

## 전자충돌로 유도된 노르니코틴에서의 폐환반응

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(1982. 5. 13 접수)

## Electron Impact Induced Ring Closure Reaction in Nornicotine

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(Received May 13, 1982)

Alkaloids isolated from a variety of tobacco species are either bicyclic or fused tricyclic nitrogenous compounds. Nornicotine is representative of the former and exhibits a characteristic fragmentation pattern in its mass spectrum<sup>1</sup>. Although some authors suggested the fragmentation mechanism of nornicotine by using a conventional mass spectrometry which is not able to elucidate the mechanism of fragmentation clearly. In contrast to conventional method of detecting the origin of fragments, a procedure for searching for related fragment ion-namely Direct Analysis of Daughter Ions (DADI)<sup>2</sup> or Mass Analyzed Ion Kinetic Energy (MIKE)<sup>3</sup> spectrometry-provides experimental data directly in order to determine the fragment genesis. The DADI/MIKE spectrometry obtained gives information on the reactions of ions which have little excess energy (between 0 and 20 kcal·mol<sup>-1</sup>) above the transition state for unimolecular dissociation, due to the relatively long life time (*ca.* 10<sup>-5</sup> s) after the formation of the reaction species<sup>4</sup>.

DADI/MIKE spectrometer is mass spectrometer with reversed Nier-Johnson geometry. The assignments of parent to daughter ion transition is somewhat difficult in conventional ion kinetic energy (IKE) spectra which must be mass

analyzed.<sup>5</sup> This disadvantage in indentifying metastable reactions is overcome when the position of the magnetic and electric sectors are reversed. In fact, one particular ion can be selected by tuning the magnetic field and the pure metastable spectrum recorded by automatic variation of the electrostatic analyzer (ESA) voltage from the initial value ( $E_0$ ) downwards. Each metastable peak arises from unimolecular decomposition in the second drift region between magnetic and electrostatic sector field in a reversed geometry instrument and occurs at an ESA voltage,  $E$ , which allows the assignment of parent ( $m_M$ ) and daughter ( $m_D$ ) mass numbers using the relationship  $m_D = m_M E / E_0$ .

In this study, the fragmentation mechanism of nornicotine was clarified by using a stepwise DADI/MIKE spectrometry.

### EXPERIMENTAL

The mass spectrum of nornicotine was determined on a Varian MAT212 double focusing mass spectrometer of reversed Nier-Johnson geometry. The spectrum was run at 70 eV and 3 kV accelerating voltage. Metastable transitions in the second drift region were observed at a nominal 3 kV, varying the ESA voltage downwards according to the DADI/MIKE spectro

metry. The sample (basic fraction of tobacco extract) was introduced via the direct inlet system with cooled sample probe. The ion source temperature was 200°C. The ESA voltage was checked by a Hewlett-Packard digital voltmeter and the DADI/MIKE spectra were recorded on a Kipp and Zonen Model BD 40 recorder.

### 3. RESULTS AND DISCUSSION

Nornicotine loses according to the conventional mass spectrum, 29 mu (mass unit) from its molecular ion at  $m/z$  148 to  $m/z$  119 (Fig. 1). The ion M-29 in nornicotine was explained via the formation of ion I and the further loss of an ethyl radical to form ion II (Fig. 2)<sup>6</sup>. However, conventional mass spectrometry cannot prove this mechanism.

The practical procedure for stepwise detection of ion generation by DADI/MIKE spectrometry is shown in Fig. 3. After electron impact ionization the species  $X^+$  ( $m/z$  148) is set by means of the magnetic field. The corresponding DADI/MIKE spectrum shows the product ions at  $m/z$  120 and  $m/z$  119. Finally, the ion  $Y^+$ , corresponding to the next ion generation, was set by the magnetic field, and a search was then made for the next product ions by DADI/MIKE spectrometry. In this procedure there was no difficulty in detecting  $m/z$  119 corresponding to the loss of hydrogen. DADI/MIKE spectra showed that a two-step process was involved. In the first step, 28 mu ( $C_2H_4$ ) are eliminated from the molecular ion at  $m/z$  148 to  $m/z$  120. In the second step, a proton is pushed out at  $m/z$  120 to  $m/z$  119.

A proton transfer occurring during a fragmentation process is the evidence for a rearrangement. Rearrangements occur very often *via* cyclic intermediate. Ring closure reactions induced by a two-step process in the salicylic

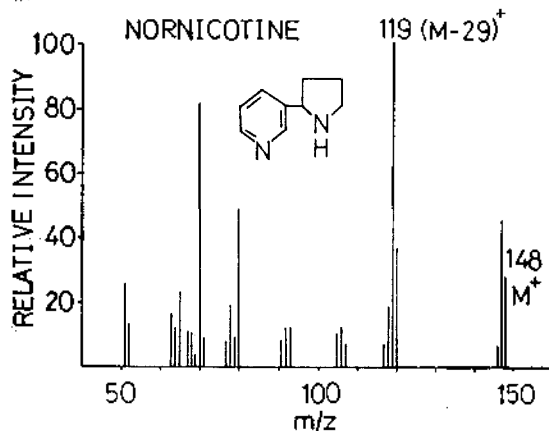


Fig. 1. Conventional mass spectrum of nornicotine (GC inlet, 20 mx · 0.25 mm SE-54 glass capillary column, column temperature 140°C).

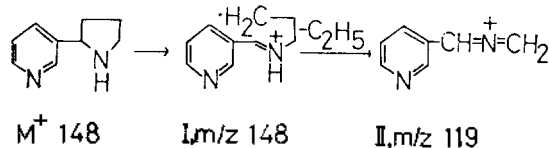
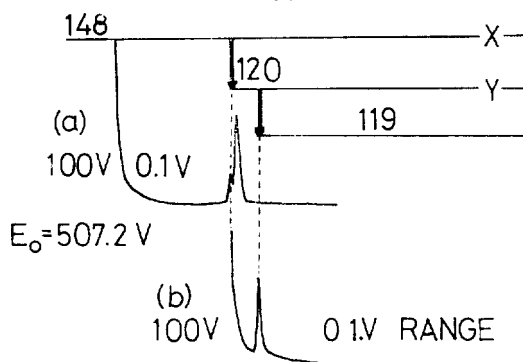


Fig. 2. Proposed mechanism of 29mu elimination from the  $M^+$  ion of nornicotine<sup>6</sup>.



	E	$E \cdot m_M / E_0$	$m_M$	$\Delta m$	
	411.5 V	120.1	120	28	$M - C_2H_4$
	408.1 V	119.1	119	29	$M - C_2H_5$
b	502.9 V	119.0	119	1	$M' - H$

Fig. 3. Stepwise analysis of different ion generations for nornicotine by DADI/MIKE spectrometry. X: First magnet setting at  $m/z$  148(M) gave spectrum (a). The unimolecular dissociation of molecular ion shows metastable transitions associated with the formation of product ions  $m/z$  120 and  $m/z$  119. Y: Second magnet setting at  $m/z$  120(M') gave spectrum (b). The elimination of hydrogen from  $m/z$  120 to  $m/z$  119.

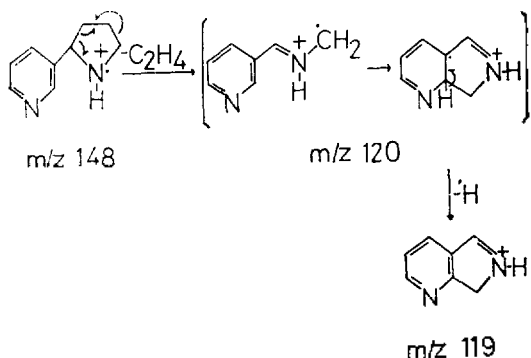


Fig. 4. The elimination of hydrogen H from the  $(M-C_2H_4)^+$  ion of nornicotine at  $m/z$  120. This mechanism could be easily explained by a ring closure.

acid derivatives and 4-( $\omega$ -phenoxy-ethyl)-tetrahydropyrene have been detected by the collision activation studies and deuterium labelling<sup>7,8</sup>. A similar ring closure reaction in the case of nornicotine can be deduced by its DADI/MIKE spectra (Fig. 4). The geometrically favourable transition state, the consequent stabilization of the resonance of the cyclic intermediate and the driving force of the rearomatization process make the ring closure with a consecutive loss of a proton be a very plausible explanation

for this reaction.

In conclusion, nornicotine exhibits a characteristic ring closure reaction in its fragmentation pathway and this reaction was readily detected by DADI/MIKE spectrometry.

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