[Contribution from the George Herbert Jones Laboratory, the University of Chicago]

REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXXIV. PHOTOCHEMICAL DISSOCIATION OF DISULFIDES INTO MERCAPTYL RADICALS[1]

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The literature contains many statements to the effect that in solution organic disulfides dissociate into free radicals (1).

$$1.\ RSSR \rightleftharpoons 2\ RS\cdot$$

The evidence upon which these statements are based does not seem to us conclusive. For example, the reaction of diphenyl disulfide with a solution of hexaphenylethane to give a thioether (2) is not adequate evidence of the dissociation of the disulfide. Neither can the reactions of disulfides with metals (3) (sodium, zinc, silver, etc.) be used as a diagnostic test of dissociation. Such dissociation, if it occurs in solution, should be demonstrable by measurement of the magnetic susceptibility of the system.

It is also possible to test the dissociation of disulfides into free radicals by noting whether (in the dark) they initiate the free radical addition of mercaptans to olefins (4), and the copolymerization in emulsion of butadiene and styrene.

Styrene and primary (lauryl and propyl) mercaptans were used in this study. With this monomer step 2 proceeds more readily than with aliphatic olefins, but step 3 is somewhat more difficult. Nevertheless, this system was considered adequate for our purpose since, in the presence of an appropriate oxidant, the addition of aliphatic mercaptans to styrene takes place readily at 30°. The product is a mixture of the one-to-one adduct, the two-to-one adduct (two styrene molecules to one of mercaptan), and higher addition-polymerization adducts (three and four molecules of styrene to one mercaptan). It was found that when an equimolar mixture of styrene and propyl or lauryl mercaptan (in a highly evacuated system) was kept for 12 hours either in the dark or exposed to the light from a 200-watt Mazda lamp,[2] 18–20% of mercaptan reacted.

$$2.\ RCH{=}CH_2 + R'S\cdot \rightarrow R\underset{\bullet}{C}HCH_2SR'$$
$$3.\ R\underset{\bullet}{C}HCH_2SR' + R'SH \rightarrow RCH_2CH_2SR' + R'S\cdot$$

The addition of small amounts of disulfides (one mole-%) had no effect on the rate of reaction of the mercaptans with styrene in the dark, but markedly

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[1] The work reported in this paper was done in connection with the Government Research Program in synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation and is abbreviated from report CR-739, June 1945, submitted to the Office of Rubber Reserve.

[2] One might of course ascribe this result to residual traces of oxygen or peroxide in spite of the precautions taken to exclude these impurities. It appears to us more probable, however, that this effect is due to the thermal activation of styrene. Note, for instance, that in the dark carefully purified styrene and bromotrichloromethane, when kept in an evacuated system, react slowly at 60° to give the one-to-one adduct.

increased the rate (Table I) when the reaction mixture was illuminated (200-watt Mazda lamp).

The data in Table I suggest that, whereas disulfides are not dissociated, when dissolved in a mixture of styrene and mercaptan, at room temperature in the dark, dissociation does occur when the mixture is illuminated, for here the disulfides initiate chain reactions. As in all chain reactions, the extent of dissociation need not be large.

TABLE I

PHOTOCHEMICAL EFFECT OF DISULFIDES ON THE ADDITION OF LAURYL MERCAPTAN TO STYRENE (12 HOURS)*

DISULFIDE (One Mole-%)	MERCAPTAN CONSUMED, %
None	23
Anisyl lauryl	57
Diphenyl	73
Dianisyl	86

* Independent experiments indicated that the 1:1 and higher addition-polymerization adducts thus formed did not differ from the adducts formed when styrene and lauryl mercaptan are allowed to react in the presence of an oxidant. It appeared convenient, therefore, in these experiments to measure the rate of disappearance of the mercaptan. This was done by an amperometric titration with silver nitrate [Kolthoff and Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946)]. In all of these experiments equimolar mixtures of the mercaptan and styrene were used. The materials were carefully purified and distilled into the reaction vessel at reduced pressure; then the system was thoroughly degassed.

TABLE II

REACTION OF STYRENE WITH LAURYL MERCAPTAN AT 90° (12 HOURS)

DISULFIDE (One Mole-%)	MERCAPTAN CONSUMED, %
None	33
Diphenyl	34
Dianisyl	31

TABLE III

PHOTOCHEMICALLY-INDUCED EMULSION COPOLYMERIZATION OF STYRENE WITH BUTADIENE IN THE PRESENCE OF DIANISYL DISULFIDES AT 50°*

DIANISYL DISULFIDE	ILLUMINATION	TIME, hours	CONVERSION, %
Absent	+	15	3
Present	−	15	0
Present	+	11	80

* Butadiene, 75 parts; Styrene, 25 parts; Distilled water, 180 parts; Potassium stearate, 5 parts; Dianisyl disulfide, 0.35 part.

It is noteworthy that light (200-watt Mazda lamp) is more effective than heat in promoting the dissociation of disulfides. Thus, experiments similar to those described in Table I were carried out in the dark at 90°. The results given in Table II indicate that disulfides are not appreciably (if at all) dissociated at 90°. The slight increase in the utilization of the mercaptan is probably due to the greater thermal activation of the styrene.

To confirm the idea that at ordinary temperatures disulfides dissociate into free radicals only when illuminated, the copolymerization of butadiene and styrene in emulsion was investigated. Some typical data indicating the efficiency of dianisyl disulfide in the presence of light as an initiator for emulsion copolymerization are given in Table III.

Optimum rate of polymerization was obtained when 0.35 gram of dianisyl disulfide was used per 100 grams of the monomers. This rate compares favorably with the rate of copolymerization (60–75% in 14 hours) obtained when persulfate is used as the initiator.

We fully recognize that the photochemical addition of mercaptans to olefins in the presence of disulfides indicates a free radical reaction, but does not preclude the formation of free radicals by the attack of the mercaptan on the disulfide.

$$\mathrm{RSSR} + \mathrm{R'SH} \xrightarrow{h\nu} \mathrm{RSH} + \mathrm{RS}\cdot + \mathrm{R'S}\cdot$$

However, since the copolymerization of styrene and butadiene is initiated by disulfides in visible light in the absence of mercaptans, it is reasonable to assume that the effect of the light is to cause the dissociation of the disulfide.

As with many other photochemical reactions, the data presented do not permit an unequivocal choice between a dissociation of the disulfide into free radicals

$$\mathrm{RSSR} \xrightarrow{h\nu} 2\mathrm{RS}\cdot,$$

and an induced dissociation of the disulfide

$$\mathrm{RSSR} + \mathrm{C_6H_5CH{=}CH_2} \xrightarrow{h\nu} \mathrm{RS}\cdot + \mathrm{C_6H_5}\underset{\bullet}{\mathrm{C}}\mathrm{HCH_2SR}.$$

EXPERIMENTAL

Materials used. The *styrene* used was obtained from the Dow Chemical Company. It was distilled from its stabilizer before use.

The *butadiene* was obtained from the Phillips Petroleum Company.

The *lauryl mercaptan* was prepared from lauryl bromide and thiourea.

The *symmetrical disulfides* were prepared by the action of powdered iodine upon the appropriate mercaptan dissolved in alkali.

The *unsymmetrical disulfides* were prepared by the action of the sulfenyl chloride of one radical upon the sodium salt of the mercaptan of the other (2).

p-Anisyl mercaptan was prepared from *p*-anisidine and potassium xanthate (5).

Addition of lauryl mercaptan to styrene. In these experiments equimolar amounts of lauryl mercaptan and styrene were allowed to react under the influence of one mole-% of various disulfides. Light was supplied by a 200-watt bulb around which the several solutions contained in 8-mm. sealed glass tubes were evenly arranged at a distance of 10 cm. from the bulb. The heat of the bulb was dissipated by an electric fan. The temperature of the surrounding air was taken by averaging the readings on two thermometers situated at opposite ends of a diameter of the circle formed by the tubes surrounding the bulb. When there was more than one tube per set, these tubes were arranged as far from one another as possible within the circle around the bulb. The purpose of this arrangement was to minimize whatever differences might exist in the different positions about the light bulb. To minimize errors involved in making up the various solutions, all tubes were filled from appropriate freshly prepared common stock solutions. In order to eliminate assumptions involving perfect solutions, the exact amount of lauryl mercaptan per portion was determined by titrating a portion at zero reaction time as a blank. The styrene used was always distilled within two hours of the time it was used. The glass tubes used as reaction vessels were flamed in a stream of dry nitrogen and then kept in a desiccator until used. The tube containing the solution was degassed twice and sealed in a high vacuum.

Emulsion-type polymerization. In a long-necked bulb of suitable size was placed 5.0 g. of potassium stearate, 180 g. of water, and 25 g. of a solution of a suitable initiator in freshly distilled styrene. When the GR-S recipe was followed, the styrene solution contained 0.5 g. of lauryl mercaptan and 0.3 g. of potassium persulfate. This mixture was degassed three times at 10^{-4} mm. mercury pressure. Into this mixture was then distilled 75 g. of butadiene which had likewise been three times degassed at 10^{-4} mm. mercury.

The degassed tubes were then sealed off and placed on a shaking machine in a constant-temperature room at 50°. Illumination was furnished by two 200-watt bulbs suspended one foot away from each of the two sides of the shaker. The dark controls were similarly treated except that the outsides of these tubes were painted black.

After a suitable time interval each tube was opened and its contents were poured with stirring into about 400 ml. of alcohol. The copolymer was collected on a filter, and dried *in vacuo*. The dry weight of copolymer was obtained and the per cent conversion of monomers to copolymer was calculated.

SUMMARY

1. It has been established that in the light, but not in the dark, dianisyl disulfide initiates the copolymerization of styrene and butadiene in emulsion in the absence of mercaptans and oxidants.

2. It has been shown that disulfides accelerate the rate of addition of lauryl and propyl mercaptans to styrene in the light but not in the dark.

3. It has been established that in the dark heat has a slight (if any) effect on the rate of addition of mercaptans to styrene in the presence of disulfides.

4. The results outlined in 1, 2, and 3 are interpreted on the basis that light causes the dissociation of disulfides into free radicals.

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