207. *The Photodecomposition of Carbon Dioxide and of Ammonia by Xenon 1470 Å Radiation.*

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The photochemical decomposition of carbon dioxide and of ammonia has been examined by the 1470 Å xenon radiation. The quantum efficiencies were found to be 1·9 ± 0·2 and 0·45 ± 0·1 molecule/quantum, respectively. The carbon dioxide decomposition is found to follow the scheme $CO_2 + h\nu \longrightarrow CO_2^*$; $CO_2^* + CO_2 \longrightarrow 2CO + O_2$. Atomic oxygen is not present. The decomposition of ammonia proceeds through the formation of NH_2 radicals, and the resulting hydrazine is photochemically decomposed.

OWING to the difficulties due to absorption inherent in radiation experiments with ultra-violet light of very short wavelength, little precise work has been published in this field. By the construction of a simple but novel xenon lamp these difficulties have been greatly reduced and it was decided to investigate the photolysis of gaseous carbon dioxide and of ammonia. According to Groth [1] carbon dioxide is decomposed photochemically into carbon monoxide and atomic oxygen. The energy required for the reaction

$$CO_2 \longrightarrow CO + O$$

is about 5·5 ev (corresponding to $\lambda \sim 2200$ Å). Carbon dioxide however only absorbs light in the extreme ultraviolet region commencing at *ca.* 1700 Å. Groth [2] evaluated the yield per quantum as nearly 1; but other investigators [3,4] have obtained either 1 or 1·5, atomic oxygen being produced in the reaction.

For the photolysis of ammonia Kuhn [5] found a quantum yield of 0·19 but other experiments lead to quantum yields between 0·5 and 11·0 for different pressures, light intensities, and temperatures.[6-9] Hydrazine was first detected among the products by Koenig and

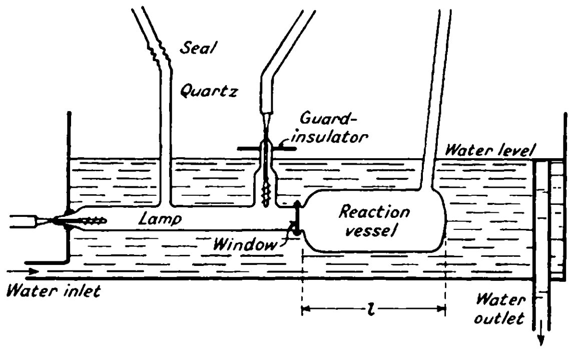
1 Groth, *Z. phys. Chem.*, 1937, *B*, **37**, 307, 315.
2 *Idem, ibid.*, 1938, *B*, **38**, 366.
3 Noyes and Leighton, "The photochemistry of gases," Reinhold, New York, 1941.
4 Harris, and Kaminsky, *J. Amer. Chem. Soc.*, 1935, **57**, 1154.
5 Kuhn, *Compt. rend.*, 1924, **177**, 956, 123.
6 Wijnen and Taylor, *J. Chem. Phys.*, 1953, **21**, 233.
7 Harteck and Oppenheimer, *Z. phys. Chem.*, 1932, *B*, **16**, 77.
8 Ogg, Leighton, and Bergstrom, *J. Amer. Chem. Soc.*, 1934, **56**, 318.
9 Wigg and Kistiakowsky, *ibid.*, 1932, **54**, 1836.

Brings,[10] and this was likewise found in the presence of mercury in a streaming system by Gedye and Rideal.[11] Hydrazine when formed can again undergo decomposition.

EXPERIMENTAL

The lamp and reaction vessel are depicted in Fig. 1. The lamp consists of a quartz tube with one end electrode and one side electrode, each made of heavy tungsten rod containing barium thorate as electron-emitting material; each electrode is wrapped with a tungsten wire spiral. They are sealed in with molybdenum seals. The side electrode is protected from shorting by a round guard insulator. To the open end of the lamp is sealed by means of picein wax a fluorite window, 22 mm. in diameter and 1 mm. thick, which also acts as the radiation entry into the reaction vessel (length, *l*, 63 mm.); the whole assembly can be immersed in a constant-temperature water-bath. Both lamp and reaction vessel are connected to vacuum pumping lines, gas reservoirs, and a two-range McLeod guage.

FIG. 1. *Lamp and reaction vessel.*



For cleaning the lamp and degassing the electrodes the lamp is run in argon which is renewed from time to time. Impurities are gradually deposited on the window and there is a slow but steady decrease in intensity. In consequence frequent calibrations of the lamp were made by means of a Cambridge Instrument Co. thermocouple of 2 cm.^{2} area mounted in the reaction vessel itself and run when the latter was evacuated. The data were plotted on an "ageing" curve. The thermocouple was tested and calibrated by means of a standard lamp provided by the National Physical Laboratory. The xenon lamp is operated directly on the a.c. mains circuit and is brought into operation by means of a high-tension Tesla coil.

The characteristic current consumption with the lamp filled to 100 mm. pressure with xenon was: maximum current 20 A, 51·0 V; usual running conditions 12 A, 36·0 V; minimum running current 4·5 A, 24·5 V. The output of 1470 Å radiation at 12 A and 36·0 V was found by means of the thermocouple to be $1{\cdot}40 \times 10^{17}$ quanta/sec.

Helium and xenon were supplied by the British Oxygen Company. The other gases were prepared and purified in the usual manner.

During the period of radiation the gas pressure was continuously recorded and analysis performed by fractionation with liquid air.

RESULTS

(a) *Carbon Dioxide.*—In Fig. 2 the initial rate of decomposition for constant light flux is plotted against pressure. As might be expected a plot of the log of the initial decomposition rate against the reciprocal of the pressure (Fig. 3) gives a linear relation in accordance with Lambert's law. A very definite falling off in the rate is noted at very low pressures. The quantum yield is $1{\cdot}9 \pm 0{\cdot}2$ molecules/quantum. This suggests that the reaction mechanism is:

$$CO_2{}^* + h\nu \longrightarrow CO_2{}^*$$

$$CO_2{}^* + CO_2 \longrightarrow 2CO + O_2$$

and that contrary to the previous view atomic oxygen is not formed in the process.

[10] Koenig and Brings, *Z. phys. Chem.*, *Bodenstein-Festband*, 1931, 541.
[11] Gedye and Rideal, *J.*, 1932, 1166.

The photochemical yield, as determined by change in pressure, rapidly decreases with time.

To investigate whether atomic oxygen is formed or not as a result of the primary act, hydrogen in various proportions was added to the carbon dioxide, the latter being maintained at a constant pressure of 100 mm. As is indicated in Fig. 4 the pressure does not remain constant, but even with a large excess of hydrogen a slight increase of pressure is still obtained.

The products of the reaction, carbon monoxide and oxygen, can undergo further photochemical reactions. These include :

$$O_2 + h\nu \longrightarrow 2O\,;\ O + O + \text{wall} \longrightarrow O_2\,;\ O + O_2 \longrightarrow O_3$$

The reaction $CO + O \longrightarrow CO_2$ requires, according to Jackson,[12] more activation energy than the others and is thus less probable.

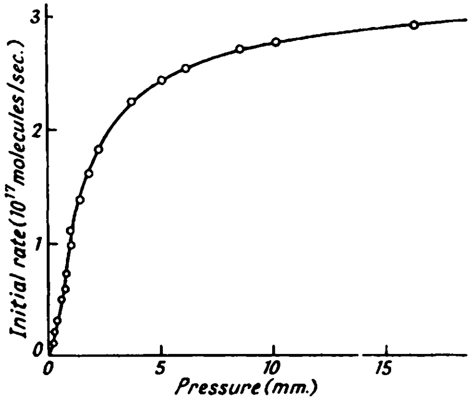


FIG. 2. *Initial rate of decomposition of carbon dioxide at different pressures.*

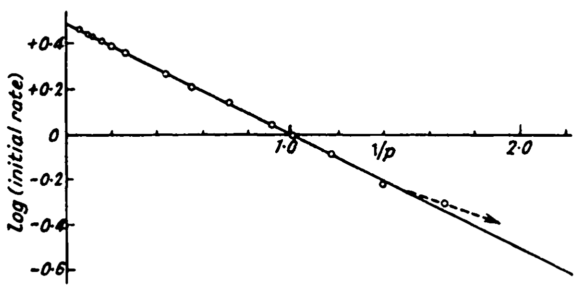


FIG. 3. *Plot of the logarithm of the initial rate of decomposition of carbon dioxide against the reciprocal of the pressure.*

The other possible reaction, $CO + h\nu \longrightarrow CO^*$, should, in the presence of hydrogen, result in the formation of formaldehyde [7], $CO^* + H_2 \longrightarrow CH_2O$, which indeed was found by freezing out the condensable gases and testing the condensate with sodium sulphite. The formaldehyde formed does not accumulate in the system as it decomposes by the mechanism

$$CH_2O + h\nu \longrightarrow HCO + H$$

and

$$CHO \longrightarrow H + CO$$

The atomic hydrogen formed in these secondary reactions can react with carbon dioxide to form formaldehyde, although as Lewis [13] showed the yield is somewhat small, as well as with the oxygen to form water. Thus no pressure change is to be expected.

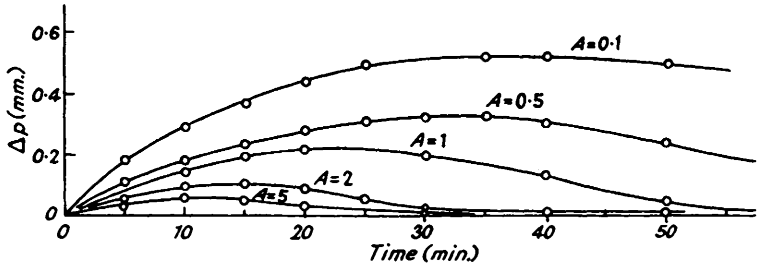
Further experiments were carried out with the lamp containing argon where the 1870 Å radiation is not absorbed by carbon monoxide. The form of the decomposition

[12] Jackson, *J. Amer. Chem. Soc.*, 1934, **56**, 2631.
[13] Lewis, *ibid.*, 1928, **50**, 27.

yield–time curves were substantially the same as with the xenon radiation but with considerably reduced slope since with the elimination of the carbon monoxide secondary reactions, carbon monoxide not being excited by this radiation, the back reactions are considerably reduced.

(b) *Ammonia.*—In Fig. 5 is plotted the decomposition rate–time curve for the photochemical decomposition of ammonia. The initial decomposition rate only obeys Lambert's law for medium pressures. At high pressures complete absorption of the radiation takes place. Under these conditions the quantum yield is $0{\cdot}45 \pm 0{\cdot}1$ molecule/quantum.

FIG. 4. *Pressure change* (Δp) *with time on irradiation of carbon dioxide–hydrogen mixtures.* [$A = p(H_2)/p(CO_2)$; $p(CO_2)$ being constant at 10 mm.]



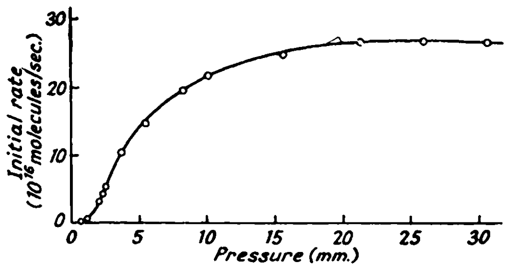


FIG. 5. *Initial rate of decomposition of ammonia at different pressures.*

It seemed probable that the primary photochemical reaction is a scission of the molecule to yield atomic hydrogen and NH_2 radicals :

$$NH_3 + h\nu \longrightarrow NH_2 + H$$

Hydrazine could readily be detected after a few minutes by cooling the trap to $-20°$ and then examining the contents.

The small observable rate of reaction at low pressures supports the view that the NH_2 radicals are adsorbed on the walls before hydrazine formation ($NH_2 + NH_2 \longrightarrow N_2H_4$) reaches a steady state. The presence of atomic hydrogen is readily established by the rapid formation of water on the addition of oxygen to the reacting gas.

The hydrazine formed reaches a stationary state by undergoing a secondary photochemical decomposition [14] to nitrogen and hydrogen. Here it appears that 2 quanta are involved, since 4 quanta are required to effect the decomposition of two molecules of

$$2N_2H_4 + 2h\nu \longrightarrow N_2 + 3H_2$$

ammonia into its final products, hydrogen and nitrogen.

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[14] Wenner and Beckman, *J. Amer. Chem. Soc.*, 1932, **54**, 2787.