this it is estimated that $E_{1a} - E_{1b} = 0.5$ kcal./mole, and $A_{1a}/A_{1b} = 1.4$. The relatively large ratio of $k_{1a}/k_{1b} = 0.61$ at 25° is consistent with the observation[4,18] that secondary free radicals have a significantly higher ratio of the rate of disproportionation to that of combination than the primary radicals. This may reflect the increased probability of the abstraction reaction for the secondary radicals (there are more H-atoms per radical which can be abstracted and lead to an olefin product), and/or the decreased rate of combination of the more sterically hindered radical.

The Mechanism of Hydrogen Formation.—For runs at a given temperature Φ_{H_2} is approximately independent of the absorbed light intensity for consecutive experiments with similar wall conditioning; compare Φ_{H_2} from runs 10 and 12, and 14 and 15 of Table I. The increase in Φ_{H_2} with temperature (Fig. 2) suggests the increasing importance of formyl radical decomposition at high temperatures. Pronounced variation in Φ_{H_2} was found in duplicate experiments separated by an extended period of photolysis. All of these facts are consistent with the formation of hydrogen in the sequence I, (5), (6) and (7). It is likely that the effectiveness of the wall for reaction (6) was altered by polymer formation; in general the cleaner the cell the higher was Φ_{H_2}, and presumably the less effective the wall for reaction (6). Compare runs 18, 19, and 20, and 23 and 24 in Table I. The yields of hydrogen are too variable in this system to provide a meaningful estimate of the activation energy of the hydrogen forming reactions.

The Configuration of Alkyl Free Radicals.—The results show that the photolysis of 2-methylbutanal is a good source of *sec*-butyl radicals. The *sec*-butyl radical is of special interest since it is the simplest alkyl radical which may contain an asymmetric carbon atom. A study of the vapor phase, iodine-inhibited photolysis of 2-methylbutanal is in progress in these laboratories. It is hoped that the information gained concerning the vapor phase reaction between the *sec*-butyl radical and molecular iodine may aid in the choice between the possible planar and tetrahedral configurations of the simple alkyl radicals.

Acknowledgment.—Grateful acknowledgment is made to Professor Melvin S. Newman for his suggestion of this problem and his helpful counsel given during the course of the work and to the Charles F. Kettering Foundation, Yellow Springs, Ohio, for the research fellowship awarded to J.T.G.

COLUMBUS 10, OHIO

---

[18] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1062 (1955).

[CONTRIBUTION FROM THE BUREAU OF MINES, PETROLEUM AND OIL-SHALE EXPERIMENT STATION]

Gaseous Decomposition Products Formed by the Action of Light on Organic Sulfur Compounds[1]

BY WILLIAM E. HAINES, GLENN L. COOK AND JOHN S. BALL

RECEIVED JUNE 11, 1956

Exposures of 30 highly purified sulfur compounds to a mercury-vapor light under identical conditions produced gaseous decomposition products that were analyzed mass spectrometically. The experiments included 13 thiols, 8 sulfides, 3 cyclic sulfides, 2 disulfides and 4 thiophenes. Decompositions, as measured by the gaseous products, ranged from 0.004 to 3.0 mole %. Thiols showed greater amounts of decomposition than the other types of sulfur compounds and gave hydrogen as the main product. Sulfides and disulfides yielded, as the predominant product, a saturated hydrocarbon corresponding to the smallest alkyl radical attached to the sulfur. Thiophenes gave hydrogen and hydrogen sulfide. These experiments show that the sulfur compounds studied must be protected from light to maintain high purity.

The action of light on highly purified organic sulfur compounds prepared by American Petroleum Institute Research Project 48 was investigated as part of a study of the stability of these compounds. The compounds, which are used for instrument calibration and research studies, often are stored for considerable periods before use, hence it is desirable to obtain information about their stability during storage, both in the dark and in the light. Work previously reported from this Laboratory[2] on 20 of the compounds has shown that no decomposition occurs upon dark storage. Only 6 of these compounds—thiacyclobutane, 2,3-dithiabutane, 3,4-dithiahexane, 2-methylthiophene, 3-methylthiophene and benzo[b]thiophene—showed instability when stored in sunlight for 1 year. These decompositions were estimated by freezing-point purity measurments,[3] which detect only the decomposition products remaining as impurities in the liquid.

Recently, interest was directed to the decomposition products that might not be detected by the methods previously used. Thirty highly purified sulfur compounds were exposed to artificial light and the gaseous decomposition products were analyzed by mass spectrometric methods. The technique developed has particular value when the amount of decomposition is small and the purity of the starting material is great enough so that the impurities may be assumed not to be responsible for the products. Some insight into the mechanism of the reaction may be drawn from the results.

---

[1] This work was done as part of API Research Project 48A on the Synthesis, Properties and Isolation of Sulfur Compounds of Petroleum carried out by the Bureau of Mines at Laramie, Wyo., and Bartlesville, Okla. The paper was presented before the Division of Petroleum Chemistry, American Chemical Society, Minneapolis, Minn., Sept. 1955.

[2] (a) W. E. Haines, R. V. Helm, C. W. Bailey and J. S. Ball, *J. Phys. Chem.*, **58**, 270 (1954); (b) W. E. Haines, R. V. Helm, G. L. Cook and J. S. Ball, *ibid.*, **60**, 549 (1956).

[3] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

TABLE I

RESULTS OF EXPOSURE OF SULFUR COMPOUNDS TO ARTIFICIAL LIGHT

Compound	Pressure in ampoule, mm.	Apparent decompn., mole %	Composition of gaseous decomposition products, mole %										
					Saturated hydrocarbons				Olefins				
			H_2	H_2S	C_1	C_2	C_3	C_4	C_2	C_3	CO	CO_2	N_2
Thiols													
Methanethiol	1018	0.7	79.9		20.2								
Ethanethiol	349	.4	98.4	0.1	0.1	1.0			0.4		0.1	0.1	
1-Propanethiol	584	.7	100	tr.									
2-Propanethiol	350	.4	99.9	0.1									
1-Butanethiol	286	.4	100	tr.									
2-Butanethiol	263	.4	99.8	0.2									
2-Methyl-1-propanethiol	454	.7	99.9	0.1									
2-Methyl-2-propanethiol	93	.1[a]	63.6	32.3	2.5			1.2				0.1	
1-Pentanethiol	191	.3	96.9	3.0									
2-Methyl-2-butanethiol	57	.1	96.9	3.1									
1-Hexanethiol	381	.8	99.0	0.1									0.9
1-Heptanethiol	487	1.1	97.4	2.6									
Benzenethiol	1762	3.2	99.1	0.9									
Sulfides													
2-Thiapropane	98	0.05	0.2		99.8								
2-Thiabutane	25	.02	0.4		92.4	6.6			.6				
2-Thiapentane	40	.03	1.2		93.8	0.3	0.7	0.1	.1	0.5	3.3		
3-Thiapentane	11	.01	2.9		19.6	54.4			11.8		11.2		
3-Methyl-2-thiabutane	32	.02	0.6		96.2		2.7			0.5			
2-Thiahexane	37	.03	2.9		94.3			0.1			2.5	0.1	
4-Thiaheptane	3.6	.004	23.3	0.6	1.9	0.9	45.5			25.5	1.8	.7	
5-Thianonane	5.2	.006[b]	60.1	.3	5.1	.7		6.3	2.5		21.7	.2	
Cyclic sulfides													
Thiacyclobutane	2762	1.7							100.0				
Thiacyclopentane	5.1	0.004	37.0	.2	0.9				60.2		1.0	.6	
Thiacyclohexane	2.5	.002	35.8	10.3	0.7				45.3	0.9		7.0	
Disulfides													
2,3-Dithiabutane	44	.03[c]	0.7		92.4	.2						0.1	0.5
3,4-Dithiahexane	12	.01	1.6		1.7	85.8	1.5		2.6		4.3	2.7	
Thiophenes													
Thiophene	3.3	.004[a]	16.0	16.4	3.5				1.3		9.5	15.5	36.5
2-Methylthiophene	4.5	.008	58.7	.9	1.5	0.6					3.2	0.5	34.5
3-Methylthiophene	4.7	.008	85.6	.5	2.8				0.4		1.0	1.4	8.3
Benzo[b]thiophene	1.6	.004[a]	22.6	52.9	1.8	7.1	.8		1.1		0.2	2.3	

[a] Includes some unidentified gases. [b] Includes butenes 3.0%. [c] Includes methanethiol 6.0%.

Experimental

The 30 sulfur compounds used were calibration standards purified by American Petroleum Institute Research Project 48. The purity of each compound exceeded 99.9 mole %, as measured by the freezing-point method. Approximately 5 ml. of each of the samples was sealed in a glass break-off-tip ampoule under vacuum. The total volume of the ampoule was approximately 12 ml., leaving 7 ml. of free space above the sample. The samples were placed in a box lined with aluminum foil and exposed to radiation from a mercury-vapor lamp placed 7 inches from the samples. The temperature in the box was approximately 50°. As preliminary experiments showed that 65 hours of exposure gave detectable decomposition, this convenient exposure time was used for all compounds.

The gaseous (at −70°) products formed during the exposure were analyzed using a Consolidated model 21-103 mass spectrometer. The gases were sampled after the ampoules were thoroughly cooled in a Dry Ice–chloroform bath to retain the original compound and the higher boiling materials in the liquid or solid state. Pressures were measured by a micromanometer after the gases had been expanded into the mass spectrometer inlet system through the break-off tip on the ampoule. The measured pressures were used to calculate the original pressure of the gas in the ampoule. The partial pressure due to the undecomposed compound was subtracted from the observed pressure on the basis of the mass spectrometer analysis. Although the absolute accuracy of the pressure measurements is probably not greater than ±10%, the internal consistency is thought to be about ±2%.

Apparent decompositions were calculated from the pressures. Assumptions were made that 2 moles of thiol or of thiophene gave 1 mole of decomposition product, while the other compounds were assumed to give a mole-to-mole ratio. These assumptions are discussed below.

Results

The data from experiments on 30 sulfur compounds are shown in Table I. The calculated decompositions are generally less than 1% for the thiols and 1 or 2 orders of magnitude lower for the other compounds. As previously observed by Thompson,[4] hydrogen was the major product from the photolytic decomposition of the thiols. This was also true of the two methylthiophenes and 5-thianonane. The gaseous decomposition products of the other sulfides and of the disulfides were primarily hydrocarbons; the cyclic sulfides yielded ethene as the principal hydrocarbon. Thiophene and

---

(4) M. Meissner and H. W. Thompson, *Trans. Faraday Soc.*, **34**, 1238 (1938); N. P. Skerrett and H. W. Thompson, *ibid.*, **37**, 81 (1941).

benzo[b]thiophene produced both hydrogen and hydrogen sulfide in important amounts.

Nitrogen, carbon dioxide and carbon monoxide are evident in several samples in which the total pressure was low. Although each sample was degassed when it was placed in the ampoule, the contribution of small amounts of impurities, such as dissolved air, becomes significant when the total gas pressure is low.

The results indicate that exposure to strong light causes decomposition of sulfur compounds. The thiols seem to be the most susceptible, but the need for protection from light is indicated for all compounds. The usual practice of storage of such calibration samples in opaque mailing tubes is shown to be necessary.

Discussion

The purpose of this investigation was to estimate the extent of photolytic decomposition of sulfur compounds. For this purpose it was unnecessary to identify the liquid decomposition products. Establishing the mechanisms of reaction is not possible without knowledge of the liquid products, but a few suggestions can be made.

Steacie,[5] in reviewing the field, indicates that the photolysis of only two of these compounds, methanethiol and ethanethiol, has been studied and gives the mechanisms proposed by Thompson, *et al.*[4]

$$\mathrm{RSH} \longrightarrow \mathrm{RS} + \mathrm{H}$$
$$\mathrm{H} + \mathrm{RSH} \longrightarrow \mathrm{RS} + \mathrm{H_2}$$
$$2\mathrm{RS} \longrightarrow \mathrm{RSSR}$$

These do not explain the formation of H_2S observed in some instances.

An alternative free radical mechanism can be obtained from work on thermal decomposition of thiols[6]

$$\mathrm{RSH} \longrightarrow \mathrm{R} + \mathrm{SH} \qquad (1)$$
$$\mathrm{R} + \mathrm{RSH} \longrightarrow \mathrm{RH} + \mathrm{RS} \qquad (2)$$
$$\mathrm{RS} \longrightarrow \text{olefin} + \mathrm{SH} \qquad (3)$$
$$\mathrm{SH} + \mathrm{RSH} \longrightarrow \mathrm{H_2S} + \mathrm{RS} \qquad (4)$$

Although these reactions explain the products of thermal decomposition, they do not explain the predominance of hydrogen observed in photolytic experiments. Hydrogen could be explained, however, by assuming that reactions 3 and 4 become negligible and that reactions 1 and 2 start a chain reaction

$$\mathrm{RS} + \mathrm{RSH} \longrightarrow \mathrm{RSSR} + \mathrm{H} \qquad (5)$$
$$\mathrm{H} + \mathrm{RSH} \longrightarrow \mathrm{RS} + \mathrm{H_2} \qquad (6)$$

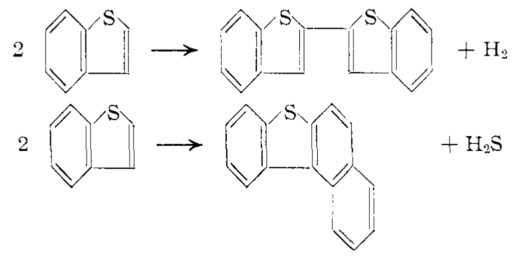
No information regarding the photolysis of sulfides was found in the literature. The meager data on thermal decomposition[7] show the products to be hydrogen sulfide, thiols and gaseous hydrocarbons. The data in Table I show that essentially no hydrogen sulfide is formed but indicate that the carbon–sulfur bond splits. The methyl sulfides break predominantly at the methyl–sulfur bond to give methane. The other products are not known, but it was necessary for the purpose of decomposition calculations to assume that they were liquid. The percentage of decomposition was then calculated from the hydrocarbon gases on a mole-for-mole basis.

Thiacyclobutane decomposed to form ethene and a white solid. The mechanism is probably analogous to that of trimethylene oxide,[8] which splits to form formaldehyde and ethene. The white solid resulting from the decomposition of thiacyclobutane is probably a trimer of H_2C–S.

The reaction for decomposition of the other cyclic sulfides in which the ring strain was negligible is impossible to postulate from the limited data. Decomposition percentages were calculated on a mole-for-mole basis.

From thermal data[7] the decomposition of disulfides is very complex, yielding hydrogen sulfide, thiol, sulfide and sometimes thiophenes. The present data indicate a split at the carbon–sulfur bond to yield hydrocarbon plus unknown products. No hydrogen sulfide was formed. The hydrocarbon gas was assumed to be a molar measure of the decomposed molecules for the purpose of calculating the extent of the decomposition.

Previous work on benzothiophene[2b] indicated that this compound underwent two reactions



The presence of both hydrogen and hydrogen sulfide in the decomposition products of the other three thiophenes suggests that they decompose by a similar mechanism. The per cent. decomposition was therefore calculated by assuming that 2 moles of the thiophene was required for each molecule of hydrogen or hydrogen sulfide produced.

Acknowledgments.—The authors wish to thank R. A. Meyer, J. C. Morris and D. G. Earnshaw, who assisted with the experimental work, and G. U. Dinneen, for helpful advice and criticisms. This work was done under a coöperative agreement between the Bureau of Mines, United States Department of the Interior, and the University of Wyoming.

LARAMIE, WYOMING

---

[5] E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. II, Reinhold Publ. Corp., New York, N. Y., 1954, pp. 785–788.

[6] W. M. Malisoff and E. M. Marks, *Ind. Eng. Chem.*, **23**, 1114 (1931).

[7] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).

[8] D. A. Bittker and W. D. Walters, THIS JOURNAL, **77**, 1429 (1955).