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

THE DECOMPOSITION OF MERCAPTANS IN ALKALI SOLUTIONS[1]

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Introduction

It is a well-established fact that the structure of the group attached to a carbon atom in combination with oxygen or a halogen has a great influence upon the strength of that bond. This has been shown by Conant and his associates,[3] who investigated the relation between the structure of organic halides and the speed of their reaction with inorganic iodides, and by Norris and his co-workers,[4] who studied the relative reactivities of the hydroxyl hydrogen atoms in certain alcohols and the effect of various substituted groups on the strength of the carbon–chloride bond.[5] It was thus considered of value to determine the effect of the structure of the alkyl group upon the strength and reactivity of the carbon–sulfur bond, and for this purpose the decomposition reaction of the aliphatic mercaptans in alkali solution was selected. It was desired to determine (1) whether mercaptans decompose in alkaline solution in any definite and reproducible manner, (2) the effect of time, temperature and concentration on this reaction, and (3) the exact course of the reaction, the products formed, and if possible its velocity constant and temperature coefficient.

Results

The aliphatic mercaptans were found to decompose in sodium hydroxide solution in a definite and reproducible manner. Three simultaneous reactions take place as follows: (1) replacement of the —SH group by hydroxyl to form an alcohol, as

$$RSH + 2NaOH = ROH + Na_2S + H_2O$$

(2) elimination of hydrogen sulfide from two molecules of mercaptan to form the alkyl sulfide, as

$$2RSH + 2NaOH = R_2S + Na_2S + 2H_2O$$

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[1] Presented at the Columbus Meeting of the American Chemical Society, May 1, 1929.

[2] From the Ph.D. dissertation of E. C. Billheimer, June, 1929.

[3] Conant and Kirner, THIS JOURNAL, **46**, 232 (1924); Conant and Hussey, *ibid.*, **47**, 476 (1925); Conant, Kirner and Hussey, *ibid.*, **47**, 488 (1925).

[4] Norris and Ashdown, *ibid.*, **47**, 837 (1925); Norris and Cortese, *ibid.*, **49**, 2640 (1927).

[5] Norris and Morton, *ibid.*, **50**, 1795 (1928); Norris and Banta, *ibid.*, **50**, 1804 (1928); Norris and Blake, *ibid.*, **50**, 1808 (1928); Norris and Gregory, *ibid.*, **50**, 1813 (1928).

(3) the elimination of hydrogen sulfide from one molecule of mercaptan to form the unsaturated hydrocarbon, as

$$CH_3CH_2SH + 2NaOH = CH_2{=}CH_2 + Na_2S + 2H_2O$$

Two further possible consecutive reactions, in which the alkyl sulfide might decompose with alkali to produce either the alcohol or the unsaturated hydrocarbon, were shown to be unimportant, as they are not given by butyl sulfide heated under the same conditions. The products of the three reactions were identified. The alkyl sulfide was oxidized to the corresponding sulfone with fuming nitric acid, according to the method of Grabowsky,[6] the product purified and identified by its melting point, which was compared with that of pure sulfone prepared in a similar manner from the particular sulfide in question. The alcohol was shown to be present by the formation of the corresponding half-ester of phthalic acid, on refluxing with phthalic anhydride, a dried benzene extraction of a steam distillate of the reaction mixture, from which the unreacted mercaptan had been removed by precipitation as mercaptide with lead acetate solution. The product was subsequently isolated and purified, and its identity proved by melting point determinations. The unsaturated hydrocarbon was easily noticeable in the case of the lower members of the mercaptan series, when it escaped as a gas, especially with ethyl mercaptan, in which case ethylene was evolved upon opening the bomb after a run. The sodium sulfide was easily distinguished by the evolution of hydrogen sulfide upon acidification.

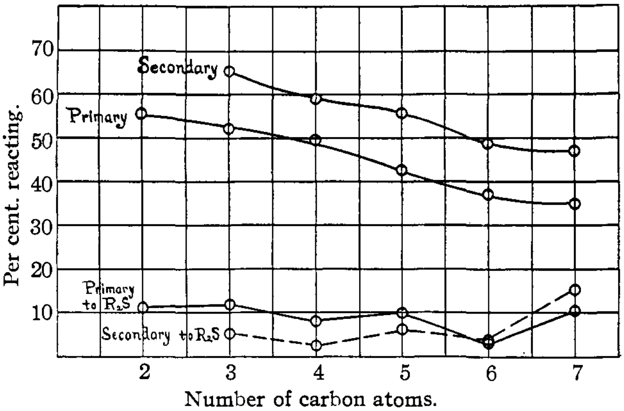

Fig. 1.—Percentage of mercaptans reacting with 3 *N* NaOH in 2 hours at 260°.

The optimum conditions for comparison of the reactivity of the different members of the mercaptan series were established with *n*-butyl mercaptan. They were so adjusted, by varying concentration, temperature and time of heating, that about half of this mercaptan was decomposed, which is the

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[6] Grabowsky, *Ann.*, **175**, 348 (1875).

case in two hours at 260° with 3*N* caustic soda solution. The runs for comparison of different mercaptans were made under these conditions. Runs with other concentrations of alkali and at other temperatures were made for other comparisons. The straight chain primary and secondary mercaptans from ethyl and isopropyl to heptyl have been studied. It was intended to include the octyl and nonyl mercaptans but their sodium derivatives were found to be insoluble, separating out immediately upon addition of the mercaptan to the alkali. This prevented complete solution of the products of the reaction at the completion of a run, and made it impossible to secure the aliquots necessary for the analytical procedure.

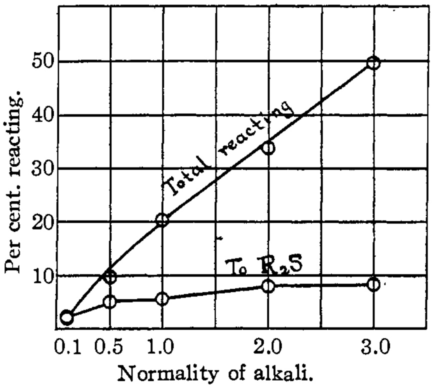

Fig. 2.—Percentage of *n*-butyl mercaptan reacting with different strengths of alkali.

The results are given in the tables below, the figures being the average percentages of the mercaptans reacting under the conditions stated. The same data are reproduced in the curves, Fig. 1 and Fig. 2.

It appears that the total decomposition decreases, with both normal and secondary mercaptans, as the number of carbon atoms increases. There is a suggestion of alternation. The secondary mercaptans react more rapidly

TABLE I

NORMAL MERCAPTANS WITH 3*N* SODIUM HYDROXIDE (2 HOURS AT 260°)

Mercaptan	Et	Pr	Bu	*Iso*-Bu	Am	Hex	Hep
Total decomposed	55.4	52.2	49.6	36.2	42.9	37.0	35.0
R_2S formed	11.0	12.1	8.1	6.1	9.9	3.1	10.4
Percentage R_2S	20	23	16	16	23	8	30

TABLE II

β-SECONDARY MERCAPTANS WITH 3*N* SODIUM HYDROXIDE (2 HOURS AT 260°)

No. carbon atoms	3	4	5	6	7
Total decomposed	65.4	59.1	56.0	48.8	47.0
R_2S formed	5.2	2.6	6.3	3.6	15.3
Percentage R_2S	8	4	11	7	33

TABLE III

VARIATION OF DECOMPOSITION OF *n*-BUTYL MERCAPTAN WITH CHANGES IN STRENGTH OF THE ALKALI

Concn. of NaOH	0	0.1	0.5	1.0	2.0	3.0
Percentage decomposed	0.0	2.1	9.8	20.2	33.8	49.6
R_2S formed	0.0	1.7	4.9	5.4	7.8	8.1
Percentage R_2S	...	81	50	27	23	16

TABLE IV

DECOMPOSITION OF *n*-BUTYL MERCAPTAN AT DIFFERENT TEMPERATURES BY 3*N* SODIUM HYDROXIDE

Temperature, °C.	250	250	260	270
Time in hours	2	4	2	2
Percentage dec.	30	47.2	49.6	63.0
R_2S formed	7.7	11.9	8.1	8.2
Percentage R_2S	26	25	16	13

than the corresponding primary, which is to be expected from the work of Norris and his co-workers, who found that reactions of alcohols in which the hydroxyl is eliminated proceed faster with secondary alcohols than with primary. The amount of sulfide formed is lower with the secondary than with the primary, which agrees with the above. With very dilute alkali the percentage of alkyl sulfide is high when it is compared with the total decomposition. Isobutyl mercaptan reacts much more slowly than *n*-butyl, just as in esterification. At 250° in four hours *n*-butyl mercaptan gives slightly less decomposition than at 260° in two hours, which shows that the reaction has about the usual temperature coefficient. The proportion of butyl sulfide formed is somewhat higher at the lower temperature.

There is a suggestion of alternation, the values for the mercaptans having an even number of carbon atoms appearing to be below the curve.

Apparatus and Materials

The special apparatus necessary for and used in the preliminary part of this investigation was exactly similar to that employed by Herndon and Reid[7] in work on the decomposition of organic compounds at high pressures and temperatures, which was itself a modification of the type developed by Morey[8] in his studies on hydrated silicates. This consisted of the special steel bomb, the furnace and the automatic temperature control. For the greater part of the present work, however, a smaller type bomb was used, of 25-cc. capacity, with threads on the outside of the body proper, allowing easier and more complete removal of the reaction products. The plunger rested atop the body proper and carried through its center a steel thermocouple tube silver-soldered to the plunger and extending a half inch into the chamber of the bomb when the latter was closed.

The mercaptans, with the exception of ethyl, *n*-butyl and isobutyl, were furnished by L. M. Ellis, Jr.[9] Normal butyl mercaptan, which was used to standardize the analytical method and establish the proper conditions for comparison, was prepared in large quantities by the method of Grabowsky and Saytzeff.[10] The mercaptan was extracted with dilute caustic soda solution, recovered by steam distillation, dried and fractionated on a tall-column still. The purity was 99.94%. The ethyl and isobutyl mercaptans were Eastman's "Certified" products. The purity of the normal and secondary mercaptans used was in no case less than 99.3%.

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[7] Herndon and Reid, THIS JOURNAL, **50**, 3066 (1928).

[8] Morey, *ibid.*, **36**, 215 (1914).

[9] Ellis, "Dissertation," Johns Hopkins University, 1929.

[10] Grabowsky and Saytzeff, *Ann.*, **171**, 251 (1874).

Experimental

The purity of the mercaptans was determined volumetrically by the method of Kimball, Kramer and Reid[11] which makes use of their reaction by titration with standard iodine solution. This reaction was also made the basis of the analytical method eventually established. The procedure was essentially as follows. The reaction mixture was washed from the bomb into a separatory funnel, from which the water layer was run into a volumetric flask and diluted to a convenient volume. The insoluble alkyl sulfide was measured and its weight calculated from its density. From the water solution aliquots were taken. First, one aliquot was titrated with 6 *N* hydrochloric acid, using methyl orange as an indicator, to determine the amount of acid necessary to neutralize the excess alkali and decompose the sodium sulfide formed. Second, an aliquot was run from a pipet with its tip below the surface of excess standard iodine solution containing hydrochloric acid in slight excess of that determined by the first operation and the excess iodine titrated with standard thiosulfate solution. This gave a value for the sum of the sodium sulfide and the unreacted mercaptan. Third, an aliquot was boiled to remove all unreacted mercaptan, diluted with water and boiled several times if necessary, and the hydrogen sulfide formed in the decomposition thus determined by washing into excess iodine solution containing the predetermined amount of hydrochloric acid and back-titrating with thiosulfate solution as before. These three sulfur values, namely, the alkyl sulfide, sodium sulfide and unreacted mercaptan, when calculated to mercaptan, gave a check on the amount originally added, and from them could be determined the percentage decomposition, since all three reactions produce sodium sulfide.

TABLE V

EXPERIMENTAL RESULTS

Col. 1, mercaptan reacted, %; Col. 2, sodium sulfide formed, %; Col. 3, mercaptan unreacted, %; Col. 4, alkyl sulfide formed, %; Col. 5, mercaptan accounted for, %.

	(1) Ethyl mercaptan, 2 hrs., 260°						(2) *n*-Propyl mercaptan, 2 hrs., 260°				
	55.5	48.7	39.1	10.9	98.7		52.3	43.3	39.4	12.5	95.2
	55.0	46.5	38.2	10.8	95.5		52.6	42.8	38.6	12.7	94.2
	55.7	48.0	38.2	11.2	97.3		51.8	44.1	41.0	11.0	96.1
Av.	55.4	47.7	38.5	11.0	97.2	Av.	52.2	43.4	39.7	12.1	95.2
	(3) *n*-Butyl mercaptan, 2 hrs., 260°						(4) Isobutyl mercaptan, 2 hrs., 260°				
	50.0	45.0	45.0	8.1	98.0		35.9	33.4	59.5	6.4	99.2
	49.4	44.6	45.7	8.1	98.5		36.5	33.9	59.0	5.8	98.8
	50.1	44.6	44.2	8.7	97.4		35.8	33.5	59.9	5.2	98.7
	48.8	43.2	45.4	7.5	96.2		36.1	33.0	58.4	6.4	97.9
	49.7	44.7	45.4	8.1	98.3		36.6	33.7	58.4	6.9	98.9
Av.	49.6	44.4	45.1	8.1	97.7	Av.	36.2	33.5	59.0	6.1	98.7

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[11] Kimball, Kramer and Reid, THIS JOURNAL, **43**, 1199 (1921).

TABLE V (*Continued*)

(5) *n*-Amyl mercaptan, 2 hrs., 260°

	42.5	37.0	50.1	10.7	97.7
	42.9	38.1	50.6	10.1	98.9
	43.3	39.6	51.7	8.4	99.5
	42.8	37.5	50.0	10.7	98.1
	43.2	37.7	49.7	9.5	96.8
Av.	42.9	38.0	50.4	9.9	98.2

(6) *n*-Hexyl mercaptan, 2 hrs., 260°

	37.1	35.4	60.2	3.2	98.8
	37.3	35.8	60.3	3.5	99.6
	36.5	35.0	60.6	2.7	98.3
Av.	37.0	35.4	60.4	3.1	98.9

(7) *n*-Heptyl mercaptan, 2 hrs., 260°

	35.0	30.4	56.4	10.6	97.3
	35.2	31.1	57.3	10.1	98.5
	34.8	30.5	57.1	10.4	98.1
Av.	35.0	30.7	56.9	10.4	98.0

(8) Isopropyl mercaptan, 2 hrs., 260°

	65.7	61.0	32.0	5.6	98.5
	65.0	61.2	32.9	5.0	99.1
	65.4	61.4	32.5	5.0	98.8
Av.	65.4	61.2	32.5	5.2	98.8

(9) *Sec.*-butyl mercaptan, 2 hrs., 260°

	58.8	56.2	39.4	3.0	98.6
	59.2	56.8	39.3	3.0	99.1
	59.3	57.2	39.0	2.5	98.7
	59.0	56.9	39.6	1.9	98.4
	59.3	56.8	38.9	2.5	98.3
Av.	59.1	56.8	39.2	2.6	98.6

(10) *Sec.*-amyl mercaptan, 2 hrs., 260°

	56.5	51.6	39.7	7.2	98.4
	56.0	52.2	40.8	6.2	99.2
	55.6	52.6	41.9	5.1	99.5
	56.3	51.8	40.4	6.2	98.5
	55.8	53.3	42.2	6.8	99.9
Av.	56.0	52.3	41.0	6.3	99.1

(11) *Sec.*-hexyl mercaptan, 2 hrs., 260°

	48.9	46.1	48.3	3.8	98.1
	48.3	45.6	48.8	3.5	97.9
	49.1	46.5	48.7	3.5	98.7
Av.	48.8	46.1	48.6	3.6	98.2

(12) *Sec.*-heptyl mercaptan, 2 hrs., 260°

	46.7	38.1	43.5	14.4	96.1
	47.0	38.3	43.2	15.2	96.7
	47.3	38.3	42.8	16.2	97.3
Av.	47.0	38.2	43.2	15.3	96.7

(A) *n*-Butyl mercaptan, 2 hrs., 250°

	30.1	26.8	62.2	7.5	96.4
	30.2	26.6	61.5	8.0	96.1
	29.5	25.6	61.5	7.5	94.8
	29.1	25.5	62.2	7.5	95.3
	30.9	27.3	61.0	8.0	96.4
Av.	30.0	26.4	61.7	7.7	95.8

(B) *n*-Butyl mercaptan, 4 hrs., 250°

	46.8	40.0	45.4	12.8	98.1
	46.3	38.7	45.0	11.6	95.3
	47.5	41.3	45.6	11.6	98.5
	48.8	42.2	44.3	12.2	98.7
	46.6	40.5	46.6	11.1	98.2
Av.	47.2	40.5	45.4	11.9	97.8

(C) *n*-Butyl mercaptan, 2 hrs., 270°

	63.0	56.5	33.2	8.7	98.3
	63.2	57.1	33.4	8.1	98.6
	62.9	57.3	33.9	8.1	99.2
	63.3	56.9	32.9	8.7	98.4
	62.8	57.5	34.1	7.5	99.1
Av.	63.0	57.1	33.5	8.2	98.7

Table V (*Concluded*)

The following runs were made between *n*-butyl mercaptan and sodium hydroxide solution of the following strengths: 2.0, 1.0, 0.5, 0.1 *N*, and finally pure water. The heating was for two hours at 260°.

n-Butyl mercaptan, 2.0 *N* NaOH

	33.8	30.3	59.3	7.7	97.4
	34.1	30.5	59.0	8.7	98.2
	33.4	30.0	59.9	7.1	97.1
Av.	33.8	30.3	59.4	7.8	97.6

n-Butyl mercaptan 1.0 *N* NaOH

	20.5	18.6	72.0	5.2	95.8
	19.8	17.9	72.4	5.1	95.4
	20.4	18.5	72.3	5.9	96.7
Av.	20.2	18.3	72.2	5.4	96.0

n-Butyl mercaptan 0.5 *N* NaOH

	9.9	9.0	81.9	4.6	95.4
	10.0	9.2	81.6	5.2	95.9
	9.4	8.7	82.2	4.9	95.7
Av.	9.8	9.0	81.9	4.9	95.7

n-Butyl mercaptan 0.1 *N* NaOH

	2.5	2.3	92.2	1.8	96.3
	1.9	1.8	95.2	1.6	98.7
	2.0	1.9	93.9	1.8	97.7
Av.	2.1	2.0	93.8	1.7	97.6

The amount of mercaptan used in each run was always 10 millimoles, which was dissolved in 12 cc. of the sodium hydroxide solution, which for the 3*N* was 3.66 equivalents. This was a convenient sized charge since the bomb held 25 cc. The results obtained are given in Table V.

In the runs with pure water, the percentage of mercaptan reacted was found to be practically zero.

Summary

1. Apparatus has been developed and a quantitative method of analysis established for the investigation of the decomposition of mercaptans in alkali solution.
2. Mercaptans have been found to decompose in alkali solution in a definite and reproducible manner.
3. The course of the decomposition has been determined and the products identified.
4. This decomposition reaction has been used as a means of studying the effect of substitution on the reactivity of the C—S bond, and the following mercaptans have been investigated in this way: ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec.*-butyl, *n*-amyl, *sec.*-amyl, *n*-hexyl, *sec.*-hexyl, *n*-heptyl, *sec.*-heptyl, *n*-octyl, *sec.*-octyl, *n*-nonyl, *sec.*-nonyl.
5. The effect of concentration of alkali on the rate of decomposition of the mercaptans has also been determined.

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