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BUDDE EFFECT IN BROMINE AND CHLORINE

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Some time ago[1] the writer described experiments intended to show that extensive drying produces neither appreciable fluorescence in chlorine on illumination, nor a change in its absorption spectrum. That the absorption spectrum remains unchanged on drying was found, independently and simultaneously, by Miss Kornfeld and Steiner.[2] The existing literature,[1] on the other hand, seemed to indicate that the Budde effect, or the heat expansion of halogens on illumination, decreases when the halogens are subjected to a more or less thorough drying. These divergent observations are difficult to reconcile and it was tentatively suggested that, while the primary photochemical process in halogens is a dissociation into atoms in the way suggested by Franck, the secondary process, a homogeneous recombination of atoms, which contributes mainly to the heating of the gas, requires the presence of water vapor, being otherwise slow. In this case the halogen atoms in highly dried gases will have time to diffuse to the walls before recombining; they will be cleaned up there and will recombine in a wall reaction, the heat liberated being conducted away by glass and little heating of the gas being produced. The present experiments were intended to test this suggestion but, first of all, to investigate generally the observations obtained elsewhere on the influence of water vapor on Budde effect. While these experiments were being conducted, Brown and Chapman[3] published their observations showing that in a mixture of bromine vapor and air very extensive drying by phosphorus pentoxide lasting over a period of several months does not produce any change in the magnitude of the Budde effect. These experiments are quite conclusive by themselves, but they do not touch on the problem of whether the Budde effect in bromine from which all impurities, particularly such as oxygen, have been removed, might not still show a dependence on the presence of water vapor. To settle this last problem, for chlorine as well as for bromine, is the object of the investigations reported here.

Experimental Details

To study the Budde effect, a cylindrical Pyrex tube 23 × 3.5 cm. with polished sealed-on end-plates was used. It was connected to an all-glass manometer, a thin caved-in glass bulb with a long pointer being used. The movements of the pointer were observed in a microscope, the sensitivity of the system being *ca.*10 divisions on the ocular scale per 1 mm. of mercury. Since such devices usually do not withstand large pressure differences, the whole manometer was sealed in a glass enclosure, which com-

[1] Kistiakowsky, THIS JOURNAL, **49**, 2194 (1927).

[2] Kornfeld and Steiner, *Z. Physik*, **45**, 385 (1927).

[3] Brown and Chapman, *J. Chem. Soc.*, **133**, 560 (1928).

municated, through a by-pass, with the illumination vessel. The whole was evacuated, baked out and filled with the halogen vapor. The outside of the manometer, however, could be disconnected, before the illumination experiments, by heating and collapsing a constriction in the by-pass. Inside the illumination vessel along its axis and at a distance of a few mm. from the side wall was suspended a loop of an almost hair-fine glass capillary through which a platinum wire was drawn. The wire acted as a resistance thermometer, its leads being carried to the outside of the vessel. The construction was such that the halogen vapors came in contact with glass only, no metal parts being exposed. A short tubing connected with the illumination vessel an inner, magnetically operated, seal which opened to a space of about 1-cc. volume filled with water vapor of atmospheric pressure.

The drying of bromine was carried out with the aid of phosphorus pentoxide. This latter was purified by a double distillation in a stream of pure oxygen and afterward by a double distillation in high vacuum. It was then distributed, by a careful sublimation in vacuum, over the walls of two wide U-tubes and their connecting tube. Bromine of C. P. grade was further purified and moderately dried by the standard chemical methods. It was then distilled twice in vacuum, the middle sections only being retained and finally was admitted to the phosphorus pentoxide tubes by breaking an inner seal. The quantity of bromine thus introduced was relatively small and it wetted only a fraction of the P_2O_5-covered surface. By cooling different parts of this surface bromine was distilled back and forth, this operation being continued for forty-eight hours. Later, an inner seal separating the illumination vessel and manometer system from the phosphorus pentoxide tubes was broken and bromine vapor admitted into the former. This inner seal was on the opposite end of the P_2O_5-tubes from that at which the undried bromine originally entered. The illumination vessel and manometer system, as well as the P_2O_5-tubes, prior to filling were baked out in vacuum for about twenty hours. The temperature was raised first to 500° for two hours and maintained at 350° the rest of the time.

Chlorine taken from a half empty tank was dried by repeated distillation in vacuum from a bath of melting ethyl bromide (−119°). In the first of the series of three experiments an attempt was made to remove traces of oxygen present by an initial prolonged bubbling of pure hydrogen through liquid chlorine at −80°. In the other two experiments a larger quantity of chlorine was condensed from the tank, about four-fifths of it was boiled away under reduced pressure and only the first half of the remaining fraction was used for the succeeding vacuum distillations. The distilling train, allowing four distillations, was divided by an inner seal into two sections with separate pumping aggregates. Inner seals separated the train from the vessel into which chlorine was originally condensed and from the illumination vessel aggregate.

It was intended to test the dryness of chlorine by the sensitivity of the hydrogen–chlorine mixture to light and the apparatus contained, therefore, besides the parts described, four small cylindrical tubes sealed in parallel which also could be filled with dry chlorine. These tubes were separated by an inner seal from the hydrogen-drying section of the apparatus. The drying of purified hydrogen was carried out by allowing it to pass through a long spiral (4-mm. tubing, 50 cm. long) immersed in liquid air. The rate of flow of hydrogen through the spiral was adjusted by a capillary and amounted to 250 cc. in twenty hours. Dried hydrogen entered in the first experiment a half-liter flask which was evacuated together with the rest of the apparatus. In the second experiment the flask was replaced by a wide glass tubing forming a closed circle. The lower part of it was immersed in liquid air and one side was gently heated (to *ca.*100°) so that hydrogen entering from the spiral was circulated continuously over liquid air. In the third experiment the flask was replaced by a vessel of a cylindrical shape which was completely immersed in liquid air for forty-eight hours.

On filling the four reaction tubes with chlorine at *ca.* 0.3 atmosphere pressure, they were sealed off from the chlorine side of the apparatus and were connected, by breaking an inner seal, to the hydrogen section which contained gas at about 0.5 atm. pressure. Chlorine was then frozen out by liquid air in each of the vessels and they were finally completely sealed from the apparatus.

The baking out of the whole apparatus was done in an electric furnace, the temperature, as in the case of bromine, being raised first to 500° and maintained later at 350°. The baking was continued for twenty-four hours in the first experiment and was extended to ten days in the last one. Here the heating was interrupted on the fifth day and all constrictions, to be sealed off afterward, were heated to the softening point and allowed to collapse almost completely; the baking was then resumed. The degassing was rather thorough in this experiment, as is shown by the fact that on the tenth day the McLeod gage, sensitive to less than 10^{-5} mm. of mercury, showed no measurable pressure after the apparatus was shut off from the pump overnight, while being heated to 350°.

For the study of the Budde effect a carbon arc burning on 20 amp. and a system of lenses and diaphragms was used by means of which a parallel beam of light of about 2 cm. diameter was separated. In front of the illumination vessel, which was rigidly fastened to the optical bench supporting the arc and the lenses, was arranged a shutter to make possible a rapid succession of illumination and darkening of the vessel.

Experimental Results

With the apparatus described three samples of bromine and three of chlorine were prepared and tested. The general procedure was to take a simultaneous series of the glass manometer and of the platinum resistance readings with the shutter alternately closed and opened, then to break the inner seal separating the water vapor compartment and take a new series of readings. Under no circumstances could even the slightest difference exceeding the experimental error be observed between the two series of readings. In the third experiment on bromine a second inner seal was attached to the illumination vessel. It separated a small evacuated volume filled with phosphorus pentoxide prepared in the same manner as the materials used in the initial drying of bromine. After the first series of readings with this bromine, the seal separating the phosphorus pentoxide was broken and the latter transferred, by shaking, into the illumination vessel. It was left there for ten days, occasional readings being taken. Then the seal separating the water vapor was broken and readings were taken immediately after and on the next day. As an example of the nature of readings obtained these series with bromine No. 3 are reproduced in Table I.

Under "glass-manometer" are given the deflections of the pointer in scale divisions of the microscope scale as caused by sudden changes from dark to light and back; under "Pt-resistance thermometer" the deflections in scale divisions of the galvanometer, which, together with a Mueller type bridge, was used to measure the resistance of the platinum wire. The temperature change and the expansion of the gas on illumination, as measured here by the two devices, agree fairly well. Ten divisions on

TABLE I

BUDDE EFFECT IN BROMINE

	Dry bromine	P_2O_5 admitted	10 days later	H_2O admitted	1 day later
Glass-manometer	+11, −10; +10, −10; +11, − 9; +10, − 9; +10, − 9; + 9, − 9; +11, − 9; +10, − 9; av. 9.7	av. 9.3	av. 10.1	av. 9.9	av. 9.3
Pt-resistance thermometer	+24, −22; +21, −20; +21, −20; +22, −20; +20, −20; +19, −20; +23, −20; +20, −21; av. 20.8	av. 21.1	av. 21.7	av. 22.0	av. 20.6

the microscope scale corresponded very nearly to 1 mm. of mercury or to approximately one degree temperature change of bromine vapor which was used at 300 mm. pressure. The thermometer had a resistance of 5.9 ohms and the galvanometer sensitivity was 18 scale divisions for 0.01 ohm. The deflection of 21 scale divisions thus corresponds roughly to 0.7° temperature change. The difference is well accounted for by the facts that only about nine-tenths of the total length of the wire in the thin capillary could be rapidly heated by the gas and that the whole wire, being outside of the actual path of the light beam, was in a somewhat cooler part of the gas.

Table I, which is quite typical of the results obtained, shows quite definitely that the Budde effect in bromine is left entirely unchanged by drying or moistening of the halogen. Thus, the experiments of Lewis and Rideal,[1] who claimed that a proportionality exists between the concentration of the water vapor and the magnitude of the Budde effect, must be incorrect. It might be suggested, of course, that a "more thorough" drying would reveal an influence of water vapor. However, the experiments of Brown and Chapman[3] are against such suggestion. Moreover, it should be pointed out here that the drying now employed must have been quite efficient. With a magnifying glass, one could see a slight trace of moisture on the first grains of the drying agent where bromine first entered the phosphorus pentoxide tubes. The moisture, which could be noticed only in this location, indicates that the phosphorus pentoxide employed was active and had extracted the main fraction of the water vapor present already within the short time of contact with bromine vapor when this was being distilled under low pressure into the phosphorus pentoxide tubes.

The experiments with chlorine yielded the same result as those with bromine: no change in Budde effect could be observed on drying. Comparing the relative care taken in drying and purifying chlorine by Coehn and Jung[1] and in the present experiments, one might conclude that the halogen was in about the same state of dryness in both sets of experiments.

However, the first of the experiments described here yielded chlorine–hydrogen mixtures which all reacted very rapidly in visible light. The experiment, therefore, was repeated twice more, each time new precautions being taken, of which a part have been mentioned before. Still, the result was the same; the photochemical reactivity of the gases was not diminished by drying. On the other hand, a critical analysis of the drying method employed fails to indicate any systematic sources of moisture in chlorine. Another explanation of the failure to prepare dry chlorine–hydrogen mixtures seems to be very likely therefore. As has been pointed out to the writer by Dr. R. N. Pease of this Laboratory, according to his experience, hydrogen reduces Pyrex glass quite readily at the temperature of its softening point. Since the last sealing of the reaction tubes in our experiments has to be undertaken with an atmosphere of hydrogen inside, it is more than likely that a sufficient quantity of water vapor is produced to cause photochemical reactivity of the gases. The quantity of water vapor required for this can be estimated, on the basis of experiments of Coehn and Jung,[1] to be of the order of 10^{-10} g. for the 10-cc. tubes employed. An action of chlorine on Pyrex glass, also followed by evolution of water, is very unlikely and it can be claimed, therefore, that the chlorine here prepared—so long as it was not mixed with hydrogen—was of the same degree of dryness as that prepared by Coehn and Jung. The latter evidently avoided our difficulties with hydrogen–chlorine mixtures by the use of soft glass.

Summary

1. No change in Budde effect could be observed on purifying and carefully drying bromine and chlorine.

2. It is pointed out that dry mixtures of hydrogen and chlorine cannot be prepared in Pyrex glass, since the latter is reduced at its softening point by hydrogen with formation of water.

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