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Reactions of nitrophenide and halonitrophenide ions with acrylonitrile and alkyl acrylates in the gas phase: The case of $[M-2]^-$ ion formation☆

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This paper is dedicated to Professor Alex Harrison on the occasion of his 80th birthday.

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ABSTRACT

The structure of $[M-2]^-$ ions formed in reactions between α,β-unsaturated compounds (acrylonitrile and alkyl acrylates) and nitro- and *p*-halonitro-phenide ions have been studied both experimentally and theoretically. Although it is not possible to prove the origin of the $[M-2]^-$ ions directly clear evidence for intermediate β-adduct formation during reaction was found. More specifically, the mechanism involves transformation of the β-adduct comprising an O-atom transfer via a six-membered intermediate, followed by the loss of an HCOR molecule (R = CN, CO_2Me, CO_2Et). This sequence leads eventually to an $[M-2]^-$ anion with an *o*-nitrosobenzylic anion structure. Further transformation of the *o*-nitrosobenzylic anion to the more stable *o*-aminobenzaldehyde anion was also considered but was ruled out.

1. Introduction

Taking into account the importance of acrylonitrile and acrylates in the manufacture of acrylic emulsion polymers used in paints, surface coatings for textiles, paper and leather, adhesives and sealants, acrylic fibers, chemical intermediates, fragrance and flavoring agent, in the synthesis of vitamin B1 [1] it is mandatory to understand the factors that determine the outcome of reactions involving these compounds.

Although such activated olefins are extensively used in organic synthesis as reactants in condense-phase nucleophilic conjugate addition (Michael reaction) [2–4] their intrinsic gas-phase reactivity, in particular with nucleophiles, is still incompletely known limited to published studies by Bartmess [5], Bowie [6] and Bernasconi [7]. One computational [8] study results showed that the stability of the initially formed β-adduct is decisive in determining reactivity. Only electron-deficient olefins reacting with nucleophiles having stabilizing groups (cyanomethyl anion, nitromethyl anion and phenyl anion) [7] give rise to adduct formation and subsequent rearrangement into conversion products. Adapting this insight we performed a number of reactions of (halo)nitrophenide ions with α,β-unsaturated compounds like acrylonitrile, methyl acrylate and ethyl acrylate as gaseous neutral reagents. The results of these reactions including product structure determination and elucidation of the corresponding reaction pathways were reported in our recent paper [9]. The most significant reaction pathways are presented in Scheme 1. It was also reported in this paper, that the gas-phase ion-molecule reactions of α,β-unsaturated compounds with nitrophenide ions and *p*-halonitrophenide ions lead to products having *m*/*z* values nominally two mass units lower than the (halo)nitrophenide ion (M). The mechanistic and structural details associated with ($[M-2]^-$) ion formation is the topic of the present work, and we report the results of mass spectrometric experiments interpreted by means of computational quantum chemistry.

2. Experimental

2.1. Mass spectrometry and quantum chemical calculations

The mass spectrometric methodology applied here was the same as in our previous paper [9], including tandem mass

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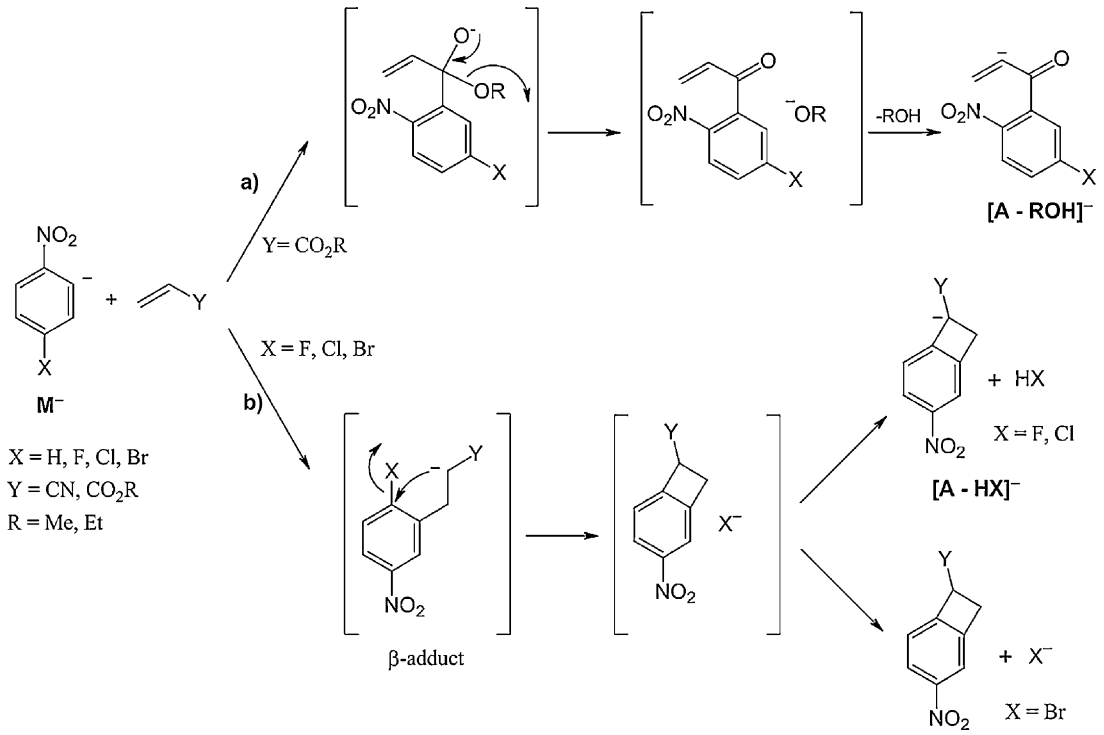


Scheme 1. General scheme of plausible pathways for the most significant reactions of α,β-unsaturated compounds with isomeric nitrophenide ions and *p*-halonitrophenide ions. Pathway (a) presents the addition of the respective nitrophenide ion to the carbonyl group of acrylate followed by the elimination of an alcohol molecule. Pathway (b) comprises the β-adduct formation followed by the intramolecular substitution of the halogen atom.

spectrometry and accurate high resolution mass measurements and is described briefly.

The gas-phase ion-molecular reactions of (halo)nitrophenide ions with α,β-unsaturated compounds as well as the fragmentations of the reaction products were studied employing an API 365 triple quadrupole mass spectrometer (Applied Biosystems) equipped with a TurboIonSpray™ electrospray ion source operated in the standard ESI mode. The examined phenide ions were generated in the ion source from appropriately substituted benzoate anions and under such ion source parameters to obtain the highest possible abundance of the (halo)nitrophenide ions. After mass selection with the use of the first quadrupole mass filter, the anions were subject to the reactions with α,β-unsaturated compounds admixed to the nitrogen introduced into the collision cell. The collision gas inlet has been modified to accommodate the introduction of vapors independently from the curtain gas of the ESI source. It is difficult to estimate the concentration of the substrate present in the collision cell with sufficient accuracy to obtain the corresponding coefficients, so our results are reported in a qualitative fashion only. However for each gas-phase reaction, we tried to keep the same increase of pressure in mass spectrometer. The nominal cell voltage was set to −5 eV relative to the immediate surroundings to suppress collisionally induced dissociation (CID). In order to obtain product CID spectra the α,β-unsaturated compound was injected directly into the medium pressure section of the ESI ion source.

Accurate high resolution mass measurements were performed using a Bruker Apex 47, FT-ICR mass spectrometer (Billerica, MA) equipped with an electrospray ion source. Ions produced in the ESI source were transferred to the FT-ICR cell, and all ions except the ion of interest were ejected using sweep pulses followed by clean up shot pulses. The substrate was charged into the FT-ICR cell through a leak valve at a constant pressure in the range 5×10^{-8} to 1×10^{-7} mbar, and mass spectra were recorded after a variable reaction time (from 5 to 10 s reaction delay).

Reaction potential energy profiles and molecular properties were computed applying density functional theory methods, at the PBE1PBE/6-311+G(d,p)//PBE1PBE/6-31+G(d) level, as described in the previous paper [9].

2.2. Reagents and reference compounds

Reagents and solvents (HPLC grade) were obtained from commercial suppliers or were synthesized according to known procedures. One reference compound which is not commercially available was synthesized as described below.

(o-Nitrobenzyl)-cyanoacetic acid – This compound was obtained in a two-step synthesis. In the first step, ethyl ester of the (*o*-nitrobenzyl)-cyanoacetic acid was prepared. To the acetone solution containing the 1.7 g (10 mmol) 2-nitrobenzyl chloride, 2.3 g (20 mmol) ethyl cyanoacetate and 0.2 g (0.5 mmol) tetrabutylammonium bromide the potassium carbonate was added. The solution was stirred at ambient temperature for 4 h and ethyl acetate was then added. Thereafter the resulting solution was washed with water and brine. The solvent was removed under reduced pressure and the residue was purified by chromatography applying silica gel using hexane–ethyl acetate (5:1) as eluent. The product obtained in this first step, the ethyl ester of (*o*-nitrobenzyl)-cyanoacetic acid, was then subject to the alkaline hydrolysis. The resulting methanol solution of the ethyl ester of (*o*-nitrobenzyl)-cyanoacetic acid (0.4 g (2 mmol)) was treated with an aqueous solution of NaOH (0.2 g NaOH in 1 ml of water). After the hydrolysis was completed the resulting solution was acidified with 10% hydrochloric acid. The precipitate was collected and washed with water to give 210 mg of the title compound.

^{1}H NMR (500 MHz, DMSO-d_6): δ [ppm] 3.38 (dd, 1H, J = 14.0, J = 9.4 Hz); 3.61 (dd, 1H, J = 14.0, J = 5.8 Hz); 4.43 (dd, 1H, J = 9.4, J = 5.8 Hz); 7.59–7.64 (m, 2H); 7.76 (td, 1H$_c$, J = 7.5, J_{a-c} = 1.3 Hz); 8.07 (dd, 1H$_a$, J_{a-b} = 8.2, J_{a-c} = 1.3 Hz).

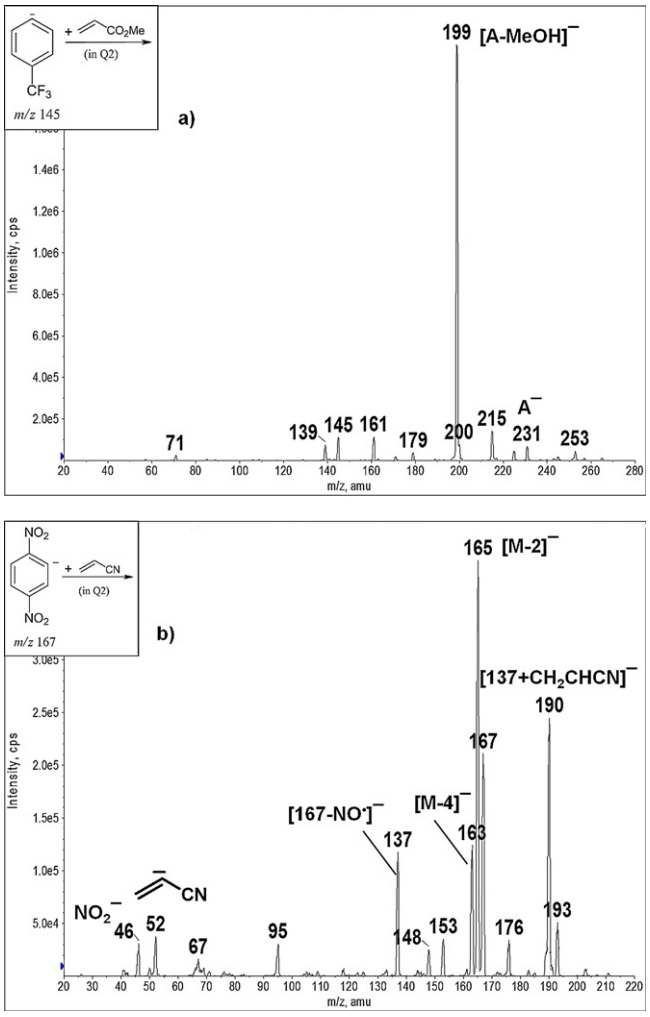


Fig. 1. Q3 mass spectra recorded for the products of the reactions in a collision cell (Q2) of (a) *p*-(trifluoromethyl)-phenide ion with methyl acrylate; (b) 2,5-dinitrophenide ion with acrylonitrile (A^- – adduct ion (the formation of different types of adducts in the reactions of (halo)nitrophenide ions with α,β-unsaturated compounds is discussed in our previous paper [9])).

^{13}C NMR (125 MHz, DMSO-d_6): δ [ppm] 117.2; 125.0; 128.9; 131.3; 132.8; 133.7; 148.8; 166.9.

3. Results and discussion

3.1. Structural requirements for $[M-2]^-$ ion formation

As a first step in a systematic effort to identify the factors that govern $[M-2]^-$ ion formation we conducted a series of reaction studies including an array of substituted olefins and substituted phenide ions. From these measurements it appears clear that the presence of a nitro group in the phenide ion is prerequisite. The situation is illustrated by the mass spectra reproduced in Fig. 1, resulting from the reaction of *p*-(trifluoromethyl)phenide ion with methyl acrylate (Fig. 1a) and the reaction of 2,5-dinitrophenide ion with acrylonitrile (Fig. 1b). In the first case no $[M-2]^-$ ion is observed. Instead, the product spectrum is dominated by the adduct (*m*/*z* 231), and its methanol elimination product (*m*/*z* 199) as discussed in our previous article [9]. In the second case formation of $[M-2]^-$ (*m*/*z* 165) is clearly evident. These two examples briefly summarizes the general observation that $[M-2]^-$ is highly specific to nitrophenide ions. In addition, the observation of $[M-4]^-$ (*m*/*z* 163) in the second case shows that the presence of the additional nitro group gives rise to two successive reactions of the same kind.

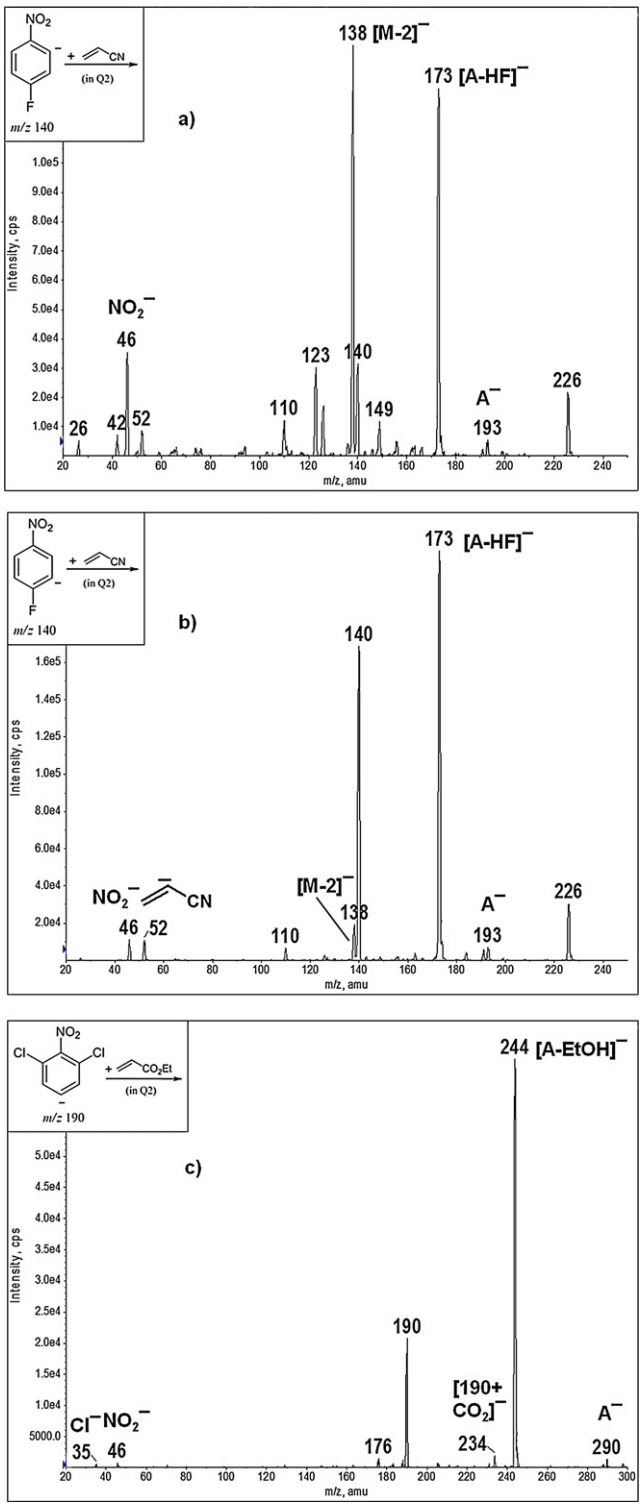
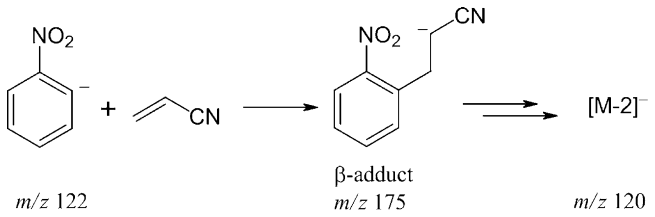


Fig. 2. Q3 mass spectra recorded for the products of the reactions in a collision cell (Q2) of acrylonitrile with Q1-selected (a) 5-fluoro-2-nitrophenide ion, (b) 2-fluoro-5-nitrophenide ion and (c) reaction of 3,5-dichloro-4-nitrophenide ion with ethyl acrylate. Collision energy was set to −5 eV in all cases.

Comparison of the intensities of the peaks corresponding to the $[M-2]^-$ ions with other products formed during the reactions of isomeric *p*-halonitrophenide ions with acrylonitrile and ethyl acrylate (Fig. 2) gives another piece of important information. The



Scheme 2. Scheme of the formation of β-adduct of 2-nitrophenide ion to acrylonitrile.

spectra show that *p*-halonitrophenide ion with the negative charge situated in the *ortho* position to the nitro group gives abundant $[M-2]^-$ ions, in stark contrast to *p*-halonitrophenide ions in which the negative charge occupies the *meta* position with respect to the nitro group. This result suggests that in the latter case a proton transfer, necessary for rearrangement into the anion having the negative charge in the *ortho* position, has to proceed prior to formation of the $[M-2]^-$ ion. To clarify this hypothesis we performed an additional experiment with 3,5-dichloro-4-nitrophenide ion (Fig. 2c). According to the hypothesis this anionic reagent in which both *ortho* positions of the nitro group are occupied by chlorine atoms should not give $[M-2]^-$ ions in the reactions with examined α,β-unsaturated compounds. The spectrum recorded during the reaction of 3,5-dichloro-4-nitrophenide ion with ethyl acrylate (Fig. 2c) confirms this suggestion. It shows the peaks corresponding to the adduct (*m*/*z* 290) and the product of elimination of ethanol molecule from the adduct (*m*/*z* 244) while there is no peak for $[M-2]^-$.

We further studied α,β-unsaturated compounds without electron withdrawing groups, more specifically allyl chloride and allyl iodide. Neither the adducts nor any decomposition product was observed, indicating that the presence of a strongly electron withdrawing group is required to make the formation of $[M-2]^-$ possible.

3.2. Discussion on the β-adduct formation

On the basis of our findings we speculate that $[M-2]^-$ formation involves formation of a β-adduct in the first step of the reaction (Scheme 2). Formation of the β-adduct occurs in the *ortho* position in accordance with the experimental observations, while in fact, according to the earlier remark, the *p*-halonitrophenide ions with the negative charge situated in *ortho* position to the nitro group give the most abundant peaks corresponding to the $[M-2]^-$ ions.

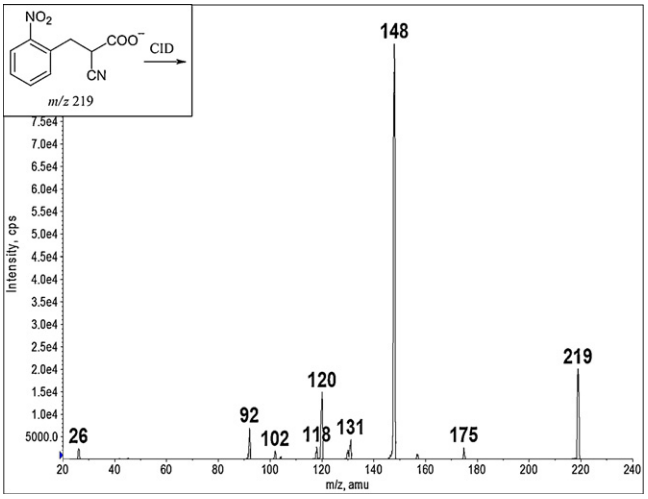


Fig. 3. The CID (CE = −5 eV) negative ion mass spectrum recorded for the (2-nitrobenzyl)-cyanoacetic acid anion (*m*/*z* 219).

To investigate this presumption we synthesized (2-nitrobenzyl)-cyanoacetic acid, which in the negative ion ESI mode after decarboxylation, was expected to give the β-adduct with the structure shown in Scheme 2. We hypothesized that transformation of this adduct could in turn lead to the $[M-2]^-$ ion. As anticipated, in the CID mass spectrum recorded for (2-nitrobenzyl)-cyanoacetic acid anion (*m*/*z* 219) presented in Fig. 3, the peak at *m*/*z* = 175 corresponding to decarboxylation is observed. Unfortunately, this fragment does not constitute the major fragmentation pathway in the represented CID mass spectrum. All attempts to generate ion with *m*/*z* 175 in reasonable abundance to enable recording its CID spectrum were ineffective.

On the other hand, one likely product of the *m*/*z* = 175 ion would be *m*/*z* 120, as actually seen in the CID spectrum of *m*/*z* 219, suggesting the intermediacy of *m*/*z* 175. As a matter of fact, the CID spectra of *m*/*z* 120 – resulting from the decomposition of (2-nitrobenzyl)-cyanoacetic acid and from the ion-molecule gas-phase reaction of 2-nitrophenide ion with acrylonitrile – give very similar spectra, as evident from Fig. 4.

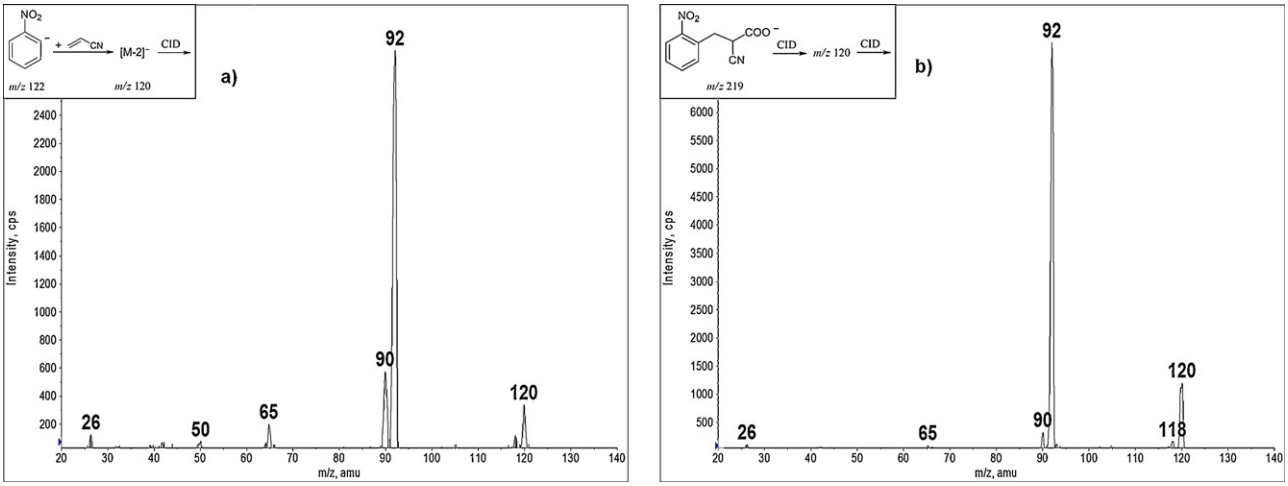
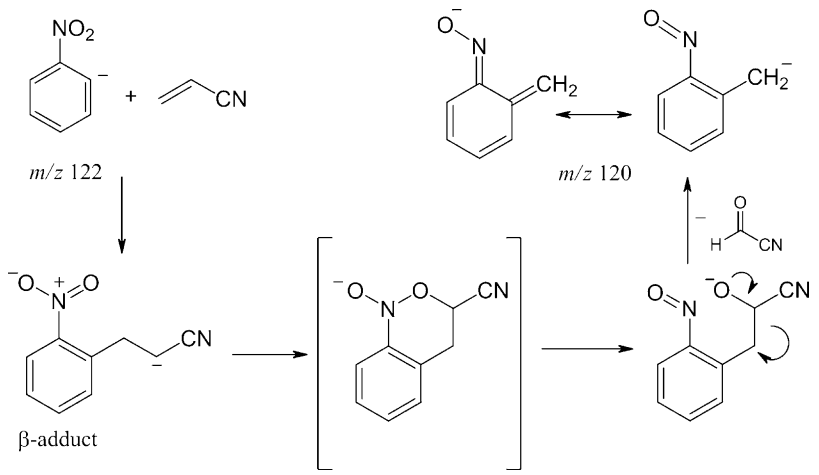


Fig. 4. CID spectra (recorded at CE = −20 eV) of ionic product (*m*/*z* 120) resulted from: (a) the reaction of 2-nitrophenide ion with acrylonitrile; (b) in-source fragmentation of (2-nitrobenzyl)-cyanoacetic acid anion.



Scheme 3. Postulated mechanism of the $[M-2]^-$ ion formation in the gas-phase reaction of 2-nitrophenide ion with acrylonitrile.

3.3. Structural properties of $[M-2]^-$ ion formation

The next set of experiments were aimed at determining the structural properties of the $[M-2]^-$ ions. The proton affinity of the $[M-2]^-$ ion resulting from the reaction of 5-chloro-2-nitrophenide ions with ethyl acrylate was bracketed by observing in-cell reactions with the following acids (*PA* of corresponding anion): acetone (369 kcal/mol), chloroacetonitrile (358 kcal/mol) and acetic acid (347 kcal/mol). Only the reaction with acetic acid gave reaction, evident from acetate ion formation, indicating a value of the proton affinity of the $[M-2]^-$ anion in the range 347–358 kcal/mol. The low reaction efficiency observed even with acetic acid indicates a value in the low end of the indicated PA range.

To verify the 2-nitrosobenzylic anion structure proposed for $[M-2]^-$ ion we computed the proton affinity of 5-chloro-2-nitrosobenzylic anion, resulting in a value 347.1 kcal/mol, only slightly higher than the PA of the acetate anion, in accordance with the bracketing experiments.

Accurate mass measurements of $[M-2]^-$ product gave the evidence that its formation is consistent with an isotopic mass shift corresponding to the replacement of O with CH_2. This finding was found to be essential in picturing out the mechanistic details, clearly showing the direct involvement of the nitro group during the order of events leading to the product formation.

3.4. Mechanism of $[M-2]^-$ ion formation

The results of the experiments described above now allow us to propose a putative mechanism leading to $[M-2]^-$, shown in Scheme 3. It consists of three steps, (i) formation of the β-adduct, (ii) cyclization of the β-adduct comprising an intramolecular nucleophilic attack of the oxygen atom of the nitro group, (iii) eventually followed by the loss of formyl cyanide molecule leading to the 2-nitrosobenzylic anion. According to the previous remark the (halo)nitrophenide ions with the negative charge situated in *meta* or *para* position to the nitro group have first to isomerize to the anion with negative charge located in *ortho* position with respect to the nitro group to make the reaction possible. Reactions involving nucleophilic addition to the oxygen atom of the nitro group are well known, as in vinyl Grignard reactions with nitroarenes [10,11]. The mechanism presented in Scheme 3 resembles the mechanism of rearrangement of 2-nitrosobenzyl compounds

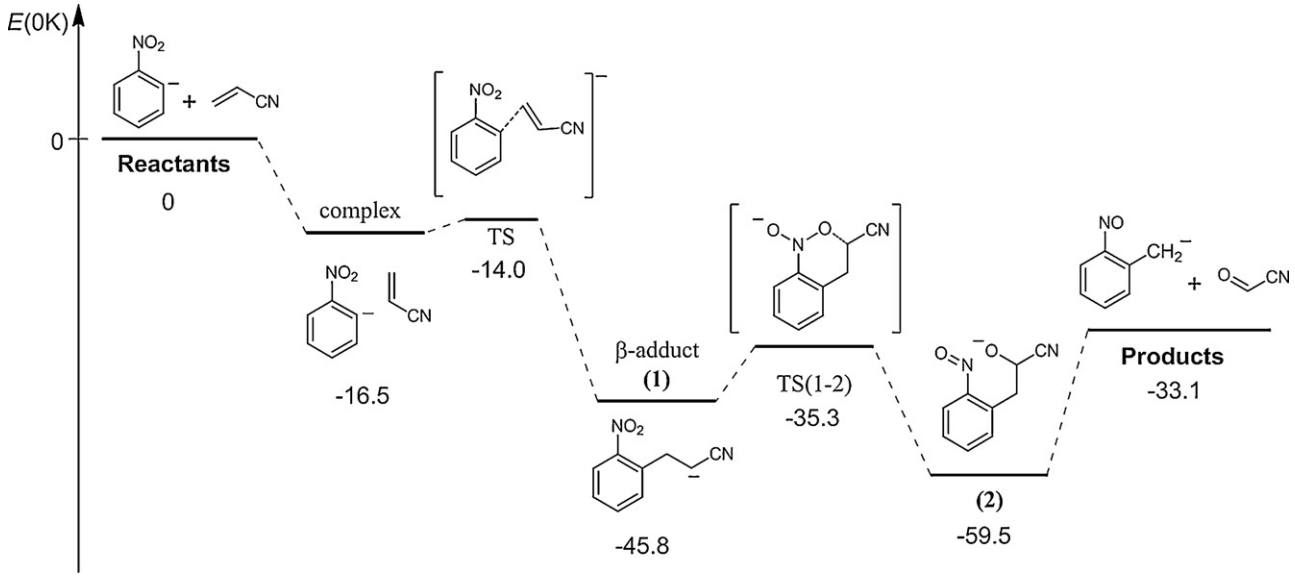


Fig. 5. Overall profile of the *E* (0 K) surface (in kcal/mol) for $[M-2]^-$ formation calculated using PBE1PBE/6-311+G(d,p)//PBE1PBE/6-31+G(d).

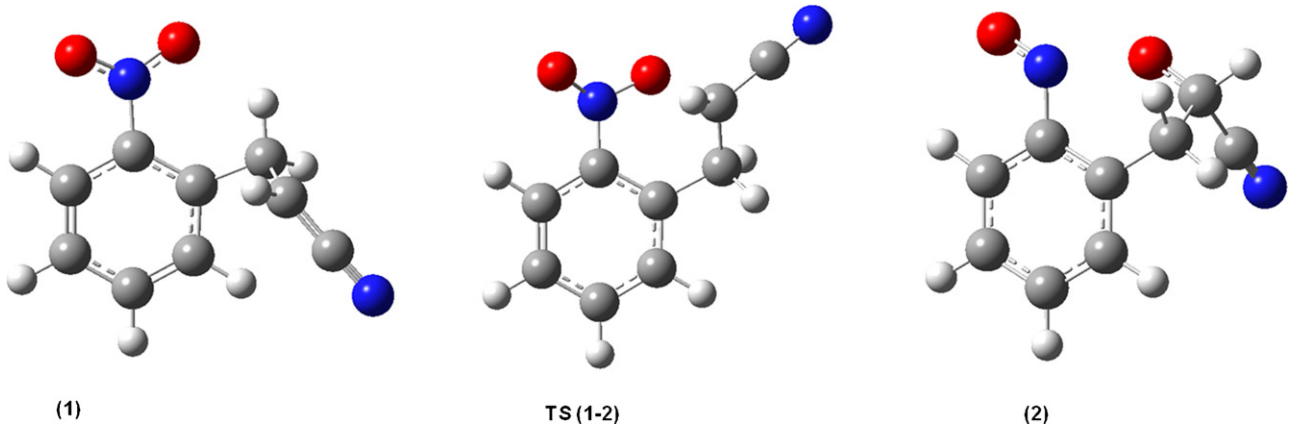


Fig. 6. PBE1PBE/6-31+G(d) optimized geometries of anions (**1**), (**2**) and TS connecting them. The C—O bond length in the transition state is computed to be 1.87 Å. It has to be noted that anions (**1**) and (**2**) are conformationaly flexible and a number of other structures with similar energy can be found.

proposed by Il'ichev and Wirz [12]. In their experimental [13–15] and theoretical [12,16] studies on the photoinduced isomerization reaction of 2-nitrosobenzyl compounds they also took under discussion the anionic version of the reaction, i.e., the isomerization of 2-nitrotoluene anion to 2-nitrosobenzyl alcohol anion via formation of bicyclic intermediate. The transformation of 2-nitrotoluene anion into 2-nitrosobenzyl anion considered formally as cyclization of deprotonated quinoid intermediate (also known as nitronic acids or aci-form) was found to occur with activation barrier of 31.3 kcal/mol (B3LYP) and 36.1 kcal/mol (BHLYP) [12]. The activation barrier for the cyclization of deprotonated species was predicted to encounter a much higher activation barrier than the analogous isomerization reaction of the quinoid intermediate. Although the relatively high activation barrier of the isomerization of 2-nitrotoluene anion was found, we suppose that in our case the transformation of β-adduct leading to the product of O-atom transfer can proceed with substantial lower activation energy due to the presence of the stabilizing group like —CN, $-CO_2Me$ and $-CO_2Et$. The formation of six-membered ring instead of five-membered ring should also influent on the stabilization of the transition state.

More significant to the discussion is the computed potential energy diagram reproduced in Fig. 5. This diagram shows that the suggested mechanism is energetically feasible, and is typical for fast addition/elimination reactions of ions in the gas-phase. According to the results of our calculations, both the β-adduct (**1**) and the intermediate O-atom transfer product (**2**), as well as the connecting transition structure TS(1-2) all lie significantly below the energy of reactants. The six-membered transition structure **TS 1-2** lies 10.5 kcal/mol above the β-adduct (**1**). The optimized geometries of anions (**1**), (**2**) and transition structure connecting them are presented in Fig. 6.

The mechanism of $[M-2]^-$ ion formation was further supported in experiments with methyl methacrylate and crotonitrile serving as the α,β-unsaturated reagents. According to the expected reaction pathways depicted in the Scheme 4 which are analogous to the proposed mechanism of Scheme 3, the reaction with methyl methacrylate (pathway a) should lead to the same anionic product as in the case of the reactions with methyl and ethyl acrylates, while in the case of the reaction with crotonitrile (pathway b) a peak at *m*/*z* 168 should be expected.

As anticipated, in the spectra recorded during the reactions of 5-fluoro-2-nitrophenide ion with methyl methacrylate (Fig. 7a) and 5-chloro-2-nitrophenide ion with crotonitrile (Fig. 7b) the peaks observed at *m*/*z* 138 and *m*/*z* 168 confirm the suggested mechanistic pathway. Moreover, the peaks corresponding to the ionic products $[A-MeOH]^-$, $[A-HX]^-$ and A^- which are also observed in the spectra presented below, are characteristic for the reactions of (halo)nitrophenide ions with activated olefins and were described in detail in the previous paper.

The last important problem which has to be addressed is the possibility of the rearrangement of the *o*-nitrosobenzylic

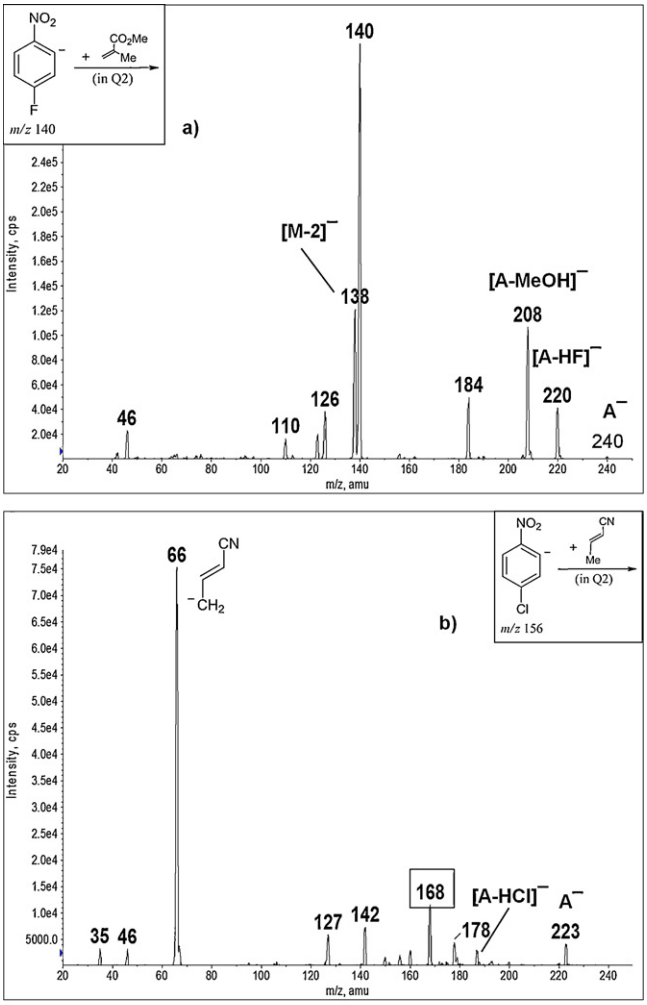
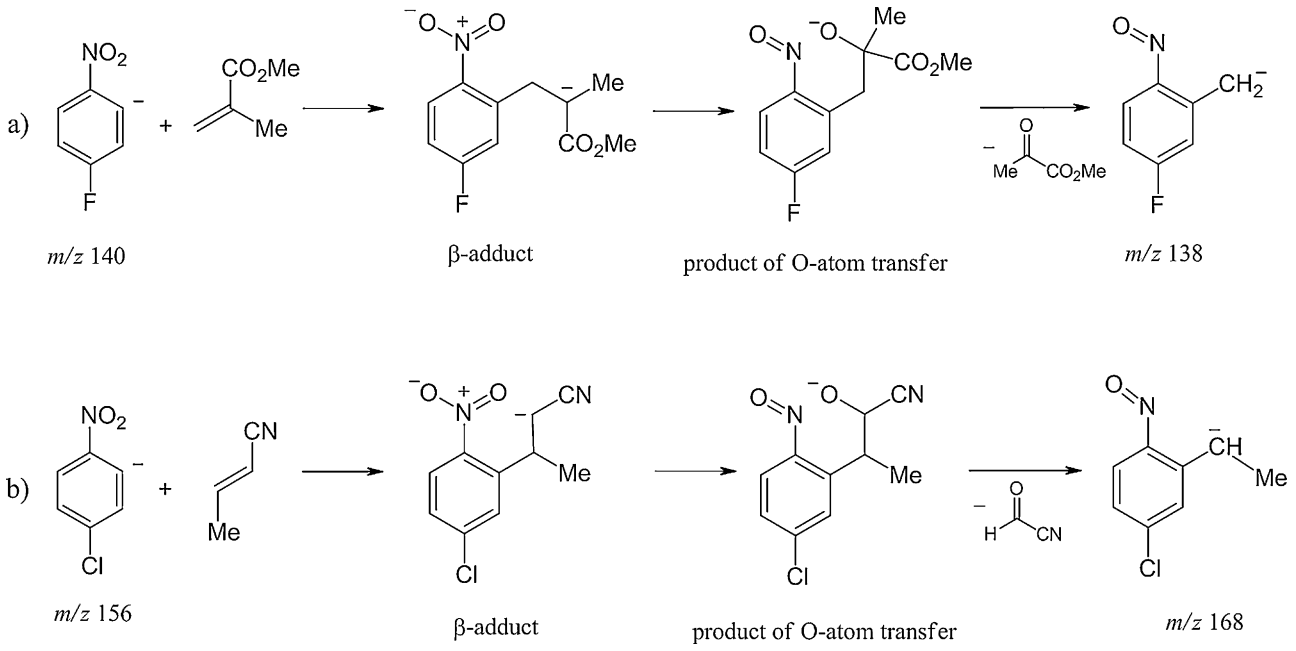


Fig. 7. Q3 mass spectra recorded for the products of the reactions of (a) 5-fluoro-2-nitrophenide ion with methyl methacrylate and (b) 5-chloro-2-nitrophenide ion with crotonitrile.



Scheme 4. The expected products of the reactions of (a) 5-fluoro-2-nitrophenide ion with methyl methacrylate and (b) 5-chloro-2-nitrophenide ion with crotonitrile.

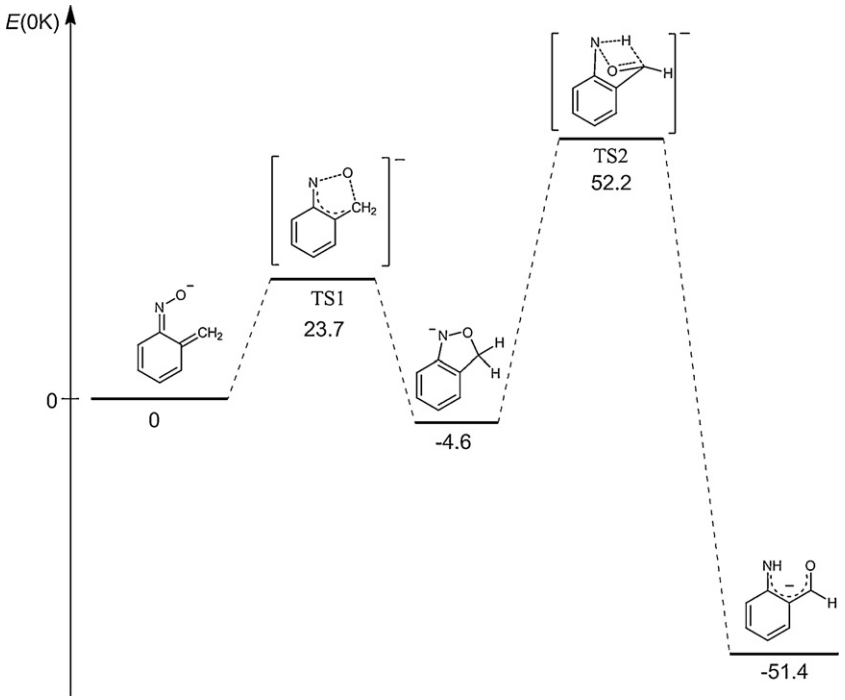


Fig. 8. Calculated energy profile (in kcal/mol) for the proposed further transformation of *o*-nitrosobenzylic anion into *o*-aminobenzaldehyde anion.

anion to the probably more stable *o*-aminobenzaldehyde anion (Fig. 8). Our quantum chemical calculations showed that *o*-aminobenzaldehyde anion indeed is 51.4 kcal/mol more stable than the *o*-nitrosobenzylic anion but the activation energy of the first reaction step is 23.7 kcal/mol and of the second step is 56.8 kcal/mol (52.2 kcal/mol respective to the energy of the substrate). This second value shows that this rearrangement is unlikely.

4. Conclusions

The study presented here provides a consistent picture of the mechanism leading to $[M-2]^-$ formation during gas-phase reactions of (halo)nitrophenide ions with acrylonitrile, methyl acrylate and ethyl acrylate. The $[M-2]^-$ ion was found to have the structure of *o*-nitrosobenzylic anion. The mechanism involves initial formation of a β-adduct of the nitrophenide ion with the activated olefin. The formation of β-adduct at the *ortho* position relative to the nitro group of the phenyl ring is prerequisite for further reaction along this pathway. The β-adducts are kinetically unstable and rearrange to derivatives of *o*-nitrosobenzylic anion accompanied by the loss of HCOR (R = CN, CO_2Me, CO_2Et).

The results presented in this part of work clearly show that the formation of $[M-2]^-$ ions is characteristic of nitrophenide ions. On this basis this reaction may be useful for analytical purposes,

i.e., identifying α,β-unsaturated compounds having electron withdrawing groups.

Acknowledgements

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