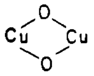
ranged from 1.77 μ_B at 290 K to 0.41 μ_B at 4.2 K. The molar magnetic susceptibility χ_M follows the Curie–Weiss law from room temperature (290 K) down to 100 K with values of 0.409 $cm^3\ mol^{-1}$ K and −13 K for the Curie and Weiss constants, respectively. The corrected molar magnetic susceptibility vs. temperature curve for **1** is indicative of antiferromagnetic exchange interaction with susceptibility maximum at 50 K. Furthermore, the increase in χ_M at the lowest temperatures is due to mononuclear impurities.

On the basis of the relatively sharp susceptibility maximum observed, a polymeric form could be excluded[10] and therefore the dimeric form seems to be the most probable one for **1**. In fact, this structure accounts well for the magnetic exchange interactions observed, which are further substantiated by suitable pathways. These pathways involve the orbital interactions (structure **4**) located on the $Cu{-}O\cdots Cu$ moieties, which actually favor the transmission of the electronic effects through intermolecular interactions. The contribution of intramolecular types of interactions to the overall magnetic behavior of **1**, if any, should be insignificant on the grounds of the EHMO calculations. Accordingly, the terephthalato bridging unit exhibits an unfavorable character to transmit the electronic effects over long distances owing to the very low electron density delocalization on the bridging unit of each magnetic orbital (structure **2**).

Finally, considering the interference of the superexchange interactions, it is expected that the 2*J* value of the $Cu{-}O\cdots Cu$ magnetic system will be about[11] one-fourth of the 2*J* value for the



magnetic systems. In fact, the calculated 2*J* value of $-51.8\ cm^{-1}$ for **1** is in the range of −35 to $-95\ cm^{-1}$, which corresponds to one-fourth of the 2*J* values observed for a number of magnetic systems with two oxygen atom bridging units.[12]

Supplementary Material Available: Table I, listing experimental magnetic susceptibility data (2 pages). Ordering information is given on any current masthead page.

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Reduction Potential of the Trinitrogen Radical As Determined by Chemical Kinetics: Novel Application of Spin Trapping

Sir:

Azide is easily oxidized in aqueous solution; its single-electron oxidation product, the trinitrogen radical (azidyl, N_3) is frequently encountered in radiation chemistry and photochemistry. However, the relationships between these two species are somewhat uncertain. The assignment of the CTTS band in the UV spectrum of N_3^-, which should link the energies of the two species, is controversial.[1] Photoelectron emission studies of N_3^- in solution have not really resolved the issue.[1d,e] The high-energy assignment of the CTTS band has been used to estimate the reduction potential of N_3 (1.87 V) and thereby to interpret the rates of fluorescence quenching of aromatic molecules[2] and aromatic ketones.[3] Electron-transfer quenching by N_3^- of nitrofurans,[4] flavins,[5] thionine,[5] and a variety of organic molecules[6] has also been interpreted by use of the CTTS band. Other estimates of the reduction potential of N_3 have ranged from 1.15[7] to 1.90 V.[8] Criteria to assign SET mechanisms to organic reactions of N_3^- rely on this poorly known potential.[9] In inorganic chemistry the radical has been implicated in photoredox studies of azido complexes[8] and in redox reactions of N_3^- with coordination complexes.[10] There appears to be only one report of simple kinetics for outer-sphere oxidation of N_3^-, and this used the strongly oxidizing species $[Ni(bpy)_3]^{3+}$.[11] Weaker oxidants such as $IrCl_6^{2-}$ gave complex and poorly understood kinetics.[7] This paper reports a reinvestigation of the reaction of $IrCl_6^{2-}$ with N_3^-, which leads to an accurate evaluation of the reduction potential for the N_3/N_3^- couple.

Qualitative studies of the reaction of excess N_3^- with $IrCl_6^{2-}$ (which yields N_2 quantitatively as determined by Toepler pumping) rapidly established that the kinetics was far from pseudo first order, consistent with prior observations.[7] Also consistent with prior observations was the observation that $IrCl_6^{3-}$ (the iridium-containing product)[7] strongly inhibited the kinetics. With excess N_3^- and $IrCl_6^{3-}$ the kinetics was pseudo second order, but the dependence on $[IrCl_6^{3-}]$ was complex. A detailed description of these observations and the overall mechanism will be presented later;[12] nevertheless, the first stages of the reaction can be represented by Scheme I.

Scheme I

$$IrCl_6^{2-} + N_3^- \rightleftarrows IrCl_6^{3-} + N_3 \quad k_f,\ k_r,\ K_{eq}$$

$$N_3,\ IrCl_6^{2-} \rightarrow \text{products}, \quad \text{slow}$$

Unusually complex kinetics arises because there is no efficient pathway for consumption of the azidyl radicals. Unlike in the oxidations of I^-, SCN^-, and $S_2O_3^{2-}$ where reaction of the free radical with the corresponding anion to form X_2^- is rapid and strongly driven.[7,13] N_3 exhibits little such tendency.[14] Dimerization of N_3 is diffusion-controlled,[15] but it is second order in $[N_3]$. NO_2 likewise has no efficient decay pathway, but in the oxidation of NO_2^- this is not a severe problem because k_r is relatively slow.[16]

Spin traps react efficiently with N_3, and the spin adduct with PBN (*N-tert*-butyl-α-phenylnitrone) has been observed by several research groups.[17] In the prior reports it was shown that PBN

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is stable in the presence of azide and that the spin adduct has a half-life of about 20 s.[17] We found that PBN was not oxidized by $IrCl_6^{2-}$. Clearly PBN was a good candidate as a scavenger of N_3 in the reaction of N_3^- with $IrCl_6^{2-}$.[18]

Stopped-flow kinetics studies were performed as previously described.[19] Reactions were performed at $\mu = 1.0$ M ($NaClO_4$), maintained at 25.0 °C, and monitored at 487 nm. Initial concentrations of $IrCl_6^{2-}$ were held at 1×10^{-4} M, while the concentrations of NaN_3 and PBN (Aldrich) were varied from 0.01 to 0.5 M and from 2.0×10^{-4} to 1.8×10^{-2} M, respectively. Under these conditions Ir(IV) decayed with excellent pseudo-first-order kinetics and at rates about 10-fold faster than in the absence of PBN. A first-order dependence on $[N_3^-]$ was found, but the kinetics was independent of the concentration of PBN, except for $[PBN] < 9 \times 10^{-4}$ M where the rates became one-half as fast. In mildly acidic media some retardation occurred as expected for protonation of N_3^-. Essentially identical results were obtained with DMPO as the spin trap. Thus by spin trapping, simple bimolecular kinetics was obtained with a rate constant of $(1.59 \pm 0.18) \times 10^2$ M^{-1} s^{-1}.

PBN's ability to clean up the kinetics indicates that it competes efficiently with $IrCl_6^{3-}$ for N_3; therefore, the rate-limiting step is k_f of Scheme I. The fate of the spin adduct, a nitroxyl radical, in unknown; however, di-*tert*-butylnitroxyl and TEMPO are instantly oxidized by $IrCl_6^{2-}$. This effect should lead to a doubling in the apparent rate constant.

Pulse radiolysis has been established as a useful method for generating transient populations of N_3; indeed, this method was used to measure the rate of oxidation of Fe^{2+} by N_3.[20] Experiments were performed as described previously[21] by monitoring the formation of $IrCl_6^{2-}$ at 487 or 434 nm. Dosimetry was performed by using the SCN^- method. Solutions of $Na_3IrCl_6 \cdot xH_2O$ and NaN_3 (0.01–0.1 M) were prepared at pH 6.5 and saturated with N_2O. Irradiation was accompanied by a prompt rise in absorbance, the magnitude of which was consistent with competition of $IrCl_6^{3-}$ and N_3^- for OH (which was generated both directly and by the reaction of N_2O with e_{aq}^-). On the microsecond time scale this was followed by a pseudo-first-order increase in absorbance, which accounted for complete reaction of N_3 with $IrCl_6^{3-}$ to form $IrCl_6^{2-}$. A first-order dependence on $[IrCl_6^{3-}]$ was found over the concentration range from 1.28×10^{-3} to 4.02×10^{-3} M, but the rate constants were independent of dose, wavelength, and $[N_3^-]$. These experiments lead to a value of $(5.5 \pm 0.6) \times 10^8$ M^{-1} s^{-1} for k_r in Scheme I. It is noteworthy that this rate constant is distinctly less than the diffusion-controlled value as this is in contrast with prior assumptions.[7]

Our measured values for $2k_f$ and k_r yield E_f for the azidyl radical. The ratio of k_f to k_r, K_{eq}, is $(1.45 \pm 0.23) \times 10^{-7}$; since E_f for $IrCl_6^{2-}$ at $\mu = 1.0$ M is 0.93 V,[22] the formal reduction potential for the N_3/N_3^- couple is 1.33 V. This potential is very close to that estimated previously on the basis of the proton affinity of N_3^-.[7]

Acknowledgment. This research was supported by the NSF (Grant CHE-8215501) and The Robert A. Welch Foundation. The experiments and analyses of the data produced in the pulse-radiolysis experiments were performed with the assistance of Steve Atherton at the Center for Fast Kinetics Research at the University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Branch of the Division of Research Resources of NIH (Grant RR00886) and by the University of Texas at Austin. We are grateful to Jim Espenson (Ames) for his continued interest and comments. Paul Engel of this department supplied samples of di-*tert*-butylnitroxyl and TEMPO and assisted with the Toepler pumping experiments.

Registry No. PBN, 3376-24-7; TEMPO, 2564-83-2; $IrCl_6^{2-}$, 16918-91-5; N_3, 12596-60-0; N_3^-, 14343-69-2.

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Articles

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Photochemistry of an Ozone Complex with Trifluoroiodomethane in Solid Argon. Infrared Spectra of CF_3IO, CF_3OI, and Two CF_2O--IF Complexes

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Codeposition of CF_3I and O_3 in excess argon on a CsI window at 17 K gave a CF_3I--O_3 molecular complex, which photodissociated upon irradiation at 470–1000 nm to yield CF_3IO. Further photolysis at 240–420 nm produced CF_3OI and two CF_2O--IF molecular complexes with a more stable structure for the CF_2O--IF complex preferred on sample annealing.

Introduction

Inorganic iodosyl compounds are considered to be polymeric in the solid state, as shown by the crystal structure of the sulfate $(IO)_2SO_4$,[1] but the vibrational spectrum of $IOSO_3CF_3$ provides evidence for a discrete IO unit.[2] Recently, monomolecular species of the type X–I–O (X = Cl, CH_3) have been prepared by photolysis of the XI--O_3 complex isolated in solid argon.[3,4] In the

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