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The Theoretical Calculated Stability of Benzoyl Ions and Their Relative Intensities in the Electron Ionization Mass Spectra of Some 2,5-Disubstituted-1,3,4-oxadiazoles

by K. Eitner[1], R. Frański[1], G. Schroeder[1*], V. Rybachenko[2] and O.P. Szwajka[2]

[1]*Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland*
[2]*National Academy of Sciences, Donetsk, Ukraine*

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2,5-Disubstituted-1,3,4-oxadiazoles are formed during gas-phase conversion of some 5-substituted tetrazoles. It was proved by comparing the mass spectrometric decomposition of the former with the decomposition of the products of gas-phase conversion of the latter [1]. 2,5-Disubstituted-1,3,4-oxadiazoles were also investigated by using electron ionization mass spectrometry. It was also demonstrated that during EIMS decomposition these compounds reveal some complex rearrangement leading to the loss of CO and N_2 molecules and H atom [2]. It is also worth to mention that 1,3,4-oxadiazoles are important because they are used as materials for scintillators in modern electronic [2]. In this paper the formation of benzoyl ions from series of 2-(4-aminophenyl)-1,3,4-oxadiazoles is investigated by using EIMS. The compounds studied **1–4** and formed benzoyl ions ($[120]^+$ and $[M\text{-}132]^+$) are shown in Figure 1. The EI mass spectra of compounds **1–4** are shown in Figure 2.

Compound	R
1	Br
2	H
3	CH_3
4	CH_3O

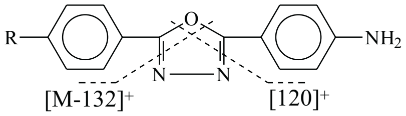

Figure 1. The compounds studied **1–4** and formed benzoyl ions ($[120]^+$ and $[M\text{-}132]^+$).

To better understanding this process (formation of benzoyl ions) the relative intensities (ri) of registered peaks corresponding to benzoyl and molecular ions are compared with their calculated stability (heat of formation). The calculated heats of formation (HoF) of molecular ions and registered 4-substituted benzoyl ($[M\text{-}132]^+$) ions are presented in Table 1. In the case of 4-aminobenzoyl ($[120]^+$) ion, the calculated heat of formation is 698 kJ/mol.

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[*] Author for correspondence. E-mail: schroede@chem.amu.edu.pl; tel: (+48 61) 8291486 fax: (+48 61) 8658008

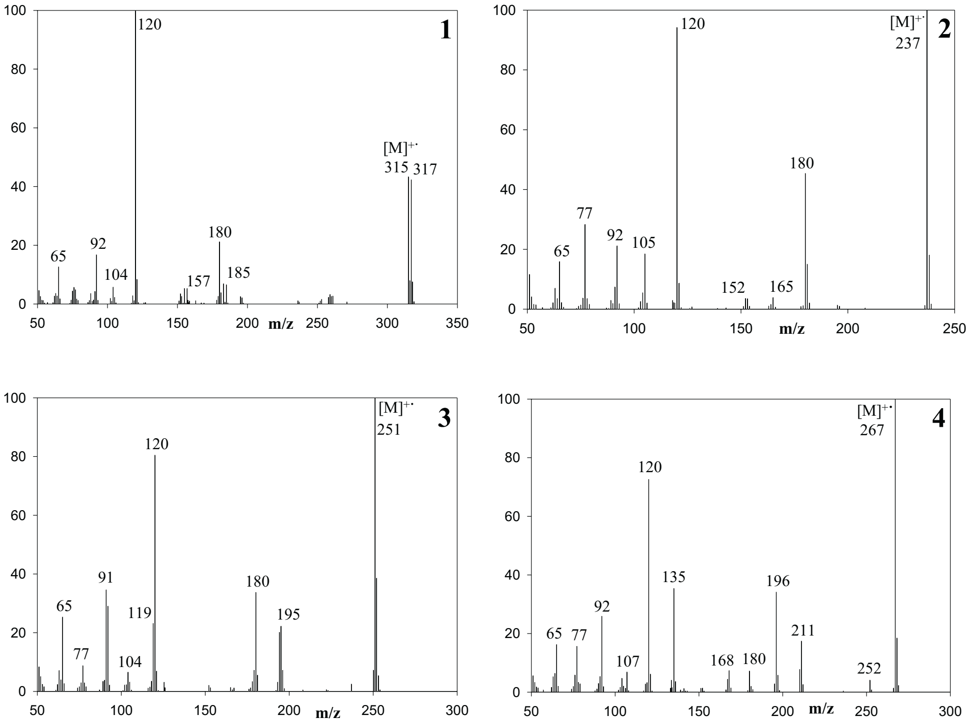

Figure 2. The EI mass spectra of studied compounds **1–4**.

Table 1. The calculated heats of formation (HoF) of molecular ions and registered 4-substituted benzoyl ($[M\text{-}132]^+$) ions.

Compound	HoF of $[M]^{+\bullet}$ kJ/mol	HoF of $[M\text{-}132]^+$ kJ/mol
1	1086	810
2	1045	764
3	1001	711
4	990	576

In each of the EI mass spectrum for studied compounds, the 4-aminobenzoyl ion at m/z = 120 was registered as the most significant fragment. The signals of other 4-substituted benzoyl ions ($[M\text{-}132]^+$) are characterized by different relative intensities in comparison to the signals of the 4-aminobenzoyl ion and to the molecular ion (Figure 2). A reasonable agreement was found between the u_n and v_n coefficients, which are defined as follow:

$u_1 = \text{ri } [M\text{-}132]^+/\text{ri } [M]^{+\bullet}$, $v_1 = \text{HoF } [M\text{-}132]^+/\text{HoF } [M]^{+\bullet}$

$u_2 = \text{ri } [120]^+/\text{ri } [M]^{+\bullet}$, $v_2 = \text{HoF } [120]^+/\text{HoF } [M]^{+\bullet}$

Correlations between these two coefficients are shown in Figure 3. In both cases, the regression coefficient (R^2) is higher than 0.97. It is a quite good result, which leads to the conclusion that the formation of benzoyl ions from studied 2,5-disubstituted-1,3,4-oxadiazoles is controlled thermodynamically. It should be stressed that this process occurs *via* an azirane as it was observed during mass spectrometric decomposition of oxazoles and isooxazoles [3].

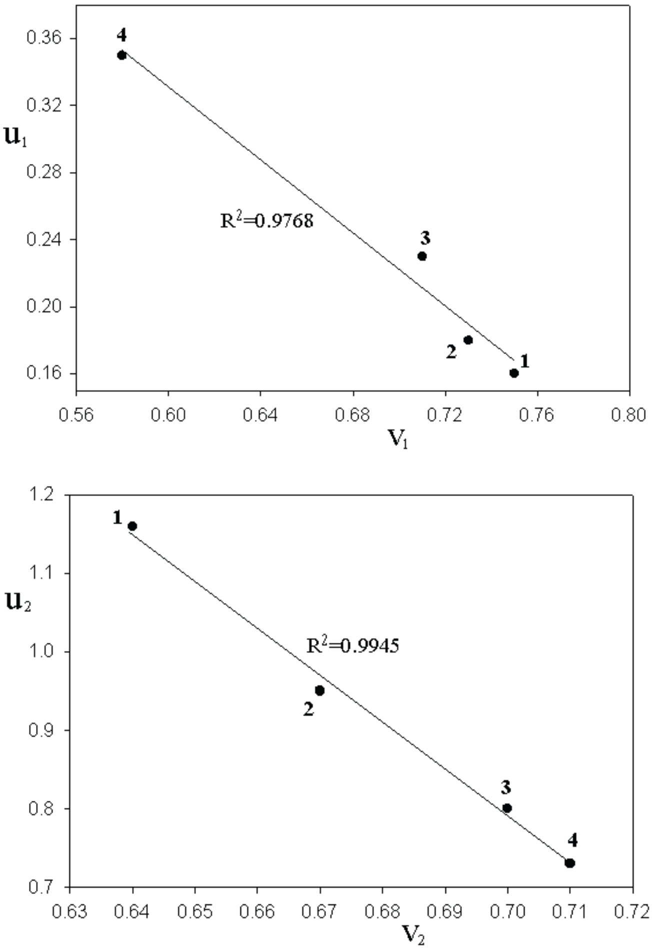

Figure 3. Correlations between u_n and v_n coefficients for compounds **1**–**4**.

The differences in relative intensities and in stabilities of benzoyl ions can also be explained on the basis of inductive effect of substituent at *para* position and possible resonance structures (mesomeric effect). These ions can exist as oxonium and/or oxocarbenium and the charge can be delocalized in aromatic ring [4]. The high relative intensity of $[120]^+$ ion is mainly caused by quinoid resonance structure, analogically as in the case of 4-aminobenzyl ion [5]. Thus, the substituent effect on the relative intensities and stabilities of benzoyl ions is clear.

It is worth to add that u_n coefficients are useful in structural elucidation of quinolizidine alkaloids [6]. However, it is the first time (to the best of our knowledge) when v_n coefficients are introduced for mass spectrometric study. It should be also pointed out that benzoyl ions are important in organic mass spectrometry and probably their most significant application is in structural elucidation of flavonoids [7,8].

The EI mass spectra were recorded on an AMD-402 two-sector mass spectrometer (AMD Intectra, Germany) of B/E geometry with an acceleration voltage of 8 kV and an electron energy 70 eV and ion source temperature of 200°C. Compounds were introduced by using direct insertion probe heated, when required, from 100 to 200°C. Semiempirical calculations were performed using the Winmopac V 2.0 package. Geometry were carried out with PM3 hamiltonian with precise key. The compounds studied were prepared according to the procedures described elsewhere [2].

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