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Formation of the Copper(II) Nitrosyl Cation, $[CuNO]^{2+}$, in Strong Acids

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In strong acids, the reaction of Cu^0, Cu^I or Cu^{II} compounds with atmospheric NO at room temperature results in the formation of the copper(II) nitrosyl cation, $[CuNO]^{2+}$, during which the oxidation of Cu^0 to Cu^{II} is accompanied by the formation of N_2 and N_2O, whereas the oxidation of Cu^I to Cu^{II} results in the formation of N_2O without a significant amount of N_2.

Nitrogen monoxide, NO, is an important bioregulatory molecule and copper-nitrosyl adducts, including $[CuNO]^{2+}$, are implicated as pivotal intermediates in biological systems.[1] Great attention has been focused on the important role that the copper-nitrosyl species have played in the environmentally significant nitrogen oxide processing using copper exchanged zeolites.[2–4] However, the direct observation for the $[CuNO]^{a+}$ (a = 1, 2) cations remains limited to the adsorbed species[4,5] or the isolated species in matrices.[6] So far there has been no evidence for the formation of metal nitrosyl cations in strong acids, with the only exception being the NO absorption by iron and copper compounds in sulfuric acid,[7,8] while there has been a rapid development in the synthesis and characterization of metal carbonyl cations, usually generated in strong acids, superacids or with weakly coordinating anions.[9–11]

In the present study, we found that in concd H_2SO_4 the reaction of Cu^0 (powder) and a variety of Cu^I and Cu^{II} compounds with atmospheric NO at room temperature results in the formation of the copper(II) nitrosyl cation, $[CuNO]^{2+}$ (for sake of brevity, a solvated cation that should exist in the form of $[CuNO(L)_m]^{a+}$ (L denotes the weakly coordinating ligand probably being the conjugate base of the solvent acid or a closely related species) is simply formulated as $[CuNO]^{a+}$), according to Scheme 1, of which the formulation is based on IR, Raman and ESR spectroscopy. An IR absorption was observed for the ν(NO) stretching at 1929 cm^{-1} with the corresponding Raman band at 1930 cm^{-1}, indicating the formation of a copper mononitrosyl complex (Fig. 1).

The reaction of Cu_2O with atmospheric CO in concd H_2SO_4 leads to the formation of $[Cu(CO)_n]^+$ (n = 1–3), which releases the reversible CO ligands upon brief evacuation to give the stable $[Cu(CO)]^+$ (ν(CO) = 2148 cm^{-1}; see Fig. 1a).[12] If atmospheric NO is introduced, the CO ligand of $[Cu(CO)]^+$ is gradually replaced by NO to give a purple heterogeneous suspension exhibiting an IR ν(NO) band at 1929 cm^{-1} (Figs. 1b–1c). The resulting complex readily releases the NO ligand upon brief evacuation (2–3 min) to give a colorless heterogeneous suspension showing no ν(CO) bands (Fig. 1d, Eq. 1), whereas NO is not desorbed from $[CuNO]^{2+}$ in the zeolite by brief evacuation at room temperature.[13] No CO species is observed by reintroducing CO into the above solution (Fig. 1e), leading to the conclusion that Cu^I has been oxidized to Cu^{II} as it is found that a Cu^I compound such as Cu_2O but not a Cu^{II} compound such as $CuSO_4$ absorbs CO in concd. H_2SO_4; CO has also been used as a probe molecule diagnostic for the Cu^+ sites on the Cu-zeolites.[14] The copper(II) nitrosyl cation, $[CuNO]^{2+}$, is reformed by reintroducing NO (Fig. 1f, Eq. 1).

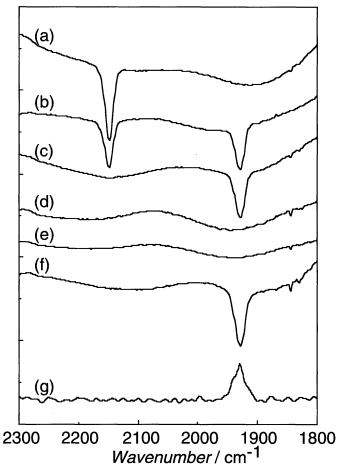
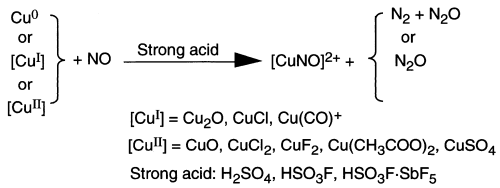


Fig. 1. IR spectra of ν(CO) and ν(NO) regions at room temperature obtained (a) after the reaction of Cu_2O in concd H_2SO_4 with atmospheric CO and subsequent evacuation; (b) after a 1-h reaction with NO following (a); (c) after a 16-h reaction with NO following (a); (d) after a 5-min evacuation following (c); (e) after stirring under a CO atmosphere for 1 h following (d); and (f) after a 30-min reaction with NO following (e); and (g) the corresponding Raman spectrum of (c).



Scheme 1.

$$[CuNO]^{2+} \underset{+NO}{\overset{-NO}{\rightleftharpoons}} Cu^{2+} \quad (1)$$

The ESR study confirmed the II oxidation state of Cu in the resulting complex. As shown in Fig. 2a, the strong resonance characteristic of Cu^{2+} is observed at g = 2.2359 for the clear solution obtained by decanting and filtering the suspension of $CuSO_4$ in concd H_2SO_4. Introducing NO to this clear solution leads to a significant decrease in the intensity of the ESR signal (Fig. 2b) owing to the formation of the diamagnetic $[CuNO]^{2+}$; the weak ESR signal remains observable due to the existence

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of a small amount of Cu^{2+} in equilibrium with $[CuNO]^{2+}$ (Eq. 1). The intensity of the ESR signal for Cu^{2+} is increased upon a brief evacuation (Fig. 2c), but significantly decreases again by reintroducing NO (Fig. 2d).

The coordination of NO to Cu^{2+} involves the electron transfer of the unpaired electron from the antibonding π^* orbital of NO to a 3d orbital of Cu^{2+}, resulting in the spin pairing between NO and Cu^{2+}, and therefore, the diamagnetism for $[CuNO]^{2+}$.[15] The observed ν(NO) value (1929 (IR); 1930 (Raman) cm^{-1}), higher than 1876 cm^{-1}, the value for free NO,[16] corresponds to a partially positive NO species and a linear Cu–N–O bond angle.[17] Although the spin pairing has occurred as revealed by ESR, the charge transfer from NO to Cu^{2+} is, however, far from being complete, which should be followed by a lone pair donation from NO and π back-bonding to the NO orbitals, as the observed ν(NO) value is lower than that of NO^+ (2340 cm^{-1});[18] hence $[CuNO]^{2+}$ may be denoted as $Cu^{(1+\delta)+}(NO)^{\delta'+}$ ($\delta + \delta' = 1$). Based on the classification proposed by Enemark et al. for MNO complexes by the number of d-type electrons present in the complex, $[CuNO]^{2+}$ would be written as $\{CuNO\}^{10}$, which may have a pseudo-tetrahedral geometry with a linear Cu–N–O group and three solvent ligands.[17]

It is worth noting that, during the formation of $[CuNO]^{2+}$ in concd H_2SO_4 at room temperature, the oxidation of Cu^0 is accompanied by the reduction of NO to N_2 and N_2O (analyzed by gas chromatography), while no significant N_2, but N_2O, is observed during the reaction of the Cu^I compounds with NO. These findings suggest the possibility that Cu^0, which may be generated by the disportionation of two Cu^+ sites, might play an important role in the catalytic decomposition of NO to N_2 and O_2. Cu^+ has been considered as the active center, and a neighboring Cu^+ site has been proposed to be important in the copper-exchanged zeolites.[5]

In HSO_3F and magic acid, $HSO_3F{\cdot}SbF_5$ (1:1), $[CuNO]^{2+}$ is also formed from the Cu^0, Cu^I or Cu^{II} compounds under an NO atmosphere. $[CuNO]^{2+}$ exhibits higher ν(NO) values in HSO_3F (1933 (IR); 1936 (Raman) cm^{-1}) and magic acid (1946 (IR); 1950 (Raman) cm^{-1}) due to a decrease in the π back-bonding as observed for metal carbonyl cations in strong acids.[9–12] It is confirmed that no IR or Raman ν(NO) bands appear in the range of 1500–2200 cm^{-1} in the absence of Cu in these acids. $[CuNO]^{2+}$ is remarkably more stable in HSO_3F and magic acid than in concd. H_2SO_4; it remains unchanged even after a prolonged evacuation of 4 h.

The present study of the copper(II) nitrosyl cation, $[CuNO]^{2+}$, in strong acids suggests the possibility that a number of metal nitrosyl cations might be prepared and isolated using strong acids and superacids or with weakly coordinating anions. The present findings might enrich the understanding of the reaction mechanism of the direct decomposition of NO into N_2 and O_2 over copper-exchanged zeolites.

Experimental

The Cu^{II} nitrosyl cation is prepared using commercial reagents. Suspensions were formed in all the cases. Standard cannula transfer techniques were used for all sample manipulations for the spectroscopic measurements. The infrared spectra were obtained at 25 °C on thin films between two silicon disks on a Bio-rad FTS 6000 spectrometer. Raman spectra were recorded at 25 °C on liquid samples contained in a 5-mm o.d. NMR tube on a Nicolet FT-Raman 960 spectrometer. ESR spectra were recorded at 25 °C using a Bruker ESP 300e spectrometer. The gases were analyzed on a gas chromatograph (SHIMADZU GC-14B) with molecular sieve 13X (3 m) (carrier gas: He; column temperature: 50–180 °C (raising rate: 10 °C/min)).

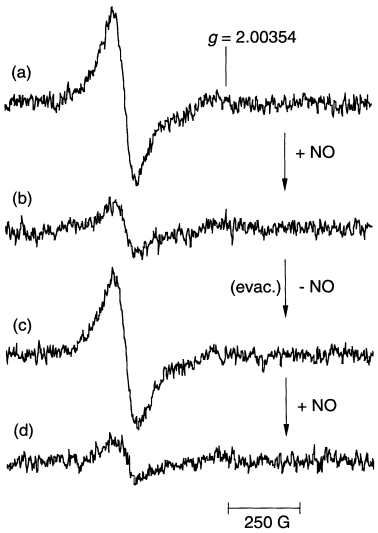

Fig. 2. ESR spectra of (a) the clear solution obtained by decanting and filtering the suspension of $CuSO_4$ in concd H_2SO_4; (b) after a 40-min reaction with NO following (a); (c) after a 30-min evacuation following (b); and (d) after a 2-h reaction with NO following (c).

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