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Nitrogen-15 NMR and Tracer Determination of Protonation Site and Mechanism of Decomposition of Aqueous Hyponitrite[1]

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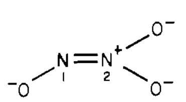
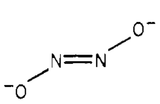
The hyponitrite anion $N_2O_2^{2-}$ shows a single ^{15}N NMR resonance at 429 ppm, referred to NH_3(l). Diprotonation to form $H_2N_2O_2$ causes an upfield shift averaging 8 ppm per proton, compared with 24 ppm observed for monoprotonation of trioxodinitrate ($N_2O_3^{2-}$). The data suggest O-protonation of $N_2O_2^{2-}$, in contrast to N-protonation of $N_2O_3^{2-}$, and this is confirmed by isotopic and chemical evidence: the anion $HN_2O_2^-$ is shown to form N_2O without N–N bond cleavage, whereas HNO and NO_2^- are the known primary products of $HN_2O_3^-$ decomposition. Despite their close similarities of rate constant, activation enthalpy, and other features, the thermal decompositions of $HN_2O_2^-$ and $HN_2O_3^-$ therefore occur via dissimilar mechanisms.

We have recently reported ^{15}N NMR evidence that the trioxodinitrate anion $N_2O_3^{2-}$ (I) binds a proton at N_1, despite the presence of charge centers at oxygen.[2] There are striking similarities of properties between I and the trans-hyponitrite anion $N_2O_2^{2-}$ (II); hence it is of interest to determine whether II exhibits a similar protonation anomaly. We now report NMR measurements that suggest O-protonation in this case and we report a confirming isotopic and chemical demonstration that $HN_2O_2^-$ decomposes to N_2O without N–N bond cleavage, whereas $HN_2O_3^-$ decomposition is known to yield HNO as a primary product.



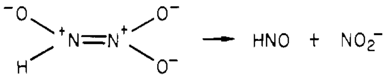
I



II

Similarities between I and II include the following: intense UV bands at λ_{max} = 250 (I) and 248 nm (II), shifting to 237 and 233 nm upon monoprotonation,[3,4] N–N stretching frequencies 1380 (II)[5] and 1397 cm^{-1} (I) (in this case not a true N–N stretch but the mode having the highest degree of such character),[6] and substantial separation of pK_1 (2.51 (I) 7.2 (II)) and pK_2 (9.7 (I) 11.5 (II)).[4,7] The dianions are stable in aqueous solution, but both are destabilized by monoprotonation, the products of decomposition being $N_2O + NO_2^-$ (I) and $N_2O + H_2O$ (II). The first-order rate constants for these decompositions are nearly identical under conditions in which the monoprotonated anion predominates: $k_1 = 6.8 \times 10^{-4}$ s^{-1} for I at pH 6.2 and 7.2×10^{-4} s^{-1} for II at pH 9.2 (25.0 °C).[4,8] The enthalpies of activation ΔH^* are 100 (I) and 95 kJ mol^{-1} (II).[4,8] Both diprotonated acids are more stable in solution than the monoprotonated anions,[4,8] although $H_2N_2O_2$ is subject to radical chain reactions[12] and $H_2N_2O_3$ to NO-producing attack by HNO_2.[8,9]

The above parallels strongly suggest closely similar mechanisms for the decompositions of monoprotonated I and II. For I, it is well established that N–N bond cleavage is rate controlling and leads to formation of HNO, which then dimerizes to N_2O (eq 1 and 2).[3,8]



(1)

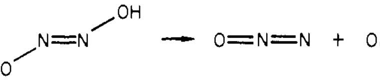
The rate of (1) is unchanged

$$HNO + HNO \rightarrow N_2O + H_2O \qquad (2)$$

by the presence of hydroxylamine, but N_2 is produced by the competing reduction eq 3.[10] Hyponitrite decomposition was

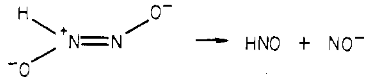
$$HNO + NH_2OH \rightarrow N_2 + 2H_2O \qquad (3)$$

described by Latimer and Zimmerman[11] as unimolecular heterolysis at N–O (eq 4), and this view is supported by the kinetic studies of Hughes and Stedman[4] and others.[12]



(4)

However, nothing in the literature precludes the possibility that II decomposes to HNO via an N-protonated anion (eq 5) and that its N_2O product arises from dimerization of HNO (eq 2) (or NO$^-$)[13] as in the case of I. The new evidence that N-protonation occurs in I[2] compels examination for this possibility in II.



(5)

$Na_2{}^{15}N_2O_2$ was prepared by NaHg reduction of $Na^{15}NO_2$ (ca. 99% ^{15}N, KOR),[14] and ^{15}N NMR spectra were obtained with a Varian XL-100 spectrometer. For each measurement ca. 0.4 mL of 0.2 M solution was employed; pH adjustment was accomplished by addition of microliter quantities of glacial HOAc. No more than 0.1 unit of pH increase was observed during the course of acquisition. All measurements on protonated species were carried out at 2 ± 2 °C, since kinetic data[4] predict a 6-h half-life at this temperature for the most unstable case (pH ca. 9). Concentration losses prevented us from acquiring satisfactory spectra at pH 7 and 9, however, and losses were also observed in samples carried through that interval for measurement in acid solution. The kinetic predictions were based on dilute solution data, and these losses may have been caused by concentration effects.

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Table I. ^{15}N Chemical Shifts of Hyponitrite at Various pH Levels

expt no.	soln	predominant species	*t*, °C	δ_{obsd}[a]	$\delta_{NH_3(l)}$[b]	$\Delta\delta$[c]
1	1 M NaOH	$N_2O_2^{2-}$	30 ± 2	61.1	428.7	
2	1 M NaOH	$N_2O_2^{2-}$	2 ± 2	59.7	427.3	
3	pH 13.0	$N_2O_2^{2-}$	30 ± 2	61.2	428.8	(0)
4	pH 12.1	$N_2O_2^{2-}$	2 ± 2	60.1	427.7	(0)
5	pH 11.3	$HN_2O_2^- + N_2O_2^{2-}$	2 ± 2	59.2	426.8	0.5
6	pH 11.0	$HN_2O_2^- + N_2O_2^{2-}$	2 ± 2	58.8	426.4	0.9
7	pH 10.1	$HN_2O_2^- + N_2O_2^{2-}$	2 ± 2	56.5	424.1	3.2
8	pH 5.0	$H_2N_2O_2$	2 ± 2	44.6	412.2	15.1
9[d]	1 M NaOH	$N_2O_2^{2-}$	30 ± 2	61.3	428.9	(0)
10	1 M $HClO_4$	$H_2N_2O_2$	30 ± 2	45.2	412.8	15.9

[a] Relative to external 6.6 M HNO_3 at 30 ± 2 °C. [b] Relative to anhydrous NH_3; correction constant = 367.6.[21] [c] $\Delta\delta = \delta_{N_2O_2^{2-}} - \delta_{sample}$, at applicable *t*. [d] Experiment 8 sample (pH 5) after treatment with NaOH.

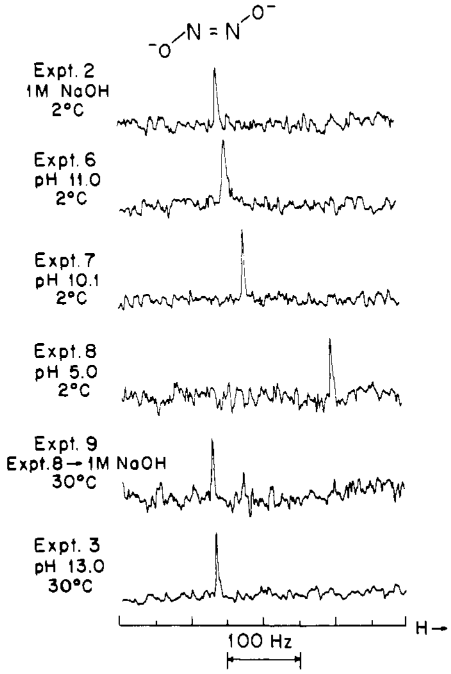

Figure 1. ^{15}N NMR spectra (10.14 MHz) of $Na_2{}^{15}N_2O_2$ solutions at several pH levels. The spectrometer was locked on external ^{19}F, with tip angle 70° and recycle time 10 s. Numbers of FID's accumulated vary from 417 (experiment 6) to 7700 (experiment 9).

A single resonance is observed in $N_2O_2^{2-}$ at 429 ppm downfield from $NH_3(l)$ (30 ± 2 °C), in some disagreement with the previously reported ^{14}N value of 463 ppm.[15] The effects of protonation are seen clearly in Figure 1 and Table I even though measurements could not be made at pH 7 and 9. After completion of the measurement at pH 5 (experiment 8), the sample was made 1 M in NaOH and its NMR reexamined (experiment 9). Since the resonance was found exactly where observed previously for $N_2O_2^{2-}$, there is no doubt that the reported effects are due to protonation.

From the values $pK_2 = 11.5$ (25 °C) and $\Delta H° = 29$ kJ mol^{-1} [4] we calculate that $HN_2O_2^-$ should constitute more than 90% of total hyponitrite at pH 10.1, yet the protonation-induced shift is only 3.2 ppm at that pH. The small difference between runs at pH 5 and at 1 M $HClO_4$ (experiments 8 and 10), on the other hand, indicates that diprotonation is nearly complete at pH 5, as expected. We conclude that the total effect of bonding two protons to $N_2O_2^{2-}$ is an upfield shift of 16 ppm, and the data also suggest a possible asymmetry of protonation effects since the full shift due to monoprotonation may be only 4–5 ppm. The average value, 8 ppm per proton, is much less than the shift observed for monoprotonation of I at N_1 (24 ppm).[2] The present data suggest O-protonation of II.

Table II. Mass Spectra[22] of N_2O Products of Complete Decomposition of $Na_2{}^{15}N_2O_2$ (Experiment 1) and Simultaneous $Na_2{}^{15}N_2O_2$ and $Na_2N_2O_3$ Decompositions (Experiments 2 and 3) in Phosphate Buffer[a]

expt no.	pH	$[Na_2N_2O_3]_0$, M	$[Na_2N_2O_2]_0$, M	*m/e* 46	*m/e* 45	*m/e* 44
1	7.80	0	0.0010	98.8	1.2	0.004
2	7.73	0.0029	0.0014	35.6	0.57	63.9
3	7.95	0.0025	0.0015	37.8	0.62	61.6

[a] Abundances are expressed as percents of total *m/e* 44–46, with neglect of small contributions at *m/e* 47 and 48.

In order to perform the test of eq 5 to be described below, it was necessary to determine whether interactions occur between monoprotonated I and II in solution. Initial rates of production of N_2O were measured for I and II, separately and together, in phosphate buffer (pH 7.8), by employing a GC method with CF_4 as internal reference.[16,17] A combined rate equal to the sum of component rates was observed,[18] no gas product other than N_2O was detected, and we conclude that the decompositions are mutually independent.

The results of experiments designed to test the possible mechanism eq 5 and 2 are shown in Table II. Experiment 1 shows that our $Na_2{}^{15}N_2O_2$ decomposes to form N_2O in which $^{15}N^{15}N^{16}O$ (*m/e* 46) is overwhelmingly abundant (% ^{15}N = 99.4). If reaction 5 occurred, cross dimerization of its product $H^{15}NO$ with $H^{14}NO$ from known reaction 1 should have produced N_2O of *m/e* 45 in substantial proportions, in experiments 2 and 3. Instead, it is quite clear from the data that N_2O arises from separate, distinct sources in these experiments, demonstrating that the N–N bond is not broken along the pathway from II to N_2O.

An additional chemical test of eq 5 was performed by addition of hydroxylamine to monoprotonated II solutions and GC examination of the decomposition product gas. The rate of decomposition was unaffected by NH_2OH in 10-fold excess. However, only trivial proportions of N_2 were detected in the presence of the N_2O product at pH 6 and 10, in contrast to the effect of NH_2OH on $HN_2O_3^-$ decomposition product (eq 3),[10] confirming the absence of HNO as intermediate in the decomposition of $HN_2O_2^-$.

The original interpretation of hyponitrite decomposition as heterolysis at N–O[11] is sustained by the above isotopic and chemical evidence. Because reaction 1 is reversible,[8,9] trioxodinitrate decomposition seems best interpreted as heterolysis at N–N of a singly bonded form of the anion $HN_2O_3^-$. It is

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(18) For $[I]_0 = 0.0112$ M, $10^6R_0 = 5.33$ mol min^{-1}; for $[II]_0 = 0.00985$, $10^6R_0 = 2.08$; for $[I]_0 = 0.0101 + [II]_0 = 0.0104$, $10^6R_0 = 7.40$.

remarkable that the two processes proceed along such dissimilar pathways when their kinetic characteristics and the structural features of the two anions show such close resemblances.

Our interpretation of the NMR data as indicating O-protonation of II is confirmed by the isotopic evidence. The N-protonation observed for I remains unique among oxoanions, and the more conventional behavior of the closely related anion II suggests that a close energetic balance is probably involved. An ab initio calculation by Cremaschi and Whitten,[19] using crystal lattice geometry and dimensions,[20] shows that the isolated $HN_2O_3^-$ anion protonated at its nitroso-like O atom should be more stable than the N_1-protonated form by about 52 kJ mol^{-1}. Any energetic accounting for the N-protonation of this species observed in solution may therefore require that a heavy burden be placed upon distortion and solvent effects, and it is interesting to note that this price is apparently not paid in the more symmetrical case of hyponitrite.

Registry No. $Na_2N_2O_2$, 60884-93-7; $Na_2N_2O_3$, 13826-64-7; $N_2O_2^{2-}$, 15435-66-2.

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Magnetic Ordering in $CoCl_2 \cdot 2P(C_6H_5)_3$ and $CoBr_2 \cdot 2P(C_6H_5)_3$

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The crystal structures of $CoCl_2 \cdot 2P(C_6H_5)_3$ and $CoBr_2 \cdot 2P(C_6H_5)_3$ are reported. Both crystals belong to the space group $P2/c$ with $Z = 2$: for the chloride, $a = 11.764$ (2) Å, $b = 8.250$ (3) Å, $c = 17.254$ (7) Å, and $\beta = 106.57$ (4)°; for the isostructural bromide, $a = 11.828$ (2) Å, $b = 8.325$ (2) Å, $c = 17.365$ (5) Å, and $\beta = 106.58$ (3)°. The crystal susceptibilities of the compounds have been measured over the temperature interval 40 mK-4 K. Antiferromagnetic ordering is observed at 0.21 ± 0.01 K (Cl) and 0.25 ± 0.01 K (Br). The specific heats have also been measured, and the ordering has been confirmed. Both compounds order with lattice dimensionality between 1 and 2, and all the data may be fit by a theoretical calculation for the rectangular Ising lattice, with $J_x/J_y = 0.31 \pm 0.02$ for the chloride and 0.10 ± 0.02 for the bromide. These results require that the $|\pm {}^3/_2\rangle$ component of the $^4A_2$ level be the ground state in both systems.

Introduction

The nature of the ground state of tetrahedral cobalt(II) complexes continues to be a problem of interest.[4-9] The determination of the sign and magnitude of the zero-field splitting of the $CoCl_4^{2-}$ ion in several lattices has attracted widespread attention as has also the concomitant magnetic ordering. We note that the tetrahedral ion in Cs_3CoCl_5, for example, exhibits a large zero-field splitting of about 10 K and the compound orders according to the three-dimensional Ising model.[10] On the other hand, the zero-field splitting in Cs_2CoCl_4 is 13.5 ± 1 K,[5,6] but it is of opposite sign to that in Cs_3CoCl_5. This leads to an anisotropy in the magnetic interaction according to the magnetic *XY* model.[5-7] This system is of further interest because it behaves as a linear-chain magnet.[5-7,11]

We report here a study of the compounds CoX_2L_2 where X is chloride or bromide and L is triphenylphosphine, $P(C_6H_5)_3$. Previous work on these compounds is limited to powder susceptibilities at high temperatures,[12] to polarized crystal spectra,[13] and to paramagnetic anisotropy measurements at 25 °C[14] and down to 20 K.[15] The crystal structures of both compounds have now been determined, and single-crystal susceptibility and specific heat measurements at low temperatures are reported. These measurements determine the sign of the zero-field splitting (ZFS) of the $^4A_2$ ground state without ambiguity, but the measurements are at temperatures too low to allow the determination of the magnitude of the ZFS. The results are also of interest because they indicate that antiferromagnetic ordering of reduced lattice dimensionality occurs in both salts.

Experimental Section

Single crystals of each material were grown from warm ethanol and oriented by means of the known morphology.[15] Susceptibilities were measured by an ac mutual-inductance technique at near zero field. Temperatures below 1 K were obtained by means of a ^3He–^4He dilution refrigerator; the experimental procedure has been reported

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