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Abstract

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TWO-QUANTUM PHOTOCHEMICAL PROCESSES IN FROZEN SOLUTIONS OF TRIPHENYLMETHANE COMPOUNDS

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In work ([1]) it was established that the yield of the triphenylmethyl radical $(C_6H_5)_3\dot{C}$ and of some of its amino derivatives $[C_6H_4N(CH_3)_2]_3\dot{C}$ upon photoirradiation of frozen (77°K) ethanolic solutions of triphenylmethane (I) and of the leuco base of crystal violet (II) is proportional to the instantaneous concentration of molecules in the triplet state ($\dot{R} \sim n_t$) and to the square ($K = 1.75 \pm 0.25$) of the intensity of the exciting flux ($\dot{R} \sim n_t I \sim I^2$). It was suggested that the intramolecular process of formation of triphenylmethyl-type radicals is a two-photon process and occurs at the triplet excited level. The hypothesis that two-photon excitation (according to the scheme $S^0 \xrightarrow{h\nu_1} S^* \rightsquigarrow T \xrightarrow{h\nu_2} T^* \rightsquigarrow R$) is responsible for a photochemical reaction was first put forward by G. Lewis and M. Kasha ([2]), who observed a quadratic dependence on the intensity of the exciting flux for the photodecomposition of α-nitronaphthalene. The same dependence of the yield of a photoprocess on the density of the exciting light was recently obtained ([1, 3]) for the amine-sensitized dehydrogenation reaction of alcohols ([4]). However, a quadratic dependence of a photoprocess on light intensity is not unambiguous proof of its two-photon character (participation of the T^* level). Photochemical processes with a quadratic dependence on light intensity are possible, but occurring according to a different scheme, not requiring participation of the excited triplet state ([5, 6]).

In the present work new experimental facts are presented which prove the participation of the T^*-state in the intramolecular process of formation of triphenylmethyl radicals during the photolysis of triphenylmethane and other $(C_6H_5)_3C{-}X$ compounds, and a possible mechanism is considered for the formation of radicals upon rupture of the central bond in amino derivatives of triphenylmethane (compound II and others).

We carried out photoirradiation of frozen, evacuated solutions of $(C_6H_5)_3C{-}H$ in ethanol ($T = 77°K$) with two ultraviolet sources. In the first channel, exci-

tation was carried out in the absorption band of triphenylmethane (λ_{max} = 260 mμ) using a UFS-1 light filter or the total light of a PRK-2 mercury lamp; corresponding to this excitation, phosphorescence of $(C_6H_5)_3 \equiv C{-}H$ ($\lambda_{max} \simeq 400$ mμ, $\tau = 5.7 \pm 0.2$ sec) was observed, as well as a time increase in the intensity of luminescence of the $(C_6H_5)_3\dot{C}$ radical (the first band of the spectrum, $\sim$ 514 mμ, was recorded) ([7]). In the absorption spectrum of the radicals recorded under these conditions, there is an intense band in the region $\sim$ 340 mμ and weak bands in the region of 500 mμ ([8], [9]). It was assumed that under the experimental conditions the luminescence intensity in the 514 mμ band is proportional to the yield of $(C_6H_5)_3\dot{C}$ radicals. In the second channel, using a more powerful DRSh-500 mercury lamp, irradiation was carried out outside the region of the main absorption bands of triphenylmethane (filters: 365, 313, and BS-4 >> 280 mμ), but could excite the luminescence of the radicals. Prolonged irradiation (5 min) only in the second channel does not lead to the appearance of triphenylmethyl radicals. However, upon simultaneous irradiation in both channels the yield of $(C_6H_5)_3\dot{C}$ radicals increases significantly—

Table 1

No.	Irradiation region and emission filter	Yield $t_{irr} = 30$ sec
	$(C_6H_5)_3C\cdot$. Luminescence intensity in the 514 mμ band	
1	> 280 mμ (BS-4)	0
2	250–400 mμ (UFS-1)	1.0
3	BS-4 after 2 and complete disappearance of phosphorescence	1.0
4	UFS-1 + BS-4 simultaneously	2.0
5	UFS-1 + ZhS-11 (> 400 mμ)	2.0
6	UFS-1 + ZhS-18 (> 500 mμ) simultaneously	1.0
	$[C_6H_4N(CH_3)_2]_3C\cdot$. Luminescence intensity in the 580 mμ band	
1	> 350 mμ (BS-7)	0
2	> 250 mμ (UFS-1)	1.0

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

No.	Irradiation region and emission filter	Yield $t_{irr} = 30$ sec
3	BS-7 after 2 and complete disappearance of phosphorescence	2.3
4	UFS-1 + BS-7 simultaneously	2.1

in comparison with the yield upon irradiation only in the region of the absorption spectrum. Such an increase in the yield of triphenylmethyl radicals is not observed in the case where irradiation in the second channel is carried out not simultaneously, but after switching off the first source, after some time (15-20 sec), necessary for the complete disappearance of the phosphorescence of triphenylmethane. The experimental facts set forth are illustrated by the data of Table 1. The kinetics of the secondary process of the increase in the luminescence intensity of the $(C_6H_5)_3C\cdot$ radical can be described, under the condition that the second source is switched on immediately after cessation

Fig. 1. Kinetics of accumulation of the $(C_6H_5)_3C\cdot$ radical (luminescence in the 514 mμ band) upon photoirradiation of an ethanolic solution of triphenylmethane, $C = 10^{-3}$ M, $T = 77°$K.
a—irradiation (1-2 min) in the region > 280 mμ (filters UFS-6, BS-4, recorded at high amplification); *b*—excitation in the long-wavelength absorption band of triphenylmethane (total irradiation, UFS-1); for the kinetics of the process see (1). *v*—irradiation in the region 313, 365 mμ (in comparison with *b*, the amplification coefficient is increased by a factor of 3). The solid curve is immediately after *b*; the dash-dotted curve is after *b* and complete disappearance of phosphorescence; the dashed curve is the decay of phosphorescence in the 400-420 mμ region.

Fig. 2. E.p.r. spectra of the photoirradiation products of an ethanolic solution of leuco-base of crystal violet (10^{-3} M, $T = 77°$K).
a—after 10 sec excitation in the 313 mμ region; *b*—after 10 sec irradiation in the 405 mμ region; *v*—after freezing to the glass-transition temperature of ethanol.

of excitation in the first channel (Fig. 1, curve *v*). In this case it turned out that the curve obtained with secondary illumination is an exponential ($e^{-t/\chi}$), and that the mean value of the exponential factor $\chi = 6 \pm 1$ sec agrees well with the lifetime of the triplet state of triphenylmethane. For comparison, Fig. 1 gives the phosphorescence decay curve of triphenylmethane, recorded under the same conditions. Increasing the concentration of the solution (in the range 10^{-4}

-10^{-2} M), as well as changing the intensity of the flux in the second channel (approximately by a factor of 30), does not

have no substantial effect on the decay curves of the phosphorescence and the growth of the luminescence of the $(C_6H_5)_3C$-radical under secondary illumination. The deviations from the mean value of χ observed in these experiments are small and may be explained by experimental errors. When polyisobutylene was used as the medium, the following data were obtained: $\tau_{\text{phosph}} = 5.5 \pm 0.5$ sec; $\chi = 6 \pm 0.5$ sec; moreover, just as for the ethanol solution, no dependence of χ on the intensity of the exciting and secondary fluxes was observed. In an isopentane solution it is not possible to obtain curve 6 for the increase in luminescence brightness of the $(C_6H_5)_3C$-radical, since even at $T = 77^\circ$ K there occurs a gradual decrease in the luminescence intensity of triphenylmethyl radicals (this process proceeds in the dark), probably owing to their recombination in the solvent cage ([10]). In an ethanol solution at 77° K there is no recombination of triphenylmethyl radicals. Recombination in isopentane excludes the possibility of observing curve 6 under additional illumination. In addition, in an isopentane solution at $T = 77^\circ$ K there is a substantial decrease in the yield and in τ of the phosphorescence ($\tau \approx 1$ sec) of triphenylmethane. In accordance with this, the yield of $(C_6H_5)_3C$-radicals decreases sharply in an isopentane solution at 77° K in comparison with the yield in an ethanol solution under irradiation under identical conditions, as we have already noted earlier ([1,7]). The absorption spectra of I in isopentane and ethanol (recorded at $T = 293^\circ$ K) differ little.

The same experiments were carried out by us with amino-substituted triphenylmethane (compound II and others). The luminescence spectra of the photolysis products of these compounds, studied by us earlier ([7]), were assigned to radicals of the triphenylmethyl type, formed from these compounds upon rupture of the $\equiv$C—H bond and obtained by Weitz ([11]) and Wieland ([12]) by chemical means. Under additional illumination (365, 405 mμ, BS-7) of frozen ethanol solutions of these compounds, as in the case of triphenylmethane, an increase is observed in the luminescence of the radical $(C_6H_4—N(CH_3)_2)_3C\cdot$ (in the band at 580 mμ); however, this process does not depend on the moment at which the secondary illumination is switched on: immediately after cessation of excitation of the initial solution in the absorption band (313 mμ; UFS-1), or after a long time following the disappearance of the phosphorescence ($\lambda_{\max} \simeq 430$ mμ, $\tau \simeq 3 \pm 0.2$ sec) (cf. Table 1). In the dark, without irradiation, process 6 does not occur.

In the absorption spectra of photoirradiated samples I and II, no substantial changes upon secondary illumination can be observed.

In studying the e.p.r. spectra on a high-resolution superheterodyne-type setup ([13]), it was found that, as we had already noted earlier ([1]), upon photoirradiation of ethanol solutions of compound II, CH_3—$\dot{C}$HOH radicals are generated in high yield (the yield of these radicals upon photoirradiation of an ethanol solution of compound I is very small). At short irradiation times this process can be subdivided into two stages: initially ($t_{\text{irr}} = 3$-5 sec, $\lambda_{\text{exc}} = 313$ mμ) a singlet

line is formed ($g \simeq 2.00$; $\Delta H \simeq 17$ oersted), then, under additional irradiation ($\lambda = 405$ mμ), the singlet in the e.p.r. disappears and a five-line spectrum of CH_3—$\dot{C}HOH$ appears. Further irradiation in the region > 380 mμ does not lead to a change in the e.p.r. spectrum, whereas under prolonged irradiation in the region ~ 300 mμ the five-line structure becomes more complicated.

A similar two-stage process of formation of matrix radicals was observed upon photoirradiation of an ethanol solution of triphenylamine ([9]) and was explained by decomposition of the radical complex formed in the primary act upon detachment of a triplet amine molecule, forming a hydrogen bond with an alcohol molecule already in the ground state ([14]), of hydrogen from the O—H group of the alcohol, with subsequent conversion into $CH_3\dot{C}HOH$ radicals ([15]). Another mechanism is also possible for the formation of alcohol $CH_3\dot{C}HOH$-radicals—as a result of a reaction of "hot" methyl radicals

radicals formed upon dissociation of the group $N(CH_3)_2$ (16), or H atoms formed upon dissociation of CH, with alcohol molecules.

This mechanism is less general, since it is not applicable to triphenylamine; moreover, it does not explain the two-stage character of the process. A comparison of data obtained from luminescence and by the EPR method under secondary illumination makes it possible to suggest that the second stages of the processes of formation of the radicals $[C_6H_4$—$N(CH_3)_2]_3 \equiv C\cdot$ and $CH_3\dot{C}HOH$ upon photoirradiation of frozen ethanolic solutions of compounds of type II are related.

However, determination of the quantum yields of the radicals led to the following results: $\gamma_{Ar_3C\cdot} \sim 3 \cdot 10^{-4}$; $\gamma_{CH_3\dot{C}HOH} \sim 2 \cdot 10^{-2}$; such a difference in quantum yields implies a difference in the mechanisms of their formation (the radicals are probably formed by competing processes). The existence of the process of formation of $Ar_3C\cdot$ in a hydrocarbon matrix leads to the same conclusion (matrix radicals are not observed under these conditions).

Triphenylmethyl-type radicals cannot be unambiguously isolated in the EPR spectrum at 77°K, probably because of the considerable relaxation time of these radicals in the solid phase (17).

The experimental data presented above can be explained on the assumption that formation of triphenylmethyl radicals occurs only after the molecule has been transferred to the triplet excited level as a result of triplet–triplet absorption, which, according to our data, should lie in the region of ~ 450 m (Table 1). In the literature, however, there are no data concerning $T \rightarrow T^*$ absorption of triphenylmethane. At the triplet excited level the molecule dissociates with formation of the radical $(C_6H_5)_3C\cdot$, which is stabilized in the solid matrix, and $H\cdot$, which diffuses readily at 77°K and then recombines with formation of H_2. Thus, $(C_6H_5)_3C\cdot$ radicals are formed in the photolysis of frozen triphenylmethane solutions by a two-photon mechanism. We are currently carrying out work to elucidate the mechanism of formation of triphenylmethyl-type radicals in amino-substituted triphenylmethane. This process probably takes place

without participation of the triplet excited level and is two-stage.

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Note: Figure translations are in progress. See original paper for figures.