
COMMUNICATIONS TO THE EDITOR

THE THERMAL REACTION BETWEEN FORMALDEHYDE AND CHLORINE

Sir:

Spence and Wild [*J. Chem. Soc.*, 1588 (1934)] report that the thermal reaction between chlorine and formaldehyde proceeds either by an explosion or by a relatively slow process, depending on temperature, pressure and the condition of the reaction vessel. They find further that any excess of formaldehyde present in an explosive mixture is decomposed into carbon monoxide and hydrogen; that the slow reaction is preceded by an induction period; that the rate of this latter reaction is somewhat affected by the walls of the reaction vessel; and that the amount of carbon monoxide produced in this reaction is apparently somewhat greater than the amount predicted from the observed pressure change. These observations accord well with results obtained for the photochemical reaction [Krauskopf and Rollefson, *THIS JOURNAL*, 56, 2542 (1934)] between the two gases, and it seems probable that the mechanism devised to account for the photochemical change may be applied successfully to the thermal process.

According to this mechanism, formyl chloride is produced from formaldehyde and chlorine: $\text{CH}_2\text{O} + \text{Cl}_2 \rightarrow \text{COHCl} + \text{HCl}$, and decomposes subsequently into carbon monoxide and hydrogen chloride. The existence and comparative stability of the intermediate have been demonstrated in photochemical reaction mixtures; its lifetime would be considerably shortened by the higher temperatures used by Spence and Wild, but its presence in their reaction mixtures seems entirely reasonable. The formation of formyl chloride according to the above reaction involves no pressure change; the observed induction period, therefore, like the corresponding period in the photochemical reaction, can be explained as the time during which the intermediate is being produced faster than it decomposes. This first reaction is a highly exothermic chain process which under favorable conditions can become explosive. The second reaction is at least partially heterogeneous, since the pressure change in either the photochemical or the thermal process is more rapid immediately after the reac-

tion vessel is cleaned. Whether increase of the surface-volume ratio produces any effect is doubtful. In the photochemical experiments an increase of surface appeared to increase the rate; but the increase may have been merely one of the erratic variations which occur so frequently in these experiments, or may have been due merely to the relative freshness of the added surface. Spence and Wild report a slight decrease of rate with increasing surface, but feel that the decrease is not significant.

Spence and Wild determined the amount of carbon monoxide formed by analysis of their gas mixtures. In every case, the amount of carbon monoxide indicated by analysis was greater than the amount calculated from the pressure change. This result they explain by assuming that the observed pressure increase is too small because of a concurrent chlorine-sensitized polymerization of formaldehyde. If formyl chloride is present, the discrepancy can be alternatively explained by supposing that during the process of analyzing the reaction mixture some formyl chloride decomposes, thus increasing the amount of carbon monoxide present.

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K. B. KRAUSKOPF
G. K. ROLLEFSON

RECEIVED JANUARY 16, 1935

THE CHEMICAL BASIS FOR SOME BIOLOGICAL EFFECTS OF HEAVY WATER

Sir:

Empirical physiological effects of heavy water require chemical explanations [*cf.* Barnes and Jahn, *Quart. Rev. Biol.*, 9, 292 (1934)]. We find the contractile vacuole of protozoa an excellent object for heavy water experiments. Thus in a race of *Paramecium caudatum* the contractile vacuole empties every 18.9 seconds in 30% D₂O compared to 11.3 seconds in controls (both at 18.8°). We have applied the Arrhenius equation: Velocity $\propto e^{-E/RT}$ to data on the rate of contraction at various temperatures and in ordinary water we find the following values of the constant *E* or energy of activation of the controlling catalyst: below 16° 24,000 calories; between 16 and 22° 17,000 calories and above 22° 14,000

calories. In 30% heavy water, however, the graph representing $\log k$ as a function of $1/T$ is an unbroken line throughout the entire temperature range with a value of E of 22,000 calories, similar to the constant for the rate in ordinary water at low temperatures (below 16°). The reduced rate of contraction and the interesting fact that the master reaction appearing only at low temperatures in ordinary water controls the rate over the entire temperature range in heavy water support the prediction of chemists that deuterium will have effects similar to those of low temperature. Assuming that the slowest master reaction of the catenary set controls the rate of water discharge from the vacuole, it appears that the catalyst in control at low temperatures in ordinary water is so slowed down in the heavy water that it governs the rate at all temperatures. The results should throw light on the chemical basis for the biological effect of heavy water and on the kinetics of the Arrhenius equation.

In green plant cells a new factor appears. Of 1088 cells of *Spirogyra* in 0.47% D₂O in the light of 60 foot candles, 72% were alive and healthy after two days but only 18% of 1129 cells survived in the dark. In ordinary water 32% of 1266 cells survived under the same light intensity and 16% of 789 cells in the dark. This suggests that heavy water in low concentration is favorable to photosynthesis. In fact, Reitz and Bonhoeffer [*Naturwiss.*, **22**, 744 (1934)] find that deuterium is taken directly into the carbohydrates of green algae. It is possible that the stronger bond between the heavy hydrogen and an adjacent atom, carbon, favors the production of a more stable intermediary product in photosynthesis (formaldehyde?) and also the C-C bonds may be strengthened slightly as in heavy acetylene.

We wish to express our thanks to Prof. L. L. Woodruff for helpful advice.

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RECEIVED JANUARY 24, 1935

n-PROPYLARSONIC ACID FOR ZIRCONIUM

Sir:

In the January issue of THIS JOURNAL there appears an article entitled "*n*-Propylarsonic Acid as a Reagent for the Determination of Zirconium," by F. W. Arnold, Jr., and G. C. Chandlee, which is an abstract of Mr. Arnold's thesis.

Further study has shown that the directions, in so far as the separation of zirconium and tin is concerned, are inadequate.

STATE COLLEGE, PA.

G. C. CHANDLEE

RECEIVED JANUARY 25, 1935

THE USE OF ARTIFICIAL RADIOACTIVE ELEMENTS AS INDICATORS IN CHEMICAL INVESTIGATIONS

Sir:

The use of the fruitful method of radioactive indicators introduced by G. v. Hevesy and F. Paneth has been limited to a very few heavy metals. The discovery of artificial radioelements by F. Joliot, I. Curie and E. Fermi extends this field to most of the common elements. The only, and surely temporary, limitation in their use is the small available activity, which necessitates the use of sensitive counters instead of the much simpler electroscope. The following experiment serves as an example of how the artificial radioelements can be put to use at the present time.

The problem was to determine whether or not the expected exchange of bromine atoms between free bromine and the bromine of sodium bromide, dissolved in water, takes place.

For this purpose 20.0 g. of sodium bromide was dissolved in 200 g. of water, placed in a 200-cc. round flask, surrounded by water (similarly to our experiment with silver) [A. V. Grosse and M. S. Agruss, *Phys. Rev.*, **47**, 91 (1935)] and bombarded for twenty-five hours with neutrons from a glass capsule placed in the center of the flask containing 100 millicuries of radon and 200 mg. of beryllium powder. After the irradiation the sodium bromide solution was divided into two equal parts: to the first 100 cc. containing 10.0 g. of sodium bromide, 24.0 g. of liquid bromine was added. Both solutions were evaporated in porcelain dishes on a boiling water-bath; the free bromine disappeared in the first solution after about half an hour. The sodium bromide obtained was dried at 150°. The activities of the two preparations were measured with a helium filled Geiger-Müller counter and a thyratron operated watch. The finely powdered preparations were evenly sieved on paper, coated with lacquer, then covered with very thin Japanese tissue paper, also coated with lacquer, and rolled into cylinders fitting the Geiger tube.

The weights of sodium bromide were about 2-4 g. and were determined by difference. Both preparations were measured for a thirty-hour period, beginning two hours after the end of