

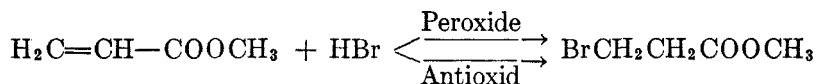
THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO  
UNSATURATED COMPOUNDS. XXVIII. THE ADDITION  
OF MERCAPTANS TO METHYL ACRYLATE

M. S. KHARASCH AND CHARLES F. FUCHS<sup>1</sup>

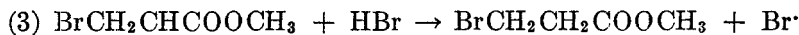
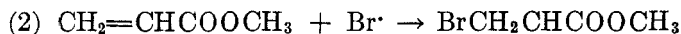
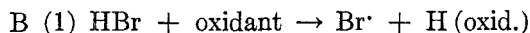
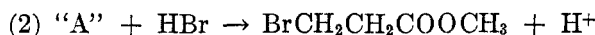
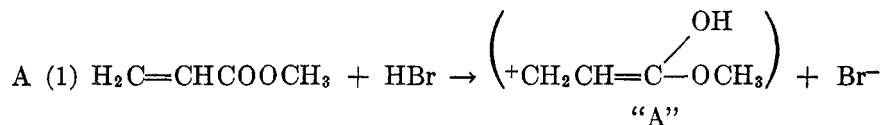
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INTRODUCTION

It has been shown that the so-called "normal" addition of hydrogen bromide to any type of unsaturated compounds may be reversed unless the double bond is conjugated with a carboxyl or a carbalkoxyl group (1). Specifically, methyl acrylate, (in the presence or absence of solvents), under both the most rigorous antioxidant and the most rigorous peroxidic conditions (1) (oxygen, ascaridol, light), gives the same product, methyl  $\beta$ -bromopropionate.



It is not known, however, whether the same compound is formed under these conditions by both of the mechanisms A and B indicated below, or by only one of them.



Unfortunately, since step B3 (see above) is very fast, it is impossible to determine whether both mechanisms operate in this reaction or whether the free-radical-chain reaction (B1,2,3) is inhibited and only the ionic type reaction (A1,2) is effective.

If hydrogen bromide were replaced by a reagent which requires a higher activation energy for step B3, it should be possible to demonstrate that the same addition product to methyl acrylate may be obtained by two different mechanisms when step B3 is slow; at the same time considerable amounts of other condensation products characteristic of a free-radical-chain mechanism should be formed. The addition of mercaptans to methyl acrylate was therefore investigated.

<sup>1</sup> Present address: Emulson Corporation, Chicago.

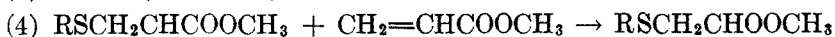
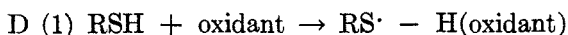
Mercaptans by themselves do not add to methyl acrylate. In the presence of small amounts of strong bases, however, rapid addition takes place; this fact indicates that the mercaptide ion adds first to the olefin.



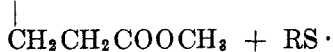
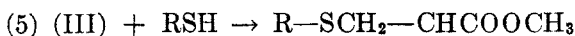
(II)

The yield of the addition product (II) is practically quantitative. This substance (II) may therefore be called the "ionic" addition product. No material containing two or more molecules of the methyl acrylate to one of the mercaptan is formed.

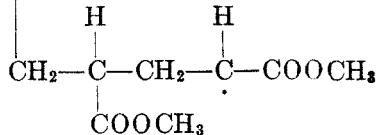
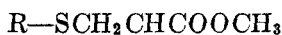
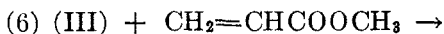
However, if a mixture of mercaptan and methyl acrylate is treated with a small amount of a peroxide (ascaridol) and the system is illuminated in a quartz tube with ultraviolet light, there is formed, besides compound II (above), compounds (IV) and (VI), containing two and three molecules of methyl acrylate per molecule of mercaptan, respectively. Small yields of compounds in which the ratio of acrylate to mercaptan is greater than three to one are also formed; the amounts obtained depend upon the relative amounts of methyl acrylate and mercaptan used in the reaction. These results are readily interpreted as follows:



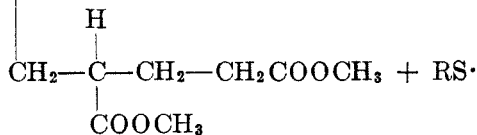
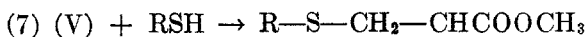
(III)



(IV)



(V)



(VI)

Apparently the "ionic" and "free radical" addition of mercaptans to methyl acrylate (and presumably to other compounds in which the double bond is conjugated with a carbalkoxyl group) yield the same product, but by two entirely different mechanisms. In these cases both the mercaptide ion (ionic addition) and the free mercaptide radical (free radical addition) add to the olefin to produce the ion or free radical of lowest energy content, *i.e.* the secondary ion or secondary free radical. This conclusion agrees with other observations on the addition of ions or free radicals to olefins.

#### EXPERIMENTAL PART

*Addition of ethyl mercaptan to methyl acrylate in the presence of a peroxide and ultraviolet light.* Methyl acrylate (10 g.), ethyl mercaptan (7.5 g.), and ascaridol (0.1 cc.) were mixed, placed in a quartz tube provided with a reflux condenser, and irradiated with ultraviolet light for 25 minutes. Since heat was evolved in the reaction, it was necessary, in order to avoid a rise in temperature beyond 40–50°, to cool the quartz flask with ice-water at frequent intervals. The reaction product was distilled at reduced pressure, and the following fractions were collected: Fraction I: 4.0 g., b.p. 90° at 745 mm. Fraction II: 6.3 g., b.p. 84° at 14 mm.,  $n_D^{20}$  1.4630. Fraction III: 3.2 g., b.p. 127–128° at 0.5 mm.,  $n_D^{20}$  1.4705. Fraction IV: Residue, 3.0 g.,  $n_D^{20}$  1.4745. Fraction I is a mixture of unreacted materials. Fraction II is the addition product of one molecule of ethyl mercaptan to one molecule of methyl acrylate, that is, methyl 2-thioethylpropionate. This compound was converted, by oxidation with 30% hydrogen peroxide in glacial acetic acid, to the sulfone of 2-thioethylpropionic acid (m.p. 112°). The recorded melting point of the sulfone is 112° (2). Fraction III is a compound formed by the condensation of one molecule of ethyl mercaptan with two molecules of methyl acrylate.

*Anal.* Calc'd for  $C_{10}H_{18}O_4S$ : C, 51.26; H, 7.75; S, 13.67. Mol. wt. 234.

Found: C, 51.71; H, 7.40; S, 13.50. Mol. wt. 232.

Fraction IV was not worked up. It is probably a compound formed from one molecule of ethyl mercaptan and three molecules of methyl acrylate. A corresponding compound was isolated in the study of the addition of propyl mercaptan to methyl acrylate.

*The addition of ethyl mercaptan to methyl acrylate in the presence of a base.* When methyl acrylate (50 g.) was mixed with pure ethyl mercaptan (36 g.), no reaction took place. However, when a very small quantity of trimethylbenzylammonium hydroxide (0.3 cc. of a 40% solution in  $H_2O$ ) was added to the mixture, it soon became quite warm, and was cooled in ice-water. The reaction is complete in a short time. In the experiment here cited, the reaction mixture was allowed to stand for 12 hours at room temperature. By distillation at reduced pressure, a 95% yield of methyl 2-thioethylpropionate was obtained (b.p. 83.4/14 mm.;  $n_D^{20}$  1.4628).

This substance was identical in every way with the material designated as Fraction II in the previous experiment, carried out by the addition of ethyl mercaptan to methyl acrylate in the presence of ultraviolet light and ascaridol. The sulfones obtained by the oxidation of the two esters with hydrogen peroxide (30%) in glacial acetic acid both melted at 112°, and gave no melting point depression.

*Addition of propyl mercaptan to methyl acrylate in the presence of ascaridol and ultraviolet light.* Two parallel experiments were conducted. Two quartz tubes were filled with mixtures of methyl acrylate (10 g.), propyl mercaptan (8.8 g.), and ascaridol (0.1 cc.). One tube (A) was sealed in air. The other tube (B) was cooled with liquid nitrogen and evacuated to  $10^{-5}$  mm. Hg pressure. It was then allowed to warm to room temperature, cooled again with liquid nitrogen and once again evacuated to  $10^{-5}$  mm. Hg pressure, to remove all oxygen. Both tubes were then warmed to 20° and irradiated (side by side) at room temperature with ultraviolet light. The temperature in both tubes rapidly rose to 50°. At that point, the illumination was interrupted, the tubes cooled to room temperature and the irradiation resumed. The total time of irradiation was 37 minutes. Both tubes were

opened and their contents subjected to distillation at reduced pressure and the following fractions were collected. Tube A (Air Present). Fraction I: 4.0 g., b.p. 37° at 151 mm. Fraction II: 7.0 g., b.p. 63° at 4 mm.,  $n_D^{20}$  1.4629. Fraction III: 1.0 g., b.p. 58° at 0.7 mm.,  $n_D^{20}$  1.4635. Fraction IV: 3.4 g., b.p. 120–123° at 0.8 mm.,  $n_D^{20}$  1.4692. Fraction V: 2.0 g., b.p. 150–155 at 0.8 mm.,  $n_D^{20}$  1.4699. Fraction VI: Residue: 1.0 g. Fraction II is the addition product of one molecule of propyl mercaptan to one molecule of methyl acrylate. Fraction IV is the addition product of one molecule of propyl mercaptan to two molecules of methyl acrylate.

*Anal.* Fraction IV. Calc'd for  $C_{11}H_{20}O_4S$ : S, 12.94; Mol. wt. 248.3.

Found: S, 13.40; Mol. wt. 241.

Tube B. (Air Absent). Fraction I: 3.9 g., b.p. 35° at 151 mm. (unreacted materials were collected in the cold trap). Fraction II: 6.0 g., b.p. 63° at 4 mm.,  $n_D^{20}$  1.4630. Fraction III: 1.6 g., b.p. 56° at 0.8 mm.,  $n_D^{20}$  1.4639. Fraction IV: 4.1 g., b.p. 118–123° at 0.8 mm.,  $n_D^{20}$  1.4699. Fraction V: 2.3 g., b.p. 150–156° at 0.8 mm.,  $n_D^{20}$  1.4719. Residue about 0.5 g.

Here [as well as in the experiment (A) in which air was present] Fraction II was shown to be methyl 2-thiopropylpropionate. Fraction IV corresponds to an addition product of one molecule of propyl mercaptan to two molecules of methyl acrylate. The probable formation of this compound is discussed in the theoretical part (D5).

*Anal.* Calc'd for  $C_{11}H_{20}O_4S$ : S, 12.94; Mol. wt. 248.3.

Found: S, 13.40; Mol. wt. 243.

Fraction V is probably a compound formed from one molecule of propyl mercaptan to three molecules of methyl acrylate (See D 7 in the theoretical part). The analyses indicate that the substance is contaminated with a small amount of the compound which occurs in Fraction IV.

*Anal.* Calc'd for  $C_{15}H_{26}O_6S$ : S, 9.60; Mol. wt. 334.

Found: S, 11.70; Mol. wt. 318.

*Addition of lauryl mercaptan to methyl acrylate.* Lauryl mercaptan (7.5 g.) and methyl acrylate (4.0 g.) were mixed in a glass-stoppered flask and 0.2 cc. of trimethylbenzylammonium hydroxide (40% solution in  $H_2O$ ) was added. A vigorous, exothermic reaction took place. After the mixture had stood for one hour, 15 cc. of alcohol and 5 cc. of a 20% sodium hydroxide solution were added. The hydrolysis of the ester was rapid and accompanied by the evolution of heat. Upon addition of hydrochloric acid, the acid, 2-thiolaurylpropionic acid, separated. The yield of this acid was 95% of the amount calculated. It melted, after crystallization from methanol, at 61–62° (uncor).

By oxidation with 30% hydrogen peroxide, the 2-thiolaurylpropionic acid was readily converted to the sulfone, which, upon crystallization from acetic acid, melted at 137–138°. This sulfone is only moderately soluble in warm dilute alkali.

*Anal.* Calc'd for  $C_{15}H_{26}O_3S$ : C, 58.80; H, 9.88

Found: C, 58.36; H, 9.84.

#### SUMMARY

1. It has been established that mercaptans add to methyl acrylate by two different mechanisms: "ionic" and "free radical." The same addition product,  $RSCH_2CH_2COOCH_3$  is obtained by both mechanisms.

2. The compound  $RSCH_2CH_2COOCH_3$  is formed in 95% yield by the "ionic" addition of mercaptans to methyl acrylate.

3. In the free radical addition of mercaptans to methyl acrylate, there are formed, besides the substance  $RSCH_2CH_2COOCH_3$ , compounds which contain two, three (and even larger number) of methyl acrylate molecules per molecule of mercaptan.

CHICAGO 37, ILL.

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- (1) WALLING, KHARASCH, AND MAYO, *J. Am. Chem. Soc.*, **61**, 2693 (1939).
- (2) OTTO AND OTTO, *Ber.*, **21**, (1888).