by the General Electric Company used in the earlier experiments. During the last year of the work the first-named author held the du Pont Fellowship of the Division of Chemistry.

Summary

The photolysis of certain uranyl oxalate solutions in nine approximately monochromatic radiations has been reinvestigated with elaborate (and in some cases novel) radiometric and analytical precautions.

The gross quantum yield ϕ at 25° for a solution 0.01 M in uranyl sulfate and 0.05 M in oxalic acid varies between 0.60 at 254 mμ to 0.58 at 435 mμ with a minimum of 0.49 at 366 mμ. These values are about half those generally in use at the present time.

ϕ is diminished by sodium sulfate, by sodium hydroxide and by sulfuric acid, in spite of the fact that the first two enhance total absorption.

The temperature coefficient, ϕ_{t+10}/ϕ_t, is 1.03 + 0.035, between 10 and 25°, both at 366 mμ and 313 mμ.

If the light presumably absorbed by uncombined uranyl sulfate is subtracted before calculating ϕ for solutions containing no great excess of oxalic acid, ϕ becomes nearly independent of their concentrations.

These calculations give some support to the view that the photolyte is $UO_2HC_2O_4^+$ or $UO_2C_2O_4$ or some optical cluster equivalent to one of these and make it seem somewhat improbable that the photolysis depends mainly upon collisions of the second kind between excited UO_2^{++} and $H_2C_2O_4$.

Detailed suggestions for actinometry in monochromatic and in polychromatic light are offered. The limitations of the latter procedure are emphasized.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 4]

THE DISSOCIATION OF CARBON DIOXIDE IN THE ELECTRODELESS DISCHARGE

BY HERSCHEL HUNT WITH WALTER C. SCHUMB

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The dissociation of carbon dioxide by the application of other than thermal energy has been studied by a number of investigators. Thus Lefebvre and Montagne[1] found that in the electric arc the dissociation proceeds in perfect accord with the prediction based upon the thermal decomposition of carbon dioxide. Carbon monoxide was unchanged when traversed by the arc or spark discharge.

Lind,[2] using alpha particles, has shown that oxygen forms O_2^- and

[1] Lefebvre and Montagne, *Bull. soc. encour. ind. nat.*, **127**, 917 (1928).

[2] Lind, *Trans. Am. Electrochem. Soc.*, **44**, 66 (1923).

thereby chemical action with carbon monoxide is promoted. Neither carbon dioxide nor carbon monoxide can accept the electron.

Busse and Daniels[3] found no relation to exist between amount of decomposition of gases, such as nitric oxide and carbon dioxide, and the heats of formation or free energies of the gases. They found that cathode rays gave the same comparative results as alpha particles, and concluded that actual decomposition was brought about by the free electron.

The present investigation was undertaken with the object of observing the influence of the electrodeless discharge upon the decomposition and the synthesis of carbon dioxide. It constitutes an extension of the work described in another article upon the dissociation of ammonia.[4]

It is not proposed in this paper to offer a complete interpretation of the phenomena observed, because at the present writing such an explanation would be largely conjectural. The experimental facts, however, we believe merit setting forth, the theoretical significance of these facts being left for subsequent clarification.

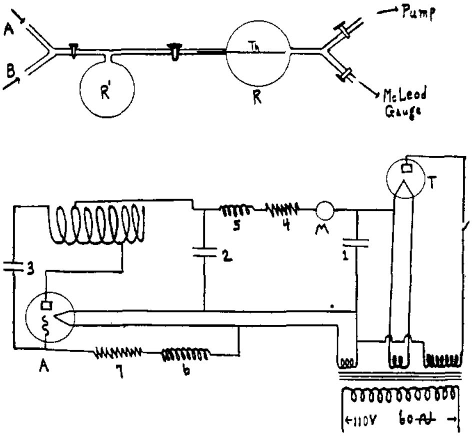

Fig. 1.—T, UX 866 mercury rectifying tube; M, 110-ma. milliammeter; A, UV 203 A power transformer tube, 50-watt; 1, 2-mfd. 1500-v. fixed condenser; 2, 0.002-mfd. 5000-v. fixed condenser; 3, 0.0005-mfd. 5000-v. fixed condenser; 4 and 7, 5000-ohm, 50-watt resistances; 5 and 6, radio frequency chokes (4″ × 5/8″, No. 22 wire).

Procedure

The apparatus employed in the earlier study has been greatly improved, and is shown diagrammatically in Fig. 1. We are indebted to Professor V. Bush of this Institute for the suggested arrangement. The wave length of the set as shown was found to be 34 meters, corresponding to a frequency of 8820 kc.

The transformer operated on a 110-v. 60-cycle circuit and supplied T with 2.5-v. filament current, A with 10 v., and T with 825 v. at 150 ma., d. c. half-wave current. The solenoid, 10 inches in diameter, was made of flat copper strip 1 cm. in width. When tapped as shown the wave length produced was 34 m. Higher wave lengths were obtained by increasing the number of turns tapped off on the solenoid.

The reaction system, shown in Fig. 1, consisted of R, a one-liter pyrex bulb in which was placed a thermometer, Th, and R′, a reservoir in which gases were mixed before using. To A and B were connected purification and drying trains for the entering gases. Gas mixtures were made up by controlling the individual partial pressures, using a

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[3] Busse and Daniels, This Journal, **50**, 3271 (1928).

[4] Schumb and Hunt, *J. Phys. Chem.*, **34**, 1919 (1930).

manometer in conjunction with the McLeod gage. R was thoroughly evacuated and swept out several times with the gas mixture. Then a sample was drawn from R′ into R and the pressure lowered to the desired value; pressure and temperature readings were taken and the discharge started. After the passage of the discharge (regularly an interval of five minutes) the bulb, R, was allowed to come to the original temperature, which process required over one hour, and the final pressure was then taken at the original temperature. Since the room temperature did not vary over 0.1° in the course of any experiment, and since the gas was always measured at the same temperature, we may assume our measurements to be accurate to within 0.2%.

The carbon dioxide was generated by heating pure sodium bicarbonate. It was carefully dried by passage through phosphorus pentoxide. The carbon monoxide was made from concd. formic acid and concd. sulfuric acid. Most of the water vapor left in the gas was condensed by strong chilling in a gas trap. Traces of carbon dioxide were then removed by passing through solid caustic potash, and the gas was finally thoroughly dried by phosphorus pentoxide. Commercial compressed oxygen was passed over potassium hydroxide and phosphorus pentoxide before use.

In Table I typical data are given for the decomposition of pure carbon dioxide at pressures ranging from 0.25 to 2.82 mm. The first two columns show, respectively, the initial and final pressures, the third column gives the calculated percentage decomposition on the basis of the relationship

$$D = \frac{2(p_f - p_i)\,(100)}{p_i}$$

and the last column gives the corresponding value of K_p, the equilibrium constant, calculated according to the equation

$$K_p = \frac{(py^3/2)^{1/2}}{(1-y)(1+y/2)^{1/2}}$$

These results are shown graphically in Fig. 2, Curve I, wherein the percentage decomposition is plotted against the equilibrium pressure.

Table I

Experimental Results

P_i, (mm.)	P_f, (mm.)	D, (%)	K_p	P_i, (mm.)	P, (mm.)	D, (%)	K_p
0.25	0.375	100.0	...	0.82	1.00	43.9	0.3320
.27	.40	96.3	9.375	0.925	1.105	38.9	.2708
.28	.41	92.86	4.690	1.06	1.25	35.85	.2436
.33	.47	84.8	2.087	1.175	1.36	31.5	.1978
.34	.48	82.35	1.739	1.36	1.555	28.68	.1776
.39	.54	76.9	1.289	1.61	1.81	24.8	.1390
.45	.60	66.67	0.7755	1.73	1.94	24.3	.1389
.495	.65	62.6	.6581	2.16	2.40	22.2	.1397
.56	.72	57.1	.5319	2.72	3.01	21.3	.1457
.67	.84	50.75	.4259	2.82	3.11	20.6	.1398
.76	.935	46.05	.3562				

Qualitatively the presence of carbon monoxide in the resulting gas after the passage of the discharge was confirmed by the blackening of palladious chloride paper, and sufficient oxygen was produced to cause a darkening of fresh alkaline pyrogallol solution.

Since the carbon dioxide is not completely decomposed at pressures greater than 0.25 mm., it is evident that an equilibrium is reached. That such is the case was definitely proved by the synthesis of the gas from a mixture of carbon monoxide and oxygen. The data obtained, using a mixture of two volumes of carbon monoxide and one volume of oxygen, are given in Table II.

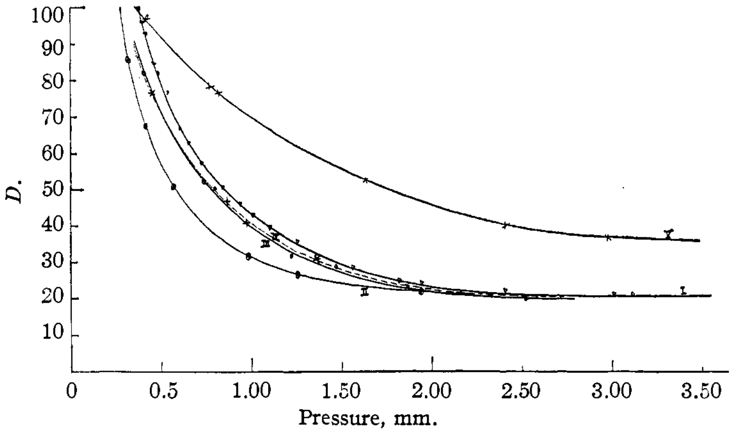

Fig. 2.—I, Decomposition of CO_2; II, synthesis: $CO/O_2 = 2$; III, decomposition: $CO_2/CO = 1$; IV, decomposition: $CO_2/O_2 = 1$; V, decomposition: $CO_2/He = 1$.

TABLE II

DATA OBTAINED

P_i	P_f	S	K_p
0.33	0.315	13.64	1.907
.46	.41	32.7	0.6613
.67	.56	49.3	.3456
1.27	.98	68.5	.1679
1.65	1.25	72.7	.1531
2.62	1.94	77.89	.1247

The third column lists the percentage of carbon monoxide converted into carbon dioxide. These data are also represented in Fig. 2, Curve II. The discharge passed for five minutes in all cases. After the discharge the gas was tested for carbon dioxide by passage through clear barium hydroxide solution. A dense turbidity was produced. A blank test made on the mixture which had not been subjected to the discharge gave a negative result.

The effect of varying composition of the gas mixture was now studied. The proportions of oxygen and of carbon monoxide in the original gas mixtures were increased above the stoichiometrical requirements and in a third experiment carbon dioxide was diluted with 50% of helium to observe the effect of an inert gas. The helium was freed before use from carbon dioxide, oxygen and water vapor. The results of these experiments are shown in Table III. *S* is based in all cases upon the fraction of carbon monoxide changed to carbon dioxide.

TABLE III

A. SYNTHESIS OF CARBON DIOXIDE WITH EXCESS OXYGEN. VOL. RATIO $CO/O_2 = 1$

P_i	P_f	S	K_p
0.31	0.29	25.8	1.0567
.45	.415	31.11	0.9627
.62	.56	38.71	.7917
1.15	.99	55.65	.5134
1.57	1.30	68.88	.3254
2.42	1.95	77.68	.2472
2.87	2.26	85.02	.1601

B. SYNTHESIS OF CARBON DIOXIDE WITH EXCESS CARBON MONOXIDE. VOL. RATIO $CO/O_2 = 4$

0.51	0.48	14.7	1.557
.62	.57	20.16	1.078
.70	.63	25.0	0.7937
1.17	1.00	36.32	.4428
1.67	1.38	43.4	.2738
2.84	2.28	49.3	.0917

C. SYNTHESIS OF CARBON DIOXIDE IN PRESENCE OF HELIUM. VOL. RATIO $He/(2CO + O_2) = 1$

0.33	0.3275	4.5
0.72	0.69	25.0
1.15	1.08	36.52
2.22	1.995	60.8

D. DECOMPOSITION OF CARBON DIOXIDE IN PRESENCE OF OXYGEN. VOL. RATIO $CO_2/O_2 = 1$

P_i	P_f	D	K_p
0.38	0.4525	76.31	1.646
.77	.86	46.76	0.6054
.88	.97	40.91	.504
1.26	1.36	31.74	.3979
1.76	1.865	23.86	.311

E. DECOMPOSITION OF CARBON DIOXIDE IN PRESENCE OF CARBON MONOXIDE. VOL. RATIO $CO_2/CO = 1$

0.34	0.41	82.35	2.731
.65	.735	52.31	0.931
.71	.80	50.70	.9169
1.13	1.22	31.85	.5802
1.37	1.47	29.2	.5771
2.40	2.525	20.83	.5393

F. DECOMPOSITION OF CARBON DIOXIDE IN PRESENCE OF HELIUM. VOL. RATIO $He/CO_2 = 1$

0.33	0.41	96.96
.64	.765	78.12
.68	.81	76.47
1.44	1.63	52.78
2.23	2.45	39.46
2.72	2.97	36.77

Preliminary experiments employing pure oxygen at pressures ranging from 0.82 to 1.8 mm. gave no pressure change, proving that ozone was not formed under these conditions. The gas gave a pale yellow glow which filled the bulb completely without the appearance of banding as in most of the other cases studied. Carbon monoxide alone gave no pressure changes when subjected to the discharge.

The passage of the discharge was in all cases accompanied by a rise in temperature, which, in a five-minute interval, amounted to about 20°. For this reason the 0.1° thermometer was enclosed in the bulb, as shown in Fig. 1, and time was allowed after each discharge for the gas to return to the initial temperature before the pressure was measured. Separate experiments on carbon dioxide carried out with and without the enclosed thermometer proved that the presence of the thermometer itself had no influence upon the establishment of the equilibrium pressures.

In the experiments recorded in Section E, Table III, a peculiar afterglow was observed which persisted for about four seconds at 0.5 mm. after the current had been cut off. The length of time varied somewhat with the pressure within the bulb. The afterglow had more of a yellowish tinge than was seen while the discharge was passing. Mixture F containing helium gave a pinkish glow, while carbon dioxide alone produced a bluish color.

To determine the effect of variation in the time of operation of the discharge, a series of experiments was conducted upon the decomposition of carbon dioxide, in which the discharge interval was varied from five seconds to ten minutes using the same initial pressure. Consideration of the following table of results shows clearly that at the end of two minutes equilibrium has been attained; the percentage decomposed, *D*, does not alter thereafter. Similar results were obtained when working at higher pressures.

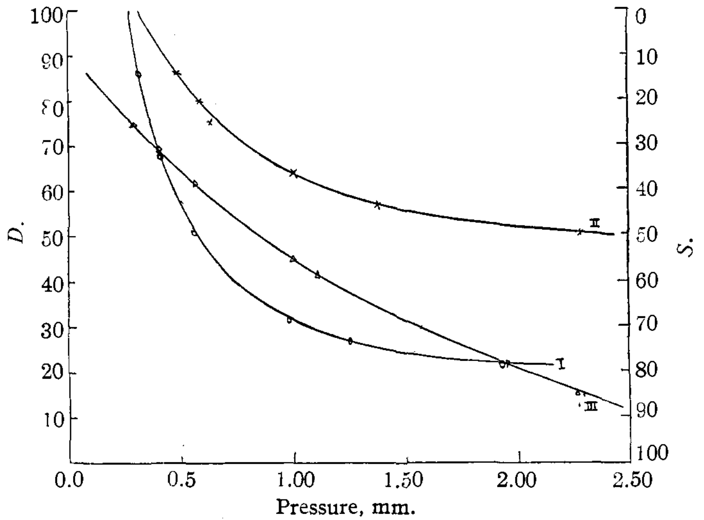

Fig. 3.—I, Synthesis: $CO/O_2 = 2$; II, synthesis: $CO/O_2 = 4$; III, synthesis: $CO/O_2 = 1$.

Finally, the effect upon the decomposition of change of wave length was observed by allowing the discharge to pass at 51 meters, the maximum afforded by the apparatus as constructed, instead of 34 meters, as in all the previous experiments. No appreciable alteration in the percentage decomposed was observed due to this change, as is indicated in Part B, Table IV.

Discussion of Results

The percentage of carbon dioxide decomposed, at a pressure *p*, plus the percentage synthesized from a mixture at a pressure, *p*, of two volumes

TABLE IV

A. EFFECT OF VARIATION IN TIME

Time	P_i	P_f	D
5 sec.	0.92	0.99	15.22
10 sec.	.92	1.035	24.9
15 sec.	.92	1.06	30.44
20 sec.	.92	1.07	32.61
30 sec.	.92	1.085	35.87
60 sec.	.92	1.09	37.0
2 min.	.92	1.10	39.13
5 min.	.92	1.10	39.13
10 min.	.92	1.10	39.13

B. EFFECT OF VARIATION IN WAVE LENGTH

P_i	P_f	D, $\lambda = 51$	D, $\lambda = 34$
0.82	1.00	43.90	43.90
1.02	1.205	36.27	36.40

of carbon monoxide plus one volume of oxygen are in all cases practically equal to 100%. Hence, we may assume that we are dealing with an equilibrium

$$2CO + O_2 \rightleftharpoons 2CO_2$$

The addition of carbon monoxide to the dissociating mixture decreases the amount of carbon dioxide decomposed and an excess of carbon monoxide in the synthesis of carbon dioxide increases the percentage of carbon dioxide synthesized.

Likewise, additional oxygen decreases the amount of decomposition of carbon dioxide but does not increase the amount of synthesis. Oxygen reduces the amount of decomposition relatively more than carbon monoxide. This is in contradiction to the mass action law, a fact which is in agreement with the observations of other workers in this field. If a complex, $[(CO_2)_x \cdot (O_2)_y]$, were formed by the union of CO_2^+ and O_2^-, we may assume that the energy used in its formation is wasted, as far as the dissociation of carbon dioxide is concerned. Similarly, the formation of $[(CO)_x \cdot (O_2)_y]$ by the union of CO^+ and O_2^- would decrease the extent of synthesis of carbon dioxide. This hypothesis is supported by the data at hand.

Helium increases the amount of decomposition of carbon dioxide and likewise decreases the amount of synthesis. Since helium has a high ionization potential, it may be assumed that it gives up any energy primarily absorbed to further disrupt carbon dioxide when it returns to its stable state.[5]

Nitrogen also caused an increase in the amount of carbon dioxide decomposed, but the process here is obscured by the probability of complicating reactions between the nitrogen and the other gases, especially

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[5] *Cf.* Brewer and Westhaver, *J. Phys. Chem.*, **34,** 153 (1930).

oxygen. It is not surprising, therefore, that in this case the amount of decomposition and amount of synthesis do not equal 100%, as with helium. In view of these facts, we have omitted the data until the phenomena can be further investigated.

Summary

1. An apparatus suitable for producing a high frequency oscillatory electrodeless discharge has been described.

2. Under the influence of this discharge, the equilibrium

$$2CO + O_2 \rightleftharpoons 2CO_2$$

has been shown to be established, and data for this equilibrium at various pressures are given.

3. Variation in the length of time of discharge indicates that the reaction is brought to equilibrium in two minutes. Five minutes was adopted as the standard interval in these experiments.

4. The results obtained by variation in the percentage composition of the gas mixtures employed are not in agreement with the law of mass action. K_p is not a constant, but shows a decrease with increasing values of the equilibrium pressures.

5. Increased pressure decreases the extent of decomposition of carbon dioxide and increases the extent of synthesis, a fact, however, which is only in qualitative agreement with the law of mass action.

6. An inert gas, such as helium, displaces the equilibrium in the direction of increased decomposition of carbon dioxide.

CAMBRIDGE, MASSACHUSETTS

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

THE VAPOR PRESSURE OF SODIUM. LOW PRESSURE MEASUREMENTS WITH THE ABSOLUTE MANOMETER

BY WORTH H. RODEBUSH AND WM. F. HENRY

RECEIVED JUNE 2, 1930 PUBLISHED AUGUST 5, 1930

The reliable measurements on the vapor pressure of sodium at pressures below 0.1 mm. have all been made by the effusion method of Knudsen and the vapor pressures can only be calculated by assuming some value for the vapor density. Rodebush and Walters[1] have shown that the assumption of normal density for sodium at low pressures is justified, but it seemed desirable to check this by a direct measurement of the vapor pressure. This measurement presented an excellent opportunity to try out the absolute manometer described by Rodebush and Coons.[2]

For the measurement of vapor pressure the design of the gage was altered from that originally described, by inverting the arrangement of

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[1] Rodebush and Walters, THIS JOURNAL, **52**, 2654 (1930).

[2] Rodebush and Coons, *ibid.*, **49**, 1953 (1927).