

of the input parameters. With this in mind, series of calculations were run in which K of eq 1, the degree of contraction of the 3d orbitals, and the matrix elements $H_{3d,3d}$ were varied. Representative results are shown in Figures 11–13. It was found that trends in overlap populations were insensitive to K , as expected, and depended far less on the 3d-orbital exponent than initially feared. Figure 13 displays the detailed response of the individual molecular orbitals of the sulfate ion to variations in the sulfur 3d-orbital exponent and

$H_{3d,3d}$ element. It is apparent that, for the adopted value of $H_{3d,3d}$, the quantities of interest change little with orbital exponent in the neighborhood of the exponent assumed in Figures 2–10. Unfortunately, less leeway for error exists for the poorly known $H_{3d,3d}$.

According to Table IV, overlap populations calculated with the inclusion of 3d orbitals exhibit only a modest dependency on the assumed bond angle, consistent with the known small energy required to bend bonds.

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The Copper(I)-Catalyzed Reduction of Nitric Oxide by Tin(II) Chloride

By THOMAS L. NUNES AND RICHARD E. POWELL

Received February 3, 1970

The reduction of NO by aqueous SnCl_2 is strongly catalyzed by Cu(I). The kinetics and stoichiometry are consistent with the sequence of reactions: dissolved NO \rightleftharpoons hydrolyzed NO \rightarrow one-nitrogen intermediate resulting from reaction with the Cu(I)–Sn(II) combination \rightarrow two-nitrogen intermediate, which competitively forms N_2O or hydroxylamine as a result of further reaction with the Cu(I)–Sn(II) combination.

Introduction

Prior attempts¹ to investigate the kinetics of the reduction of gaseous NO by aqueous tin(II) salts have not succeeded in agitating the aqueous phase vigorously enough to eliminate the effect of gas–liquid mass transfer on the observed rates.² We find that the reaction can be followed in a reaction vessel equipped with a vibratory mixer, rather like that used by Schmid and Bähr,³ to give kinetics demonstrably unaffected by mass transfer, down to a half-life for aqueous NO of 5 sec or less.

Experimental Section

Apparatus.—The reaction vessel (Figure 1) was a Virtis 250-ml freeze-drying flask, only modified by addition of a side arm leading to the manometer and gas-handling system. It was equipped with a Vibro-Mixer (A. G. für Chemie-Apparatebau, Zurich; Chemapec, Inc., Hoboken, N. J.). Although the Vibro-Mixer became a much less efficient stirrer whenever the gas pressure was less than the vapor pressure of water, full efficiency could easily be recovered by adding a few Torr of an inert gas such as nitrogen.

Three lines of evidence indicate that the stirring was vigorous enough to keep the aqueous phase saturated with gas. (1) Reaction rates were, within experimental scatter, independent of stirrer amplitude. (2) The rate measured for reaction of CO_2 with a buffer solution of pH 9.15 ± 0.05 was $(16.0 \pm 0.15) \times 10^{-2} \text{ sec}^{-1}$, in good agreement with the literature value ob-

tained from a fast-flow study,⁴ $(16.0 \pm 1.2) \times 10^{-2} \text{ sec}^{-1}$. (3) At high concentrations of copper(I) or tin(II), the rate of reaction appears to approach a ceiling determined by a hydrolytic reaction of NO (*vide infra*) whose rate at 0° is 0.13 sec^{-1} . We have also measured the kinetics of the reaction of NO with aqueous sulfite⁵ and observed a two-term rate law, with one term proportional to sulfite concentration and the other independent of it. The term independent of sulfite, which presumably corresponds to a sequence whose rate-determining step is the hydrolytic reaction of NO, has at 0° the same value, $0.13 \pm 0.01 \text{ sec}^{-1}$.

Reagents.—Tank nitric oxide was condensed at liquid nitrogen temperature, pumped on, and distilled at the temperature of *n*-pentane slush, after which it had no contaminants detectable by gas chromatographic or mass spectrometric analysis. All other chemicals were reagent grade, used without further purification. Stannous chloride dihydrate was assayed iodometrically at $99 \pm 0.5\%$ purity. All reaction mixtures were degassed before use by freezing and thawing five times under vacuum.

Analyses.—Gases were analyzed on an Aerograph gas chromatograph with a 6-ft column of 30–60 mesh 5A molecular sieve, at 25 or 100°. Tin(II) was titrated under carbon dioxide with triiodide solution standardized against arsenic trioxide. Free acid was determined by titration with standard sodium hydroxide, using a glass electrode pH meter, 2 equiv of base being subtracted for each mole of tin(II) present.

Soluble nitrogenous products were analyzed as follows. One aliquot was boiled for 1 hr to allow the tin(II) to reduce any hydroxylamine to ammonia,⁶ which upon Kjeldahl analysis gave the total of ammonia and hydroxylamine originally present. A second aliquot was neutralized with base, the tin(II) hydroxide was centrifuged down, and the supernatant solution was acidified and treated with copper(II) chloride and boiled for 1 hr to drive off nitrous oxide resulting from any hydroxylamine present. Kjeldahl analysis of the remaining solution then gave the amount of ammonia originally present.

(1) (a) M. L. Nichols and C. W. Morse, *J. Phys. Chem.*, **36**, 1239 (1931); (b) J. E. Chilton, Dissertation, University of California, Berkeley, Calif., 1960; (c) J. N. Cooper, Dissertation, University of California, Berkeley, Calif., 1964.

(2) There is a large chemical engineering literature on the rates of diffusion-affected gas–liquid reactions. Cf. H. L. Toor and S. H. Chiang, *A.I.Ch.E. J.*, **5**, 339 (1959); P. V. Dankwerts, *ibid.*, **1**, 456 (1955); F. J. W. Roughton, *J. Biol. Chem.*, **141**, 129 (1941).

(3) G. Schmid and G. Bähr, *Z. Phys. Chem. (Frankfurt am Main)*, **41**, 8 (1964).

(4) C. Ho and J. M. Sturtevant, *J. Biol. Chem.*, **238**, 3499 (1963).

(5) T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1916 (1970).

(6) L. H. Milligan and G. R. Gillette, *J. Phys. Chem.*, **28**, 747 (1924).

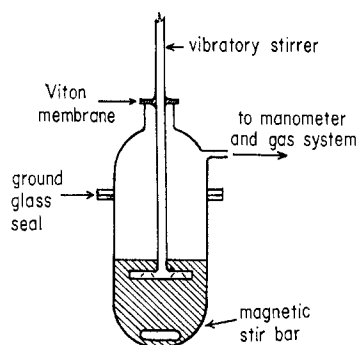


Figure 1.—Reactor, schematic.

Reaction Mixtures.—Small measured amounts of copper(II) chloride were added to 0.07, 0.335, 1.00, or 2.17 *M* tin(II) chloride. For each tin solution, enough HCl was added to give the desired acidity and enough KCl to bring the ionic strength to approximately 1.2 *M*. In order to calculate ionic strengths, it was necessary to calculate the population of each tin(II) species, for which purpose literature values^{7,8} of the stability constants were used. The compositions of the mixtures are tabulated in Table I.

TABLE I
COMPOSITION OF TIN(II) CHLORIDE SOLUTIONS

[Sn ^{II}] ^a	0.07	0.335	1.00	2.17
[KCl, HCl]	1.18	1.13	1.00	0.68
[Sn ²⁺]	0.00071	0.0044	0.019	0.064
[SnCl ⁺]	0.0077	0.043	0.16	0.43
[SnCl ₂]	0.034	0.17	0.52	1.13
[SnCl ₃ ⁻]	0.027	0.12	0.31	0.55
[Cl ⁻]	1.19	1.06	0.90	0.72

^a The notation [Sn^{II}] or [Cu^I] is used to designate the stoichiometric molar concentration of tin(II) or copper(I), respectively.

Treatment of Kinetic Data.—The raw kinetic data were manometric. Each observed total pressure was recalculated to the corresponding partial pressure of nitric oxide by analyzing for the total nitrous oxide at completion of reaction, correcting for dissolved nitrous oxide to obtain its partial pressure at completion of reaction, and subtracting its *pro rata* partial pressure from the total pressure at each stage of reaction. The disappearance of nitric oxide was then cleanly first order for at least 3 half-lives.

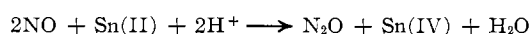
The apparent first-order rate constant as observed by disappearance of gaseous nitric oxide was recalculated to the rate constant per unit liquid volume by dividing the apparent constant by the fraction of nitric oxide present in the liquid phase. For a gas volume of 140 cm³, a liquid volume of 50 ml, and the literature values for Henry's law constant for nitric oxide in distilled water, the fraction of NO in the aqueous phase was 0.02568, 0.01657, and 0.1434 at 0, 25, and 50°, respectively. One may question the validity of the Henry's law constant for distilled water in these rather concentrated salt solutions, but if there be a discrepancy, our qualitative conclusions at any one temperature are unaffected, although a substantial error in the apparent temperature coefficient of reaction may well be introduced thereby.

Results and Discussion

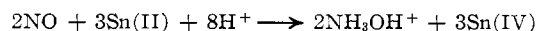
Catalysis by Copper(I).—The reaction of NO with tin(II) chloride in the presence of even a low concentration of copper(I) is strikingly faster than its reaction with either of them alone. At pressures of NO below about 150 Torr, its uncatalyzed reaction with tin(II)

chloride has a half-life measured in weeks. The reaction of NO with CuCl₂⁻ solutions alone is almost imperceptible, yet the reaction of NO with the combination of reagents has a half-life measured in seconds. The copper salt added may be a copper(II) salt, which is rapidly reduced by tin(II). So far as we are aware, the only previous report of the catalytic effect of copper(I) on reductions by tin(II) is that by Reznik, *et al.*,⁹ on the reduction of iron(III). The catalytic effect of molybdate on reductions of nitrogen species by tin(II) has been extensively studied by Haight and coworkers.¹⁰ We have made only a cursory search for other metallic ions with similar catalytic effect, but neither Mn²⁺, Ni²⁺, Fe²⁺, Zn²⁺, nor Ag⁺ has any.

Stoichiometry.—In the limit of low concentration of copper(I) or tin(II), the reaction approaches the stoichiometry



No gaseous product but nitrous oxide is observed, and the nitrous oxide, once formed, is inert to further attack by the aqueous reagents. In the limit of high concentration of copper(I) or tin(II), the reaction approaches the stoichiometry



Hydroxylamine in acid solution, once formed, does not react with gaseous NO. It does react, very slowly, with the aqueous reducing agent to form NH₄⁺, which is always found in traces among the products,^{10a} but the extent of this subsequent reaction is so small that it can be ignored.

The relative yield of N₂O and hydroxylamine depends markedly on the composition of the reducing solution. The ratio of yield of hydroxylamine to yield of N₂O is proportional to the concentration of copper(I) and of tin(II) and at least approximately to the second power of the concentration of free chloride ion (Figure 2). So far as the effects of copper and tin are concerned, this observation can be reported with good confidence, inasmuch as each of them was varied over a wide range. The effect of chloride ion is somewhat less certain, since we were unable systematically to vary its concentration over a wide range and still keep ionic strength constant, and the second-power dependence merely represents the best fit to the relative-yield data for the four chloride concentrations given in Table I. The stoichiometry does not depend upon acidity (within the range 0.1–1 *M*), nor upon the NO pressure (within the range 50–150 Torr).

This 300-fold change in the relative stoichiometry is not accompanied by any change in the form of the kinetic law. The most general interpretation consistent with these observations appears to be that there is an intermediate product of the reaction, formed by or subsequent to the rate-determining step, which is sub-

(9) B. E. Reznik, N. A. Bidnyak, and M. V. Pchelkina, *Izv. Vyssh. Icheb. Zaved., Khim. Khim. Tekhnol.*, **6** (2), 209 (1963); *Chem. Abstr.*, **59**, 5834d (1963).

(10) (a) G. P. Haight, Jr., and C. von Frankenberg, *Acta Chem. Scand.*, **15**, 2026 (1961); (b) G. P. Haight, Jr., P. Mohilner, and A. Katz, *ibid.*, **16**, 221 (1962); (c) G. P. Haight, Jr., and A. Katz, *ibid.*, **16**, 659 (1962).

(7) G. P. Haight, J. Zoltewicz, and W. Evans, *Acta Chem. Scand.*, **16**, 811 (1962).

(8) L. G. Sillén, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

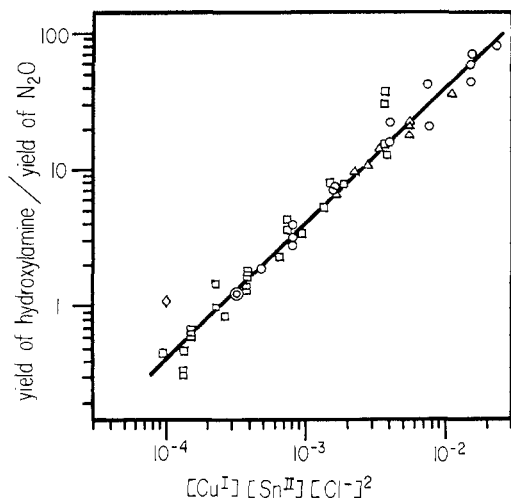
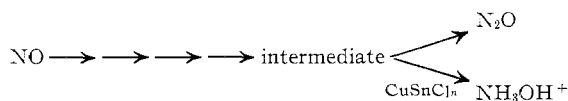


Figure 2.—Ratio of moles of NO converted to hydroxylamine to moles of NO converted to N_2O . Tin(II) concentration: triangles, 2.17 M ; circles, 1.00 M ; squares, 0.335 M ; diamond, 0.07 M .

ject to the competitive processes of either decomposing directly to N_2O or being reduced by copper(I)—tin(II) to hydroxylamine. The reducing moiety involves one copper(I), one tin(II), and, at least tentatively, two more chloride ions than are associated with the principal species in solution; it may be, but is not necessarily, a single species $CuSnCl_n$. The corresponding skeletal mechanism for the late stages of the reaction sequence is



Kinetic Law. (a) Dependence on NO pressure.—For all runs, a first-order plot (namely, $\log P_{NO}$ vs. time) was linear for at least 3 half-lives. Moreover, the initial rate was proportional to the initial NO pressure when the latter was varied from 50 to 100 to 150 Torr. The activated complex therefore involves only one molecule of NO for the slowest as well as the fastest reactions measured.

(b) The Kinetic Ceiling Phenomenon and the Copper Threshold Phenomenon.—For each concentration of tin(II) and acid, the rate was measured for concentrations of copper(I) from below 10^{-4} M to above 10^{-2} M . Typical results are shown in Figure 3. There are two peculiarities about this type of kinetic dependence. The first is that, whenever the rate is increased by addition of Cu(I), it asymptotically approaches a limiting or "ceiling" value and is thenceforward independent of additional Cu(I). The same ceiling is approached, whatever the concentration of Sn(II) or of acid. Therefore the ceiling must be set by the reaction of one molecule of NO with one or more molecules of water and no other reagent. In other words, the reversible hydrolysis of NO is a compulsory first step in the reaction sequence

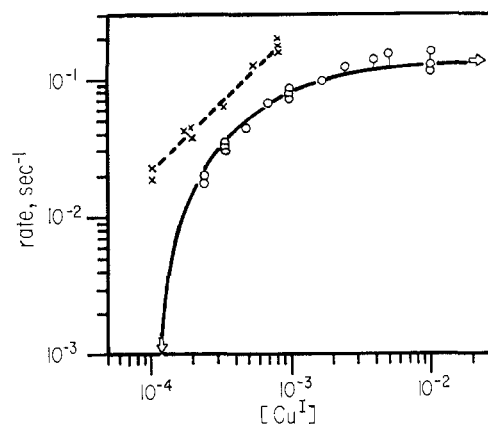
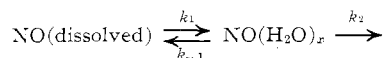


Figure 3.—Pseudo-first-order rate constants for reaction at 0° , $[Sn^{II}] = 0.335$ M , and $[H^+] = 0.5$ M . Circles with the solid curve represent raw data. The upper arrow indicates the ceiling rate; the lower arrow, the threshold copper concentration. Crosses with dashed line indicate values of k_2k_1/k_{-1} calculated as described in text.

It must be emphasized that this ceiling process is not merely the dissolution of gaseous NO to form dissolved NO, a process which in the reactor at hand requires only a small fraction of 1 sec. It is, presumably, more like the hydrolysis of aqueous CO_2 to form H_2CO_3 .

The ceiling rate at 0, 25, and 50° is 0.136, 0.141, and 0.15 sec^{-1} , respectively. The activation parameters corresponding to these data are $\Delta H^\ddagger = \sim 0$ and $\Delta S^\ddagger = -63$ $\text{cal deg}^{-1} \text{mol}^{-1}$ referred to 1 M aqueous NO; however, inasmuch as the rates involve the possibly uncertain Henry's law constants at the three temperatures, it is inadvisable to draw firm conclusions from the temperature dependence.

The steady-state condition for $NO(H_2O)_x$ gives the relation between the raw pseudo-first-order rate constant, call it k , and the individual rate constants k_1 , k_{-1} , and k_2 which may be written in the form

$$k_2k_1/k_{-1} = \frac{k}{1 - k/k_1}$$

With the aid of this relation, the ceiling rate k_1 being known, each raw k value can be recalculated to give the corresponding value of k_2k_1/k_{-1} , which can then be examined to discover the dependence of k_2 upon the concentrations of the various aqueous reagents, *i.e.*, the rate law for the reduction of $NO(H_2O)_x$.

There is a second peculiarity in the copper(I) dependence. For each tin(II) concentration, there appears to be a lower threshold to copper(I) concentration, below which the reaction does not proceed at all. The rate appears to be proportional to the concentration of copper(I) over and above this threshold. The threshold increases with increasing tin(II) concentration (Table II), being approximately equal to 1/2800 the

$[Sn^{II}], M$	$[Cu^I]$ (threshold), M
0.07	$(2 \pm 1) \times 10^{-5}$
0.335	$(1.5 \pm 0.5) \times 10^{-4}$
1.00	$(3 \pm 0.5) \times 10^{-4}$
2.17	$(1 \pm 0.1) \times 10^{-3}$

molar concentration of the tin(II). We can see no alternative to the inference that our (Baker and Adamson, reagent grade) SnCl₂ contained 1/2800 mole fraction of some impurity which was able to react irreversibly with copper(I) and convert it to a form not reactive toward NO(H₂O)₂. We are, unfortunately, unable to suggest what that impurity might be. Recrystallizing the SnCl₂ once from distilled water did not change the threshold. This phenomenon, although intriguing for its own sake, has a fairly small effect on the observed kinetics, and our qualitative conclusions would not be changed even if it were ignored.

(c) **Dependence on Copper(I).**—The dashed line in Figure 3 shows the typical dependence of k_2k_1/k_{-1} on the first power of copper(I) concentration. Similar results were obtained at all tin(II) concentrations.

(d) **Dependence on Acidity.**—As Table III shows, k_2k_1/k_{-1} corrected for [Cu^I] and at a fixed value of [Sn^{II}] and of [Cl⁻] is proportional to the first power of [H⁺].

[H ⁺], M	k_2k_1/k_{-1} [Cu ^I], sec ⁻¹ M ⁻¹
0.1	45 ± 10
0.5	200 ± 60
1.0	350 ± 60

^a At 0°, 0.335 M Sn^{II}, and 1.06 M Cl⁻.

(e) **Dependence on Chloride.**—The data in Table IV are consistent with a second-power dependence of k_2k_1/k_{-1} on [Cl⁻] at fixed values of the concentrations of other reagents. This result is not entirely unambiguous, in part because the computation of free chloride ion concentration involves literature values of complexing constants for tin chlorides and in part because the ionic strength was somewhat changed.

[Cl ⁻], M	k_2k_1/k_{-1} , sec ⁻¹
1.06	32 × 10 ⁻⁴
0.55	8.2 × 10 ⁻⁴

^a At 0°, 0.335 M, Sn^{II}, 7 × 10⁻⁴ M Cu^I, and 0.5 M H⁺.

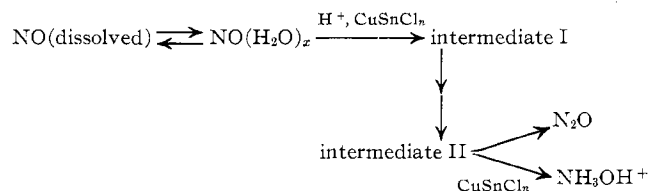
(f) **Dependence on Tin(II).**—As Table V shows, k_2k_1/k_{-1} corrected for the kinetic dependence on other species is proportional to the first power of [Sn^{II}].

[Sn ^{II}], M	k_2k_1/k_{-1} [Cu ^I][H ⁺][Cl ⁻] ² , sec ⁻¹ M ⁻⁴
0.07	55 ± 5
0.335	350 ± 50
1.00	800 ± 300
2.17	1800 ± 200

(g) **Summary of Kinetic Dependence.**—In summary, the activated complex for the second step in the reaction sequence is made up of one molecule of hydrolyzed NO, one ion each of H⁺, Sn(II), and Cu(I), and two Cl⁻ ions over and above the number associated with the principal stannous and cuprous species in so-

lution. The average value of k_2k_1/k_{-1} at 0° is 910 sec⁻¹ M⁻⁵.

A skeletal mechanism consistent with the kinetics and the stoichiometry is



Related Phenomena.—Our kinetic and stoichiometric results cannot carry us farther than the foregoing skeletal reaction scheme, but there are various auxiliary data that permit some conjectures on the chemical nature of the intermediate species.

The reactive combination of metal ions in the second step and in the hydroxylamine-producing step are the same, namely, one ion of tin(II), one of copper(I), and two chloride ions more than those associated with the principal species in solution. Inasmuch as the principal cuprous species is CuCl₂⁻ and the principal stannous species is SnCl₂, this would make the reactive combination SnCuCl₆³⁻. Bearing in mind the ability of SnCl₃⁻ to act as a ligand to other metal ions, we note that the reactive combination is equivalent to a CuCl₄³⁻ ion one of whose chloro groups has been replaced by a SnCl₃⁻ group, to wit, Cl₃Sn-CuCl₃³⁻. On this hypothesis, the role of the SnCl₃⁻ group is first to labilize the cuprous complex toward substitution and later to act as a reducing moiety in an intramolecular oxidation-reduction.

If the first step, the hydrolysis of NO, involves only one molecule of water, the plausible product is the dihydroxynitrene N(OH)₂. If this be so, the oxygen atom of NO ought to exchange rapidly with the oxygen atoms of water. Taylor and Clarke¹¹ have observed the exchange of oxygen-18 between NO and 6 M HNO₃ at 25°, but it is conceivable that in their experiment the nitrate ion is implicated. We have repeated their experiment at 0° using 1 M HCl made up with oxygen-18-enriched water and can report that the exchange does take place rapidly.

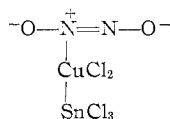
Inasmuch as there is no likely site for a proton in the complex Cl₃Sn-CuCl₃³⁻, the acid catalysis of the second step is presumably attributable to protonation of the N(OH)₂.

Intermediate I, the primary product of the second step, cannot involve more species than those in its activated complex but may involve fewer. Thus, it must be a single-nitrogen species. It might be, for example, the nitrosyl complex resulting from displacement of one of the chloro groups from cuprous, Cl₃Sn-CuCl₂(NO)²⁻.

Intermediate II, being an immediate precursor of N₂O, is almost certainly a two-nitrogen species. Such a species could readily be formed by the fast addition of another NO molecule to intermediate I. By analogy with the well-known species R₂N(NO)NO⁻, ⁻O₃S-(NO)NO⁻, R(NO)NO⁻, formed rapidly when NO is

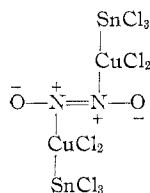
(11) T. I. Taylor and J. C. Clarke, *J. Chem. Phys.*, **31**, 277 (1959).

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



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

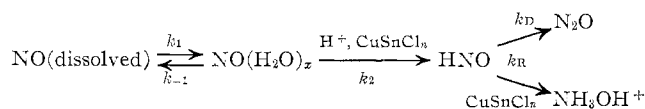


Analogous structures have been proposed for the red dimer of $\text{Co}(\text{NH}_3)_5\text{NO}^{2+}$ and for the dimer of $\text{Fe}(\text{NO})_4$.¹² In order to account for the stoichiometry, this complex has to be supposed unstable with respect to hydroxylamine, Sn(IV), and Cu(II).

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



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 $\text{NO}(\text{H}_2\text{O})_x$ and HNO, one obtains the following expression for the relative yields

$$\left(\frac{\text{N}_2\text{O yield}}{\text{NH}_2\text{OH}^+ \text{ yield}} \right)^2 + \left(\frac{\text{N}_2\text{O yield}}{\text{NH}_2\text{OH}^+ \text{ yield}} \right) = \frac{k_D k_1 k_2}{k_R^2} \frac{(\text{NO})}{k_{-1} S + k_2 S^2}$$

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 $k_{-1} + k_2 S$. 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.

Acknowledgment.—T. L. N. gratefully acknowledges the tenure of National Science Foundation fellowships during the academic years 1964–1966.

Notes

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Kinetics of the Reaction of Nitric Oxide with Sulfite

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Received February 3, 1970

NO reacts very rapidly and quantitatively¹ with alkaline sulfite to yield N-nitrosohydroxylamine-N-sulfo-

nate,² $-\text{O}_3\text{S}(\text{NO})\text{NO}^-$. Apart from a study³ 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.

(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).

(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.