Communications to the Editor

Spectroscopic Detection of Two Neutral [CHNO$_2$] Isomers: Nitrocarbene and Nitrosoformaldehyde

P. E. O'Bannon, Detlev Sülzle, William P. Dailey,[1] and Helmut Schwarz*

Institut für Organische Chemie
Technische Universität Berlin, Strasse des 17 Juni 135
1000 Berlin 12, Federal Republic of Germany
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

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There are several interesting [C,H,N,O$_2$] isomers. We have reported a computational study of nitrocarbene (**1**) and nitrosoformaldehyde (**2**).[2] Extensive calculations have also been reported for several other [C,H,N,O$_2$] isomers.[3]

There is a dearth of experimental data regarding the [C,H,N,O$_2$] isomers. We have presented indirect evidence that nitrocarbene rearranges to nitrosoformaldehyde in solution;[4] otherwise, there is no experimental data on nitrocarbenes. The solution chemistry of acyl nitroso compounds, however, has been well studied.[5] Still, all attempts to date to spectroscopically detect these species have failed.

Here, we present charge-reversal[6] and neutralization–reionization mass spectra (NRMS)[7] for two isomeric [C,H,N,O$_2$] anions. The NRMS data indicate that both nitrocarbene and nitrosoformaldehyde are clearly distinguishable on the time scale of the experimentally stable neutral molecules.

Since rearrangement processes are of minor importance in radical anions,[8] we have chosen structurally well defined precursors for generating the two isomeric [C,H,N,O$_2$]$^{\bullet+}$ ions. Anions with $m/z = 59$ were generated in the source of a modified VG-ZAB tandem mass spectrometer of BEBE configuration[9] by 70-eV electron impact of ethyl nitrodiazoacetate[10] in the presence of ammonia as a moderator gas. The charge-reversal (CR) mass spectrum of $m/z = 59$ is shown in Figure 1a. The neutralization–reionization mass spectrum is shown in Figure 1b. The presence of a weak recovery signal at $m/z = 59$ in the NRMS is proof that [C,H,N,O$_2$] does exist as a stable neutral molecule in the dilute gas phase for at least 0.5 μs.

Heating the Diels–Alder adduct of nitrosoformaldehyde and 9,10-dimethylanthracene[4] to 80 °C in the source of the mass spectrometer under similar conditions yielded an intense signal at $m/z = 59$. The CR mass spectrum is shown in Figure 2a, and the NR mass spectrum is shown in Figure 2b. Here too, a recovery signal at $m/z = 59$ is observed.

The four spectra are similar, yet telltale peaks indicate two distinctly different species. In Figure 1a,b there are signals at $m/z = 46$ and 43. These peaks are absent in Figure 2a,b. The peak at $m/z = 46$ can *only* be assigned to NO$_2^+$ and strongly suggests the presence of an intact nitro (or nitrito) group in the parent ion.[11] The peak at $m/z = 43$ can only be assigned to [H,C,N,O]$^+$ and indicates that these atoms are connected in the parent ion. These signals are most compatible with a nitrocarbene or a nitritocarbene connectivity. The presence of signals at $m/z = 26$ and 27 (CN and HCN) are inconsistent with a nitritocarbene connectivity.

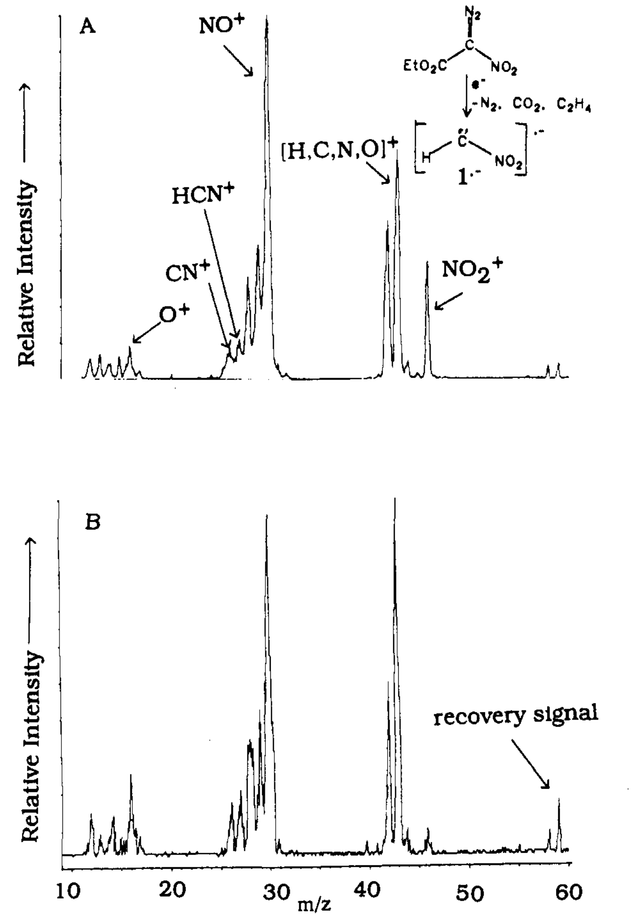

Figure 1. Charge-reversal (CR) spectrum of [C,H,N,O$_2$]$^{\bullet -}$ generated from ethyl nitrodiazoacetate in the presence of NH$_3$ (oxygen, 80% transmission (T)) (a); neutralization–reionization (NR) mass spectrum of [C,H,N,O$_2$]$^{\bullet -}$ (oxygen, 80% T//oxygen, 80% T) (b).

The peak at $m/z = 46$ is much weaker in the NR spectrum (Figure 1b) relative to the CR spectrum (Figure 1a). It appears that the peak at $m/z = 43$ has increased at the expense of the $m/z = 46$ peak. The fragmentation of the parent ion to [H,C,N,O]$^+$ and O is thermodynamically favored over the fragmentation to NO$_2^+$ and CH by 50 kcal/mol.[12] The charge-reversal process generates highly energetic ions,[13] and it may be that more product from the higher energy fragmentation pathway (NO$_2^+$ formation) is observed in the CR spectrum. Also, fragmentation of the neutral [CHNO$_2$] to neutral HCNO and O is thermodynamically favored over fragmentation to neutral CH and NO$_2$ by 40 kcal/mol.[12]

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*Author to whom correspondence should be addressed at the Technische Universität Berlin.

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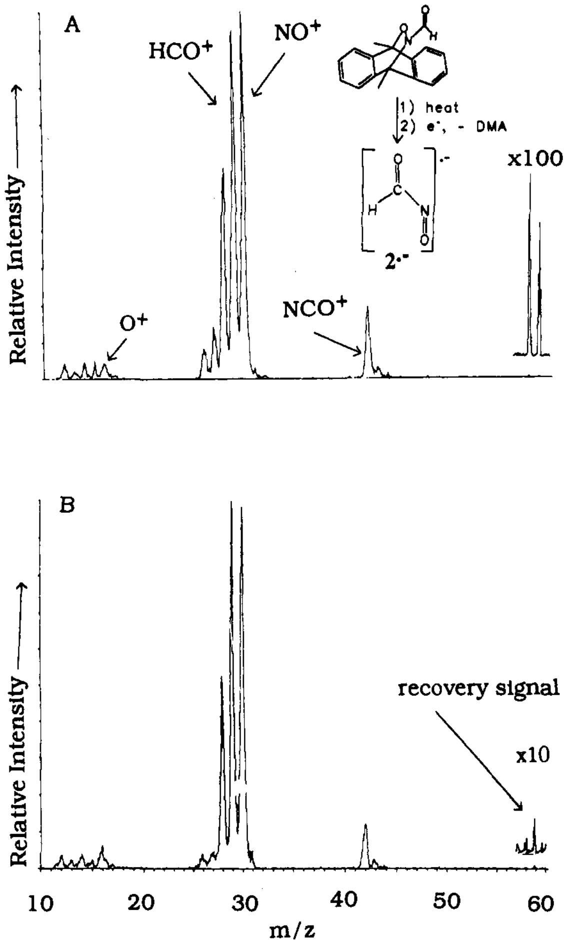

Figure 2. CR spectrum of $[C,H,N,O_2]^{\bullet-}$ generated by heating the Diels–Alder adduct of nitrosoformaldehyde with 9,10-dimethylanthracene, followed by electron impact ionization in the presence of NH_3 (a); NR mass spectrum of $[C,H,N,O_2]^{\bullet-}$ (b).

In the present experiment, we cannot address the multiplicity of nitrocarbene. Triplet nitrocarbene has a calculated [ROHF-(D95**)] energy of −242.438 20 au. Singlet nitrocarbene has a calculated [TCSCF(D95**)] energy of −242.434 22 au. The barrier for the rearrangement of singlet nitrocarbene to nitrosoformaldehyde is calculated to be less than 1 kcal/mol.[2] Thus, our experiments suggest that it is the triplet species of **1** which is generated in the electron detachment of $\mathbf{1}^{\bullet-}$.[14]

Figures 2a and 2b are very similar. The abundant signal at $m/z = 29$ is most informative, since it is relatively weak in Figure 1a,b. The intense peaks at $m/z = 30$, 29, and 28 account for the bulk of the signals from this isomer. These signals are best accommodated by the nitrosoformaldehyde (**2**) structure, because simple cleavage of the CN single bond will give rise to the signals at $m/z = 30$ (NO^+) and 29 (HCO^+).

In summary, we have provided the first direct spectroscopic measurements of the neutral molecules nitrocarbene (**1**) and nitrosoformaldehyde (**2**).

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Registry No. 1, 19527-13-0; **2**, 5187-67-7; ethyl nitrodiazoacetate, 1572-59-4; 9,10-dihydro-9,10-dimethyl-10,9-(epoxyimino)anthracene-12-carboxaldehyde, 120290-28-0.

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[14] As suggested by a reviewer, the formation of *singlet* nitrocarbene cannot be ruled out in the electron detachment from $[HCNO_2]^{\bullet-}$. The so-formed $[HCNO_2]$ will undergo isomerization to [HC(O)NO] (**2**), followed by rapid dissociation. This sequence would also explain the decreased intensity of the reionized NO_2^+ signal in Figure 1b.

A Polyoxometalate Incorporating an Organoimido Ligand: Preparation and Structure of $[Mo_5O_{18}(MoNC_6H_4CH_3)]^{2-}$

Yuhua Du,[†] Arnold L. Rheingold,[‡] and Eric A. Maatta*[,†]

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506
Department of Chemistry, University of Delaware
Newark, Delaware 19716

Received August 30, 1991

A flourishing subdiscipline of the burgeoning field of polyoxometalate chemistry involves the derivatization of polyoxometalate frameworks by incorporation of organic and organometallic fragments.[1] The resulting species are often of interest as models for catalytic processes employing metal oxides. In conjunction with our ongoing studies directed at modeling ammoxidation chemistry,[2] we sought to prepare an imido derivative of a polyoxometalate system since imido species have been invoked as key surface intermediates in postulated ammoxidation mechanisms.[3] We report the achievement of this goal through the synthesis and X-ray structural determination of a *p*-tolylimido derivative of the $[Mo_6O_{19}]^{2-}$ system, namely, $[(n\text{-}Bu)_4N]_2[Mo_5O_{18}(MoNC_6H_4CH_3)]$ (**1**). Of particular importance is the fact that, unlike preparations of other $[(L_nM)Mo_5O_{18}]^{x-}$ systems[4,5] which rely on cluster assembly reactions, the synthesis of **1** is achieved *directly* from the hexamolybdate salt itself.

The reaction of equimolar amounts of $[(n\text{-}Bu)_4N]_2[Mo_6O_{19}]$[6] and $Ph_3P{=}Ntol$ (prepared from the reaction of *p*-tolyl azide and Ph_3P in ether) in strictly anhydrous pyridine at 85 °C proceeds as shown in eq 1. Complete conversion to the bright orange

$$[(n\text{-}Bu)_4N]_2[Mo_6O_{19}] + Ph_3P{=}Ntol \rightarrow \underset{\mathbf{1}}{[(n\text{-}Bu)_4N]_2[Mo_5O_{18}(MoNtol)]} + Ph_3P{=}O \quad (1)$$

tolylimido derivative is achieved within 48 h as determined by ^1H NMR monitoring. Separation of $Ph_3P{=}O$ is achieved by first precipitating **1** by addition of benzene, then dissolving the crude product in CH_3CN, and reprecipitating by addition of Et_2O. Crystals of **1** are readily grown by slow diffusion of Et_2O into a CH_3CN solution.[7] **1** is reasonably stable in air as a solid, but undergoes hydrolysis in solution to produce *p*-toluidine and the hexamolybdate salt. The IR spectrum of **1** closely resembles that of its hexamolybdate parent, except for the appearance of a strong, sharp absorption at 980 cm⁻¹; while this feature *may* derive from the molybdenum–nitrogen stretching vibration, such assignments

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[†] Kansas State University.

[‡] University of Delaware.

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[7] Anal. Calcd for $C_{39}H_{79}N_3O_{18}Mo_6$: C, 32.22; H, 5.48; N, 2.89. Found: C, 32.05; H, 5.33; N, 2.76. ^1H NMR (C_5D_5N, 23 °C): δ 7.22, 7.21, 6.95, 6.94 (AA′BB′ "quartet", C_6H_4, 4 H), 3.45 (m, CH_2, 16 H), 2.14 (s, $C_6H_4CH_3$, 3 H), 1.78 (m, CH_2, 16 H), 1.44 (m, CH_2, 16 H), 0.93 (m, CH_3, 24 H). ^{13}C NMR (CD_3CN, 23 °C): δ 140.1 (C_{ipso}), 131.3 (C_{para}), 130.1 (C_{ortho}), 126.8 (C_{meta}), 59.3 (NCH_2), 24.4 (CH_2), 21.3 ($C_6H_4CH_3$), 20.3 (CH_2), 13.9 (CH_2CH_3). Electronic spectrum (200–850 nm; CH_3CN): 348 (log ε = 4.3), 244 (log ε = 4.6), 223 (log ε = 4.5) nm. IR (Nujol mull): 980 (s), 959 (s), 885 (m), 790 (br, s), 590 (br, m), 440 (br, s) cm⁻¹.

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