

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Mercury-Sensitized Decomposition in Light of $\lambda 1849 \text{ \AA}$. I. Carbon Dioxide

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The possibility that carbon dioxide can be decomposed by light was first considered by Chapman, Chadwick and Ramsbottom,¹ who surrounded their reaction chamber with the luminous column of a mercury vapor lamp. The gas was confined over mercury, and special precautions were taken to avoid thermal effects. After a long exposure, dry carbon dioxide at one atmosphere was three per cent. decomposed, but at 36 mm. the reaction ran nearly half way to completion. In other words, decomposition in moles was (roughly) independent of pressure in spite of the fact that light absorption was very small in both cases. Of course the possibility of photosensitization was not considered at that time. When moist gas was exposed, the pressure increase was negligible.

Herschfinkel² exposed carbon dioxide, in a quartz tube containing mercury, to the radiation of a quartz mercury lamp and obtained mercuric oxide as well as carbon monoxide. No reaction occurred in a glass vessel.

The role of moisture in carbon dioxide decomposition had a part in the historic controversy between Bodenstein and Coehn concerning effects of drying upon photochemical activity of gases. Coehn and Sieper³ reported that after drying over concentrated sulfuric acid and also phosphorus pentoxide a steady state was easily reached in the reversible reaction $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$ with 7-34% decomposition, dependent on pressure and temperature. The methods of preparation and photolysis by no means precluded the presence of mercury vapor. Coehn and May⁴ and Coehn and Spitta⁵ dried carbon monoxide and oxygen at liquid air temperature, partially combined them in light, and then showed that the product had very low photosensitivity. In one experiment mercury vapor was purposely introduced as a test for oxygen formation⁴ more sensitive, so they hoped, than the pressure increase as read on their manometer. Yellow mercuric oxide promptly appeared on the walls, so they considered the pos-

sibility of decomposition of carbon dioxide by mercury excited by resonance radiation of $\lambda 2537 \text{ \AA}$. The above-described process for producing "dry" carbon dioxide would have removed mercury as well as water vapor. Whenever photolysis was pronounced the procedure was apparently such that mercury vapor would not have been eliminated.

Kreusler⁶ states that 20.45 cm. of carbon dioxide at one atmosphere absorbs 13.6% of light from an aluminum spark, $\lambda 1860 \text{ \AA}$. Leifson⁷ detected, in a 1.5-cm. layer, a series of absorption bands beginning at $\lambda 1712 \text{ \AA}$. and found absorption "complete" at $\lambda 1610 \text{ \AA}$. In view of these results it is not surprising that Groth⁸ could readily measure the quantum yield (0.96 in terms of the ozonization reaction as 2.0) in the light of a xenon lamp, which radiates strongly at $\lambda 1295$ and 1470 \AA .

Our roughly quantitative investigation proves that mercury atoms excited by resonance radiation of $\lambda 1849 \text{ \AA}$., but not those excited by $\lambda 2537 \text{ \AA}$., readily decompose carbon dioxide. In all probability, unsensitized photolysis also occurs in the former spectral region to the extent that light absorption is in evidence.

Apparatus and Method.—Radiation of $\lambda 1849 \text{ \AA}$. from mercury vapor lamps has been detected repeatedly including those containing argon and neon. Our spectrograms of an argon-filled "Fluorolight"⁹ resonance lamp (Braun Corporation, Los Angeles) showed, as well as $\lambda \lambda 2537$ and 1849 \AA ., fainter images for the mercury lines at $\lambda \lambda 2483, 2464, 2408, 2390, 2354, 2323, 2302, 2262, 2230, 2225, 2053, 2028, 1973, \text{ and } 1942 \text{ \AA}$. In addition there was a faint background having a banded structure.

An apparatus^{10,11} was developed recently in this Laboratory suitable for accurate measurement of very small amounts of "permanent" gas produced by photolysis of a readily condensable gas. It was used for present purposes without any important alterations except that no provision had to be made for rotation of the cell during photolysis.

Commercial solid carbon dioxide was placed in a large side-necked test-tube provided with a tight cork. The tube was immersed in liquid air, and most of the air pumped out. Replacing the liquid air with carbon dioxide snow, the first tenth was distilled into the first trap of an all-glass apparatus. It was held there by liquid air while

(1) Chapman, Chadwick and Ramsbottom, *J. Chem. Soc.*, **91**, 951 (1907).

(2) Herschfinkel, *Compt. rend.*, **149**, 395 (1909).

(3) Coehn and Sieper, *Z. physik. Chem.*, **91**, 347 (1916).

(4) Coehn and May, *ibid.*, **B26**, 117 (1934).

(5) Coehn and Spitta, *ibid.*, **B9**, 401 (1930).

(6) Kreisler, *Ann. Phys.*, **6**, 412 (1901).

(7) Leifson, *Astrophys. J.*, **63**, 73 (1926).

(8) Groth, *Z. physik. Chem.*, **B37**, 307 (1937).

(9) Leighton and Leighton, *J. Chem. Education*, **12**, 139 (1935).

(10) Forbes, Cline and Bradshaw, *THIS JOURNAL*, **60**, 1431 (1938).

(11) Forbes and Cline, *ibid.*, **61**, 151 (1939).

the test-tube was sealed off and the system evacuated on the mercury diffusion pump to remove permanent gases. Next a part of the solid was evaporated and pumped off. About half of the residue was then sublimed into a second trap, after which the first trap with its remaining solid was sealed off and discarded. The middle portion of the solid in the second trap was again exposed to high vacuum and evaporated into a large storage bulb. While passing from this bulb to the cylindrical reaction cell (of 400 cc. capacity) it traversed a trap cooled with dry-ice as an additional protection against water vapor. This cell was first set up with a few grams of liquid mercury. Before filling with carbon dioxide the cell was pumped out to a high vacuum while a flame was applied to various parts of its surface in succession so as to vaporize the condensed mercury several times. Experiments 17-19 were made with a new sample of gas similarly prepared. The carbon dioxide was introduced just like the carbonyl sulfide of the previous research.¹¹ To ensure saturation with mercury vapor the cell was always allowed to stand overnight before proceeding. The measurement of permanent gas produced by photolysis has been described sufficiently.¹¹

Resolution of the radiation from the resonance lamp adequate for present purposes was attained by the use of filter solutions contained in a quartz test-tube of 25-mm. internal diameter. The luminous column of the lamp, 7 mm. in external diameter, was coaxial with the test-tube. Nine mm. of 0.167 *M* acetic acid transmits light of $\lambda 2537$ completely, but absorbs strongly from $\lambda 2300$ on.¹² Substituting 0.0016 *M* sodium acetate, all light of wave length exceeding 1942 Å. is transmitted quite freely, judging from our spectrograms; but at $\lambda 1849$ Å. $\log_{10} \epsilon$ is 3.4,¹² so that about 1% was transmitted by our filter.

Table I shows the results obtained with the above-mentioned combinations. The lamp was 2 cm. from the cell, and was backed up by a curved sheet of aluminum metal. Pressures are in millimeters of mercury and time in minutes; p' corresponds to permanent gas, for the most part carbon monoxide and oxygen.

TABLE I
EXPOSURES OF CARBON DIOXIDE CONTAINING MERCURY VAPOR

Expt.	p_{CO_2}	Filter	Time	p'
18	1.7	NaAc	138	0.0035
8	239	HAc	125	0.0002
1	264	None	346	1 ± 0.5
7	239	None	98	0.120
9	239	None	100	.135
13	23.5	None	100	.186
17	1.7	None	100	.095

Experiment 1 produced too much gas for the McLeod gage, so pressure was estimated merely by difference of mercury levels in a manometer. The figures show conclusively that resonance radiation of $\lambda 2537$ Å. produces no sensitized decomposition. The approximate constancy of p' in experiments 7, 9, 13, 17 over a hundred-fold pressure change is convincing evidence that mer-

(12) Ley and Arends, *Z. Physik. Chem.*, **B17**, 177 (1932).

cury atoms excited at $\lambda 1849$ Å. readily decompose carbon dioxide. Experiment 17 suggests a quenching not very different from that of the fluorescence of mercury atoms excited at $\lambda 2537$ Å. in the presence of 2 mm. of carbon dioxide, as observed by Stuart.¹³

Yellow mercuric oxide was deposited only when radiation at $\lambda 1849$ Å. was present. We did not attempt to ascertain how complete was the "cleanup" of oxygen by mercury but it is possible that p' is due almost entirely to carbon monoxide. The absorption of radiation by the yellow product, in spite of the considerable area (about 200 sq. cm.) over which it was distributed, must have further depressed p' in all such experiments.

The percentage of radiation, at $\lambda 1849$ Å., from the resonance lamp was estimated by exposing a thermopile (a) with an acetic acid filter and (b) with pure water filter. Without correction for radiation of $\lambda \lambda 2262-1942$ Å. inclusive, radiation at $\lambda 1849$ is 2% of the whole—a maximum value.

Experiments 5 and 11 were similar to those in Table I except that two slits in tandem were used to minimize divergence. The radiant flux beyond the slits was measured radiometrically, and 2% of the total was attributed to $\lambda 1849$ Å. Molecules of permanent gas are denoted by n . The quantum yields ϕ are destitute of all the corrections suggested above—simply the molecules of permanent gas found, n , divided by q , the light quanta entering the gas. The pressure of carbon dioxide was about 240 mm.

TABLE II
QUANTUM YIELDS IN CARBON DIOXIDE CONTAINING MERCURY VAPOR

Expt.	Filter	Time	n ($\times 10^{16}$)	q_{total} ($\times 10^{16}$)	q_{1849}	ϕ_{total}	ϕ_{1849}
5	HAc	544	1.00	33.2	...	0.0003	...
11	None	219	4.06	3.34	5×10^{16}	.012	0.8

Additional experiments were undertaken, in which we resolved the radiation of the resonance lamp (Hg), and of the zinc spark¹⁴ (Zn) by a crystal quartz monochromator, also that of the aluminum spark¹⁴ by focal isolation.¹⁵ In Table III q' denotes merely total quanta entering the gas, which absorbed but little of the radiation, and ϕ' is n/q' . If q , the quanta absorbed, are calculated from Kreuzer's⁶ absorption data for $\lambda 1860$ Å., the true quantum yield is of the order of unity.

(13) Stuart, *Z. Physik*, **32**, 262 (1925).

(14) Forbes and Brackett, *THIS JOURNAL*, **53**, 3973 (1931).

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

For interpretation of experiments 4, 2 and 19 especially, it should be noted that experimental errors are of the order of 10^{16} molecules.

TABLE III
APPROXIMATE UNSENSITIZED QUANTUM YIELDS

Expt.	p_{CO_2}	Source	λ (m μ)	Time ($\times 10^{10}$)	n ($\times 10^{17}$)	q' ($\times 10^{17}$)	ϕ'
4	235	Zn	253	142	2.46	1.05	0.0023
2	264	Hg	254	117	0.528	4.78	.009
10	241	Al	186, etc.	139	37.1	104	.036
12	241	Al	186, etc.	132	15.2	57.7	.026
14	23.5	Al	186, etc.	130	22.0	102	.022
15	23.5	Al	186, etc.	130	4.31	141	.0029
19	1.7	Al	186, etc.	141	1.79	146	.0012

All the experiments undertaken by us are now accounted for except 3, 6 and 16 which were lost through breakage of the apparatus.

We intend to continue work in the field opened up by this investigation. We suspect that other reactions can be attributed to mercury atoms excited by radiation of $\lambda 1849 \text{ \AA}$. rather than $\lambda 2537 \text{ \AA}$., and intend, without delay, to examine certain of these from this standpoint.

Summary

Purified carbon dioxide freed from water vapor at -78° and saturated with mercury vapor is unaffected by resonance radiation of $\lambda 2537 \text{ \AA}$. provided that radiation of $\lambda 1849 \text{ \AA}$. is entirely excluded by suitable filters. It is rapidly decomposed, however, when radiation of $\lambda 1849$ is admitted.

The quantum yield of the decomposition sensitized at $\lambda 1849$ is at least as great as 0.8 and very possibly could become unity if certain suggested corrections could be applied.

Assuming that mercury vapor is not at all excited by the radiation of the aluminum spark at $\lambda 1860 \text{ \AA}$. the unsensitized quantum yield estimated with the help of Kreuzler's absorption data is of the order of unity.

We intend, without delay, to determine the relative importance of radiations of $\lambda 2537$ and 1849 \AA ., respectively, in certain reactions sensitized by mercury vapor.

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RECEIVED FEBRUARY 6, 1939

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The Dielectric Behavior of Solutions of the Protein Zein¹

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There are now available several methods which are useful in the determination of the size or distribution of size of macromolecules. Less well developed are the methods for the study of the shapes of such molecules. Several attempts have been made to make available for certain classes of compounds these kinds of information by a study of the frequency variation of dielectric constant for dilute solutions containing such molecules, since from the dispersion of dielectric constant of their solutions there may be calculated, among other things, the relaxation time or times of the solute. As is now known these constants are related to the size and shape of the molecule. In so far as we now know, protein systems always show the anomalous dispersion. Also, due to the achievements of Svedberg and his associates with proteins, it was considered desirable to work with a member of this class of compounds since com-

parisons with sedimentation behavior can then be made.

In order to subject the dielectric constant methods to test in this way, it is desirable, at least for the early work, to select for observation a protein system having extremely low electrical conductivity. For the purpose we have chosen, as did Wyman² before us, studies of the plant protein zein prepared from the seeds of maize or from corn gluten in 72% aqueous ethyl alcohol.

Since the application of the Debye theory to the anomalous dispersion of dielectric constant of macromolecular solutions has been given in detail in previous publications,³⁻⁵ it will be necessary to give only a brief outline here. The dielectric constant, ϵ , of a solution can be said to consist of a real and an imaginary part

$$\epsilon = \epsilon' - i\epsilon'' \quad (1)$$

(2) Wyman, *J. Biol. Chem.*, **90**, 443 (1931).

(3) Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929.

(4) Williams, *Trans. Faraday Soc.*, **30**, 723 (1934).

(5) Oncley, *THIS JOURNAL*, **60**, 1115 (1938).

(1) More complete details of this work are to be found in the thesis of Myron A. Elliott submitted to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree in June, 1938.