moved by the reaction of the organic halide with the adjacent atoms of magnesium. If the film is magnesium hydroxide its disappearance on standing might be explained by the reaction with the magnesium bromide from the Grignard equilibrium to produce basic magnesium bromide which is soluble in ether.

Summary

(1) Magnesium amalgam electrodes gave zero dark voltage and no light sensitivity with ether solutions of either phenylmagnesium bromide or ethylmagnesium bromide. (2) Magnesium electrodes which had been cleaned by reacting with the organic halide gave the same results. (3) Magnesium electrodes which had not been cleaned in this manner showed variable dark voltages and variable photo-voltaic responses. Both of these could be destroyed by adding the organic halide or by allowing the cell to stand for several days. (4) "Cleaned" magnesium electrodes were made sensitive to light by exposure to oxygen.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Addition of Sulfur, Hydrogen Sulfide and Mercaptans to Unsaturated Hydrocarbons

BY S. O. JONES[1] AND E. EMMET REID

There have been many investigations of the action of sulfur and hydrogen sulfide on unsaturated hydrocarbons[2] and a few on the addition of mercaptans[3] but so many points have not been cleared up that further study seemed desirable.

Curiously enough the end-products are much the same whether an unsaturated hydrocarbon is treated with sulfur, hydrogen sulfide or a mercaptan. Thus with ethylene, sulfur gives hydrogen sulfide which reacts with more ethylene to form ethyl mercaptan which then adds to more ethylene to form ethyl sulfide.

Our results help to explain the presence of ethyl, *i*-propyl and other mercaptans and the corresponding sulfides in petroleum distillates but do not account for the presence of methyl mercaptan and methyl sulfide.

The Action of Sulfur.—Quite different results are obtained from the reaction with sulfur according to the conditions and whether free sulfur or a compound which readily liberates sulfur is used. When ethylene was passed over pyrites at 350° about 1% of thiophene was isolated along with hydrogen sulfide and ethyl mercaptan, while when it was bubbled through sulfur at 325° much hydrogen sulfide was formed along with 3% of ethyl mercaptan and small amounts of carbon disulfide and ethyl sulfide. We found it advantageous to use ethyl tetrasulfide as a sulfur donor. This is a liquid which mixes well with organic compounds and decomposes on heating, giving off what may be assumed to be atomic sulfur. The proportions were calculated on the basis of the tetrasulfide going down to the disulfide. A noteworthy difference is that with it, appreciable yields of the cyclic sulfides were obtained.

When ethylene was bubbled slowly through ethyl tetrasulfide kept at about 150°, the main product isolated was ethyl mercaptan with some ethyl sulfide and in addition some ethylene sulfide. The results of heating several hydrocarbons in a bomb with ethyl tetrasulfide are given in Table I.

TABLE I

Hydrocarbons with Et_2S_4, 10 hrs. at 180°

Hydrocarbon	Yields of products, %		
	Mercaptan	Sulfide	Cyclic sulfide
Ethylene	5	18	1
Propylene	6	20	15
Heptene-1	20	..	..
Octene-1	19	..	..
Cyclohexene	8	..	8

The mercaptans, except from ethylene, and sulfides were all secondary.

The Addition of Hydrogen Sulfide.—The addition of hydrogen sulfide was effected by heating in the bomb for ten hours at 180°. Sulfur was added as a catalyst for without it there was little if any addition. The results are given in Table II. The sulfur is found on the secondary or tertiary carbon atom in accordance with Markownikow's rule.

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[1] Taken from the Ph. D. dissertation of S. O. Jones, R. J. Reynolds Tobacco Co. Fellow, The Johns Hopkins University, June, 1936.

[2] Mailhe and Renaudie, *Compt. rend.*, **195**, 391 (1932); Duffey, Snow and Keyes, *Ind. Eng. Chem.*, **26**, 91 (1934).

[3] Posner, *Ber.*, **38**, 646 (1905); Nicolet, THIS JOURNAL, **57**, 1098 (1935).

TABLE II

Addition of hydrogen sulfide, 10 hrs. at 180°

Hydrocarbon	Yields of products, %	
	Mercaptan	Sulfide
Ethylene	11	80
Propylene	7	90
i-Butylene	23	6
Octene-1	9	35
Cyclohexene	7	5

The addition takes place according to Markownikow's rule. In all cases the mercaptan that is first formed adds to a second molecule of the hydrocarbon to form the sulfide. In the case of the simple unsaturates this second reaction must be rapid as compared to the first addition as little of the mercaptans is left over. *t*-Butyl and cyclohexyl mercaptans evidently do not add so readily to the hydrocarbons.

The Addition of Mercaptans.—The unexpected observation was made in the course of our experiments that peroxides influence the mode of addition of mercaptans to unsaturates just as Kharasch[4] found that they influence the addition of hydrogen bromide. When we heated ethyl mercaptan with propylene we obtained ethyl *i*-propyl sulfide, but with octylene the product was ethyl *n*-octyl sulfide. The propylene had never been exposed to the air while the octylene had been stored for some time in a partly filled bottle and gave a strong test for peroxides. By adding ethyl mercaptan to propylene in the presence of added peroxides, we obtained ethyl *n*-propyl sulfide.

It has been observed by Posner and Nicolet[3] that thiophenol and *p*-thiocresol add to unsaturates contrary to Markownikow's rule. We have verified this in a large number of cases, but by using freshly distilled thiophenol and *p*-thiocresol we were able to reverse the mode of addition. Kharasch[4] observed that *p*-thiocresol was not effective as an anti-oxidant unless it was freshly distilled. It appears that only very small amounts of peroxides such as are usually present in the hydrocarbon or in the *p*-thiocresol itself are sufficient to influence the addition of mercaptans while for hydrogen bromide much larger amounts are required. In the absence of catalysts scarcely any addition takes place even on heating for twenty-four hours at 180°. Sulfur catalyzes the normal addition and peroxides the abnormal. It is difficult to suppress the abnormal addition entirely. Into each of 3 tubes of 2-cc. capacity were placed 0.25 g. of *p*-thiocresol and 0.4 cc. of tridecene. The *p*-thiocresol had been distilled recently *in vacuo* and the tridecene had just been distilled over sodium. To the first tube was added a trace of ascaridole, to the second a trace of sulfur and nothing to the third. After the usual heating the product in the first tube was solid and on recrystallization gave 0.3 g. which melted at 39.9°, the melting point of *p*-thiocresyl *n*-tridecyl sulfide made from *n*-tridecyl bromide in the usual way. From the liquid products in the other two tubes it was possible to isolate 0.01 and 0.08 g., respectively, of the sulfide melting at the same point.

In a number of experiments the products were identified by their boiling points and by oxidation to known solid sulfones but for positive proof of structure unsaturated hydrocarbons[5] and mercaptans were chosen that would give known crystalline sulfides which previously had been prepared from the potassium salt of the mercaptans and the normal alkyl bromides.[6] The tubes were of 2-cc. capacity and the hydrocarbon was in slight excess. The heating was for ten hours and 180°. The results given in Table III show conclusively that the abnormal addition took place with these hydrocarbons which had been exposed to air for some weeks.

In another series tridecylene was added to dimercaptans.[7] The results are given in Table IV.

In one experiment lauryl mercaptan was added to allyl lauryl sulfide $C_{12}H_{25}SCH_2CH{=}CH_2$ and the product was $C_{12}H_{25}S(CH_2)_3SC_{12}H_{25}$, m. p. 47°, proved by melting point and mixed melting point to be identical with that from lauryl bromide and trimethylene mercaptan.

Experimental

Ten moles of ethylene bubbled at the rate of 50 cc. per minute through a 25-cm. layer of sulfur in a vertical tube kept at 325° gave much hydrogen sulfide. The 25 cc. of condensate gave 15 g. of ethyl mercaptan, b. p. 34–37°, $Hg(SEt)_2$, m. p. 76°, 2 g. of carbon disulfide and 3 g. of ethyl sulfide, b. p. 91–92°, $Et_2S{\cdot}HgCl_2$, m. p. 76.5°. Five moles passed at the rate of 20 cc. per minute through a 20-cm. column of ethyl tetrasulfide at 140–150° gave 30 g. of condensate, largely ethyl sulfide but containing 10 g. of ethyl mercaptan $Hg(SEt)_2$, m. p. 76°, and 1.5 g. of ethylene sulfide,[8] b. p. 54–57°, S calcd. 53.36, found 53.09 and 53.12.

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(4) Kharasch and Hannum, THIS JOURNAL, **56**, 712 (1934).

(5) Prepared by Kozacik and Reid, *ibid.*, **60**, 2436 (1938).

(6) The alkyl bromides were those described by Meyer and Reid, *ibid.*, **55**, 1574 (1933).

(7) Hall and Reid, unpublished results.

(8) Delépine, *Bull. soc. chim.*, **733**, 03 (1923).

TABLE III

MELTING POINTS AND ANALYSES OF SULFIDES OBTAINED BY ADDITION COMPARED WITH THOSE OF SYNTHETIC SULFIDES

Mercaptan	Unsaturate	Sulfide	Synthetic M. p., °C.	By addition M. p., °C.	Sulfur, % Calcd.	Sulfur, % Found	
C_6H_5SH	$CH_3(CH_2)_8CH=CH_2$	$C_6H_5S(CH_2)_{10}CH_3$	33.8	33.8	12.13	11.90	11.93
p-$CH_3C_6H_4SH$	$CH_3(CH_2)_8CH=CH_2$	$CH_3C_6H_4S(CH_2)_{10}CH_3$	29.8	29.8	11.52	11.58	11.49
β-$C_{10}H_7SH$	$CH_3(CH_2)_8CH=CH_2$	$C_{10}H_7S(CH_2)_{10}CH_3$	46.8	46.8	10.00	10.01	10.10
$C_{12}H_{25}SH$	$CH_3(CH_2)_8CH=CH_2$	$C_{12}H_{25}S(CH_2)_{10}CH_3$	37.2	37.2	8.99	9.14	9.10
C_6H_5SH	$CH_3(CH_2)_{10}CH=CH_2$	$C_6H_5S(CH_2)_{12}CH_3$	43.8	43.9	10.95	10.69	10.78
p-$CH_3C_6H_4SH$	$CH_3(CH_2)_{10}CH=CH_2$	$CH_3C_6H_4S(CH_2)_{12}CH_3$	40.2	40.2	10.46	10.57	10.40
β-$C_{10}H_7SH$	$CH_3(CH_2)_{10}CH=CH_2$	$C_{10}H_7S(CH_2)_{12}CH_3$	54.6	54.5	9.36	9.10	9.21
$C_{12}H_{25}SH$	$CH_3(CH_2)_{10}CH=CH_2$	$C_{12}H_{25}S(CH_2)_{12}CH_3$	39.2	39.8	8.35	8.33	8.30
C_6H_5SH	$CH_3(CH_2)_{12}CH=CH_2$	$C_6H_5(CH_2)_{14}CH_3$	51.0	51.1	10.07	10.07	10.01
p-$CH_3C_6H_4SH$	$CH_3(CH_2)_{12}CH=CH_2$	$CH_3C_6H_4S(CH_2)_{14}CH_3$	48.0	48.8	9.58	9.83	9.60
β-$C_{10}H_7SH$	$CH_3(CH_2)_{13}CH=CH_2$	$C_{10}H_7S(CH_2)_{14}CH_3$	61.0	60.9	8.65	8.39	8.45
$C_{12}H_{25}SH$	$CH_3(CH_2)_{12}CH=CH_2$	$C_{12}H_{25}(CH_2)_{14}CH_3$	49.2	49.2	7.77	7.60	7.62
C_6H_5SH	$CH_3(CH_2)_{14}CH=CH_2$	$C_6H_5S(CH_2)_{16}CH_3$	57.6	57.6	9.20	8.91	8.98
p-$CH_3C_6H_4SH$	$CH_3(CH_2)_{14}CH=CH_2$	$CH_3C_6H_4S(CH_2)_{16}CH_3$	56.0	55.8	8.84	8.70	8.65
β-$C_{10}H_7SH$	$CH_3(CH_2)_{14}CH=CH_2$	$C_{10}H_7S(CH_2)_{16}CH_3$	66.2	66.2	8.29	8.10	8.19
$C_{12}H_{25}SH$	$CH_3(CH_2)_{14}CH=CH_2$	$C_{12}H_{25}S(CH_2)_{16}CH_3$	53.6	52.1	7.25	7.10	7.13
C_6H_5SH	$CH_3(CH_2)_{16}CH=CH_2$	$C_6H_5S(CH_2)_{18}CH_3$	62.4	60.5	8.49	8.28	8.35
p-$CH_3C_6H_4SH$	$CH_3(CH_2)_{16}CH=CH_2$	$CH_3C_6H_4S(CH_2)_{18}CH_3$	61.0	59.5	8.21	8.08	8.12
β-$C_{10}H_7SH$	$CH_3(CH_2)_{16}CH=CH_2$	$C_{10}H_7S(CH_2)_{18}CH_3$	71.2	70.0	7.52	7.32	7.40
$C_{12}H_{25}SH$	$CH_3(CH_2)_{16}CH=CH_2$	$C_{12}H_{25}S(CH_2)_{18}CH_3$	..	53.2	6.84	6.80	6.75

TABLE IV

MELTING POINTS AND ANALYSES OF SULFIDES OBTAINED BY ADDITION OF TRIDECENE TO DIMERCAPTANS AND MELTING POINTS OF SYNTHETIC SULFIDES. $R = n\text{-}C_{13}H_{27}$

Mercaptan	Sulfide	Synthetic	By addition	Sulfur, % Calcd.	Sulfur, % Found	
$HS(CH_2)_2SH$	$RS(CH_2)_2SR$	64	63.9	13.98	13.69	13.75
$HS(CH_2)_3SH$	$RS(CH_2)_3SR$	53	53	13.37	13.30	13.36
$HS(CH_2)_4SH$	$RS(CH_2)_4SR$	56.2	56.2	13.17	13.47	13.10
$HS(CH_2)_5SH$	$RS(CH_2)_5SR$	57.4	57.3	12.80	12.70	12.65
$HS(CH_2)_6SH$	$RS(CH_2)_6SR$	59.2	59.2	12.45	12.50	12.40
$HS(CH_2)_7SH$	$RS(CH_2)_7SR$	60.4	60.4	12.13	12.10	12.09
$HS(CH_2)_8SH$	$RS(CH_2)_8SR$	61.2	59.4	11.81	11.91	11.99
$HS(CH_2)_9SH$	$RS(CH_2)_9SR$	63.8	63.8	11.51	11.62	11.44
$HS(CH_2)_{10}SH$	$RS(CH_2)_{10}SR$	64.2	64.2	11.23	11.01	11.19
$HS(CH_2)_{11}SH$	$RS(CH_2)_{11}SR$	66.6	65	10.96	10.80	10.74
$HS(CH_2)_{12}SH$	$RS(CH_2)_{12}SR$	67.0	65.5	10.71	11.01	10.89
$HS(CH_2)_{18}SH$	$RS(CH_2)_{18}SR$	73.6	73	9.31	9.21	9.25

This was identical with a preparation by the method of Delépine.

All other experiments unless otherwise stated were made by heating in a steel bomb for ten hours at 180°. From 30 g. of propylene and 45 g. of ethyl tetrasulfide we obtained: 1 g. of carbon disulfide, 3 g. of i-PrSH, Hg(i-PrS)$_2$, m. p. 62°; 21 g. of i-Pr$_2$S, b. p. 118–121°; oxidized to sulfone, m. p. 36.4°; i-Pr$_2$SO$_2$, m. p. 36°,[9] and 10 g. of cyclic propylene sulfide, S calcd. 43.26, found 43.14. Under the same conditions, substituting sulfur for the ethyl tetrasulfide, the same products were found except that there was none of the cyclic sulfide.

Isobutylene, 14 g., and 23 g. of ethyl tetrasulfide in the bomb eight hours at 160° gave 1 g. of carbon disulfide, 5 g. of ethyl disulfide and a mixture of unsaturated hydrocarbons from which no sulfur compounds could be isolated.

From 27 g. of heptene-1 and 15 g. of Et_2S_4, we obtained 5 g. of carbon disulfide, 2 g. of ethyl disulfide, and 10.5 g., b. p. 140–170°, from which, by extraction with potassium hydroxide solution, heptane-thiol-2, b. p. 163–165°, $n^{25}D$ 1.4459, was obtained, agreeing with the data in the literature. There was much carbonization.

From 56 g. of octene-1 and 45 g. of Et_2S_4 10 g. of octylene was recovered along with 8 g. of carbon disulfide, 5 g. of ethyl disulfide and 30 g. of which half was hydrocarbon and half octanethiol-2. This was identified by treating it with octadecyl bromide, the resulting $C_8H_{17}SC_{18}H_{37}$ had m. p. 24° and was identical with that made from authentic octanethiol-2; n-$C_8H_{17}SC_{18}H_{37}$, m. p. 42.6°. There was much carbonization.

Cyclohexene, 82 g., and 32 g. of sulfur gave 6 g. of carbon disulfide and 15 g. of cyclohexyl mercaptan, b. p. 153–155°, S calcd. 27.60, found by I titration 27.45 and 27.49. Five runs were made using in each the same amount of cyclohexene with 93 g. of ethyl tetrasulfide, equivalent to 32 g. of sulfur. The products, united and fractionated, gave 34 g. of carbon disulfide, 105 g., b. p. 80–84°, of chiefly unreacted cyclohexene, 45 g., b. p. 154–155°, of cyclohexyl mercaptan and 50 g., b. p. 180°, of cyclohexene sulfide. This had $d^0{}_4$ 0.9466, $d^{25}{}_4$ 0.9274; $n^{25}D$ 1.4881; S calcd. 28.10, found 28.00 and 28.05%. Besides these there were 15 g. of ethyl disulfide, b. p. 151–154°, and 40 g. of ethyl trisulfide, b. p. 85° at 15 mm.

Addition of Hydrogen Sulfide.—From 28 g. of ethylene and 34 g. of hydrogen sulfide liquefied in the bomb, with 5 g. of sulfur, there were obtained 7 cc. of ethanethiol, b. p. 34–7°, and 77 cc. of ethyl sulfide, b. p. 90.5–93°.

From 21 g. of propylene, 17 g. of hydrogen sulfide and 5 g. of sulfur, we obtained 2.5 g., b. p. 57–60°, which gave Hg(i-PrS)$_2$, melting at 62°, and 25 g., b. p. 117–121°, oxidized to sulfone, m. p. 35.5°, i-Pr$_2$SO$_2$ melting at 36°. This was repeated after thoroughly cleaning the bomb and leaving out the sulfur catalyst. The liquid product was only 3 cc., b. p. 60–180°, and contained mercaptan and sulfide.

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(9) Delépine, *Compt. rend.*, **172**, 158 (1921).

From 14 g. of isobutylene, 8.5 g. of hydrogen sulfide and 3 g. of sulfur we obtained 6 g. of *t*-butyl mercaptan, b. p. 65–67°, S calcd. 35.56, found by I titration 35.48 and 35.44, and 6 g., b. p. 115–160°, of *t*-butyl sulfide. This was refractionated, 1.8 g., b. p. 72° at 71 mm., S calcd. for t-Bu$_2$S 21.92, found 21.63 and 21.76. The remainder was hydrocarbons.

From 46 g. of octene-1, 17 g. of hydrogen sulfide and 3 g. of sulfur were recovered 20 g. of octylene and 5 g., b. p. 89° at 30 mm., identified as octane-thiol-2, $n^{25}\mathrm{D}$ 1.4480. Titrated with I, found S, 21.69 and 21.78, calcd. 21.92. With octadecyl bromide it gave a sulfide melting at 24°. The sulfide fraction boiled at 281–283°.

From 82 g. of cyclohexene, 34 g. of hydrogen sulfide and 3 g. of sulfur, 40 g. of cyclohexene was recovered along with 8 g. of the mercaptan, b. p. 153–155°, and 4 g. of the sulfide, b. p. 180° at 50 mm., S calcd. 16.17, found by Br titration 16.08 and 16.01, $n^{25}\mathrm{D}$ 1.50473, sulfone m. p. 126°.

Addition of Mercaptans.—All runs were made in a steel bomb for ten hours at 180°. Small samples for Tables III and IV were sealed in glass tubes which were surrounded in the bomb by a liquid of the proper vapor pressure. The solid sulfides from these were recrystallized from alcohol.

From 20 g. of thiophenol, 8 g. of propylene and 1 g. of sulfur were obtained 1 g. of *i*-PrSH, boiling at 57–59°, 2 g. of i-Pr$_2$S boiling at 118–120° and 12 g. of *i*-PrSPh which gave a liquid sulfone, n-PrSO$_2$Ph, m. p. 46°.

From 28 g. of ethylene and 62 g. of ethanethiol with 3 g. of sulfur the yield of diethyl sulfide was 93% but without the sulfur catalyst there was no condensation, Propylene and ethyl mercaptan did not combine without the catalyst but from 3 g. of sulfur, 21 g. of propylene and 31 g. of ethanethiol, 44 g. of *i*-PrSEt boiling at 103–104°, 4 g. of PrSEt boiling at 115–117° and 4 g. of i-Pr$_2$S boiling at 120–121° were obtained. From 21 g. of the same propylene mixed with 61 g. of octene-2, 3 g. of ascaridole and 62 g. of ethanethiol the products were: 2 g. of *i*-PrSEt, b. p. 103–110°; 25 g. of *n*-PrSEt, b. p. 115–117°; sulfone, m. p. 25°; and 13 g. of EtSOct, b. p. 102–103° at 11 mm.; sulfone, m. p. 68°.

Starting with 56 g. of octene-1 containing peroxides and 31 g. of ethanethiol we obtained 14 g., b. p. 145–154° at 100 mm., of which 75% was *n*-octyl SEt, and 14 g., b. p. 154–156°, pure *n*-octyl SEt identified as sulfone, m. p. 68°. The same materials with the addition of 4 g. of hydroquinone gave only 4 g. of sulfide which was not increased by twenty-four hours of heating. When the same were heated with 4 g. of sulfur the products were 5 g., b. p. 109° at 70 mm., of octane-thiol-2; 50 g., b. p. 145–147° at 100 mm., of *s*-octyl ethyl sulfide of which the sulfone was a liquid; and 5 g., b. p. 281–283°, 175° at 20 mm. of di-*s*-octyl sulfide; and 5 g., b. p. 281–283°, 175° at 20 mm. of di-*s*-octyl sulfide.

Cyclohexene, 7 cc., and ethanethiol 5 cc. were sealed in a glass tube which was surrounded in the bomb by a like mixture containing hydroquinone. From the sealed tube 5 cc. of cyclohexyl SEt was isolated but there was no reaction in the outside mixture. Two runs were made with half mole each of these reactants. With sulfur as catalyst the yield was 60% and with peroxides 40%.

Ethyl mercaptan, 0.5 mole, and 0.25 mole of *n*-butylacetylene with 2 g. of sulfur were heated. Fractionation of the product gave 4 g., b. p. 133°, and 16 g., b. p. 95–110° at 150 mm. The first of these took up 2Br$_2$ and gave 2HBr on hydrolysis, showing the presence of 1 = and 1 S. The other took up 2Br$_2$ and gave 4HBr, showing the presence of 2 S. The constitutions of these were not determined.

Summary

1. Sulfur strips hydrogen from unsaturates even to form hydrogen sulfide a part of which adds to the double bond producing a mercaptan which adds to more of the unsaturate to give a sulfide.

2. The addition of hydrogen sulfide takes place readily and follows Markownikow's rule. Sulfur is an effective catalyst.

3. Mercaptans add to double bonds in accordance with Markownikow's rule if peroxides are eliminated or sulfur used as a catalyst. In the presence of peroxides the abnormal addition takes place. The amount of peroxide required is small.

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