[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Photochemical Reactions Involving Hydrogen Sulfide and Chloromethanes

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The present research was the outgrowth of an experiment made to learn whether carbon tetrachloride would serve as an inert medium for photolyses involving hydrogen sulfide. The question was decided in the negative, since hydrogen chloride was readily detected after irradiation with ultraviolet light. Subsequent quantitative experiments upon solutions of hydrogen sulfide in methylene chloride, chloroform and carbon tetrachloride clarified the mechanism of the secondary reactions, and that of the primary act as well.

Berthelot and Gaudechon,[1] also Smits and Aten,[2] found that hydrogen and sulfur were formed, in ultraviolet light, from hydrogen sulfide. Warburg and Rump[3] studied its photolysis in hexane and in water solution. In hexane, the quantum yield, Φ, was close to unity, independent of concentration, and of wave length between λ 254 and λ 207 mμ at least. In water, Φ was 0.2 at λ 254 mμ and 0.4 at λ 207 mμ. They proposed the mechanism (1) $H_2S + h\nu \longrightarrow H_2 + S$ followed by (2) $S + S \longrightarrow S_2$, which did not of itself explain the low values of Φ in water. They introduced hydrogen gas under increasing pressure without noting any decrease in Φ attributable to a reverse reaction, and also illuminated a suspension of sulfur in water saturated with hydrogen without detecting any hydrogen sulfide. Their contention that some interaction between hydrogen sulfide and water might be responsible for the low quantum yield in this solvent appeared to be supported by their own measurements of absorption coefficients of hydrogen sulfide in hexane and in water. But Ley and Arends,[4] who used an improved technique, found the two absorption curves to be identical.

Goodeve and Stein[5] state that the absorption threshold of the gas, 37,000 cm.$^{-1}$, corresponds to the energy of the thermal dissociation $H_2S \longrightarrow H_2 + S$ where the sulfur atom is in the ^1D state, and that the reaction $H_2S + h\nu \longrightarrow HS + H$ would require less energy than the observed threshold value. Their failure to detect hydrogen disulfide after irradiation appeared to be a further objection to the second equation. Stein[6] photolyzed gaseous hydrogen sulfide in light of wave length 205 mμ, and found Φ to increase from 2.2 at 75 mm. pressure to 3.5 at 1350 mm.—much higher than any yields observed in solution. He mentions no effort to prevent deposition of solid sulfur upon the cell window, so that the above must be regarded as minimum values. Stein does not reject either dissociation mechanism, but points out an improbability of hydrogen molecule formation from two atoms separated by a bond angle of 110°.

Experimental

The method, in outline, was as follows: solutions of hydrogen sulfide were prepared in known concentrations in a suitable quartz cell. The hydrogen chloride resulting from absorption of a measured number of quanta was transferred by a stream of nitrogen to an absorption train, and there determined by acidimetry. As only a few millionths of a mole of hydrogen chloride resulted from the average experiment, a mere trace of any impurity yielding this substance through hydrolysis or photochemical reaction would have been disastrous. Oxygen dissolved in methylene chloride or chloroform proved to be particularly objectionable so that complete elimination of air before photolysis was imperative.

Purification of Materials.—Commercial liquid hydrogen sulfide was distilled in a fractionating column of the "Standard Precision" type described by Podbielniak,[7] 135 cm. in length and 0.6 cm. in internal diameter, packed with a spiral of No. 16 nichrome wire, four and a half turns to the inch. Thermal insulation for the column was provided by a silvered vacuum jacket. The reflux ratio exceeded ten to one, and the middle fraction boiled within 0.02° as measured by a copper–constantan couple and a type K potentiometer. The melting point, kindly determined by Dr. W. E. Vaughan, was −85.1°, 0.4° higher than that reported by Giauque and Blue.[8] Mercury in contact with a sample of the best fraction remained untarnished for months.

For removal of sulfur compounds from carbon tetrachloride, refluxing under sodium plumbite solution, previously recommended[9] merely as a test reagent, proved the only dependable process. After treatment with concentrated sulfuric acid, dilute potassium hydroxide, distilled water and calcium chloride, it was fractionated in the Podbielniak column.

Commercial chloroform often contains phosgene, carbon

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(1) D. Berthelot and Gaudechon, *Compt. rend.*, **150**, 1517 (1910).

(2) Smits and Aten, *Z. Elektrochem.*, **16**, 264 (1910).

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

(4) Ley and Arends, *Z. physik. Chem.*, **B15**, 311 (1932).

(5) Goodeve and Stein, *Trans. Faraday Soc.*, **27**, 395 (1931).

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

(7) Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 119 (1933).

(8) Giauque and Blue, THIS JOURNAL, **58**, 831 (1936).

(9) Weissberger and Proskauer, "Organic Solvents," Oxford-Clarendon Press, p. 156.

tetrachloride and perhaps other, unidentified, impurities strongly absorbing resonance radiation, λ 254 mμ. Treatment with sulfuric acid was omitted as it would have removed at the start the alcohol, an effective inhibitor of phosgene formation. Only distilled water and calcium chloride were used before fractionation. Transmission, by the best samples in a 1-cm. layer, of 92% of resonance radiation (referred to transmission by water in the same cell) was adopted, and is now proposed, as a standard of purity. The calculated lowering of the transmission by 0.001% of phosgene, is about 5%. All samples of chloroform photolyzed in final experiments had been fractionated within four days.

Methylene chloride was first shaken with concentrated sulfuric acid, and then treated like the chloroform. No measurable absorption of resonance radiation was detected.

Tank nitrogen was passed over hot copper turnings freed from grease first by a solvent and then through oxidation followed by reduction.

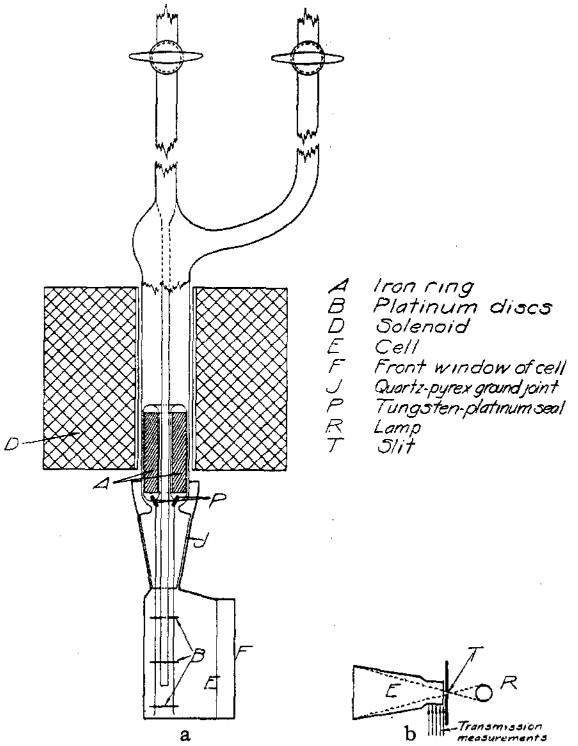

Fig. 1.

Apparatus.—A small mercury vapor lamp of the argon-filled type (Braun Corporation "Fluorolight") consumed about 30 watts in the primary of the small attached transformer. The mercury vapor, at very low pressure, was excited in the spaces between the walls of a quartz tube and a longitudinal partition. Its spectral energy distribution was measured with the usual precautions. Resonance radiation, λ 254 mμ, was 82.6% of the whole, and only about 3% of the remainder lay between λλ 297 and 313 mμ. Since the absorption of hydrogen sulfide is negligible in this region, and begins only at λ 280 mμ, the solutions were exposed directly to the full radiation of the lamp, and a monochromator was used for absorption measurements only.

A zinc spark between rotating disks[10] was also employed. The lines λλ 206 and 210 mμ (with much smaller contributions from the lines λλ 203 and 216 mμ) were separated by a crystal quartz monochromator having a Cornu prism. Ten per cent. or less of the total radiation was transmitted by 1 cm. of chloroform and so would not have been photochemically efficient. Most of this was in the visible spectrum.

The energy absorbed by the hydrogen sulfide solutions was estimated by alternate exposures of a uranyl oxalate actinometer.[11] Since the total uranium concentration was only 0.001 *M*, and the layer only 5 mm. in thickness, practically all the visible light, and most of the stray ultraviolet light of wave length exceeding 280 mμ, from either light source, must have been transmitted without photochemical action.

The horizontal section of the trapezoidal cell is shown in Fig. 1 (b). For 7 mm. from the front window the sides were pressed in and ground parallel to each other, to permit measurements of the extinction coefficients of the contents. The vertical section, Fig. 1 (a) with legend, makes clear the essential features. The magnetic stirrer consisting of the glass-enclosed iron ring A was connected by platinum wires to the platinum disks B beyond the zone of light absorption and was actuated by an intermittent current in the solenoid.

The apparatus shown in Fig. 2 served for the removal of dissolved oxygen from the solvents, for production of solutions of hydrogen sulfide of known concentrations and for the quantitative determination of hydrogen chloride formed by photolysis. The cell E filled with purified solvent was evacuated through stopcocks 4, 5 and 9. Nitrogen, entering through stopcocks 1, 2 and 3, bubbled through the solution under reduced pressure until a quarter of the solution had evaporated. The nitrogen was then shut off, and the solvent was boiled under the pressure of its own vapor for fifteen seconds. Stopcock 4 was closed and the line completely evacuated. Unless this entire process was carried out, hydrogen chloride formed by photoöxidation of chloroform or methylene chloride could always be detected after irradiation.

The transmission of light by the cell filled with methylene chloride or chloroform was measured with the help of the lamp R, the monochromator C, thermopile B and a high-sensitivity galvanometer with scale at five meters (not shown). The concentration of hydrogen sulfide was figured using its extinction coefficient, at the given wave length, as measured by Arends and Ley in *hexane.* But the extinction coefficient of carbon tetrachloride is so high that its solutions transmitted no measurable radiation. Therefore all solutions were saturated at known pressure and temperature by four hours' contact with the gas, stirring meanwhile. The corresponding concentration was determined in special experiments by transferring the gas to a bubbler with standard sodium hydroxide, oxidizing the sodium sulfide to sulfate with excess peroxide and then titrating back with standard acid. The result, at 25°, corrected to 20° by the Clapeyron–Clausius equation, agreed with that given by Bell.[12]

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[10] Wiig and Kistiakowsky, This Journal, **54**, 1806 (1932).

[11] Forbes and Heidt, *ibid.*, **56**, 2363 (1934).

[12] Bell, *J. Chem. Soc.*, 1377 (1931).

Without changing the position of the cell or of the radiometric apparatus, one atmosphere of hydrogen sulfide was admitted to a system of measured volume bounded by stopcocks 1, 3, 4, 8, 9 and the quartz spiral manometer. The pressure was measured accurately enough to give a rough estimate of the quantity of gas present. Upon opening stopcock 3, a part of the hydrogen sulfide dissolved in the stirred solution. After closing it, the pressure was read again and the amount dissolved found by difference.

The transmission of light by the solution was measured and compared with that of the solvent. The hydrogen sulfide content was then calculated, not omitting a correction for the dilution of the solvent upon introduction of gas.

The lamp was transferred to a reproducible position such that the slit T which was rigidly attached to it was flush against the front window of the cell as in Fig. 1 (b) and the solution irradiated for a measured time. The thermopile had been mounted, meanwhile, in a new fixed position on the other side of the lamp. Galvanometer deflections were read from time to time which were proportional to the total light flux behind the slit. Quanta per second were estimated by actinometry with uranyl oxalate, as described above, while small fluctuations in light intensity were followed with the help of thermopile and galvanometer. The ratio between the total light energies in the two exposures (expressed as products of deflections and times) multiplied by the decomposition, and quantum yield of uranyl oxalate at λ 254 mμ, gave the number of quanta entering the hydrogen sulfide solution.

The hydrogen sulfide remaining in the line was pumped out, and the line flushed with nitrogen. Stopcocks 5 and 6 were then closed, and 8, 3 and 4 opened in this order. A test-tube containing 5 cc. of distilled water was fitted over the spiral N, forming a bubbler of the Friedrich type. A slow stream of nitrogen admitted under the solution through stopcock 1 now swept out the hydrogen chloride formed by photolysis into the bubbler together with the undecomposed hydrogen sulfide. The nitrogen finally eliminated the hydrogen sulfide, but not hydrochloric acid. After boiling, the acid solution was titrated with 0.003 *N* potassium hydroxide to a brom thymol blue end-point. The procedure just described was repeated, once or even twice, until no hydrochloric acid could be detected in the bubbler. It was proved by experiments upon samples of solvent containing known amounts of hydrogen chloride that this substance was removed completely by the technique described. In addition, blank experiments on each pure solvent showed that no hydrochloric acid was produced, even upon boiling, by hydrolysis of the solvent vapor dissolved in the bubbler. The high absorption coefficient of the solutions for light of wave length 208 mμ required operation of the stirrer throughout photolysis. After saturation with hydrogen sulfide the cell was disconnected at the ground joints D, and relocated behind the exit slit of a second monochromator (not shown) during photolysis only.

To determine the photochemical temperature coefficients, experiments were also performed at 5° and at −30°. Photolyses were conducted in a "cold room" at 5°, disconnecting the cell, after filling, at DD′. The number of quanta incident upon the solution was determined by actinometry only. At −30°, the apparatus and method of Forbes and Nelson[13] were duplicated, with minor changes.

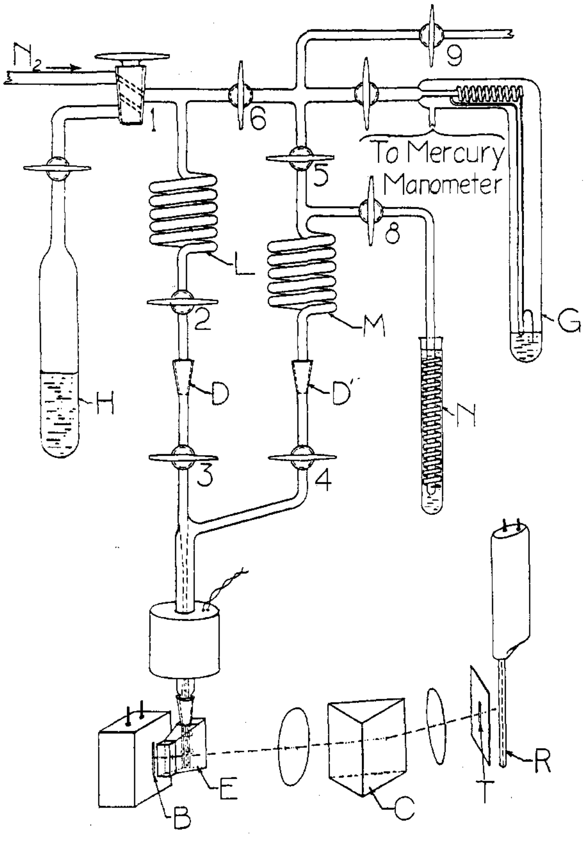

Fig. 2.

Table I contains the data of all final experiments and suggests the method of calculation. L_{H_2S}/L_0 is the fraction of total light energy incident upon the solution which is absorbed by the hydrogen sulfide present. $L_0/L = 10^{Kcd}$ referred to moles per liter, and centimeters of light path. At wave length 254 mμ the extinction coefficients are: $K_{H_2S} = 3.86$, $K_{CH_2Cl_2} = 0$, $K_{CHCl_3} = 0.0115$, $K_{CCl_4} = 1.18$. At λ 208 mμ, $K_{H_2S} = 525$, $K_{CH_2Cl_2} = 3.1$, $K_{CHCl_3} = 47.5$, $K_{CCl_4} = 4650$. A subscript attached to the symbol Φ indicates, unless stated to the contrary, that the total number of molecules of hydrogen chloride formed has been divided by the number of quanta absorbed by the substance designated.

Identification of reaction products was not undertaken except in carbon tetrachloride because a simple outcome could be expected in this solvent only. Sufficient quantities were obtained by direct immersion of the luminous column of the "Fluorolight" in the reaction mixture. After

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[13] Forbes and Nelson, THIS JOURNAL, **59**, 693 (1937).

TABLE I

Solvent	[H_2S]	[Solvent]	t°	λ, mμ	$\frac{L_{H_2S}}{L_0}$	Molecules, HCl × 10^{-18}	Quanta, H_2S × 10^{-18}	Φ_{H_2S}	Φ_{gross}
CH_2Cl_2	0.074	15.7	25 ± 2	254	0.86	1.67	3.83	0.44	..
CH_2Cl_2	.140	15.6	25 ± 2	254	.98	1.45	2.77	.52	..
CH_2Cl_2	.225	15.5	25 ± 2	254	1.00	1.71	4.06	.42	0.42
CH_2Cl_2	.139	15.6	25 ± 2	208	0.60	1.17	0.77	1.52	.91
CH_2Cl_2	.127	15.6	25 ± 2	208	.58	1.21	.92	1.32	.77
CH_2Cl_2	.037	15.7	25 ± 2	208	.29	1.11	.32	3.5	1.0
CH_2Cl_2	.014	15.7	25 ± 2	208	.13	0.93	.14	7.0	0.9
CH_2Cl_2	.155	15.6	4 ± 1	254	.98	2.15	6.11	0.35	.34
CH_2Cl_2	.161	15.6	5 ± 1	254	.98	1.54	4.12	.38	.37
$CHCl_3$	.260	12.3	25 ± 2	254	.88	3.14	5.70	.55	.48
$CHCl_3$	0	12.5	25 ± 2	254	0	0.39	4.08	..	.10
10% C_2H_5OH 90% $CHCl_3$	.245	11.1	25 ± 2	254	.88	3.30	4.55	.73	.64
$CHCl_3$	.242	12.3	25 ± 2	254	.87	0.60	0.93	.64	.56
$CHCl_3$	.362	12.2	25 ± 2	254	.91	1.43	2.04	.70	.64
$CHCl_3$	.260	12.3	25 ± 2	254	.88	1.74	2.67	.65	.57
$CHCl_3$	.22	12.3	−37 ± 3	254	.9	3.30	5.77	.6	.5
$CHCl_3$	.2	12.3	−30 ± 5	254	.9	2.38	6.33	.4	.3
CHCl	.16	12.4	28 ± 2	208	.125	4.6	0.65	7.1	.9
$CHCl_3$	.35	12.2	25 ± 2	208	.24	7.66	1.91	4.0	1.0
CCl_4	.348	10.0	25 ± 2	254	.07	3.60	0.185	19	1.4
CCl_4	.358	10.0	25 ± 2	254	.07	1.62	.128	12	0.9
CCl_4	.321	10.0	25 ± 2	254	.065	2.40	.21	11	.8
CCl_4	.360	10.0	25 ± 2	208	.004	0.64	.0034	190	.76
CCl_4	.292	10.0	25 ± 2	208	.003	.10	.0014	70	.21
CH_2Cl_2	0	3.1	25 ± 2	210	0	3.17	3.5	..	.9

three hours the liquid was transferred, by tilting, to a still which with the reaction vessel formed a closed system from which air was excluded. The hydrogen sulfide and unchanged solvent were distilled back into the reaction vessel, exposed for three hours more, and so on. Photolytic decomposition of the original products was thus largely avoided, and these products, so far as they were involatile, accumulated in the still as a dark brown oil. This oil was fractionated in a vacuum in an all-glass micro-still having a bulb of about 1-cc. capacity connected with four small U-tubes in series. Selective condensation was achieved by suitable freezing mixtures. We are greatly indebted to Dr. G. H. Carlson of Converse Laboratory for planning this apparatus and the technique of using it. Three products were isolated, thanks to advantageous differences in volatility. Hexachloroethane and sulfur, each about 10% of the total, were identified by mixed melting points. The intermediate fraction, nearly 80% of the total, a yellow oil of disgusting odor, was subjected to microanalysis by Mrs. Gertrude M. Wellwood of Converse Laboratory.

	C	H	S	Cl
Found	8.18	0.79	23.97	69.7
	8.24	.69		
Calculated for CCl_3SH	7.90	.66	21.1	7

Trichloromethyl mercaptan has been described by Connolly and Dyson.[14] Any products of about the same volatility as carbon tetrachloride would not have been isolated in the course of the above treatment. Thiophosgene (b. p. 73.5°) would have colored the first distillate deep red, and the highly penetrating odor of hydrogen disulfide (b. p. 74.5°) was absent from that liquid. Weiss and Fishgold[15] have found R_2S_2 as a final product of the photolysis of organic and inorganic compounds of the general formula RSH with production of RH and S from some (unspecified) compounds. Of course the disulfide might have decomposed, at the temperature employed in the distillation, to yield the sulfur finally recovered.

Except for hydrogen chloride, the photolytic products in methylene chloride and in chloroform were not identified in detail. But as the odor of a mercaptan was detected readily after photolysis, and sulfur could be deposited by prolonged exposure, it was assumed that these were of the same nature as in carbon tetrachloride.

Discussion

An adequate explanation of the data must not

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(14) Connolly and Dyson, *J. Chem. Soc.*, 822 (1934).

(15) Weiss and Fishgold, *Nature*, **137**, 71 (1936).

only account for the reaction products detected, or inferred, but must predict values of quantum yields which are largest in carbon tetrachloride and smallest in methylene chloride.

The two mechanisms previously proposed for the primary photochemical reactions are

$$H_2S + h\nu \longrightarrow H + HS \tag{1}$$
$$H_2S + h\nu \longrightarrow H_2 + S \tag{2}$$

The greater plausibility of (1) is apparent, for hydrogen molecules are not known to react with carbon tetrachloride at room temperature. But Cremer, Curry and Polanyi[16] have shown that hydrogen atoms in the gas phase react upon every collision with carbon tetrachloride.

$$H + CCl_4 \longrightarrow CCl_3 + HCl$$

They observed no substitution reaction. We have attempted to explain the products obtained by us in the liquid phase, starting in each case with analogous reactions in the three solvents, respectively.

$$H_2S + h\nu \longrightarrow H + HS \tag{1}$$
$$H + CH_2Cl_2 \longrightarrow HCl + CH_2Cl \tag{2a}$$
$$H + CHCl_3 \longrightarrow HCl + CHCl_2 \tag{2b}$$
$$H + CCl_4 \longrightarrow HCl + CCl_3 \tag{2c}$$

By analogy with the gas reactions of Cremer, Curry and Polanyi[16]

$$H + CH_2Cl_2 \longrightarrow H_2 + CHCl_2 \tag{3a}$$
$$H + CHCl_3 \longrightarrow H_2 + CCl_3 \tag{3b}$$
$$H + H_2S \longrightarrow H_2 + SH \tag{4}$$

In methylene chloride $\Phi = 0.46$. This would be predicted if reactions 3a and 2a are equally probable in the liquid phase, as they appear to be in the gas phase.[16] In chloroform $\Phi = 0.68$, suggesting that the probability of 3b is one-third that of 2b, though Cremer, Curry and Polanyi[16] assign equal probabilities in the gas phase.

The following reactions in methylene chloride involving free radicals appear reasonable and in addition lead to products analogous to those established by the analyses described above. In addition to reactions 1, 2a and 3a and 4

$$CHCl_2 + SH \longrightarrow CHCl_2SH$$
$$CH_2Cl + SH \longrightarrow CH_2ClSH$$
$$CHCl_2 + CHCl_2 \longrightarrow C_2H_2Cl_4$$
$$CH_2Cl + CH_2Cl \longrightarrow C_2H_4Cl_2$$
$$CHCl_2 + CH_2Cl \longrightarrow C_2H_3Cl_3$$
$$SH + SH \longrightarrow H_2S + S \text{ or } H_2S_2 \text{ or } H_2 + S_2$$

The corresponding reaction scheme in chloroform leads to CCl_3SH, $CHCl_2SH$, $C_2H_2Cl_4$, C_2HCl_5 and C_2Cl_6.

If no additional reaction occurs to produce hydrogen chloride, the net quantum yield, Φ_{H_2S}, of hydrogen chloride in carbon tetrachloride should be less than unity because some part of the hydrogen atoms must be ineffective because of combination with hydrogen sulfide, (4). The high observed value of Φ_{H_2S}, 14, could be ascribed either to photochemical activity on the part of the solvent which absorbs 93% of the light, or to a chain reaction with a length of fourteen. If Φ_{CCl_4} is unity, Φ_{H_2S} must be unity also to account for the fact that $\Phi_{\text{gross}} = 1.0$. Such an outcome corresponds to the reactions

$$CCl_4 + h\nu = Cl + CCl_3 \tag{1'}$$
$$H_2S + Cl \longrightarrow HCl + HS \tag{2'}$$

Reaction 2′ is exothermic to the extent of 16 kcal. Thereupon

$$CCl_3 + SH \longrightarrow CCl_3SH \tag{5}$$
$$2CCl_3 \longrightarrow C_2Cl_6 \tag{6}$$
$$SH + SH \longrightarrow H_2S_2 \text{ or } H_2S + S \text{ or } H_2 + S_2 \tag{7}$$

But reactions 1 and 2c, following absorption of a quantum by hydrogen sulfide, also yield CCl_3 and SH, so that the same final products will result from 5, 6 and 7 as if hydrogen sulfide had absorbed the quantum, and analysis of the irradiated mixture will not identify the primary act or acts.

On the other hand, reaction 1′ suggests that chlorine and hexachloroethane might be detected after irradiation of pure carbon tetrachloride. Lyons and Dickinson[17] have proved that this solvent, if free from oxygen and water, is not decomposed by resonance radiation whence it might appear that the energy of the quantum is partitioned among several degrees of freedom of the molecule, or that recombination of Cl and CCl_3 usually occurs before these become separated by solvent molecules.

But Lyons and Dickinson remark—"The failure of pure carbon tetrachloride to decompose might be attributed to a much higher specific rate for the process $Cl + CCl_3 = CCl_4$ than for either of the processes $2Cl \longrightarrow Cl_2$ or $2CCl_3 \longrightarrow C_2Cl_6$. An alternative would be to suppose that with λ 2537 a small concentration of Cl_2 is built up, but that the process $CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl$ occurs with a high specific rate, so that little net decomposition results." Either of these mechanisms permits absorption of light by carbon tetrachloride to produce hydrogen chloride from hydrogen sulfide when it is present. However, if the quantum yield for reaction 1′ followed by 2′ is unity at λ 254 mμ, one

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[16] Cremer, Curry and Polanyi, *Z. physik. Chem.*, **B23**, 445 (1933).

[17] Lyons and Dickinson, THIS JOURNAL, **57**, 443 (1935).

should expect at least as large a value at λ 208 mμ, where the energy of the quantum is greater by 24 kcal. The observed quantum yield at λ 208 mμ, however, is only 0.5. Unless both these reactions invariably follow the absorption of a quantum by carbon tetrachloride, which seems improbable in view of the above considerations, the net quantum yield for the process initiated by reaction 2c or 2′ must exceed unity to account for the fact that Φ_{gross} is unity. No chain is predicted by the sequence 5, 6, 7. Of several imaginable schemes the following appear least objectionable.

$$
\begin{array}{rcll}
H_2S + h\nu & = & H + SH & (1) \\
H + CCl_4 & = & HCl + CCl_3 & (2c) \\
SH + CCl_4 & \longrightarrow & CCl_3SH + Cl & (8c) \\
Cl + H_2S & \longrightarrow & HCl + SH & (9c) \\
SH + SH & \longrightarrow & H_2S + S \text{ or } H_2S_2 \text{ or } H_2 + S_2 & (7) \\
CCl_3 + SH & \longrightarrow & CCl_3SH & (5) \\
CCl_3 + CCl_3 & \longrightarrow & C_2Cl_6 & (6)
\end{array}
$$

Reactions 8c and 9c are the chain-carrying steps in this mechanism. The chains are broken by reactions 5 and 7. Step 8c might at first sight appear inconsistent with the statement of Rollefson and Libby[18] that irradiated radioactive chlorine does not exchange with the ordinary chlorine of carbon tetrachloride. But the sulfhydryl radical produced in 1 should have kinetic and excess of vibrational energy amounting to (112 − 80)/2 or 16 kcal. Here 112 kcal. is the einstein at 254 mμ, and 80 kcal. is somewhat less than half the total dissociation energy of hydrogen sulfide, 170 kcal.[19] Sixteen kilocalories greatly exceeds the kinetic energy of chlorine atoms produced by dissociation of chlorine atoms produced by visible light. Even in the violet, 404 mμ, this is only (70 − 57)/2 or 6.5 kcal.,[19] and if the plate glass interposed by Rollefson and Libby between their mercury vapor lamp and the vessel containing chlorine transmitted some light, λ = 366 mμ, relatively few chlorine atoms would have had kinetic energy as great as (78 − 57)/2 or 10.5 kcal. Again, the kinetic and excess vibrational energy of SH following 9c should be approximately (101 − 80)/2 or 10.5 kcal.,[19] so that the propagation of a chain is possible from the energetic standpoint at least.

Two experiments in carbon tetrachloride solution, performed in light λ = 208 mμ, indicate that a chain initiated by reaction 1 must attain the improbable length of 130 if no reaction involving hydrogen sulfide follows the absorption of a quantum by carbon tetrachloride. This outcome can be avoided only if Φ_{CCl_4} is much nearer 0.5 than zero. As one einstein at λ 208 mμ, has 24 kcal. more energy than one at λ 254 mμ, such a result is not surprising. It is regrettable that Lyons and Dickinson did not repeat their experiment in light of 208 mμ also. Günther, von der Horst and Cronheim[20] state that chlorine (though in extremely small amounts) was detected after exposure of carbon tetrachloride to X-rays.

If a chain exists in carbon tetrachloride (λ = 254 mμ), it might be predicted that the reaction in chloroform

$$SH + CHCl_3 \longrightarrow CHCl_2SH + Cl \qquad (8b)$$

would also occur unless it had an activation energy higher than the corresponding reaction 8c in carbon tetrachloride, so that the propagation of a chain in chloroform would be hindered, if not inhibited altogether. Such a relation was actually found by Cremer, Curry and Polanyi[16] to hold for the analogous reactions in the gas phase

$$
\begin{array}{ll}
CCl_4 + H \longrightarrow HCl + CCl_3 & (E = 0) \\
CHCl_3 + H \longrightarrow HCl + CHCl_2 & (E = 2.5)
\end{array}
$$

When hydrogen sulfide is photolyzed in chloroform, and λ = 208 mμ, $\Phi_{\text{gross}} = 0.95$ for total light absorbed by the solution. As it is hardly to be expected that the efficiency of reactions 1, 2b, . . . 6 (8b excepted) will be much greater than at λ 254 mμ, the high gross quantum yield is plausibly attributed to photochemical decomposition of the solvent. Hill[21] has found a quantum yield of 4.0, at λ 208 mμ, for decomposition of pure chloroform in the gas phase, independent of pressure.

A similar argument holds for methylene chloride, in which $\Phi_{CH_2Cl_2}$ measured in the pure liquid solvent was 0.9. In a typical experiment the solvent absorbed six-tenths of the incident light and the hydrogen sulfide four-tenths; the observed net quantum yield for each was 0.9.

$$
\begin{array}{l}
\Phi_{\text{gross}} \text{ (calcd.)} = 0.6 \times 0.9 + 0.4 \times 0.9 = 0.9 \\
\Phi_{\text{gross}} \text{ (obsd.)} = 0.9
\end{array}
$$

The ten-degree temperature coefficients of the quantum yields, as measured, were 1.06 in chloroform and 1.13 in methylene chloride. As the experimental error in any single value of Φ might amount to 10%, this difference cannot be considered significant.

Summary

Solutions of hydrogen sulfide in methylene

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[18] Rollefson and Libby, *J. Chem. Phys.*, **5**, 569 (1937).

[19] Bonhoeffer and Harteck, "Grundlagen der Photochemie," Steinkopff, Dresden, 1933, table, page 80.

[20] Günther, von der Horst and Cronheim, *Z. Elektrochem.*, **34**, 616 (1928).

[21] Hill, THIS JOURNAL, **54**, 32 (1932).

chloride, chloroform and carbon tetrachloride were photolyzed in monochromatic light of wave lengths 254 and 208 mμ. The molar percentage and the absorption of each component were always evaluated. All materials were highly purified, and air was rigorously excluded.

Hydrogen chloride was a product of every photolysis, and quantum yields based upon molecules of this substance formed per quantum absorbed by hydrogen sulfide were worked out for the various solutions and wave lengths. These were largest in carbon tetrachloride and smallest in methylene chloride. Quantum yields in pure methylene chloride, and chloroform, were determined similarly.

Enough of the reaction products in carbon tetrachloride were obtained for micro-fractionation and for identification of components by mixed melting point or by quantitative micro-analysis. These proved to be sulfur, hexachloroethane and trichloromethyl mercaptan. Qualitative evidence was available that analogous products were formed in the other two solvents.

Reaction mechanisms were worked out with due regard for thermodynamical considerations, by which the relative magnitudes, and in some cases the actual magnitudes, of quantum yields were accounted for. All reactions resulting from primary absorption of light by hydrogen sulfide can be interpreted in terms of the primary act $H_2S + h\nu \longrightarrow H + HS$ but not in terms of $H_2S + h\nu = H_2 + S$. Corresponding secondary reactions possibly initiated by the products of primary light absorption by carbon tetrachloride, also, were considered.

The temperature coefficients were normal, within experimental error.

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[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, THE UNIVERSITY OF CHICAGO]

The Preparation of *dl*-α,β-Diacetoxyisobutyric Aldehyde[1]

BY J. W. E. GLATTFELD AND WALTER E. MOCHEL

The preparation of the eleven theoretically possible C_4-saccharinic acids of molecular formula $C_4H_8O_4$ has now been accomplished.[2] This work was undertaken as a preliminary to the study of the saccharinic acid rearrangement of the tetroses. Work on the preparation of the tetroses by reduction of the corresponding tetronic acids is now being carried on as the next step in the rearrangement program.

The transformation of the C_4-saccharinic acids into the corresponding aldehydes would make available hydroxy aldehydes which might be of great usefulness in this study of saccharinic acid formation from sugars. Furthermore, these aldehydes would serve as sources for the preparation of some of the important C_5-saccharinic acids by means of the Kiliani reaction. It was for these reasons that the preparation of some of them was undertaken.

The work reported below was directed toward the preparation of the aldehyde corresponding to the acid first prepared by Glattfeld and Sherman and called by them *dl*-1,2-dihydroxyisobutyric acid.[3] A name for this substance more consistent with common usage is *dl*-α,β-dihydroxyisobutyric acid. This name henceforth will be used; in the present paper it will be shortened to α,β-iso acid.

Some success has been attained in the catalytic reduction of certain aldonic acid lactones in this Laboratory.[4] As acid lactones are internal esters, it was thought worth while to try the reduction of some of the esters of the α,β-iso acid. A series of the normal esters accordingly was prepared[5] and their reduction attempted. Catalytic reductions under widely varying conditions, with pressures from 30 to 2600 lb. (2 to 173 atm.) of hydrogen were tried. Sodium and sodium amalgams were also tried but neither the aldehyde nor the alcohol was obtained in any case. The apparatus used in these catalytic reduction attempts, and the general procedure, are described elsewhere.[6]

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(1) This article is condensed from a dissertation presented by Walter E. Mochel in partial fulfilment of the requirements for the doctorate degree in The University of Chicago.

(2) Glattfeld and co-workers, THIS JOURNAL, **42**, 2314 (1920); **43**, 2675 (1921); **47**, 1742 (1925); **49**, 2309 (1927); **53**, 3164 (1931); **55**, 1114 (1933); **55**, 3663 (1933); **60**, 415 (1938).

(3) Glattfeld and Sherman, *ibid.*, **47**, 1742 (1925).

(4) Glattfeld and Shaver, *ibid.*, **49**, 2305 (1927); Glattfeld and Schimpff, *ibid.*, **57**, 2204 (1935).

(5) Mochel, Masters Thesis, The University of Chicago, 1935.

(6) Glattfeld and Stack, THIS JOURNAL, **59**, 753 (1937).