(i) With regard to ethylene loss, the reaction is highly specific, involving the terminal CH_3CH_2 unit with β-hydrogen transfer from the methyl group, analogous to Scheme III. Hydrogen scrambling amounts to less than 5%.

(ii) The generation of C_3H_6 (presumably propene) requires a double-bond isomerization, corresponding formally to a partial isomerization **12** → **16**. Not surprisingly, hydrogen atoms of the terminal methyl group are not involved in this process. In contrast, hydrogens of the CC double bond and the allylic methylene group of the propyl unit participate in the double-bond migration.

(iii) The elimination of C_4H_8 (presumably butene) requires in a formal sense a twofold double-bond isomerization prior to the neutral formation. The high specificity (all neutral isotopomers are formed with >99% isotopic purity) is worth mentioning.

Acknowledgment. The continued financial support of our work by the Deutsche Forschungsgemeinschaft, Stiftung Volkswagenwerk, Fonds der Chemischen Industrie, and Gesellschaft von Freunden der Technischen Universität Berlin is gratefully acknowledged. Professor W. P. Fehlhammer, Freie Universität Berlin, kindly provided us with pertinent references on structural studies of nitriles in the condensed phase.

Gas-Phase Electron Photodetachment Spectroscopy of the Molecular Anions of Nitroaromatic Hydrocarbons at Atmospheric Pressure

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Abstract: Low-resolution, electron photodetachment (PD) spectra of the molecular radical anions of nitrobenzene and 30 other nitroaromatic hydrocarbons bearing methyl, fluoro, chloro, bromo, and cyano substituents are reported for the first time. A unique feature of these measurements is that they have been obtained at atmospheric pressure by use of a specialized electron capture detector (ECD) in which the molecular anions are formed by resonance electron capture at 200 °C. Absolute PD cross sections, σ_d, for these anions over the spectral range 300 to 1200 nm have been obtained by use of I^- as a calibration reference. It is shown that the nitroaromatic anions undergo photodetachment by two mechanisms, direct PD and resonance PD. Through measurements of direct PD in the spectral region of photodetachment onset, the minimum photon energy, E_{th}, necessary to cause PD has been determined for each nitroaromatic anion. These measurements have been compared with the adiabatic electron affinities (EA) of the corresponding molecules which had been determined previously from studies of gas-phase electron transfer equilibria. This comparison indicates a high level of agreement between these two data sets and is consistent with a simple model of the energetics and structural changes which are thought to accompany the negative ionization of the nitroaromatic hydrocarbons. The occurrence of resonance PD for these anions is supported by a comparison of several of the PD spectra with UV-vis absorption spectra of the corresponding anions previously measured in τ-irradiated frozen glassy solutions. By the resonance PD mechanism, peak maxima of high absolute cross section are observed for many of the nitroaromatic anions. The largest PD cross section observed here was that of the 9-nitroanthracene anion for which $\sigma_d = 0.42$ Å^2 at 600 nm. For several instances in which σ_d was not large relative to the absorption cross section at peak maxima, low quantum efficiency for resonance PD is thought to result from poor Frank-Condon overlap of the excited molecular anion and the neutral molecule.

Electron photodetachment from atomic and polyatomic anions has proven to be a useful means of studying thermochemical and spectroscopic properties of negative ions and their photoproducts.[1-5] In particular, PD has been extensively used for the measurement of gas-phase electron affinities (EA), an application of considerable importance to a wide variety of chemical disciplines.[6,7] The photodetachment spectra of polyatomic negative ions has also been shown to provide information concerning the excited states of the negative ions and the neutral products involved in the PD process. We have recently shown in our laboratory[8] that PD may also be of considerable use in the field of analytical chemistry when used in conjunction with an electron capture detector (ECD) for gas chromatographic detection.

While a number of experimental techniques have been used for observing PD in the gas phase, those using the ion cyclotron resonance mass spectrometer (ICR-MS) in conjunction with a light source have been most extensively applied to the study of relatively large polyatomic negative ions.[1,4] The ICR-MS is well-suited to the study of PD because of its ability to generate a variety of mass-identified negative ions and then to trap and study them for a relatively long period of time. Certain limitations, however, are also recognized in the use of the ICR-MS for PD measurements. One of these is that the internal energy of the negative ions which can be readily produced in an ICR cavity are generally not under tight experimental control, and this fact can complicate the interpretation of PD spectra.[1,4] The negative ions are typically formed by energetic chemical means, and the excess internal energy thereby imparted to the product ions is not efficiently removed by collisions in the 10^{-8} to 10^{-5} Torr low-pressure environment of the ICR cavity.[9-11] This problem is expected to be particularly severe when a negative ion is formed through resonance electron capture, as shown in reaction 1, from a molecule, M, of high electron affinity (EA).

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$$e + M \rightleftharpoons M^{-*} \qquad (1)$$

Since the EA of molecules which readily lead to negative ions can be quite high, up to and exceeding 3 eV, the internal energy imparted to the molecular anion, M^{-*}, by reaction 1 will be correspondingly high.

Another related problem can arise if the natural lifetime of the initially formed excited anion, M^{-*}, is too short against autodetachment, the reverse of reaction 1. For example, Christophorou[12] has shown that the lifetimes of the molecular negative ions of nitrobenzene and substituted nitrobenzenes formed by capture of low-energy electrons are only on the order of tens of microseconds. Since stabilizing collisions can occur in an ICR cavity no faster than about one per millisecond, the natural lifetimes of these initially formed negative ions may not be sufficiently long as to allow their PD spectra to be reliably measured. Perhaps for this reason, the PD spectra of only a few molecular radical anions have been reported by the ICR method. Photodetachment studies of the resonance electron capture product of SF_6, for example, have been reported by ICR-MS[13] and appear to have been made possible in this case by the existence of one of several excited states of SF_6^{-*} which has an unusually long lifetime against autodetachment.[12,14-16] Most of the PD measurements of polyatomic negative ions measured to date by the ICR method have been performed on negative ions formed by dissociative EC reactions or by ion-molecule reactions in which an even electron anion is irreversibly formed.

In 1983 Dovichi and Keller[17] described the use of a direct current electron capture detector (ECD) for the measurement of the PD spectrum of NO_2^- at atmospheric pressure. We have recently described[8] an improvement of this general approach for performing gas-phase electron photodetachment spectroscopy at atmospheric pressure by use of an ECD which was operated in the pulsed mode of signal processing. It was demonstrated that the PD spectra of Cl^-, Br^-, and I^- and absolute PD cross sections of I^- could then be accurately measured. In the present study we describe the application of the photodetachment-modulated electron capture detector (PDM-ECD) to the measurement of the PD spectra of the molecular anions of nitrobenzene and 30 substituted nitroaromatic hydrocarbons, none of which have been previously reported. These anions are readily formed in an ECD due to rapid quenching of the initially formed excited molecular anion, M^{-*}, by collisions with the atmospheric pressure buffer gas, B, as shown in reaction 2,

$$M^{-*} \xrightarrow{B} M^- \qquad (2)$$

This process serves to overwhelm the reverse of reaction 1, which can destroy M^{-*} in low-pressure mass spectrometers. Furthermore, at atmospheric pressure reaction 2 is sufficiently effective in removing excess internal energy from the electron capture products that it is certain to bring them into thermal equilibrium with the buffer gas. This fact is expected to greatly facilitate the interpretation of PD spectra and should allow meaningful comparisons to be made between our results and those of previous studies in which the thermodynamic and spectroscopic properties of the corresponding ground-state species have been investigated. In particular, a comparison of 24 of the threshold PD measurements reported here with the corresponding EA values reported by Kebarle and co-workers[7,18,19] using the pulsed high-pressure mass spectrometry (PHPMS) method will be of interest. Also, comparisons of PD spectra reported here with the condensed-phase absorption spectra of several nitroaromatic anions measured previously by Shida and Iwata[20] will be made.

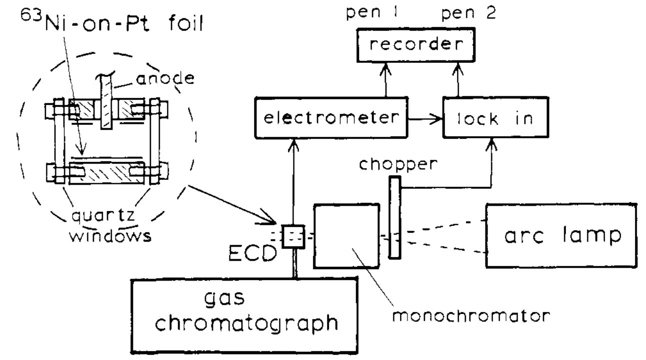

Figure 1. A schematic diagram of the apparatus used for photodetachment-modulated pulsed electron capture detector (PDM-ECD) measurements.

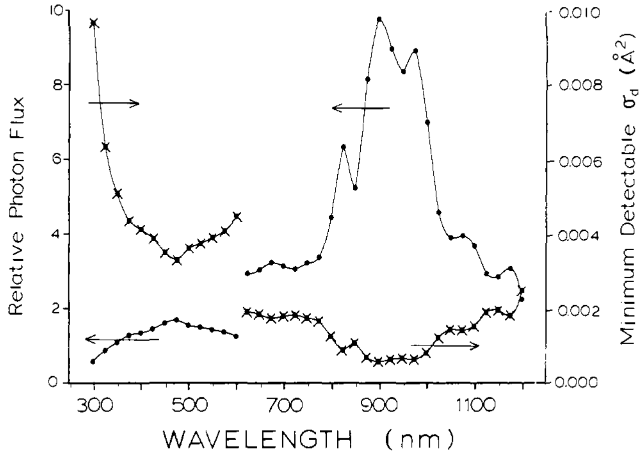

Figure 2. Relative magnitude of light flux (photons per second per unit area) and minimum detectable PD cross section throughout the spectral range of PD measurements. The discontinuity at 600 nm is due to a change in the grating used at this wavelength.

Experimental Section

The PDM-ECD experiment has been previously described in considerable detail.[8] A schematic representation of the apparatus is shown in Figure 1. A mechanically chopped beam of light, produced by a 1000-W Xe arc lamp, is passed through a grating monochromator and into a pulsed electron capture detector. The slits of the monochromator are typically set to a width of 5 mm. The cross-sectional area of the light beam formed is then sufficiently large so that all the negative ions present within the ECD are being irradiated by a relatively uniform photon flux. With this slit width the effective bandwidth of the monochromator is 20 nm when a grating with 1200 lines/mm is used for the spectral range of 250 to 600 nm, and is 40 nm when a grating with 600 lines/mm is used for the range 600 to 1200 nm. Relative light power (watts per unit area) was measured at each wavelength setting using a volume absorbing disk calorimeter (Scientech, Inc., Model 38-0101) which was placed in the position normally occupied by the ECD. These measurements were converted to values of relative light flux (*f*, photons per second per unit area). A plot of relative photon flux thereby obtained over the spectral range used is shown in Figure 2. The variations of flux with wavelength shown are due to a combination of factors including the spectral emission of the Xe arc lamp, the transmission efficiency of the monochromator, the change of grating which occurs at 600 nm, and the use of various cutoff filters which ensure the absence of unwanted light of higher order wavelengths.

The compounds of interest are introduced to the ECD by gas chromatography using a wide-bore 3-m capillary column (Hewlett-Parkard, 50% phenylmethylsilicone stationary phase). The chromatographic effluent is mixed with an excess flow of detector make-up gas so that the total gas flow rate is about 40 mL min^{-1}. Both gas streams consist of a mixture of 10% methane in argon (Matheson) and were first passed through water- and oxygen-removing traps (Altech). In order to ensure

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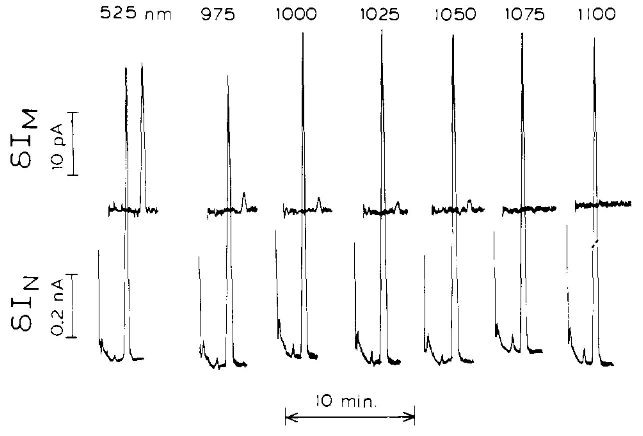

Figure 3. Repeated gas chromatographic analyses by the PDM–ECD of a sample containing 400 pg of nitrobenzene using the various settings of the monochromator shown. The two responses simultaneously obtained are the normal ECD response, δI_N, and the PD-modulated component of the ECD response, δI_M. The series of long-wavelength analyses shown illustrate the determination of the first detectable PD onset which occurs at λ_{th} = 1050 nm for the nitrobenzene anion.

that atmospheric oxygen does not enter the flow system, a positive pressure of about 100 Torr above atmospheric pressure (630 Torr in Bozeman) was maintained within the ECD at all times by placement of a flow restrictor at the detector gas outlet port. The expected chromatographic retention times of all compounds studied were known either from previous studies using these compounds and this column[21] or by parallel analyses of the samples by GC–MS. The highest column temperature used was 160 °C and the ECD was maintained at 200 °C at all times. All compounds studied were obtained from commercial suppliers and required no additional purification since they were introduced to the ECD with chromatographic separation from potential impurities, including isomers of the compound being studied. Typically, about 0.5 ng of the compound of interest was injected for each analysis. The precise amount used was adjusted so that uniform responses to all compounds studied were created.

The ion chemistry which occurs in the ECD is initiated by continuous β-radiation emitted by a ^{63}Ni-on-Pt foil which forms the cylindrical wall of the cell.[22] The secondary electrons created by this radiation are rapidly thermalized in the atmospheric pressure buffer gas and are contained within the central region of the reaction volume by a positive ion space-charge field.[22,23] When a molecule of high EA enters the cell, some of the electrons will be captured to form stable negative ions by the combination of reactions 1 and 2, shown above. This will tend to decrease the average electron population within the ECD. The negative ions formed will also be contained within the central region of the ECD by the positive ion space charge and, therefore, will not be lost by nonchemical processes such as wall neutralization or ventilation out of the cell. In the absence of light all negative ions and the electrons will be lost by recombination with positive ions. The rates of all of these processes are reasonably well-known under the conditions existing within a pulsed ECD.[8,24-26] If an intense flux of light is then passed through the ECD, photodetachment reaction 3 may also occur.

$$M^- + h\nu \rightarrow M + e \qquad (3)$$

This process offers an alternate fate for M⁻ which, if it occurs, will tend to increase the instantaneous electron population within the ECD during the period of photon illumination.

A measure of the average electron density existing within the cell is continuously provided by the fixed-frequency, pulsed method of ECD operation[22] in which all of the free electrons are periodically (4000 times per second in these experiments) collected at the anode. The time-averaged current thereby provided by the electrometer shown in Figure 1 provides the normal ECD response, δI_N, to a compound and is sent to pen 1 of a dual-pen recorder. The light beam is chopped at a frequency of 23 Hz,[8] and any PD caused by this light and reaction 3 will create a modulation of the time-averaged current measurement at this frequency. This component of the signal, called δI_M, is extracted by a lock-in amplifier and is sent to pen 2 of the recorder.

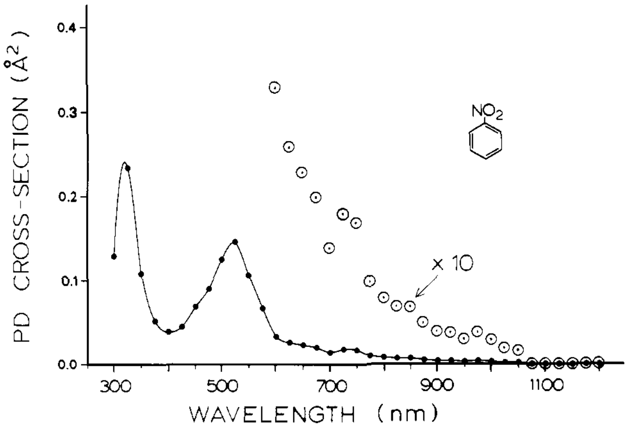

Figure 4. Electron photodetachment spectrum of the molecular anion of nitrobenzene measured by the PDM–ECD at 200 °C. Absolute PD cross sections have been determined by comparisons with PD measurements of I⁻ at 365 nm. Measurements have been taken at 25-nm intervals between 300 and 1200 nm. The effective bandwidth of the monochromator is 20 nm for wavelength settings below 600 nm and 40 nm above 600 nm. The solid line shown is a computer-generated smooth curve passing through the data points.

Typical measurements obtained in this way are shown in Figure 3 where the analysis of a sample containing 400 pg of nitrobenzene is repeated several times using different monochromator settings. The magnitude of the δI_N response is about 1.0 nA for all cases (total standing current is 4.0 nA). In the first case shown, light of 525 nm has been used and a relatively strong δI_M response is observed, reflecting a relatively large PD cross section for the nitrobenzene anion at this wavelength. For the remaining six analyses shown in Figure 3, much longer wavelengths have been used. While the PDM–ECD responses are not large in these cases, they are of considerable interest because they reveal the first detectable onset of PD, λ_{th}, in the threshold region for the nitrobenzene anion and will be used here in comparisons with the EA of the molecule. The determination of λ_{th} for nitrobenzene anion illustrated in Figure 3 is one of the most difficult encountered in this study because the onset of PD in its threshold region is very weak and gradual. Nevertheless, the absence of a PD response in Figure 3 with use of 1075-nm and longer wavelengths relative to the responses observed with use of 1050-nm and shorter wavelength light is distinctly observable above the baseline noise.

In order to obtain a full PD spectrum for a given compound, gas chromatographic analyses such as the ones shown in Figure 3 were repeated 37 times using 25-nm variations in wavelength from 300 to 1200 nm. A measure of relative PD cross section, rel σ, at each wavelength is obtained from the combination of the PDM–ECD measurements with that of relative light flux, f, shown in Figure 2, in accordance with the equation,[8] rel $\sigma = \delta I_M/(\delta I_N \times f)$. By comparison of relative cross sections thereby obtained for any negative ion with that observed for I⁻ at 365 nm under identical experimental conditions, absolute cross sections, σ_d, are obtained at all wavelengths assuming that the absolute PD cross section for I⁻ at 365 nm is accurately given by σ_d = 0.20 ± 0.05 Å^2.[8,27] The PD spectrum of I⁻ was obtained when desired by inclusion of 1-iodooctane in the nitroaromatic sample introduced to the gas chromatograph. The minimum σ_d value detectable over the entire spectral range investigated here is shown in Figure 2 and bears an inverse relation to the intensity of light at each setting of the monochromator.

In order to identify the negative ions produced by EC in the above experiments, the electron capture mass spectra of all compounds were determined in separate experiments using an atmospheric pressure ionization mass spectrometer (APIMS). This instrument is also home-built[22] and includes a ^{63}Ni-based ion source in which conditions can be made essentially identical with those existing in the PDM–ECD. These measurements were also carried out with capillary GC introduction to the APIMS ion source which was maintained at 200 °C.

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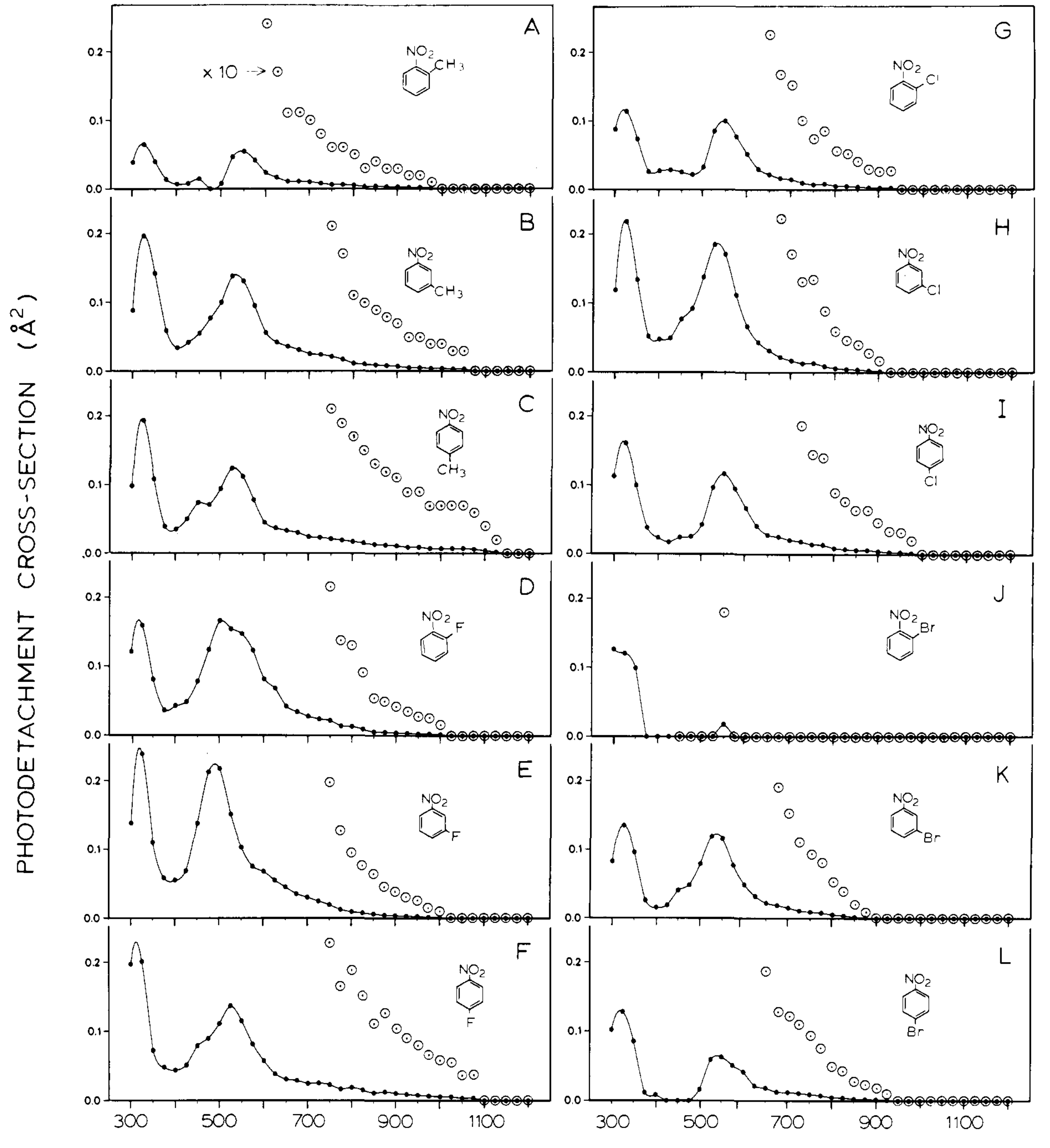

Figure 5. Electron photodetachment spectra observed for 12 substituted nitrobenzenes by the PDM–ECD at 200 °C.

Results

The PD spectra obtained by the PDM–ECD for nitrobenzene and 30 other nitroaromatic hydrocarbons at 200 °C are shown in Figures 4–7. For all spectra the cross sections measured in the wavelength region of initial PD onset out to 1200 nm are also indicated with ×10 amplification by the circled data points. The threshold wavelength, λ_{th}, at which PD is first observed for each case is also indicated in Table I along with the energy, E_{th}, of individual photons of that wavelength. The uncertainty in the λ_{th} measurements is estimated to be ±20 nm and is determined primarily by the bandwidth of the monochromator.

In order to verify the identity of the negative ions formed by electron capture in the PDM–ECD, the atmospheric pressure electron capture mass spectra of all of the compounds in this study group were measured by the APIMS described in the Experimental Section. With only two exceptions, electron capture produced a prominent M^- molecular anion and no other fragment ions of intensity greater than 0.1 relative abundance. The only compound for which the M^- ion was not the most abundant was *o*-bromonitrobenzene, for which the Br^- ion was approximately 10 times greater in intensity. This observation is consistent with its PD spectrum, shown in Figure 5J, which differs entirely from those of the other halogenated nitrobenzenes, but is essentially identical with that previously reported for Br^-.[8] The second exception was *m*-bromonitrobenzene for which the Br^- ion was 0.3 as intense as the M^- ion. The APIMS measurements also revealed the tendency of *p*-chloronitrobenzene and *p*-bromonitrobenzene to form ions of the type $(M + O - Cl)^-$ and $(M + O - Br)^-$, respectively, if great care was not taken to reduce the oxygen concentration in the carrier gas to the lowest possible levels.[29]

Discussion

Many of the PD spectra shown in Figures 4–7 bear two general characteristics which have been previously observed in other PD

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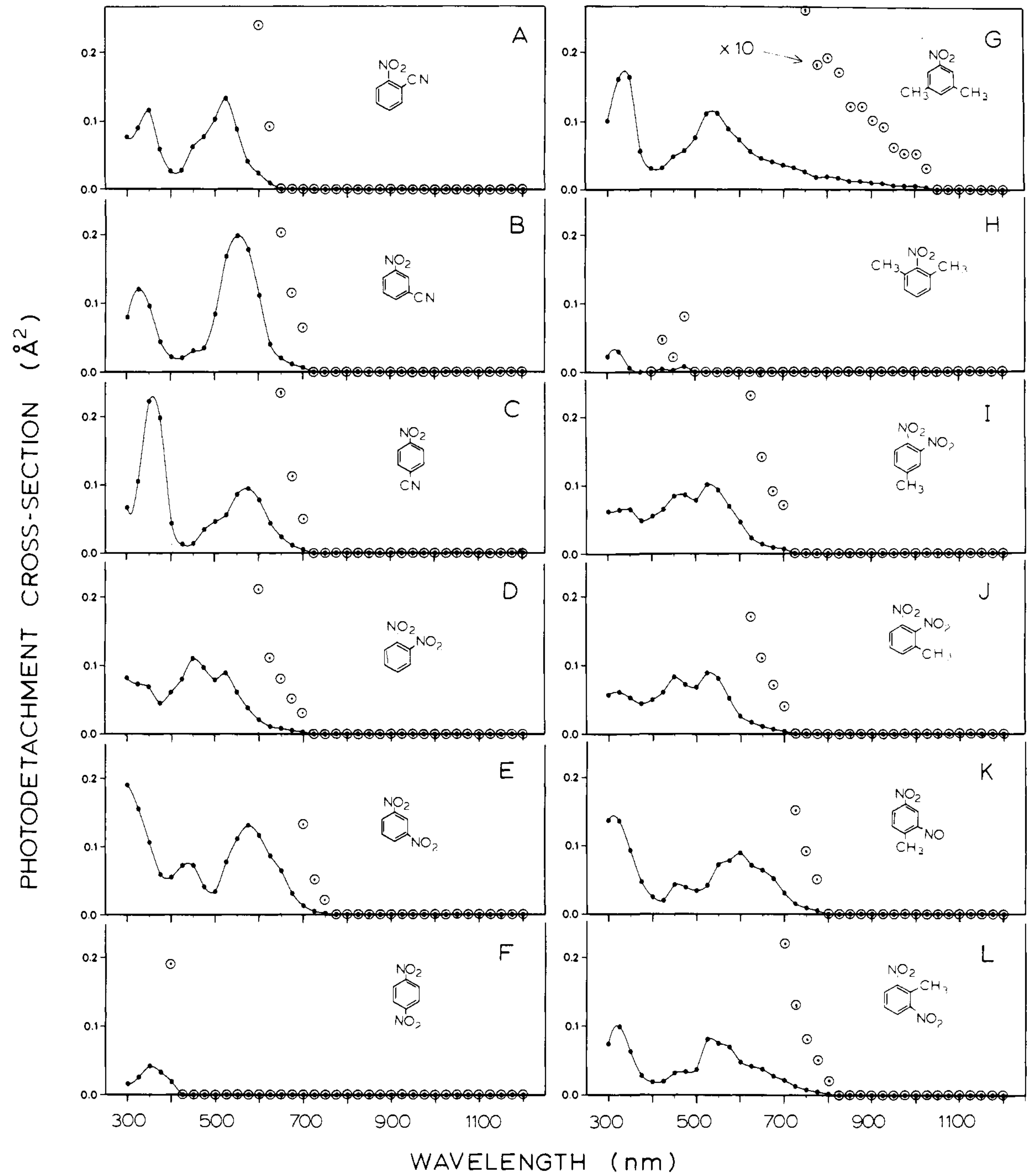

Figure 6. Electron photodetachment spectra observed for 12 substituted nitrobenzenes and dinitrobenzenes by the PDM-ECD at 200 °C.

studies.[30,31] These two characteristics are (1) a gradual and continuous increase in the PD cross section with use of increasingly shorter wavelengths and (2) the superimposition on this curve of peaks and maxima. Two PD mechanisms which have previously been associated with these two characteristics are direct photodetachment and resonance photodetachment, respectively. A symbolic representation of these two mechanisms is shown in Figure 8 and will provide a basis for the discussions below which are presented in two parts, one dealing with the direct PD mechanism and electron affinities and the other, with the resonance PD mechanism.

Direct Photodetachment and Electron Affinities. Process 1 in Figure 8 represents the direct photon-induced transition of the negative ion M^- to the neutral product M and a free electron. This process is generally expected to be operative in the threshold region of the PD spectra with use of photons whose energies are near that of the adiabatic electron affinity (EA) of M. With photons of progressively higher energy, the PD cross section is expected to increase in a manner described by the "threshold law" for that system. In order to most accurately determine the EA of a neutral from PD data, one would ideally like to know the exact threshold law, $\sigma_d(E) = f(E - EA)$, where E is the photon energy, for that system. This knowledge is especially useful if the increase in σ_d with increasing E is very gradual in the region of initial PD onset. Brauman and his collaborators[1] have developed considerable understanding of the shapes of PD threshold curves for polyatomic negative ions. They have found that the threshold law for several systems is determined primarily by the symmetry of the highest occupied molecular orbital of the negative ion. They have also shown, however, that additional factors, such as the existence of a strong dipole moment in the neutral, absorption resonances related to excited states of the negative ion and the neutral, and structural differences between the negative ion and the neutral

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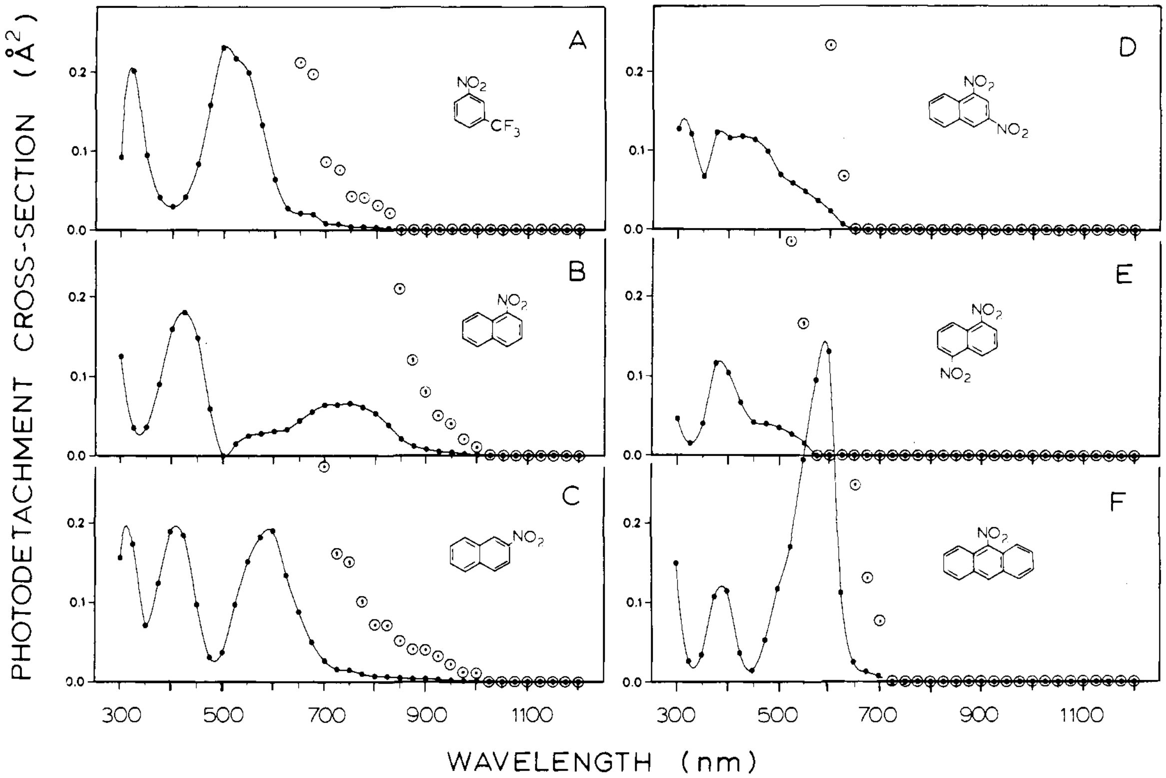


Figure 7. Electron photodetachment spectra observed for six nitroaromatic and dinitroaromatic hydrocarbons by the PDM-ECD at 200 °C.

Table 1. Photodetachment Thresholds of Nitroaromatic Anions

		PDM-ECD[a]		PHPMS[d]	
fig	anion	λ_{th} (±20 nm)[b]	E_{th} (±0.05 eV)[c]	EA (±0.1 eV)[e]	$\Delta S°$[f]
4	nitrobenzene (NB)	1050	1.18	1.01	−1.0
5A	*o*-methyl-NB	1000	1.24	0.92	−1.6
5B	*m*-methyl-NB	1050	1.18	0.99	
5C	*p*-methyl-NB	1125	1.10	0.95	
5D	*o*-fluoro-NB	1000	1.24	1.07	
5E	*m*-fluoro-NB	1000	1.24	1.23	−1.7
5F	*p*-fluoro-NB	1075	1.15	1.12	
5G	*o*-chloro-NB	925	1.34	1.14	−1.6
5H	*m*-chloro-NB	900	1.38	1.28	
5I	*p*-chloro-NB	975	1.27	1.26	−2.0
5K	*m*-bromo-NB	875	1.42	1.32	
5L	*p*-bromo-NB	925	1.34	1.29	
6A	*o*-cyano-NB	625	1.98	1.61	
6B	*m*-cyano-NB	700	1.77	1.56	
6C	*p*-cyano-NB	700	1.77	1.72	−2.7
6D	*o*-dinitrobenzene	700	1.77	1.65	
6E	*m*-dinitrobenzene	750	1.65	1.65	
6F	*p*-dinitrobenzene	400	3.10	2.00	−4.5
6G	3,5-dimethyl-NB	1025	1.21		
6H	2,6-dimethyl-NB	475	2.61		
6I	3,4-dinitrotoluene	700	1.77		
6J	2,3-dinitrotoluene	700	1.77		
6K	2,4-dinitrotoluene	775	1.60		
6L	2,6-dinitrotoluene	800	1.55		
7A	*m*-trifluoromethyl-NB	825	1.50	1.41	−2.5
7B	1-nitronaphthalene	1000	1.24	1.23	−0.9
7C	2-nitronaphthalene	1000	1.24	1.18	
7D	1,3-dinitronaphthalene	625	1.98	1.78	
7E	1,5-dinitronaphthalene	550	2.25	1.77	
7F	9-nitroanthracene	700	1.77	1.43	−2.9

[a] Present work, from Figures 4–7. [b] Highest wavelength setting of monochromator at which photodetachment is observed. [c] Photon energy corresponding to λ_{th}. [d] Pulsed high-pressure mass spectrometry measurements from ref 19. [e] Electron affinity. [f] Entropy change associated with negative ionization of molecule, M → M^-.

can also strongly influence the shape and intensity of PD spectra in the threshold region. For the nitroaromatic hydrocarbons studied here, we suspect that some of these complicating factors are operative and would affect any threshold laws which might be derived for them. Since these calculations have not yet been done for the nitroaromatic hydrocarbons, threshold laws cannot be effectively used here. Therefore, only the first detectable onset of PD, λ_{th}, will be used here for comparison with the EA of each molecule, while it is recognized that the energy, E_{th}, associated with this wavelength is not necessarily expected to be equal to EA of the molecule.

The M^- ion shown in Figure 8 has been assumed to be in its electronic and vibrational ground state, while the photoproduct, M, may be formed in any of a number of vibrational and rotational excited states of its electronic ground state. If the most stable geometries of M^- and M are exactly the same, the first onset of photodetachment of M^- would be observed with photons of energy equal to the EA of M. However, if the stable geometries of M^- and M are significantly different (that is, the Franck–Condon overlap is poor), as suggested in the case illustrated in Figure 8, the energy, E_{th}, of the photons at the PD threshold will be greater than EA. For the case symbolized in Figure 8, the stable configuration of M^- is characterized by internuclear distances which are shorter and intramolecular motions which are more constrained than those of the parent molecule. We have chosen this representation because Kebarle and co-workers[7,19] have shown that the entropy of negative ionization, i.e., $\Delta S°$ for the process M → M^-, is consistently negative for nitrobenzene and for substituted nitroaromatic hydrocarbons, in general. They suggest that this loss of entropy upon addition of an electron to these molecules is due to a stiffening of the internal rotation of the NO_2 groups due to increased π density in the C–N bond of the anion.

For all of the nitroaromatic hydrocarbons studied here, with the exception of *o*-bromonitrobenzene as noted in Results, the first onset of photodetachment indicated in Figures 4–7 is thought to be due to the photodetachment of the M^- species. These threshold measurements, λ_{th} and E_{th}, are listed in Table I along with values for the adiabatic EA and the entropy of negative ionization for many of the nitroaromatic hydrocarbons. These thermochemical properties have recently been determined by Kebarle and co-workers[7,18,19] through observations of gas-phase electron transfer equilibria by pulsed high-pressure mass spectrometry (PHPMS). A comparison of the E_{th} values observed here with Kebarle's EA determinations is also provided graphically in Figure 9. The dashed line shown in Figure 9 has unity slope and is the line on which all points would fall if E_{th} = EA.

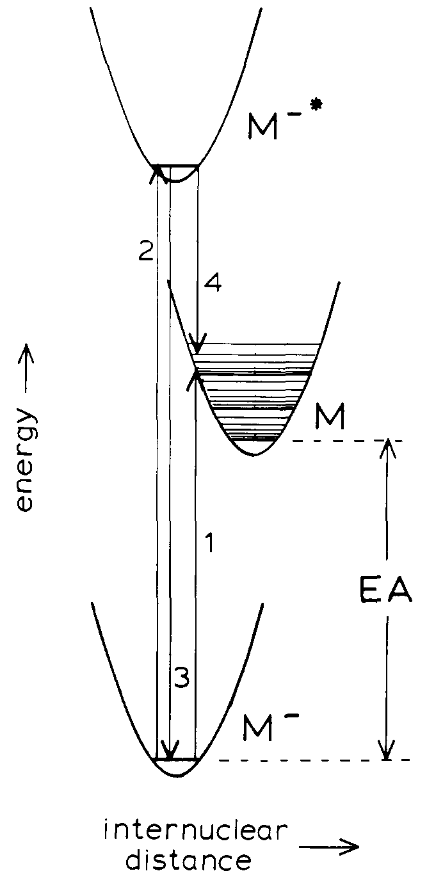


Figure 8. A simple model for the electron photodetachment of nitroaromatic anions. Direct PD is represented by process 1 in which absorption of a photon by M⁻ leads directly to the neutral molecule and a free electron. Resonance PD is represented by the combination of processes 2 and 4 in which absorption of a photon promotes M⁻ to an excited electronic state of the negative ion followed either by autodetachment of M⁻*, process 4, or by relaxation of M⁻*, process 3. The electron affinity (EA) of M is the energy difference between the M and M⁻ species in their ground electronic, vibrational, and rotational states. The stable structure of the negative ion is shown to be slightly different and somewhat more constrained than that of the neutral molecule.

Given the estimated uncertainty indicated with each set of energy measurements, many of the comparisons made in Figure 9 do lie sufficiently close to the dashed line as to indicate that the measurements of E_{th} for these are essentially equal to the corresponding adiabatic EA values of Kebarle. Nevertheless, approximately one-half of the data set clearly indicates that E_{th} exceeds EA by an amount greater than the uncertainty of the two measurements. In view of expected geometry differences between the M⁻ and M species of the nitroaromatic hydrocarbons,[7,19] the result that E_{th} exceeds EA is not unexpected. The only result which would not have been consistent with the simple model shown in Figure 8 would have been if E_{th} had been found to be less than EA for any of the compounds studied. This result would be expected only if the M⁻ ion in Figure 8 possessed sufficient additional internal energy so that its higher vibrational states were well-populated and photons having less energy than the adiabatic EA could cause direct PD. As has been previously explained, however, only ions of relatively low internal energy will be present in our atmospheric pressure ion source.

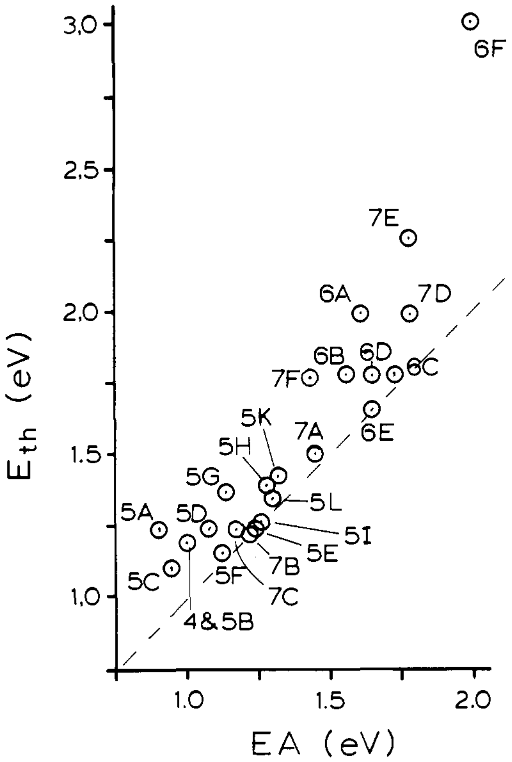
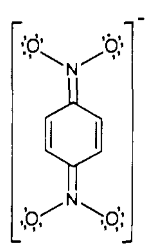


Figure 9. Photodetachment threshold energies, measured here, plotted against the adiabatic electron affinity (EA) of the corresponding nitroaromatic molecules determined from the electron transfer reactions by Kebarle and co-workers.[7,18,19] The numbers shown indicate the compound and PD spectra in Figures 4–7 associated with each data point. The dashed line is the line on which all points would lie if E_{th} = EA for each case.

One might expect a correlation to exist between the magnitude of the difference between the E_{th} and EA values discussed above and Kebarle's $\Delta S°$ values[7,19] for negative ionization, since both of these are thought to be related to the magntidue of structural differences in the M⁻ and M species. Unfortunately, the estimated uncertainty of the $\Delta S°$ values and the differences in E_{th} and EA values are too large to allow a meaningful comparison of this type to be made for many of the cases indicated in Table I and Figure 9. Nevertheless, for a few cases in which the differences between E_{th} and EA are unusually large, comparisons with the corresponding $\Delta S°$ values do suggest the existence of a direct correlation. For example, the greatest departure from the dashed line in Figure 9 is data point 6F for *p*-dinitrobenzene. In strong contrast, data points 6D and 6E for the ortho and meta isomers of dinitrobenzene lie very close to the unity slope dashed line. As indicated in Table I, Kebarle and co-workers[7,19] found *p*-dinitrobenzene to possess the most negative $\Delta S°$ value, −4.5 cal/K, of the group of compounds they studied (unfortunately, the ortho and meta isomers of dinitrobenzene were not included in that study). Therefore, both experiments involving the PDM-ECD and the PHPMS indicate that an unusually great geometry change accompanies the addition of an electron to *p*-dinitrobenzene.



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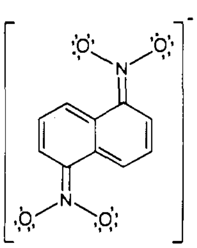

II

The significant structural change which occurs in the negative ionization of *p*-dinitrobenzene may be due to the relative importance of resonance form I in determining the structure of the molecular anion, while the analogous resonance form of the neutral molecule would not be expected to be as important in influencing its structure. In the resonance form I, considerable stiffening of both C–N bonds and the hindered rotation of both NO_2 groups is expected due to the double-bond π character assumed by both C–N bonds. Other reasonable resonance forms can written for this anion in which one or both of the C–N bonds have σ character. However, none of these would include a larger number of conjugated double bonds than the four shown in resonance form I and, therefore, would not necessarily be favored over form I. By removal of one electron from form I, a potential resonance structure for neutral *p*-dinitrobenzene can be written which also has four conjugated double bonds. In the case of the neutral, however, competing resonance structures having C–N bonds of σ characters can be written in which five conjugated double bonds are present.

The above argument concerning *p*-dinitrobenzene is also consistent with the results reported here for other dinitroaromatic hydrocarbons. A resonance form of type I, in which both C–N bonds assume π character, is not possible for *m*-dinitrobenzene and no anomalously large structure change was suggested by its E_{th} measurement. For *o*-dinitrobenzene, a resonance form analogous to type I would not be favored due to steric hindrance and, again, E_{th} for this compound was not found to be significantly larger than its EA. The case of 1,5-dinitronaphthalene indicated by data point 7E in Figure 9 deviates significantly from the unity slope dashed line, thereby suggesting that a significant structure change accompanies its negative ionization. For the 1,5-dinitronaphthalene anion, resonance form II is possible in which the π-resonance system is extended over the entire molecule by six conjugated double bonds, two of which are the C–N bonds. Competing resonance forms having a greater number of double bonds cannot be written for this anion. On the other hand, the resonance form of type II for the neutral molecule will have one fewer double bonds than its competing resonance structures and is not expected to be as important in determining the structure of the neutral. A resonance form of type II is not possible for the 1,3-dinitronaphthalene anion and, as shown by data point 7D in Figure 9, the departure of its E_{th} value from the unity slope dashed line is much less severe than that of the 1,5 isomer, even though the EA values of these two isomers are identical.

Another systematic trend, consistently noted in Table I and in Figure 9, is that the difference between E_{th} and EA for all of the methyl-, fluoro-, chloro-, and cyano-substituted nitrobenzenes is always greatest for the ortho isomer. This suggests that the magnitude of geometry change upon the negative ionization of these molecules is greatest for the ortho isomers. Unfortunately, this trend in the PD spectra cannot presently be compared with parallel $\Delta S°$ determinations from PHPMS because too few of these have been made to date.

Resonance Photodetachment. The peaks and maxima observed in the PD spectra of the nitroaromatic anions cannot be attributed to an alternate form of the direct PD mechanism in which a transition from M^- to an electronically excited state of M might be envisioned. Resonances and peak maxima are not expected to be associated with transitions of this type[4,5] and, furthermore, electronic excited states of sufficiently low energy are not thought to exist for most of the neutral nitroaromatic hydrocarbons studied here. For example, the peak at 525 nm in the PD spectrum of nitrobenzene anion shown in Figure 4 cannot be attributed to direct PD of M^- to form an excited electronic state of M. The UV-vis absorption spectrum of molecular nitrobenzene contains no absorption in the wavelength range greater than 400 nm[32] which indicates that no excited states of nitrobenzene exist within 3.0 eV of its ground state.

As shown in Figure 8, the other mechanism by which PD can occur is initiated by process 2, the absorption of light by M^- to form the electronic excited state, M^{-*}. The excited negative ion can then either relax back to the its ground state by radiative or nonradiative processes, shown collectively as reaction 3, or can undergo autodetachment to form the neutral molecule and an electron, shown as reaction 4. Since the energies of excited electronic states of negative ions are often greater than the EA of the neutrals, this process is potentially available to most negative ions. The criteria required for this mechanism to lead to intense resonances and peaks are that the cross sections for absorption, σ_a, must be larger than the cross sections for direct PD somewhere in the spectral region above E_{th}, and the quantum efficiency for autodetachment, given by $\Phi = k_4/(k_3 + k_4)$, must be acceptably high.

If the photodetachment peaks in Figures 4–7 are due to resonance PD, the PD spectrum observed for each case should resemble the absorption spectrum of the negative ion. Shida and Iwata[20] have provided the absorption spectra of numerous nitroaromatic anions which were made and contained in τ-irradiated glassy solutions frozen at 77 K. Some of their results have been plotted in Figure 10 (continuous curves) in a form (molar absorptivity coefficients have been converted to cross sections, wavenumbers to wavelengths) which facilitates their comparison with the corresponding PD spectra reported in Figures 4–7. The gas-phase PD measurements for each anion are also shown (points) in Figure 10.

The absorption spectrum of nitrobenzene anion, shown in Figure 10A, bears an obvious and convincing resemblance to its PD spectrum. In both spectra a large peak is noted at 325 nm and another, in the 500-nm region. The latter peak is red-shifted about 50 nm in the PD spectrum relative to that of the absorption spectrum. Red shifts of this magnitude have been observed previously in comparisons of gas-phase to condensed-phase electronic spectra[31] and have been attributed to solvation effects which can increase the energy of certain electronic transitions by destabilizing an excited state relative to the ground state.[33] The σ_a values for absorption at the two-peak maxima in Figure 10A are very large (a σ_a value of 0.6 Å^2 corresponds to a molar absorptivity of $\epsilon = 1.6 \times 10^4$ cm^{-1} M^{-1}) and are either equal to or about twice as great as the two corresponding σ_d values at the peak maxima. Because of the considerable differences in physical conditions under which the absorption and the PD measurements were made, quantitative deductions as to the relative rates of processes 2–4 in Figure 8 in terms of the observed σ_a and σ_d values for nitrobenzene would not be expected to be very accurate. Nevertheless, these cross-section measurements at the absorbance and PD maxima do clearly indicate that process 2 is very efficient for the gas phase nitrobenzene anion and that the quantum efficiency, Φ, for PD is quite high for both of the excited states of the negative ion indicated in the spectrum (using the σ_a and σ_d values without correction for phase and temperature differences indicates $\Phi = \sigma_d/\sigma_a \approx 0.5$ at 325 nm).

Shida and Iwata[20] also measured the absorption spectra of the three isomers of methylnitrobenzene anion and found that they differed very little from that shown for nitrobenzene anion in Figure 10A. In Figure 5A–C the PD spectra of the three isomers of methylnitrobenzene are shown, and these also are quite similar to the PD spectrum of nitrobenzene anion. Contrary to the absorption spectra reported by Shida and Iwata, however, the PD cross sections for the ortho isomer in Figure 5A are significantly reduced relative to those of nitrobenzene and the meta and para isomers of methylnitrobenzene anion. The absorption spectrum of 2,6-dimethylnitrobenzene in Figure 10E shows the effect on absorption of having two methyl groups adjacent to the nitro group. Only the higher energy absorption maximum observed at 325 nm is noticeably weakened relative to that of the nitrobenzene anion. While the absorption maximum at 575 nm has been red-shifted about 100 nm, its intensity is undiminished. The PD spectrum of 2,6-dimethylnitrobenzene anion shown in Figure 6H indicates that the σ_d values are greatly reduced at all peak maxima relative to that of nitrobenzene anion. The PD spectrum of 3,5-dimethylnitrobenzene anion, shown in Figure 6G, exhibits peak maxima as intense as that of nitrobenzene anion. The results indicate that methyl substitution adjacent to the nitro group tends to decrease σ_d much more than it does σ_a at the peak maxima. In terms of our model for PD illustrated in Figure 8, this result suggests that methyl substitution in the ortho position has relatively little effect on process 2, but substantially decreases the quantum efficiency for resonance PD by decreasing the rate of autodetachment, reaction 4, relative to that of relaxation, reaction 3. It will be recalled that in the previous section dealing with direct

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(32) *UV Atlas of Organic Compounds*; Plenum Press: New York, 1966; p D8/5.

(33) Amos, A. T.; Burrows, B. L. *Adv. Quantum Chem.* **1973**, *7*, 289.

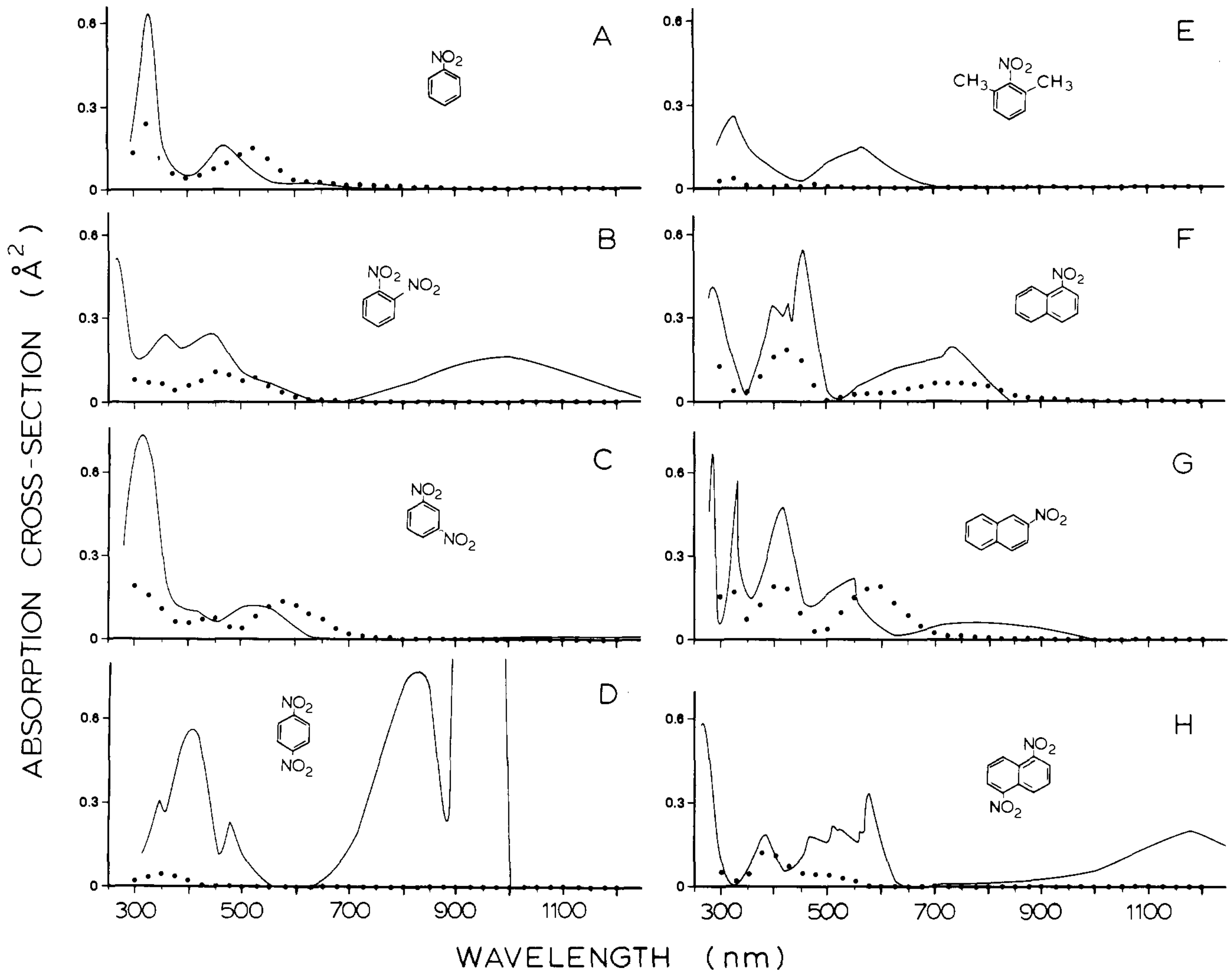

Figure 10. The absorption spectra (continuous curves) of the molecular radical anions of several nitroaromatic hydrocarbons reported previously by Shida and Iwata.[20] The molecular anions were formed by γ-irradiation of glassy solutions frozen at 77 K. These data have been converted to a form which facilitates their comparison with the PD spectra of the corresponding molecular anions which were reported in Figures 4–7 and have been replotted here (points).

PD, methyl substitution at the ortho position of nitrobenzene was shown to cause E_{th} to significantly exceed EA; this was suggested to be caused by poor Franck–Condon overlap of the M^- and M species. Poor Franck–Condon overlap of the M^{-*} and M species would also be expected if the M^- and M^{-*} states of the anions have very similar structures as implied in Figure 8. Therefore, it is reasonable to suggest that the lower σ_d values observed here with methyl substitution at the ortho position are also caused by poor Franck–Condon factors and, for the resonance PD mechanism, this causes the rate of reaction 4 and the magnitude of Φ to be decreased. That the M^- and M^{-*} species of *o*-nitrobenzene anion do, in fact, have similar structures is supported by the fact that σ_a of its two absorption maxima[20] are large.

The matrix absorption spectra of the ortho and meta isomers of dinitrobenzene anion, shown in Figure 10B,C, also bear considerable resemblance to the gas-phase PD spectra of these anions. The ortho isomer, for example, has a unique multiplicity of peaks in the short wavelength region which is evident also in its PD spectrum shown in Figure 6D. For this anion, the broad absorption which reaches a maximum at 1000 nm in Figure 10B is not expected to be seen in the corresponding PD spectrum because the excited electronic state of the negative ion involved in this transition lies below the EA of this molecule, and, therefore, it is not capable of autodetachment. These low-energy excited electronic states are present in other molecules as well. For example, the intense absorption peaks shown in Figure 10D for *p*-dinitrobenzene anion at wavelengths longer than 700 nm are not expected to be seen in the PD spectrum because the very high EA of *p*-dinitrobenzene (2.0 eV) prohibits resonance PD with use of wavelengths greater than about 600 nm.

It is also noted in Figure 10D that σ_d for the peak maximum at 350 nm is greatly reduced relative to σ_a for the absorption peak of this anion at 400 nm. This result is consistent with the effects of *o*-methyl substitution, discussed above, in which a decrease in σ_d at peak maxima was attributed to poor Franck–Condon factors. It will be recalled that in the section concerning direct PD, particularly poor Franck–Condon factors were indicated for *p*-dinitrobenzene.

The PD spectra of several methyl-substituted dinitrobenzenes are also shown in Figure 6. A comparison of D, I, and J in Figure 6 indicates that little change in the PD spectrum of *o*-dinitrobenzene is caused by the addition of a methyl group to either of the two possible positions on its ring. On the other hand, a comparison of PD spectra E, K, and L in Figure 6 indicates a progressive decrease in σ_d of the *m*-dinitro isomer at the peak maxima as the methyl group is placed first adjacent to one and then adjacent to both of the nitro groups. This result for methyl-substituted *m*-dinitrobenzene is consistent with the effects of *o*-methyl substitution on the σ_d of the nitrobenzene anion, discussed above The fact that a much smaller effect on σ_d is caused by methyl substitution in *o*-dinitrobenzene anion is undoubtedly due to the large degree of steric hindrance already caused by adjacent NO_2 groups. Therefore, the additional steric effect caused by an added methyl group is not as important.

The absorption spectra of 1- and 2-nitronaphthalene anions shown in F and G of Figure 10 provide a particularly interesting comparison with their PD spectra. The absorption spectrum of each of these is unique and relatively complex. Nevertheless, their essential features are apparent in the PD spectra of these two anions shown most clearly in B and C of Figure 7.

Conclusions

We have described and demonstrated a means for measuring the electron photodetachment spectra of polyatomic negative ions at atmospheric pressure. Several significant advantages have been demonstrated to accompany the use of the PDM-ECD for PD measurements. Stable molecular radical anions can be easily generated by resonance electron capture. The internal energy of the ions being studied is under good experimental control since they are in thermal equilibrium with the buffer gas. Absolute PD cross sections are readily determined by the PDM-ECD. While in this study absolute σ_d measurements were made using a reference negative ion whose σ_d was known at a specific wavelength, we have previously shown[8] that absolute PD cross sections can also be accurately determined by the PDM-ECD method without use of a calibration standard. Although these PD spectra were obtained with a low-resolution light system, the PDM-ECD should be equally applicable to the measurement of high-resolution PD spectra with lasers. The most apparent disadvantage of the PDM-ECD method for PD measurements is that the identities of the ions are not indicated by the instrument and must be determined by other means. In the present study this complementary information was readily provided by an atmospheric pressure ionization mass spectrometer.

Both the direct PD and resonance PD mechanisms have been shown to be operative in the PD spectra of 31 different nitroaromatic anions studied here. From measurements involving direct PD, the first detectable onset for photodetachment was determined for 30 molecular anions and 24 of these were compared with known adiabatic electron affinities of the molecules which had been previously determined through measurements of gas-phase electron transfer equilibria.[7,18,19] This comparison of spectroscopic and thermodynamic measurements was found to be consistent with a simple model of direct PD for the nitroaromatic hydrocarbons in which the structures of some of the anions were envisioned to be different and more constrained than those of the molecules. Additional evidence concerning the unusually large geometry change which has been previously suggested[19] to accompany the negative ionization of *p*-dinitrobenzene has been provided here. A systematic tendency for ortho-substituted nitrobenzenes to undergo significant geometry change upon negative ionization was also noted.

A comparison of the gas-phase PD spectra measured here at 200 °C with UV-vis absorption spectra of several of the nitroaromatic anions previously measured[20] in frozen glassy matrices at 77 K indicate that resonance PD is operative and efficient for many of the nitroaromatic anions. Since the peaks and resonances observed are initiated by electronic transitions of the molecular anions, the PD spectra provide a wealth of information concerning the molecular orbitals of the numerous substituted nitroaromatic anions studied here. The resonance PD mechanism accounts for the very high PD cross sections which were frequently observed. The largest PD cross section measured was for 9-nitroanthracene anion, where $\sigma_d = 0.42$ Å^2 at 600 nm. It was concluded that structural differences between the molecule and anion have a strong influence on the facility of the resonance PD mechanism and significantly decrease the magnitude of σ_d at peak maxima whenever poor Franck-Condon factors are suspected.

In our initial report of the PDM-ECD,[8] its application to the sensitive and specific analysis of trace quantities of organic iodides and bromides in the presence of organic chlorides was demonstrated. The discovery here of large and varied PD cross sections for nitroaromatic anions suggests that the PDM-ECD, when used in combination with gas chromatography, also possesses high potential for the selective and sensitive analysis of these molecules. It seems likely that this potential for trace organic analysis might also extend to other classes of compounds of environmental or biomedical interest which can be made to undergo electron capture and photodetachment rapidly under the influence of a specific bandwidth of light.

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Selective, Zirconium-Mediated Cross-Coupling of Alkynes: Synthesis of Isomerically Pure 1,3-Dienes and 1,4-Diiodo 1,3-Dienes

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Abstract: The coupling reaction of zirconocene alkyne complexes with a second alkyne provides a general method for the preparation of asymmetrically substituted zirconacyclopentadienes. The overall transformation is the chemoselective and regioselective *intermolecular* cross-coupling of two alkynes, a goal that has not been achieved with other methodology. Isomerically pure 1,3-dienes or 1,4-diiodo 1,3-dienes are obtained upon treatment of the metallacyclopentadienes with aqueous acid or iodine. Because this synthesis can be carried out as a one-pot procedure starting from the alkynes and Schwartz's reagent (Cp_2ZrHCl), it is an attractive alternative to other transition-metal-based methods for the synthesis of dienes from vinyl halides and isolated vinylmetal starting materials.

Recent advances in organopalladium and organonickel chemistry have led to the development of several preparatively useful methods for the synthesis of isomerically pure 1,3-dienes.[1] Although these methods have the advantage that they are often

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