

## Electron Impact-induced Fragmentation of 5-Aminotetrazole

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Sir:

Occurrence of "metastable ions" (1,2) in mass spectra of organic compounds is frequently used to elucidate fragmentation routes. This paper describes experiments showing that fragmentation of the 5-aminotetrazole molecular radical-ion in the mass spectrometer proceeds by two parallel pathways which include an unusually high proportion of energetic transitions.

Direct introduction of 5-aminotetrazole (3) into the ion source of the mass spectrometer by means of a heated sample probe allows production of a sudden pressure surge as the solid vaporizes. By adjusting the rate of heating, it is possible to control the extent of the pressure surge so that satisfactorily high concentrations of metastable ions occur without appearance of peaks due to ion-molecule reactions.

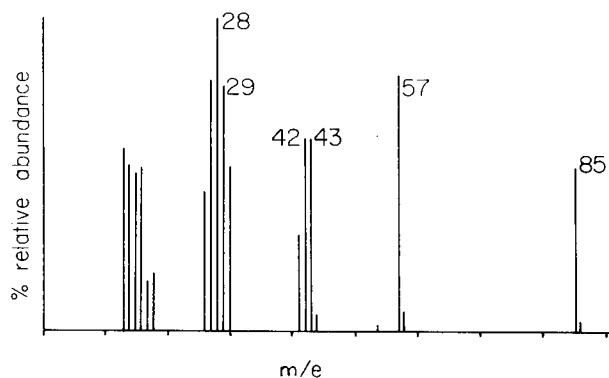


Figure 1. Mass Spectrum of 5-Aminotetrazole

The normal mass spectrum (Figure 1) of 5-aminotetrazole is altered upon increasing ion source pressure by appearance of no less than seven peaks (Table I) due to metastable transitions in the fragmentation of this nine-atom (molecular weight 85) molecule.

Calculations relating the apparent  $m/e$  values of metastable ion signals to the more prominent "normal" lines (integral  $m/e$ , intensity  $> 10\%$  of base peak) make possible the deduction of sequential stepwise fragmentation routes (Figure 2).

In addition, six of these seven metastable transitions give rise to "flat-topped" peaks. The apparent width  $d$

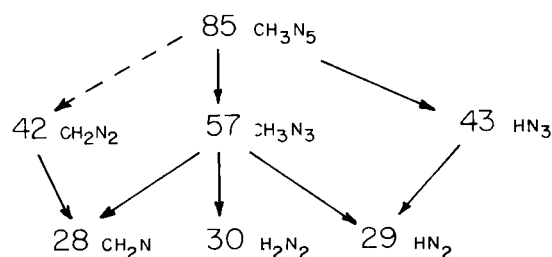


Figure 2. Decomposition Paths (5-Aminotetrazole)

(in mass numbers) of the flat-topped signal, the  $m/e$  values of the parent- and daughter-ions, and the ion accelerating voltage are used (eq. 1) in computation of the excess kinetic energy associated with each such transition (4,5).

$$T = \frac{d^2 m_1^2 V}{16m_2^3 (m_1 - m_2)} \quad (1)$$

Ejection of a neutral nitrogen atom, a mass spectroscopic fragmentation step until recently believed "unusual" (6) and "surprising" (7), is clearly shown to occur in two energetic metastable transitions in the mass spectrum of 5-aminotetrazole ( $42^+ \rightarrow 28^+ + 14$  and  $43^+ \rightarrow 29^+ + 14$ ). A recent article (8) summarizes a number of previously reported instances of such transitions; separation of neutral nitrogen atom with excess kinetic energy in the range 0.45 to 0.57 eV is there postulated to result from predissociation onto a repulsive energy surface with subsequent ejection of a quartet nitrogen atom. Since the two cases of loss of a neutral nitrogen atom described in the present work involve release of excess kinetic energy of 0.51 and 0.53 eV, respectively, it seems not unreasonable to consider them as further examples of such a predissociation-fragmentation process.

Assignment of summary formulas to certain of the fragment ions in this scheme has been facilitated in the absence of double-focusing capability by use of deuterium-labeled 5-aminotetrazole. In recognition of the possibility that the  $85^+ \rightarrow 43^+ + 42$  step might conceivably represent production of either  $\text{HN}_3^+$  or  $\text{CH}_3\text{N}_2^+$ , attention has been focused upon the subsequent  $43^+ \rightarrow 29^+ + 14$  step. Metastable transitions numerically corresponding to ejection of a nitrogen atom from  $\text{N}_3^+$ , from  $\text{CD}_2\text{N}_2^+$  and from  $\text{DN}_3^+$

TABLE I

Metastable Transitions in the Mass Spectrum of 5-Aminotetrazole

$m_1$	$m_2$	$m_{\text{neut.}}$	$m^*$ calcd.	$m^*$ obsd.	T (ev)
57	28	29	13.75	13.8	0.08
57	29	28	14.75	14.8	0.10
57	30	27	15.79	15.8	none
42	28	14	18.67	18.7	0.53
43	29	14	19.56	19.6	0.51
85	43	42	21.75	21.8	0.31
85	57	28	38.22	38.3	0.38

TABLE II

Comparison of Excess Kinetic Energy Values

5-Aminotetrazole	5-Aminotetrazole-d <sub>2</sub>	5-Aminotetrazole-d <sub>3</sub>
$85^+ \rightarrow 57^+ + 28$ T = 0.38 ev	$87^+ \rightarrow 59^+ + 28$ T = 0.36 ev	$88^+ \rightarrow 60^+ + 28$ T = 0.36 ev
$42^+ \rightarrow 28^+ + 14$ T = 0.53 ev	$43^+ \rightarrow 29^+ + 14$ T = 0.51 ev	$44^+ \rightarrow 30^+ + 14$ T = 0.56 ev

(the last-named two being numerically the same) are indeed observed, however, the  $\text{CD}_3\text{N}_2^+$  transition ( $46^+ \rightarrow 32^+ + 14$ ) is completely absent. This confirms the supposition that the measured  $85^+ \rightarrow 43^+$  transition represents formation of  $\text{HN}_3^+$  rather than  $\text{CH}_3\text{N}_2^+$ .

The ion source of the mass spectrometer used in this work is thermally hot, usually above  $250^\circ$ . In view of the known thermal instability of 5-aminotetrazole, the possibility of a thermolytic pathway parallel with the electron impact-induced fragmentation must be allowed. In fact; production of radical-cation of  $m/e$  42 from the molecular radical-ion is shown (Figure 2) with a dashed arrow as indication of present uncertainty regarding its immediate origin; formation of the  $\text{CH}_2\text{N}_2^+$  fragment is *not* accompanied by a corresponding  $85^+ \rightarrow 42^+$  metastable transition. This radical-ion could result from secondary ionization of cyanamide molecules; cyanamide might be produced either as the neutral fragment of the  $85^+ \rightarrow 43^+$  transition or (together with hydrogen azide) by direct thermolysis of 5-aminotetrazole (9).

Identification of the  $m/e$  42 ion as  $\text{CH}_2\text{N}_2^+$  and description of the  $42^+ \rightarrow 28^+ + 14$  transition as  $\text{CH}_2\text{N}_2^+ \rightarrow \text{CH}_2\text{N}^+ + \text{N}$  (rather than  $\text{CH}_2\text{N}_2^+ \rightarrow \text{N}_2^+ + \text{CH}_2$ ) are also substantiated by the deuteration experiments. Metastable transitions  $43^+ \rightarrow 29^+$  and  $44^+ \rightarrow 30^+$  are observed, but are not diagnostic since they can logically be ascribed to loss of a neutral nitrogen atom from  $\text{HN}_3^+$  and  $\text{DN}_3^+$ , respec-

tively, as well as from  $\text{CHDN}_2^+$  and  $\text{CD}_2\text{N}_2^+$ . The alternate (10) fragmentation possibility, ejection of a neutral methylene, is refuted by the complete absence of metastable transitions at  $m^*$  18.23 and 17.82, the values calculated for  $\text{CHDN}_2^+ \rightarrow \text{N}_2^+ + \text{CHD}$  and  $\text{CD}_2\text{N}_2^+ \rightarrow \text{N}_2^+ + \text{CD}_2$ .

Excess kinetic energy values computed for metastable transitions in fragmentation of some deuterated species are essentially identical (see Table II) with excess kinetic energy values obtained in fragmentation of the corresponding non-deuterated ions.

## EXPERIMENTAL

All mass spectra were measured with a Nuclide 12-90-G mass spectrometer, using a heated probe for direct introduction of samples into the ion source. While measurement of the actual source pressures involved is not possible, it has been observed that satisfactorily high concentrations of metastable ions apparently occur when the source-housing ionization gauge indicates greater than ten-fold pressure change, e.g. from  $5 \times 10^{-7}$  to over  $5 \times 10^{-6}$  torr. Greater pressure increases lead to appearance of peaks due to ion-molecule reactions. Ionization potential was 70 ev. Accelerating potential used was ordinarily 4 Kv except for determination of excess kinetic energies, when experiments using two or three different accelerating potentials (usually 3.5, 4.0 and 4.5 Kv) were run to increase the reliability of the energy figures reported.

Computation of excess kinetic energy values (eq. 1) and peak-matching analysis of experimental spectral data for fitting parent-daughter relationships to observed metastable signals were done with a PDP-8/I laboratory computer (11).

5-Aminotetrazole was prepared by the method of Mihina and Herbst (3).

Deuteration of 5-aminotetrazole was accomplished by recrystallization of 5-aminotetrazole from deuterium oxide. The extent of exchange was indicated by diminution of the infrared N-H stretching absorption at  $3540\text{-}2920\text{ cm}^{-1}$  and appearance of the N-D stretching absorption bands at  $2600\text{-}1910\text{ cm}^{-1}$ . Integrated intensity measurements were carried out by use of a K&E compensating polar planimeter on spectra produced with a Perkin-Elmer Model 621 infrared spectrophotometer. The results indicated that four successive recrystallizations from deuterium oxide gave 5-aminotetrazole in which slightly over 92% of the protium had been replaced by deuterium. The mass spectra of deuterated samples invariably contained weak metastable ion peaks corresponding to fragmentation of  $\text{CHD}_2\text{N}_5$  as well as those from  $\text{CD}_3\text{N}_5$ . Re-exchange with background water in the source was inferred from the observation that the apparent proportion of 5-aminotetrazole-d<sub>2</sub> to fully deuterated material was higher in the mass spectra than in infrared measurements.

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(9) This thermolysis is presently under investigation.

(10) Suggested by a referee.

(11) On request, the Author will furnish copies of PDP-8 FOCAL programs written for these applications.

Received February 23, 1970

Revised July 20, 1970

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