit [6, 7]. The fact that the influence of substituents is responsible for this effect has been confirmed by measurements with cellulose triacetate which has C-1 signals with a δ_r maximum at 100.6 ppm.

The δ_r region between 60 ppm and 70 ppm belongs to the C-6 carbon atoms and the $-CH_2-CH_2-$ group. We may state that the signals of carbon atoms directly bonded to the acetyl group appear in ^{13}C-n.m.r. spectrum at $\delta_r = 63.4$ ppm which is characteristic of esters [6]. In the range 169—172 ppm, we observed four different bands which were the result of acetylation in four different positions of the β-D-glucopyranose units of HEC. It resulted from the shift in integral intensities of the $-COO$ groups towards the C-1 and C-4 carbon atoms that the acetylation proceeded to a high degree. As for the product *III*, we can expect signals of the aromatic carbon atoms in the substituted benzene rings as well as a signal of the methylene group in $C_6H_4(NO_2)-CH_2-O-$ in the ^{13}C-n.m.r. spectrum. The measurements carried out with this product gave six signals in the δ_r region 120—140 ppm for which the aromatic carbon atoms were responsible and a signal at $\delta_r = 43.27$ ppm which belonged to carbon atom of the methylene group bonded directly to aromatic ring and polymer chain. An addition of small amount of free

2-nitrobenzyl chloride into polymer manifested itself in the spectrum by a new signal at $\delta_r = 45.22$ ppm which also belonged to the —CH_2— group. As for the product *II*, we observed signals in the ^{13}C-n.m.r. spectrum like with the product *III*, but their intensities were much lower, which was consistent with the measured values of $DS_{nitroaryl}$ (Table 1).

In further investigations, we tried to clear up the mechanism of phototransformation reactions of the synthesized derivatives of cellulose. Figs. 2 and 3 represent the change in electronic absorption spectra of products *II* and *III* in the course of irradiation. The radiation caused a rapid change in electronic absorption spectrum of product *II* (Fig. 2) and the photolysis was accompanied by appearance of two new absorption bands with $\lambda_{max} = 277$ nm and 315 nm in the spectrum. On the basis of latest studies of photochemical reactions of 2-nitrobenzaldehyde with alcohols [8], we may assign these bands to the esters of 2-nitrobenzoic acid which are final products of the photolysis of the intermediate hemiacetal arising already in dark reaction [9]. As for the product *III*, the absorption bands of the products of photolysis overlap the band at $\lambda_{max} = 267$ nm. The characteristic increase in absorbance in the right shoulder of spectrum may be observed even in this case but without any identifiable maximum which would characterize the presence of the nitroso esters of benzoic acid. On the basis of literature data describing the photolysis of 2-nitrobenzyl compounds [3], we may assume that the mechanism of photodestructive processes is in this case different from that of product *II* and may be explained by the formation of nitroso aromatic compounds which undergo further dimerization to give azoxy and azo products. This assumption is also confirmed by brown-red colour of the original colourless film.
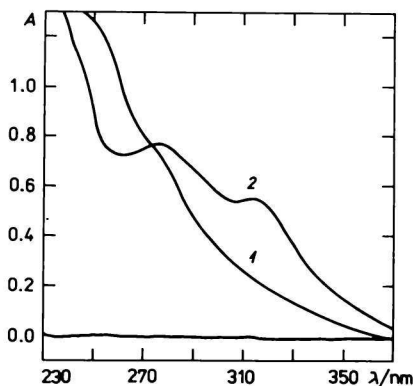

Fig. 2. Temporal change in electronic absorption spectrum of product *II* in the course of exposure: *1.* 0 min; *2.* 16 min.
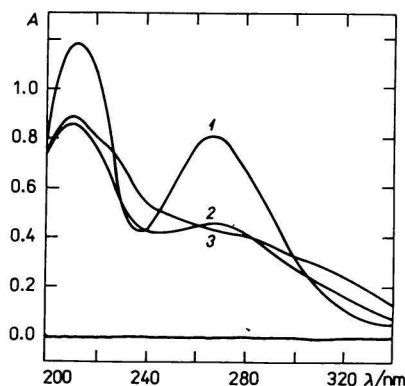
Fig. 3. Temporal change in electronic absorption spectrum of product *III* in the course of exposure: *1.* 0 min; *2.* 4 min; *3.* 32 min.

By exposing a film of acetylated HEC, we observed an increase in absorbance in the wavelength region 250—300 nm, which was characteristic of the substances containing aldehydic, ketonic, carboxylic and ester chromophores. In the infrared spectra of products *II* and *III* we observed in the course of photolysis a rapid growth of the absorption band in the wavenumber region 3100—3500 cm^{-1} with a maximum at 3440 cm^{-1}. In the wavenumber region 1600—1700 cm^{-1} a rise of the absorption band with a maximum at 1665 cm^{-1} was also observed. A rapid decrease in intensity of the bands $\tilde{v}_{as}(NO)_2 = 1540$ cm^{-1} and 1525 cm^{-1} of these derivatives took place during irradiation, which did not appear with the derivative *IV* ($\tilde{v}_{as}(NO_2) = 1530$ cm^{-1}). The kinetic curve representing the decrease in NO$_2$ groups of product *II* is shown in Fig. 4. An increase in absorption band with the maximum at $\tilde{v} = 3440$ cm^{-1} as well as in band with the maximum at $\tilde{v} = 1665$ cm^{-1} during irradiation was also observed in the infrared spectrum of acetylated hydroxyethylcellulose. These changes may be explained by photodestruction of the polymer chain which is succeeded by oxidation as evidenced by the
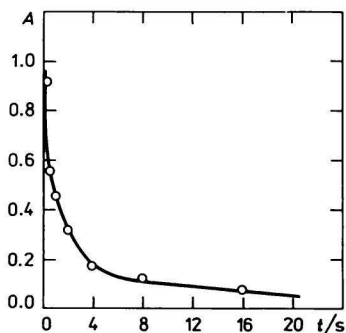

Fig. 4. Kinetic curve describing the decrease in NO$_2$ groups of product *II* at $\tilde{v}_{as}(NO_2) = 1540$ cm^{-1} of the infrared spectrum.

measured changes in ultraviolet spectrum during exposure. Similar conclusions are also presented in papers [10—12] which describe the photolysis of cellulose and its derivatives in the presence of air oxygen. After interruption of irradiation, no insoluble fractions were formed. The decrease in limiting viscosity numbers with irradiation time of products *I* and *II* is given in Table 3.

The photolysis of products *I* and *II* followed by gel permeation chromatography is represented in Figs. 5 and 6. A short-time effect of ultraviolet radiation on acetylated HEC did not bring about more significant changes in high-molecular fraction (Fig. 5, elution curves *1* and *2*). After 2 h, the high-molecular fraction increased in the region of elution volume of 90—150 cm^3 (elution curve *3*). More significant change is to be observed in composition of the low-molecular photodestruction products of acetylated HEC. Their identification is the topic of further experiments. On the other hand, the photolysis of product *II*, even after 15 min,

Table 3

Decrease in limiting viscosity numbers of products *I* and *II* measured in 1,2-dichloroethane in the course of irradiation

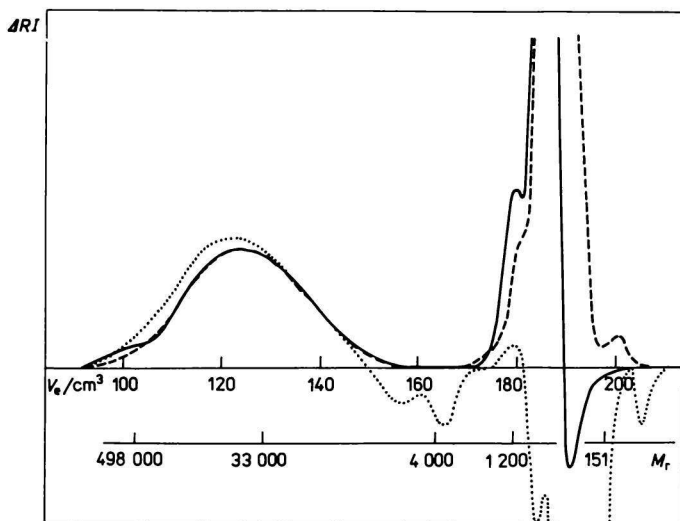| Irradiation time	$[\eta]/(100 \text{ cm}^3 \text{ g}^{-1})$	
min	*I*	*II*
0	0.898	0.268
4	—	0.229
8	0.765	0.185
16	0.732	0.172
32	0.606	0.164
64	0.508	0.160

Fig. 5. G.p.c. elution curves: original acetylated HEC (———); after 15 min irradiation (– – –); after 2 h irradiation (· · ·).

resulted in elimination of the maximum corresponding to the fraction with the highest molecular mass owing to photodestruction of the high-molecular fraction (Fig. 6, V_e region 110 cm³).

The assumption of intramolecular reduction of the nitro group was confirmed by measuring the e.s.r. spectra of irradiated products *II* and *III* in chloroform. The
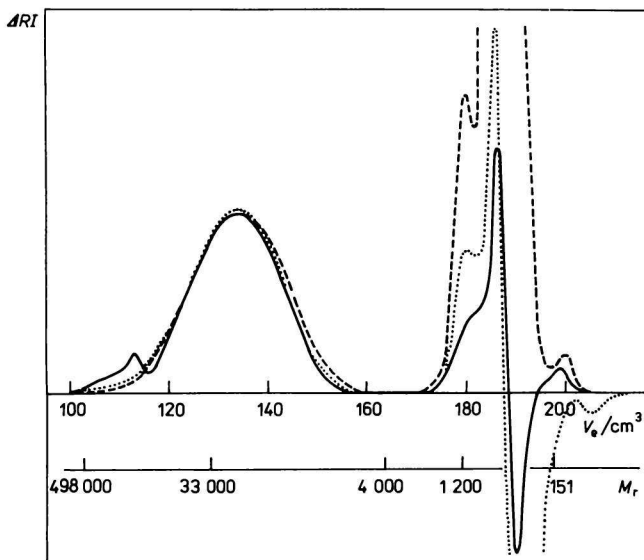
Fig. 6. G.p.c. elution curves: condensation product of acetylated HEC with 2-nitrobenzaldehyde (———); after 15 min irradiation (– – –); after 2 h irradiation (   ).

measured and simulated spectra of the trapped radical as well as the interaction constants are represented in Fig. 7. On the basis of literature data [13—15], this spectrum may be attributed to the phenylnitroxide radical which was revealed as intermediate in photoreduction of aromatic nitro compounds [16, 17]. This spectrum was not obtained with product *IV*. These results evidence that a hydrogen atom of the methylene or methine group directly bonded to aromatic ring participates in phototransformation reaction of the *o*-nitroaromatic chromophore and the reaction proceeds as intramolecular abstraction of hydrogen by the excited triplet of the nitro group like it is with 2-nitrobenzaldehyde or other derivatives of 2-nitrobenzene [3, 4, 8]. If these groups are replaced by other chromophore (*e.g.* —CO in product *IV*), the internal photoreduction of the nitro group does not take place.

On the basis of the changes in synthesized derivatives observed during irradiation, we may state that the pertinent photochemical transformations are connected with photodestruction and photooxidation of the arising intermediates. If some active 2-nitroaryl chromophores are present, a simultaneous photoreduction of the nitro group takes place.

By applying the synthesized derivatives to photomechanical reproduction, we laid these substances in the form of a thin film on anodically oxidized aluminium
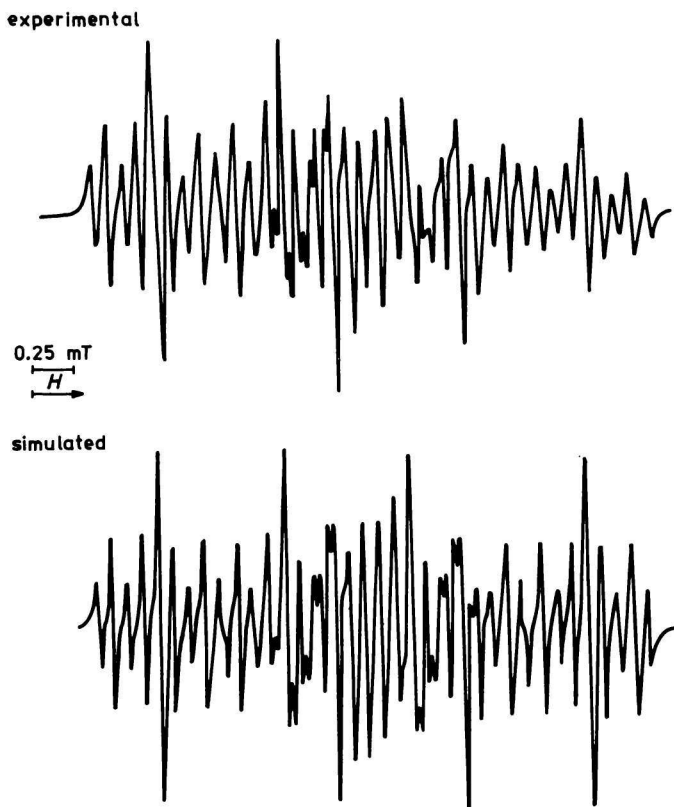
experimental

0.25 mT

$\overrightarrow{H}$

simulated

Fig. 7. Experimental and simulated spectrum of the phenylnitroxide radical.
(1 H) $a_H = 1.189$ mT; (1 N) $a_N = 0.844$ mT;
(2 H) $a_H = 0.307$ mT; (2 H) $a_H = 0.100$ mT;
p/p = 0.032 mT.

surface. By exposing through a positive stencil and developing in a 0.5 % aqueous solution of sodium hydroxide, we obtained a positive copy. By the use of derivatives *II* and *III*, the exposure time necessary for printing was reduced ten times when compared with the exposure time corresponding to derivative *I*.

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