

## Steric Effects on Gas-Phase Negative Ion Resonances of Phthalates

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**Abstract:** The interaction of low-energy electrons with eight phthalates was studied using an electron monochromator–mass spectrometer (EM–MS). Each phthalate captures electrons of discrete energy to yield negative ions by resonance or dissociative electron capture. Two negative ion resonances are generally observed for each ion. Electrons with energies of  $\sim 0.6$  and  $\sim 1.1$  eV result in maximum molecular ion intensity for *o*-phthalates, while higher energy electrons produce  $(M-R_1)^-$ ,  $(M-R_1-R_2 + H)^-$ , and phthalic anhydride ions. *m*-Dimethyl phthalate yields a molecular ion with electrons of energies 0.19 and 0.87 eV, but no fragment ions. Electron attachment energies calculated with the HF/D95//HF/6-31G basis set and a scaling constant are in reasonable agreement with the experimental values for the first molecular ion state of each phthalate. Semiempirical calculations show that the optimum geometry for *m*-dimethyl phthalate results when both ester groups are coplanar with the benzene ring, while steric interactions force the ester groups of *o*-phthalates into noncoplanar orientations relative to the benzene ring. It is suggested that this geometry leads to efficient  $\pi^*-\sigma^*$  orbital interaction in the transient radical anion and facile fragmentation, producing product anions and radicals. Larger R groups result in a lowering of the electron energies required to produce  $(M-R_1)^-$ , a result which is interpreted on the basis of greater steric compression of the ester groups in the transient negative ion.

## Introduction

The interaction of electrons with electrophilic molecules in the production of negative ions represents an important chemical process. Despite the crucial role of negative ions in so many chemical reactions, far less is known about them particularly in the gas phase than their counterpart, the positive ions. One of the chief barriers to investigating the formation and structure of negative ions has been the lack of techniques with which to form large numbers of them in configurations stable enough and sufficiently free of complicating reactions to permit the kinds of measurements routinely performed on positive ions.

Several decades ago, it became possible to produce low-energy electrons (0–50 eV) having nearly monoenergetic (0.005–0.1 eV) distributions with a device called an electron monochromator (EM).<sup>1,2</sup> The earliest electron monochromators were used for the most part to accurately determine ionization potentials and to record negative ion resonances of theoretical interest. Negative ion resonances are now widely studied by electron transmission spectroscopy (ETS) in which the derivative of the transmitted electron current is recorded.<sup>3</sup> The electron monochromator, however, was also introduced into the mass spectrometer's ion source early on,<sup>4</sup> thereby permitting mass spectrometric investigations of ions produced with monoenergetic electron beams. Several research groups have used these systems to study the gas-phase interaction of electrons with electrophilic molecules, particularly halogenated organics. Reviews on gas-phase negative ions studied by both ETS and electron monochromator–mass spectrometer (EM–MS) systems have been published.<sup>5–9</sup>

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In the EM–MS instrument the energy of the electrons produced by the monochromator is scanned, and the specific energies at which an electrophilic compound captures electrons are measured by using the mass spectrometer to detect and specifically identify the respective negative ions produced. These measurements can be used to provide an additional dimension of analytical information with which to identify the molecules.<sup>9</sup> Additionally, it has been shown that the experimental electron attachment energies for both the molecular and dissociative capture ions of polychlorodibenzo-*p*-dioxins can be correlated with their calculated  $\pi$  virtual orbital energies.<sup>10</sup> In this paper evidence is presented that steric requirements of the targeted molecules have a very decided effect on the electron attachment energies producing negative ions. The ubiquitous phthalates proved to be desirable compounds for this kind of investigation because the different ester groups provided a convenient variety of functionalities to test for the effects of steric interactions. Moreover, these compounds have recently come under scrutiny because of their estrogenic<sup>11</sup> effects and are, therefore, of some concern as environmental agents for which new analytical techniques would be desirable. The investigation of phthalates by negative ion mass spectrometry seems not to have received much attention, but studies on the interaction of low-energy electrons with phthalic anhydride<sup>12</sup> and aryl phthalides have been reported.<sup>13,14</sup>

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## Experimental Section

**Electron Monochromator—Mass Spectrometer Instrument.** The EM—MS system consists of an in-house-constructed monochromator source interfaced to a Hewlett-Packard 5982A quadrupole mass spectrometer. This system has been described previously.<sup>15</sup>

Data were acquired by counting and storing pulses from a Detech spiraltron detector in an Ortec multichannel analyzer inside a Hewlett-Packard 386 personal computer. The electron energy scale was generated by converting the channel number from the data generated by the multichannel analyzer into electron energy after an empirical linear relationship was established between channel number and electron energy using hexafluorobenzene as calibrant. The electron energies required to produce its ions in electron capture experiments are generally agreed to be 0.03, 4.55, and 8.3 eV.<sup>16</sup>

In most experiments the quadrupole was operated in the single ion monitoring (SIM) mode, while the filament potential was ramped quickly from  $-2$  to  $+10$  eV by means of a function generator. The data generated were converted from an intensity versus filament potential plot to an intensity versus electron energy plot using commercial peak-fitting software (Peakfit, Jandel Scientific). Using standard nonlinear curve-fitting routines, the peaks observed were deconvoluted using Gaussian functions. In all cases the single values reported for vertical attachment energies represent the maximum value of the curve-fitted Gaussian function ( $\epsilon_{\max}$  value). All attachment energy values are averages of 3–20 runs for any given ion. For comparison all compounds were also analyzed on a Finnegan 4023 EI/NCI mass spectrometer in the negative ion electron capture mode using a DB-5  $10\text{ m} \times 0.25\text{ mm}$  i.d. capillary column programmed between 70 and  $320\text{ }^\circ\text{C}$  to introduce the samples.

**Chemicals.** Phthalates were purchased from Chem Service, Inc. All were certified 99% pure and were not purified further. NCI spectra were obtained on a Finnegan 4023 instrument prior to analysis on the EM—MS system. The compounds studied on this system were introduced into the instrument via a direct insertion probe.

**Computational Studies.** Ab initio calculations were performed using the Gaussian 94 program.<sup>17</sup> This program was run on a DEC Alpha and an Intel Pentium Pro 200 MHz personal computer. Molecular structures were built using Hyperchem (Hypercube, Inc.) and Chem3D (Cambridgesoft, Corp.). Schematic representations of molecular orbitals were produced using Chem3D and the Molden program (Gjits Schaftelander, The Netherlands). Schematic diagrams of molecular structures were rendered using the POV-RAY ray-tracing engine (POV, Inc.).

Geometry optimizations on the phthalates were typically performed using only a Hartree—Fock wave function. Frequency calculations were done on selected molecules to ensure that minimized geometries were global minima. All other computational parameters were left at the default Gaussian 94 values including the use of direct inversion of iterative subspace (DIIS) and the direct SCF method.

**Dihedral Angles of Ester Groups.** Upon completion of the Gaussian 94 calculations the checkpoint files were converted to ASCII using the internal formchk utility available in G94. These checkpoint files were converted to PDB format using Chem 3D (Cambridgesoft). The PDB files produced were examined using the WebLab Viewer Lite program (Molecular Simulations, Inc.) at [www.msi.com](http://www.msi.com). The ester groups of *o*-phthalates are forced apart in the plane of the aromatic ring, thus complicating the measurement of their deviation relative to

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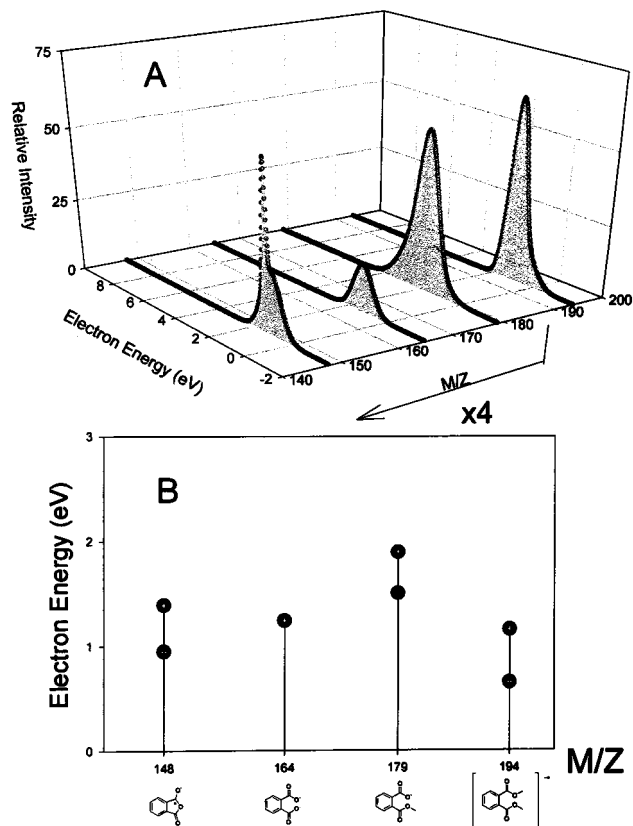
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**Table 1.** Vertical Attachment Energies (eV) for the Production of Phthalate Molecular Ions

<i>o</i> -phthalate	1st NIR state		2nd NIR state
	AE (exptl)	AE (calcd) <sup>a</sup>	AE (exptl)
R <sub>1</sub> = methyl, R <sub>2</sub> = methyl	0.62	0.45	1.03
R <sub>1</sub> = ethyl, R <sub>2</sub> = ethyl	0.63	0.49	1.15
R <sub>1</sub> = <i>n</i> -butyl, R <sub>2</sub> = <i>n</i> -butyl	0.60	0.51	1.14
R <sub>1</sub> = isobutyl, R <sub>2</sub> = isobutyl	0.65	0.52	1.15
R <sub>1</sub> = <i>n</i> -amyl, R <sub>2</sub> = <i>n</i> -amyl	0.48	0.52	1.01
R <sub>1</sub> = <i>n</i> -butyl, R <sub>2</sub> = cyclohexyl	0.57	0.51	1.07
R <sub>1</sub> = <i>n</i> -butyl, R <sub>2</sub> = benzyl	0.78	0.53	1.27
<i>m</i> -dimethyl phthalate	0.19	0.21	0.87

<sup>a</sup> Calculated using HF/D95//HF/6-31G and a scaling constant (see eq 4).

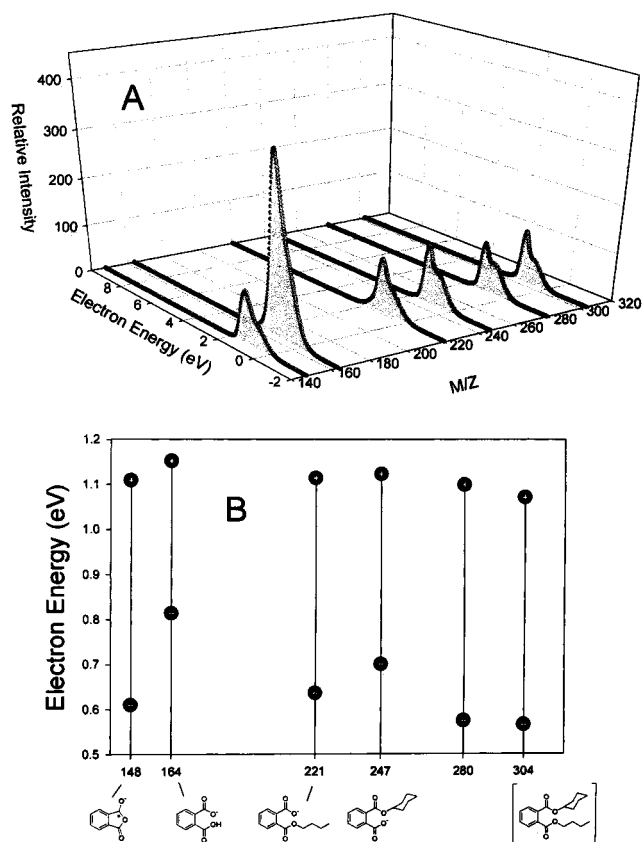


**Figure 1.** Electron energy mass spectra of *o*-methyl phthalate. (A) Three-dimensional electron energy vs ion mass/charge ratio vs ion relative intensity spectrum. (B) Two-dimensional electron energy vs ion mass/charge spectrum.

the benzene plane. Two angles were, therefore, measured. The first was measured using the plane defined by the carbonyl oxygen, the carbonyl carbon, the aromatic carbon, and the adjacent aromatic carbon that gives the smaller dihedral angle. The second angle comprises the plane defined by the alkyl oxygen, the carbonyl carbon, the aromatic carbon, and the adjacent aromatic carbon that gives the smaller dihedral angle.

## Results

Eight phthalates were examined in this study (Table 1). All are in common use as plasticizers with the exception of methyl isophthalate, the meta diester, which was included for comparison with the *o*-phthalates. Three-dimensional electron energy—ion mass/charge—ion intensity spectra (Figures 1–3) of phthalates were recorded under electron capture negative ion mass spectrometry conditions using the electron monochromator to generate slow monoenergetic electrons. These spectra reveal significant differences among the compounds within the class,



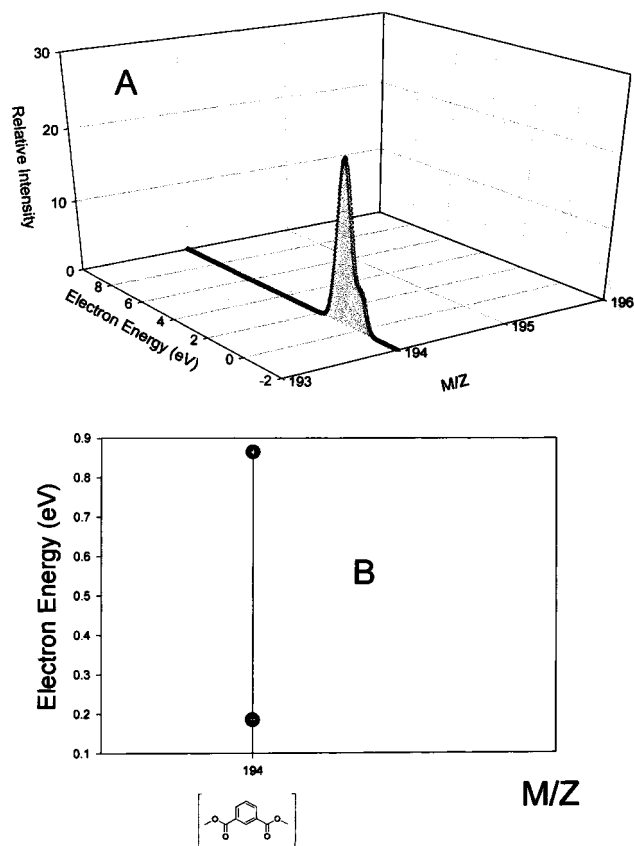
**Figure 2.** Electron energy mass spectra of *o*-butyl cyclohexyl phthalate. (A) Three-dimensional electron energy vs ion mass/charge ratio vs ion relative intensity spectrum. (B) Two-dimensional electron energy vs ion mass/charge spectrum.

despite the constancy of the parent phthalate structure. All of the phthalates studied show molecular ions (Table 1), and without exception each compound shows two negative ion resonances (NIR) associated with the generation of these ions. Only minor differences are observed in the electron energies required to produce the first and second NIR states for the alkyl series. The benzyl group has a somewhat greater effect, but the largest departure from the series in the electron energy required for molecular ion formation is observed for *m*-dimethyl phthalate. Both the first and second NIRs are associated with distinctly lower electron energies than are required for *o*-phthalates.

**Common Fragment ( $M-R^*$ )<sup>-</sup>.** Several dissociative attachment ions are common to most of the phthalates studied. First, all of the *o*-phthalates undergo cleavage of the alkyl-oxygen bond (Scheme 1). The electron energies required for resonances associated with this cleavage range between 0.62 and 2.17 eV. These results show that, as the size of the R group increases, the electron attachment energy required to produce the ( $M-R$ )<sup>-</sup> ion decreases (Figure 4). To understand this trend, it is important to understand the thermodynamic quantities that influence the electron attachment energy. The dissociative electron attachment energy ( $\epsilon_1$ ) is the minimum energy required for anion formation and is defined as

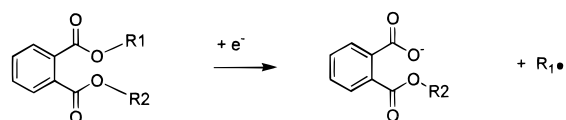
$$\epsilon_1 = \Delta H_0 + \epsilon_x \quad (1)$$

where  $\epsilon_x$  is the excess energy carried away by the fragments after bond dissociation.<sup>6</sup> The electron attachment energies (AE) (Table 2) are  $\epsilon_{\max}$  values, which correspond to the energies of maximum ion production. The minimum heat of reaction for dissociation ( $\Delta H_0$ ) of a molecule, A-B, by electron capture is



**Figure 3.** Electron energy mass spectra of *m*-dimethyl phthalate. (A) Three-dimensional electron energy vs ion mass/charge ratio vs ion relative intensity spectrum. (B) Two-dimensional electron energy vs ion mass/charge spectrum.

#### Scheme 1

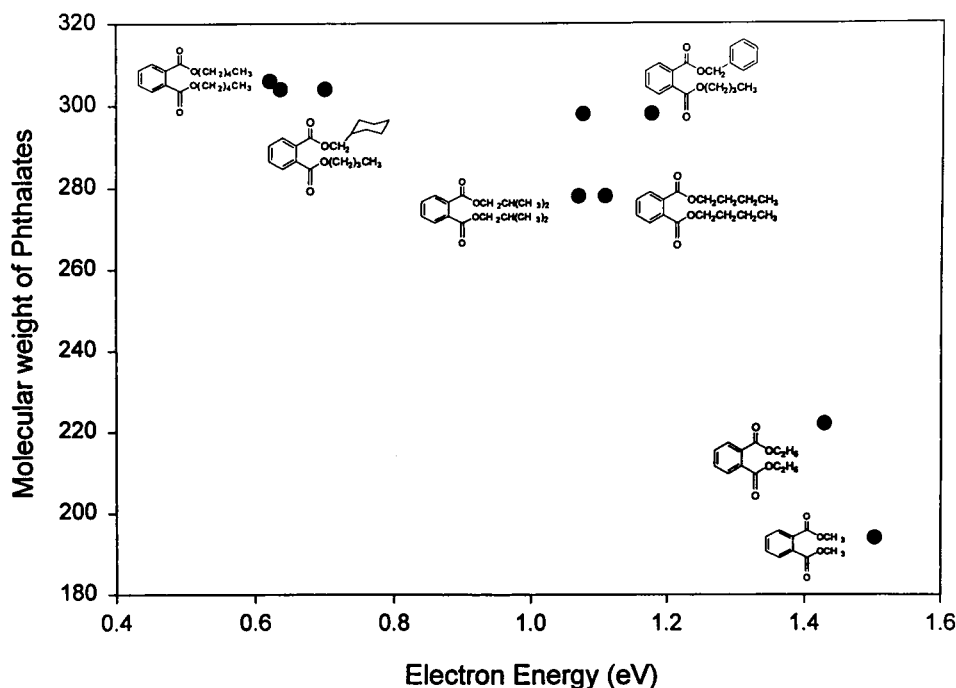


the difference between the bond dissociation energy of AB and the electron affinity of B<sup>\*</sup>. In this case it is the electron affinity of the phthalate radical which should not change much from one phthalate to another.

$$\Delta H_0 = D(A-B) - EA(B^*) \quad (2)$$

Several phthalates, i.e., di-*n*-butyl, *n*-butyl benzyl, and *n*-butyl cyclohexyl, produce the same *n*-butyl radical, but the electron energies required to produce them are not the same (Figure 4). This indicates there is a steric relief factor affecting the energies of these resonances. The molecule with the highest molecular weight, diamyl phthalate, requires the lowest electron energy to fragment, while the smallest molecule, dimethyl phthalate, requires the highest energy. Butyl benzyl phthalate is also less sterically demanding than diamyl phthalate, and this compound requires electrons of distinctly higher energy, but it occupies a unique position on the electron energy-molecular weight curve as it requires at least 0.4–0.5 eV greater electron energies than might be predicted from an examination of the electron energy-molecular weight relationship (Figure 4).

**Common Fragment ( $M-R_1-R_2 + H$ )<sup>-</sup>.** Another fragmentation observed in several phthalates is cleavage of both alkyl-oxygen bonds with transfer of a hydrogen atom to form the phthalic acid residue. These phthalic acid ions, if present, are



**Figure 4.** Electron energy required for R cleavage in phthalates versus the molecular weights of phthalates.

**Table 2.** Dissociative Electron Capture Attachment Energies (eV)<sup>a</sup> for Substituted Phthalates

<i>o</i> -phthalate	1st AE for (M-R <sub>1</sub> ) <sup>-</sup>	2nd AE for (M-R <sub>1</sub> ) <sup>-</sup>	1st AE for (M-R <sub>1</sub> -R <sub>2</sub> +H) <sup>-b</sup>	2nd AE for (M-R <sub>1</sub> -R <sub>2</sub> +H) <sup>-b</sup>	1st AE for phthalic anhydride ion	2nd AE for phthalic anhydride ion
R <sub>1</sub> = methyl, R <sub>2</sub> = methyl	1.50	1.90	1.24 <sup>c</sup>	<i>d</i>	0.95	1.4
R <sub>1</sub> = ethyl, R <sub>2</sub> = ethyl	1.43	2.17	<i>d</i>	<i>d</i>	0.48	<i>d</i>
R <sub>1</sub> = <i>n</i> -butyl, R <sub>2</sub> = <i>n</i> -butyl	1.11	1.48	<i>d</i>	<i>d</i>	0.70	<i>d</i>
R <sub>1</sub> = isobutyl, R <sub>2</sub> = isobutyl	1.07	<i>d</i>	0.54	1.20	0.70	<i>d</i>
R <sub>1</sub> = <i>n</i> -amyl, R <sub>2</sub> = <i>n</i> -amyl	0.62	1.04	0.66	1.13	0.54	1.04
R <sub>1</sub> = <i>n</i> -butyl, R <sub>2</sub> = cyclohexyl	0.70	1.12	0.81	1.15	0.61	1.11
R <sub>1</sub> = cyclohexyl, R <sub>2</sub> = <i>n</i> -butyl	0.64	1.11	na <sup>e</sup>	na	na	na
R <sub>1</sub> = <i>n</i> -butyl, R <sub>2</sub> = benzyl	1.18	1.37	0.85	1.22	1.04	<i>d</i>
R <sub>1</sub> = benzyl, R <sub>2</sub> = <i>n</i> -butyl	1.08	1.43	na	na	na	na
<i>m</i> -dimethyl phthalate	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>

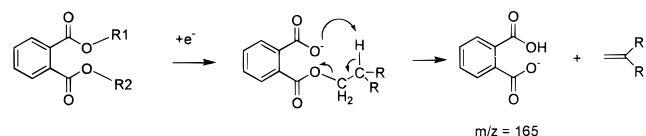
<sup>a</sup> AE = attachment energies for maximum ion production. Sometimes referred to as  $\epsilon_{\max}$  values. <sup>b</sup> *m/z* 165. <sup>c</sup> *m/z* 164. <sup>d</sup> Not observed. <sup>e</sup> na = not applicable.

produced over a small range of electron energies. Phthalates with smaller alkyl substituents are less likely to form phthalic acid ions (Table 2). The electron energies required to produce the first resonance peaks appear to depend less on steric considerations than in the case of the (M-R)<sup>-</sup> resonances, and the second resonances show almost no variation with the alkyl groups. Comparison of the electron attachment energies for single alkyl group cleavage (Table 2) with those for dual alkyl cleavages reveals that the formation of the ions (M-R<sub>1</sub>-R<sub>2</sub>+H)<sup>-</sup> occur either at lower electron energies or at about the same energies as those required to produce (M-R)<sup>-</sup>. Assuming that these ions do not arise from the same resonance state, the tendency toward lower energy requirements may be a result of a rearrangement reaction involving the formation of a bond in the fragmentation process (Scheme 2).<sup>18</sup> A possible mechanism to account for this reaction is cleavage of the first carbon-oxygen ester bond after initial electron capture, followed by  $\beta$  elimination with hydrogen atom transfer to give the phthalic acid anion and neutral alkene. Such a reaction would be analogous to the well-known E2 elimination reaction<sup>19</sup> (Scheme 2).

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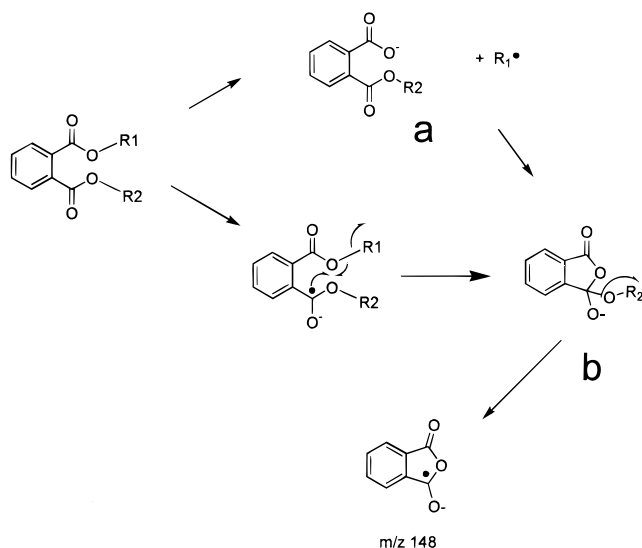
### Scheme 2



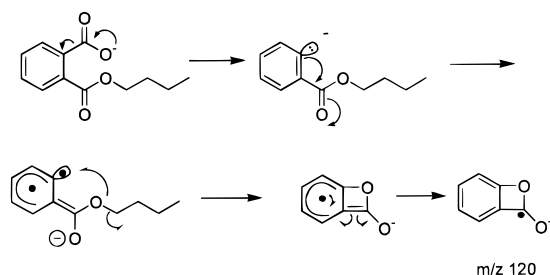
All phthalates except *o*-dimethyl phthalate show the resultant (M-R<sub>1</sub>-R<sub>2</sub>+H)<sup>-</sup> with *m/z* 165. Since there is no  $\beta$  hydrogen, dimethyl phthalate cannot form this ion, but instead forms an ion with *m/z* 164. The mechanism for its formation is not apparent, but the higher energy resonance (Table 2) is consistent with a pathway that does not involve a rearrangement reaction.

**Phthalic Anhydride Ion.** The formation of a phthalic anhydride radical anion (*m/z* 148) is common to all phthalates studied. The electron energies required to produce these ions vary over a relatively broad range (Table 2). Two mechanisms for the cleavage (Scheme 3) can be considered. The reaction could proceed through intermediate **a**, i.e., (M-R<sub>1</sub>)<sup>-</sup>, followed by nucleophilic attack of the carboxyl anion on the adjacent carbonyl group to give **b**, which then fragments to give the product ion (*m/z* 148) (Scheme 3). Alternatively, it could proceed via a concerted mechanism that forms **b** directly. Semiempirical calculations by MOPAC 97<sup>20</sup> indicate that intermediate **a** ( $\Delta H_f$

## Scheme 3



## Scheme 4

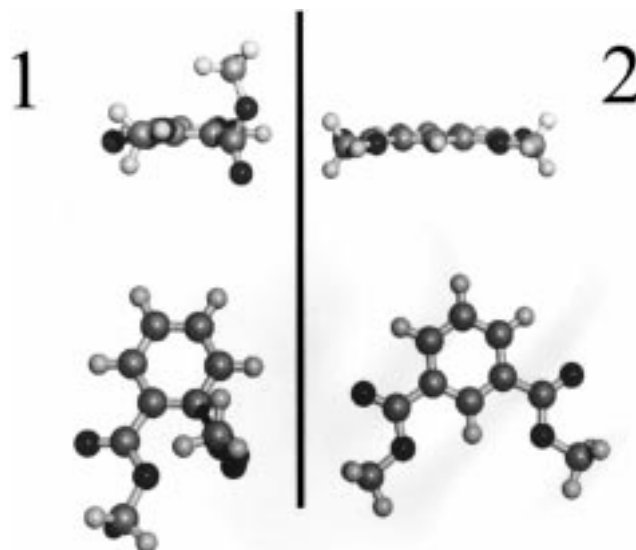


$= -177.4$  kcal/mol) is more stable than intermediate **b** ( $\Delta H_f = -170.5$  kcal/mol), suggesting that **b** might be formed via the stepwise mechanism. However, if this were the case, one would expect that the resonances that produce  $(M-R_1)^-$  also would be responsible for producing the phthalic anhydride ion. Only diamyl and *n*-butyl cyclohexyl phthalates have similar resonance energies.

In general considerably lower energy electrons are involved in the formation of the phthalic anhydride ions in comparison to the other fragment ions. These results support the concerted mechanism. The lower energies may be attributed in part to a bond being formed during the ion's production. It is well-known that rearrangement reactions involving fragmentation are lower energy processes.<sup>18</sup> Diamyl and *n*-butyl cyclohexyl phthalates, on the other hand, may be unique in this series and arise from  $(M-R_1)^-$ . There is no simple experimental procedure to test for these mechanisms without some method for following the course of metastable ion decomposition, but perhaps the recording of resonance electron energies provides a new method for elucidating fragmentation mechanisms of this type.

**Other Ions.** In addition to the common ions described above, there are a few ions unique to individual phthalates. An intense ion with *m/z* 120, for example, is formed from *n*-butyl benzyl phthalate. This ion is formed with an electron attachment energy of 1.42 eV, which is exactly the value of the high-energy resonance of the anionic fragment produced by cleavage of the alkyl-oxygen bond (Table 2, column 2, row 9), suggesting that the ion with *m/z* 120 originates from the  $(M-R_1)^-$  ion (Scheme 4).

*n*-Butyl cyclohexyl phthalate also produces a unique ion with *m/z* 280, which is just 14 amu below the molecular ion or the



**Figure 5.** Comparison of (1) *o*-dimethyl phthalate and (2) *m*-dimethyl phthalate geometry.

apparent loss of a methylene group. It is difficult to explain the origin of this ion, but it appears to be produced from a metastable ion since the electron energies producing it are 0.57 and 1.09 eV, which are identical to the energies required to form the molecular ion (Table 1).

## Discussion

To understand the behavior of these molecules under electron capture conditions, it is necessary to examine their electronic states. Koopmans' theorem<sup>21</sup> states that the wave function obtained by removing an electron from an occupied orbital or adding an electron to a virtual MO in a Hartree-Fock wave function is stable with respect to any subsequent variation in either of the orbitals. It does not follow that these orbitals remain optimized, but Koopmans' theorem provides a useful model that allows an approximate description of the electronic states of a molecule that has an added electron.

Recently, Staley and Strnad<sup>22</sup> used Koopmans' theorem in a study of a series of electron-capturing compounds involving several popular SCF basis sets. In their approach, the experimental attachment energy was scaled to the energy of the appropriate SCF virtual orbital energy ( $\epsilon_{vo}$ ):

$$AE = m\epsilon_{vo} + b \quad (3)$$

The approach was successful for a wide range of experimental attachment energies measured by ETS for  $\pi^*$  negative ion resonances of unsaturated molecules. The best correlation was found using HF/D95//HF/6-31G calculations. Using a similar approach, evidence was obtained for the involvement of  $\pi^*$  orbitals in dissociative electron attachment to polychlorodibenzo-*p*-dioxins, with chloride ion production postulated to arise from  $\pi^*-o^*$  mixing.<sup>10</sup> A priori one can assume that dissociative electron attachment for phthalates involves localized aromatic  $\pi^*$  orbitals and the loss of the alkyl radicals requires  $\pi^*-o^*$  orbital interactions.

An examination of the optimized geometries of the phthalates reveals an important structural feature that supports this mechanism. Steric interactions cause the ester groups of *o*-phthalates to twist out of the plane of the benzene ring (Figure 5). The

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**Table 3.** Calculated Angles between the Benzene Plane and the Plane Formed by the Carbonyl Group of Phthalates

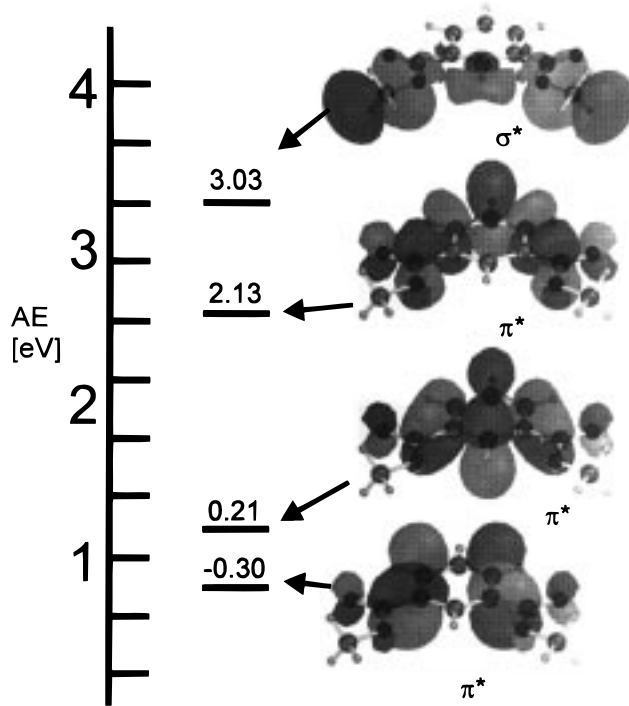
phthalate <sup>a</sup>	first ester group		second ester group	
	angle 1 <sup>b</sup>	angle 2 <sup>c</sup>	angle 1 <sup>b</sup>	angle 2 <sup>c</sup>
methyl	89.2	78.5	14.6	15.6
ethyl	87.0	76.3	17.3	15.6
<i>n</i> -butyl	87.8	77.1	15.0	16.5
isobutyl	89.2	85.0	5.3	4.9
<i>n</i> -amyl	87.8	77.2	15.0	16.5
<i>n</i> -butyl benzyl <sup>d</sup>	89.6	85.3	4.9	5.4
<i>n</i> -butyl cyclohexyl <sup>d</sup>	88.9	84.9	5.2	5.7
<i>m</i> -dimethyl	0	0	0	0

<sup>a</sup> *o*-Phthalates unless otherwise indicated. <sup>b</sup> Angle in degrees between the benzene plane and the plane formed by the carbonyl oxygen, carbonyl carbon, and aromatic carbon. <sup>c</sup> Angle in degrees between the benzene plane and the plane formed by the alkyl oxygen, carbonyl carbon, and aromatic carbon. <sup>d</sup> Butyl is part of the first ester group.

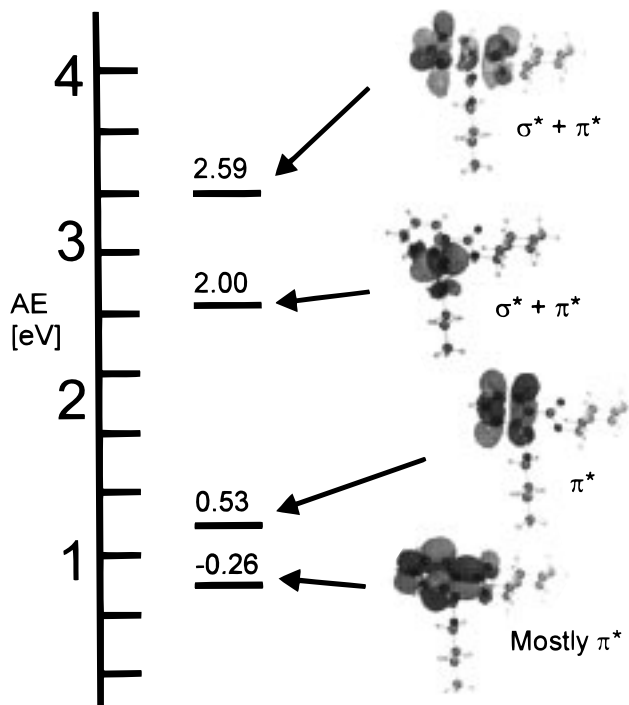
angles formed between the planes of the benzene ring and the ester groups in the geometry-optimized structures (Table 3) clearly reveal this orthogonality. *o*-Dimethyl phthalate, for example, shows that the plane formed by the alkyl oxygen, the carbonyl carbon, and the aromatic carbon to which the ester group is attached is displaced 78.5° from the plane of the benzene ring for one of the ester groups and 15.6° for the other one. In *m*-dimethyl phthalate the ester groups and aromatic ring are coplanar and conjugated (Figure 5). Steric compression in *o*-phthalates leads to not only a series of fragment ions and radicals but also a lowering of the resonance energies in the dissociative electron capture reactions as the ester groups become larger. The dihedral angles (Table 3) do not appear to vary systematically with the size of the alkyl substituent, and a correlation with the electron energy necessary to cause fragmentation is not evident. This may be because the geometry optimization convergence criteria cannot be made tight enough for compounds with long floppy alkyl chains to arrive at global minima on the shallow surfaces within reasonable computation times. Nevertheless, the sterically crowded isobutyl and *n*-butyl cyclohexyl phthalates have larger angles for the first ester group and smaller ones for the second. It appears that increased steric crowding may be a factor in the larger angles and consequent lowering of the electron energies required to form the (M-R<sub>1</sub>)<sup>-</sup> ions from these compounds. Butyl benzyl phthalate also has a larger dihedral angle, but this compound has to be considered separately because of the extra  $\pi$  system.

The relative conformations for *o*- and *m*-phthalates must affect the orbitals and orbital energies. Calculations show that *m*-dimethyl phthalate has virtual orbitals that are either completely  $\pi^*$  or completely  $\sigma^*$  in character (Figure 6), while *o*-phthalates have  $\sigma^*-\pi^*$  character for some states (Figure 7). Mixing of  $\pi^*$  and  $\sigma^*$  states has been implicated in dissociative electron capture processes of several other systems. Recent studies by Burrow and co-workers<sup>23</sup> found that the absolute Cl<sup>-</sup> yield from chloronornornenes under dissociative electron capture conditions with monoenergetic electrons depends on the relative orientation of the chlorine atoms with respect to the olefinic  $\pi$  orbitals. In *exo*-5-chloro-2-norbornene, the chlorine is attached so that coupling of the  $\sigma^*$  orbital of the CX bond can occur with the olefinic  $\pi^*$  orbital. The resulting Cl<sup>-</sup> yield was found to be 2 orders of magnitude higher than that for *syn*-5-chloro-2-norbornene, where the CX bond lies in the nodal plane of the  $\pi^*$  orbital.

(23) Pearl, D. M.; Burrow, P. D.; Nash, J. J.; Morrison, H.; Jordan, K. *J. Am. Chem. Soc.* **1993**, *115*, 9876–9877.



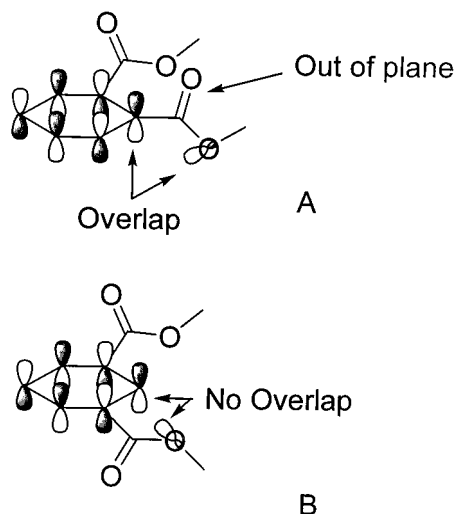
**Figure 6.** Vertical attachment energies for *m*-dimethyl phthalate calculated using Koopmans' theorem with an empirical linear scaling relationship at the HF/D95//HF/6-31G level of theory. Orbitals were drawn with Chem3D Pro at an isosurface value of 0.03.



**Figure 7.** Vertical attachment energies for butyl cyclohexyl phthalate calculated using Koopmans' theorem with an empirical linear scaling relationship at the HF/D95//HF/6-31G level of theory. Orbitals were drawn with Chem3D Pro at an isosurface value of 0.03.

Allan and co-workers<sup>24</sup> found that the relative yields of halide ion from the benzylic position of halobenzyl halides is much greater than it is from the phenylic position. This observation was rationalized on the basis that the halogen on the tetrahedral carbon atom can freely orient to allow efficient  $\pi^*-\sigma^*$  coupling.

(24) Bulliard, C.; Allan, M.; Haselbach, E. *J. Phys. Chem.* **1994**, *98*, 11040–11045.



**Figure 8.** Orbital overlap between the carbon–oxygen  $\sigma$  bond in *o*-dimethyl phthalate, A, allows for  $\pi^*-\sigma^*$  interaction, while the coplanar substituents in *m*-dimethyl phthalate, B, cause the  $\sigma$  antibonding orbital to retain an orientation orthogonal to the  $\pi^*$  system of the aromatic ring, thereby preventing  $\sigma^*-\pi^*$  orbital interaction.

Coupling between the  $\sigma^*$  orbitals with the  $\pi^*$  orbitals of the phenylic halogens is symmetry forbidden.

The experimental data showing a stable NIR for *m*-dimethyl phthalate and fragments for *o*-phthalates (Table 1) are consistent with the models described above. The noncoplanarity of the ester groups and aromatic ring can result in through-space interaction between a  $\sigma^*$  orbital located on the ester oxygen and the  $\pi^*$  orbital of the benzene ring (Figure 8). This  $\pi^*-\sigma^*$  interaction promotes fragmentation between the ester oxygen and the alkyl groups. In *m*-dimethyl phthalate, the  $\pi^*-\sigma^*$  interaction does not occur and only the molecular ion is observed.

The  $(M-R_1-R_2+H)^-$  ion may also involve initial association of the ionizing electron with the aromatic  $\pi$  system followed by  $\pi^*\sigma^*$  mixing. The generally lower electron energies required for this reaction may be an indication that the loss of  $R_1^*$  is concerted with the elimination reaction associated with the loss of  $R_2^*$  (Scheme 2).

It is significant that the electron attachment energy for the dissociative loss of either R group from benzyl butyl phthalate is at least 0.4 eV greater than expected on the basis of the electron energy–molecular mass relationship (Figure 4). The captured electron can be localized in the  $\pi$  system of the benzyl group with interaction now occurring between the  $\pi^*$  orbital of the benzyl group and the  $\sigma^*$  orbital of the ester oxygen. The first NIR for loss of the benzyl radical occurs at a lower energy than that required for loss of the butyl group (Table 2), which

is consistent with the electron being associated with the benzyl group. In fact, this dissociation can be viewed much as the loss of the halide ion from the benzylic position of halobenzyl halides.<sup>24</sup> It would be interesting to know if *m*-benzyl butyl phthalate would undergo dissociative electron attachment to yield fragment ions.

If the values,  $x$ , of the molecular orbitals ( $\pi^*_2$ ) calculated with the SCF basis set discussed above are adjusted using the empirical correction (eq 4) formulated by Staley and Strnad,<sup>22</sup>

$$\hat{\epsilon} = (x + 1.5273)/0.7415 \quad (4)$$

one finds reasonably good agreement between the experimental  $AE_1$  and calculated resonance energies,  $\epsilon_{\max}$ , for the phthalate molecular ions (Table 1). It is assumed that in applying the scaling factor (eq 4), the electron associates with the aromatic  $\pi$  system and not with the carbonyl group. The application of eq 4 to the second set of molecular ion resonances was not successful, which leads to speculation that these NIRs arise from electron association with the  $\pi$  orbitals of the carbonyl groups. The formation of the phthalic anhydride ion also is best rationalized on the basis of the electron entering the carbonyl  $\pi$  orbital.

## Conclusions

The dissociative electron capture events that lead to the production of  $(M-R_1)^-$  and other fragment ions in *o*-phthalates appear to be driven by steric interactions that cause the ester functionalities to adopt noncoplanar orientations with the benzene ring. This loss of coplanarity of the ester groups with the aromatic ring can lead to significant  $\pi^*-\sigma^*$  orbit mixing and energetically favorable routes to fragment ions. If the molecule has ester functionalities coplanar with the benzene ring, as in the case of *m*-dimethyl phthalate, then  $\pi^*$  and  $\sigma^*$  orbitals are orthogonal and no energetically favorable pathways exist for fragmentation; hence, only an intense molecular ion is observed.

Several fragment ions appear to be predissociation ions, as the electron energies necessary to produce them are close to or identical with the energies required to produce the molecular ions. An EM–MS instrument capable of metastable ion scanning will be necessary to be certain of the origin of these ions. Open shell calculations are also needed to gain a better understanding of the nature of the transition states.

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