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Copper-Mediated Oxygenation of Nitronate to Nitrite and Acetone in a Copper(I) Nitronate Complex

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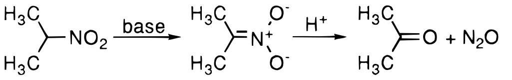
Introduction

Primary and secondary but not tertiary aliphatic nitro compounds can be transformed to aldehydes or ketones by treatment of their conjugate bases with sulfuric acid. This is called the Nef reaction and involves hydrolysis of the $C{=}N$ double bond (eq 1a).[2,3] There are several alternative methods for converting nitroalkanes to carbonyl compounds that give better yields and fewer side reactions. Such methods are the reaction of aliphatic nitro compounds with aqueous $TiCl_3$,[4] cetyltrimethylammonium permanganate,[5] tin complexes and $NaHSO_3$,[6] activated dry silica gel,[7] or 30% $H_2O_2-K_2CO_3$,[8] and the treatment of the conjugate base of the nitro compound with $KMnO_4$,[9] *t*-BuOOH and a catalyst,[10] ceric ammonium nitrate,[11] MoO_5−pyridine−HMPA,[12] ozone,[13] or singlet oxygen.[14]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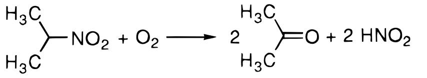
(1b)

In biological systems, the oxygenation of nitroalkanes—with the concomitant loss of nitrite—is facilitated by species formed upon oxygenation of flavoenzymes with molecular oxygen.[15] Glucose oxidase and D- and L-amino acid oxidase accept nitroalkane anions as substrates.[16] The mechanism of flavoenzyme-catalyzed oxidation of nitroalkanes has been established to involve an N(5)-adduct as an intermediate.[16,17] Electron-deficient flavins will also oxidize nitroalkane anions in model reactions.[18]

Extracts of *Neurospora crassa* and pea seedlings oxidatively degrade nitroethane and nitropropane,[19] and those from the hyphae of a nitrifying strain of *Aspergillus flavus* produce nitrite and nitrate from 3-nitropropionate.[20] 2-Nitropropane and some other nitroalkanes are oxidatively metabolized by an intracellular enzyme of *Hansenula mraki*.[21] It has been purified and characterized as 2-nitropropane dioxygenase presumably possessing iron ions in its active center.[22] The action of this enzyme can be best described as an intermolecular dioxygenation reaction (eq 1b).[23] In this report we describe preliminary results obtained from similar reactions using a copper(I) *aci*-2-nitropropanate complex.

Experimental Section

Preparation of $Cu((CH_3)_2CNO_2)(PPh_3)_2$. To a stirred solution of 2-nitropropane (356 mg, 4 mmol) in anhydrous acetonitrile (60 mL) were added copper(I) mesityl (732 mg, 4 mmol) and triphenylphosphine (2.096 g, 8 mmol) under argon. The mixture was stirred for 8 h, and a white precipitate formed, which was filtered off, washed with small amount of acetonitrile, and dried under vacuum. Recrystallization from ether give colorless diamagnetic crystals of $Cu((CH_3)_2CNO_2)(PPh_3)_2$ (2.32 g) in 86% yield based on initial quantities of Cu.

Characterization. Mp: 217−219 °C. IR (Nujol) [ν (cm^{-1})]: 1602, 1478, 1458, 1431, 1374, 1145, 1134, 1085, 1030, 1000, 938, 858, 755, 700, 502. UV−vis (CH_3CN) [λ_{max} (log ϵ)]: 214 nm (4.68), 226 (4.61), 265 (4.08).^{1}H NMR ($CDCl_3$) [ppm]: 1.94 (s, 6H, CH_3), 7.16−7.40 (m, 30H, ArH). ^{13}C NMR ($CDCl_3$) [ppm]: 133.9, 133.7, 133.5, 133.3, 133.2, 129.5, 128.5, 128.4, 23.0. ^{31}P NMR ($CDCl_3$) [ppm]: −2.66. Anal. Calcd for $C_{39}H_{36}NP_2O_2Cu$: C, 69.27; H, 5.36; N, 2.07. Found: C, 69.36; H, 5.41; N, 1.98.

Crystallography. Colorless crystals of $Cu((CH_3)_2CNO_2)(PPh_3)_2$ were obtained from ether. They form in the monoclinic crystal system, space group *C*2/*c*, in a unit cell of the dimensions listed in Table 1. Data were collected on a Siemens (Nicolet Syntex) R3m/V diffractometer, and the structure was solved by direct methods. Refinement converged with $R = 0.0555$ and $R_w(F^2) = 0.155$ for 3806 measured, 3216 independent ($R_{int} = 0.0220$), and 2606 observed reflections [$I > 2\sigma(I)$]. Positions for selected atoms of the structure are listed in Table 2.

Reaction of $Cu((CH_3)_2CNO_2)(PPh_3)_2$ with Dioxygen. A suspension of $Cu((CH_3)_2CNO_2)(PPh_3)_2$ (169 mg, 0.25 mmol) in anhydrous acetonitrile (10 mL) was stirred under dioxygen at room temperature. The uptake of dioxygen was measured manometrically. After 8 h 3.1 mL (0.127 mmol) of dioxygen was consumed. GLC analysis of the solvent shows the presence of acetone (9 mg, 62%). The solvent was

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Table 1. Crystallographic Data for Cu($(CH_3)_2CNO_2$)(PPh_3)$_2$

empirical formula	$C_{19.50}H_{18}Cu_{0.50}N_{0.50}OP$
fw	676.16
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	15.280(8)
b (Å)	9.804(7)
c (Å)	22.783(11)
β (deg)	101.15(4)
V (Å$^{3)}$	3349(3)
Z	4
T (K)	190
λ (Mo Kα) (Å)	0.710 73
D_{calcd} (Mg m^{-3})	1.341
μ (mm^{-1})	0.783
R_1	0.056
$R_w(F^2)$	0.155
GOF(F^2)	1.325

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Cu($(CH_3)_2CNO_2$)(PPh_3)$_2$

	x	*y*	*z*	U_{eq}[a]
Cu	5000	1970(1)	2500	23(1)
P(1)	5313(1)	2862(1)	3428(1)	21(1)
O(1)	4305(2)	101(2)	2571(1)	33(1)
N(1)	5000	−634(4)	2500	29(1)
C(1)	5000	−1947(5)	2500	39(1)
C(2)	5803(4)	−2667(4)	2384(2)	64(1)
C(3)	5670(2)	1629(3)	4029(1)	26(1)
C(4)	6253(2)	1950(4)	4565(2)	30(1)
C(5)	6485(2)	974(4)	5003(2)	38(1)
C(6)	6147(2)	−331(4)	4918(2)	38(1)
C(7)	5567(2)	−653(4)	4394(2)	35(1)
C(8)	5333(2)	317(3)	3952(1)	28(1)
C(9)	6198(2)	4129(3)	3552(1)	26(1)
C(10)	6127(2)	5397(4)	3810(2)	37(1)
C(11)	6809(3)	6339(4)	3857(2)	47(1)
C(12)	7563(3)	6031(4)	3644(2)	42(1)
C(13)	7656(2)	4776(4)	3399(2)	39(1)
C(14)	6982(2)	3827(4)	3355(2)	31(1)
C(15)	4363(2)	3690(3)	3656(1)	24(1)
C(16)	3682(2)	4158(3)	3210(2)	31(1)
C(17)	2928(2)	4752(4)	3345(2)	39(1)
C(18)	2852(3)	4895(4)	3928(2)	42(1)
C(19)	3530(3)	4451(4)	4384(2)	42(1)
C(20)	4281(4)	3846(4)	4252(2)	35(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

evaporated off in a vacuum, and the residue was recrystallized from ethanol to give colorless crystals of Cu(NO_2)(PPh_3)$_2$ (130 mg) in 82% yield.

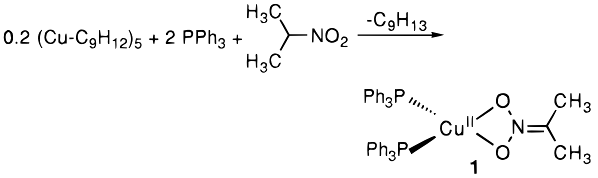
Characterization of Cu(NO_2)(PPh_3)$_2$. Mp 212−214 °C. IR (Nujol) [ν(cm^{-1})]: 1481, 1461, 1434, 1380, 1221, 1094, 1028, 1000, 854, 748, 693, 524, 505. UV−vis (CH_3CN) [λ_{max} (log ϵ)]: 214 nm (4.73), 263 (4.26). ^{1}H NMR ($CDCl_3$) [ppm]: 7.20−7.72 (m, ArH). ^{13}C NMR ($CDCl_3$) [ppm]: 133.7, 132.1, 132.0, 129.9, 128.6. ^{31}P NMR ($CDCl_3$) [ppm]: −1.75. Anal. Calcd for $C_{36}H_{30}NO_2P_2Cu$: C, 68.18; H, 4.76; N, 2.20. Found: C, 68.10; H, 4.64; N, 2.15.

$^{18}O_2$ Labeling Experiments. A suspension of Cu($(CH_3)_2CNO_2$)(PPh_3)$_2$ (169 mg, 0.25 mmol) in anhydrous acetonitrile (10 mL) was stirred under a mixture of $^{18}O_2$ and $^{16}O_2$ (60%:40%) at room temperature. After the reactants had stirred for 8 h, GC−MS and IR analysis of the solution showed the presence of ^{18}O- and ^{16}O-acetone.

Kinetic Measurements. Standard volumetric methods were used in the kinetic measurements. Pyridine was placed under dioxygen in a thermostated reaction vessel, connected to a thermostated gas buret and stirred until saturated. The consumption of dioxygen was measured after adding and dissolving the Cu($(CH_3)_2CNO_2$)(PPh_3)$_2$ complex at 18.5 °C and constant O_2 pressure. The log[Cu($(CH_3)_2CNO_2$)(PPh_3)$_2$] vs time plots gave straight lines with pseudo-first-order rate constants k_{obs}. With various O_2 pressures the k_{obs} vs [O_2] plots resulted also in straight lines.

Results and Discussion

Our studies on the activation of dioxygen[24] and on model systems mimicking dioxygenases[25] and the fact that nitronate salts of nonredox metals can be converted to nitro compounds and carbonyls with singlet oxygen inspired us to prepare nitronato copper complexes, possessing a redox-active metal ion, and oxygenate it with triplet dioxygen. Nitroalkanes are known to exhibit tautomerism to yield nitronic acids and equilibria lay well on the side of the latter.[26] Deprotonation of both tautomers leads to nitronate ions. Mesitylcopper(I)[27] reacts with 2-nitropropane and triphenylphosphine in anhydrous acetonitrile under an atmosphere of argon at room temperature (eq 2). After 8 h a white precipitate formed which was filtered, dried, and crystallized from ether to give colorless crystals of the copper(I) *aci*-2-nitropropanate complex Cu($C_3H_6NO_2$)(PPh_3)$_2$ (**1**). This complex is moderately soluble in polar organic solvents, and its solutions are not very sensitive toward oxygen due to the facts that the PPh_3 stabilizes the copper in the 1+ oxidation state and that the coordinated nitronato ligand is not susceptible to oxidation. Characteristic NMR features of complex **1** in $CDCl_3$ solution include a single CH_3 resonance downfield shifted by 0.4 ppm from the free 2-nitropropane and a multiplet resonance of the aromatic protons of the phosphine ligands in the ^{1}H NMR, downfield shifts of coordinated nitronato carbons in the ^{13}C NMR together with a single peak in the ^{31}P NMR spectrum, and intense sharp IR bands assigned to ν(C=N) at 1602, ν_{as}(NO_2) at 1145 and 1134, and ν_s(NO_2) at 938 cm^{-1}. Single-crystal X-ray analysis of compound **1** revealed a distorted tetrahedral geometry around copper(I) with a Cu−O distance of 2.139(3) Å and a Cu−P distance of 2.2510(13) Å with a 2-fold axis through Cu and N(1) (Figure 1). The atoms O(1) and O(1A) form strong bonds with the copper atom having short bond distances and consequently the O(1)−N−O(1A) angle is rather small. The *aci*-2-nitropropanate ion is planar and the observed C−N distance is somewhat shorter than those found by bis(propane-2-nitronato)copper(II)[28] (1.34(4), 1.35(4) Å) and in α-nitro-α-*aci*-nitrotoluenebis(triphenylphosphine)copper(I)[29] (1.36(1) Å) and lie between those for oximes (1.26−1.31 Å)[30] and for nitro compounds (1.46−1.55 Å).[31] It seems likely that these bonds have appreciable double bond character. A comparison of the N−O distance with those of oximes (1.36−1.42 Å)[30] and of nitro compounds (1.22−



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(2)

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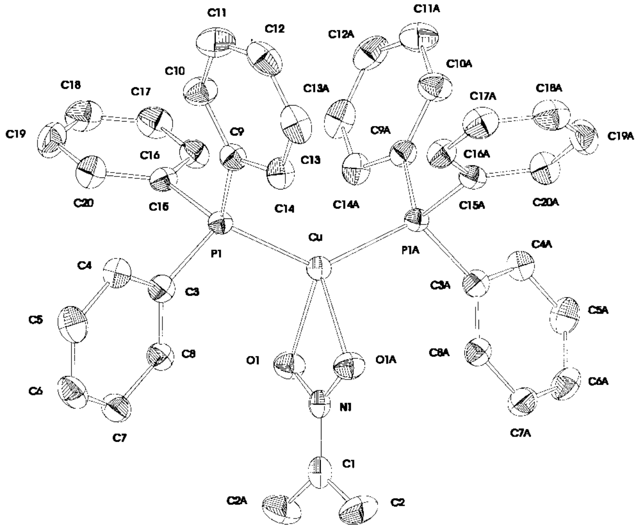
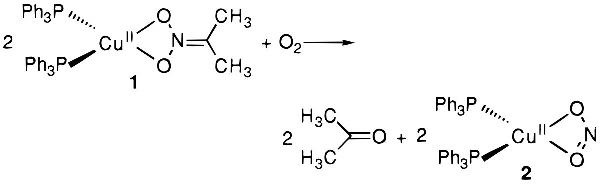


Figure 1. View showing the structure of $Cu(C_3H_6NO_2)(PPh_3)_2$. Important bond distances (Å) and angles (deg): Cu−O(1), 2.139(3); Cu−O(1A), 2.139(3); Cu−P(1), 2.2510(13); Cu−P(1A), 2.2510(13); N(1)−O(1), 1.319(3); N(1)−O(1A), 1.319(3); N(1)−C(1), 1.287(7); C(1)−C(2), 1.483(5); O(1)−Cu−O(1A), 62.17(13); O(1)−Cu−P(1), 106.28(7); O(1)−Cu−P(1A), 112.63(7); P(1)−Cu−P(1A), 134.31(6); O(1)−N(1)−O(1A), 113.7(4).

1.25 Å)[31] indicates that the bonds between the nitrogen and oxygen atoms in complex **1** are basically single.

Motivated by our original goal to oxygenate a nitronato redox-metal complex we investigated the reactivity of **1** toward dioxygen. A slurry of $Cu(C_3H_6NO_2)(PPh_3)_2$ (**1**) in acetonitrile reacts with dioxygen slowly in a 2:1 stoichiometry with the concomitant formation of $Cu(NO_2)(PPh_3)_2$ (**2**) and acetone (eq 3). When oxygenated 0.25 mmol of **1** took up 3.1 mL of O_2 at 23 °C (stoichiometry 2:1) during 8 h, then the reaction was stopped to avoid unwanted oxidation of Cu(I). The presence of acetone was proved and quantified by GC−MS (yield 62%), and after evaporation of the solvent and recrystallization from ethanol pure, colorless crystals of **2** in 82% yield were obtained. The diamagnetic compound exhibits simple NMR spectroscopic features showing only signals characteristic for PPh_3 in the ^1H, ^{13}C, and ^{31}P NMR spectra and $\nu(NO_2)$ bands in IR due to coordinated nitrito ligand. Single-crystal X-ray analysis data of the complex **2** was identical to those found earlier.[32]

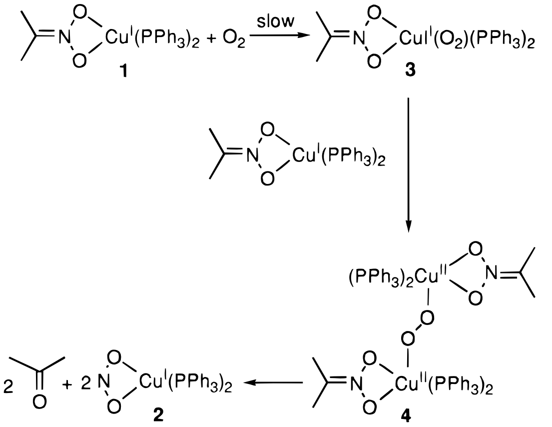


(3)

$^{18}O_2$ labeling experiments of the oxygenation of **1** were carried out with a mixture of $^{18}O_2$ and $^{16}O_2$ (60%:40%). After the reactants had stirred at 25 °C in CH_3CN suspension for 8 h GC−MS analysis of the solution showed the presence of ^{18}O- and ^{16}O-acetone. The ^{18}O-acetone gave a molecular ion at *m*/*z* 60 with a base peak at *m*/*z* 45, indicating the incorporation of ^{18}O atom into the nitropropane moiety. The relative abundance of *m*/*z* 45 (100) and *m*/*z* 43 (61) parallels the $^{18}O_2$ enrichment used. In the IR spectra of the acetone formed peaks to $\nu(C^{16}O)$ (1714 cm^{-1}) and $\nu(C^{18}O)$ (1684 cm^{-1}) and no new bands in that of **2** due to $\nu(N^{18}O^{16}O)$ or $\nu(N^{18}O^{18}O)$ were found showing that $^{18}O_2$ has been incorporated only into acetone.

Kinetic measurements on the oxygenation of **1** in pyridine solution (reasonable solubility in other solvents could not be found) under ambient conditions (18.5 °C, 1 bar O_2 pressure) were shown to be first order with respect to **1** and dioxygen with a second-order rate constant of k_2 (M^{-1} s^{-1}) = 2.48×10^{-2}.

The *aci*-2-nitropropanato anion is inactive against $^3O_2$[14] but the Cu(I) is redox-active in complex **1**, even in the presence of strong Cu(I)-stabilizing ligand such as PPh_3.[25,34] The rate-limiting reaction step seems to be the interaction of dioxygen with **1** leading to a superoxocopper(II) complex **3**, as found in the case of many other copper(I) complexes,[35] and finally to an intermolecular peroxidic species **4**. A fast breakdown of **4** may result in the copper nitrite complex and acetone (eq 4).



(4)

Labeling with $^{18}O_2$ and the stoichiometry of the oxygenation reaction gives unequivocal evidence for the incorporation of both oxygen atoms of O_2 into two substrate molecules reminiscent of intermolecular dioxygenase.[36]

On the basis of the stoichiometry, kinetics, and labeling experiments on reaction 3, the mechanism shown in eq 4 can be proposed. The copper-assisted intermolecular oxygenation of the C═N double bond of the coordinated *aci*-2-nitropropanato ligand with triplet dioxygen may indicate that the presence of copper(I) is essential in the activation of triplet dioxygen, and the reduced oxygen species is ready for oxidative splitting of the C═N double bond.

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Supporting Information Available: Stoichiometry and kinetics of dioxygen uptake, spectral characterization for new compounds, and details of the X-ray structure determination (13 pages). Ordering information is given on any current masthead page.

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