$(C_6H_5)_3C_5H_{11}$, 302. The polymer was not oxidized by twenty hours of boiling with neutral permanganate solution, conditions which were effective in converting hexylbenzene to benzoic acid in six hours. No immediate decoloration with bromine occurred.

Diphenylpropane.—To benzylsodium, prepared as in experiment 9, was added gradually 30 ml. of methylene dichloride. The mixture was stirred for one-half hour after addition and then carbonated to ensure complete reaction of the organosodium compound. After the usual decomposition no acids could be found. Crude diphenylpropane (270–285°) 11 g. (18%), decane 5 g. (12%), and liquid boiling from 175–270°, 7 g. were obtained.

Hexyl-, Benzyl-, and Phenylethyl Alcohols.—Amylsodium, phenylsodium, and benzylsodium were prepared in the customary manner used in the reactions described in Tables I and II. Trioxymethylene, 30 g., suspended in the appropriate hydrocarbon solvent was added and the mixture stirred until the color of the organosodium compound was discharged, after which the mixture was heated to ensure completion of the reaction. The mixture was then carbonated and decomposed with ice. No acids were obtained. Upon fractionation of the hydrocarbon layer obtained in each experiment there was isolated 16 g. (28%), 11 g. (17%), and 13 g. (17%) of *n*-hexyl, benzyl, and phenylethyl alcohols, respectively. The corresponding decane and high boiling contents were 18, 20, and 14 g. The 3-nitrophthalic acid monoester derivative of this hexyl alcohol (boiling 149–152°) melted without further purification at 119–121° (pure 121°); that of the 190–200° boiling benzyl alcohol at 167–174° and when recrystallized at 172–176° (pure 176°). The phenylethyl alcohol which boiled at 205–212° was shown to be free from *o*-methylbenzyl alcohol by the absence of phthalic acid and the presence of benzoic acid after oxidation with neutral permanganate solution.

Summary

Possible combinations of organosodium compounds and organic chlorides in the Wurtz–Fittig synthesis of amylbenzene have been studied. The reaction is capable of giving high yields of products other than the expected coupling.

Benzylsodium reacts more smoothly and gives far better yields with alkyl halides than does amyl- or phenylsodium. In general its use is preferred where the nature of the product permits.

Diphenylpropane can be prepared by reaction of benzyl sodium with methylene dichloride.

Trioxymethylene reacts with amyl-, phenyl-, or benzylsodium yielding hexyl, benzyl, and phenylethyl alcohols, respectively.

CAMBRIDGE, MASS. RECEIVED APRIL 2, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photolysis of Gaseous Hydrogen Sulfide

BY GEORGE S. FORBES, JAMES E. CLINE AND BENJAMIN C. BRADSHAW

Warburg and Rump,[1] in 1929, photolyzed hydrogen sulfide in hexane and in water. In hexane the quantum yield ϕ (molecules of hydrogen produced per light quantum absorbed by hydrogen sulfide) was close to unity, but in water it ranged from 0.2 to 0.3. The lower value in water they attributed to hydration of the photolyte. This conclusion appeared at first to be supported by differences in the absorption curves of hydrogen sulfide in the two solvents, respectively, but Arends and Ley,[2] using a more refined procedure, found the two curves to be identical.

Goodeve and Stein,[3] in 1931, investigated the absorption spectra of hydrogen sulfide, selenide and telluride, and concluded that the energy at the threshold of the optical dissociation, of hydrogen sulfide at least, indicated the reaction $H_2S + h\nu \longrightarrow H_2 + S\ (^1D)$.

Herzberg[4] dissented, pointing out that both hydrogen atoms should not be split off in a single act, since they are not bound together in the original molecule. Furthermore, the analogous dissociation $H_2O + h\nu \longrightarrow H_2 + O\ (^1D)$ requires 163.3 kcal., in contrast with the observed dissociation threshold at 153 kcal. Herzberg preferred to write $H_2S + h\nu \longrightarrow H + HS$ followed by $H + H_2S = H_2 + HS$, and by $HS + HS \longrightarrow H_2S + S$ to explain the formation of sulfur.

Stein,[5] in 1933, photolyzed gaseous hydrogen sulfide in approximately monochromatic light, $\lambda = 205$ mμ, and measured with a Pirani gage the very small quantity of hydrogen produced. When P_{H_2S} lay between 75 and 250 mm., ϕ was close to 2 but rose to 3.5 for a pressure of 1350 mm. These high values Stein attributed to short chains initiated by excited sulfur atoms or molecules, a hypothesis not entirely satisfactory.

In 1934, a preliminary series of quantitative photolyses in light of λ 208 mμ was undertaken (B. C. B.) using carefully purified gas. To spread

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(1) Warburg and Rump, *Z. Physik*, **58**, 291 (1929).

(2) Arends and Ley, *Z. physik. Chem.*, **15B**, 311 (1932).

(3) Goodeve and Stein, *Trans. Faraday Soc.*, **27**, 393 (1931).

(4) Herzberg, *ibid.*, **27**, 402 (1931).

(5) Stein, *ibid.*, **29**, 583 (1933).

out over as large a surface as possible the inevitable deposit of sulfur which absorbs and scatters incident light, a spherical bulb containing the gas at about 5 mm. pressure was rotated just behind the exit slit of a crystal quartz monochromator. In other respects the experimental method resembled quite closely that described below, except that the light flux was measured by alternate exposures of a uranyl oxalate actinometer. Because it was desired to preserve the bulb for further experiments, the average transmission by the zone illuminated during photolysis was not then compared with that of the actinometer window. In 1937 the bulb was sawed apart, and one of us (J. E. C.) made the necessary measurements. The uncorrected average value of ϕ, 1.07, was thus raised to 1.15. Owing to the disagreement with Stein's figure, publication was postponed pending an opportunity to clear up certain minor uncertainties, and to make additional experiments at higher pressures.

Fig. 1.—Rotating photolytic cell.

In 1935–37, Dr. William H. Avery and one of us[6] investigated in this Laboratory the photolysis of hydrogen sulfide dissolved in chloromethanes. The final reaction products in carbon tetrachloride were isolated and shown to include sulfhydryl radical. In fact, all the secondary reactions initiated by primary dissociation of hydrogen sulfide could be explained in terms of $H_2S + h\nu = H + SH$, but not in terms of $H_2S + h\nu \longrightarrow H_2 + S$.

Mund and van Tiggelen,[7] in 1937, undertook to find the number of hydrogen atoms (here designated as X) formed per ion pair produced by an α particle in hydrogen containing a small amount of hydrogen sulfide. They measured the number of molecules of hydrogen sulfide disappearing per ion pair and found it to be 2.1. If the reaction is $H + H_2S \longrightarrow H_2 + HS$ followed by $2HS = H_2 + S_2$, X must have been 2.1. But if the reaction is $H + H_2S \longrightarrow H_2 + HS$ followed by $2HS \longrightarrow H_2S + S$, X must have been 4.2. These authors argued from Stein's high quantum yields that the first mechanism is the more probable, but if our preliminary results were sound, the second reaction is indicated, and X becomes four, in better agreement with the value $X = 6$ calculated by Eyring, Hirschfelder and Taylor[8] upon the basis of Capron's[9] work on the influence of α particles upon para–ortho conversion.

Experimental

The Cylindrical Quartz Reaction Cell.—Since hydrogen sulfide at atmospheric pressure absorbs about 90% of radiation, $\lambda = 208$ mμ, in a layer 0.1 mm. deep, the photochemical reaction is localized at the window of the reaction cell. Fine particles of sulfur precipitate out upon this window, diminishing the light flux transmitted to the gas. A reaction cell was therefore designed to distribute the sulfur over as large an area as possible. A quartz cylinder (Fig. 1) 10 cm. high and 6.2 cm. in diameter was connected through a graded seal to a Pyrex cross-arm bearing three inner capillary seals L_1 L_2 L_3 which could be broken with magnetic hammers as described below. The volume was about 400 cc. By rotating this cylinder at six different heights during each photolysis six zones each about 1 cm. high and 20 sq. cm. in area were successively employed for transmission of light. Under these conditions the sulfur was deposited in a uniform layer so thin that it was invisible. Its effect upon light transmission was too small to be detected, as shown below.

The mechanism for rotating the cell during a photolysis is shown in Fig. 1. A heavy iron yoke, Y, holds the cell and the motor, M, as a unit which can be raised or lowered on the ringstand, R, so that different zones of the cylindrical window, W, can be exposed to the radiation. The lower end of the cell is tapered off into a tail, T, which is fitted into a brass pulley, P, with a rubber lining for frictional contact. The upper part of the cell rotates within three small rubber wheels, B, B' and B''. The arm A, holding the wheel B, can be swung aside to permit the cell to be removed easily or put into place. There is very little

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(6) Avery and Forbes, THIS JOURNAL, 60, 1005 (1938).

(7) Mund and van Tiggelen, *Bull. soc. chim. Belg.*, 46, 129 (1937).

(8) Eyring, Hirschfelder and Taylor, *J. Chem. Phys.*, 4, 479 (1936).

(9) Capron, *Ann. soc. sci. Bruxelles*, 55B, 222 (1935).

vibration of the cylinder at 60–120 r. p. m., the rate of rotation used.

The earlier cell (B. C. B.) consisted of a spherical bulb, connected likewise with three inner capillary seals, but rotated by hand during photolysis. Only one zone of limited area was available for transmission, so that each photolysis had to be interrupted twice to freeze out the hydrogen sulfide, and to sublime the sulfur deposit away from the zone in question by application of hot water.

As we later discovered, the principle of rotating the cell, *during a photolysis producing a solid deposit upon the* wall, had been originated by Melville[10] in connection with his work upon phosphine. Even thus a correction for light absorption by deposited phosphorus was required. His spherical cell was rotated about a ground joint connecting it with an apparatus for measurement of the hydrogen produced. As the cell could not be detached during an experiment, the actinometer had to be placed on the opposite side of the light source.

Apparatus for Filling the Cylindrical Cell.—The hydrogen sulfide used in these experiments was a sample[6] carefully purified in this Laboratory. In addition it was redistilled and the non-condensable gases pumped off to a pressure of 10^{-6} mm. or lower. After this hydrogen sulfide had been stored over mercury for five months, the mercury surface was still bright and untarnished.

Figure 2 is a diagram of the apparatus used to introduce a predetermined amount of hydrogen sulfide into the reaction vessel, and to measure the hydrogen produced by a photolysis. A part of the system had been constructed by Dr. Lawrence J. Heidt in 1935 while collaborating with one of us. The purified hydrogen sulfide was distilled in a vacuum from a trap not shown cooled by carbon dioxide snow into the trap E cooled by liquid air. Before this operation the two-liter bulb S and connections had been flamed and pumped out. After condensation of hydrogen sulfide in E, this assembly was pumped down to 10^{-6} mm. of permanent gases according to the McLeod gage, and sealed off from the line at O. With the capillary inner seal at P still unbroken, the assembly was fused to the main apparatus at U (Fig. 2). After pumping the latter down to 10^{-6} mm. the seal at P was broken by a magnetic hammer (not shown) whereupon the gas entered the main apparatus. The mercury valves A, B and C were used in place of stopcocks. To close off the line at a desired point, mercury was forced by means of air pressure up into the *proper Y-tube (90 cm. in height)*.

The cell Q was next sealed on to the system at G. The mercury valves A and B were kept closed, and C was kept open. The cell with connecting tubes was evacuated by a two-stage mercury diffusion pump backed up by an oil pump. The trap H was immersed in solid carbon dioxide. After a few hours the pressure was 10^{-6} mm. or lower as read on the McLeod gage connected at N. In order to exclude mercury vapor from the cell Q, the trap F, packed with short pieces of glass, was surrounded by solid carbon dioxide.

With the system thoroughly evacuated, the hydrogen sulfide was frozen out from bulb S in the trap E, cooled by liquid air. The valve C was then closed, and B was opened. The desired amount of hydrogen sulfide was allowed to evaporate from E before B was again closed. The pressure of gas in the cell Q and connecting tubing could be read from the difference in levels of the mercury in the two arms of the valve C. The left-hand arm was under high vacuum. The pressure of hydrogen sulfide in the cell was corrected for the volume of the tubing and the McLeod gage since all of the gas in the tubing was condensed by liquid air into the lower part of the cell T. After the hydrogen sulfide was frozen, the valve C was opened and any residual gases were pumped down to a pressure of 10^{-6} *mm. Then the cell was sealed off at G, and after the* seal was cold the gas was allowed to evaporate from T. At no time was any tube containing hydrogen sulfide sealed off or even heated.

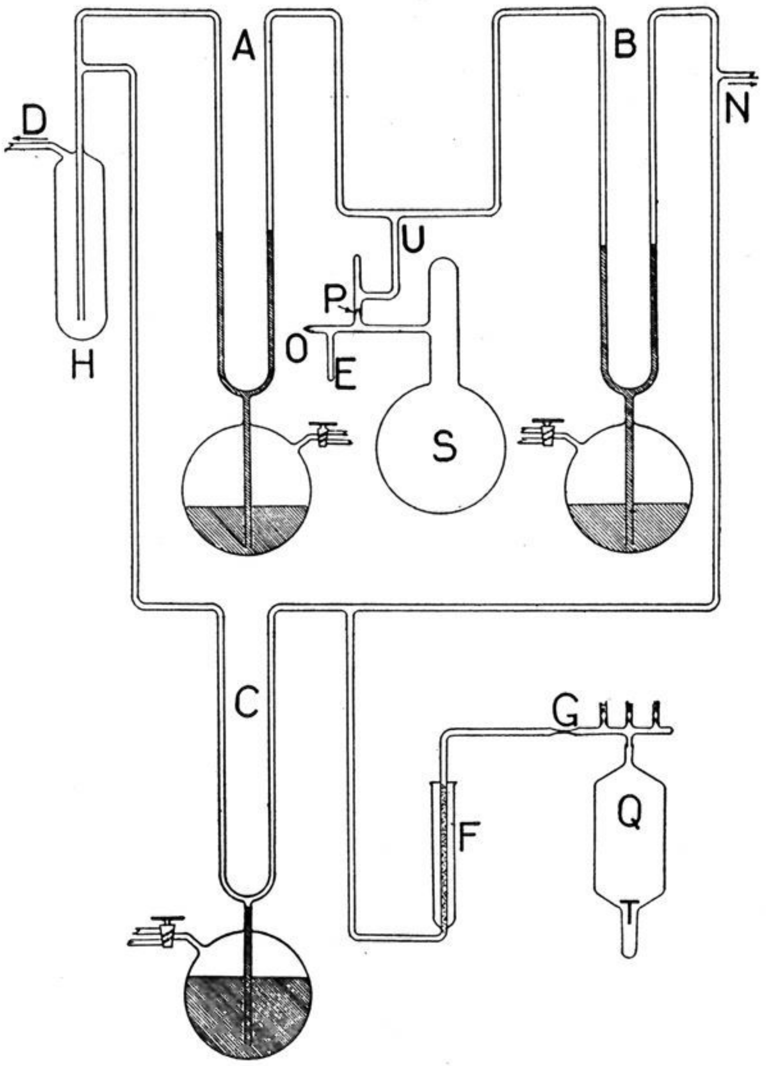

Fig. 2.—Gas-transference apparatus.

Measurement of Hydrogen Pressure.—After a photolysis the cell was again connected to the apparatus at point G, but this time through one of the side-arms J, shown in Fig. 1. A magnetic hammer, not shown, consisting of a nail in a glass tube, was lowered into the tube K by means of a solenoid and allowed to rest on the bent capillary L. The top of K was then sealed off and the system evacuated, with valves A and B closed and C open. Dry-Ice was placed around the trap F. The hydrogen sulfide in the cell was condensed into the tail T by action of liquid air extending over an hour at least. Doubling this time allowed for condensation before breaking the capillary L appeared to have no effect upon the quantum yield. Then C was closed and a blank reading of the McLeod gage was taken. The cell Q was opened to the system by breaking the capillary L with the magnetic hammer. The pressure

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(10) Melville, *Proc. Roy. Soc.* (London), **A139**, 541 (1933).

of permanent gas, assumed to be hydrogen, was calculated from the reading of the McLeod gage corrected for capillarity. A leveled telescope was used to eliminate parallax. The total volume of this gage, cell and connecting tubing was estimated at 786 ± 20 cc. From this volume and the calculated pressure of hydrogen the number of moles of hydrogen produced by the photolysis was determined. These hydrogen pressures were of the order of 0.01 mm., and each reading was reproducible within two or three per cent.

Since the cell carried three capillary seals, L_1 L_2 and L_3, it was possible to run three separate photolyses on one sample of hydrogen sulfide. After the hydrogen produced by the first photolysis had thus been measured, at least 99.5% of it was pumped off, and the sulfur was sublimed away from the cylindrical part of Q which was heated nearly to redness. The cell was sealed off at the constriction below the capillary while still holding the hydrogen sulfide condensed in liquid air. Then a second photolysis was carried out using the same sample of gas, and the hydrogen produced was measured through L_2. Finally, a third photolysis was conducted, using L_3.

Two blank determinations of permanent gases obtained by the above procedures, omitting only the exposure of hydrogen sulfide to ultraviolet radiation, showed almost negligible amounts of such gases. The larger amount, less than 0.5% of the hydrogen pressure produced by an average photolysis, was used as a correction.

Radiometry.—According to the method of Forbes and Brackett[11] a spark between zinc bars moving in troughs was used. About 5 kilowatts were consumed. In one run aluminum bars were used to secure the wave length 237 mμ. In the other the zinc lines 206–210 mμ were used. Since the upper bar is eaten away by the spark much faster than the lower one, an aluminum bar above a zinc bar was used in some of the later runs. Under these conditions the aluminum lines between 213 and 237 mμ were not apparent on a fluorescent screen and the zinc lines between 203 and 214 mμ were very strong.

The monochromator consisted of crystal quartz lenses working at F 1.5 and a Cornu prism. When a glass plate was placed over the exit slit, the thermopile deflection was negligible, indicating that less than 1% of the radiation was in the visible or long ultraviolet region.

The light flux at the exit slit of the monochromator was determined before and after each run, using a linear thermopile–galvanometer system, and the method of integration customary in this Laboratory. After each run the sensitivity of the thermopile–galvanometer system was checked against a carbon lamp run at unvaried current and voltage, which served as a secondary standard. Our two primary radiation standards had been certified by the Bureau of Standards. The secondary standard compared three times with a primary standard showed no variation exceeding 1%. Our initial comparison agreed with one made by Mr. J. W. Tamblyn of this Laboratory four months previously, one month before the first photolysis (J. E. C.). The final comparison was made about a month after the close of our experimental work.

The total number of quanta in each run was calculated from the time the thermopile readings and the data on the sensitivity of the thermopile–galvanometer system. The gross quantum yield, ϕ_{gross}, was determined by dividing the number of molecules of hydrogen produced by the number of quanta absorbed, assuming total absorption in each case. This value neglected the ratio R_0 of the average transmission of the wall of the cylindrical cell to that of the thermopile window—certainly less than unity. It appeared that R_0 could not be measured directly with any great precision. Although it was presumed that R_0 was not far from 0.9, the measured value for the spherical cell, no attempt was made to correct the results in the cylindrical cell by use of such a factor.

To cancel out R_0, and other possible systematic errors (especially the uncertainty in the volume of the McLeod gage and connections), hydrogen bromide was photolyzed in the cylindrical cell, following a procedure identical with that employed for hydrogen sulfide. The quantum yield for hydrogen bromide photolysis has been accurately determined by E. Warburg.[12] It was expressed as 1.00 molecule of hydrogen produced per quantum absorbed, instead of the customary value 2.00 referred to molecules of hydrogen bromide decomposed.

Preparation and Manipulation of Hydrogen Bromide.—The anhydrous hydrogen bromide was prepared from the elements according to the method of Ruhoff, Burnett and Reid.[13] Hydrogen was bubbled through bromine, and the mixed gases combined in a Pyrex tube heated by a Bunsen burner. Any free bromine was removed by a tower of copper filings, and the hydrogen bromide was condensed out in a trap cooled by liquid air. The hydrogen in excess was pumped off by the mercury vapor pump. A suitable amount of hydrogen bromide was then distilled from the trap at about −80° into the side-tube of a two-liter bulb, where it was condensed by liquid air. The bulb had been provided with inner capillary seals similar to those shown at L in Fig. 1. The bulb was sealed off from the hydrogen bromide supply and the residual gases again pumped off. Then the bulb was sealed off from the pump, and the hydrogen bromide was stored in a bulb at about one atmosphere pressure.

In order to fill the cell with hydrogen bromide, the side-arm of one of the capillary seals of the storage vessel was fused to the apparatus shown in Fig. 2 between C and F. After the apparatus had been evacuated and the hydrogen bromide frozen out, the seal was broken. Then the gas was allowed to evaporate to the desired pressure and the storage vessel sealed off. The hydrogen bromide was then condensed in the trap T of the cylindrical cell and the residual gases pumped off to 10^{-6} mm. as usual. The subsequent procedures and corrections were identical with those described above in connection with photolyses of hydrogen sulfide.

Results

The preliminary results (B. C. B.) on hydrogen sulfide appear in Table I.

The wave length of the (approximately) monochromatic light was 208 mμ. In the actinometer 0.48 molecule of oxalate was decomposed per

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[11] Forbes and Brackett, THIS JOURNAL, 53, 3973 (1931).

[12] Warburg, *Sitzb. kgl. preuss. Akad. Wiss.*, 314 (1916).

[13] Ruhoff, Burnett and Reid, *Org. Syntheses*, 15, 35 (1935).

TABLE I

PRELIMINARY PHOTOLYSES OF HYDROGEN SULFIDE

Expt.	P_{H_2S}, mm.	Moles actinometer decomposed	Actinometer exposure, sec.	Moles H_2 formed	H_2S exposure, sec.	ϕ_{H_2S} gross	ϕ_{H_2S} (corr.)
4	5	1.44×10^{-6}	2400	0.704×10^{-6}	540	1.04	1.12
6	5	1.32×10^{-6}	2400	0.657×10^{-6}	540	1.06	1.14
8	5	2.02×10^{-6}	2400	1.011×10^{-6}	540	1.07	1.15
9	5	2.12×10^{-6}	2400	$.966 \times 10^{-6}$	480	1.09	1.17

quantum absorbed by the solution.[14] The average transmission of the spherical cell at λ 208 mμ was 8% worse than that of the actinometer window.

In addition, five experiments were carried out in focally isolated light[15] from an aluminum spark, λ (average) = 191 mμ. There was great uncertainty in the measurement of transmission by the actinometer window. Without any correction for the transmission ratio, ϕ_{gross} (averaged) was 0.8.

Final results (J. E. C.) on hydrogen sulfide appear in Table II. All experiments are included except the first, which was lost through breakage of the apparatus by a magnetic hammer. Corrections for R_c are not included in this table.

TABLE II

FINAL PHOTOLYSES OF HYDROGEN SULFIDE

Expt.	H_2S pres., mm.	λ mμ	Quanta per sec. (× 10^{14})	Quanta (× 10^{17})	P_{H_2}, mm.	H_2 molecules (× 10^{17})	H_2 molecules corrected (× 10^{17})	H_2 molecules quantum
2	8.2	208	3.71	4.01	0.01569	4.08	4.06	1.013
3	9.5	208	7.28	7.87	.02459	6.41	6.39	0.812
4	7.5	208	10.66	3.84	.01342	3.50	3.48	.907
5	7.5	208	11.48	4.13	.01423	3.71	3.69	.894
6	7.5	...	0	0	7×10^{-5}	0.018	0	...
7	900	208	6.97	5.01	0.01854	4.83	4.81	.960
8	900	208	5.15	3.71	.01380	3.60	3.56	.966
9	900	237	2.04	3.68	.01236	3.22	3.20	.869
10	1400	208	4.80	4.32	.01596	4.16	4.14	.958
11	1400	208	5.01	4.51	.01832	4.77	4.75	1.052
12	1400	210	0.799	2.30	.00941	2.45	2.43	1.055
13	94	208	7.89	5.68	.0208	5.42	5.40	0.951
14	94	208	7.27	5.24	.01859	4.82	4.80	0.917
15	94	...	0	0	.....	..	..	...
							Mean	0.946 ± 0.016

Experiment 2 suffered by reason of excessive fluctuations of the light source. In Experiment 5, two hours instead of one were allowed for condensation of hydrogen sulfide before measuring hydrogen. Experiments 6 and 15 are the blanks. The sulfur deposited in Experiment 10 was not removed before carrying out Experiment 11. Although the *average* amount of sulfur must have been about *three* times as great in 11 as in 10, the quantum yield in 11 is *higher* than in 10, good evidence that the effect upon light transmission of the sulfur deposit was negligible in other experiments as well.

Results (J. E. C.) on hydrogen bromide, P = 408 mm., appear in Table III. The average wave length of the two zinc lines employed was 208 mμ as before.

Discussion of Results

The gross quantum yield, ϕ_{gross}, in the photolysis of hydrogen bromide expressed as hydrogen *molecules* per quantum is found to be 0.93 with an accidental error estimated at ±0.03. Assuming the true quantum yield to be exactly 1.00, it appears that ϕ_{gross} should be raised 7.6% to eliminate the effects of R_c and other systematic errors.

Since the hydrogen sulfide was photolyzed under exactly the same conditions as the hydrogen bromide, it is evident that ϕ_{H_2S}, the true quantum yield, is $(0.95 \pm 0.02)/(0.93 \pm 0.03) = 1.02 \pm 0.05$, evidently unity within experimental error.

This outcome is quite different from Stein's,[5] who found yields of approximately 2 rising to 3.8 at the higher pressures. In our work there was no apparent variation of ϕ over the range 8 to

TABLE III

PHOTOLYSES OF HYDROGEN BROMIDE

Run	Exposure, sec.	Quanta (× 10^{17})	H_2 molecules (× 10^{17})	P_{H_2}, mm.	H_2 molecules corrected (× 10^{17})	H_2 molecules quantum
1a	900	4.53	4.33	0.01703	4.31	0.952
2a	720	4.97	4.45	.01711	4.43	.893
3a	720	4.83	4.57	.01754	4.55	.943
					Mean	0.929 ± 0.03

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(14) Brackett and Forbes, THIS JOURNAL, **55**, 4459 (1933).

(15) Forbes, Heidt and Spooner, *Rev. Sci. Instruments*, **5**, 253 (1934).

1400 mm.—greater than the range covered by Stein. Also, there is no apparent trend in ϕ over a fourteen-fold increase in light flux. The value $\phi = 1.15$ reported by Bradshaw agrees well with the average of the final series, but we can offer no convincing explanation of the disagreement between our results and those of Stein. Liberal use of greased stopcocks, and the very small amount of hydrogen produced (always less than 10^{-7} mole) were possible disadvantages of his method.

Mechanisms.—There are two mechanisms that can be used to explain our quantum yield of unity over a considerable pressure range.

$$\begin{aligned} H_2S + h\nu &= H + HS \qquad (1)\\ H + H_2S &= H_2 + HS \\ HS + HS &= H_2S + S \text{ or } H_2S_2 \\ H_2S + h\nu &= H_2 + S \qquad (2) \end{aligned}$$

The first mechanism, recommended by Herzberg,[4] seems to be much the more probable. The work of Avery and Forbes,[6] as noted above, supports the same conclusion. The secondary reaction $HS + HS = H_2 + S_2$ must be infrequent at least, otherwise ϕ could become as great as two.

Ion Pairs in Hydrogen.—Mund and van Tiggelen,[7] as stated above, found that 2.1 molecules of hydrogen sulfide disappeared for each ion pair formed from hydrogen through action of α particles. If mechanism (1) is correct, *two* hydrogen atoms are required per molecule of hydrogen sulfide decomposed, unless stable H_2S_2 is formed in appreciable quantities. Then 4.2 hydrogen atoms must have been produced per ion pair, in better agreement with six, the number calculated by Eyring, Hirschfelder and Taylor.[8]

Summary

Highly purified hydrogen sulfide and hydrogen bromide were photolyzed successively, under identical conditions, in a rotating quartz cell of special design. Sulfur formed in any photolysis was distributed over a cylindrical surface 120 sq. cm. in area, and was proved to have negligible influence upon light transmission.

Stopcocks were avoided altogether by free use of breakable inner capillary seals, mercury valves and liquid air. High vacuum technique was employed consistently. Corrections for permanent gases obtained in blank experiments were less than 0.5%.

Assuming that one quantum produces exactly one molecule of hydrogen from hydrogen bromide at 400 mm., the quantum yield of hydrogen sulfide, referred to that of hydrogen bromide, is 1.02 ± 0.05 molecules of hydrogen per quantum. All systematic errors are canceled by means of this comparison.

This outcome agrees, within 13%, with that of preliminary experiments conducted in a rather similar apparatus in 1934.

Within experimental error, this quantum yield is independent of pressure, 8 to 1400 mm., and also of light flux ($\lambda = 208\ m\mu$) over a fourteen-fold range.

Correlation of our results with Herzberg's reaction mechanism, and with Mund and van Tiggelen's work, indicates that when α particles act upon hydrogen gas, 4.2 hydrogen atoms are produced per ion pair.

CAMBRIDGE, MASS. RECEIVED MARCH 18, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Specific Heats and Heat of Fusion of Iodine

BY K. J. FREDERICK AND J. H. HILDEBRAND

A careful search of the literature reveals the rather astounding fact that no direct determination of the heat of fusion of iodine has ever been reported, although varied indeed are the indirect determinations that appear in the works of reference. It is obviously desirable to have a direct determination of this important constant, and this we have carried out, employing the method of mixtures. This method also afforded us an opportunity to ascertain the heat capacities of both solid and liquid iodine.

According to Regnault[1] the mean specific heat of solid iodine between 9 and 98° is 0.05412 cal. per gram. This gives a mean molal heat capacity of 13.74 cal. per mole. Nernst and coworkers[2] give a value of 13.30 cal. per mole for the temperature 20°. Recently Carpenter and Harle[3] have measured the heat capacity of solid

(1) Regnault, *Ann. chim. phys.*, [2] **73**, 3 (1840), and [3] **26**, 268 (1849).

(2) (a) Nernst, *Berlin Sitsber.*, 247 (1910); (b) Nernst, *Ann. Physik*, [4] **36**, 395 (1911).

(3) Carpenter and Harle, *Phil. Mag.*, **23**, 193 (1937).