CHRONOMETRIC CATALYTIC METHOD FOR THE DETERMINATION OF MICRO QUANTITIES OF IODINE

Sir:

We have found that very small amounts of iodine as iodide can be detected and determined by making use of the catalytic effect of the element on the reaction between arsenious acid and ceric sulfate in sulfuric acid solution

$$As^{3+} + 2Ce^{4+} \longrightarrow As^{5+} + 2Ce^{3+}$$

In the absence of iodide this reaction proceeds with extreme slowness [*cf.* Browning and Cutler, *Z. anorg. allgem Chem.*, **22**, 303 (1900); other literature references having a bearing on this matter will be considered in a detailed account of the method]. Traces of iodide increase the speed of the reaction enormously, the rate being directly proportional, or nearly so, to the iodide concentration, other factors being constant. Thus, if 1 ml. of potassium iodide solution containing 5 microgram of iodine is added to a mixture of 2 ml. of 0.1 N arsenious acid, 1 ml. of 0.1 N ceric ammonium sulfate, and 1 ml. of 6 N sulfuric acid, the reaction between ceric ions and arsenious acid is found to be complete in 0.9 to 1.0 min. (25°) as indicated by the disappearance of the yellow color of ceric cerium; with 2.5 microgram of iodine the time required for the reduction of the ceric cerium is 1.8 min. under the same conditions; with 1 microgram, 4.5 min., etc. In the absence of iodine the reaction requires 36 hours or more for completion. It is thus possible to determine the amount of iodide added by noting the time required for the yellow color due to ceric ions to disappear, since the time is inversely proportional to the amount of iodine present. The end-point of the reaction can be determined more precisely by using *o*-phenanthroline ferrous sulfate as indicator; the solution then assumes a pink color when the ceric cerium has been reduced, whereas the indicator is practically colorless in the presence of a slight excess of ceric cerium. Alkali chlorides and bromides, and other salts also, have a relatively slight effect, and by a special procedure it is possible to determine iodine in quantities ranging from 0.01 to 1 microgram in a dilution of $1:10^7$ in the presence of 10^5 times as much chloride or bromide with an accuracy of about 20%.

The test is quite specific for iodine, since osmium and presumably ruthenium, are the only other elements showing similar behavior [*cf.* Gleu, *Z. anal. Chem.*, **95**, 305 (1933)]. Micro quantities of osmium can be determined in the same way as iodine.

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I. M. KOLTHOFF

RECEIVED MAY 21, 1934

AN ISOTOPIC EXCHANGE BETWEEN H^2_2O AND $C_2H^1_2$

Sir:

Preliminary to the preparation of $C_2H^2_2$ it was decided that a study of the possible isotopic exchange between acetylene and water was essential to the proper set up of a purification system. The weakly acidic character of acetylene has been demonstrated by several investigators,[1] as for example in the formation of metallic acetylides. Billitzer[2] claims to have evidence for an acetylenic anion. Accordingly we passed tank acetylene through a purification train as recommended by McIntosh[3] and then through water containing a high concentration of H^2_2O. In the first experiment acetylene was bubbled for three hours at a rate of 3.5 liters per hour through about 3 cc. of water containing 18.5% of H^2_2O. In order to minimize evaporation the bubble tube was immersed in an ice-bath and any vapor escaping was frozen out in a trap immersed in a salt–ice bath. The acetylene was swept out of the system by purified air in the first experiments and nitrogen was later substituted with no detectable change in results. The water in the trap and bubbler was combined and doubly distilled before the density determination. No detectable change in density was observed.

A similar experiment was carried out using 3 cc. of 18.5% solution of H^2_2O to which was added sufficient anhydrous phosphorus pentoxide to make approximately a 1 N solution of phosphoric acid. After passing acetylene through this solution for five hours sufficient sodium oxide was added to more than neutralize the acid and excess alkalinity was removed by carbon dioxide. After the elimination of the gases the water was again doubly distilled and its density determined. Again there was no detectable change in composition.

To 3.5 cc. of 18.5% solution of H^2_2O, enough sodium oxide was added to make the solution

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(1) Keiser, *Am. Chem. J.*, **14**, 285–290 (1892); **15**, 535–539 (1893); Jones and Allen, *Chem. News*, **74**, 18–19 (1896); Bredig and Usoff, *Z. Elektrochem.*, **3**, 116–117 (1896).

(2) Billitzer, *Monatsh*, **23**, 489–501 (1902); **23**, 502–511 (1902).

(3) McIntosh, *J. Phys. Chem.*, **11**, 306 (1907).

approximately 1 *N* with respect to sodium hydroxide. Purified acetylene was passed through this solution for eight hours. The hydroxide was then converted to the carbonate by carbon dioxide. In the same manner as above the water was purified and its density determined. This water was found to contain 10.9% of H_2^2O. A check experiment was run for twelve hours on water containing 12.1% H_2^2O. (The strength of the alkali was somewhat greater in this experiment than in the previous one.) The concentration of H_2^2O was found to be 2.7% at the end of this experiment.

Feeling that an isotopic exchange was occurring too slowly in neutral water, to be detected in the original experiment, acetylene was bubbled through water containing 12.1% H_2^2O for thirty-six hours. Again there was no detectable change in the density of the water.

It is evident from these experiments that a remarkable isotopic exchange occurs between acetylene and solutions of H_2^2O containing an alkali. If the same exchange occurs in neutral and acid solutions of H_2^2O the rate must be extremely slow. These experiments offer additional confirmatory evidence for the acidic nature of acetylene. Further work is in progress on this exchange reaction.

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RECEIVED MAY 22, 1934

THE ELECTRONIC MECHANISM OF INTRAMOLECULAR REARRANGEMENT

Sir:

On page 177 of the "Annual Reports" of the Chemical Society for 1933, it is implied that the work of one of us [Wallis and Moyer, THIS JOURNAL, **55,** 2598 (1933)] constitutes evidence against the electronic conception of rearrangements [*cf.* Whitmore, *ibid.*, **54,** 3274 (1932)]. We do not agree with this implication; in fact careful reflection will show that the reaction of Wallis and Moyer, in which the optically active amide of a sterically hindered diphenyl derivative (*d*-3,5-dinitro-6-α-naphthylbenzamide) gives an optically active amine (3,5-dinitro-6-α-naphthylaniline), is the strongest existing evidence for the correctness of this modern electronic viewpoint as contrasted with the older ionic mechanisms. The impression that our work is in conflict undoubtedly arises from the too brief statement of the application of the current hypothesis to the Hofmann rearrangement [Whitmore and Homeyer, *ibid.*, **54,** 3435 (1932)]. A fuller statement of this application seems desirable. In the reaction of a base with an N-bromoamide, the bromine appears as a bromide with a complete octet of electrons. Regardless of the mechanism of the process, this change leaves the nitrogen with only six electrons, a condition which necessitates a change to a more stable arrangement. The electronically deficient nitrogen atom attracts an electron pair from the adjacent carbon atom. This transfer requires no special mechanism; certainly the electron pair and its attached group never leave the molecule. Thus, in the reaction of Wallis and Moyer, the ortho position in the diphenyl derivative is not left free at any time and, consequently, there is no opportunity for racemization. The change is thus truly intramolecular.

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RECEIVED MAY 22, 1934

THE POLARITY OF THE NITROGEN TETROXIDE AND NITROGEN DIOXIDE MOLECULES

Sir:

During the course of extended experimental studies of the temperature variation of the dielectric constant and density for equilibrium mixtures of nitrogen tetroxide and nitrogen dioxide there appeared an article by Zahn [*Physik. Z.*, **34,** 461 (1933)] in which there was anticipated that portion of our work which has to do with observations on this system in the vapor phase. As the result of his measurements and calculations, Zahn assigned the electric moment values $\mu = 0.55 \times 10^{-18}$ e. s. u. to nitrogen tetroxide and $\mu = 0.39 \times 10^{-18}$ e. s. u. to nitrogen dioxide. Because earlier and preliminary work of this type with the equilibrium mixture in carbon tetrachloride solution [Fogelberg, Dissertation, University of Wisconsin (1931)] had led to the conclusion that nitrogen tetroxide is non-polar and because our experiments in the vapor phase were nearing the stage where definite conclusions could be drawn from them, it was felt worth while to continue the observations. Work with the vapors between the temperatures 25 and 125° has now progressed to the point where electric moment calculations can be made. Since further observations are impossible for the present, we wish to make brief statement of our conclusions.