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: $CH_2O + Cl_2 \longrightarrow COHCl + HCl$, 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 reaction 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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University of California
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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% D_2O compared to 11.3 seconds in controls (both at 18.8°). We have applied the Arrhenius equation: Velocity α $e^{-E/RT}$ 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% D_2O 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.

OSBORN ZOÖLOGICAL LABORATORY T. CUNLIFFE BARNES
YALE UNIVERSITY H. Z. GAW
NEW HAVEN, CONN.

RECEIVED JANUARY 24, 1935

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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 irradiation; they both showed, after the first hour, an activity regularly decaying with a half period of about six hours, corresponding to E. Fermi's radiobromine [E. Fermi and co-workers, *Proc. Roy. Soc.* (London), **146,** 483 (1934)]. The other radiobromine, with a period of thirty minutes, as well as the sodium products, had mostly decayed in the first two hours. The activity of the *first* preparation, treated with bromine, *was 2.5 times smaller,* than the *second,* proving that an exchange of bromine atoms had taken place.

It is most probable that the exchange mechanism is described by the reactions

$$\begin{tikzcd}
\mathrm{NaBr} \arrow[r, shift left] & \mathrm{Na^+} + \mathrm{Br^-} \arrow[l, shift left] \arrow[d, shift right] \\
\mathrm{Br_2} + \mathrm{H_2O} \arrow[r, shift left] & \mathrm{Br^-} + \mathrm{H^+} + \mathrm{HOBr} \arrow[l, shift left] \arrow[u, shift right]
\end{tikzcd}$$

If complete exchange has taken place, the ratio of activities should correspond to the mass ratio of free bromine to bromide bromine or equal 3.0:1. The observed deviation is surely due to the fact that part of the bromine has escaped the exchange mechanism, probably because the rate of evaporation was faster than the slow rate of hydrolysis [see W. C. Bray, THIS JOURNAL, **32,** 938 (1910); W. C. Bray and E. L. Connolly, *ibid.*, **33,** 1487 (1911); G. Jones and M. L. Hartmann, *Trans. Am. Electrochem. Soc.*, **30,** 295 (1917)]. This point shows that it also will be possible to measure, besides exchanges, reaction velocities and other phenomena.

The artificial radioelements will be of great value for the investigation of the mechanism of catalytic reactions. Especially radio-isotopes of carbon, nitrogen and oxygen (?) will, like the heavier stable isotopes of these elements, open, if available in sufficient quantity, an unlimited field of investigation in organic and biological chemistry.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to Dr. M. Cutler, of Michael Reese Hospital, and to Dr. H. Scott and Dr. E. Williams of Hines Veterans Hospital for the radon source, to Dr. W. D. Harkins for the loan of beryllium and to Mr. J. Allen, of the Physics Department, for his advice and help in building the counter. This work was partly supported by a grant from the Chemical Foundation.

KENT CHEMICAL LABORATORY A. V. GROSSE
UNIVERSITY OF CHICAGO M. S. AGRUSS[1]
CHICAGO, ILL.

RECEIVED JANUARY 29, 1935

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[1] Julius Stieglitz Fellow.

CATALYTIC EXCHANGE OF DEUTERIUM AND METHANE

Sir:

The researches of Hollings and Griffith [*Nature,* **129,** 834 (1932)] and of Turkevich, Howard and Taylor [THIS JOURNAL, **56,** 2254, 2259 (1934)] have shown, by adsorption measurements, that, on a variety of catalysts, activated adsorption of hydrocarbons may occur. The latter work shows that activated adsorption of ethylene occurs generally in a much lower range of temperature than that of the saturated hydrocarbons. Recent studies of Farkas, Farkas and Rideal [*Proc. Roy. Soc.* (London), **A146,** 630 (1934)] and of Horiuti, Ogden and Polanyi [*Trans. Faraday Soc.*, **30,** 663, 1164 (1934)] indicate that exchange between deuterium and unsaturated hydrocarbons can be achieved readily at surfaces of platinum, nickel and copper. These workers also show that the exchange with saturated hydrocarbons does not occur under conditions where the exchange with ethylene occurs rapidly. Using the technique developed in our earlier photochemical studies [THIS JOURNAL, **57,** 383 (1935)] we have examined the exchange, at reduced nickel catalyst surfaces, between deuterium and methane, choosing this latter as probably the most refractory and thermodynamically most stable of the hydrocarbons. By examining the infra-red absorption spectra of the products we have shown that deuterium and methane exchange to yield deutero-methanes in the temperature range 184–305°. At the upper temperature, equilibrium, which is on the heavy methane side, is established within twenty hours. At 218°, in the same time, the equilibrium position is not yet established, but, in fifty hours, equilibrium is obtained. The conversions are slower still at 184°. At 110° even in ninety hours no measurable formation of deutero-methane can be established. Curves of reaction velocity indicate very slow rates of exchange below 170°. We believe that this is evidence that the exchange reaction requires activated adsorption of methane, since other researches [Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2,** 362 (1934)] indicate abundant activation of the deuterium at such surfaces under the given conditions. If our assumption is correct, the activated adsorption of methane is thus demonstrable at temperatures as low as 170°, which is at least 200 degrees lower than this is detectable by adsorption measurements. We assume that activated adsorption is accompanied by a dissociation into fragments, *e. g.*, CH_3 and H from which, by recombination with adsorbed deuterium and subsequent repetition of the several processes, equilibrium concentrations of the deutero-methanes finally result. We are prosecuting this study in a quantitative direction and also catalytically, since we have, in this exchange reaction, an important tool for catalytic research in the important field of saturated hydrocarbon reactions. We are again indebted to Dr. R. B. Barnes of the Palmer Physics Laboratory for the use of his infra-red spectrometer.

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K. MORIKAWA
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H. S. TAYLOR

RECEIVED FEBRUARY 21, 1935

THE BETA-PARTICLE FROM ACTINIUM

Sir:

Through the use of a screen-wall tube counter [Libby, *Phys. Rev.*, **46,** 196 (1934)] the upper limit of the energy spectrum of the previously undetected actinium electron has been determined. The actinium was shown to be free from members of the radium and thorium series by precipitating lead sulfide from the sample and measuring the decay curve of the gamma activity. This curve was exponential with a half-life of thirty-seven minutes, in excellent agreement with the known half-life of actinium B. A sample sufficient to give a count of approximately 100 electrons per minute was mounted in a very thin layer. The magnetic field strength necessary to bend out the most energetic electrons corresponds to an $H\rho$ of about 1750 gauss.-cm., or an energy of about 220,000 electron-volts. The fact that 60% of the particles are absorbed by an aluminum screen with a thickness of 0.0023 g./cm.^{2} is in agreement with this value. This energy limit would place actinium on the lower Sargent curve [Sargent, *Proc. Roy. Soc.* (London), **A139,** 659 (1933)].

The actinium sample was prepared by extraction from Colorado uranium residues and is chiefly cerium and other rare earth chlorides. The sample was treated as follows. Small amounts of salts of barium, lead, and thorium were added, as bodies for the precipitation of the decay products of actinium. The precipitation of barium chromate removed actinium X, the actinium B and C was carried down with lead sulfide, and finally the radioactinium was coprecipitated with thorium peroxyhydroxide. The thorium was previously purified to remove mesothorium I and II, to prevent contamination of the sample with the latter, which is isotopic with actinium. The other decay products are so short-lived that their effect disappears before the activity can be observed.

It is planned to measure the energy spectrum of the disintegration electrons by means of an apparatus to deflect beams of definite energy into a counter.

DEPARTMENT OF CHEMISTRY
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D. E. HULL
W. F. LIBBY
W. M. LATIMER

RECEIVED FEBRUARY 4, 1935

NEW BOOKS

A Textbook of Inorganic Chemistry. By FRITZ EPHRAIM. Second edition, revised and enlarged, translated from the fourth German edition by P. C. L. Thorne. Gurney and Jackson, 33 Paternoster Row, London, E. C. 4, England, 1934. 873 pp. Price, 28s./- net.

This second English edition, based on the fourth German edition, is larger than the first edition by nearly one hundred pages. This is due, not to any major change, since the titles and arrangement of the thirty individual chapters remain unaltered, but rather to the insertion throughout of many items representing the progress in inorganic chemistry achieved in the interim. The new edition, therefore, retains the characteristics and outstanding virtues of the earlier edition and of the German original, namely, a simplified and eminently readable presentation of a great amount of information in a relatively brief compass.

ARTHUR B. LAMB

Anwendungen der Röntgen- und Elektronenstrahlen, mit besonderer Berücksichtigung organisch-chemischer Probleme. (Application of Röntgen and Electron Rays, with Particular Consideration of Organo-chemical Problems.) By Professor Dr. J. EGGERT, Berlin, and Professor Dr. E. SCHIEBOLD, Leipzig. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany, 1934. vii + 190 pp. 101 figs. 16 × 23.5 cm. Price, RM. 18.00; bound, RM. 19.50.

Some lectures delivered at the meeting of the "Deutsche Bunsengesellschaft" in Bonn on May 19, 1934, are here