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Fragmentation processes in phthalimide- and pyridine-2,3-dicarboimidoalkyl-α-diazoketones under resonant electron capture

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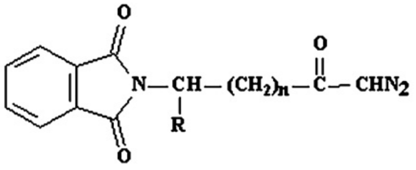
ABSTRACT

Resonant electron capture (REC) mass spectra of phthalimide- and pyridine-2,3-dicarboimidoalkyl-α-diazoketones have been investigated. Based on calculations using the Hartree–Fock method and density functional theory with the B3LYP functional the structure of the negative ions (NIs) $[M–N_2]^-$ and $[M–N_2–C_3H_3RO]^-$ as well as the reactions leading to their formation have been proposed.

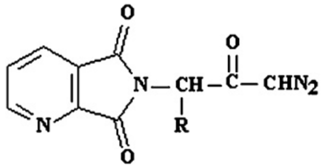
1. Introduction

In the NIs mass spectra of phthalimide containing sulfur ylids and sulfides [1] long-living molecular NIs are present. The ionization of phthalimidoalkyl-α-diazoketones leads to the separation of a nitrogen molecule and the formation of the instable carbenic cation which transforms into a linear ketene type ion as a result of the Wolff rearrangement [2].

In the present work some phthalimidoalkyl-α-diazoketones (**1a**–**e**) and pyridine-2,3-dicarboimidoalkyl-α-diazoketones (**2a**–**c**) have been investigated by means of REC NI mass spectrometry and quantum chemistry methods.



n=0, R=H (**1a**),
n=0, R=Me (**1b**),
n=0, R=i-Pr (**1c**),
n=1, R=H (**1d**),
n=2, R=H (**1e**),



n=0, R=Me (**2a**),
n=0, R=i-Bu (**2b**),
n=0, R=Bn (**2c**)

2. Experiment

NI mass spectra have been obtained using a modified [3,4] MI-1201 mass spectrometer under the following conditions: accelerating voltage 2.8 kV, electron trap current ~1 μA, FWHM of electron energy distribution $\Delta E_{1/2} = 0.3$ eV, electron energy (E_{el}) varied in the range of 0–15 eV. The vaporization temperature of compounds under investigation was in the range of 330–370 K. The calibration of the E_{el} scale has been carried out at the maxima of the curves of effective yield (CEYs) of SF_6^- ions from SF_6 (0 eV) and NH_2^- ions from NH_3 (5.65 eV).

2.1. Computational details

The calculations have been performed using the Hartree–Fock method and density functional theory with the B3LYP functional (with the basis sets 3-21+G(d,p) and 6-31++G(d,p)) in Gamess program [5]. The optimization of geometry has been carried out without a restriction on symmetry. The diazoketones have been synthesized using the procedure described in Ref. [6].

The calculation of the enthalpy of the formation of NIs' neutral analogues for the following thermochemical estimations has been carried out using additive schemes [7].

3. Results

At REC the molecules of phthalimidoalkyl-α-diazoketones and pyridine-2,3-dicarboimidoalkyl-α-diazoketones do not form long-living molecular NIs (Table 1). In the NI mass spectra of these

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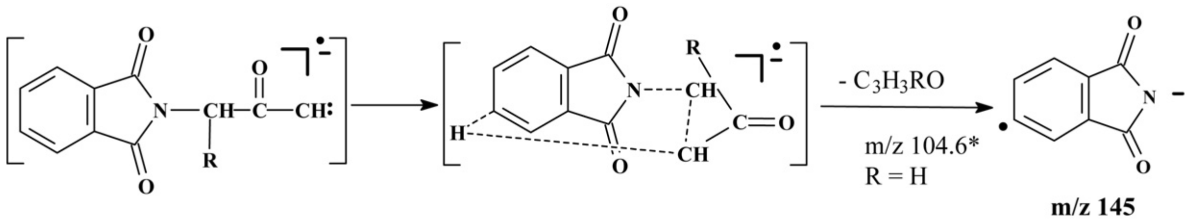
Table 1
NI mass spectra of diazoketones **1a–e** and **2a–c**.

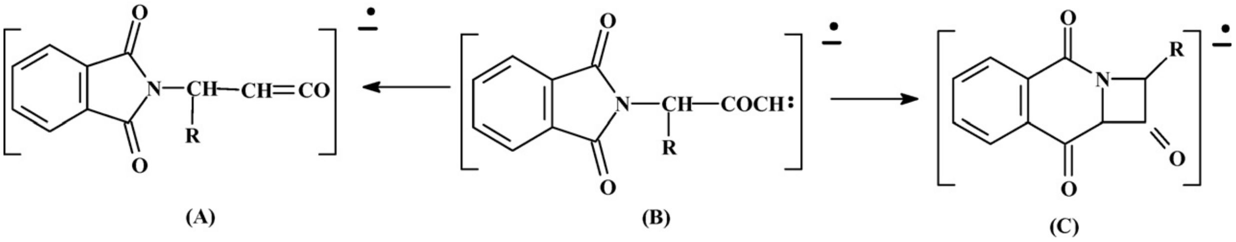
Compound	m/z Structure (relative intensity I, %)/E_{max}, eV
1a	228 $(M-H)^-$ (0.2)/6.8; 201 $(M-N_2)^-$ (0.7)/0.3; 200 $(M-N_2-H)^-$ (1.8)/0.3, (0.8)/3.6; 173 $(M-N_2-CO)^-$ (7.2)/0.3, (0.38)/3.8; 159 $(M-N_2-CH_2CO)^-$ (0.2)/0.3; 158 $(M-N_2-CH_3CO)^-$ (0.6)/0.3; 157 $(M-N_2-CO_2)^-$ (2.7)/0.3; 146 $PhtN^-$ (12)/4.4; **145 $(M-N_2-C_3H_3RO)^-$ (100)/0.4, (4.3)/3.7**; 41 $CHCO^-$ (1.0)/0.6, (10)/4.5, (5.0)/6.3; 121.5* (0.15)/0.4, (0.03)/3.7, (173 → 145); 104.6* (0.15)/0.5, (201 → 145).
1b	242 $(M-H)^-$ (0.8)/6.9; 215 $(M-N_2)^-$ (0.4)/0.3, (0.6)/3.8; 214 $(M-N_2-H)^-$ (1.6)/0.4, (1.9)/3.8; 187 $(M-N_2-CO)^-$ (12)/0.4; 173 $(M-N_2-CH_2CO)^-$ (3.7)/0.4; 172 $(M-N_2-CH_3CO)^-$ (3.3)/0.4; 171 $(M-N_2-CO_2)^-$ (4.2)/0.4; 159 $(M-N_2-2CO)^-$ (2.0)/0.5, (3.5)/6.5; 146 $PhtN^-$ (11)/4.6; **145 $(M-N_2-C_3H_3RO)^-$ (100)/0.3, (18)/3.8**; 69 (0.01)/5.0, (0.01)/6.0; 41 $CHCO^-$ (0.8)/0.5, (5.0)/4.6, (4.5)/6.1; 162.6*, (215→187); 135.2*, (187→159); 98.2*, (215→145).
1c	243 $(M-N_2)^-$ (12.5)/0.4; 215 $(M-N_2-CO)^-$ (22)/0.4; 201 $(M-N_2-CH_2CO)^-$ (3.5)/0.4; 200 $(M-N_2-CH_3CO)^-$ (3.5)/0.4; 199 $(M-N_2-CO_2)^-$ (8.5)/0.4; 187 $(M-N_2-2CO)^-$ (4.0)/0.4; 159 $(M-N_2-RCHCO)^-$ (1.5)/0.4; **145 $(M-N_2-C_3H_3RO)^-$ (100)/0.4**; 41 $CHCO^-$ (0.6)/0.5, (5.0)/4.6, (3.5)/6.3.
1d	242 $(M-H)^-$ (0.5)/7.0; 215 $(M-N_2)^-$ (59.5)/0.4; **214 $(M-N_2-H)^-$ (100)/0.5, (12)/3.6**; 159 $(M-N_2-C_3H_3RO)^-$ (66)/0.7, (41)/3.8; 158 $(M-N_2-C_3H_3RO-H)^-$ (2.1)/4.9; 146 $PhtN^-$ (21)/0.5, (28)/4.5, (25)/6.0; 41 $CHCO^-$ (5.5)/0.6, (18.5)/4.5, (12)/6.0.
1e	256 $(M-H)^-$ (2.0)/6.9; 229 $(M-N_2)^-$ (58)/0.3; 228 $(M-N_2-H)^-$ (21)/0.3, (4.5)/3.5; 173 $(M-N_2-C_3H_3RO)^-$ (60)/0.4, (19)/3.3; 146 $PhtN^-$ (25)/0.3, (80)/4.6, (65)/5.9, (35)/8.2; **41 $CHCO^-$ (100)/4.4, (83.7)/6.0**.
2a	216 $(M-N_2)^-$ (59)/0.2; 215 $(M-N_2-H)^-$ (1.2)/0.3, (0.08)/3.0, (0.03)/4.0; 174 $(M-N_2-CH_2CO)^-$ (12.3)/0.2; 188 $(M-N_2-CO)^-$ (7.5)/0.2; 160 $(M-N_2-2CO)^-$ (10.2)/0.2; 147 $(C_7H_4O_2N_2)^-$ (2.7)/3.1, (3.9)/4.2; **146 $(M-N_2-C_3H_3RO)^-$ (100)/0.2, (2.9)/2.6, (2.4)/4.1**; 41 $CHCO^($ (0.6)/0.2, (0.9)/4.1, (0.3)/6.0, 98.8* (216→146).
2b	258 $(M-N_2)^-$ (25)/0.5; 257 $(M-N_2-H)^-$ (0.25)/0.5, (0.04)/3.4; 230 $(M-N_2-CO)^-$ (6.7)/0.5; 216 $(M-N_2-CH_2CO)^-$ (20)/0.5; 202 $(M-N_2-2CO)^-$ (4.2)/0.5; 160 $(M-N_2-RCHCO)^-$ (0.5)/0.5, (0.05)/2.9, (0.1)/4.3; 147 $(C_7H_4O_2N_2)^-$ (12.5)/0.5, (6.3)/4.2; **146 $(M-N_2-C_3H_3RO)^-$ (100)/0.5, (6.1)/2.7, (6.1)/3.9**; 42 NCO^- (0.6)/0.5, (1.2)/4.2, (0.3)/6.1; 41 $CHCO^-$ (12)/4.2, (4.0)/7.4; 82.6* (0.2)/0.5, (258→146).
2c	292 $(M-N_2)^-$ (35)/0.3; 264 $(M-N_2-CO)^-$ (10)/0.4; 250 $(M-N_2-CH_2CO)^-$ (3.5)/0.3; 249 $(M-N_2-CH_3CO)^-$ (2.5)/0.3; 248 $(M-N_2-CO_2)^-$ (2.0)/0.3; 236 $(M-N_2-2CO)^-$ (1)/0.3; 160 $(M-N_2-RCHCO)^-$ (11)/0.3; **146 $(M-N_2-C_3H_3RO)^-$ (100)/0.3, (2.9)/2.6, (2.4)/4.1**; 41 $CHCO^-$ (0.6)/0.3, (0.9)/4.1, (0.3)/6.0.

m/z^* is a metastable peak from $(m/z' \rightarrow m/z'')$ reaction.



Scheme 1.

compounds in the range of thermal electron energy peaks of ions $[M-N_2]^-$, $[M-N_2-H]^-$ and $[M-N_2-C_3H_3RO]^-$, $[M-N_2-CH_2CO]^-$, $[M-N_2-CO]^-$, $[M-N_2-2CO]^-$, $PhtN^-$ ($[C_8H_4O_2N]^-$ m/z 146), $[C_7H_4O_2N_2]^-$ (m/z 147) are registered. The peaks of ions $[M-H]^-$, $[M-N_2-H]^-$, $PhtN^-$, $[C_7H_4O_2N_2]^-$, C_2HO^- (m/z 41) are also observed at higher electron energies.



Probably, originally the structure of ions $[M-N_2]^-$ (**1a**–**c** and **2a**–**c**) was **B**, which then can isomerize into ketene ions **A** and (or) cycle **C** [7,8]. Ab initio calculations of these ions of compound **1a** showed, that their stability increases in line **A** > **C** > **B** (the internal energy (E) relative values of the given ions are equal to 0, 1.62 and 0.6 eV, respectively). Thus, the structure **A** formed from **B** as a result of the Wolff rearrangement is the most stable one. However, in contrast to the positive ion mass spectra of phthalimidoalkyl-α-diazoketones [2], in the NI mass spectra of compounds **1a**–**c** and **2a**–**c** peaks formed due to the fragmentation of the ketene type ions were not observed. Therefore, it is quite possible to assume that ions $[M-N_2-C_3H_3RO]^-$ (m/z 145 (**1a**–**c**) and m/z 146 (**2a**–**c**)) form from **B**-type ions due to the cyclopropanone molecule (C_3H_3RO) elimination (see Table 1 and Scheme 1[1]).

The quantum chemical computations have shown that the $[M-N_2-C_3H_3RO]^-$ ions (m/z 145 from **1a**–**c**) without hydrogen atom in β-position of the benzene ring relative to a CO group of phthalimide fragment possess the minimal internal energy.

The elimination of cyclopropanone molecules from $[M-N_2]^-$ ions in the range of thermal electron energy is also typical for compounds (**1d** and **1e**) containing lengthened hydrocarbon bridge between the phthalimide and diazoketone fragments. In this case the cyclopropanone molecule detachment proceeds with the participation of hydrogen atoms of the specified bridge (Scheme 2).

Indeed, for the ion with m/z 159 (**1d**) similar to the $[M-N_2-CH_2CO]^-$ one from **1a** the cyclic structure **D** is calculated to be lower in energy than the carbene structure **E** by 0.5 eV at the

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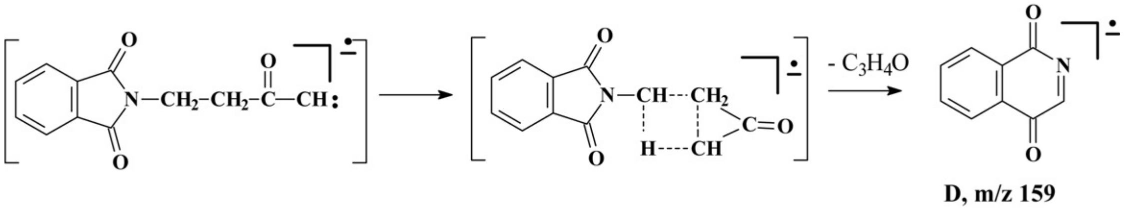
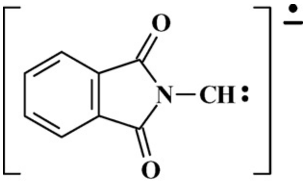
[1] The structures of ions made in brackets represent assumed intermediates.



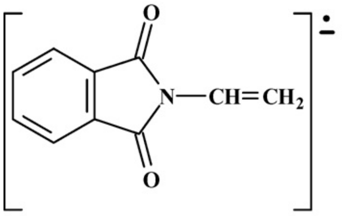
Scheme 2.

HF/6-31++G(d,p) and by 0.74 eV at the B3LYP/6-31++G(d,p) level of theory.

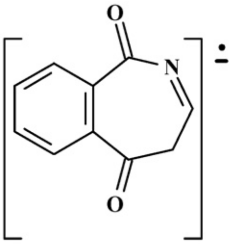


m/z 159 (E)

On the contrary, the ion with *m*/*z* 173 formed from **1e** by a similar process has more stable linear structure **F** (the difference between *E* values for the structures **G** and **F** is 1.2 eV at the HF/6-31++G(d,p) and 0.56 eV at the B3LYP/6-31++G(d,p) level of theory).

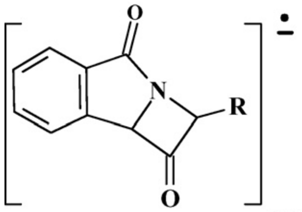


m/z 173 (F)

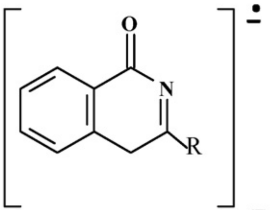


m/z 173 (G)

Probably, the decarbonylation processes also proceeded due to the **C**-type ions fragmentation yielding $[M–N_2–CO]^-$ and $[M–N_2–2CO]^-$ ions, but it is only the case when the hydrocarbon chain between phthalimide and diazoketone groups of α-diazoketone will consist of one methylene link (**1a**–**c** and **2a**–**c**). According to the calculations, $[M–N_2–CO]^-$ and $[M–N_2–2CO]^-$ ions have the following structures:



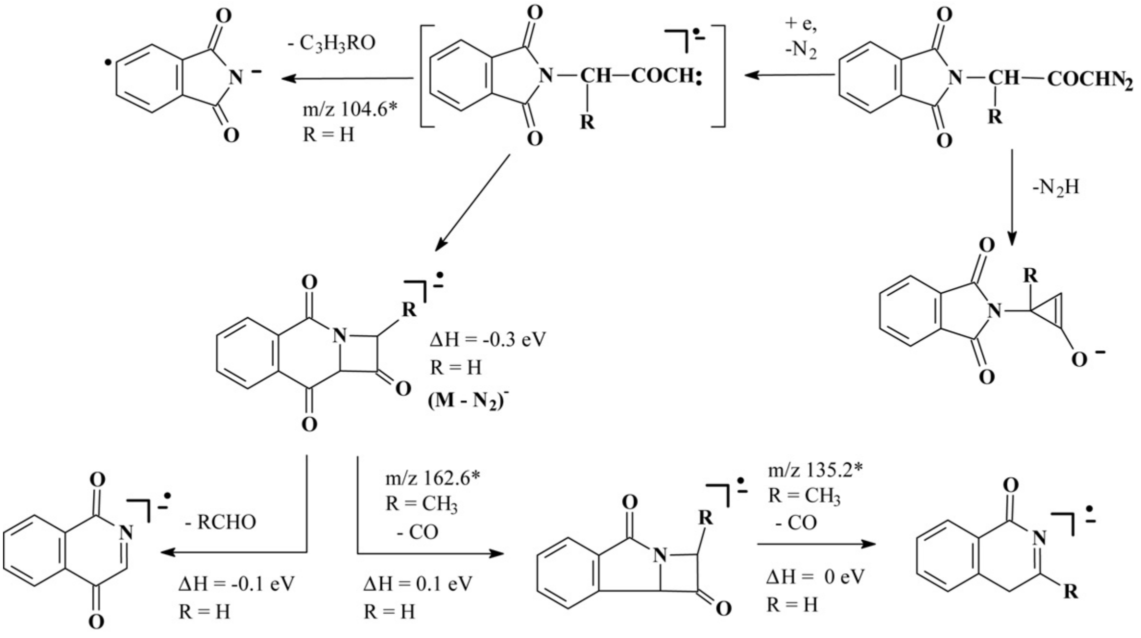
(H)



(I)

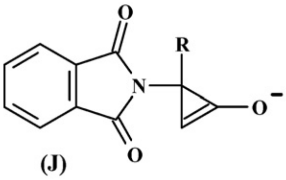
The **C**-type NIs from α-diazoketones **1d** and **1e** are likely to have structures containing five- and six-membered cycles, respectively, instead of four-membered ones in the case of **1a**–**c** and **2a**–**c** and therefore do not undergo decarbonylation: peaks of $[M–N_2–CO]^-$ and $[M–N_2–2CO]^-$ ions are not observed in the mass spectra.

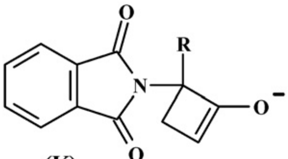
In the range of thermal electron energy of NI mass spectra of all compounds researched the peaks of $[M–N_2H]^-$ ions are observed, which have greater intensity in the case of longer molecules (**1d** and **1e**) and form by the separation of N_2H species directly from molecular ion because the consecutive emission of N_2 and H is energetically less favorable near the zero electron energy. According to

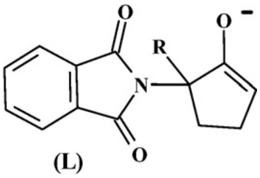


Scheme 3.

the quantum chemical calculations the structure **J** is the most stable for $[M–N_2H]^-$ ions from compounds **1a** and **1b**. The increase of $[M–N_2H]^-$ peak intensity accompanying the lengthening of hydrocarbon bridge between the phthalimide and diazoketone groups (compounds **1d** and **1e**) is probably caused by the presence of more stable four- and five-membered cycles in ion structure (**K** and **L**).


(J)


(K)


(L)

Based on the obtained results, common fragmentation scheme of α-diazoketones researched has been proposed on the example of compounds **1a** and **1b** (Scheme 3).

At the same time, for some reactions such as $AB \rightarrow A^\bullet + B^\bullet$ of the proposed fragmentation scheme appropriate enthalpies (ΔH) have been calculated from the equation of thermal equilibrium:

$$\Delta H = \Delta H_f(A^\bullet) + \Delta H_f(B^\bullet) - \Delta H_f(AB)$$

It can be seen that ΔH values are different from each other within 0.4 eV and do not contradict the given scheme.

In the mass spectra of researched diazoketones several dissociation channels of $[M–N_2]^-$ ions are testified by the presence of metastable peaks. The high relative intensity of the metastable peak indicates a relatively long lifetime of the NI with respect to dissociation (τ_d) which may be estimated based on the general procedure [9]. Based on this procedure life times of $[M–N_2]^-$ ions from **1a**, **b** and **2a**, **b** with respect to dissociation followed by the cyclopropanone molecule elimination have been estimated. In all cases the τ_d value (~15–40 μs) appreciably exceeds the average time of the presence of ions in the ionization chamber (≈3 μs [10]). And since the intensity of fragment ions in the mass spectra appreciably exceeds the intensity of parent ions, the majority of them dissolute in much shorter times, than τ_d value. Therefore, alongside with the slow channel of $[M–N_2]^-$ ions' dissociation, which is proved by the presence of the appropriate peak of metastable ion, much faster channel of the dissociation of above-mentioned ions exists, or their formation also originates directly from molecular negative ions.

4. Conclusion

Thus, under REC the mass spectra of phthalimide- and pyridine-2,3-dicarboimidoalkyl-α-diazoketones in the range of thermal electron energy consist of peaks of ions formed both by the dissociation of a molecular ion and by the processes of consistent dissociation of $[M–N_2]^-$ ions to form ions of a cyclic structure.

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