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Electron Impact Studies. C. Doubly Charged Negative Ions[1]

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Abstract: Doubly charged negative ions may be produced in the analyzer region of a conventional mass spectrometer. Evidence is presented which suggests that the formation of the doubly charged ions occurs by the capture process $A^- + e \rightarrow A^{2-}$ and that the ions detected in the mass spectrometer are produced in the electric sector when the sample pressure in that region is greater than 10^{-5} Torr. The most abundant doubly charged molecular anions occur when $n = 3$ or 4 for the series p-NO_2-C_6H_4-$(CH_2)_n$-CO_2R (R = H or Me).

Stuckey and Kiser[2a] made the first observations of doubly charged negative ions in the gas phase using an omegatron. They reported the formation of O^{2-} and X^{2-} (X = halogen) with lifetimes of 10^{-4} s. This claim was questioned[2b] but later verified.[3,4] Other doubly charged ions have since been reported including H^{2-},[5] and P^{2-}, As^{2-}, Sb^{2-}, Te^{2-}, and Bi^{2-}.[3] Kancerenicius[6] using multiconfigurational approximations calculated the energies and orbitals of doubly-charged ions of the 2nd and 3rd row elements and concluded that such ions (e.g., B^{2-}, C^{2-}, N^{2-}, O^{2-}, Al^{2-}, Si^{2-}, P^{2-}, and S^{2-}) are unstable and cannot exist as free radicals. The only report of a doubly charged negative ion from an organic substrate is that claimed[7] for a dimer of benzo[*cd*]pyren-6-one.

Doubly charged ions should be stable if the additional binding energy due to the second electron exceeds the Coulombic repulsion of the ion. Such ions have however not been observed in the *conventional* negative ion spectra of organic compounds (produced by thermal electron capture[8]), obtained in either of our laboratories[9] or in those of von Ardenne.[8b] This is not surprising, since electron capture by a singly charged anion is unlikely in the ion source because of (a) the low concentration of anions relative to molecules in that region and (b) the short residence time of ions in the source. Simultaneous two-electron capture in the ion source is an even more unlikely process.

Doubly charged cations of small abundance are common in conventional positive ion mass spectra, particularly in those of highly conjugated systems.[10] The production and the study of reactions of doubly charged cations produced by high-energy ion–molecule reactions in the analyzer regions of a double focusing mass spectrometer has been pioneered by Beynon, Cooks, and colleagues.[11] Such reactions include (a) $A^+ + N \rightarrow A^{2+} + N^-$ (an $E/2$ spectrum[12]) and (b) $A^{2+} + N \rightarrow A^+ + N^+$ (a $2E$ spectrum), where A^+ is any positive ion and N is the target gas, generally maintained at a pressure of ca. 10^{-4} Torr in the appropriate collision region.

We suggested previously[13] that it should be possible to produce doubly charged negative ions in the analyzer regions of a mass spectrometer (i.e., a $-E/2$ spectrum), and we chose quinones and dinitrobenzenes to test this proposal. Doubly charged anions were not detected;[14] instead, the charge inversion reaction $M\cdot^- \rightarrow M\cdot^+$ was observed. In retrospect, it is clear that the nonobservance of doubly charged negative ions in the previous study was due to an incorrect choice of substrate molecules.

Our first observation of doubly charged anions was accidental. The collision-induced dissociations[15] of the molecular anions of methyl esters of p-nitrobenzoyl amino acids[16] were being monitored using the negative ion kinetic energy (ike) technique.[17] The negative ike spectra showed strong peaks at ca. $-E/2$, and mass analysis showed that these were due to the respective doubly charged parent anions M^{2-}. This discovery led us to investigate the formation of doubly charged negative ions with a view to determine: (i) the types of molecule which form doubly charged anions, and (ii) the mechanism of formation of such ions.

Results and Discussion

$-E/2$ spectra were measured with an Hitachi Perkin-Elmer RMU 7D spectrometer (modified as previously described[17]) operating at 70 eV using an accelerating potential of 3.6 kV (unless otherwise specified), a sector voltage in the range $-(0.502–0.512)E$, and a sample pressure of $3\text{-}5 \times 10^{-5}$ Torr measured in the first field-free region of the spectrometer. The doubly charged ions are observed at mass $m_{(A^-)}/4$ for the process $A^- \rightarrow A^{2-}$.[18]

(a) The Formation of Doubly Charged Negative Ions. The type of organic molecule that would be expected to form a

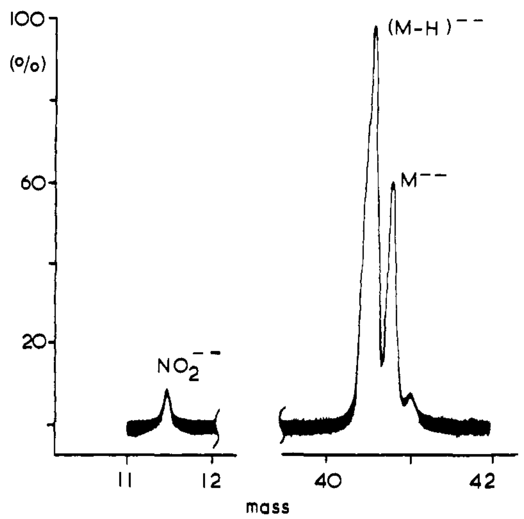


Figure 1. $-E/2$ spectrum of *p*-nitrobenzoic acid: pressure in the first field-free region = 3×10^{-5} Torr, $V = 3.6$ kV, electron beam 70 eV, and sector voltage $-0.506E$.

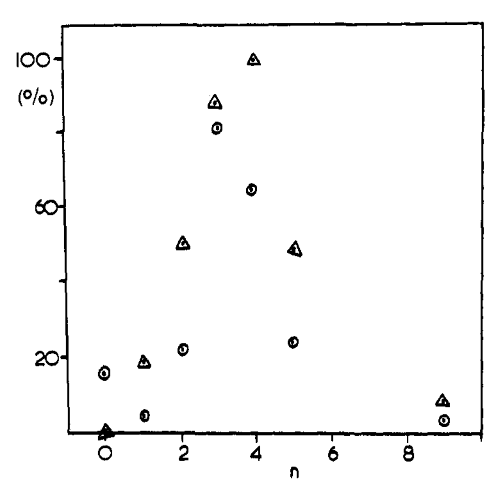
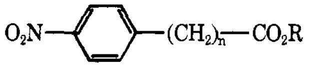


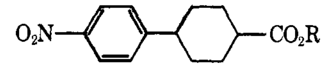
Figure 2. Plot of relative abundances of M^{2-} ions from **1** and **2** as a function of the length of the side chain. All spectra were determined at $-0.506E$, at pressures of 2–3 × 10^{-5} Torr. The pressures of all compounds were adjusted so that the ion current produced by singly charged negative ions was the same for each compound: (⊙) acids, (▲) esters.

doubly charged molecular anion would be one which forms an intense molecular anion[19] and which contains at least two electron-withdrawing substituents capable of capturing low-energy electrons. The following compounds fulfill these prerequisites, but do *not* yield detectable doubly charged molecular or fragment anions: 1,4-naphthoquinone, α-diketones, aryl anhydrides, diacetylbenzenes, dinitrobenzenes (cf. ref 14), nitrobenzaldehydes, nitroacetophenones, nitrobenzophenones, nitrobenzoates, nitrophenylamides, nitrophenyl sulfoxides, nitrophenylsulfonamides, and nitrophenyl sulfones. It appears that benzenoid derivatives with two electron-withdrawing substituents *directly* attached to the ring are generally unable to produce doubly charged molecular anions. Exceptions to this generalization are the nitrobenzoic and cyanobenzoic acids, which produce quite intense $-E/2$ spectra.

The $-E/2$ spectrum of *p*-nitrobenzoic acid is reproduced in Figure 1. M^{2-}, $[M\text{-}H\cdot]^{2-}$, and NO_2^{2-} ions are observed, and the abundance ratio $[M^{2-}]/[M^-]$ is 10^{-3} at 3.6 kV. The spectra of all three nitrobenzoic acids are similar except for the intensity of the spectra; i.e., the abundances of $[M^{2-}]$ at 3×10^{-5} Torr in the first field-free region for the ortho, meta, and para isomers are observed in the relative ratio 1:15:35. The cyanobenzoic acids yield M^{2-} and $[M\text{-}H\cdot]^{2-}$ ions.



1, R = H
2, R = Me

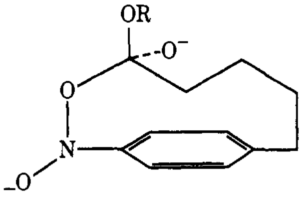


3, R = H
4, R = Me

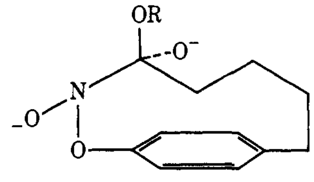
The abundance of a doubly charged anion will depend upon (i) the ability of the singly charged anion to accept an electron, (ii) the energetics of that process, (iii) the separation between the two charges,[20] and (iv) the overall stability of the dianion. In order to study the formation of doubly charged molecular anions as a function of the distance between the two charged sites, we initially chose system **1** (n = 0–5 and 9), because of the $-E/2$ spectra given by the nitrobenzoic acids. The $-E/2$ spectra of the acids **1** show peaks due to M^{2-} and $[M\text{-}H\cdot]^{2-}$ ions. The ester derivatives **2** ($n \geqslant 1$) also give pronounced $-E/2$ spectra but yield only M^{2-} ions. The abundances of M^{2-} ions as a function of n are shown for both acids and esters in Figure 2.[21] The most abundant peaks occur when $n = 3$ and 4. The most intense M^{2-} ion is produced from methyl 5-(*p*-nitrophenyl)pentanoate, where the abundance ratio $[M^{2-}]/[M^-] = 1 \times 10^{-2}$ at 3.6 kV.[22]

There could be two possible explanations to account for the pronounced M^{2-} ions from **1** and **2** (n = 3 and 4); viz. either (i) there is maximum stability of M^{2-} when the nitro and carbonyl charged centers are 11–12 Å apart (i.e., when the side chain is in the fully extended conformation), or (ii) that stabilization is occurring because suitable coiling of the side chain enables the charged centers to interact.[23] In order to distinguish between these possibilities we measured the abundances of M^{2-} ions from **3** and **4**, where the charged nitro and carbonyl groups cannot approach each other closely. The following relative abundances of M^{2-} were obtained: compounds **3**:**1** ($n = 3$) = 1:60 and compounds **4**:**2** ($n = 4$) = 1:20. This experiment clearly eliminates proposal (i).

The M^{2-} ions are at least initially diradical dianions, and the enhanced stability of those ions from **1** and **2** (n = 3 and 4) may be due to intramolecular bond formation between the radical centers. An examination of molecular models shows that this can only occur when $n > 3$ and that the most stable structure occurs when $n = 4$. The M^{2-} ion could correspond to a (for $n = 4$)[24] or to b, formed from the charged nitrite group, which is known[25] to correspond to the structure of the intermediate through which the negatively charged nitro group decomposes.



a



b

We described above how most nitrophenyl derivatives with an additional electron-withdrawing substituent attached to the ring did not form detectable M^{2-} ions. However, if one (or more) CH_2 groups is interposed between the phenyl ring and the second substituent, then all such compounds do yield parent dianions. In *general*, it would seem that in these systems, the two charged sites should be at least 7–8 Å apart, except when favorable interactions between the two charged sites may occur.

Doubly charged fragment anions (typically monoradical dianions) are also observed. $[M\text{-}H\cdot]^{2-}$ ions from acids and NO_2^{2-} have already been mentioned. Some molecules are unable to form M^{2-} species but can form fragment dianions. For example, Cl^{2-}, Br^{2-}, and I^{2-} are produced *in small abundance* from suitable alkyl halides; e.g., CH_3X (X = Cl, Br, I), CHX_3 (X = Cl, Br), and CCl_4 (substantiating earlier work[2a,3,4]), and *p*-nitroanisole and *p*-nitrobenzylmethyl ether, which produce abundant $M\cdot^-$ and $[M-Me\cdot]^-$ ions,[26] yield only $[M-Me\cdot]^{2-}$ ions.

(b) The Mechanism of Doubly Charged Anion Formation. There are two plausible mechanisms to explain the formation of doubly charged anions in the analyzer region of a double-focusing mass spectrometer. These are: (i) $A^- + N \rightarrow A^{2-} + N^+$; (ii) $A^- + e \rightarrow A^{2-}$. The first is a collision-induced reaction, dependent upon the nature of the collision gas N which is ionized in the reaction; the second, an electron capture process, is analogous to the capture of secondary electrons by suitable neutral molecules.[19]

The collision process can be eliminated on the following grounds. The abundance of A^{2-} increases as the sample pressure of the neutral substrate (A) increases and is a maximum between $3\text{-}5 \times 10^{-5}$ Torr after which it decreases in abundance due to collisional scattering. Addition of a collision gas N into the first field-free region *decreases* the abundance of M^{2-} from *p*-nitrobenzoic acid to about 50–60% of its value at 5×10^{-5} Torr and the decrease is not strongly dependent upon the nature of N. For example, toluene (IP = 8.8 eV), argon (IP = 15.8 eV), and He (IP = 24.6 eV) reduce the abundance of M^{2-} within the above range. Similar behavior is noted for other doubly charged anions.

As the formation of A^{2-} is not enhanced by addition of any collision gas different from the sample, the electron capture process is therefore the more plausible explanation for doubly charged anion formation.[27] In addition, the lifetimes of A^{2-} ions must be at least 10^{-5} s in order that these ions may reach the collector plate. Consequently, the internal energy of ions must be low, which in turn means that the captured electrons should have low energies.[28]

If the slit assemblies of the R.M.U. 7D are set to allow maximum transmission of singly charged negative ions, then the value of the electric sector voltage necessary to transmit all types of A^{2-} ions is $-0.506E$ at 3.6 kV.[29] It would appear that such ions have an additional 1.2% of translational energy when compared with that of the A^- precursors. If this is so, then that *fraction* of the sector voltage necessary to transmit A^{2-} should change with changing accelerating voltage V, e.g., $-0.512E$ at 1.8 kV for a value of $-0.506E$ at 3.6 kV. In a typical experiment, the parent ion M^{2-} from *p*-nitrobenzoic acid was transmitted at $-0.5058E$ at 3.6 kV, $-0.5056E$ at 2.4 kV, and $-0.5060E$ at 1.8 kV.[30] This means that there is *no translational energy gain* and that doubly charged anions are being produced *solely in that region inside the entrance of the electric sector.*[31-33]

When the sector potential is $-E/2$, singly charged ions A^- will be deflected to the negative sector plate and, in addition, may also collide with the grounded sector terminal plates. Secondary electrons will be released and stream to the positive plates, their position probably not being strongly localized. Some of these will intersect the deviating A^- beam near the entrance to the sector on their journey. Some electrons will be captured to yield A^{2-} ions. The enhanced value of the sector potential above $-E/2$ is necessary to straighten the A^{2-} beam in order to allow it to be transmitted through the sector.[34] If these reactions do take place in the electric sector, then an alteration in the lateral position of the slit before that sector will alter the transmission function, thus resulting in an alteration in sector voltage necessary to transmit the A^{2-} ions. Systematic movement of this slit over a 2-mm range changed the transmission voltage for the M^{2-} ion from *p*-nitrobenzoic acid from $-0.502E$ to $-0.512E$. Particular fractional values of E were again independent of the value of V.

Conclusions

Three distinct types of doubly charged negative ions are produced by direct electron capture from singly charged anions: (1) those ions where both electrons are found on one atom (e.g., X^{2-}), or where they occupy sites close to the central atom (e.g., $NO_2{}^{2-}$); (2) ions where the two charged sites are >7 Å apart; (3) ions which owe their stability to interaction between the two charged sites.

Experimental Section

Except for those compounds listed below, all materials used for this study were either commercially available or prepared by reported procedures.

10-(*p*-Nitrophenyl)decanoic acid (**1**, *n* = 9) was prepared by the nitration[35] of 10-phenyldecanoic acid in 22% yield and was crystallized from carbon tetrachloride as colorless prisms, mp 59–61 °C. Anal. Calcd: C, 65.2; H, 7.7; N, 4.81. $C_{16}H_{23}NO_4$ requires: C, 65.5; H, 7.9; N, 4.8.

The methyl esters, methyl 3-(*p*-nitrophenyl)propionate (**2**, *n* = 2), methyl 5-(*p*-nitrophenyl)pentanoate (**2**, *n* = 4), methyl 6-(*p*-nitrophenyl)hexanoate (**2**, *n* = 5) and methyl 10-(*p*-nitrophenyl)decanoate (**2**, *n* = 9), were prepared by a standard method[36] in quantitative yield and were either crystallized from carbon tetrachloride as colorless needles or distilled *in vacuo* (**2**, *n* = 5).

Table I

2, *n* =	Mp °C (n^{16}D)	Found C	Found H	Found N	Calcd C	Calcd H	Calcd N	Mol formula
2	74–75	57.8	5.3	6.5	57.4	5.3	6.7	$C_{10}H_{11}NO_4$
4	42–44	60.7	6.4	5.9	60.7	6.5	5.6	$C_{12}H_{15}NO_4$
5	(1.5229)	62.3	6.8	5.4	62.1	6.8	5.6	$C_{13}H_{17}NO_4$
9	62–63	66.5	8.3	4.4	66.4	8.2	4.6	$C_{17}H_{25}NO_4$

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(14) This feature has been substantiated in this study, except for the case of

p-dinitrobenzene which yields an NO_2^{2-} ion of small abundance (see below), overlooked in the previous study.[13]

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(20) The effect of charge separation is also of particular importance for doubly charged positive ions, see, for example T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, **6**, 741, 749 (1972), and references cited therein.

(21) Similar plots are obtained for M^{2-} and $[M-H\cdot]^{2-}$ ions from the acids.

(22) The geometry of these compounds is similar to those of the amino acid derivatives p-O_2N-C_6H_4-CO-NH-CH(R)-CO_2Me for which we first observed $-E/2$ spectra (see the introductory section).

(23) Bond formation reactions which precede the unimolecular decompositions of singly charged positive ions have also been noted, see, e.g., S. Meyerson and L. C. Leitch, *J. Am. Chem. Soc.*, **93**, 2244 (1971), and references cited therein.

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(27) The Coulomb barrier must be overcome in order for the electron-capture process to occur.

(28) (a) If some dianions are produced with excess energy, then this energy must be dissipated in some way. Collision stabilization is unlikely, as these ions are thought to be formed near the entrance of the electric sector (see below). Perhaps dianions with *excess* energy are simply unstable and reform A^-. To date, no reactions of A^{2-} ions have been observed. (b) A referee has stated that we have not proven unequivocally the electron capture mechanism. We would like to stress that we propose it as a plausible mechanism, arrived at because of elimination of mechanisms involving collision gases.

(29) The defocusing unit[17] has been carefully calibrated for known metastable transitions and is correct to $\pm 0.0002E$.

(30) The $[M^{2-}]/[M^-]$ ratio is however dependent on the value of V; i.e., for *p*-nitrobenzoic acid at 2×10^{-5} Torr the ratio $= 1 \times 10^{-3}$ (3.6 kV), 3×10^{-4} (2.4 kV), and 1×10^{-4} (1.8 kV).

(31) This suggestion was initially made by Professor R. G. Cooks who also suggested the experiments (see below) necessary to substantiate the proposal.

(32) Unimolecular positive ion dissociations in the electric sector have been reported previously. R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973, p 51. Decomposition of positive ions near the entrance to the electric sector has been described recently [R. G. Cooks, T. Ast, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, **16**, 348 (1975)].

(33) The α slit is kept wide open during this experiment, thus limiting the possibility of electron capture in the slit region.

(34) A referee has commented that this is a very simplistic explanation. He points out that any reaction involving a change in the charge of a fast ion in an electric field would give rise to a continuum in the energy or mass spectrum if all ions are transmitted. Reaction $A^- \rightarrow A^{2-}$ at the entrance and exit of the sector would appear at exactly $-E/2$ and $-E$, respectively. The observed usual value of $-0.506E$ can be ascribed to the fact that capture occurs with *high probability of product ion transmission* once the ion has entered the sector. Transmission is maximized at the interface with the field-free region, hence the observed result.

(35) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **71**, 779 (1949).

(36) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 705.

Shape and Angle Strain in Organic Intermediates. A Model Study of Alkyl Radicals, Anions, and Cations

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Abstract: The Walsh-Mulliken diagrams for methyl are constructed from ab initio wave functions and are used to explain the shape and energetics of alkyl cations, radicals, and anions. Two angles, HCH and the out-of-plane CH bend, define the energy surfaces. The minimum energy conformation of the cation is always planar and that of the radical is also planar except for an HCH angle of 90°, in which case CH is bent out-of-plane by 32.4°. For the anion, HCH angles of 90, 109.47, 120, and 135° lead to minimum energy out-of-plane CH angles of 72, 63.4, 56.6, and 32.8°, respectively. It is shown that the entire energy surface can be explained solely in terms of the occupancy and hybridization of the highest occupied molecular orbital. It is expected that the shape of all alkyl intermediates will be governed by the simple rules established in this model study and it is shown that existing experimental and computational data fit this pattern.

A central goal of physical organic chemistry is detailed understanding of the relationship between structure and energy for organic intermediates. The methyl cation, radical, and anion exemplify the problems involved: Only indirect experimental information is available concerning the structures of the ionized species. Whether or not the methyl radical is planar has not been settled with certainty experimentally.[2] Inferences regarding structures are typically drawn from more stable isoelectronic molecules; e.g., CH_3^- is compared with NH_3 and $(CH_3)_3C^+$ with $(CH_3)_3B$. Chemical reactions involving intermediates also provide indirect structural information, but obviously not of a detailed character; e.g., carbenium ion reactions are inhibited at the bridgeheads of small polycyclic ring systems and from this it is inferred that carbenium ions prefer planarity.[3]

Theoretical calculations provide insights not currently accessible experimentally. In this paper, we study the effect of angle deformation on energies and electronic structure of CH_3^-, $CH_3\cdot$, and CH_3^+ as models for larger systems. Numerous ab initio calculations have already been performed on these methyl species, but these studies have been carried out for only a limited range of geometries, usually C_{3v} or D_{3h} conformations. A unique feature of the present work is that the same basis set has been applied to all three species under a considerable variety of geometrical constraints. In addition, the potential energy surfaces which have been computed are analyzed in terms of Walsh-Mulliken diagrams[4] resulting in a simple picture for the behavior of these intermediates.

Computational Aspects

The results presented here were obtained with standard single determinant LCAO-SCF-MO theory, using the GAUSSIAN-70 program[5] with the 4-31G basis set where each inner shell is represented by a four-term Gaussian expansion and each valence shell orbital is split into three and one term expansions for the inner and outer parts, respectively. For open shell cases, the unrestricted procedure of Pople and Nesbet was used.[6] A series of calculations at high symmetry conformations

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