193. Characterization of Nitrosocarbonyl Compounds by Neutralization-Reionization Mass Spectrometry

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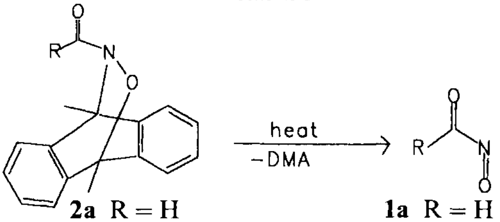
The neutral molecules nitrosoformaldehyde (**1a**), 1-nitrosoacetaldehyde (**1b**), and 2,2,2-trifluoro-1-nitrosoacetaldehyde (**1c**) have been generated and detected by neutralization-reionization mass spectrometry (NR-MS).

Introduction. – Nitrosocarbonyl compounds **1** are a class of reactive intermediates that have been known for nearly 30 years. In 1962, *Beckwith* and *Evans* first postulated that these species are formed in the thermal decomposition of alkyl nitrites [1], although 1-nitrosobenzaldehyde (**1d**) probably was first generated in 1926 by the oxidation of benzohydroxamic acid by bromine-water [2]. In recent years, *Kirby* has thoroughly studied the chemistry of these compounds [3]. Typically, these species are generated by the periodate oxidation of hydroxamic acids and are trapped *in situ* by H_2O, alcohols, dienes, and alkenes. Alternatively, the 9,10-dimethylanthracene (DMA) derivatives **2** serve as mild sources of nitrosocarbonyl compounds, for they undergo a *retro-Diels-Alder* reaction at moderate temperatures, liberating the nitrosocarbonyl moiety. These species undergo rapid inter- and intramolecular *Diels-Alder* and ene reactions. *Keck et al.* used these reactions in the synthesis of natural products [4].

Scheme 1



2a R = H
b R = CH_3
c R = CF_3

1a R = H
b R = CH_3
c R = CF_3
d R = Ph

Although *Napier* and *Norrish* have presented UV data that nitrosoformaldehyde (**1a**) is formed as a transient in the pyrolyses of simple aldehydes with methyl nitrite [5], concrete *spectroscopic* detection of these well studied intermediates is still lacking. Even using a combination of flash-vacuum-pyrolysis techniques with microwave [6] or IR spectroscopy [7], the isolated species could not be detected. Moreover, nitrodiazo compounds have been shown to be good precursors to nitrosocarbonyl compounds [8], yet irradiation of isolated nitro(trifluoromethyl)diazomethane in an Ar matrix at 12 K afforded only CF_3NO and CO (by IR spectroscopy) [9]. Thus, even this very powerful technique [10] for the detection of reactive intermediates does not lend itself to the study of nitrosocarbonyl compounds.

Here, we describe the spectroscopic detection of three prototypical nitrosocarbonyl compounds: nitrosoformaldehyde (**1a**), 1-nitrosoacetaldehyde (**1b**), and 2,2,2-trifluoro-1-nitrosoacetaldehyde (**1c**). The technique we used is neutralization-reionization (NR) mass spectrometry [11].

NR-MS has been proven to be an extremely sensitive method for the detection of reactive neutral species. In work from our group and others, NR-MS has been used for the detection of cumulenes [12], unsaturated silicon and aluminum species [13], and long sought after elusive organic molecules1).

In the NR-MS experiment a beam of positive or negative ions with a given mass is generated and mass-selected within a mass spectrometer and directed through a collision cell containing a gas (in this case, O_2). An electron is transferred, neutralizing the ion. The beam of neutrals and fragment ions pass an electrode, and all the charged species are deflected. The beam of neutrals are then ionized on collision with a gas in a second chamber and detected with a second mass spectrometer. The time of flight from the neutralization chamber to the reionization chamber is *ca.* 0.5 μs. The presence of a recovery signal indicates that the parent neutral species does exist. Structural information is obtained by comparing the fragmentation pattern of the NR-MS with a collisional activation (CA) mass spectrum [15] or a charge reversal (CR) mass spectrum [16] of the parent ion.

Results and Discussion. – Since 9,10-dimethylanthracene (DMA) adducts **2** are excellent sources of nitrosocarbonyl compounds in solution, we reasoned that they should also serve us well for our gas-phase experiments. Heating adducts **2** in the source of a modified four-sector mass spectrometer of BEBE (B: magnetic sector; E: electrostatic sector) configuration2) in the positive-ion mode did not give rise to the desired radical cations. In the negative-ion mode, however, using ammonia or dinitrogen oxide as a moderator gas, intense signals were observed at *m/z* 206 $(DMA)^{\cdot -}$ and for **1a** at *m/z* 59 $(C,H,N,O_2)^{\cdot -}$; for **1b** at *m/z* 73 $(C_2,H_3,N,O_2)^{\cdot -}$; for **1c** at *m/z* 127 $(C_2,F_3,N,O_2)^{\cdot -}$.

The ions of interest were mass-selected with the first two sectors and their charge-reversal (CR) mass spectra recorded by scanning B(2). These spectra are reproduced in *Figs. 1a, 2a,* and *3a*. There is no doubt that the species we have isolated have the assigned atomic composition. Since the precursors to the radical anions are well characterized, and since rearrangement processes in radical anions are of minor importance [18], we are confident that these signals arise from the radical anions of nitrosocarbonyl compounds **1a–c**. Moreover, in a preliminary communication [19], we have presented the CR-MS and NR-MS of nitrosoformaldehyde (**1a**) and its isomer, nitrocarbene. The two isomers yield distinctly different spectra, indicating that the two radical anions and their neutral counterparts do not interconvert. Using simple connectivity arguments, we were able to rule out a major contribution from other (C,H,N,O_2) isomers.

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1) Cyclobutadiene: [14a]; methylideneoxirane: [14b]; thiofulminic acid: [14c].

2) For a description of the machine, see [17].

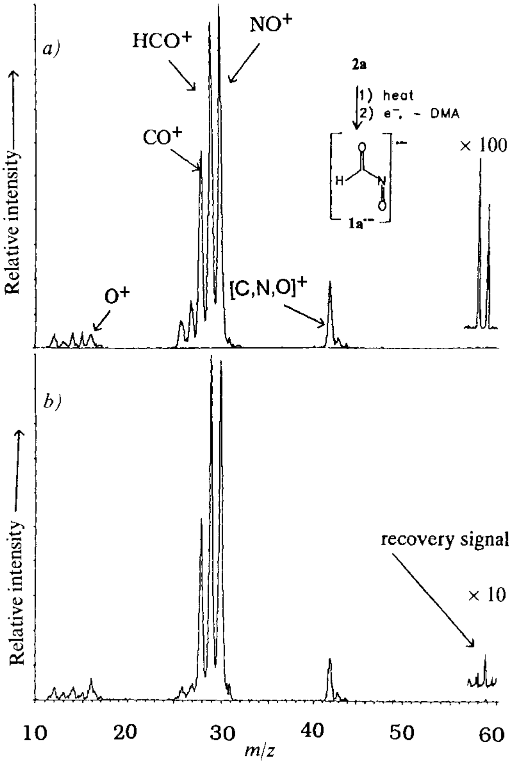


Fig. 1. a) *CR Mass spectrum of* $[C,H,N,O_2]^{\cdot-}$ *generated by heating the* Diels-Alder *adduct* **2a** *of nitrosoformaldehyde with 9,10-dimethylanthracene, followed by electron-impact ionization in the presence of* NH_3 (O_2, 80% transmission (T)). b) *NR Mass spectrum of* $[C,H,N,O_2]^{\cdot-}$ (O_2, 80% T/O_2, 80% T).

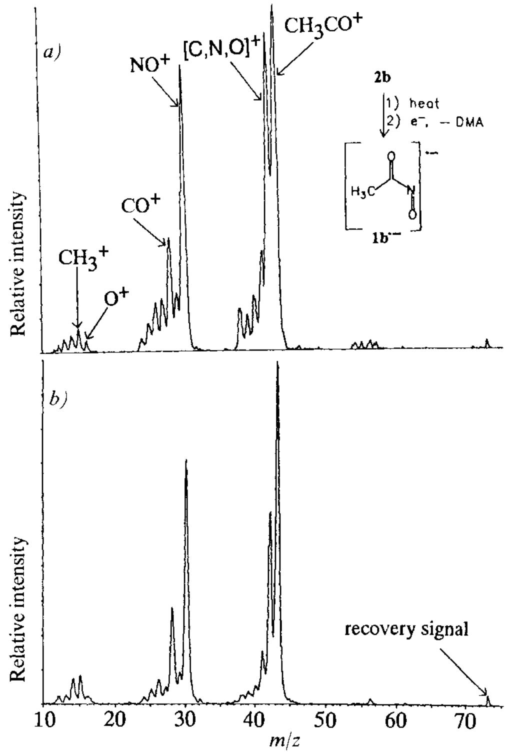


Fig. 2. a) *CR Mass spectrum of* $[C_2,H_3,N,O_2]^{\cdot-}$ *generated from* Diels-Alder *adduct* **2b** *in the presence of* NH_3 (O_2, 80% transmission (T)). *b) NR Mass spectrum of* $[C_2,H_3,N,O_2]^{\cdot-}$ (O_2, 80% T/O_2, 80% T).

The NR mass spectra of $\mathbf{1a}^{\cdot-}$, $\mathbf{1b}^{\cdot-}$, and $\mathbf{1c}^{\cdot-}$ are shown in *Figs. 1b, 2b*, and *3b*. The NR and CR mass spectra for all three species are quite similar. Small differences in NR and CR spectra are not uncommon, for the CR-MS experiment is a one-collision process and the NR-MS experiment is a two-collision process, separated in space and time. In NR-MS experiments the additional possibility exists that the parent neutral decomposes to neutral fragments. Reionization of the neutral fragments is often the source of discrepancy between NR and CR spectra.

Poorer intensities are also observed in NR mass spectra relative to CA or CR mass spectra. Nevertheless, the presence of distinct, albeit weak, recovery signals indicates that these three species **1a–c** are indeed stable molecules in the dilute gas phase.

The dominant signals in all of the spectra arise from the cleavage of single bonds in the nitrosocarbonyl moiety (*Scheme 2*).

All three molecules fragment to give rise to strong signals at *m/z* 42 (C, N, O)$^+$, *m/z* 30 (NO^+), and *m/z* 28 (CO^+). The acylium ions RCO^+ are present in strong intensities for **1a**

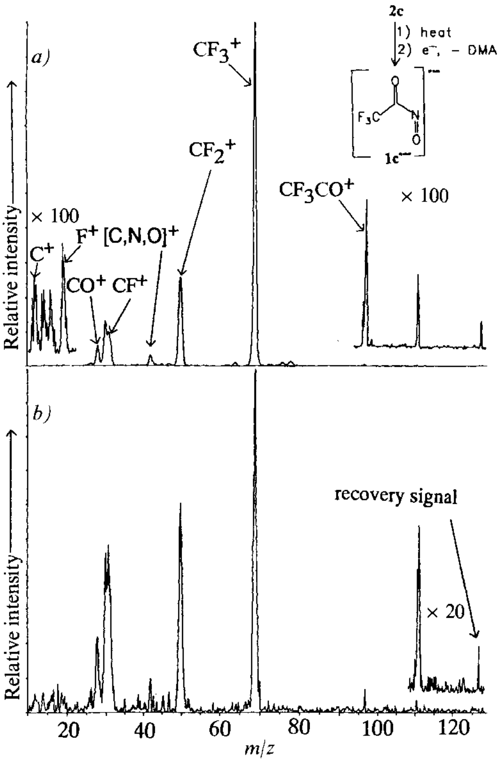
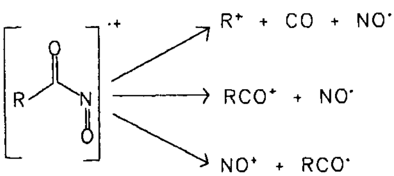


Fig. 3. a) *CR Mass spectrum of* $[C_2,F_3,N,O_2]^{\bullet-}$ *generated from* Diels-Alder *adduct* **2c** *in the presence of* N_2O (O_2, 80% transmission (T)). b) *NR Mass spectrum of* $[C_2,F_3,N,O_2]^{\bullet-}$ (O_2, 80% T/O_2, 80% T).

(HCO^+, *m/z* 29) and **1b** (CH_3CO^+; *m/z* 43). In the spectra for **1c**, however, CF_3CO^+ (*m/z* 96) is very weak. In fact, the spectra for **1c** (*Fig. 3a* and *b*) are dominated by the stable fluorinated cations CF_3^+ (*m/z* 69), CF_2^+ (*m/z* 50), and CF^+ (*m/z* 31). The fragmentation of positive ions containing a CF_3 or a CF_3CO group to give CF_3^+ as the base peak is common [20].

Scheme 2



In summary, we have shown that compounds **2** are good precursors to the radical anions of three prototypical nitrosocarbonyl compounds **1a–c**. NR-MS experiments show that the neutral nitrosocarbonyl compounds are stable molecules in the dilute gas phase.

Experimental. – Compounds **2a–c** were prepared as described in [21]. The MS experiments were carried out using standard techniques (see text).

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