these studies; also to Messrs. E. S. Lamar and J. W. Westhaver, for assistance in the experimental work.

Summary

The decomposition of ammonia on tungsten, molybdenum and nickel has been investigated as a part of a program designed to give further information in regard to the ammonia reaction and the role played by the catalyst in this reaction. The results are expressed in terms of the A and E constants of Arrhenius' equation.

The decomposition of ammonia on tungsten and molybdenum was apparently of zero order. The reaction rate was decreased at the lower temperatures by both hydrogen and nitrogen.

The value of E as determined from the temperature coefficient was approximately constant for all surfaces at the lower reaction rates, about 45,000, decreasing for the higher temperatures to 35,000 for tungsten, 32,000 for molybdenum and 26,000 for nickel.

The relative catalytic activity of the surface investigated was not given by the observed temperature coefficient of the reaction expressed in terms of E but was given rather in terms of the surface, that is, in terms of A, in so far as comparisons can be made from the measured dimensions of the hot catalyst surfaces.

In general, the conclusions herein reached agree with the results obtained on promoted iron catalysts, which are to be published soon.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

INFRA-RED ABSORPTION BY THE S–H BOND

BY JOSEPH W. ELLIS

RECEIVED APRIL 26, 1928 PUBLISHED AUGUST 4, 1928

The apparent possibility of identifying the carbon–hydrogen[1] and the nitrogen–hydrogen[2] atom pairs as the probable origins of certain series of absorption frequencies in the near infra-red spectra of organic molecules has suggested a search for corresponding frequencies characteristic of the sulfur–hydrogen linkage. The spectra of the mercaptans suggest possible sources in which to look for such absorption bands. Bell[3] has obtained the spectra of several alkyl and aryl mercaptans and sulfides in the spectral region from 1–12μ. The general appearance of these spectra is strikingly similar to that of the corresponding alkyl or aryl amines recorded by Bell.[4]

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[1] (a) Ellis, *Phys. Rev.*, **23,** 48 (1924); (b) **27,** 298 (1926).

[2] (a) Ellis, THIS JOURNAL, **49,** 347 (1927); (b) **50,** 685 (1928).

[3] (a) Bell, *Ber.*, **60,** 1749 (1927); (b) private communication.

[4] (a) Bell, THIS JOURNAL, **47,** 2192 (1925); (b) **47,** 3009 (1925); (c) **48,** 813 (1926); (d) **48,** 818 (1926); (e) **49,** 1837 (1927).

This suggests that the main features of the spectra are assignable to origins within the substituted organic radical, some of them doubtless to the C–H linkages.

In the spectrum of a mercaptan, however, there is one band at 3.8–3.9μ which disappears, or practically disappears, in the spectrum of the corresponding sulfide. It was the opinion of the present author that this band might represent a fundamental frequency characteristic of the S–H atom pair, corresponding to the 3.4μ, 3.2–3.3μ and 2.8–3.0μ band ascribed by him and others to alkyl C–H, aryl C–H and N–H linkages, respectively.

The present investigation was undertaken to search for possible harmonics of this 3.8–3.9μ band. The recording quartz spectrograph used in previous studies was employed here. The compounds studied were ethyl, *n*-propyl, *n*-butyl, *iso*-amyl, phenyl (thiophenol) and benzyl mercaptans and the corresponding sulfides. These were supplied by the Eastman Kodak Company.

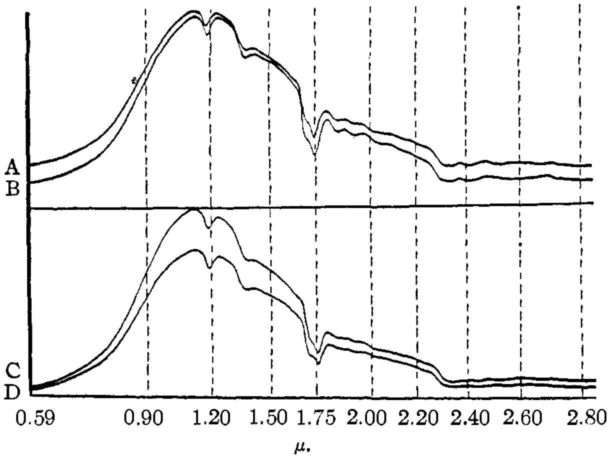

Fig. 1.—A. Ethyl mercaptan, T = 1 mm. B. Ethyl sulfide, T = 1 mm. C. *n*-Propyl mercaptan, T = 1 mm. D. *n*-Propyl sulfide, T = 1 mm.

The records of these spectra are shown in Figs. 1–4. In reproducing these records the plate containing the photographic tracing of the mercaptan was placed over that of the sulfide and these were photographed together by transmitted light. There seems to be but one distinguishing feature in the spectra of the mercaptans, namely, a band at 1.99–2.00μ. This is regarded as the first harmonic of the 3.8–3.9μ band. Both of these bands are strongest in the spectra of thiophenol and benzyl mercaptan. The presence of the overtone band may be considered uncertain in the records of 1-mm. cells of ethyl and *n*-propyl mercaptans, Fig. 1. However, it appears quite strongly when a 1-cm. cell of the latter substance is used, Fig. 2. An inspection of the original record of *n*-butyl mercaptan removes any doubt of its presence in that substance, and it is very noticeably present in the record of *iso*-amyl mercaptan in Fig. 3.

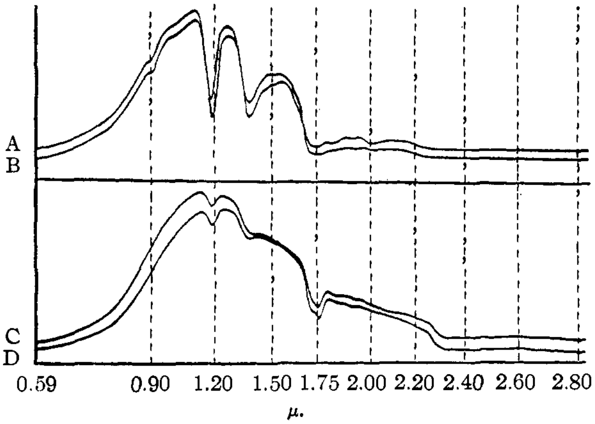

Fig. 2.—A. *n*-Propyl mercaptan, $T = 10$ mm. B. *n*-Propyl sulfide, $T = 10$ mm. C. *n*-Butyl mercaptan, $T = 1$ mm. D. *n*-Butyl sulfide, $T = 1$ mm.

A possible second harmonic would be superimposed upon the 1.4μ absorption region characteristic of both the mercaptan and the sulfide and hence could not be expected to be capable of detection.

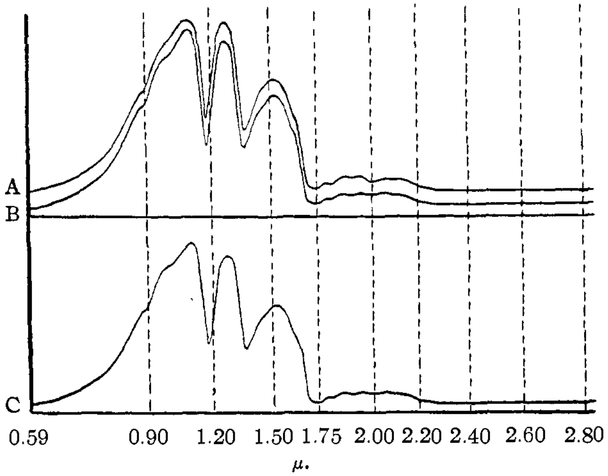

Fig. 3.—A. *Iso*-amyl mercaptan, $T = 10$ mm. B. *Iso*-amyl sulfide, $T = 10$ mm. C. *Iso*-amyl disulfide, $T = 10$ mm.

The deviation from true multiple relationship between the 3.8μ and the 1.99μ wave lengths for the alkyl mercaptans seems slightly greater than would be expected from comparisons with the fundamental and first overtone bands assigned to C–H and N–H atom pairs. However, the deviation is quite comparable with these latter cases in the case of the two aryl mercaptans; in these instances Bell's value (unpublished) varies from 3.85μ to 3.90μ and the overtone value from the present investigation is 2.00μ.

The main features of the spectra of the mercaptan and of the corresponding sulfide are quite similar over the whole region in which they have been studied. The main bands which occur are also found in the spectra of the corresponding primary, secondary and tertiary amines.[2,4] Certain of these, which have already been assigned to the C–H linkages, are tabulated, together with the bands assignable to S–H pairs, for the mercaptans and sulfides in Table I. Inspection of the table reveals the fact that the 3.30–3.35μ alkyl C–H value seems to be a trifle low as compared with the integral multiples of the corresponding overtone wave lengths. This fact, taken with the slight discrepancies in the S–H values discussed above, suggests a possible small systematic error in Bell's investigation of the alkyl mercaptans and sulfides.

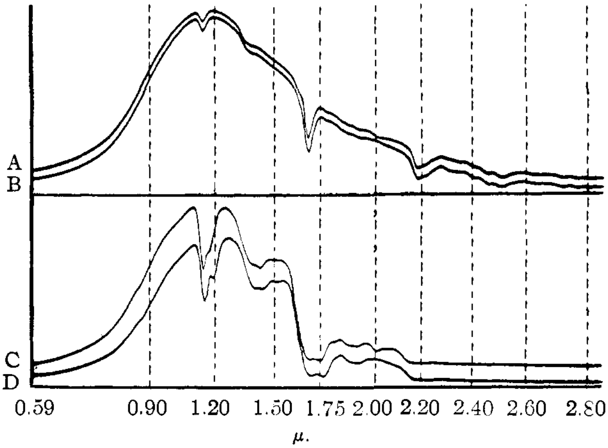

Fig. 4.—A. Thiophenol, $T = 1$ mm. B. Phenyl sulfide, $T = 1$ mm. C. Benzyl mercaptan, $T = 10$ mm. D. Benzyl sulfide, $T = 10$ mm.

The record of di-*iso*-amyl sulfide, Fig. 3, reveals nothing not shown by *iso*-amyl sulfide. Consequently, a study of the disulfides was pursued no further.

The doubling of the 1.145–1.19μ and 1.69–1.76μ bands in benzyl mercaptan and benzyl sulfide is probably due, as in the corresponding amines, to the presence of both phenyl and alkyl types of C–H bonds. The doubling of the 1.7μ alkyl band, more noticeable here than in the corresponding records heretofore published by the author, has been brought about by an increase in the resolving power of the spectrograph. This increased resolution has been produced largely by focusing the spectrum upon the slit in front of the thermopile rather than upon the thermoelements themselves. The possible significance of this revealed doubling here and in other instances will be discussed elsewhere.

All of the compounds examined are liquids at room temperature with the exception of benzyl sulfide. The record shown for this compound in Fig. 4 was taken through a 1-cm. cell of the molten substance maintained at a temperature just above the melting point. Upon cooling in an open dish, benzyl sulfide crystallizes in rhombohedral plates. A record was taken through such a specimen about 2 mm. in thickness. It was found necessary to open the slits considerably to get sufficient intensity, but the positions of the bands were found to be unchanged. This would seem to indicate that the force constants and the energy associated with the C–H bond, at least in this instance, remain unchanged during crystallization.

Table I

Bands Characteristic of Mercaptans and Sulfides

	Bands assignable to C–H, μ							to S–H, μ	
Ethyl mercaptan			1.18	1.38	1.70, 1.74			2.00	
Ethyl sulfide			1.185	1.38	1.70, 1.74				
n-Propyl mercaptan	0.91	1.01	1.19	1.385	1.71, 1.75	3.3	6.8	1.99	3.80
n-Propyl sulfide	.91	1.01	1.19	1.385	1.71, 1.75	3.35	6.85		
n-Butyl mercaptan			1.19	1.395	1.71, 1.75	3.3	6.8	1.99	3.80
n-Butyl sulfide			1.19	1.385	1.71, 1.75	3.35	6.85		
Iso-amyl mercaptan	.90	1.00	1.18	1.38	1.73	3.3	6.8	1.99	3.80
Iso-amyl sulfide	.90	1.00	1.18	1.37	1.73	3.4	6.85		
Iso-amyl disulfide	.90	1.00	1.18	1.37	1.73				
Thiophenol			1.145	1.39	1.685	3.25	6.8	2.00	3.90
Phenyl sulfide			1.145	1.39	1.685	3.25	6.8		
Benzyl mercaptan			1.145	1.39	1.69, 1.75	3.25	6.6, 6.9	2.00	3.85
Benzyl sulfide			1.145	1.39	1.69, 1.76	3.25	6.7, 6.9		

The spectrum of hydrogen sulfide has been recorded beyond 3μ by Coblentz.[5] Inasmuch as the mercaptans are mono derivatives of hydrogen sulfide, it might be expected that the spectrum of this latter substance would show a band analogous to that at 3.8–3.9μ. A band at 4.2μ might

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[5] Coblentz, *Carnegie Inst. Pub.*, **1905**, 35.

be interpreted as such. However, the complexity of the hydrogen sulfide spectrum beyond 4μ tends to make this comparison uncertain.

Summary

1. The infra-red absorption spectra of several alkyl and aryl mercaptans and sulfides have been examined with a recording quartz spectrograph.

2. A single band at 1.99–2.00μ differentiates the spectrum of a mercaptan from the corresponding sulfide. This band is regarded as the first harmonic of one found by Bell at 3.8–3.9μ, and both are interpreted as originating in the S–H bond.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GALLIUM. III. QUANTITATIVE SEPARATION OF IRON FROM GALLIUM BY MEANS OF ALPHA-NITROSO-BETA-NAPHTHOL[1]

BY JACOB PAPISH AND L. E. HOAG

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The method frequently employed for separating iron from gallium is based on the property of trivalent iron to form a precipitate on the addition of an excess of fixed alkali hydroxide while gallium, being amphoteric, passes into solution as alkali gallate. This method was first used by de Boisbaudran,[2] the discoverer of gallium, and in so far as the preparation of iron-free gallium is concerned it will be found satisfactory; the resulting alkali gallate and the gallium hydroxide and oxide ultimately obtained from it will be found on spectroscopic examination to contain negligible traces of iron, provided care is taken to prevent contamination through reagents and containers. A similar examination of the residual ferric hydroxide will reveal that even after thorough washing, small quantities of gallium are retained. This can be undoubtedly ascribed to the strong adsorptive power of ferric hydroxide, a phenomenon frequently observed in similar cases.

In extracting gallium from a natural mineral or in recovering it from commercial products, iron which is always present will accompany the

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[1] This article is a corollary of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. It is respectfully dedicated by the authors to Professor L. M. Dennis, and will be reprinted as article No. 9 in the Louis Munroe Dennis Quarter Century Volume to be published in 1928 in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University.

[2] De Boisbaudran, *Compt. rend.*, **94,** 1439, 1625 (1882).