

different types of matings) deviate widely from those expected on the basis of ordinary Mendelian inheritance, but are readily interpreted when allowance is made for the aberrant chromosome behavior in the males.

<sup>1</sup> Metz, C. W. 1925. "Chromosome Behavior in *Sciara* (Diptera)," *Anat. Rec.*, 31, 346. Cf. also *Science*, 61, 212 and 63, 190.

<sup>2</sup> A detailed account is in press in the *Zs. ind. Abst. Vererb.*

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## DECOMPOSITION OF AMMONIA BY OPTICALLY EXCITED MERCURY ATOMS.

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*Introduction.*—Recently there have been studied various chemical reactions sensitized by mercury vapor activated by the absorption of the line 2537 Å. These reactions are often so complicated as to make their mechanism difficult to elucidate. For instance, in the case of the hydrogen-oxygen reaction, which has been studied by ourselves and later by others, there is the possibility of activating oxygen as well as hydrogen and the possibility of forming hydrogen peroxide and ozone as well as water; this reaction is further complicated by the removal of mercury vapor through oxidation. Consequently, it was desirable to study a reaction which *a priori* seemed relatively simple. It was known that ammonia can be decomposed photochemically<sup>1</sup> by the absorption of light of wave-lengths 2025 to 2140 Å. Preliminary experiments showed that ammonia decomposition could also be brought about by the wave-length 2537 Å when mercury vapor was present, although ammonia itself does not absorb this line. The decomposition products of both the sensitized and unsensitized reactions have been examined.

*Experimental Procedure.*—Light from a quartz-mercury arc was allowed to shine on two concentric cylindrical quartz tubes. The inner tube was connected to a mercury-vapor pump and McLeod gauge and could be filled with ammonia at any desired pressure. In the annular space between the two tubes a solution could be placed to serve as a light filter. In a side-arm connected to the inner quartz tube was placed about 2 cc. of mercury, in order to give a partial pressure of mercury corresponding to its vapor-pressure at room temperature. Through a liquid-air trap a quartz-fibre manometer, whose purpose was the examination of the reaction-products, was also connected to the inner tube. This manometer had two quartz fibres fused together at one end to prevent Lissajou

motion, as suggested by Coolidge.<sup>2</sup> At the low gas pressures used here the logarithmic decay constant  $\lambda$  of the amplitude of vibration of the fibre has been shown by Haber and Kerschbaum<sup>3</sup> to be given by the relation

$$A \cdot \sum(p\sqrt{M}) + B = \lambda = \frac{0.693}{\tau_{1/2}}$$

Here  $A$  and  $B$  are apparatus constants,  $\tau_{1/2}$  is the time required for the vibration to decrease to half amplitude, and  $\sum(p\sqrt{M})$  is the sum of the products of the partial pressures of the separate components of the gas into the square-roots of their molecular weights. The gauge was calibrated against the McLeod gauge using both hydrogen and air, care being taken to exclude mercury vapor; and a nearly straight-line calibration curve was drawn having  $\lambda$  as ordinates and  $\sum(p\sqrt{M})$  as abscissae.

SENSITIZED DECOMPOSITION OF AMMONIA			
INITIAL PRESSURE OF NH <sub>3</sub>	FINAL PRESSURE OF RESIDUAL GAS	$\Sigma(p\sqrt{M})$	MOL.-FRACTION OF HYDROGEN
0.138 mm.	0.0055 mm.*	0.0124 mm.	0.786
0.137	0.0069	0.0171	0.727
0.770	0.0171*	0.0388	0.782
0.137	0.0097	0.0254	0.691
0.238	0.0165	0.0431	0.694
0.490	0.0286	0.0761	0.681
0.191	0.0124	0.0328	0.685
0.488	0.0348	0.0937	0.673
0.429	0.0303	0.0830	0.660
0.461	0.0190	0.0551	0.619
0.450	0.0234	0.0613	0.690
		Mean	0.699

\* Time of illumination, 5 minutes.

DIRECT PHOTOCHEMICAL DECOMPOSITION OF AMMONIA			
0.140	0.0062	0.0109	0.913
0.132	0.0075	0.0127	0.930
0.229	0.0134	0.0238	0.908
0.497	0.0232	0.0395	0.925
0.480	0.0327	0.0700	0.814
0.426	0.0226	0.0458	0.843
0.497	0.0289	0.0601	0.835
14.0	0.147	....	....
0.135	0.0058	0.0132	0.789
		Mean	0.870

The experimental procedure was as follows. After pumping out the whole system, ammonia manufactured by the Fixed Nitrogen Research Laboratory was admitted through suitable stopcocks and condensed in the liquid-air trap, the non-condensable impurities being then pumped off.

With the apparatus closed from the pumps, the liquid air was removed, and the ammonia pressure was measured on the McLeod gauge. In case the sensitized reaction was to be studied, a 1.7 per cent solution of tartaric acid was placed in the 5 mm. annular space to filter off radiation below 2340 Å; the arc was water-cooled and a magnet used to deflect the discharge against the front wall of the lamp. In case the direct photochemical decomposition was to be studied, no filter was used and the arc was run without water-cooling or a magnetic field. After ten minutes' illumination the liquid air was replaced on the trap to condense out the remaining ammonia, and the pressure of the residual gases was read on the McLeod gauge. Several half-periods were taken on the quartz-fibre manometer and the value of  $\sum(p\sqrt{M})$  read off the calibration plot.

In both these types of experiment appreciable quantities of residual gas were found; however, when a tartaric acid filter was used and the arc run hot with no magnetic field (in order to reverse the core of the resonance line 2537 Å), no residual gas was found.

*The Experimental Results.*—A summary of the experimental results is given in the table. The values of  $\sum(p\sqrt{M})$  considered in relation to the pressure  $\sum p$  of the residual gases are much lower, both for the sensitized and unsensitized reaction, than corresponds to the molecular weight of any gas which could have been present except hydrogen. They consequently demonstrate the presence of a considerable proportion of hydrogen in the residual gas. The mol-fraction  $x$  of hydrogen was calculated by the following equation, which assumes that the non-condensable products are hydrogen and nitrogen:

$$x = \frac{\frac{1}{\sum p} \sum(p\sqrt{M}) - \sqrt{M_{N_2}}}{\sqrt{M_{H_2}} - \sqrt{M_{N_2}}}$$

where  $M_{H_2}$  and  $M_{N_2}$  are the molecular weights of hydrogen and nitrogen, respectively.

The average mol-fraction of hydrogen, computed from eight experiments on the direct photochemical decomposition of ammonia, is 0.870, while 0.75 corresponds to the reaction  $2NH_3 = 3H_2 + N_2$ . This high value may indicate the formation of some condensable product, such as hydrazine, containing more nitrogen than does ammonia. However, we found that the quartz tube, when illuminated with the unfiltered radiation, gave out gas to some extent. Thus the evacuated tube developed, on illumination, a pressure amounting to several per cent of the residual gas pressure developed in the ammonia experiments. This fact renders a closer interpretation of the value 0.870 impossible.

The fact that the filtered radiation from the cooled arc produced non-condensable gases, while that from the hot arc gave none, shows that

optical excitation of the mercury vapor by the line 2537 Å is the first step in the sensitized decomposition.

The average of eleven experiments on the sensitized decomposition gave 0.699 for the mol-fraction of hydrogen in the non-condensable products. This is somewhat lower than the value 0.75 for an ammonia mixture. It is known, however, from the work of Cario and Franck<sup>4</sup> and others that hydrogen activated by collision with excited mercury "cleans up" on the walls of a quartz vessel. Since hydrogen is one of the decomposition products of ammonia, it may be expected to adsorb on the walls. This would leave a residual gas with a somewhat smaller mol-fraction of hydrogen than corresponds to an ammonia mixture, and thus account for our low results. We have no evidence of other products than hydrogen and nitrogen in the sensitized decomposition.

A greenish fluorescence, bright at first and dying out somewhat as the reaction proceeded, was noticed when the lamp was cooled, but not when it was hot. On observing with a direct-vision spectroscope, the fluorescence was found to be a diffuse band with a maximum around 5100 Å. On photographing with a quartz-prism spectrograph an additional diffuse band was found in the ultra-violet with a maximum around 3370 Å. Similar photographs taken with no ammonia in the tube, and one taken with about the same pressure of air in the tube, showed no bands. Visual observations were made with the tube filled with nitrogen and the green fluorescence found. Comparative observations in which two quartz tubes were placed side by side, one containing nitrogen at 3 mm. and the other ammonia at the same pressure, showed that the fluorescence in the tube containing nitrogen was markedly more intense. Similar observations with hydrogen showed no visible fluorescence. The interposition of a glass plate between the mercury arc and the quartz tubes caused the fluorescence to cease. In all these experiments the mercury was at room temperature and not distilling. These diffuse bands appear to be identical with those observed by Phillips<sup>5</sup> in a stream of distilling mercury vapor, excited by the line 2537 Å. Van der Lingen and Wood<sup>6</sup> have also excited the same bands in distilling mercury by means of a zinc spark. These bands were also noted by Wood<sup>7</sup> when light from a cooled mercury arc was allowed to shine on a tube containing mercury vapor at room temperature, and a few millimeters of nitrogen. He further found that this gas mixture absorbed the line 4046 Å ( $2p_3 - 2s$ ) while fluorescing, indicating the presence of mercury atoms in the  $2p_3$  state. It seems likely that ammonia as well as nitrogen can produce this band fluorescence of mercury, since in our experiments the fluorescence was visible at the very beginning of the illumination of the ammonia-mercury mixture. Contrary to the observation of Wood, we found these bands unaccompanied by the "water band" just below 3125 Å.

*Summary.*—It has been shown that the photochemical decomposition of ammonia at low pressure into nitrogen and hydrogen is sensitized by mercury vapor when the radiation used is from a cooled quartz mercury-arc lamp and is filtered so as to remove wave-lengths below 2340 Å. The so sensitized decomposition has been found to be accompanied by diffuse-band fluorescence in the green and ultra-violet.

<sup>1</sup> Kuhn, *Compt. Rend.*, 177, 956 (1923).

<sup>2</sup> Coolidge, *J. Am. Chem. Soc.*, 45, 1637 (1923).

<sup>3</sup> Haber and Kerschbaum, *Zt. Elektrochem.*, 20, 296 (1924).

<sup>4</sup> G. Cario and J. Franck, *Zt. Physik*, 11, 161 (1922).

<sup>5</sup> Phillips, *Proc. Roy. Soc.*, 89, 44 (1913).

<sup>6</sup> Van der Lingen and Wood, *Astrophys. J.*, 54, 149 (1921).

<sup>7</sup> Wood, *Phil. Mag.*, 50, 774 (1925).

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## THE CONCENTRATION AND IDENTIFICATION OF THE ELEMENT OF ATOMIC NUMBER 61

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In making measurements of the wave-lengths of the X-ray *K* emission lines for the rare-earth elements,<sup>1</sup> very faint traces of lines corresponding to the *K* series of the element of atomic number 61 appeared on the plate with certain specimens of samarium (atomic number 62) and neodymium (atomic number 60). In tracing these compounds to their source a consistent effort has been made over a period of two years to increase the concentration of the element of atomic number 61. Many of the samples obtained have shown definite traces of lines where they should be expected in both the *K* and *L* X-ray wave-length regions but the photographic spectra have until now never been strong enough to permit photographic reproduction in a printed article and this was deemed necessary before the announcement of the discovery of the element was made.

In 1923, two of the authors commenced examining rare earth minerals for element 61. The minerals, which have been thoroughly investigated by employing large quantities, comprise gadolinite, xenotime (ytterspar) and monazite. These three minerals show an interesting variation in their rare earth constituents. Monazite is essentially a phosphate of the cerium group elements carrying a few per cent of the yttrium earths; gadolinite consists largely of the yttrium group with some of the cerium