# Observations on the Reactions of Normal and Excited Ions of Cyanogen and the Persistent Complex $C_4N_4^+$ *

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The mass spectrum of cyanogen at a pressure of 1 mm. Hg in the ionization chamber has been reported to contain all ions of the type $(CN)_x$ $(1 \leqq x \leqq 10)$ [1]. At this pressure successive ion-molecule reactions occur. Unstable bimolecular collision complexes are deactivated by collisions with gas molecules before being extracted from the ionization chamber. We have studied the complex formation and other ion-molecule reactions in cyanogen in the more conventional pressure region where only bimolecular processes can be observed. These experiments have been carried out with both an Atlas Model CH4 and a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. Secondary ions were recognized by the linear dependence of the current ratio $i_{sec.}/i_{prim.}$ on the gas pressure and by the decrease of this ratio with increasing repeller field strength. Appearance potential measurements have been used to identify the precursors of the secondary ions.

The relative intensities and appearance potentials of the primary and secondary ions in cyanogen are listed in Table 1. The reactions which must be postulated to explain the formation of the secondary ions are shown in Table 2. Special attention should be called to reaction a) which illustrates the formation of a persistent molecular ion complex and to the processes b) and c) which illustrate reactions of an excited ion.

The secondary ion $C_4N_4^+$ is a persistent complex from the collision of a $C_2N_2^+$ ion with a $C_2N_2$ molecule. Although a large number of ion-molecule reactions is already known only a few persistent complexes have been found to date [2–4]. Among all these complexes $C_4N_4^+$ consists of the smallest number of atoms. The lifetime of a complex is in general considered to be described by

$$t \approx 10^{-13} \left(\frac{E}{E-E_1}\right)^{\alpha-1} \qquad (1)$$

where $\alpha$ is the number of vibrational degrees of freedom, $E$ is the total internal energy and $E_1$ is the strength of the weakest bond in the complex. The nature of the bonds and atoms is usually disregarded in this and even more elaborate expressions. Since the complexes reported to date belong to certain classes of compounds, i. e., alkyl halides [2, 3] and unsaturated molecules [4] (including the presently described cyanogen), it is concluded that certain groups favour a long-lived complex. Although our present knowledge of persistent complexes is too incomplete to draw any further conclusions it may be noted that the concept of "inactive" degrees of vibrational freedom [5, 6] could explain the relatively infrequent observation of complexes in studies of ion-molecule reactions. If only a small fraction of the degrees of freedom allows the flow of internal energy through a complex, its lifetime will be much shorter than calculated from Eq. (1). Certain groups may facilitate the energy flow by increasing the number of active degrees of freedom. On the other hand, certain bounds of high strength may belong to the more "adiabatic" degrees of freedom [5]. They would act as energy sinks thus preventing the weaker bonds from being overloaded.

| Mass | Ion | AP | Intensity |
|---|---|---|---|
| Primary Ions | | | |
| 12 | $C^+$ | $25.0 \pm 1.0$ | 4.0 |
| 14 | $N^+$ | $26.0 \pm 1.5$ | 0.78 |
| 24 | $C_2^+$ | $18.7 \pm 0.5$ | 3.8 |
| 26 | $CN^+$ | $21.3 \pm 0.5$ and $25 \pm 1.0$ | 10.7 |
| 28 | $N_2^+$ | 18.0 and 23.0 | 0.1 |
| 38 | $C_2N^+$ | $19.5 \pm 0.5$ | 2.4 |
| 40 | $CN_2^+$ | $23.0 \pm 0.5$ | 0.1 |
| 52 | $C_2N_2^+$ | $14.0 \pm 0.5$ | 100 |
| Secondary Ions | | | |
| 48 | $C_4^+$ | $19.0 \pm 0.5$ | 0.0012 |
| 50 | $C_3N^+$ | $19.3 \pm 0.5$ | 0.051 |
| 62 | $C_4N^+$ | $19.5 \pm 0.5$ | 0.0014 |
| 64 | $C_3N_2^+$ | $23.0 \pm 1.0$ and $25.5 \pm 1.0$ | 0.026 |
| 76 | $C_4N_2^+$ | $15 \pm 1.0$ and $18.5 \pm 1.0$ | 0.0008 |
| 78 | $C_3N_3^+$ | $16.0 \pm 0.5$ | 0.024 |
| 104 | $C_4N_4^+$ | $14.0 \pm 0.5$ | 0.004 |

Table 1. Mass Spectrum of Cyanogen at 70 eV of Electron Accelerating Voltage, taken in an Atlas Model CH 4 Mass Spectrometer at a pressure of 1.7 mm. Hg in the gas reservoir.

The secondary ion $C_3N_3^+$ appears at $(16 \pm 0.5)$ volts, i. e., about 2.0 volts above the ionization potential of $C_2N_2$ and about $2-3$ volts below the first dissociation limits of $C_2N_2^+$. Similarly, the secondary ion $C_4N_2^+$ shows a first appearance potential of $(15 \pm 1.0)$ volts.

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| Secondary Ion | Reaction | $i_s/i_p$* |
|---|---|---|
| $C_4N_4^+$ | a) $C_2N_2^+ + C_2N_2 \rightarrow C_4N_4^+$ | $4 \cdot 10^{-5}$ |
| $C_3N_3^+$ | b) $C_2N_2^{+*} + C_2N_2 \rightarrow C_3N_3^+ + CN$ | $> 2.4 \cdot 10^{-4}$ |
| $C_4N_2^+$ | c) $C_2N_2^{+*} + C_2N_2 \rightarrow C_4N_2^+ + N_2$ (20%) | $\sim 1.6 \cdot 10^{-6}$ |
| | d) $C_2^+ + C_2N_2 \rightarrow C_4N_2^+$ and/or<br>e) $C_2N^+ + C_2N_2 \rightarrow C_4N_2^+ + N$ (80%) | $\sim 2 \cdot 10^{-4}$ |
| $C_3N_2^+$ | f) $CN^+ + C_2N_2 \rightarrow C_3N_2^+ + N$ | $2.4 \cdot 10^{-3}$ |
| $C_4N^+$ | g) $C_2N^+ + C_2N_2 \rightarrow C_4N^+ + N_2$ and/or<br>h) $C_2^+ + C_2N_2 \rightarrow C_4N^+ + N$ | $\sim 5.0 \cdot 10^{-4}$ |
| $C_3N^+$ | i) $C_2N^+ + C_2N_2 \rightarrow C_3N^+ + CN_2$ and/or<br>j) $C_2^+ + C_2N_2 \rightarrow C_3N^+ + CN$ | $\sim 1.8 \cdot 10^{-2}$ |
| $C_4^+$ | k) $C_2N^+ + C_2N_2 \rightarrow C_4^+ + N_2 + N$ and/or<br>l) $C_2^+ + C_2N_2 \rightarrow C_4^+ + N_2$ | $\sim 4.0 \cdot 10^{-4}$ |

* $i_s/i_p$ of the reaction $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ was equal to $2 \cdot 10^{-2}$ at the same pressure in the gas reservoir and the same repeller field strength.

Table 2. Ion-Molecule Reactions in Cyanogen.

The only possible precursor of these ions would seem to be an excited $C_2N_2^+$ carrying about 2.0 eV of excess energy. Reactions of excited ions with molecules have recently been found in a number of aromatic and double or triple bond containing compounds as well as in iodine [7–9]. It seems that ions having relatively long-lived excitational energy are quite frequently formed by electron impact in types of molecules such as these.

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## $O^{\ominus}$-Radikalionen bei der Radiolyse von alkalischem Eis

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In zahlreichen Arbeiten über die Radiolyse wäßriger Lösungen konnte sichergestellt werden, daß das H-Radikal in Abhängigkeit vom $p_H$ in einer sauren [1a–e], einer neutralen [2a–d] und einer basischen [3a–i] Form vorliegen kann:

$$H^{\oplus} + e_{solv.}^{\ominus} \rightleftharpoons H^{\cdot} \rightleftharpoons H_2^{\oplus} - H^{\oplus}. \qquad (1)$$

Die basische Form des H-Radikals stellt das solvatisierte Elektron dar, die saure das positiv geladene Wasserstoffmolekülion.

Analog dazu sollte auch das OH-Radikal in Abhängigkeit vom $p_H$-Wert in verschiedenen Formen auftreten:

$$H^{\oplus} + O^{\ominus} \rightleftharpoons {}^{\cdot}OH \rightleftharpoons H_2O^{\oplus} - H^{\oplus}. \qquad (2)$$

Nach (2) besteht die basische Form des OH-Radikals aus einem einfach negativ geladenen Sauerstoffatomion und die saure Form aus dem positiv geladenen Wassermolekülion.

Für das Auftreten des $O^{\ominus}$-Radikalions [4] in $\gamma$-bestrahlten, wäßrigen Lösungen gibt es bisher nur Hinweise aus kinetischen Untersuchungen. Hart, Gordon und Hutchinson [5] haben beobachtet, daß unter $\gamma$-Bestrahlung schwerer Sauerstoff (*O) mit Wasser nur dann mit großer Geschwindigkeit austauscht, wenn der $p_H$-

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