The spectrophotometric determination of hyponitrite

A spectrophotometric method for the determination of hyponitrite ($N_2O_2^{2-}$) in alkaline solution has been proposed by ADDISON *et al.*[1], who reviewed the previous literature on the absorption spectra of hyponitrites; these investigators found $\log \varepsilon_{max} = 3.60$ for the species $N_2O_2^{2-}$ at 248 nm but this value seems to require revision.

Moderate concentrations of hyponitrous acid in acidic solution can be determined[2] by the old precipitation method. No spectrophotometric method for this species seems to have been available; a procedure is suggested below.

Reagents and equipment

Sodium hyponitrite and pure $Ag_2N_2O_2$ were prepared by published methods[3]. To obtain a stable solution of hyponitrous acid by the interaction of hydrochloric acid and silver hyponitrite, it is essential to use an excess of as pure as possible silver hyponitrite. The first filtrate usually contains colloidal silver chloride. A convenient method of removing the colloidal suspension is to let the solution pass through the same filter repeatedly.

The concentration of the hyponitrous acid solution (usually around 0.04 *M*) was determined by the precipitation method[2] with the normal titrimetric accuracy. The room temperature was kept at 20°. To check for the stability of the solutions, each time 4 precipitations were made within a few minutes (the back-titrations could be performed later). Between the second and third precipitations, a sample of the hyponitrous acid solution was diluted, or dropped into 50 ml of 2 *M* sodium hydroxide and then diluted to the appropriate concentration.

Three U.V.-spectrophotometers were used in order to establish the reproducibility of the results: Hilger H.700, Cary M14, and Zeiss PM QII.

Absorption spectra

The species $N_2O_2^{2-}$ in alkaline solution shows a normally shaped peak. The maximum has been reported as lying at 248 nm[1,4] and at 247 nm[5]. In the present work, this maximum was found at 247 nm, and the half band width, $\Delta\nu$, was 36 nm.

The spectra of $H_2N_2O_2$ and $HN_2O_2^-$ exhibit a peak accompanied by a weak shoulder. The spectra of the following mixtures were studied: (*a*) $H_2N_2O_2$ in pure aqueous solution, (*b*) $H_2N_2O_2$ in 10^{-2} and 10^{-3} *M* hydrochloric acid, and (*c*) $HN_2O_2^-$ in 10^{-2} *M* borax (pH 9.2). The peak maximum of $H_2N_2O_2$ was found at 208 nm with $\Delta\nu = 27$ nm, and its shoulder at 242 ± 2 nm when hydrochloric acid was present. Pure aqueous solutions of hyponitrous acid have a pH around 4. In such solutions the ratio $(HN_2O_2^-)/(H_2N_2O_2)$ becomes appreciable and the peak of $HN_2O_2^-$ overlaps with the shoulder of $H_2N_2O_2$. At pH 9.2, the peak maximum of $HN_2O_2^-$ was found at 232 nm with $\Delta\nu = 47$ nm, and its shoulder at 280 ± 3 nm. BUCHHOLZ *et al.*[5] reported the peak maximum of $H_2N_2O_2$ at 207 nm and that of $HN_2O_2^-$ at 232 nm.

Molar extinction coefficients

In the acidic solutions of hyponitrous acid, a little ethanol was added (1%, v/v) to secure stabilization[5]. For the peak of hyponitrous acid at 208 nm, ε_{max} was found to be $4.61 (\pm 0.02) \cdot 10^3$. This value is not affected by a variation in the hydrochloric acid concentration in the region 10^{-3}–10^{-2} *M*. Beer's law is obeyed up to hyponitrous acid

concentrations of at least $3 \cdot 10^{-4}$ *M*. Higher concentrations of hyponitrous acid in acidic solution can be measured at 240 nm, where ε_{240} was found to be $2.4 (\pm 0.1) \cdot 10^2$. These two values of ε are based on the determination of the hyponitrous acid concentration by the precipitation method. The value given for ε_{240} expresses the resultant absorption caused by both the bands with λ_{max} 208 nm (strong) and 242 nm (very weak) respectively. The latter seems to have ε_{max} considerably less than ε_{240}. This makes the analysis of the shoulder into components unreliable.

Owing to the very well known instability of $HN_2O_2^-$ there can be no question of accurate measurement of the ε_{232} value of this species. For general spectroscopic considerations the value $\varepsilon_{232} = 7.7 (\pm 0.4) \cdot 10^3$ is satisfactory. This was estimated by extrapolation of the measurements back to the moment when 10 ml of a standard aqueous solution of hyponitrous acid were added to a borax solution. If the shoulder is analyzed into a component band with $\lambda_{max} = 280$ nm, this weak band seems to have a molar extinction coefficient equal to $0.25 \cdot \varepsilon_{232}$ and a $\Delta\nu$ of 41 nm.

Two independent methods were used (each in triplicate) to determine the molar extinction coefficient of the species $N_2O_2^{2-}$.

Method I. 20.00 ml of an aqueous *ca.* 0.04 *M* hyponitrous acid solution (accurately determined by 4 precipitations as described above) were added dropwise and with good agitation to a 100-ml volumetric flask containing 50 ml of 2 *M* sodium hydroxide. This was diluted to obtain a series of appropriate concentrations of sodium hyponitrite in 1 *M* sodium hydroxide.

Method II. Single perfectly grown crystals[6] of $Na_2N_2O_2 \cdot 6H_2O$ were used as a standard.

Both methods gave the same results: $\varepsilon_{max} = 6.55 (\pm 0.2) \cdot 10^3$ for $N_2O_2^{2-}$. Beer's law was obeyed up to a concentration of $1.5 \cdot 10^{-4}$ *M*.

To ensure stability and suppress hydrolysis of $N_2O_2^{2-}$ to $HN_2O_2^-$, alkali concentrations as high as 1 *M* are recommended. In 0.2 *M* sodium hydroxide, ε_{max} was found to be smaller by 4%.

Discussion

ADDISON *et al.*[1] reported $\log \varepsilon_{max} = 3.60$, which corresponds to $\varepsilon_{max} = 4.0 \cdot 10^3$ for the hyponitrite ion; this value is less than two-thirds of the value found in this work. These investigators used as a standard pure anhydrous sodium hyponitrite. However, when this anhydrous salt is mixed with water, heat is evolved (calorimetric measurements on this reaction are not available); some of the hyponitrite may thus decompose during dissolution and this may be the reason why ADDISON *et al.* found low values for the extinction coefficient. Presumably hyponitrite does not decompose during the dissolution of $Na_2N_2O_2 \cdot 6H_2O$ because it is hydrated already.

Another partial cause for the discrepancy may be that ADDISON *et al.* used 0.1 *M* sodium hydroxide as solvent. Technical instrumental defects can be ignored, because their results for sodium nitrite agree with those found in the present work ($\varepsilon_{max} = 23.0$ and $22.64 (\pm 0.1)$ in 0.1–1 *M* sodium hydroxide, respectively).

The precipitation method is not likely to produce high values for hyponitrous acid in acidic solution by a coprecipitation of atmospheric carbon dioxide; silver carbonate cannot coprecipitate with silver hyponitrite at pH 4.5–5[2], unless the carbonate concentration exceeds 0.01 *M*. Low results might be expected because of the slight solubility of silver hyponitrite, but this is suppressed by the excess of silver(I).

Finally, the concordance of the molar extinction value of hyponitrite, as determined by the precipitation method, with that based on the theoretical composition of $Na_2N_2O_2 \cdot 6H_2O$, suggests that the precipitation method is sufficiently accurate, within the limits of its precision (1%)[2].

The authors gratefully acknowledge the support of this work by the Royal Hellenic Research Foundation. They are also indebted to the Greek Atomic Energy Committee for permission to use their equipment.

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(Received May 31st, 1967)

Anal. Chim. Acta, 40 (1968) 170–172

BOOK REVIEW

Organometallic Compounds. Methods of Synthesis, Physical Constants, and Chemical Reactions. Vol. II. Compounds of Germanium, Tin and Lead, Edited by M. DUB, 2nd Edn., Springer-Verlag, Berlin, 1967, xix+697 pp., price DM 98,—; $24.50.

This second volume in the series covers the literature on germanium, tin and lead compounds from 1937 to 1964. As in the first volume, the survey is comprehensive and uncritical. In addition to references covering methods of preparation, properties and reactions, there are various references to biological and physiological activity and to commercial applications. These last serve to emphasize the practical importance of these compounds and the intensive industrial work which has been done in this area of chemistry.

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