

## STABILIZATION AND PHOTOCHEMICAL REACTIONS OF THIYL RADICALS IN GLASSY MATRICES AT 77 K

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### Summary

The possibility of stabilization of thiyl radicals formed during the photolysis of thiol solutions at a wavelength  $\lambda = 253.7$  nm in glassy matrices at 77 K was shown by means of electron spin resonance and UV spectroscopy. The main alternative process is the formation of adducts  $\text{RSS}(\text{H})\text{R}$  ( $\text{R} \equiv \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, \text{tert-C}_4\text{H}_9$ ) in thiol self-associate. Stabilized alkylthiyl radicals are able to enter into photochemical reactions leading to C—C or C—H bond rupture in the position  $\beta$  to the sulphur atom. The ability of stabilized thiyl radicals to enter into photochemical reactions is suggested as the reason for their low concentrations in dilute thiol solutions in alcohol and hydrocarbon matrices subjected to photolysis at  $\lambda = 253.7$  nm at 77 K.

### 1. Introduction

Thiyl radicals are widely known to be the primary products of photodissociation of thiols, sulphides and disulphides [1]. However, reliable data on the stabilization of thiyl radicals formed during photolysis of sulphur-containing compounds in glassy matrices are lacking. From an analysis of data reported in the literature it is possible to give two main explanations of the situation. First, the thiyl radicals are difficult to detect; a considerable anisotropy of the  $g$  tensor [2 - 8] leads to a wide electron spin resonance (ESR) spectrum in glassy matrices, and small extinction coefficients ( $290 - 580 \text{ M}^{-1} \text{ cm}^{-1}$  [9]) make it difficult to register the radicals by UV absorption spectroscopy. Second, thiyl radicals are able to enter into secondary reactions, yielding products which have sometimes been incorrectly identified as thiyl radicals. One of these reactions may be the formation of adducts with thiols or sulphides [8, 10, 11]:



where  $\text{R} \equiv$  alkyl. Further reactions of the adducts produce perthiyl radicals  $\text{R}\dot{\text{S}}_2$ . In addition, thiyl radicals are able to enter into photochemical reactions by the action of light with a wavelength  $\lambda < 360$  nm [3, 5].

The aims of our investigation were (1) to elucidate the effect of the nature of the matrix on the effectiveness of the stabilization of the thiyl radicals formed in the photolysis of thiol solutions in various matrices and (2) to establish the mechanism of the secondary photochemical and thermal reactions of the thiyl radicals formed in the photolysis of sulphur-containing compounds.

## 2. Experimental details

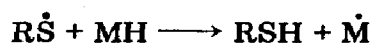
The initial thiols RSH ( $R \equiv H, CH_3, C_2H_4, i-C_3H_7, tert-C_4H_9$ ), the solvents 3-methylpentane (3MP), perfluorodimethylcyclohexane (PFDMCH) and 4-methylheptan-4-ol (4MH) and the salts LiCl and NaClO<sub>4</sub> were purified by standard methods. The purified solvents did not absorb light with  $\lambda > 250$  nm and when frozen formed good glasses. The techniques of sample preparation and spectral measurements were described earlier [11]. Low pressure mercury lamps with high frequency excitation ( $\lambda = 253.7$  nm) and high pressure mercury lamps equipped with filters to separate the mercury spectral lines were used as sources of light. Ferrioxalate actinometry was conducted under conditions similar to those of the sample photolysis.

## 3. Results and discussion

The primary photochemical process taking place in the absorption of light with  $\lambda = 253.7$  nm by thiols is known to be the dissociation of the S—H bond [1]:

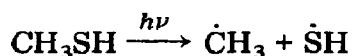


To establish whether thiyl radicals in glassy matrices can be registered by ESR and UV spectroscopy, we investigated the photolysis at  $\lambda = 253.7$  nm of dilute (about 0.05 M) solutions of hydrogen sulphide and methane thiol in inert matrices (aqueous 5 M LiCl or 8 M NaClO<sub>4</sub> frozen at 77 K) and of a solution of methane thiol (about 0.05 M) in a PFDMCH matrix. We chose 5 M LiCl and 8 M NaClO<sub>4</sub> matrices on the basis of the following considerations. First, the ability of these matrices to form hydrogen bonds with thiols may facilitate the ESR registration of the radicals R $\dot{S}$  produced in the photolysis because of the partial elimination of the  $\pi$  orbital degeneracy of the thiyl radicals in the media [8]. Second, because the matrices form hydrogen bonds with RSH the self-association of thiols in aqueous salt matrices decreases compared with that in hydrocarbon matrices and thus the probability of secondary reactions of the thiyl radicals in the thiol self-associates decreases. Third, the reaction



which is considered to be the main reaction in the photolysis of dilute solutions of thiols and sulphides in the 3MP matrix [10, 12] cannot take place in aqueous salt matrices. A further advantage of the 8 M NaClO<sub>4</sub> matrix is its ability to stabilize hydrogen atoms produced in the photolysis of thiol solutions (eqn. (1)).

Irradiation of hydrogen sulphide and methane thiol solutions at  $\lambda = 253.7$  nm in 8 M NaClO<sub>4</sub> at 77 K produces intense signals for the hydrogen atoms, whose concentration reached  $3 \times 10^{16}$  cm<sup>-3</sup>. In PFDMCH and 5 M LiCl matrices the signals due to the hydrogen atoms quickly disappeared after the photolysis was stopped. No other significant changes were observed in the ESR spectra for the UV photolysis at 77 K of hydrogen sulphide in 5 M LiCl, hydrogen sulphide and methane thiol in 8 M NaClO<sub>4</sub> or methane thiol in PFDMCH solutions. The ESR spectra of the photolysed solution of methane thiol in 5 M LiCl shows signals due to  $\dot{\text{C}}\text{H}_2\text{SH}$  radicals (triplet,  $a_{\text{H}}^{\alpha} = 19$  G (2 H)), the concentration of which depends linearly on time for short photolysis durations, and signals due to  $\dot{\text{C}}\text{H}_3$  radicals, for which the dependence of the concentration on the photolysis duration exhibits an induction period (Fig. 1). The kinetics for the accumulation of the methyl radicals exclude the possibility that their formation is predominant in the primary photochemical process, as was supposed earlier [13]:



The ESR spectra of radicals with spin localized on the sulphur atom were not registered either.

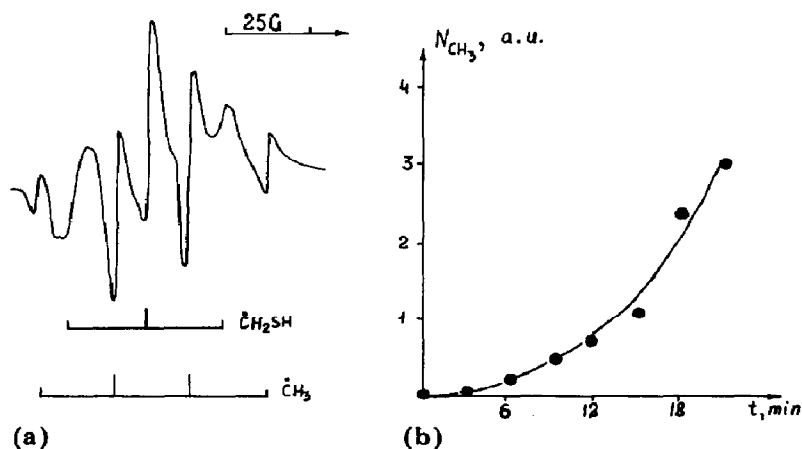


Fig. 1. (a) ESR spectrum of a solution of methane thiol UV irradiated ( $\lambda = 253.7$  nm) at 77 K in a 5 M LiCl matrix; (b) kinetics for methyl radical formation in this system.

Photolysis of the hydrogen sulphide and methane thiol solutions in 5 M LiCl and of the methane thiol solution in PFDMCH generates an absorption band in the UV spectra in the region  $\lambda < 400$  nm with a maximum at 300 - 330 nm (Fig. 2). The intensity of the absorption bands depends linearly on time for short photolysis durations. This allows us to assign the absorption

bands to the primary products of the photolysis of hydrogen sulphide and methane thiol, *i.e.* stabilized thiyl radicals which absorb light in this spectral region [9, 14].

The changes in the UV absorption spectra of the photolysed solutions of hydrogen sulphide and methane thiol in the 8 M NaClO<sub>4</sub> matrix are within the measurement error. This should probably be attributed to the low concentration of stabilized thiyl radicals resulting from the poor solubility of thiols and possibly from the low quantum yields of photolysis in this matrix.

The results obtained support the conclusion of Wheaton and Ormerod [3] that the ESR spectra of randomly oriented thiyl radicals cannot be registered at relatively low concentrations because the spectrum is too wide. In this case reactions of thiyl radicals producing other radicals which are easily registered by ESR spectroscopy should be accompanied by an increase in the integral intensity of the signals in the spectra. In addition to the recombination of thiyl radicals, the following reactions may also take place in aqueous salt matrices:



The predominant course of the reactions depends on the pH of the medium. Indeed, when hydrogen sulphide solutions in 8 M NaClO<sub>4</sub> and 5 M LiCl matrices and methane thiol solutions in 5 M LiCl and PFDMCH matrices are UV irradiated at 77 K ( $\lambda = 253.7$  nm) and the temperature is then increased until the matrices soften, bands are generated at  $\lambda_{\max} = 370 - 380$  nm and  $\lambda_{\max} = 390 - 410$  nm respectively (Fig. 3). Figure 4 represents the ESR spectra of particles formed in these systems. Their formation becomes more prominent with increasing pH of the medium and is accompanied by an increase in the integral intensity of the ESR spectra. By comparing the observed ESR and UV absorption spectra with the UV [9, 15] and ESR [16] spectra reported in the literature we consider that thawing of the UV-

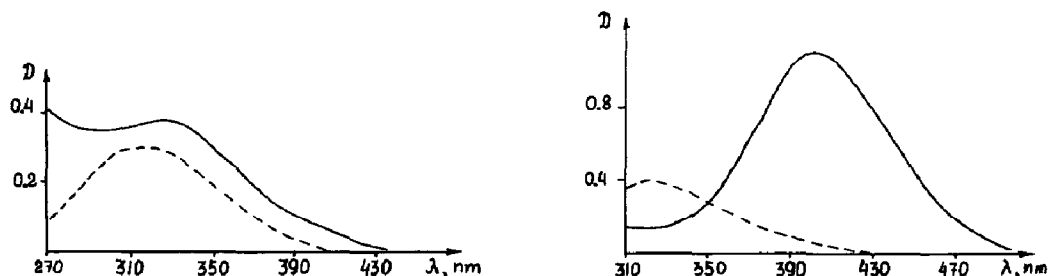


Fig. 2. UV absorption spectra after the action of light with  $\lambda = 253.7$  nm on solutions of methane thiol (—) and hydrogen sulphide (---) in a 5 M LiCl matrix at 77 K.

Fig. 3. Absorption spectra of solutions of methane thiol UV irradiated ( $\lambda = 253.7$  nm) at 77 K in 5 M LiCl before (—) and after (---) the sample has been heated to the temperature at which the matrix softens.

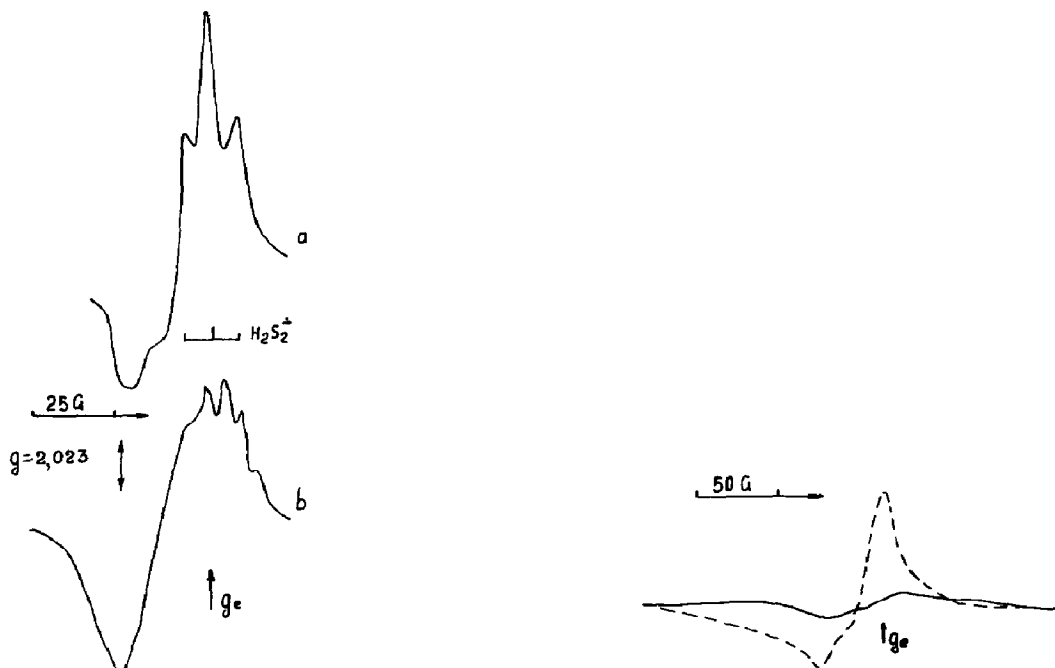


Fig. 4. ESR spectra of solutions of hydrogen sulphide (curve a) and methane thiol (curve b) UV irradiated ( $\lambda = 253.7$  nm) at 77 K in 5 M LiCl after the samples have been heated to the temperature at which the matrix softens and subsequently cooled to 77 K.

Fig. 5. ESR spectra of solutions of methane thiol UV irradiated ( $\lambda = 253.7$  nm) at 77 K in PFDMCH before (—) and after (---) the sample has been heated to the temperature at which the matrix softens.

irradiated solutions of hydrogen sulphide and methane thiol in the aqueous salt matrices produces disulphide anions  $\text{H}_2\text{S}_2^-$  and  $\text{CH}_3\text{SSCH}_3^-$  by reaction (3). This confirms the presence of stabilized thiyl radicals in the matrices after photolysis of the thiol solutions at 77 K.

As reported in refs. 10, 11 and 17 - 19, photolysis of concentrated solutions of thiols in hydrocarbon matrices at 77 K generates absorption bands with a maximum near 400 nm. These bands were assigned either to the thiyl radicals [10, 17, 18] or to the adducts of structure  $\text{RSS}(\text{H})\text{R}$  [11, 19]. A wide asymmetric signal in the ESR spectrum [11] corresponds to the bands. Thawed UV-irradiated ( $\lambda = 253.7$  nm) solutions of methane thiol in PFDMCH give a similar ESR spectrum (Fig. 5). Neither the ESR spectrum nor the absorption spectrum of the particles coincides with the data reported in the literature for thiyl radicals. We are of the opinion that the absorption bands at  $\lambda = 400$  nm and the wide asymmetric signals in the ESR spectra of UV-irradiated solutions of thiols in the hydrocarbon matrices should be assigned to adducts  $\text{RSS}(\text{H})\text{R}$ . The shape of the absorption band is independent of the thiol concentration within the *tert*-butyl thiol concentration range investigated in the 3MP matrix (0.05 - 1 M). This means that the spectrum must be assigned to the same radical at all *tert*-butyl thiol concentra-

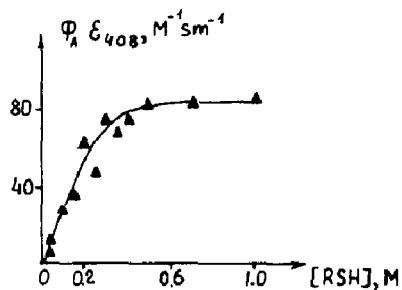
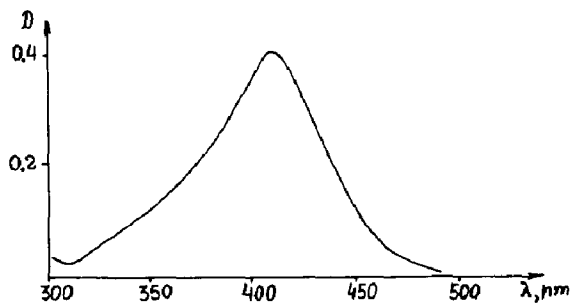


Fig. 6. UV absorption spectrum of  $(\text{CH}_3)_3\text{CS}(\text{H})\text{C}(\text{CH}_3)_3$  radicals in a 3MP matrix at 77 K.

Fig. 7. Effectiveness of  $\text{RSS}(\text{H})\text{R}$  adduct formation under the action of light ( $\lambda = 253.7$  nm) on *tert*-butyl thiol solutions in a 3MP matrix.

tions (Fig. 6). We determined  $\phi_A \epsilon_{408}$  (where  $\phi_A$  is the quantum yield of the adducts and  $\epsilon_{408}$  is the extinction coefficient of the adducts at the maximum of the absorption band) for various concentrations of *tert*-butyl thiol in 3MP (Fig. 7) from the initial linear plots of the dependence of the optical density at the maximum of the absorption band at  $\lambda = 408$  nm on the time of photolysis.  $\phi_A$  was determined using the ESR spectroscopy data as the difference

$$\phi_A = \phi_R - \phi_M$$

where  $\phi_R$  and  $\phi_M$  are the quantum yields of the paramagnetic centres and 3-methylpentyl radicals respectively in the photolysis of *tert*-butyl thiol solutions in 3MP. The possible route to the formation of 3-methylpentyl radicals is the reaction between hydrogen atoms formed in the primary photochemical process and matrix molecules:



In the calculation of  $\phi_A$  we supposed, in accordance with the results discussed earlier, that the thiol radicals which may be stabilized under the given conditions do not contribute considerably to the net ESR spectrum. Using  $\phi_A$  we calculated the extinction coefficient  $\epsilon_{408} = 7100 \pm 600 \text{ M}^{-1} \text{ cm}^{-1}$  for adducts  $\text{RSS}(\text{H})\text{R}$  in solutions of *tert*-butyl thiol in 3MP. The value obtained is in good agreement with that of the extinction coefficient attributed to the radical  $\text{RSS}(\text{H})\text{R}$  formed by the pulse radiolysis of aqueous acid solutions of DL-lipoic acid ( $\lambda_{\text{max}} = 385$  nm;  $\epsilon_{385} = 6900 \text{ M}^{-1} \text{ cm}^{-1}$  [9]). The photolysis of the thiol and hydrogen sulphide solutions in the 4MH matrix yields adducts of an analogous structure. The maxima of the absorption bands of the adducts  $\text{RSS}(\text{H})\text{R}$  in 4MH lie at 355 nm ( $\text{R} \equiv \text{H}$ ), 395 nm ( $\text{R} \equiv \text{CH}_3$ , *i*- $\text{C}_3\text{H}_7$ ) and 390 nm ( $\text{R} \equiv \text{C}_2\text{H}_5$ , *tert*- $\text{C}_4\text{H}_9$ ).

By assuming that the extinction coefficients of the adducts in the 3MP and 4MH matrices are equal, we obtain a quantum yield for adduct formation in 3MP 6.1 times greater than that for the same concentration of *tert*-butyl thiol in the 4MH matrix. This is in good agreement with the supposi-

tion that, in matrices which form hydrogen bonds with thiols, the thiols self-associate to a lesser degree.

The presence of hex-1-ene (0.2 M) in 0.2 M solutions of thiols in 4MH reduces the formation of adducts by nearly 50%. Hex-1-ene acting as an acceptor of thiyl radicals



competes with thiol to capture the thiyl radicals.

Thus the stabilization of the thiyl radicals is most probable in matrices which inhibit the thiol self-association by forming hydrogen bonds with the thiol. The thiyl radicals are stabilized with difficulty in hydrocarbon matrices. In particular, when the concentration of *tert*-butyl thiol in 3MP exceeds 0.2 M,  $\phi_A \geq \phi_M$ , and this is indicative of the almost complete self-association of the thiol.

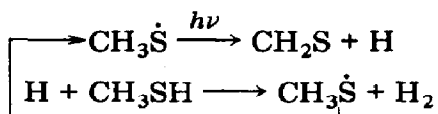
Thiyl radicals in hydrocarbon and alcohol matrices may form not only as a result of the primary photochemical process but also as a result of secondary reactions between the radicals of the matrix and the thiol:



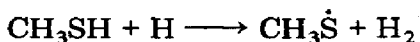
In fact, the concentration of 3-methylpentyl radicals produced by the photolysis of the thiol solutions in 3MP decreases as the samples are maintained at 77 K. This is accompanied by the formation of a number of  $\text{RSS}(\text{H})\text{R}$  adducts and a reduction in the total number of paramagnetic centres. The latter takes place to the greatest degree in dilute solutions (up to 50% in a 0.01 M solution of *tert*-butyl thiol in 3MP). A further increase in the temperature to 88 K, however, leads to the formation of an additional number of adducts and the integral intensity of the ESR spectra increases. This may be the result of further reactions of the stabilized thiyl radicals produced in reaction (6). The observed effect is greatest at *tert*-butyl thiol concentrations of 0.1 - 0.15 M in 3MP. The effect is reduced at low concentrations possibly because of the increased contribution of the recombination reactions to the processes occurring during thawing. High concentrations of thiol decrease the probability of production of the stabilized thiyl radicals by reaction (6) owing to the thiol self-association. In this case the adducts are already formed at 77 K. Therefore, the number of paramagnetic centres in the concentrated solutions of thiols maintained at 77 K after photolysis is reduced to a lesser extent.

To investigate the photochemical reactions of the thiyl radicals, solutions of thiols in various matrices were subjected to photolysis by light with  $\lambda = 253.7$  nm and to the action of light with  $\lambda > 400$  nm to remove the  $\text{RSS}(\text{H})\text{R}$  adducts produced in a number of cases. Further action of light with  $\lambda = 365$  nm on solutions of hydrogen sulphide and thiols in 4MH and 5 M LiCl and of methane thiol in PFDMCH increases the integral intensity of the ESR spectra of the specimens. In the latter case, the effect can be almost completely attributed to the formation of  $\dot{\text{C}}\text{H}_2\text{SH}$  radicals. This also

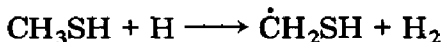
increases the absorption at  $\lambda < 300$  nm [20]. In addition, the ESR spectra exhibited a low intensity hydrogen atom signal. We obtained an extinction coefficient  $\epsilon_{330} = 580 \text{ M}^{-1} \text{ cm}^{-1}$  for the photolysed particle (which adequately correlates with the data reported in the literature for the thiyl radicals [9]) by comparing the change in the intensity of the absorption band with a maximum at 330 nm with the increase in the concentration of  $\dot{\text{C}}\text{H}_2\text{SH}$  radicals. The quantum yield for  $\dot{\text{C}}\text{H}_2\text{SH}$  radical formation under the given conditions is greater than 0.1. The action of light with  $\lambda = 365$  nm on the solutions of methane thiol in 4MH produces matrix radicals together with  $\dot{\text{C}}\text{H}_2\text{SH}$  radicals. Simultaneously, the absorption band with  $\lambda_{\text{max}} = 330$  nm disappears in the UV spectrum (Fig. 8). We obtained a coefficient  $\epsilon_{330} = 550 \text{ M}^{-1} \text{ cm}^{-1}$  by comparing changes in the ESR and UV absorption spectra. The above-mentioned results allow us to assign the photochemical reactions to conversions of the thiyl radicals. Mass spectrometry analysis of the gases produced by the photolysis of methylthiyl radicals in the PFDMCH matrix by light with  $\lambda = 365$  nm shows that the process yields hydrogen and methane; the amount of hydrogen is ten times greater than the amount of  $\dot{\text{C}}\text{H}_2\text{SH}$  radicals formed in the photolysis. The ESR spectra of the methylthiyl radicals in the PFDMCH matrix subjected to the action of light with  $\lambda = 365$  nm exhibit a signal due to the hydrogen atoms. This and the results discussed earlier indicate that the thiyl radicals photodissociate and the photoradical chain reaction takes place in the system investigated:



The reaction

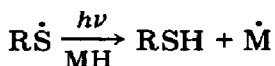


is at least ten times more effective than the reaction

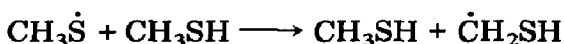


and this is in good agreement with the ratio of the velocity constants for the analogous reactions in the liquid phase [21].

Hydrogen atoms which react with molecules of the 4MH matrix should form radicals of the matrix. This supposition is confirmed by experiment. A possible abstraction of the hydrogen from the molecules of the matrix by the excited thiyl radical should not be excluded either:



It seems to be quite probable that some of the  $\dot{\text{C}}\text{H}_2\text{SH}$  radicals form as a result of photosubstitution and in the photolysis of the methylthiyl radicals in the PFDMCH matrix:





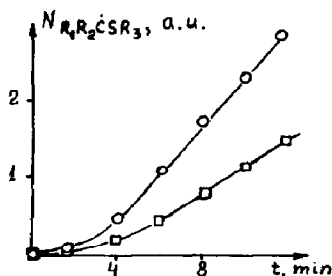
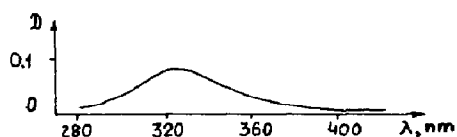
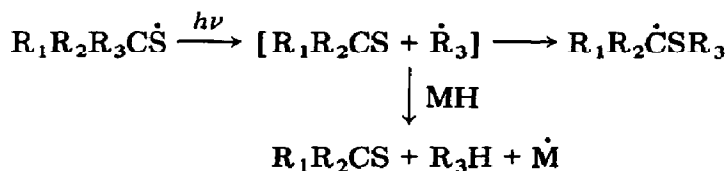


Fig. 8. Changes in the absorption spectrum of a solution of methane thiol UV irradiated ( $\lambda = 253.7$  nm) at 77 K in a 4MH matrix produced by light with  $\lambda = 365$  nm.

Fig. 9. Kinetics of  $R_1R_2\dot{C}SR_3$  radical accumulation in the photolysis of a 0.2 M solution of *tert*-butyl thiol in 4MH by light with  $\lambda = 253.7$  nm in the absence ( $\circ$ ) and presence ( $\square$ ) of 0.2 M hex-1-ene at 77 K.

The action of light with  $\lambda = 365$  nm on solutions of thiols RSH ( $R \equiv C_2H_5$ , *i*- $C_3H_7$ , *tert*- $C_4H_9$ ) in 4MH yields radicals with the spin located at the carbon atom (the ESR spectra of the radicals have an odd number of component hyperfine structures ( $a_H = 20$  G)) and radicals of the matrix. For methane thiol, the signals may be assigned to the radicals of type  $R_1R_2\dot{C}SR_3$  formed as the C—C bond is cleaved at the  $\beta$  position of the corresponding excited thiyl radicals. Cage reactions of the primary products of photolysis of the thiyl radicals



probably play an essential role in the formation of the  $R_1R_2\dot{C}SR_3$  radicals.

Photolysis of the initial solutions of thiols in 4MH by light with  $\lambda = 253.7$  nm at 77 K also produces  $R_1R_2\dot{C}SR_3$  radicals. The kinetics of their accumulation exhibit an induction period. The presence of 0.2 M hex-1-ene, which reduces the quantum yield for the stabilized thiyl radicals (reaction (5)), considerably retards the process (Fig. 9). This indicates that the thiyl radicals can also be photolysed under the action of light with  $\lambda = 253.7$  nm.

The integral intensity of the ESR spectra of the solutions of thiols in 4MH photolysed and subjected to the action of visible light does not increase, or increases only slightly, under the action of light with  $\lambda = 365$  nm when 0.2 M hex-1-ene is present in the solution.

Photolysis of the ethylthiyl radicals in the 5 M LiCl matrix yields methyl radicals. This indicates that the thiyl radicals photodissociate, cleaving the C—C bond in the  $\beta$  position. The action of light with  $\lambda = 253.7$  nm and  $\lambda = 365$  nm on the methylthiyl radicals produces the same effect. A wide singlet component at  $g \approx 2.12$  also appears in the last case. The ESR spectrum of the photolysed  $H\dot{S}$  radicals ( $\lambda = 365$  nm) in the 5 M LiCl matrix

also shows a similar component. The mechanism of the reactions is not clear so far and needs further investigation.

The ability of the thiyl radicals to enter into photochemical reactions leads to their low stationary concentrations in the photolysis of dilute solutions of thiols in 3MP and 4MH. The self-association of thiols inhibits the stabilization of the thiyl radicals when the concentration of the thiols in 3MP is high. This explains why the action of light with  $\lambda = 365$  nm on solutions of *tert*-butyl thiol in 3MP UV irradiated ( $\lambda = 253.7$  nm) and photolysed by light with  $\lambda \geq 400$  nm does not increase the number of paramagnetic centres at concentrations below 0.1 M and above 0.2 M. Further action of light with  $\lambda = 365$  nm on solutions of *tert*-butyl thiol in 3MP of all concentrations heated to 88 K does not increase the number of paramagnetic centres because the stabilized thiyl radicals produced both by photolysis and by thermal reactions form adducts with the thiol.

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