Photodissociation Dynamics of Nitrobenzene Molecular Ion on a Nanosecond Time Scale

Wan Goo Hwang,[†] Myung Soo Kim,^{*,†} and Joong Chul Choe^{*,‡}

Department of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea, and Department of Chemistry, University of Suwon, Kyunggi 445-743, Korea

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Photodissociation dynamics of nitrobenzene molecular ion has been investigated on a nanosecond time scale by mass-analyzed ion kinetic energy spectrometry. Photodissociation has been found to occur through various reaction channels. Three dissociation channels to $C_6H_5O^+$, $C_6H_5^+$, and NO^+ have been observed together with a consecutive dissociation to $C_5H_5^+$ via $C_6H_5O^+$. The photodissociation rate constant of the molecular ion and the kinetic energy release distributions in each channel have been determined. The rate constant of the second step of the consecutive reaction has been determined in real time also. It has been found that the direct bond cleavage to $C_6H_5^+$ occurs in competition with the rearrangement processes to $C_6H_5O^+$ and NO^+ on a nanosecond time scale. Statistical theories have been used to gain insight into the dynamics of the reactions.

I. Introduction

Nitrobenzene has been among the most attractive systems studied in the fields of both ionic¹⁻¹⁸ and neutral¹⁹⁻²⁴ dissociation dynamics. A number of possible dissociation pathways of the nitrobenzene or its molecular ion have been the main motivation for such research efforts. To understand the dynamics and mechanism of the nitrobenzene ion dissociation, various experimental techniques have been employed such as photoelectron-photoion-coincidence (PEPICO) spectrometry,¹⁻³ laser photodissociation,3-7 infrared multiphoton dissociation (IRM-PD),^{8,9} and conventional mass spectrometry.¹⁰⁻¹⁸ Also, the experimental rate constant and kinetic energy release data have been compared with theoretical predictions based on statistical theories such as Rice-Ramsperger-Kassel-Marcus (RRKM) theory,²⁵ which is equivalent to quasi-equilibrium theory (QET or RRKM-QET)²⁶ in ionic field and phase space theory.²⁷ Despite such efforts, its dissociation dynamics and mechanism have not been fully understood yet, and some controversy still remains.

The major fragment ions in the dissociation of nitrobenzene ions are $C_6H_5O^+$, $C_6H_5^+$, and NO^+ . In addition, consecutive dissociation via C₆H₅O⁺ results in abundant C₅H₅⁺. Rate constants for the main channels, namely, the productions of C₆H₅O⁺, C₆H₅⁺, and NO⁺, in the dissociation of the energyselected nitrobenzene ions with an internal energy of 1.3-1.9 eV were measured with PEPICO by two research groups.^{1,2} In the earlier study by Panczel and Baer,¹ it was reported that the rate for the appearance of $C_6H_5^+$ was much faster than those for C₆H₅O⁺ and NO⁺, indicating that these two groups of channels are not in direct competition. This result combined with the earlier report⁴⁻⁶ that $C_6H_5^+$, but not $C_6H_5O^+$ and NO^+ , was observed in the photodissociation of nitrobenzene ion at 514.5 nm led the above investigators to suggest that the production of C₆H₅⁺ occurs from an excited electronic state. On the other hand, in the later study by Nishimura et al.,² all the above three channels were found to occur competitively and could be explained by RRKM-QET.

Production of $C_6H_5^+$ from nitrobenzene ion has been the focus of some research efforts since the first report by Panczel and

ion by Moini and Eyler,⁹ $C_6H_5^+$ product was not observed at all even though its appearance energy was comparable to those for other product ions. This was taken as evidence for the excited state hypothesis mentioned above. In a recent study by Osterheld *et al.*,⁸ however, production of $C_6H_5^+$ was observed in pulsed IRMPD, indicating that it occurs in the ground electronic state. To accommodate this result with the previous rate measurement with PEPICO by Panczel and Baer, Osterheld *et al.* proposed an ion-dipole intermediate (IDI) mechanism. In this mechanism, nitrobenzene ion first forms IDI, which either dissociates to $C_6H_5^+$ directly or reassociates to an isomeric structure (nitrite form) followed by dissociation to $C_6H_5O^+$ or NO⁺.

Baer.¹ In the continuous-wave IRMPD study of nitrobenzene

Another interesting feature in the nitrobenzene ion dissociation is the production of $C_5H_5^+$. It is well known that $C_5H_5^+$ is produced by a consecutive reaction via $C_6H_5O^+$. In particular, in the previous visible laser photodissociation studies carried out with a double-focusing mass spectrometer,^{4–6} PEPICO,³ and an ion cyclotron resonance mass spectrometer,⁷ the major fragment ions observed were $C_6H_5^+$ and $C_5H_5^+$. Absence of $C_6H_5O^+$ was explained by its further dissociation to $C_5H_5^+$ at a nitrobenzene ion internal energy higher than 2.5 eV.^{3,7}

In the present study, the dissociation dynamics of nitrobenzene ions at the internal energy 2.48-2.98 eV has been investigated with the recently developed photodissociation method using mass-analyzed ion kinetic energy spectrometry (PD-MIKES).²⁸⁻³³ Nanosecond rate data can be obtained with the present technique. We observed that the production of $C_6H_5^+$ is competitive with the dissociation channels leading to NO⁺ and $C_6H_5O^+$. In this paper, the dynamics in the individual dissociation channels is to be discussed on the basis of the measured and theoretically calculated rate constants and kinetic energy release distributions.

II. Experimental Section

The experimental setup has been described in detail elsewhere²⁸ and will be reviewed only briefly here. A doublefocusing mass spectrometer with reversed geometry (VG Analytical Model ZAB-E) modified for photodissociation study was used. Nitrobenzene ions generated by charge exchange in the ion source and accelerated to 8 keV were mass-analyzed

^{*} Authors to whom correspondence should be addressed.

Seoul National University.

[‡] University of Suwon.

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Figure 1. PD-MIKE spectra for dissociation of nitrobenzene molecular ion at the photoexcitation wavelengths of (a) 607.5, (b) 514.5, and (c) 488.0 nm. The molecular ions with 8 keV translational energy entered the electrode assembly floated at 1.85 kV. Chemical formula and m/z of the photofragment ion corresponding to each peak are indicated.

by the magnetic sector. Then, the ion beam was crossed with the laser beam in the field region of an electrode assembly located near the intermediate focal point of the instrument. The 607.5 nm output of a dye laser (Spectra Physics Model 375B) and the 514.5 and 488.0 nm lines of an argon ion laser (Spectra Physics Model 164-09) were used. The translational kinetic energy of the fragment ions was analyzed by the electric sector. This is called mass-analyzed ion kinetic energy spectrometry (MIKES). Since a MIKE spectrum contains contributions from metastable ion decomposition (MID) and collision-induced dissociation (CID) by residual gas, phase-sensitive detection was adopted to record a MIKE spectrum originating from photodissociation, namely, a PD-MIKE spectrum. To improve the quality of a PD-MIKE spectrum, signal averaging was carried out for repetitive scans. Errors quoted in this work were estimated from several duplicate experiments at 95% confidence limits.

 CS_2 was used as a reagent gas for charge exchange ionization. The ion source chamber was maintained at 140 °C.

III. Results

A. General Appearance of the PD-MIKE Spectrum. To measure the photodissociation rate constant, a high voltage was applied on the electrode assembly and the parent ions were photoexcited in the field region of the assembly. The PD-MIKE spectrum for the nitrobenzene ion obtained at 1.85 kV applied voltage using a 607.5 nm photon is shown in Figure 1a. Four photofragment ions are identified and assigned at m/z (massto-charge ratio) 30, 65, 77, and 93 in Figure 1a, which correspond to NO⁺, C₅H₅⁺, C₆H₅⁺, and C₆H₅O⁺, respectively. Considerable noise between the peaks is due to strong backgrounds originating from MID and CID by residual gas. At photon wavelengths of 514.5 and 488.0 nm, $C_6H_5O^+$ and NO^+ peaks were not observed in the PD-MIKE spectra as shown in Figure 1b,c. The results at 514.5 and 488.0 nm are consistent with the previous laser photodissociation results,³⁻⁷ as mentioned in a previous section. Photofragment ions with a particular m/z value formed at different positions in the field

 TABLE 1: Relative Abundances (%) of Fragment Ions in the Photodissociation of the Nitrobenzene Ion

photodissociation	fragment ion (m/z)			
wavelength (nm)	$\overline{C_{6}H_{5}O^{+}(93)}$	$C_{6}H_{5}^{+}(77)$	$C_5H_5^+(65)$	NO ⁺ (30)
607.5	11 ± 3	68 ± 5	19 ± 4	2 ± 1
514.5	0	78 ± 3	22 ± 3	0
488.0	0	80 ± 3	20 ± 3	0

region appear at different translational energies in the PD-MIKE spectrum. Therefore, the fact that the peaks at m/z 30, 77, and 93 are asymmetrically broadened in Figure 1a (enlargements are shown in Figure 2) indicates that the photodissociation rate constant of the molecular ion can be determined for the experiment with 607.5 nm excitation. At higher photon energies, however, the $C_6H_5^+$ peak is symmetric, as shown in Figure 1b,c. This means that the dissociation rate of the molecular ion after the absorption of a 514.5 or 488.0 nm photon is too fast to be measured with the present method. The photofragment ion with m/z 65 appears as two peaks designated A and B in Figure 1, which will be assigned later. Its spectral pattern changes dramatically with wavelength as can be seen more clearly in Figure 3. Relative abundance of each photofragment signal was determined after various calibrations to account for the instrumental effects as previously.³¹ The results are listed in Table 1.

B. Rate Constants. The photodissociation rate constants have been determined by analyzing PD-MIKE peak shapes as described in detail previously.²⁸⁻³⁰ Instead of a single value of rate constant, its distribution was determined, which is mainly due to internal energy distribution of the molecular ions. The average value will be taken as the rate constant representative of the distribution. In our previous photodissociation studies,^{30,32–33} not only the thermal energy of the parent molecules but also the collisional relaxation of the molecular ions occurring in the ion source were found to affect the internal energy and its distribution of the molecular ion. An experimental technique to correct for the latter in the rate data was developed.³⁰ Such a correction was not needed here because the effect of the collisional relaxation on the rate data was not significant. This is thought to be due to the fact that the internal energy of nitrobenzene ions generated by charge exchange with $CS_2^{\bullet+}$ is small (0.21 eV ignoring the thermal energy, *vide infra*).

Figure 2 shows the PD-MIKE peak shapes for NO⁺, $C_6H_5^+$, and $C_6H_5O^+$ at 607.5 nm excitation which have been analyzed to obtain rate constants. The peak shapes recalculated with the rate constant distributions thus obtained are also shown. The average photodissociation rate constants obtained from the three peaks are listed in Table 2. It is to be noted that the average total rate constants determined from C₆H₅⁺ and NO⁺ peaks are essentially the same. This means that these channels are in direct competition. Since the production of $C_6H_5O^+$ and NO^+ are known to be in direct competition, one expects that the rate constant determined from $C_6H_5O^+$ would be the same as the other two. However, the former rate constant tends to be a little smaller than the latter two, even though still within experimental error. This, we believe, is due to consecutive dissociation of $C_6H_5NO_2^{\bullet+}$ to $C_5H_5^+$ via $C_6H_5O^+$. In the second step of this consecutive reaction, $C_6H_5O^+$ ions with higher internal energy will dissociate more readily. Then, the signal detected as the PD-MIKE peak of $C_6H_5O^+$ is due to those ions with lifetimes longer than the flight time to the detector ($\sim 8 \mu s$). Among the molecular ions with some internal energy distribution, those ions with lower internal energy, on the average, will contribute to this signal. Then, it is reasonable to observe that the average total rate constant determined from C₆H₅O⁺ channel is smaller than those from NO⁺ and $C_6H_5^+$. To summarize, the average



Figure 2. PD-MIKE profiles for (a) NO⁺, (b) $C_6H_5^+$, and (c) $C_6H_5O^+$ at 607.5 nm excitation. Experimental conditions are the same as in Figure 1. Experimental and calculated results are shown as filled circles and solid curves, respectively.

 TABLE 2: Dissociation Rate Constants Derived from

 PD-MIKE Peaks

photodissociation		rate const	ant (10^8 s^{-1})	
wavelength (nm)	$C_6H_5O^{+a}$	$C_6H_5^{+a}$	NO^{+a}	$C_{5}H_{5}^{+b}$
607.5	5.7 ± 2.9	8.6 ± 0.4	7.9 ± 1.5	0.52 ± 0.21
514.5		с		2.6 ± 1.0
488.0		С		3.5 ± 1.1

^{*a*} Total dissociation rate constant (k_T). ^{*b*} Second step rate constant (k_{65}) of the consecutive reaction $123^{*+} \rightarrow 93^+ \rightarrow 65^+$. ^{*c*} Higher than 10^9 s^{-1} .

total rate constants determined from the three channels show that all these channels are in direct competition, on a nanosecond time scale.

The total dissociation rate constant, $k_{\rm T}$, is the sum of the individual rate constants for competitive channels. The individual rate constants for the above channels, k_{30} , k_{77} , and k_{93} can be evaluated from $k_{\rm T}$ and branching ratios. Here, $k_{\rm T}$ has been estimated by averaging the total rate constants determined from NO^+ and $C_6H_5^+$ channels. In estimating the relative abundances and hence the branching ratios, the intensity of $C_5H_5^+$ has been added to that of $C_6H_5O^+$ because the former ion originates from the latter (consecutive production of C5H5⁺ via $C_6H_5O^+$ is evident, as will be shown below). The resultant values for k_{93} , k_{77} , and k_{30} are $(2.4 \pm 0.6) \times 10^8$, $(5.7 \pm 1.1) \times$ 10^8 , and $(1.7 \pm 0.3) \times 10^7 \text{ s}^{-1}$, respectively, for the experiment with 607.5 nm excitation. For the experiments with 514.5 and 488.0 nm excitations, the fact that the $C_6H_5^+$ peak is symmetric means that $k_{\rm T}$ is larger than the maximum ($\sim 1 \times 10^9 \text{ s}^{-1}$) that can be determined with the present method.

The PD-MIKE peak shape for $C_5H_5^+$ is different from the others, as shown in Figure 1 and also in Figure 3. The methods to identify a consecutive channel and analyze the PD-MIKE peak to evaluate the rate constant have been described in detail in our previous study on *n*-heptane molecular ion.²⁹ Following the same method, it can be readily shown that peak A in Figure 3 is due to $C_5H_5^+$ generated by the consecutive reaction $123^{\bullet+} \rightarrow 93^+ \rightarrow 65^+$ occurring in the field region of the electrode



Figure 3. PD-MIKE spectra for production of $C_5H_5^+$ ion from nitrobenzene ion obtained with 1.85 kV applied on the electrode assembly. (a) 607.5, (b) 514.5, and (c) 488.0 nm excitations. Experimental and calculated results are shown as filled circles and solid curves, respectively. The arrow denotes the translational energy of $C_5H_5^+$ if it were produced directly from the molecular ion outside the field region of the electrode assembly.

assembly and peak B is that occurring outside the field region. If $C_5H_5^+$ were produced directly from the molecular ion, the peak corresponding to dissociation outside the field region would appear at 4233 eV, as marked with an arrow in Figure 3. Figure 3 shows that the relative abundance of peak A to peak B increases with decreasing wavelength or increasing photon energy. This means that the second step of the consecutive reaction occurs faster as the internal energy increases, as will be shown later.

Full analysis of a PD-MIKE peak shape arising from a consecutive reaction is rather complicated because two rate constants and their distributions are involved. The rate constant for the first step, which is $k_{\rm T}$, is not available for photodissociation at 514.5 and 488.0 nm. Even for photodissociation at 607.5 nm, it is likely that the effective rate constant for the first step is larger than $k_{\rm T}$ determined from NO⁺ and C₆H₅⁺ channels for the reason explained above. Fortunately, however, the consecutive reaction can be treated easily by considering the second step only since the second step rate constant is much smaller than $k_{\rm T}$. Then, a simple first-order kinetics applies and the rate constant or its distribution can be determined just as for a direct reaction.^{25b} The PD-MIKE profiles recalculated from the rate constant distributions thus obtained are shown as solid curves in Figure 3. A successful analysis as is evident in Figure 3 further supports that all the $C_5H_5^+$ ions are produced consecutively via $C_6H_5O^+$. The average values of the second step rate constant, k_{65} , at three photon wavelengths are listed in Table 2.

C. Kinetic Energy Release Distributions. In our previous investigations on the photodissociation dynamics of molecular ion beam, a kinetic energy release distribution (KERD) was evaluated from a PD-MIKE profile recorded without applied voltage on the electrode assembly.^{28,30,32–33} This is to avoid the peak tailing arising from kinetic reasons. The same method has been used here to obtain KERD in the production of $C_6H_5^+$. KERD thus obtained at 607.5 nm excitation is shown in Figure 4b. The average kinetic energy release evaluated from the



Figure 4. Kinetic energy release distributions in the photodissociation of nitrobenzene ion to (a) NO⁺, (b) $C_6H_5^+$, and (c) $C_6H_5O^+$ with 607.5 nm excitation. Experimental results are shown as circles. Theoretical (PST) results are shown as solid curves. Bars represent error limits.

distribution increases with the photon energy. These are 0.089, 0.133, and 0.134 eV, respectively, in the photodissociation at 607.5, 514.5, and 488.0 nm. KERD in the production of $C_6H_5O^+$ at 607.5 nm has been determined similarly. The result is shown in Figure 4c. The average kinetic energy release evaluated from the distribution is 0.66 eV. In the case of NO⁺, which appears as a very weak signal in the spectrum, determination of the KERD from the PD-MIKE profile recorded without the field was rather difficult due to the presence of metastable noise. In the PD-MIKE spectrum recorded with the field, the peak does not suffer from the above noise, as shown in Figure 3. Since the peak tailing is not severe, the higher energy half of the peak has been used to determine KERD. The result is shown in Figure 4a. The average kinetic energy release evaluated from the distribution is 0.29 eV.

IV. Discussion

The internal energy of the molecular ion generated by charge exchange ionization and then photoexcited can be estimated by the following relation.

$$E = RE - IE + E_{th} + h\nu \tag{1}$$

Here, RE is the recombination energy of CS₂ and IE is the ionization energy for nitrobenzene. Their best literature values³⁴ are 10.07 and 9.86 eV, respectively. Hence, charge exchange alone results in the production of nitrobenzene molecular ion with 0.21 eV internal energy. $E_{\rm th}$ is the thermal internal energy of nitrobenzene ion at 140 °C, which can be estimated from the molecular parameters. The average vibrational internal energy was 0.23 eV at 140 °C. Thus, the average total internal energies for the photoexcited molecular ions are 2.48, 2.85, and 2.98 eV with 607.5, 514.5, and 488.0 nm excitations, respectively.

TABLE 3: Thermochemical Data

species	(structure)	$\Delta H_{\rm f}{}^{\circ}{}_{0{ m K}}{}^a$ (kJ/mol)
$C_6H_5NO_2^{\bullet+}$		1045^{b}
$C_6H_5ONO^{+}$	(phenylnitrite ion)	900 ^c
$C_6H_5O^+$	(phenoxy ion)	888^{b}
$C_6H_5^+$	(phenyl ion)	1143.8^{b}
$C_5H_5^+$	(cyclopentadien-1,3-yl-5 ion)	1064^{d}
NO^+		987.7^{d}
$C_6H_5O^{\bullet}$	(phenoxy)	66^d
NO_2 •		36.0^{b}
NO•		90.78^{b}
CO		-113.80^{b}

^{*a*} Heat of formation at 0 K. ^{*b*} Reference 34. ^{*c*} AM1 calculation in ref 1. ^{*d*} Values converted from 298 K data in ref 34.

The results from the photodissociation experiment described in the previous section show that the following dissociation pathways are acceptable.

$$k_{77} \rightarrow C_6 H_5^+ (m/z \ 77) + NO_2^{\bullet}$$
 (2a)

$$C_6H_5NO_2^{\bullet+}$$
 $(m/z \ 30) + C_6H_5O^{\bullet}$ (2b)

$$\stackrel{(93)}{\longrightarrow} C_6 H_5 O^+ (m/z \ 93) + NO^{\bullet}$$
(2c)

$$k_{65} \rightarrow C_6 H_5^+ (m/z \ 65) + CO$$
 (2d)

Dissociation dynamics for the individual channels is discussed below.

A. Production of C_6H_5^+. To gain insight on the dynamics of this channel, the experimental rate constant and KERD have been compared with predictions from the statistical theories. KERD for this reaction has been calculated by phase space theory formalism.²⁷

$$n(T;J,E) \propto \int_{\mathbb{R}^{\neq}}^{E-E_0-T} \rho'(E-E_0-T-R)P'(T,J,R) \, \mathrm{d}R \quad (3)$$

Here, n(T;J,E) is the distribution, namely, KERD, of the kinetic energy release (T) at a given angular momentum J and internal energy E. The root-mean-square average J value evaluated at the ion source temperature has been used.^{27g} ρ' and P' are the product vibrational and angular momentum state densities, respectively. R is the product rotational energy, and R^{\neq} is its minimum. E_0 is the reaction critical energy. Assuming that the reverse barrier for this channel is negligible as suggested in the PEPICO study by Nishimura *et al.*,² E_0 has been taken as the endoergicity at 0 K of 1.37 eV estimated from the thermochemical data listed in Table 3. The molecular parameters used in the calculation of KERD are listed in Table 4. KERD calculated with eq 3 is shown in Figure 4b, which is in excellent agreement with the experimental result. This indicates that the production of $C_6H_5^+$ occurs statistically on the ground electronic state potential energy surface without significant reverse barrier. The statistical nature of the kinetic energy release in this channel was also reported by Nishimura et al.² and by Bunn et al.,³ who compared average kinetic energy release determined by PEPICO and PEPICO-PD, respectively, with the phase space theory calculation.

The rate constant for this reaction has been calculated by RRKM-QET formalism. 25

$$k(E) = \sigma \frac{W^{\neq}(E - E_0)}{h\rho(E)} \tag{4}$$

Here, ρ is the density of states of the reactant ion, W^{\neq} is the state sum at the transition state, and σ is the reaction path

 TABLE 4: Molecular Parameters Used in the Calculations of KERDs

	vibrational frequencies ^{<i>a</i>} (cm ⁻¹)
$C_6H_5^{+b}$	3080, 3060(2), 3050(2), 1600(2), 1490(2), 1330, 1310,
	1180, 1150, 1040(2), 1010, 1000, 990, 970(2), 850,
	700, 670, 610(2), 410(2)
$NO_2^{\bullet b}$	1620, 1320, 750
$C_6H_5O^{c,d}$	3070, 3060(2), 3050(2), 1720, 1600(2), 1490(2), 1330,
	1310, 1180(2), 1150, 1040(2), 1010, 990(2), 970(2)
	850(2), 670, 610(2), 560, 410(2)
$NO^{c,e}$	1900

	rotational constants (cm ⁻¹)	polarizability (10 ⁻²⁴ cm ³)
$C_6H_5NO_2^{+\bullet}$	0.057^{b}	
$C_6H_5O^+$	0.086^{f}	
$C_6H_5^+$	0.152^{b}	
NO^+	2.00^{e}	
C ₆ H ₅ O•	0.101^{f}	10.5^{g}
NO_2^{\bullet}	1.121^{b}	2.5^{b}
NO•	1.67^{e}	0.0171^{e}

^{*a*} Numbers in parentheses denote the degeneracies of vibrational modes. ^{*b*} Reference 2. ^{*c*} The same values are used for the ion and radical. ^{*d*} Reference 1. ^{*e*} Reference 35. ^{*f*} Estimated value. ^{*s*} Reference 36.



Figure 5. Rate-energy dependence for the dissociation of nitrobenzene ion to $C_6H_5^+$. The present photodissociation result is shown as a filled circle (\bullet). The experimental rate-energy data of Nishimura *et al.* (\Box) are also shown. The theoretical result (RRKM-QET) is shown as a solid curve. Rate parameters used in the calculation are $E_0 = 1.37 \text{ eV}$ and $\Delta S^{\ddagger} = 6.4$ eu. The bar represents error limit.

degeneracy. In a usual RRKM-QET fitting of rate-energy data for a particular channel, the critical energy and the activation entropy at 1000 K (ΔS^{\ddagger}) are treated as two parameters to be adjusted.³⁷ In the present case, E_0 of 1.37 eV has been adopted, as in the calculation of KERD, and ΔS^{\ddagger} has been adjusted to fit the present experimental data. Also, an attempt has been made such that the RRKM fitting for this channel and the fittings for other channels (to be described below) result in branching ratios at 514.5 and 488.0 nm excitations, which are in agreement with the experimental data. The best fit has been obtained when ΔS^{\dagger} is 6.4 eu, as shown in Figure 5. The vibrational frequencies used in the calculation are listed in Table 5. The large positive entropy of activation means that the reaction occurs statistically via a loose transition state. This accords well with the above analysis of KERD. According to the rate-energy curve in Figure 5, the rate constant at the internal energy of 2.85 eV corresponding to the experiment with 514.5 nm excitation is $3 \times$ 10^9 s⁻¹, which is larger than the maximum rate constant (1 ×

TABLE 5: Vibrational Frequencies Used in the Calculations of Rate Constants (cm⁻¹) for the Production of $C_6H_5^+$, NO^+ , and $C_6H_5O^+$

$C_6H_5NO_2^{\bullet+b}$	3080(4), 3050, 1610, 1590, 1520, 1480, 1460,
	1350, 1320, 1310, 1180, 1170, 1160, 1120,
	1110, 1000(2), 970, 940, 850, 840, 790,
	700, 680, 670, 610, 530, 420, 400(2), 260,
	180, 140
$C_6H_5NO_2^{\bullet+}(TS1)^{c,d}$	3080(4), 3050, 1610, 1590, 1520, 1480, 1460,
	1350, 1320, 1310, 1180, 1170, 1160, 1120,
	1110, 1000(2), 970, 940, 840, 790, 600, 500,
	400, 380, 350, 300, 270, 180, 160, 150, 120
$C_6H_5NO_2^{\bullet+}(TS2)^{e,f}$	3080(4), 3050, 1610, 1590, 1520, 1480, 1460,
	1350, 1320, 1310, 1180, 1170, 1160, 1120,
	1110, 1000(2), 970, 940, 850, 840, 790, 700,
	680, 670, 610, 530, 420, 400(3), 320
$C_6H_5NO_2^{\bullet+}(TS3)^{f,g}$	3080(4), 3050, 1610, 1590, 1520, 1480, 1460,
	1350, 1320, 1310, 1180, 1170, 1160, 1120,
	1110, 1000(2), 970, 940, 850, 840, 790, 700,
	600, 470, 420, 350, 330, 310, 300, 240, 180

^{*a*} Numbers in parentheses denote the degeneracies of vibrational modes. ^{*b*} Reference 1. ^{*c*} Transition state for the production of C₆H₅⁺. ^{*d*} The C–N stretching mode at 850 cm⁻¹ was taken as the reaction coordinate. ^{*e*} Transition state for the production of NO⁺. ^{*f*} The NO₂ torsional mode at 140 cm⁻¹ was taken as the reaction coordinate for production of NO⁺ and C₆H₅O⁺. ^{*g*} Transition state for the production of C₆H₅O⁺ ion.

 10^9 s^{-1}) that can be measured with the present method. This explains why the experimental PD-MIKE peak for $C_6H_5^+$ appears symmetric at 514.5 and 488.0 nm.

Nishimura et al. measured the rate constant for this channel on a microsecond time scale using PEPICO.² RRKM-QET fitting of their experimental data required a tight transition state with E_0 less than the endoergicity. On the other hand, the experimental kinetic energy release could be well explained by phase space theory, indicating involvement of a loose transition state. The transition state switching model^{27f} was invoked to explain the results. In their study, however, the thermal internal energy of the nitrobenzene ion (~0.1 eV) was not considered and the thermochemical data at 298 K instead of those at 0 K were used in the calculation of the endoergicity. In addition, improved thermochemical data have appeared since their study. Hence, the rate-energy data of Nishimura et al. have been corrected here, and the results are shown in Figure 5. The corrected results are in excellent agreement with the present **RRKM-QET** calculation.

In the other PEPICO study by Panczel and Baer,¹ the rate constant for this channel was found to be larger than could be determined by the technique. The fact that the productions of $C_6H_5O^+$ and NO^+ occurred on a much longer (microsecond) time scale than this channel was attributed to the lack of competition between these two groups of channels. In particular, the production of $C_6H_5^+$ from an excited electronic state was suggested. This is in sharp contrast with the present result on a nanosecond time scale that all three channels compete and that the production of $C_6H_5^+$ occurs statistically from the ground electronic state of the molecular ion.

B. Production of NO⁺. The rate constants for reaction 2b were determined on a microsecond time scale in the previous two PEPICO studies.^{1,2} In the study of Panczel and Baer,¹ a faster channel in addition to the regular statistical one was reported even though its origin was not clear. Hence, its time-of-flight was analyzed using two-component rate constants. The fast component was not observed in the PEPICO study of Nishmura *et al.*² carried out under a similar condition. In the present study, a one-component rate constant with distribution has been found to be adequate for data analysis. The RRKM-QET calculation has been carried out to fit the present and the



Figure 6. Rate-energy dependence for the dissociation of nitrobenzene ion to NO⁺. The present photodissociation result is shown as a filled circle (\bullet). The experimental rate-energy data of Nishimura *et al.* (\Box) and those of Panczel and Baer (\bigcirc) are also shown. The theoretical result (RRKM-QET) is shown as a solid curve. Rate parameters used in the calculation are $E_0 = 1.21$ eV and $\Delta S^{\ddagger} = -7.1$ eu. The bar represents error limit.

two PEPICO rate data. The slow component rate constants of Panczel and Baer have been used, and the data of Nishimura *et al.* have been corrected for the thermal energy, as mentioned above. The best fit was obtained using the parameters $E_0 =$ 1.21 eV and $\Delta S^{\ddagger} = -7.1$ eu, as shown in Figure 6. The vibrational frequencies used in the calculation are listed in Table 5. E_0 adopted here is similar to the one (1.27 eV) used in the RRKM-QET analysis by Panczel and Baer, but higher than that (1.02 eV) by Nishimura *et al.* The latter discrepancy is thought to be due to the fact that thermal energy was ignored in the estimation of internal energy. The large negative activation entropy means that this channel occurs via a tight transition state in accordance with the previous RRKM-QET analyses.^{1,2}

Assuming the phenoxy structure of the neutral fragment $C_6H_5O^{\bullet}$, the reaction endoergicity of ~0.09 eV is estimated from the thermochemical data in Table 3. The fact that this is well below the critical energy of 1.21 eV obtained above means that a substantial reverse barrier is present. Then, the kinetic energy release in this reaction will be larger than statistically expected. In this regard, KERD has been calculated with phase space theory to compare with the experimental one shown in Figure 4a. The molecular parameters used in the calculation are listed in Table 4. The calculated KERD which is also shown in Figure 4a is significantly narrower than the experimental one. Namely, the analysis of KERD suggests that the reaction occurs via a tight transition state with a substantial reverse barrier, in agreement with the result from the above rate constant analysis. Nishmura *et al.* suggested that the production of NO⁺ occurs via two different channels;² it occurs consecutively via phenylnitrite ion intermediate near the threshold energy with a small average kinetic energy release, and it occurs directly at higher internal energy with a large average kinetic energy release. Since the average internal energy of photoexcited nitrobenzene ions is well above the threshold, the latter of the two mechanisms would apply in the present case, in agreement with the observation of large kinetic energy release. The present result does not allow us, however, to tell whether switching of the pathway would occur near the threshold.

C. Production of $C_6H_5O^+$. RRKM-QET calculation has been carried out to fit the present and PEPICO^{1,2} rate data for



Figure 7. Rate-energy dependence for the dissociation of nitrobenzene ion to $C_6H_5O^+$. The present photodissociation result is shown as a filled circle (\bullet). The experimental rate-energy data of Nishimura *et al.* (\Box) and those of Panczel and Baer (\bigcirc) are also shown. The theoretical result (RRKM-QET) is shown as a solid curve. Rate parameters used in the calculation are $E_0 = 1.20$ eV and $\Delta S^{\ddagger} = -1.1$ eu. The bar represents error limit.

reaction 2c. The best fit has been obtained using E_0 of 1.20 eV and ΔS^{\ddagger} of -1.1 eu as shown in Figure 7. The vibrational frequencies used in the calculation are listed in Table 5. This E_0 value is the same as that reported by Panczel and Baer.¹ The negative activation entropy indicates that the reaction occurs via a tight transition state. In Figure 4c, the experimental KERD is compared to the theoretical one calculated by phase space theory using the parameters listed in Table 4. Phenoxy structure of $C_6H_5O^+$ was assumed in the calculation. The experimental KERD deviates significantly from the statistical prediction. One of the reasons for such a deviation is due to the fact that $C_6H_5O^+$ further dissociates to C₅H₅⁺. Namely, C₆H₅O⁺ ions generated with a smaller kinetic energy release would possess a larger amount of internal energy than those with a larger kinetic energy release. Thus, the former ions will dissociate more readily, which results in smaller probability at the smaller kinetic energy release in the experimental data. Even though such an effect cannot be ignored, the substantial probability for large kinetic energy release in the experimental data indicates that a considerable reverse barrier is present in this reaction. This is in accordance with the result of the above rate constant analysis.

D. Production of $C_5H_5^+$. The present work has confirmed in real time that $C_5H_5^+$ is produced by the consecutive reaction via $C_6H_5O^+$ (reactions 2c and 2d). As shown by the data in Table 2, the rate constant for the second channel (reaction 2d) increases with the photon energy, indicating that the internal energy of the intermediate, $C_6H_5O^+$, also increases. Detailed analysis of the dynamics of the second step is not easy, however, because the structure of $C_6H_5O^+$ and its internal energy content are uncertain. It is assumed here that $C_6H_5O^+$ has the phenoxy structure, whose thermochemical data are available.³⁴ Its average internal energy has been estimated in two opposite extreme situations. In the first method, the total energy available for the products in reaction 2c, namely, the sum of the excess energy at the transition state and the reverse barrier, has been assumed to be partitioned statistically. Such an assumption is in contradiction with the experimental observation that the average kinetic energy release is much larger than statistical prediction. Hence, the internal energy of $C_6H_5O^+$ estimated in this way will be an upper limit to the true value. The total



Internal Energy, eV

Figure 8. Rate-energy dependence for production of $C_5H_5^+$ from $C_6H_5O^+$ The internal energy is that of $C_6H_5O^+$. The same experimental rate data are plotted with two different internal energy scales (see text for details). The rate-energy data using the upper-limit internal energy scale are shown as solid circles (\bullet) together with the corresponding RRKM-QET fit (-). E_0 of 1.76 eV and ΔS^+ of 1.8 eu have been used in the calculation. The rate-energy data using the lower limit internal energy scale are shown as open circles (\bigcirc) together with the corresponding RRKM-QET fit(--). E_0 of 1.45 eV and ΔS^+ of -1.1 eu have been used in the calculation. Bars represent error limits.

available energy has been estimated from the thermochemical data of the related species in Table 3. Then, its statistical partitioning has been calculated using the relation proposed by Klots.³⁸

$$E^* = kT^* + \left(\frac{r-1}{2}\right)kT^* + \sum_{i=1}^n h\nu_i [\exp(h\nu_i/kT^*) - 1]^{-1}$$
 (5)

Here, E^* is the total energy available for partitioning, *r* is the number of rotational degrees of freedom of the products, the v_i 's are the product vibrational frequencies, and kT^* is the total average translational energy in the dissociation. The average internal energies of C₆H₅O⁺ thus estimated are 2.76, 3.09, and 3.21 eV, respectively, at 607.5, 514.5, and 488.0 nm excitations. The RRKM-QET calculation has been carried out to fit the rateenergy data thus obtained for reaction 2d varying both the critical energy and the activation entropy at 1000 K. A good fit has been obtained with the critical energy of 1.76 eV and the activation entropy of 1.8 eu. The result is shown in Figure 8.

In the second method, it has been assumed that KERD of $C_6H_5O^+$ which dissociates further to $C_5H_5^+$ is the same as that of $C_6H_5O^+$ which remains undissociated, namely, Figure 4c. At a particular value of the kinetic energy release, the difference between the total available energy and the kinetic energy release becomes the energy available for partitioning in the vibrational and rotational degrees of freedom of $C_6H_5O^+$ and NO. This energy has been partitioned statistically over the pertinent degrees of freedom using the Klots formula. The internal energy of C₆H₅O⁺ thus estimated has been averaged over the experimental KERD in Figure 4c. These are 2.28, 2.62, and 2.74 eV, respectively, at 607.5, 514.5, and 488 nm excitations. Since it is very likely that $C_6H_5O^+$ generated with less kinetic energy release will dissociate more easily, the internal energy estimated in this way will be only a lower limit to the true value. The rate-energy data for the second step have been plotted in Figure 8 with this internal energy scale. A good RRKM-QET fit is

also shown which has been achieved with the critical energy of 1.45 eV and the activation entropy of -1.1 eu.

The RRKM-QET analyses of the rate-energy data for reaction 2d estimated with two different internal energy scales require critical energies which are noticeably different. The critical energy of 1.91 eV estimated from the data reported by Nishimura *et al.*² agrees better with the one obtained with the former method of internal energy estimation. However, we are not in a position to support this method at all because the estimation of the critical energy for the second step of a consecutive reaction from an appearance energy measurement can be erroneous. Reliable critical energy information will be very helpful in this regard. Fortunately, the activation entropies obtained from the two analyses are not significantly different, both having values near zero. Hence, one can tell that reaction 2d occurs via a slightly tight transition state, as is expected from the reorganization of the reactant structure needed in the reaction.

E. Overall Dissociation Mechanism. From the data presented so far, it is clear that the direct bond cleavage to $C_6H_5^+$ competes with the rearrangement processes to NO⁺ and $C_6H_5O^+$ on a nanosecond time scale. Such an overall picture is in general agreement with the PEPICO study by Nishimura *et al.* carried out on a microsecond time scale. Namely, even though the rearrangement channels to $C_6H_5O^+$ and NO⁺ dominate near the threshold energy, the rate constant for the direct bond cleavage to $C_6H_5^+$ increases more rapidly with the internal energy and becomes dominant in the photodissociation at 514.5 and 488.0 nm. Such a changeover is well-known in the dissociations of molecular ions where direct bond cleavage and rearrangement compete.

Even though the conclusion drawn from the present nanosecond result does not agree with the microsecond result reported by Panczel and Baer, it is worthwhile to examine whether the ion-dipole intermediate (IDI) mechanism proposed by Osterheld *et al.*⁸ is still applicable to the present result. As was mentioned in the introductory section, the IDI mechanism shown below was devised to explain the result of Panczel and Baer that the production of $C_6H_5^+$ did not compete with the other rearrangement channels.



Here, the ion-dipole intermediate (IDI) may either dissociate to $C_6H_5^+$ and NO_2^{\bullet} or isomerize to the phenylnitrite structure. If $k_2 \gg k_3$, k_4 , NO^+ and $C_6H_5O^+$ will be observed with a smaller apparent total rate constant ($k_3 + k_4$) than that ($k_1 + k_2$) for $C_6H_5^+$. Then, it would look as if the direct and rearrangement channels do not compete, as was pointed out by Osterheld *et al.*

In the present result obtained on a nanosecond time scale, however, all three channels have been found to compete. Within the IDI mechanism, such a situation can arise only when the total rate constant for IDI, $k_T = k_1 + k_2$, is much smaller than that $(k_3 + k_4)$ for the dissociation of the phenylnitrite ion. Namely, appearance kinetics of all three ions will be governed by k_T in this case. Predominance of the C₆H₅⁺ channel would require $k_1 \gg k_2$. The above consideration means that k_3 and/or k_4 should increase rapidly with the internal energy for the IDI mechanism to be applicable from a microsecond to nanosecond time scale. To check such a possibility, we have calculated the rate constant k_4 on the basis of the PEPICO rate-energy data of Panczel and Baer. The heat of formation of phenylnitrite ion has been estimated as ~900 kJ mol⁻¹ from an AM1 calculation by Osterheld et al.8 Our own semiempirical calculations resulted in similar values. The best RRKM-QET calculation for k_4 to fit the PEPICO data has been obtained using E_0 of 2.35 eV and ΔS^{\ddagger} of 12 eu. Then, k_4 at the internal energy corresponding to photoexcitation at 607.5 nm has been evaluated with the RRKM-QET calculation using the same parameters. Finally, the branching ratio information in Table 2 has been utilized, which has resulted in $k_3 + k_4$ of $2.0 \times 10^8 \text{ s}^{-1}$. This is much smaller than $k_{\rm T}$ of $8.3 \times 10^8 \, {\rm s}^{-1}$ observed in the present work, invalidating the applicability of the IDI mechanism on a nanosecond time scale.

V. Conclusions

Photodissociation of nitrobenzene molecular ions with a visible photon occurs via several reaction channels. The first generation dissociation channels producing $C_6H_5O^+$, $C_6H_5^+$, and NO⁺ have been found to occur competitively. Among the $C_6H_5O^+$ ions produced, those with high internal energy dissociate further to $C_5H_5^+$, which has been observed in real time in this work. The photodissociation rate constant has been determined at the molecular ion internal energy of 2.48 eV on a nanosecond time scale together with KERDs in each channel. It has been found that the production of $C_6H_5^+$ on this time scale occurs statistically on the ground electronic state potential energy surface in accordance with RRKM-QET. The rearrangement channels producing $C_6H_5O^+$ and NO^+ also occur statistically. Namely, the results on a nanosecond time scale are quite typical for cases when direct cleavages and rearrangements compete in the dissociation of a molecular ion. In particular, no evidence has been found on a nanosecond time scale to support the ion-dipole intermediate mechanism proposed by Osterheld et al.⁸ The possibility of this mechanism on a microsecond time scale cannot be completely ruled out, however, because some of the nitrobenzene ion dissociation pathways which can be ignored at high internal energies may become important at low internal energies. Further investigation, both experimental and theoretical, seems to be needed in this regard. Analysis of the rate-energy data for the second step of the consecutive reaction to $C_5H_5^+$ indicates that the reaction occurs statistically also, even though lack of reliable knowledge on the structure and internal energy content of the intermediate makes such a conclusion provisional.

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