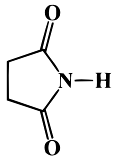
JOURNAL OF MASS SPECTROMETRY, VOL. 32, 1137–1139 (1997)

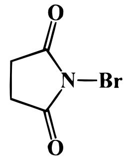
JMS Letters

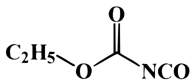
Dear Sir,

On the Structure of the *m/z* 70 Ions from *N*-H- and *N*-Br-succinimide: O=C=N=C=O$^+$?

In the course of an investigation on the gas phase chemistry of the heterocumulene ion O=C=N$^+$=C=O (**1**) and its isomer O=C=C=N$^+$=O (**2**),[1] we were looking for appropriate precursors of **1**. Schwarz and coworkers,[2] when applying high-energy CID, NRMS and charge-reversed MS for the structural characterization of $C_2NO_2^+$ heterocumulene ions, concluded that *N*-H-succinimide produces **1** as the main 70 eV EI fragment ion of *m/z* 70. However, this ion is of quite moderate abundance, which led us to consider *N*-Br-succinimide and ethoxycarbonyl isocyanate[3] (see below) as possible and more adequate precursors of **1**. Both these precursors produce more intense *m/z* 70 ions on 70 eV EI and display structures with the correct OCNCO connectivity.







We have recently demonstrated[1] by low-energy CID, high-level *ab initio* calculations and structurally diagnostic ion/molecule reactions performed via multi-stage pentaquadrupole mass spectrometry[4–6] that **1** is indeed the major *m/z* 70 fragment ion of ethoxycarbonyl isocyanate. Low-energy collisions (5–50 eV) with argon induce dissociation of **1** [Fig. 1(a)] exclusively to *m/z* 42 (CO loss), whereas the isomeric **2** dissociates under the same conditions mainly to ions of *m/z* 54, 42 and 30.[1] Ion **1** is also the main constituent of the *m/z* 70 population from *N*-H-succinimide, as indicated by its low-energy CID spectrum [Fig. 1(b)]. The *m/z* 70 ion of *N*-Br-succinimide, however, behaves quite differently on low-energy collisions. At lower collision energies (less than 30 eV) it dissociates to a set of fragment ions of *m/z* 42, 43 and 44 [Fig. 1(c)]. The fragment ions of *m/z* 43 and 44 are of course not in accordance with structure **1**. A drastic drop in intensity is noted for the *m/z* 43 and 44 fragments as the collision energy increases [Fig. 1(d)], a trend that is clearly observed in the energy-resolved mass spectrometry (ERMS)[7] plot (Fig. 2). It is interesting to note that the ion of *m/z* 42 becomes the only observed fragment at collision energies greater than 30 eV. Therefore the *m/z* 70 ion from *N*-Br-succinimide displays under these conditions very similar CID behavior to that of 'pure' **1**. Thus care should be taken when using low-energy CID for structural assignments of possible $C_2NO_2^+$ ions.

It is therefore evident from the data just discussed that a mixture of isomeric or isobaric ions of *m/z* 70 is produced from *N*-Br-succinimide. High-resolution mass measurements were then performed on a Micromass Autospec mass spectrometer to address the isobaric composition of *m/z* 70 ions from the three precursors. The data show that the *m/z* 70 ionic beam from ethoxycarbonyl isocyanate consists of pure (greater than 99.99%) $C_2NO_2^+$ ions. On the other hand, ions of *m/z* 70 from *N*-H- and *N*-Br-succinimide are shown to be mixtures of both $C_2NO_2^+$ (69.9929 u) and $C_3H_4NO^+$ (70.02929 u) ions. The abundance of $C_3H_4NO^+$ ions is quite low for *N*-H-succinimide (1%) but very significant for *N*-Br-succinimide (36%). Co-generation of $C_3H_4NO^+$ therefore explains the unexpected fragments observed in the 'very'-low-energy CID experiments [Figs 1(c) and 1(d)], i.e. *m/z* 43 (loss of HCN or $C_2H_3^{\cdot}$) and *m/z* 44 (loss of C_2H_2). The ERMS data (Fig. 2) indicate that the co-generated $C_3H_4NO^+$ ion dissociates at very low collision energies mainly to *m/z* 43 and 44, but it displays at higher collision energies a similar CID behavior to that of the $C_2NO_2^+$ ion, i.e. it dissociates mainly to *m/z* 42 by loss of CO (or C_2H_4). Therefore dissociation of the $C_3H_4NO^+$ ion to *m/z* 43 and 44 probably involves rearrangements, which are not favored at higher collision energies. The quite high reactivity of the *m/z* 70 ion from *N*-Br-succinimide towards adduct formation in ion/molecule reactions with pyridine (Fig. 3) confirms that the $C_2NO_2^+$ ionic population consists mainly of **1**. This is so because **1** from both ethoxycarbonyl isocyanate and *N*-H-succinimide behaves similarly, whereas the isomeric **2** forms no adduct in reactions with pyridine, reacting instead by CN$^+$ and CNO$^+$ transfer.[1]

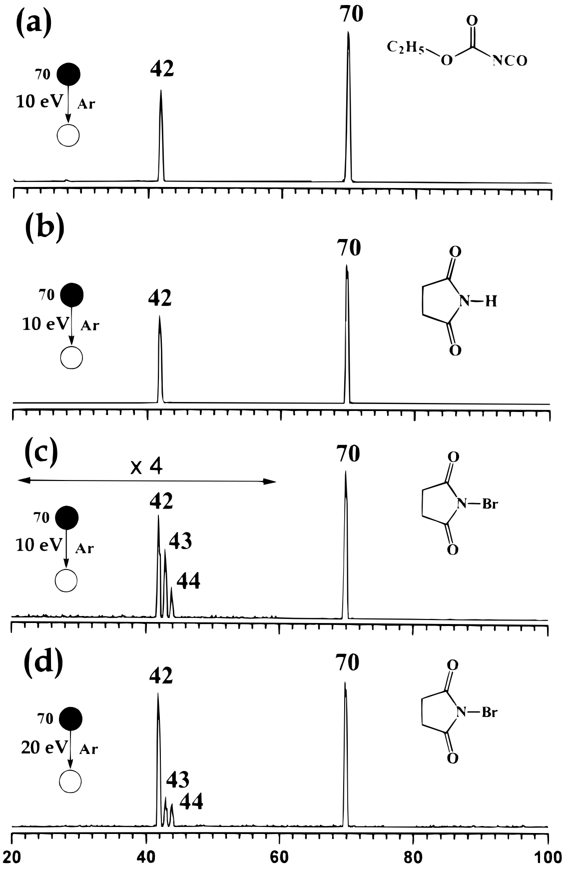


Figure 1. MS^2 collision-induced dissociation (CID) spectra of ions of *m/z* 70 produced from 70 eV EI of (a) ethoxycarbonyl isocyanate, (b) *N*-H-succinimide and (c, d) *N*-Br-succinimide.

One possible explanation for the formation of *m/z* 70 ionic populations of different $C_2NO_2^+$ and $C_3H_4NO^+$ compositions from *N*-H- and *N*-Br-succinimide could be related to the competition of different ionization sites (Scheme 1). Radical and charge localization on the nitrogen atom in the molecular ion of the former and on the bromine atom in the latter are favored owing to the lower electronegativity of these heteroatoms, i.e. Br < N < O. In both cases, subsequent dissociations initiated by α-cleavage account for the observed fragments.

CCC 1076–5174/97/101137–03 $17.50

Received 2 June 1997
Accepted 24 June 1997

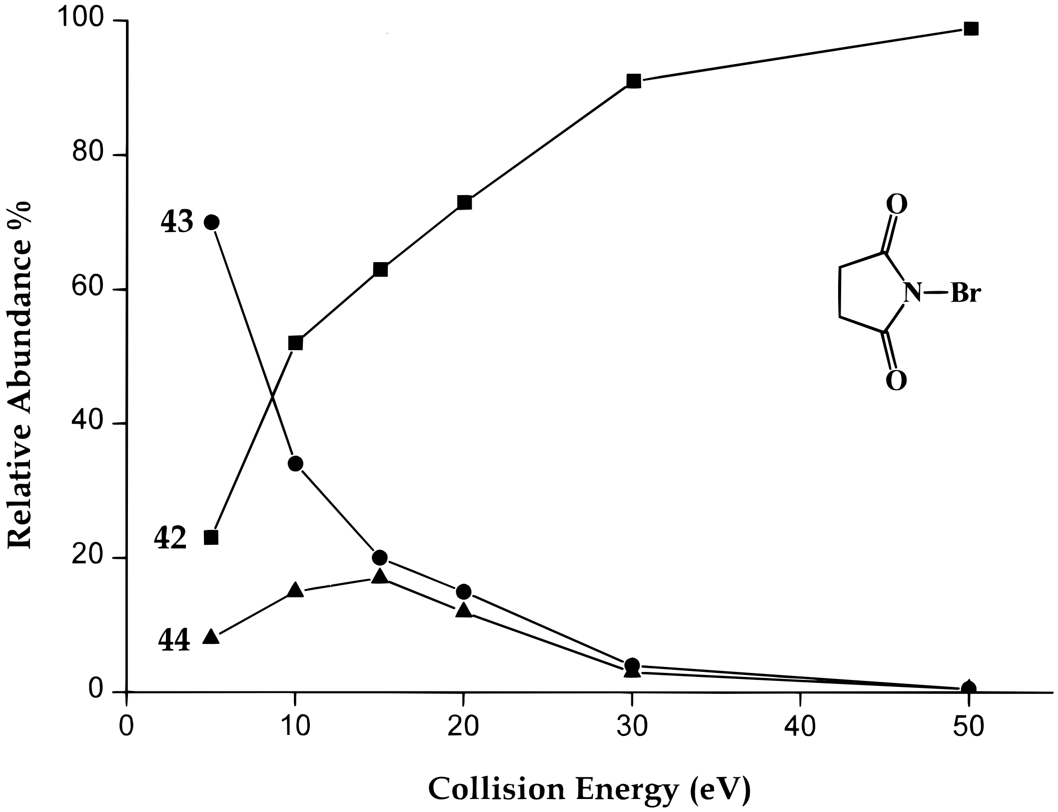


Figure 2. Energy-resolved (5–50 eV) mass spectrometry (ERMS) plot for the ion of *m/z* 70 produced from 70 eV EI of *N*-Br-succinimide.

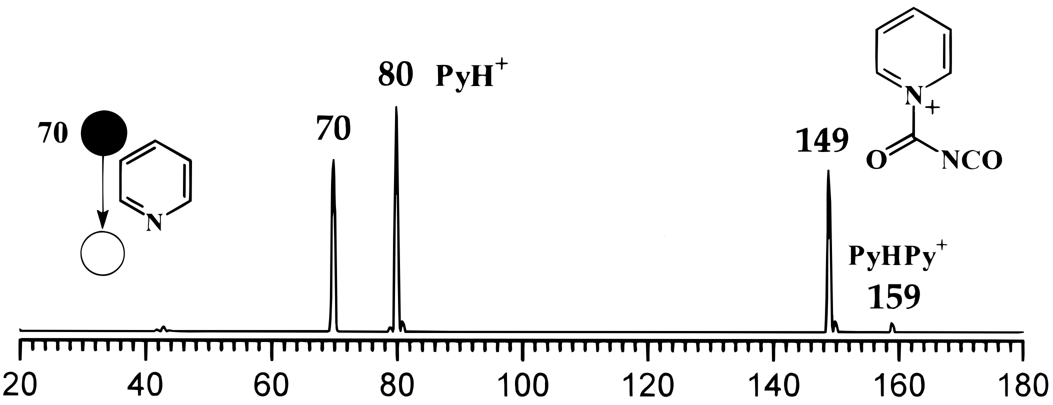
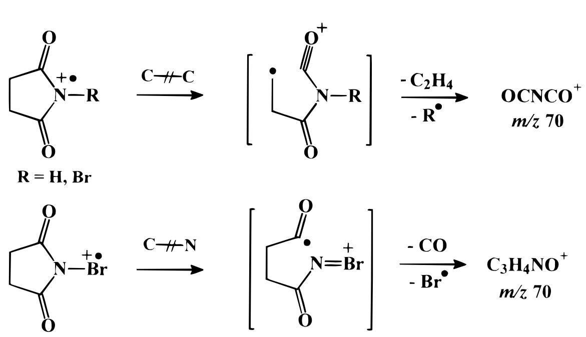


Figure 3. Double-stage (MS^2) product spectrum for reactions of pyridine with the ion of *m/z* 70 produced from 70 eV EI of *N*-Br-succinimide.



Scheme 1.

This work has been supported by the Research Support Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq).

Yours,

MÁRCIA C. CARVALHO, LUIZ ALBERTO B. MORAES, CONCETTA KASCHERES and M. N. EBERLIN*
Institute of Chemistry,
State University of Campinas—UNICAMP,
CP 6154, 13083-970 Campinas, SP, Brazil

---

* Correspondence to: M. N. Eberlin, Institute of Chemistry, State University of Campinas—UNICAMP, CP 6154, 13083-970 Campinas, SP, Brazil.

Contract grant sponsor: Research Support Foundation of the State of São Paulo (FAPESP).
Contract grant sponsor: Brazilian National Research Council (CNP$_q$).

References

1. M. C. Carvalho, V. F. Juliano, C. Kascheres and M. N. Eberlin, *J. Chem. Soc., Perkin Trans. 2* in press.
2. D. Sülzle, P. E. O'Bannon and H. Schwarz, *Chem. Ber.* **125**, 279 (1992).
3. S. S. Yang, G. Chen, S. Ma, R. G. Cooks, F. C. Gozzo and M. N. Eberlin, *J. Mass Spectrom.* **30**, 807 (1995).
4. M. N. Eberlin, *Mass Spectrom. Rev.* in press.
5. V. F. Juliano, F. C. Gozzo, M. N. Eberlin, C. Kascheres and C. L. Lago, *Anal. Chem.* **68**, 1328 (1996).
6. (a) F. C. Gozzo and M. N. Eberlin, *J. Am. Soc. Mass Spectrom.* **6**, 554 (1995); (b) F. C. Gozzo and M. N. Eberlin, *J. Mass Spectrom.* **30**, 1553 (1995); (c) A. E. P. M. Sorrilha, F. C. Gozzo, R. S. Pimpim and M. N. Eberlin, *J. Am. Soc. Mass Spectrom.* **7**, 1126 (1996); (d) L. A. B. Moraes, R. S. Pimpim and M. N. Eberlin, *J. Org. Chem.* **61**, 8726 (1996); (e) M. N. Eberlin, A. E. P. M. Sorrilha, R. S. Pimpim and F. C. Gozzo, *J. Am. Chem. Soc.* **119**, 3550 (1997); (f) L. A. B. Moraes, F. C. Gozzo, M. N. Eberlin and P. Vaniotalo, *J. Org. Chem.* **62**, 5096 (1997).
7. S. A. McLuckey, L. Sallans, R. B. Cody, R. C. Burnier, S. Verma, B. S. Freiser and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.* **44**, 215 (1982).