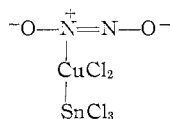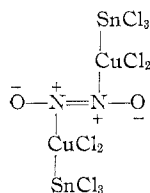passed into solutions of secondary amines, $SO_3{}^{2-}$, or Grignard reagents, respectively, we suggest for intermediate II the structure of an N-substituted nitrosohydroxylamine

$$^-O—\overset{+}{N}{=}N—O^-$$
$$\underset{\underset{SnCl_3}{|}}{\overset{|}{CuCl_2}}$$

Molecules of such structure are known to decompose to yield N_2O and the two-electron oxidation product of the N substituent. The sulfonate, for example, yields N_2O and $SO_4{}^{2-}$; the products from triphenylphosphine and NO are N_2O and triphenylphosphine oxide. The proposed intermediate would yield N_2O and $Sn(IV)$, regenerating $Cu(I)$.

The activated complex for the hydroxylamine-producing reaction involves intermediate II and one more of the reactive combination of metal ions. A structure consistent with this requirement is
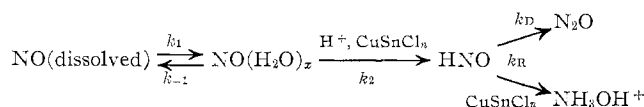
$$\overset{SnCl_3}{\underset{\overset{|}{\underset{\overset{CuCl_2}{|}}{\overset{+}{N}{=}\overset{+}{N}—O}}}{\overset{|}{CuCl_2}}}$$
$$\bar O—\overset{+}{N}{=}\overset{+}{N}—O^-$$
$$\underset{\underset{SnCl_3}{|}}{\overset{|}{CuCl_2}}$$

Analogous structures have been proposed for the red dimer of $Co(NH_3)_5NO^{2+}$ and for the dimer of $Fe(NO)_4$.[12] In order to account for the stoichiometry, this complex has to be supposed unstable with respect to hydroxylamine, Sn (IV), and Cu (II).

In the foregoing paragraphs, we have proposed a scheme in which the precursor of both N_2O and hydroxylamine is a two-nitrogen species. In such a scheme, the ratio of the yield of hydroxylamine to the yield of N_2O is independent of the steady-state concentration of

(12) J. B. Raynor, *J. Chem. Soc.*, 8, 997 (1966).

precursor. An alternative scheme, as proposed by Haight, *et al.*,[10b] postulates a one-nitrogen precursor, HNO, which upon reduction yields hydroxylamine or upon dimerization yields N_2O. The corresponding skeletal scheme would be

$$NO(dissolved) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO(H_2O)_x \xrightarrow[k_2]{H^+, CuSnCl_n} HNO \overset{\overset{k_D}{\longrightarrow} N_2O}{\underset{\underset{CuSnCl_n}{\searrow} NH_3OH^+}{k_R}}$$

The elegance and plausibility of the Haight scheme led us to favor it as a working hypothesis early in our investigation. However, it leads to the difficulty that, there being a competition between dimerization and reduction of the monomer, the relative yield of products would be predicted to be sensitive to the steady-state concentration of intermediate. Upon making the steady-state approximation with respect to $NO(H_2O)_x$ and HNO, one obtains the following expression for the relative yields

$$\left(\frac{N_2O\ yield}{NH_3OH^+yield}\right)^2 + \left(\frac{N_2O\ yield}{NH_3OH^+yield}\right) = \frac{k_Dk_1k_2}{k_R{}^2}\frac{(NO)}{k_{-1}S + k_2S^2}$$

where S has been written for the concentration of the stannous–cuprous reducing moiety. This scheme predicts that the ratio of N_2O to hydroxylamine will be an increasing function of NO pressure. We searched for this effect and found it absent. This scheme also predicts that S divided by the left-hand side of the foregoing equation will be a linear function of S, namely, proportional to $k_{-1} + k_2S$. When the data of Figure 2 were replotted in this way, nothing resembling a linear plot resulted. We therefore conclude that a two-nitrogen precursor is more consistent with the product–composition data than a one-nitrogen precursor.

Notes

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Kinetics of the Reaction of Nitric Oxide with Sulfite

BY THOMAS L. NUNES AND RICHARD E. POWELL

NO reacts very rapidly and quantitatively[1] with alkaline sulfite to yield N-nitrosohydroxylamine-N-sulfonate,[2] $^-O_3S(NO)NO^-$. Apart from a study[3] made in 1934 with an unstirred reaction vessel, the kinetics of the reaction has not been reported. Having at hand a stirred reactor suitable for such fast gas–liquid reactions, we have investigated it.

Experimental Section

The apparatus and general procedure have been described previously. Ordinary visual reading of the manometer was sufficient to follow the kinetics.[4] Reagent grade sodium sulfite was used without further purification, the alkalinity adjusted with sodium hydroxide, and the ionic strength brought to 4 M with sodium sulfate or potassium chloride.

(1) As a preparative reaction, this gives a high yield. When carried out with a measured amount of NO and the product assayed by its absorption at 2580 Å (M. N. Ackermann and R. E. Powell, *Inorg. Chem.*, **6**, 1718 (1967)), the yield was 100% within the accuracy of our analysis.

(2) In alkaline solution, the product is stable indefinitely, although it liberates N_2O as the solution becomes more acidic (reference cited in footnote 1).

(3) E. Terres and H. Lichti, *Angew. Chem.*, **47**, 511 (1934).

(4) T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1912 (1970).

Results and Discussion

All runs were kinetically first order with respect to NO pressure. The pseudo-first-order rate constant for disappearance of dissolved NO depends on th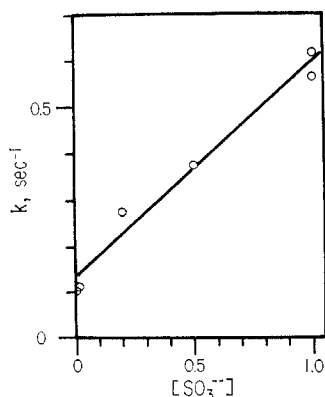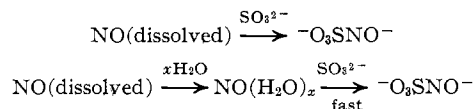e concentration of sulfite as illustrated in Figure 1, corresponding to a rate law $k = 0.13_2 + 0.45[SO_3^{2-}]$ sec^{-1}.

Figure 1.—Pseudo-first-order rate constant for the reaction of aqueous NO with sulfite at 25°.

At 50° the values are $k = 0.12 + 1.32[SO_3^{2-}]$ sec^{-1}. Within the range of concentration 0.1 to 1.0 M, the rate is independent of hydroxide.

This form of rate law is consistent with a mechanism involving two parallel paths. The sulfite-dependent term corresponds to direct combination of dissolved NO with sulfite ion, while the sulfite-independent term corresponds to a rate-determining reaction of dissolved NO with water to form a hydrolyzed species, followed by the relatively fast reaction of that species with sulfite

$$NO(\text{dissolved}) \xrightarrow{SO_3^{2-}} {}^-O_3SNO^-$$

$$NO(\text{dissolved}) \xrightarrow{xH_2O} NO(H_2O)_x \xrightarrow[\text{fast}]{SO_3^{2-}} {}^-O_3SNO^-$$

In either case, the primary product must be supposed to react rapidly with a second molecule of NO to yield the final product.

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## The Kinetics of Complexing of Nickel(II) Ion with 8-Hydroxyquinoline and 8-Hydroxyquinoline-5-sulfonate

By WILLIAM A. JOHNSON AND R. G. WILKINS

The kinetics of formation of nickel(II) complexes with a large number and variety of ligands have been studied.[1] In our investigations of the effect of proto-

(1) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965); N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966); L. I. Budarin and K. B. Yatsimirskii, *Russ. Chem. Rev.*, **37**, 209 (1968); A. McAuley and J. Hill, *Quart. Rev., Chem. Soc.*, **23**, 18 (1969)

nation of a ligand on its reactivity, a striking result has been the low rate constant for reaction of the zwitterion form of amino acids with nickel(II).[2] This may result from the internal hydrogen bonding present in the zwitterion, and in this connection it seemed worthwhile to examine the behavior of 8-hydroxyquinoline. This important ligand can exist in three forms, I–III, R = H, $pK_I = 9.9$ and $pK_{II} = 5.1$.[3] II has been reported to exist in the H-bonded form,[4] although its high rate constant for reaction with OH$^-$ ($\gtrsim 1.5 \times 10^9$ M^{-1} sec^{-1}) does not support this idea.[5] It was therefore of interest to study the complexation kinetics of I–III. We also examined the 5-sulfonated derivative, in which R = SO$_3^-$ over the whole pH range of our study ($pK_I = 8.4$, $pK_{II} = 3.8$).[3] The kinetics of complex formation of a number of magnesium complexes with 8-hydroxyquinoline have been investigated previously.[5]
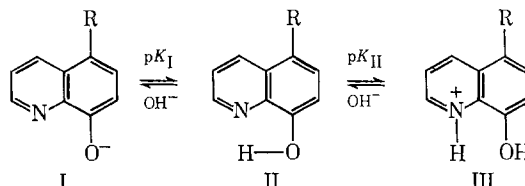
Experimental Section

Materials.—These were commercially available, reagent grade. 8-Hydroxyquinoline was recrystallized three times from aqueous ethanol and 8-hydroxyquinoline-5-sulfonic acid dihydrate was recrystallized twice from water, using decolorizing charcoal. 2,6-Lutidine was redistilled and a center fraction, bp 142°, was used.

Kinetic Experiments.—The concentration of nickel and copper ions was estimated by EDTA titrations, and that of the ligand by direct weighing. The formation and dissociation of the complexes were followed spectrally in the region of 370 mμ, using a glass–Lucite stopped-flow apparatus. In the formation experiment, metal ion at the appropriate pH (using acid alone, or buffer if necessary) was mixed with ligand at the correct pH, both solutions containing sodium nitrate to bring to the ionic strength used in all the studies (0.30 M). A large ratio of metal ion (usually 5×10^{-3} M) to ligand concentration (10^{-4} M) ensured pseudo-first-order kinetics and halted the reaction at the monocomplex stage, thus preventing precipitation of the sparingly soluble bis compound. The observed second-order rate constants [$k_{obsd} = 0.693/(t_{1/2}[Ni^{2+}])$, where $t_{1/2}$ is the half-life for the first-order reaction] are shown in Table I, and are the means of several runs.

In the dissociation experiments, complex prepared from excess Ni^{2+} at pH ~5 was plunged into perchloric acid at the lower pH or into solutions containing Cu^{2+} at pH 4–5. From a knowledge of the formation constants for the complexes with the two ligands,[3] it could be shown (and was checked spectrally) that both formation and dissociation reactions went to ($\geq 95\%$) completion. The temperature was controlled to $\pm 0.1°$. Spectra were recorded with a Cary 14 in a thermostated room (25 $\pm$ 0.5°).

Results and Discussion

Complex Formation.—The major forms of the ligand

(2) J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968).

(3) L. G. Sillén and A. E. Martell, Ed., "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

(4) A. Albert, "Heterocyclic Chemistry," The Athlone Press, London, 1968, p 91. The enol form is favored with respect to the charge-separated form, $^+NH\cdots O^-$, K_t = [zwitterion]/[enol] = 0.035: S. F. Mason, *J. Chem. Soc.*, 5010 (1957).

(5) D. N. Hague and M. Eigen, *Trans. Faraday Soc.*, **62**, 1236 (1966).