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The Study of Photochemical Reactions in Polyoximurethane

E. M. Lipskerova and M. Ya. Melnikov

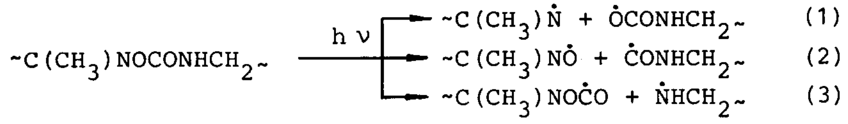
Department of Chemistry, Moscow State University, Leninskie Gory,
Moscow 117234, USSR

SUMMARY

The irradiation of polyoximurethane at 77K yields only iminoxy radicals. The gaseous products are CO and CO_2. The mechanism of photodegradation, including 2 initial processes of N-O and C-O bond scission is discussed. The ratio between the initial processes depends on the wavelength of the light used. Only the C-O bond cleavage results in polymer degradation.

INTRODUCTION

Photodegradative polyoximurethans with N-O bonds in the main chain have been obtained and an attempt was made to estimate the mechanism of photodegradation by analysing the photolysis products of a benzophenon oximphenyl urethane solution. It was found, that under UV irradiation the cleavage of N-O bond occured preferentially. The following 3 initial processes were suggested (Hong et al., 1972):



$$\sim C(CH_3)NOCONHCH_2\sim \xrightarrow{h\nu} \sim C(CH_3)\dot{N} + \dot{O}CONHCH_2\sim \quad (1)$$

$$\sim C(CH_3)NOCONHCH_2\sim \xrightarrow{h\nu} \sim C(CH_3)N\dot{O} + \dot{C}ONHCH_2\sim \quad (2)$$

$$\sim C(CH_3)NOCONHCH_2\sim \xrightarrow{h\nu} \sim C(CH_3)NO\dot{C}O + \dot{N}HCH_2\sim \quad (3)$$

The photodegradation of the polyoximurethane prepared from dimethylglyoxime and hexamethylene diisocyanate (POU) was studied at 77K, as it was excepted that the mechanism could be elucidated from the nature and reactions of the free radicals produced and from the gaseous product contents.

Experimental

The experiments were performed in thin-walled quartz tubes, evacuated to a pressure of 10^{-3} torr. High-pressure mercoury lamps with or without additional filters were used as UV and visible light

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sources. The ESR spectra were determined with a Varian E-3 ESR spectrometer using Varian variable temperature accessory. The nature and quantity of gases evolved were evaluated with a mass-spectrometer.

RESULTS AND DISCUSSION

Figure 1a presents the ESR spectrum of POU exposed either to light of a high-pressure mercury lamp without filter (λ >250 nm), or to light of wavelength longer than 280 nm at 77K.

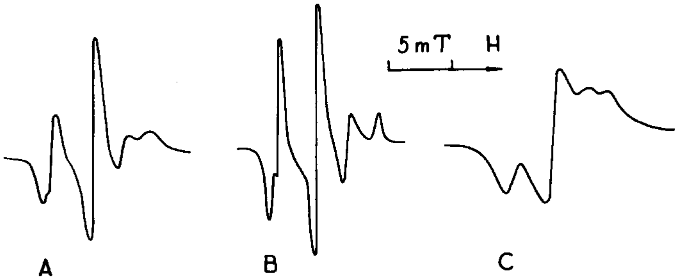

Fig. 1. The ESR spectra in polyoximurethane after irradiation with UV and visible light (λ >250 nm) at 77K (A); at 300K (B); after photolysis at 240 nm $\leq \lambda \leq$ nm (C)

It can be attributed to the iminoxy radical C(CH$_3$)NO. The coupling constant A = 44,4 and g-value 2,0028 are in substantial agreement with parameters, obtained for the iminoxy radical in γ-irradiated dimethylglyoxime (Miyagawa and Gordy, 1959). On heating the irradiated sample, or on irradiating the sample at room temperature, a better resolved hyperfine structure is obtained (Fig. 1b). A completely resolved spectrum can not be obtained, as the radicals disappear at 330K. The stable di-tert-butylnitroxy radical introduced into POU also does not produce a completely resolved spectrum below 360K. The rate of CO evolution correlates with the rate of radical formation (Table). The rate of CO$_2$ evolution is higher for the samples exposed to light of λ >280 nm.

Wavelength	The CO formation rate $\frac{\text{molecules}}{\text{sec}}$	The radicals formation rate $\frac{\text{radicals}}{\text{sec}}$	CO : CO_2
$240 \text{ nm} < \lambda < 270$ nm	$(1-3)\ 10^{13}$	$(1,5-2)\ 10^{13}$	1,4 - 1,6
$\lambda > 250$ nm	$(1-3)\ 10^{13}$	$(1-1,5)\ 10^{13}$	0,2 - 0,6
$\lambda > 280$ nm	10^{12}	$(2-3)\ 10^{12}$	0,1

Photolysis at $240 \text{ nm} \leq \lambda \leq 270$ nm produces a poorly resolved spectrum (Fig. 1c). The rate of CO_2 evolution is the lowest. Better resolution (Fig. 1a) can be obtained by subsequent exposure of the irradiated sample to light of $\lambda = 313$ nm (the total radical concentration being constant), or by heating the sample to 200K (the decrease in total radical concentration is about 50%). These results seem to contradict the mechanism, proposed by Hong et al.

The cleavage of N-O bond (1) should result in formation of the imino radical $\sim C(CH_3)\dot{N}$ stable at 77K and slowly photolysed (Neta and Fessenden, 1970) and of the $\sim CH_2NHCO\dot{O}$ radical which is known to decarboxylate immediately to produce the $\sim CH_2\dot{N}H$ radical. Since the CO_2 formation is found, but the ESR spectrum of imino radical is not observed, we suggest recombination of the radicals produced:

$$\sim C(CH_3)NOCONHCH_2\sim \xrightarrow{h\nu} \sim C(CH_3)\dot{N} + \dot{O}CONHCH_2\sim \longrightarrow$$

$$\sim C(CH_3)NNHCH_2\sim + CO_2 \qquad (4)$$

The formation of corresponding hydrazone was detected by Hong et al. A similar reaction can not be suggested for the initial cleavage of C-N bond (3), as spontaneous decarboxylation of $\sim C(CH_3)NO\dot{C}O$ radical is impossible (Griller and Roberts, 1972). Therefore we consider that reaction (3) is not essential in the POU photodegradation process. Reaction (4), however, would not result in a molecular weight decrease. Hence, the decrease in viscosity observed by Hong et al. should proceed by some other reaction.

The C-O bond scission (2) should produce an iminoxy radical, actually detected by its ESR spectrum and a $\sim CH_2NH\dot{C}O$ radical. The latter removes CO to produce a $\sim CH_2NH$ radical (Lipskerova and Melnikov, 1980). The CO liberation data indicates that reaction (2) prevails, when POU is irradiated with light of

240 nm $\leq \lambda \leq 270$ nm. The $\sim CH_2\dot{N}H$ radical produced reacts with the neighbour molecule to abstract the H atom. It was found that the most abstractable H atom in polyurethans was the H atom adjacent to the C atom, next to the NH group (Beachell and Chang, 1972). Therefore the $\sim C(CH_3)NOCONH\dot{C}HCH_2\sim$ radical should be formed. Since neither the ESR spectrum of this radical, nor the spectra of the radicals formed in its photodissociation ($\sim C(CH_3)NO\dot{C}O$, $\sim C(CH_3)\dot{N}$) are observed, we suggest, that the H atom, adjacent to the N atom, is abstracted to form the $\sim C(CH_3)NOCO\dot{N}CH_2\sim$ radical (R_1). Irradiating with UV light would dissociate R_1 to produce the iminoxy radical:

$$\sim C(CH_3)NOCO\dot{N}CH_2\sim \xrightarrow{h\nu} \sim C(CH_3)N\dot{O} + O\dot{C}NCH_2\sim \qquad (5)$$

The stationary concentration of R_1 can be estimated from the rate of iminoxy radical formation. When R_1 concentration is stationary, the rates of the iminoxy radical formation in reactions (2) and (5) are equal and the rate of the iminoxy radical formation observed is twice as large as the initial rate of R_1 formation. The following assumptions are made: the extinction coefficient of R_1 $\varepsilon = 10^3$ l mol^{-1} cm^{-1} (for a $CH_3CO\dot{N}H$ radical $\varepsilon = 2 \times 10^3$ l mol^{-1} cm^{-1} - Hayon et al., 1970). The quantum yield of reaction (5) is $10^{-1} - 10^{-2}$, which is typical for such reactions (Lipskerova and Melnikov, 1980). The R_1 concentration is estimated to be about 5% of the total radical concentration after 10 minutes exposure of POU to light of 240 nm $\leq \lambda \leq 270$ nm. It is too low to be detected by ESR. An acceleration in the iminoxy radicals formation also can not be observed. Reactions (2) and (5) should result in POU degradation.

The formation of 2 excited states with different electron density distribution can be the reason of the 2 simultaneous initial processes (1) and (2). This suggestion is supported by the fact, that the absorption spectrum of POU exhibits 2 bands, the absorption maxima being 280 nm and 230 nm (Hong et al., 1972).

The cause of the poor resolution of the spectrum 1C is not clear. Perhaps, the 2 iminoxy radicals produced from the 2 neighbour H-bonded molecules in reaction (2) and (5) are so close to each other that the dipole widening is possible. Subsequent irradiation with light absorbed by iminoxy radicals, but not by POU ($\lambda = 313$ nm) induces syn- anti-isomerisation of the radicals increasing their separation. On heating the sample the neighbouring radicals recombine improving the spectrum resolution.

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