Resonance Electron Capture Rate Constants for Substituted Nitrobenzenes

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We report here a new method for the determination of electron capture (EC) rate constants that utilizes a pulsed electron beam mass spectrometer. The method is first tested by measurements of the known dissociative electron capture rate constants for several halogenated methanes that have been extensively studied by other techniques. The resonance electron capture (REC) rate constants of nitrobenzene (NB) and 23 substituted nitrobenzenes (SNB's) are then determined for the first time at 125 °C in 10 Torr of methane buffer gas. The SNB's studied here include several sets of closely related structural isomers whose electron affinities (EA's) have been previously determined. It is shown that the REC rate constants of these compounds bear little systematic relationship with the EA's of these compounds. The REC rate constants of the SNB's are also compared with other previously reported characteristics associated with the negative ionization of these compounds, including their entropies of negative ionization, the lifetimes against autodetachment of their initially formed molecular anions, and the rates of autodetachment from electronically excited states of their molecular anions.

Introduction

A large number of polyatomic molecules that have positive electron affinities (EA's) are capable of capturing thermal and low-energy electrons (k_a) in the gas phase by a nondissociative resonance electron capture (REC) process in which a molecular anion is formed. This process is made possible by the initial formation of long-lived, nuclear-excited Feshbach states, M^{-*} , as shown in reaction 1,^{1,2}where the electron is initially trapped

$$e^{-} + M \underset{k}{\stackrel{k_{a}}{\rightleftharpoons}} M^{-*} \xrightarrow{k_{b}[B]} M^{-}$$
(1)

by losing energy to the nuclear motion of $M^{-*.1}$ If this reaction is carried out under conditions of very low pressure, M^{-*} will autodetach with rate constant k_{-a} .¹ However, if this reaction is carried out in the presence of a buffer gas (B), the high internal energy of M^{-*} can be removed by collisions with the buffer gas to form a stable molecular anion, M^- . (If the EA of M is about 1 eV or greater, the rate of thermal electron detachment by the stabilized anion, M^- , will be negligible at temperatures less than 200 °C.³⁻⁵) With use of moderate to high buffer gas pressures (about 0.1 Torr and greater), the rate of collisional stabilization of M^{-*} , k_b [B], will generally exceed the autodetachment rate constant, k_{-a} , for polyatomic anions, so that the overall observed rate constant for the REC mechanism, k_{rec} , becomes equivalent to the initial attachment rate constant, k_a , as shown by eq 2.

$$k_{\rm rec} = k_{\rm a} k_{\rm b}[{\bf B}]/(k_{\rm -a} + k_{\rm b}[{\bf B}]) \approx k_{\rm a}$$
 (at high pressure) (2)

The REC reaction has been used extensively in various instruments, such as mass spectrometers,⁶ electron capture detectors,⁷ and ion mobility spectrometers,⁸ for the trace detection of selected organic compounds in environmental or biomedical samples. In these applications, several features of the REC process are invaluable. First, molecular anions are formed that are directly representative of the compound of interest. Second, high chemical specificity for target compounds of relatively high EA can be achieved against other uninteresting compounds of low or negative EA. Third, k_a can be extremely large, often exceeding the rate constants for fast ion-molecule reactions by 2 orders of magnitude.⁹ These combinations of factors have allowed unsurpassed detection sensitivity to be achieved by methods based on REC.

In view of the apparent simplicity of the REC mechanism and its importance for chemical analysis, it is surprising to note that relatively little is presently known about the factors that determine the initial and high-pressure rate-controlling step, k_a , in reaction 1. REC rate constants have previously been measured for relatively few compounds under a limited range of physical conditions,^{2,9} and from these measurements, no clear understanding of the factors that determine the magnitude of k_a has emerged. Consider, for example, the following five compounds which are listed in order of increasing EA along with their respective k_a values at room temperature: perfluorobenzene (EA = 0.52 eV^{10}) $k_a = 1.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1,11}$ nitrobenzene (EA = 1.01 eV^{12,13}) k_a = $6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, ¹⁴ SF₆ (EA = 1.05 eV¹⁵) $k_{\text{a}} = 3.1 \times 10^{-7} \text{ cm}^3$ s^{-1} ,¹⁶ SF₄ (EA = 1.5 eV¹⁷) $k_a = 1.5 \times 10^{-9}$ cm³ s⁻¹,¹⁸ and *p*-benzoquinone (EA = 1.91 eV¹³) $k_a \approx 2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.^{19,20} While it is recognized that a positive EA is necessary for REC to occur, the above data set indicates that the relative magnitudes of the k_a 's for these compounds are not related in a straightforward manner to the relative magnitudes of the EA's. For example, while the EA of p-benzoquinone is the greatest of the five compounds listed, its k_a is 7 orders of magnitude lower than that of perfluorobenzene, the compound with the lowest EA. Also, it is noted that k_a for SF₆ is 2 orders of magnitude greater than that of SF₄, even though the EA of SF₆ is less than that of SF₄. It is interesting to note that the geometry of the SF_6^- ion is thought to differ very significantly from that of the SF₆ molecule.^{21,22} This geometry change results in a large positive entropy change in the negative ionization of SF₆ ($\Delta S_a^\circ = 13 \text{ cal/K}$).^{13,15} While this structural change is thought to contribute to the very slow electron-transfer rates observed for SF₆ and SF₆⁻ with various electron donors and acceptors, 15,23,24 it clearly does not retard the REC rate constant of SF_6 , which is as large as any that has even been reported.^{16,25} Within the data set provided above, it is also noted that the dipole moment of M is not an important factor in determining k_a . For example, while both SF₆ and p-benzoquinone have no permanent dipole moment, they have the highest and lowest k_a values, respectively. While nitrobenzene has a very large dipole moment (4.2 D (ref 26)), its k_a is of moderate magnitude.

To our knowledge, the only theoretical model for the dynamics associated with the resonance EC reactions of polyatomic molecules is that proposed by Compton *et al.*¹⁴ in 1966. Their prediction is expressed by eq 3 for the specific case involving the capture of very low-energy (thermalized) electrons.

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Electron Capture Rate Constants for Nitrobenzenes

$$k_{\rm a}\tau = \rho^{-}/\rho^{0} = \frac{2\pi^{2}h^{3}}{m^{2}v} \frac{(\rm EA + a\beta_{z})^{N-1}}{(N-1)! \sum_{i} h\nu_{i}}$$
(3)

This equation predicts that the product of k_a and $\tau = 1/k_{-a}$ (the lifetime of M-* against autodetachment) will be equivalent to the ratios of the density of states of the negative ion, ρ^{-} , and that of the electron plus molecule, ρ^0 . Compton *et al.*¹⁴ then derived an expression for the density of states ratio in terms of the mass, m, and velocity, v, of the electron, the EA of the molecule M, and the zero-point energy, β_z , the number of vibrational degrees of freedom, N, and the vibrational frequencies, v_i , of the negative ion M^{-*}. The term a is an empirical correction factor. By eq 3 and measurements of k_a and τ for SF₆, Compton *et al.*¹⁴ predicted that the EA of SF_6 would be about 1.1 eV. This is in excellent agreement with the recent measurements by electron-transfer equilibria¹⁵ that indicate EA = 1.05 eV for SF₆. Johnson *et al.*¹ have also shown that a simplified form of eq 3 provides a useful means of correlating measurements of τ for substituted nitrobenzenes with their electron affinities. However, Babcock and Streit¹⁸ have shown that eq 3 does not provide a useful prediction of the magnitude of k_a for SF₄ (discussed in previous paragraph).

In the present study, we provide additional characterizations of the REC process by measurements of the REC rate constants of nitrobenzene (NB) and 23 substituted nitrobenzenes (SNB's) by a new method based on a pulsed electron beam mass spectrometer. This study is unique among previous investigations of the REC process in that it provides relative k_a values of numerous compounds that are structurally closely related and it includes several sets of positional isomers. The SNB's have previously been shown¹ to form excited molecular anions, M^{-*}, upon electron capture (reaction 1) that have relatively long lifetimes against autodissociation ($k_{-a} = \tau^{-1} < 10^5 \,\mathrm{s}^{-1}$). Therefore, at the buffer gas pressure used in the present study (10 Torr), the pseudo-first-order rate constant for collisions of M-* with the buffer gas $(k_b[B] \approx 3 \times 10^8 \text{ s}^{-1})$ can reasonably be assumed to greatly exceed k_{-a} so that the present measurements provide a determination of the initial capture rate constant, k_{a} , for each compound (see eq 2).

Two fundamental properties that must be associated with the negative ionization of a molecule are the electron affinity (EA) and entropy of negative ionization (ΔS_a°) of that molecule. The electron affinities of most of the SNB's studied here are now accurately known and range from about 0.9 to 2.0 eV.13 The entropies of negative ionization of several of the SNB's included here have also been reported.¹³ While EA and ΔS_a° values were shown above to not determine the relative k_a values for the set of five compounds considered there, it is possible that the considerably different structures and elemental compositions of those compounds masked subtle affects of EA and ΔS_a° on k_a . Therefore, the present set of measurements provide an additional and perhaps more valid means of assessing the role of these individual molecular properties on the k_a values of a set of closely related compounds. The present measurements of k_a along with previous measurements of molecular anion lifetimes ($\tau = 1/k_{-a}$) will also allow the model for the EC process given by eq 3 to be further tested. Finally, from previous studies of the photodetachment²⁷ and absorption²⁸ spectra of the molecular anions of the SNB's, dynamic properties of their electronically excited molecular anions will be deduced and compared with k_a values.

Experimental Section

All experiments to be reported here were performed with a pulsed electron beam high-pressure mass spectrometer (PHPMS) that has previously been described in detail.^{29,30} For the present experiments, a modified ion source that was specifically designed



Figure 1. Pulsed electron beam ion source used for the present measurements. A pulsed electron beam enters through an aperture in the back wall of the source. Ions are sampled through an aperture on the front wall. A 2-mm Cu gasket determines the depth of the active source volume.

for buffer gas pressures in excess of the low Torr range was used for the first time and is shown in Figure 1.

In order to operate at higher pressures and still allow ions to diffuse rapidly to the ion source walls (as required by the PHPMS method for observing gas-phase ion chemistry), it is necessary to decrease the characteristic length of the ion source. As shown in Figure 1, a small characteristic length has been established by a thin (2 mm) copper gasket that separates the faces of two Conflat flanges. The interior volume of the ion source thereby formed is disk-shaped. A prepared gaseous mixture is passed into this source volume through a hole drilled into one of the flanges. At the center of the back side of the ion source, a 50- μ m aperture allows the entrance of a 3000-V pulsed electron beam. At the center of the front side of the ion source, another $50-\mu m$ aperture allows a portion of the ionic contents of the source to diffuse out of the source and then to be mass analyzed and detected. For the present measurements, the ion source was maintained at a pressure of 10 Torr with methane buffer gas and at a temperature of 125 °C.

Electron capture rate constants were measured in the following manner. A gaseous mixture was prepared in a 6.4-L gas handling plant by adding small amounts of CH₃I (reference compound) and the SNB of interest to methane. The total initial pressure of methane in the gas handling plant was 800 Torr. Standardized solutions of CH₃I and the SNB's in toluene solvent were injected into the gas handling plant by syringe and allowed to vaporize and equilibrate at 150 °C. This gaseous mixture was then allowed to flow continuously through the ion source at a rate sufficient to maintain a total pressure of 10 Torr in the ion source. The absolute concentrations (molecules cm⁻³) of CH₃I and the SNB in the ion source were calculated from their known mole fractions in the gas handling plant and the total ion source pressure. With CH₃I and a SNB simultaneously present in the ion source, competitive electron capture reactions lead to the formation of the negative ions, I⁻ and SNB⁻. The relative intensities of these negative ions were then used to determine the relative k_a values of the two parent molecules. CH₃I was chosen as a reference compound for two reasons. One is that the EC rate constant of CH₃I is known at 125 °C.³¹ The other is that, with CH₃I as the reference compound, no ion-molecule reactions will occur in the ion source after the initial EC reactions of interest.³⁰ That is, we know that the I⁻ ion formed by the EC reaction of CH_3I will not react with SNB and that the SNB-ion formed by the EC reaction of the SNB will not react with CH₃I.³⁰ That post-EC chemistry does not, in fact, occur for any of the systems examined here was verified in each experiment, as illustrated in the following example.

In Figure 2, a typical measurement (shown here for the case of nitrobenzene with reference compound CH_3I) is illustrated. Following an electron beam pulse at time = 0.0 ms, the negative



Figure 2. Typical temporal profiles measured by the pulsed electron beam mass spectrometer. The ion source contains 0.030 mTorr of CH_{3I} and 0.18 mTorr of nitrobenzene in 10 Torr of methane buffer gas at 125 °C. The two ions shown are formed by competitive electron capture and are destroyed by diffusion to the walls. The temporal profiles provide proof that no ion-molecule reactions between I⁻ and NB or between NB⁻ with CH_{3I} occur following the initial EC reactions of interest.



Figure 3. Mass spectral scan of the pulsed electron beam ion source under conditions identical to those described in Figure 2.

ions, NB⁻ and I⁻, are initially formed by their respective EC reactions. These negative ions are then observed by the mass spectrometer slightly later in time as a positive ion space charge field associated with the initial presence of the electrons collapses and allows the negative ions to diffuse to the walls of the ions source.³² After about 0.3 ms, the time dependence of both ions is determined simply by the rates at which these ions diffuse to the walls. Since no post-EC chemistry occurs over the entire time of the measurement, the relative areas under the two intensity-time curves provide a direct measure of the relative rates of the two EC reactions. Alternatively, the relative ion abundance could be obtained from the relative areas of the peaks in the mass spectrum shown in Figure 3.

The absence of post-EC reactions was experimentally verified by changing the concentrations of both compounds introduced to the source. For example, if an ion-molecule reaction of the type NB⁻ + CH₃I \rightarrow NB + CH₃ + I⁻ was occurring, the slope of the NB⁻ decay would be increased with increased [CH₃I]. As expected,³⁰ no changes in the slopes of the NB⁻ or I⁻ decay curves were detected with changes in the concentration of either parent molecule, thereby proving that the ions formed by the initial EC reactions do not undergo additional reactions of any kind.

In addition to the expected molecular anions, other negative ions of minor relative intensity were sometimes observed in the EC spectra of the SNB. However, as illustrated for the case of NB in Figure 3 for which the ion, $(NB-O)^-$, is also formed by a competitive dissociative EC process, secondary ions of this type never exceeded 0.10 abundance relative to the molecular anion. It was assumed that these dissociative EC products are formed

TABLE 1: Dissociative Electron Capture Rate Constants of
Various Halogenated Methanes Measured against Reference
Compound SF6 at 125 °C in 10 Torr of Methane Buffer Gas

compound	k_{dec} (present)	k_{dec} (literature) ^a		
CH ₃ I	1.4 × 10 ⁻⁷	1.8 × 10 ⁻⁷		
CH ₂ Br ₂	1.5×10^{-7}	1.57×10^{-7}		
CF ₃ Br	3.7 × 10−8	4.3 × 10 ⁻⁸		
CHCl ₃	1.3×10^{-8}	1.4 × 10− ⁸		
CFCl	3.3×10^{-7}	3.2 × 10⁻ ⁷		
CCl ₄	3.7×10^{-7}	4.5×10^{-7}		

^a By the FALP method.^{16,31}

through the same intermediate species (M^{-*}) in reaction 1. Therefore, in determining k_a , the integrated intensity (area of peaks in Figure 3) of any secondary ions was added to the integrated intensity of the M^- ion before comparison with the abundance of the reference I⁻ ion by eq 4.

$$\frac{I_{\rm M-}}{I_{\rm I-}} = \frac{k_{\rm a}[{\rm M}]}{k_{\rm cc}[{\rm CH}_{\rm 3}{\rm I}]}$$
(4)

By eq 4, the k_a for M is determined from the ratio of measured ion intensities, the ratio of the concentrations of M and CH₃I added to the gas handling plant, and the known EC rate constant, k_{ec} , for CH₃I at 125 °C.

Results and Discussion

In order to test the validity of the experimental method introduced here, the EC rate constants of several previously studied halogenated methanes were first measured using SF₆ as a reference compound. All of the halogenated methanes capture electrons by the dissociative EC mechanism forming a halide negative ion, X⁻. In these experiments also, no post-EC chemistry occurs because X⁻ does not react with SF₆ and SF₆⁻ does not react with any of the halogenated methanes. Therefore, the observed relative signal intensities again provide a direct measure of the relative EC rates. In these experiments, SF₆ was assumed to have an electron capture rate constant of 4.5×10^{-7} cm³ s⁻¹ at 125 °C.¹⁶

The results of these measurements are shown in Table 1, along with literature values previously determined by the flowing afterglow with the Langmuir probe (FALP) technique (16,31) at the same temperature. The dissociative EC rate constants of these compounds have also been measured by a variety of other techniques at specific temperatures, and a complete summary of these other measurements can be found in the recent FALP studies.^{16,31} We have chosen to use the FALP measurements in Table 1 because the FALP technique is a relatively definitive method, including unambiguous measurements of both the reagent electron density and the product ion density along its reaction volume. In addition, the FALP measurements provide EC rate constants under conditions of temperature and pressure that are most similar to those used in the present study.

A comparison of the present and FALP measurements indicates very good agreement and, therefore, supports the validity of the present method. The one compound for which the discrepancy slightly exceeds our estimates of experimental uncertainty is CH₃I, which is the compound that will serve as a reference compound in the present study. In our use of CH₃I as a reference compound, its EC rate constant determined here, 1.4×10^{-7} cm³ s⁻¹, will be used rather that the literature value, 1.8×10^{-7} cm³ s⁻¹. This choice is made because the present determination for CH₃I is directly linked to that of SF₆, the EC-active compound that has been most extensively studied by others and whose k_a is assumed to be most accurately known. In this way all EC rate constants reported in Tables 1 and 2 are anchored either directly or indirectly to that of SF₆ at 125 °C.

EC Rate Constants of the SNB's. The rate constants, k_a , determined here for NB and 23 SNB's are listed in Table 2. It

TABLE 2: Resonance Electron Capture Rate Constants, k_a ,Measured against Reference Compound CH₃I at 125 °C in 10Torr of Methane Buffer Gas

substituted nitrobenzene (NB)	$k_{\rm a} \times 10^7$ (cm ³ s ⁻¹)	rel k _a	EA ^a (eV)	$\Delta S_{a}^{\circ b}$ (cal/K)	k** _{auto} c
NB	0.26	1.00	1.01	-1.0	$\gg k_r$
2-CH₃−NB	0.26	1.00	0.92	-1.6	$0.75k_{\rm r}$
3-CH ₃ -NB	0.25	0.96	0.99		$\gg k_r$
4-CH₃−NB	0.42	1.61	0.95		≫kr
2-F-NB	0.44	1.69	1.07		
3-F-NB	0.11	0.42	1.23	-1.7	
4-F–NB	0.35	1.34	1.12		
2-Cl–NB	1.00	3.8	1.14		
3-C1–NB	0.90	3.5	1.28		
4-CI-NB	0.85	3.3	1.26	-2.0	
2-CF ₃ -NB	1.40	5.4	1.33		
3-CF ₃ -NB	0.80	3.1	1.41	-2.5	
4-CF ₃ -NB	1.20	4.6	1.47		
2-CN-NB	0.46	1.77	1.61		
3-CN-NB	0.53	2.00	1.56	-3.2	≫kr
4-CN-NB	1.34	5.1	1.72		$0.35k_{r}$
2-NO ₂ -NB	1.33	5.1	1.65		$1k_r$
3-NO ₂ -NB	0.22	0.85	1.65		≫k₁
4-NO ₂ -NB	1.40	5.4	2.00	-4.5	$0.1k_{\rm r}$
2-NO ₂ -3-CH ₃ -NB	1.40	5.4			
3-NO ₂ -4-CH ₃ -NB	0.50	1.92			
3-NO ₂ -2-CH ₃ -NB	1.0	3.8			
2,6-diCH ₃ -NB	0.42	1.61			$0.07k_{\rm r}$
3,5-diCH ₃ -NB	0.21	0.81			

^a Electron affinities determined by the electron-transfer equilibria method.¹³ Estimated uncertainty is ± 0.10 eV. ^b Entropy of negative ionization determined by the electron-transfer equilibria method.¹³ ^c Rate constant for electron autodetachment by electronically excited molecular anion; see text.

is seen that the k_a values vary by more than 1 order of magnitude, from 0.11 × 10⁻⁷ cm³ s⁻¹ for 3-F-NB to 1.4 × 10⁻⁷ cm³ s⁻¹ for 3-CF₃-NB, 4-NO₂-NB, and 2-NO₂-3-CH₃-NB. The fastest EC rate constants measured here for the SNB's are about 1/3 as great as those of the most EC-active compounds, such as SF₆ and CCl₄. The slowest are about 1/40 as great. Since the rate constants reported in Table 2 have not been previously measured under the present conditions, no meaningful comparisons of the present measurements with literature values can be made. One previous measurement of k_a for NB in 1966¹⁴ indicated $k_a = 6$ × 10⁻¹⁰ cm³ s⁻¹ at room temperature, about 1/40 as great as the present measurement of k_a for NB at 125 °C.

Relative EC rate constants, normalized with respect to the case of NB, are also listed in Table 2 under the heading "rel k_a ". The effects of the various substituents on relative k_a are seen in Table 2 to be generally much greater than experimental uncertainties estimated for the individual relative k_a measurements $(\pm 15\%)$. Therefore, the present set of data provide a valid means of assessing the effects of each substituent on k_a . A cursory inspection of the relative k_a values for the singly substituted NB's in Table 2 reveals the following effects on k_a : CH₃ substitution causes a significant change for only the para isomer; F substitution causes both an increase (ortho and para) and a decrease (meta); Cl, CF₃, and CN substitutions cause an increase; and NO_2 substitution causes either a large increase (ortho and para) or no change (meta). It is interesting to note that, among the singly substituted NB's, the meta isomers tend to have the lowest k_a . Among the multiply substituted NB's listed at the bottom of Table 2, it is interesting to note that the addition of a methyl group to 3-NO₂-NB at the 4-position and particularly at the 2-position greatly increases k_a . Also, the addition of two ortho methyl groups to NB (to form 2,6-diCH₃NB) significantly increases k_a while the addition of two meta methyl groups (to form 3,5-diCH₃NB) does not.

Correlation of k_a Values with Molecular Properties. Electron Affinities. The electron affinities of all of the monosubstituted NB's studied here have previously been determined in studies of



Figure 4. EC rate constants, k_a , determined here for NB and singly substituted nitrobenzenes plotted against their electron affinities.

their electron-transfer equilibria reactions,13 and these EA values are also listed in Table 2. In Figure 4 the k_a values for the monosubstituted NB's have been plotted against their respective EA values. Inspection of Figure 4 indicates that only a very rough correlation exists between the magnitudes of k_a and EA for the individual SNB's. The addition of one of the electronwithdrawing substituents, F, Cl, CF₃, CN, or NO₂, consistently leads to higher EA's and this usually leads to an increased $k_{\rm s}$. For example, 4-NO₂-NB has the highest EA of all of the compounds studied here, and it also has the greatest k_a . However, some exceptions to this expected tend are also noted, and even within a given isomeric set of compounds, it is noted that the increase in k_a is not generally in proportion to the EA values. For example, while the EA's of all three isomers of NO₂-NB are very great, the k_a 's of only the ortho and para isomers are enhanced relative to that of NB. The k_a of the meta isomer is either unchanged or slightly decreased relative to that of NB. Similarly, it is noted that while the ortho isomer of FNB has the lowest EA, it has the greatest k_a , and while the meta isomer of FNB has the greatest EA, it has a k_a that is actually suppressed relative to that of unsubstituted NB. The meta isomers for the CF₃- and CNnitrobenzenes also are seen to have distinctly lower than expected k_a values. For the CN-NB's, k_a of the ortho isomer is also surprisingly low relative to that of the para isomer.

Steric Ortho Effects. It is instructive to consider whether or not a steric ortho effect on k_a is indicated in the data in Table 2. The negative ionization of NB might be expected to lead to an increase in the π -bond character of the C-N bond.³³ This, in turn, would lead to a stiffening of the C-N bond of the negative ion so that the plane of the nitro group would tend to align itself with that of the benzene ring. In that case, a bulky substituent placed at the ortho position of NB might be expected to cause a steric hindrance to its negative ionization and, for this reason, might be expected to diminish k_a . It is noted in Table 2, however, that k_a for 2-CH₃-NB is unchanged relative to that of NB even though its EA is somewhat less than that of NB. Also, it is noted that the k_a values for 2-CF₃-NB and 2-NO₂-NB are both about 5 times greater than that of NB and are not significantly lower than those of their meta and para isomers. In addition, the results obtained for 3-NO₂-4-CH₃-NB and 3-NO₂-2-CH₃-NB clearly indicate that the addition of a methyl group adjacent to or between the nitro groups in 3-NO₂-NB greatly increases the EC rate constant of this compound. These results suggest that a steric ortho effect is, indeed, operative in electron capture by the substituted NB's. However, this effect appears to increase rather than decrease k_a and, therefore, is in the opposite direction of that initially expected.

Entropies of Negative Ionization. The entropies of negative ionization, ΔS_a° , for some of the substituted NB's have also been



Figure 5. EC rate constants, k_a , plotted against the lifetimes, τ , of the initially formed molecular anions. The τ values were obtained from ref 1.

previously determined from studies of electron-transfer equilibria¹³ and are listed in Table 2. It is seen that the ΔS_a° values are negative for these compounds and range from a low value of -1.0cal/K for NB to a high value of -4.5 cal/K for 4-NO₂-NB. The loss of entropy associated with the negative ionization of these compounds has been suggested to be caused by a decrease in rotational motion about the C-N bond(s) as this bond acquires increased π character in the negative ion state.³³ As indicated most clearly by the case of 4-NO2-NB, however, a large decreased entropy change upon negative ionization does not appear to retard the rate of electron capture. While this compound has an unusually large negative ΔS_a° , it also has the greatest k_a value measured here. It is interesting to recall that SF_6 is known to have an unusually large positive entropy change (13, 15) upon negative ionization ($\Delta S_a^{\circ} = +13 \text{ cal/k}$) and also has one of the largest k_a 's ever measured. Clearly, large structural changes leading to either "loose" or "tight" molecular anions do not necessarily retard the rates of resonance electron capture.

Dipole Moments. Inspection of the k_a values in Table 2 also reveals that the permanent dipole moment of the SNB molecule plays no obvious role in determining the magnitude of k_a . Perhaps the most striking illustration of this is provided by the relative k_a values of the ortho versus para isomers of NO₂-NB. While these two compounds are expected to have the largest and smallest (none) dipole moments of the SNB's studied here, their k_a values are both extremely large and of similar magnitude.

Correlation of k_a Values with Other Dynamic Properties. As mentioned in the Introduction, Johnson *et al.*¹ have previously measured the lifetimes ($\tau = 1/k_{-a}$) of the initially formed anions, M^{-*}, of numerous SNB's at 25 °C (reaction 1). Assuming that the difference in temperatures used in the present study (125 °C) and that used by Johnson *et al.* would not change the relative orders of reactivity, it is interesting to consider whether a correlation exists between these two sets of measurements. As shown in Figure 5, however, no meaningful correlation between k_a and τ appears to exist. For example, it is noted that unusually large τ values were detected for all three isomers of NO₂-NB, while unusually large k_a values were noted for only the ortho and para isomers of NO₂-NB and not the meta isomer.

According to the model of the REC process developed by Compton *et al.*,¹⁴ a more meaningful correlation between k_a and τ might be expected if they are combined and plotted against the combination of anion properties, including EA, as shown in eq 3. Unfortunately, the vibrational frequencies of the molecular anions of the SNB's are not known, and therefore, eq 3 cannot be rigorously applied. However, Johnson *et al.*¹ have applied the following simplified version of eq 3 to their measurements of τ



Figure 6. Present k_a determinations and previous τ determinations (ref 1) for the SNB's plotted against electron affinity in the form predicted by eq 6. N is the number of vibrational modes present in the molecular anion ($N = 3 \times$ number of atoms - 6). The units of $(k_a \tau)^{1/(N-1)}$ are (cm³)^{1/(N-1)}.

for SNB's.

$$\tau^{1/(N-1)} \propto EA \tag{5}$$

In applying this equation, Johnson *et al.* assumed that all SNB had the same k_a and that the EA of each SNB could be accurately estimated from solution-phase electrochemical reduction potentials. A reasonably good correlation between $\tau^{1/(N-1)}$ and EA was obtained.¹

At the present time, we have the opportunity to test the applicability of the Compton model to the EC chemistry of the SNB's somewhat more completely than Johnson *et al.* did by eq 5 because we now know the k_a values of each SNB at 125 °C and the EAs of each SNB in the gas phase. Accordingly, in eq 6 we have modified eq 5 to include k_a in accordance with the more complete expression of Compton (eq 3).

$$(k_{\rm a}\tau)^{1/(N-1)} \propto \rm EA \tag{6}$$

In Figure 6, we have plotted $(k_a \tau)^{1/(N-1)}$ versus the gas-phase EA of each compound using the present measurements of k_a and the previous measurements of τ by Johnson *et al*. The degree of scatter in Figure 6 is greater than that obtained by Johnson et al.,1 and therefore, the present treatment of these data does not provide additional support for the applicability of the general model for REC by Compton et al. to the SNB's. It is possible that this failure results from the omission of several terms in eq 6 that appear in the complete eq 3. Those additional terms in eq 3 are primarily related to the vibrational degrees of freedom of the anions and their frequencies. These terms might reasonably be expected to be of similar magnitude and, therefore, not of significance within sets of geometric isomers. It is therefore important to note in Figure 6 that, even within each set of geometric isomers, a positive correlation of $(k_a \tau)^{1/(N-1)}$, as predicted by eq 6, is not generally observed.

It is also interesting to compare the present set of k_a measurements against the lifetimes of electronically excited molecular anions that can be deduced from absorption (ABS)²⁸ and photodetachment (PD)³⁴ spectra of the SNB molecular anions. The ABS and PD spectra of the three dinitrobenzenes are reproduced in Figure 7. Also shown (arrows) are the wavelengths corresponding to the known EA of each molecule. The ABS and PD spectra can be interpreted in terms of the simple model shown by reaction 7



wavelength (nm)

Figure 7. Absorption (continuous curve) and photodetachment spectra (points) of the molecular anions of the three isomers of dinitrobenzene. The ABS spectra are obtained from frozen glassy solutions at 77 K (taken from ref 28), and the PD spectra (taken from ref 34) were measured in the gas phase at 200 °C. The arrow in each spectra indicates the wavelength corresponding to the electron affinity of the molecule.

$$M^{-} \underset{k_{r}}{\overset{\sigma_{ABS}}{\rightleftharpoons}} M^{-**} \xrightarrow{k^{**}_{auto}} M^{*} + e^{-}$$
(7)

where the exited molecular anion, M^{-**} , is formed by the absorption of a photon of energy somewhat greater than the EA of the molecule. M^{-**} will then be quickly altered by one of two competing processes. It either will relax back to its ground state with rate constant k_r or will undergo electron autodetachment with rate constant k^{**}_{auto} . The PD cross section, σ_{PD} , at each wavelength is related to the absorption cross section, σ_{ABS} , by the relation³⁴ $\sigma_{PD} = k_r \sigma_{ABS} k^{**}_{auto} (k^{**}_{auto} + k_r)^{-1}$. Therefore, k^{**}_{auto} can be determined at each wavelength by eq 8.

$$k^{**}_{auto} = k_r \sigma_{PD} / (\sigma_{ABS} - \sigma_{PD})$$
(8)

Under the condition of 1 atm pressure in which the PD spectra were measured, it can be assumed that k_r will be determined by the rate of collisions of M^{**} with the buffer gas molecules and, therefore, that k_r will be identical ($k_r \approx 10^{10} \text{ s}^{-1}$) for all SNB's.

For the case of 3-NO₂-NB, the first ABS and PD maximum that appear at photon energies greater than the EA of this compound have nearly identical σ_{ABS} and σ_{PD} (at approximately 525 nm). In terms of eq 8, this indicates that $k^{**}_{auto} \gg k_r$ for 3-NO₂-NB. For 2-NO₂-NB and 4-NO₂-NB, however, the first PD maxima above the EA is significantly smaller than the corresponding maxima in the ABS spectra. Therefore, application of eq 8 to the spectra of these two compounds leads to significantly smaller values of k^{**}_{auto} , about $1.0k_r$ and $0.1k_r$, respectively. A comparison of k^{**}_{auto} thereby obtained (Table 2) with the measurements of k_a reported here suggests a correlation for the three isomers of dinitrobenzene. That is, the meta isomer of dinitrobenzene has a k_a that is uniquely low and a k^{**}_{auto} that is uniquely large. Perhaps the properties of the M^{-**} species for 3-NO₂-NB that cause its rapid autodetachment relative to that of the ortho and para isomers are the same ones that cause its slower rate of electron capture. It would be interesting to be able to pursue this potential correlation between k^{**}_{auto} and k_a for the other SNB's studies here. Unfortunately, both the ABS and PD spectra of molecular anions have been reported for only a few of the other SNB's. The k^{**}_{auto} values obtained from these few

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measurements are also listed in Table 2, and some of these tend to reinforce an inverse relationship between k_a and k^{**}_{auto} . For example, it is noted that k_a significantly increases and k_{auto} significantly decreases upon change of a CN substituent from the meta to para position. Also, the addition of methyl groups to the two ortho positions of NB (forming 2,6-diCH₃-NB) greatly decreases k^{**}_{auto} and slightly increases k_a . While the addition of one methyl group to an ortho position of NB results in a detectable decrease in k^{**}_{auto} , no change in k_a is observed. Therefore, 2-CH₃-NB is the only compound of the several considered here for which an inverse relation between k_a and k^{**}_{auto} is not observed.

As first described by Johnson et al.,¹ we have also considered the possibility that $k_{\rm a}$ is dependent on the existence of electronically excited states of M-* having energies below that of the thermalized M and electron. The presence of such electronic states would increase the density of states available to the incoming electron and might thereby cause an increase in k_{a} relative to those compounds which can offer only vibrationally excited states of the ground electronic state to the incoming electron. Some support for this suggestion can be seen in the absorption spectra of the three isomers of NO₂-NB⁻ shown in Figure 7. In each of these spectra, the wavelength corresponding to the energy of the reactants, equal to the EA of M, is indicated by an arrow. The presence of absorption bands at wavelengths greater than that of the EA indicates the presence of low-lying excited electronic states of M-. The spectra in Figure 7 indicate the presence of such states only for the ortho and para isomers of NO2-NB- and not for the meta isomer. This might contribute to the lower $k_{\rm s}$ reported here for the meta isomer. We have also applied the same consideration to the k_a values measured here for the meta and para isomers of CN-NB, since the absorption spectra of the molecular anions of these two compounds have also been reported.28 For these compounds, however, the absorption spectra do not indicate the presence of low-lying electronic states for 4-CN-NB, and therefore, the existence of such states does not account for the greater k_a of this isomer.

Conclusions

A versatile method for the determination of electron capture rate constants has been described. The resonance electron capture rate constants of numerous substituted nitrobenzenes have been reported for the first time. It has been shown that the relative values of the capture constants, k_a , for these closely related compounds vary significantly and that these variations are not readily explained by consideration of the electron affinities of the individual molecules alone. It has also been noted that the $k_{\rm a}$ values are not diminished for those SNB's that experience unusually great structural change and decrease of entropy upon negative ionization. While the present measurements of $k_{\rm s}$ do not appear to bear a systematic relationship with previous measurements of autodetachment rate constants previously reported by Johnson *et al.*,¹ they do appear to bear an inverse correlation with estimates of autodetachment rate constants for the electronically excited molecular anions of several of the substituted nitrobenzenes studied here. It is clear, however, that a great deal of additional experimental and theoretical insight is needed before a detailed understanding of the factors that control the rates of resonance electron capture reactions can emerge. It is perhaps not an exaggeration to state that the resonance electron capture reaction is presently among the least well understood of all simple, fundamental processes in chemistry.

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