PHOTOCHEMICAL RESTITUTION OF THE RADIOTHERMAL LUMINESCENCE PEAK IN DIETHYL SULFOXIDE

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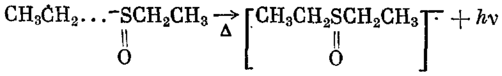
An anion-radical pair (addition product) has previously been detected in γ-irradiated DMSO-d_6 [1]. We have observed stabilization of the addition product $CH_3\dot{C}H_2\ldots{}^{-}\underset{\underset{O}{\|}}{S}CH_2\dot{C}H_3$ (I) in γ-irradiated diethyl sulfoxide (DESO) at 77°K.

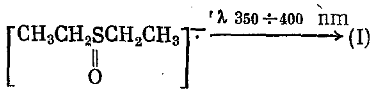
The addition product (I) is associated with a red coloration of DESO specimens and an anomalous EPR spectrum for the ethyl radical with a hyperfine interaction constant on the β-protons $a_{\beta\text{-}H} = 21$ Oe. There is a peak at 153°K on the radiothermal luminescence (RTL) curve of γ-irradiated DESO. Examination of the temperature variations of the EPR spectrum enables us to link this peak with transformation reactions of (I) to the molecular anion radical



$$CH_3\dot{C}H_2\ldots{}^{-}\underset{\underset{O}{\|}}{S}CH_2CH_3 \xrightarrow[\Delta]{} \left[CH_3CH_2\underset{\underset{O}{\|}}{S}CH_2CH_3\right]^{\dot{-}} + h\nu$$

(I)

The action of 350-400 nm light (DRSh-1000 lamp, UFS-1 filter) on the γ-irradiated DESO specimens which had first been heated to 173°K (a temperature above the RTL peak) results in restoring the signal of addition product (I) in the EPR spectrum and correspondingly the RTL peak at 153°K. In this case, the molecular anion radical is once more converted to (I)



$$\left[CH_3CH_2\underset{\underset{O}{\|}}{S}CH_2CH_3\right]^{\dot{-}} \xrightarrow{\lambda\ 350\div400\ \mathrm{nm}} (I)$$

Thus, we have detected a rare example of photochemical reversibility of radiothermal luminescence. We should expect a similar restitution of RTL peaks in other cases of anion-radical pair stabilization as well.

LITERATURE CITED

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