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STUDIES IN PHOTOSENSITIZATION. II. A SOURCE OF CADMIUM RESONANCE RADIATION

BY JOHN R. BATES AND HUGH S. TAYLOR

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With the broadening of the phenomenon of mercury photosensitized processes to a larger number of reactions[1] it becomes of interest to attempt to extend the field to include other metallic vapors than mercury. A consideration of chemical properties, vapor pressure and resonance potentials shows that sensitization by means of excited cadmium atoms not only ought to prove practical, but also ought to yield valuable results. The resonance lines of mercury, cadmium and zinc, together with their equivalents in gram calories and volts, and the temperature at which the vapor pressure is equal to 0.012 mm. are given in the following table.

TABLE I

RESONANCE DATA AND VOLATILITY OF ZINC, CADMIUM AND MERCURY

Metal	Line	λ	Cals./mole	Volts	T, °C., v.p. = 0.012 mm.
Hg	$1S\text{–}2^3P_1$	2536.7	112,000	4.86	50
	$1S\text{–}2^1P$	1849.6	152,000	6.67	
Cd	$1S\text{–}2^3P_1$	3262.1	87,000	3.78	240
	$1S\text{–}2^1P$	2288.8	124,000	5.39	
Zn	$1S\text{–}2^3P_1$	3076.9	92,400	4.01	350
	$1S\text{–}2^1P$	2139.3	133,000	5.77	

As can be seen, while only one of the resonance lines of mercury is in a region available for use, cadmium and zinc have both in a very convenient part of the spectrum. Moreover, a study of the effects on reactions of quanta of various energy content should prove of interest. Unfortunately, the low vapor pressure of zinc makes this metal less useful for such purposes.

This paper deals with the effect of cadmium atoms in the 2^3P_1 state (3262.1 Å.) on ammonia and hydrogen-ethylene mixtures.

Experimental

A source of cadmium resonance light was sought which would be fairly intense and steady enough for such work. Cadmium arcs of the type of the ordinary quartz mercury arc cannot be made with the pure metal, which tends to wet glass and quartz and to break it when it expands upon solidification. Bates[2] has found that a small amount of pure gallium prevents this. To avoid the use of this element, which is difficult to obtain in pure condition, we have discovered that a 50% cadmium-tin alloy

[1] Taylor and Bates, THIS JOURNAL, 49, 2438 (1927).

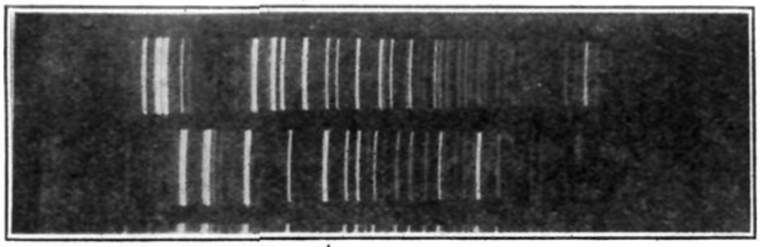
[2] Bates, *Bur. Stand. Sci. Paper No. 37*, 1920.

serves the purpose. The alloy melts from 176–200° and does not crack the arc upon cooling. The light emitted is almost entirely that of the cadmium spectrum, because of the low vapor pressure of the tin. A photograph of the spectrum, with one of mercury for comparison, is shown in Fig. 1.

The arc in use in this work was of the Cooper Hewitt type, has been run for over 50 hours and allowed to solidify many times without cracking and has proved in every way satisfactory. It runs at from 7–10 amperes and has the non-restricted character of the cooled mercury arc as used by us for earlier photosensitized reactions.

The experimental arrangement was the same as that used in Part I of this work and described as the static system. The reaction vessel, however, was placed in an electric furnace with a window fitted with a filter of G986A Corning, 5 mm. in thickness, to transmit only the line at 3262 Å. and absorb completely 2288 Å. Filings and shavings of cadmium were placed in the reaction tube, which was brought close to the window and the arc placed on the other side as close as could be without causing local overheating and consequent cracking of the filter.

Cd



Hg

Fig. 1.

Preliminary runs with ammonia and ethylene-hydrogen in the presence of cadmium at 250–260° showed that neither the decomposition of ammonia nor the formation of ethane nor the decomposition of ethylene took place as purely thermal reactions under these conditions. No change of pressure was observed after three to four hours. Before every run the reaction vessel was baked out *in vacuo* above the temperature used for the reactions.

Ammonia, in the presence of cadmium vapor, showed no decomposition after five hours' exposure to the 3262 Å. line at 255–260°.

An ethylene-hydrogen mixture, 545 mm. total pressure and consisting of 273 mm. of ethylene and 272 mm. of hydrogen decreased to 452 mm. after 9 hours' illumination in the presence of cadmium vapor at 255–260°. Forty-seven per cent. of the resulting gas was condensable in liquid air. If the reaction were solely condensation of ethylene, 33% should condense; if the formation of ethane were the sole reaction, 60% should condense. The cooling effect of the liquid air was probably large and so the 47% is probably a high value. For this and other reasons we are led to believe that ethylene condensation is practically the sole reaction.

Theoretical

The probability that two colliding atoms or molecules will have an amount of energy Q available for chemical change, due to their energy of translation, that is, whole component of relative velocity parallel to the line of centers is greater than a value necessary to obtain the energy Q, is equal to $e^{-Q/RT}$.[3] Taking the best value for the heat of dissociation of hydrogen as 101,000 calories, we find the Q necessary for the dissociation of a hydrogen molecule by an excited cadmium atom in the 2^3P_1 state to be equal to 14,000 calories. At 260° the ratio of collisions possessing this energy to the total number would be $N_Q/N = 1/10^6$. The reaction of the formation of ethane from hydrogen and ethylene under the influence of excited cadmium atoms would be one millionth of that reported for excited mercury atoms. This would not be detectable with our apparatus.

Cario and Franck,[4] in studying the cadmium fluorescence spectrum excited by mercury atoms in the 2^3P_1 state, report cases where, at high temperatures, they obtained the 4800° Å. line of cadmium, due to cadmium atoms in the 2^3S_1 state, which is 1.4 volts (32,000 cal.) higher than the 2^3P_1 for mercury. But, at the same time, the 2258 Å. (2^1P) resonance line, which calls for excitation only 0.5 volt higher than that possessed by the excited mercury atoms *did not* appear. This would seem to show that the 1.4 volts are not the result of purely thermal excitation. An explanation may possibly lie in the formation of metastable 2^3P states and subsequent collision.

The vibrational states of the hydrogen molecules do not enter into the thermal excitation at as low temperatures as 500–600° absolute.

In the case of ammonia the heat of an N-H linkage, calculated from the heats of decomposition of nitrogen (263 kg. cal.), hydrogen (101 kg. cal.) and the heat of formation of ammonia from the molecules (22 kg. cal.), is 98 kg. cal. Here the value of N_Q/N would equal $10^{-4.4}$ and the rate of decomposition would be too small to be measured.

The polymerization of ethylene is in entire accord with Part I of this paper, which showed that the initial reaction is probably the formation of acetylene and molecular hydrogen.

Summary

1. A new type of cadmium quartz lamp is described.
2. Ammonia and probably hydrogen are unaffected by the action of cadmium atoms in the 2^3P_1 state at 255°, but ethylene is polymerized.
3. Theoretical considerations of the reactions are in agreement with these results.

PRINCETON, NEW JERSEY

[3] Foote, *Phys. Rev.*, **30**, 292 (1927).

[4] Cario and Franck, *Z. Physik*, **17**, 202 (1923).