by using the large-curvature approximation of Garrett et al.<sup>51</sup> In this formalism, the tunneling path for heavy-light-heavy mass combinations is a direct straight-line path across the potential energy surface from one end atom to the other. Bondi et al.<sup>50</sup> have shown that improved canonical variational transition-state theory with large-curvature ground-state transmission coefficients (ICVT/LCG) provide rate constants that are accurate to within a factor of 1.7 for the Cl + HCl, Cl + DCl, and Cl + MuCl (Mu = muonium) reactions. Their results indicated that the rate coefficients and KIEs for heavy-light-heavy reactions should be interpreted in terms of tunneling with large end-atom separation instead of in the region of the saddle point.

After an examination of the experimental and theoretical results, it appears that the mechanism of the  $F + H_2O$  reaction is more complicated than a simple abstraction and requires a careful analysis on both the macroscopic and the microscopic levels. The results of the ab initio and simple TST plus tunneling calculations presented here indicate that tunneling may play an important role in the mechanism of this reaction. However, the experimental results for this simple hydrogen-transfer reaction cannot be interpreted directly by using simple models. Clearly a more detailed analysis of the potential energy surface and more accurate transition-state theory rate constants, including transmission coefficients, are needed to confirm the conclusions that have been drawn from these simple models.

#### Summary

The enhanced experimental kinetic isotope effect and abnormally low activation energies for the reactions  $F + H_2O/D_2O$  indicate that quantum mechanical tunneling may be important in these abstraction mechanisms. Both ab initio methods and a semiempirical BEBO potential are unable to accurately reproduce the experimental parameters using standard transition-state theory and a one-dimensional tunneling model. The best ab initio calculation overestimated the size of the classical barrier and as a result overestimated the KIE and  $E_a$  for the reaction when tunneling was included. The BEBO model quantitatively reproduced the thermal activation energy but underestimated the experimental KIE, suggesting that the method underestimated the size of the classical barrier and the magnitude of tunneling.

The best fit of the experimental  $E_a$  and KIE suggests that the true classical barrier height for reaction is on the order of 4 kcal/mol and that the abnormally low activation energy and enhanced KIE are consequences of tunneling through this barrier. This mechanism is not unreasonable based on the correlation of activation energy with exothermicity for hydrogen abstraction reactions and the nature of reactive tunneling in heavy-light-heavy mass systems.

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# Kinetics for Reactions of the Nitrate Radical (NO<sub>3</sub>) with Aldehydes in Acetonitrile

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The rate constants for the reactions of NO<sub>3</sub> with RCHO (R: H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, and C(CH<sub>3</sub>)<sub>3</sub>) and XC<sub>6</sub>H<sub>4</sub>CHO (X: NO<sub>2</sub>, CN, Cl, H, CH<sub>3</sub>, and OCH<sub>3</sub>) have been measured by following the decay of the transient absorption band of  $NO_3^{\circ}$  generated by flash photolysis of  $K_2[Ce(NO_3)_6]$  in acetonitrile. Representative rate constants (in unit of  $M^{-1} s^{-1}$ ) at 20 °C in acetonitrile are  $2.3 \times 10^7$  for CH<sub>3</sub>CHO and  $2.4 \times 10^7$  for PhCHO. The hydrogen-atom abstraction reaction of NO3<sup>\*</sup> from the aldehydic C-H was confirmed by the similarity of the above two rate constants and by the higher reactivities than those of acetone and benzene. The rate constants for HCHO and CH<sub>3</sub>CHO in aqueous solution are smaller than the corresponding values in acetonitrile, because of the hydration. For aliphatic aldehydes, the methyl substitutions on the vicinal carbon to aldehydic carbon slightly increase the reactivity of aldehydic C-H with NO3. A large negative Hammett reaction constant ( $\rho = -1.3$ ) for any aldehydes indicates the high electrophilicity of NO<sub>3</sub><sup>•</sup>. The polar substituents strongly affect the orientation factors rather than the activation energies, which were obtained by the Arrhenius plots. The rate constants in acetonitrile, however, are ca. 30 times larger than the corresponding ones reported in the gas phase: a polar medium affects the distribution of an unpaired electron and the polar nature of the reaction.

#### Introduction

The nitrate radical  $(NO_3^{\bullet})$  has been recognized as a common constituent of the trophosphere during nighttime hours.<sup>1-4</sup> From many kinetic studies, the importance of the reactions of NO3° with aldehydes in the gas phase was revealed.<sup>5-10</sup> The kinetic data

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and product analysis data indicate that the hydrogen-atom abstraction from aldehydic C-H (reaction 1) occurs first, followed

•0 - 
$$N^{*}$$
 - 0 + RCHO + HNO<sub>3</sub> + RC = 0 (1)

by CO formation in the case of NO<sub>3</sub> -HCHO-O<sub>2</sub> reaction system<sup>8,9</sup> or by peroxyacetyl nitrate formation in the case of  $NO_3\ensuremath{^\circ-CH_3CHO-O_2}$  in the presence of  $N_2O_5$   $^{5,7,10}$ 

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Figure 1. (a) Absorption spectrum of  $K_2[Ce(NO_3)_6]$  in acetonitrile; (b) transient absorption spectrum 20  $\mu$ s after the flash photolysis of  $10^{-3}$  M of  $K_2[Ce(NO_3)_6]$ . First-order plots of absorbances of NO<sub>3</sub><sup>•</sup> at 635 nm; (a) in acidic aqueous solution and (b) in acetonitrile at 20 °C.

Since NO<sub>3</sub><sup>•</sup> is presumed to be a polar and electrophilic radical from the canonical structure I, it is interesting to investigate the reactivities of NO3<sup>•</sup> in solution and to compare them with those in gas phase. Especially, it is expected that the reaction medium affects the distribution of the unpaired electron of NO<sub>3</sub><sup>•</sup> and the polar nature of the reaction. Martin et al. found that NO3 was produced by the flash photolysis of  $(NH_4)_2[Ce(NO_3)_6]$  in acidic aqueous solution;<sup>11,12</sup> some rate constants for the reaction of NO<sub>3</sub>. with alcohols were reported by Dogliotti and Hayon.<sup>13</sup> To investigate the effect of the substituent effect on the rate constants of aryl aldehydes, it is essential to find an appropriate nonaqueous solvent to follow the decay kinetics of NO<sub>3</sub><sup>•</sup>. Recently, the flash photolysis method was applied to the generation of NO3<sup>•</sup> in acetonitrile.14,15 in which both the radical source and most aldehydes are soluble. Thus, it became possible to investigate the medium effect by comparing the reactivities in aqueous and nonaqueous solutions and in the gas phase. Furthermore, the substituent effect was examined on the basis of the Arrhenius parameters, which can be obtained by the flash photolysis method.

### **Experimental Section**

 $K_2[Ce^{IV}(NO_3)_6]$  was used as a radical source of  $NO_3^{\bullet}$  in acetonitrile; the potassium salt was prepared from the commercially available ammonium salt by adding KOH. Commercially available aqueous formaldehyde (37 wt %) and acetaldehyde (85 wt %) were used as received; other aliphatic aldehydes and liquid aryl aldehydes were purified by distillation. Solid aryl aldehydes were purified by recrystallization before use. Acetonitrile was purified by refluxing over  $P_2O_5$  followed by distillation under  $N_2$  before use. Distilled water was also used as a solvent.

The flash photolysis apparatus was a standard design having two xenon flash lamps (Xenon Corp. N-851C) with input energy of 100 J and half-duration of 8  $\mu$ s.<sup>16</sup> The reaction temperature was controlled by immersing the flash cell (10-cm optical path) in a bath filled with cooled methanol. For each flash exposure, a fresh solution containing a known amount of aldehydes was used. For aldehydes used in this study, no decrease of the absorbances of the reactants was observed by mixing for a few hours, indicating that no spontaneous reaction occurs at 20 °C, which was the highest measurement temperature of our experiments.

### **Results and Discussion**

Figure 1 shows the absorption spectra of the radical source  $K_2[Ce(NO_3)_6]$  in acetonitrile and the transient species produced



Figure 2. First-order plots for decay of  $NO_3^{\bullet}$  (at 635 nm) in the presence of CH<sub>3</sub>CHO in acetonitrile at 20 °C: (a) 0, (b) 0.9, (c) 4.8, (d) 9.5, and (e) 14.0 mM.



Figure 3. Pseudo-first-order plots for some aldehydes in acetonitrile at 20 °C: (a)  $(CH_3)_3CCHO$ , (b)  $CH_3CHO$ , and (c) m- $ClC_6H_4CHO$ .

by the flash photolysis with light between 310 and 430 nm (To-shiba C-40C). Photodissociation reaction 2 can be confirmed even

$$K_2[Ce(NO_3)_6] \xrightarrow{h_{\nu}} K_2[Ce(NO_3)_5] + NO_3^{\bullet}$$
(2)

in acetonitrile, since these absorption bands with vibronic structure were similar to those of observed in aqueous solution.  $^{13,17}\,$ 

The absorption bands in the gas phase were sharper than those in solution, but the positions were similar.<sup>18,19</sup> The strongest peak in solution is 635 nm in the visible region, but in the gas phase the peak at 665 nm is strongest; this suggests some differences in the electron distributions in the two media.

In the insert in Figure 1, the first-order plots of the decay of  $NO_3^{\bullet}$  in acetonitrile and in aqueous solution are shown; in acetonitrile without additive, the decay of  $NO_3^{\bullet}$  obeys first-order kinetics, whereas in aqueous solution, the decay obeys second-order kinetics. Slow reaction between  $NO_3^{\bullet}$  and acetonitrile may occur. Both decay rates are slow, indicating that these solvents are appropriate to kinetic study by using flash photolysis with an 8- $\mu$ s flash lamp.

For the reaction systems that contain aldehydes, the first-order plots for the decay of NO<sub>3</sub><sup>•</sup> in acetonitrile are shown in Figure 2. The linear decay curves were obtained; the slopes yield the first-order rate constants ( $k_{\rm first-order}$ ). From the reported extinction coefficient of NO<sub>3</sub><sup>•</sup> in the gas phase,<sup>19</sup> the initial concentration of NO<sub>3</sub><sup>•</sup> generated by each flash exposure was calculated to be ca.  $3 \times 10^{-6}$  M; thus, addition of aldehydes more than  $5 \times 10^{-5}$ M is enough to yield the pseudo-first-order kinetics. In Figure 2, addition of acetaldehyde more than ca. 1 mM accelerated the decay rates with increasing concentrations of additives. Fairly

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TABLE I: Rate Constants for Reactions of NO<sub>3</sub><sup>•</sup> with Aldehydes and Related Compounds in Various Media (Bond-Dissociation Energy (BDE)<sup>a</sup> and Ionization Energy (IE)<sup>b</sup>)

		$10^{-6}k$ , M <sup>-1</sup> s <sup>-1</sup>			
compd	in acetonitrile <sup>c</sup>	in water <sup>c</sup>	gas phase <sup>d</sup>	BDE, kJ/mol	IE, eV
нсно	8.4	0.49 (2 N HNO <sub>3</sub> ) 1.1 (6 N HNO <sub>3</sub> )	0.19 <sup>e</sup> 0.36 <sup>f</sup>	364	
CH3CHO	23	4.9 (2 N HNO₃) 6.2 (6 N HNO₃)	0.80 <sup>e</sup> 0.78 <sup>g</sup>	360 (-C(O)-H)	
			1	397 (-CH <sub>2</sub> -H)	~ <b>*</b> •
PhCHO (CH <sub>3</sub> ) <sub>2</sub> CO	24 0.24	<0.003 (6 N HNO <sub>3</sub> )	0.66 <sup>n</sup>	364 411 (-CH <sub>2</sub> -H)	9.52
PhH PhCN	1.0 <0.12		<0.01 <sup>e</sup>	461	9.24 9.71
PhOCH <sub>3</sub>	2300	3200 <sup><i>i</i></sup>	0.03 <sup>h</sup>	389	8.21

<sup>a</sup>Reference 20. <sup>b</sup>Reference 25. <sup>c</sup>The rate constants evaluated in this study contain an estimation error of  $\pm 5\%$ . <sup>d</sup>The rate constants reported in the gas phase are converted from cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 25 °C. <sup>e</sup>Reference 7. <sup>f</sup>Reference 9. <sup>g</sup>Reference 10. <sup>h</sup>Reference 8. <sup>i</sup>Reference 15.

good linear lines in Figure 2 also indicate that contribution of secondary reactions between  $NO_3^{\bullet}$  and RCO from reaction 1 is small; if there is such a contribution, downward curvature will be observed. The presence of oxygen molecules in solution did not affect the decay rates.

Figure 3 shows the pseudo-first-order relations; good linear lines can be obtained between  $k_{\text{first-order}}$  and the concentrations of aldehydes. The intercept at [aldehyde] = 0 corresponds to the decay rate in acetonitrile without aldehydes. From the slopes, the second-order rate constants  $(k_{\text{H}})$  for reaction 1 were obtained.

The rate constants for some representative aldehydes and related compounds in acetonitrile at 20 °C are summarized in Table I, in which the rate constants in acidic aqueous solution and reported rate constants in the gas phase are also given. In acetonitrile, the rate constant for HCHO is slightly smaller than those for CH<sub>3</sub>CHO and PhCHO. The rate constants in aqueous solution are considerably smaller than the corresponding values in acetonitrile; this is attributed to the hydrated form. Most of the formaldehyde is present as  $H_2C(OH)_2$  in aqueous solution; even in acetonitrile, the hydrated form is predominant. In the case of acetaldehyde, although the hydrated form is ca. 50% in aqueous solution, in acetonitrile the aldehyde form is ca. 100% as found from the UV spectra. Since the rate constants in aliphatic alcohols are smaller than those of aldehydes, 13,17 the low reactivities in aqueous solution can be attributed to the hydrated form. Dependence of the rate constants in aqueous solution on acid concentration may be due to the acid effect on the equilibrium between both forms. Low reactivities in the gas phase compared with those in acetonitrile will be discussed in the later part of this paper.

From the similarity of the rate constants for CH<sub>3</sub>CHO and PhCHO in acetonitrile combined with the bond-dissociation energies (Table I),<sup>20</sup> it is confirmed that reaction 1 is a main path. Since the rate constant for acetone in acetonitrile is about  $1/_{100}$  of that for acetaldehyde, the attack of NO<sub>3</sub> to >C=O of aldehydes forming >C-O-O-NO<sub>2</sub> may not occur.

The rate constant for benzene (probably addition of  $NO_3^{\bullet}$  to the phenyl ring) is ca.  $1/_{20}$  of  $k_{\rm H}$  of benzaldehyde. This indicates that the addition of  $NO_3^{\bullet}$  to phenyl rings of PhCHO is a minor path. By the introduction of electron-withdrawing substituent such as CN to benzene, a further decrease in the rate constant was observed, suggesting that the reaction path does not change from reaction 1 by introducing electron-withdrawing substituents to phenyl aldehyde. On the other hand, an electron-donating substituent on the benzene ring accelerated the rate constants for the reaction with  $NO_3^{\bullet}$  as found for anisole.<sup>15,17</sup> For anisaldehyde, change in reaction path may occur.

Figure 4 shows some examples for the Arrhenius plots; in the range of temperature from -35 to 20 °C, the rate constants increase about twice, which is larger than the experimental errors in this method. The rate constants and Arrhenius parameters are summarized in Table II for aliphatic aldehydes and in Table III for aryl aldehydes. By the variation of  $E_a$  of  $\pm 1$  kJ/mol, the A





Figure 4. Arrhenius plots for  $k_{\rm H}$  of some aldehydes in acetonitrile: (a) (CH<sub>3</sub>)<sub>3</sub>CCHO, (b) CH<sub>3</sub>CHO, and (c) *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO.

TABLE II: Rate Constants at 20  $^{\circ}$ C and Arrhenius Parameters for Reactions of NO<sub>3</sub><sup>•</sup> with Aldehydes in Acetonitrile

compd	$10^{-6} k_{\rm H}, M^{-1} {\rm s}^{-1}$	$\frac{\log A,^a}{M^{-1} s^{-1}}$	E₂ª kJ∕mol	BDE, <sup>b</sup> kJ/mol	IE, <sup>c</sup> eV
НСНО	8.4	7.93	5.6	363	10.88
CH <sub>3</sub> CHO <sup>d</sup>	23	8.15	4.5	360	10.20
CH <sub>3</sub> CH <sub>2</sub> CHO	38	8.32	4.2	366	9.98
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	61	8.57	4.4		9.74
(CH <sub>3</sub> ) <sub>3</sub> CCHO	68	8.58	4.2		9.50

<sup>*a*</sup>Estimation error in  $E_a$  is ±1 kJ/mol; that in log A is ±0.18. <sup>*b*</sup>Reference 20. <sup>*c*</sup>Reference 25. <sup>*d*</sup> $E_a$  for acetonitrile in the gas phase is 36.5 kJ/mol.<sup>8</sup>

TABLE III: Rate Constants at 20 °C and Arrhenius Parameters for  $X-C_6H_4$ -CHO in Acetonitrile

•••					
 x	$10^{-6}k_{\rm H},$ M <sup>-1</sup> s <sup>-1</sup>	log <i>A</i> , M <sup>-1</sup> s <sup>-1</sup>	$E_{a}$ , kJ/mol	IE, eV	
p-NO <sub>2</sub>	3.2	7.92	8.0	(10.4) <sup>a</sup>	
m-NO <sub>2</sub>	2.1	7.61	7.3	(10.4) <sup>a</sup>	
p-CN	4.0	7.92	7.4		
m-CN	7.9	8.04	6.5		
m-Cl	7.6	8.18	7.0	(9.90) <sup>a</sup>	
p-Cl	17	8.36	7.2	(9.60) <sup>a</sup>	
Н	24	8.56	5.5	9.52	
p-CH <sub>3</sub>	25			9.33	
p-CH <sub>3</sub> O	1200			8.60	

<sup>a</sup>Estimated from the figures in ref 26; others are from ref 25.

values vary by ca. 50%; thus, the log A values are shown in the tables. The activation energies of 4-8 kJ/mol are smaller than those for the hydrogen-atom abstraction by the carbon-centered radicals.<sup>21</sup> For the oxygen-centered radicals, however, similar

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Figure 5. Hammett plots for log  $k_{\rm H}$  (at 20 °C), log A, and  $E_{\rm a}$  for X-C<sub>6</sub>H<sub>4</sub>CHO in acetonitrile against  $\sigma$  of X.

activation energies were frequently reported;<sup>21</sup> i.e., the  $E_a$  values for t-BuO'-ArOH,<sup>22</sup> having rate constants similar to those for  $NO_3$  -aldehydes, are close to the  $E_a$  values for  $NO_3$  -aldehydes.

In aliphatic aldehydes, the rate constants at 20 °C increase with the methyl substituents; although there seems to be a tendency of the activation energies decreasing with the methyl substituents, the variations are small. The activation energy was generally governed by the bond-dissociation energy of the C-H bond of the hydrogen donor. For aldehydes, however, the variations of the bond-dissociation energies of the aldehydic C-H's are considerably smaller when changing the number of the methyl substituents on the vicinal carbon atom of CHO (Table II).20 For nucleophilic methyl radical, an opposite tendency was reported with the methyl substitutions.<sup>23,24</sup> This suggests that the methyl substitution affects the polar nature of aldehydic C-H, which was supported by the ionization potentials of aldehydes.<sup>25,26</sup> In Table II, it seems that the frequency factors mainly determine the rate constants at ambient temperature, suggesting some relationships between the orientation factors and the polar nature of the aldehydic C-H. To estimate this type of polar effect, further investigation by using the Hammett correlation for aryl aldehydes, in which the polar effect is quantitatively evaluated, was performed.

The Hammett plots for the rate constants and Arrhenius parameters for any aldehydes against  $\sigma$  are shown in Figure 5, in which the data for p-CH<sub>3</sub>O and p-CH<sub>3</sub> are excluded, since the reaction path may change. In the case of anisaldehyde with a low ionization energy (8.60 eV),<sup>25</sup> electron transfer from anisaldehyde to  $NO_3^{\bullet}$  may occur.<sup>15</sup> For tolualdehyde, hydrogen-atom abstraction from the CH<sub>3</sub> group by NO<sub>3</sub><sup>•</sup> is also possible.

For log  $k_{\rm H}$  of seven derivatives, a linear correlation was obtained yielding  $\rho(\log k_{\rm H}) = -1.3$ . For the hydrogen-atom abstraction reactions from aryl aldehyde by other radicals, the Hammett correlations were reported: for *t*-BuO<sup>•</sup>,  $\rho = -0.32$ ,<sup>27</sup> for <sup>•</sup>SO<sub>2</sub>Cl,  $\rho = -0.48$ ,<sup>28</sup> and for <sup>•</sup>CCl<sub>3</sub>,  $\rho = -0.75$ .<sup>29</sup> The high electrophilicity can be presumed from the oxygen-centered radical substituted by the highly electron-withdrawing nitro group as can be shown by the resonance between canonical structures I and II, but not by resonance structure like III.

In Figure 5, log A and  $E_a$  also give linear correlations against  $\sigma$  yielding  $\rho(\log A) = -1.0$  and  $\rho(E_a) = 1.5$  kJ/mol, although the

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dots in the plot for  $E_a$  seem to scatter. In general, the negative slopes of the Hammett plots for the reactivities imply that charge transfer occurs from hydrogen donor to the attacking radical; for the reaction system between NO3<sup>•</sup> and ArCHO, this can be shown by polar resonance structures IV-VI.30

$$(ArC:H^{\bullet}O_{NO_{2}}) \xrightarrow{} (ArC^{\bullet}H^{\bullet}O_{NO_{2}}) \xrightarrow{} (ArC^{+}HO^{-}_{NO_{2}})$$

$$IV \qquad V \qquad VI$$

It has been presumed that the contribution of these polar resonance structures lowers the barrier of the transition state of the reaction.<sup>31</sup> In the case of the reaction system of  $NO_3$  -aryl aldehydes, since the activation energies vary only slightly with the substituents, the contribution of this effect to the variations of the rate constants is small; i.e., assuming the frequency factor to be constant,  $\rho(E_a) = 1.5 \text{ kJ/mol corresponds to } \rho(\log k_H) =$ -0.3, which is in good agreement with the observed difference  $\{\rho(\log k_{\rm H}) - \rho(\log A)\}$ . This small contribution of the  $E_a$  values to the rate constants may be a reflection of small variation in the bond-dissociation energies of the aldehydic C-H's with the change of the substituents on the phenyl ring as can be presumed by the IR band due to the aldehydic C-H;<sup>32</sup> for both p-nitrobenzaldehyde and p-anisaldehyde, the position of the absorption peak of aldehydic C-H is the same ( $\bar{\nu} = 2730 \text{ cm}^{-1}$ ).<sup>33</sup> The rate constants at 20 °C are mainly determined by the frequency factors.

In the case of halogen abstraction by the triethylsilyl radical, it was recently pointed out that the frequency factors were influenced by the polar substituents more greatly than were the activation energies.<sup>34</sup> For this interpretation, the following hypothesis was introduced: the charge separation occurs between Et<sub>3</sub>Si<sup>•</sup> and RX before reaching the transition state of the reaction. For relatively electron-rich R-X, the charge separation facilitates the orientation between the attacking radical center and transferring halogen. If this idea can be applied to the reaction system of NO<sub>3</sub><sup>•</sup>-RCHO, the large substituent effect on the rate constants at room temperature is determined by the polar effect on the orientation factors as shown:

$$(R - C - H \cdots O - N^{+} - O^{-}) \longrightarrow$$
VII
$$(R - C - H^{\delta +} \cdots O^{\delta^{-}} - N^{+} - O^{-}) \longrightarrow$$
transition state
VIII

For aryl aldehydes, the electron-withdrawing substituents interfere with the above charge transfer, resulting in a decrease in the rate constants. In aliphatic aldehydes, methyl substitution increases the above charge separation. In the gas phase, such polar effects may be small; this is one of the reasons for the smaller rate constants in the gas phase than those in acetonitrile as seen in Table I. Since  $NO_3^{\bullet}$  in the gas phase was reported to be a planar triangle,<sup>35</sup> the minus charge and unpaired electron may

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be delocalized in the three oxygen atoms of NO<sub>3</sub> like the resonance structure III, which may be less electrophilic and less reactive. In the condensed phase, NO3' is reported to be a Yshaped structure,<sup>36</sup> in which an unpaired electron is localized on one oxygen atom like the canonical structures I and II. This radical center is quite reactive and electrophilic. This change of the electronic distribution may also be one of the causes for the medium effect.

For the reaction of  $NO_3^{\bullet}$  with phenol in the gas phase,<sup>37</sup> it is assumed that the addition of NO<sub>3</sub><sup>•</sup> to the benzene ring occurs first followed by the elimination of phenolic hydrogen. In the case of

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aryl aldehydes in acetonitrile, although direct evidence for the formation of a cyclohexadienyl radical was not observed by our flash photolysis experiments, the smaller values in  $\log A$  and  $E_a$ suggests the complex formation between NO<sub>3</sub> and  $\pi$ -bonds in the phenyl ring or/and the C=O group in the transition state.

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Registry No. K<sub>2</sub>(Ce(NO<sub>3</sub>)<sub>6</sub>), 17126-44-2; NO<sub>3</sub><sup>•</sup>, 12033-49-7; HCHO, 50-00-0; CH3CHO, 75-07-0; PhCHO, 100-52-7; (CH3)2CO, 67-64-1; PhH, 71-43-2; PhCN, 100-47-0; PhOCH<sub>3</sub>, 100-66-3; CH<sub>3</sub>CH<sub>2</sub>CHO, 123-38-6; (CH<sub>3</sub>)<sub>2</sub>CHCHO, 78-84-2; (CH<sub>3</sub>)<sub>3</sub>CCHO, 630-19-3; p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO, 555-16-8; *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO, 99-61-6; *p*-CNC<sub>6</sub>H<sub>4</sub>CHO, 105-07-7; *m*-CNC<sub>6</sub>H<sub>4</sub>CHO, 24964-64-5; *m*-ClC<sub>6</sub>H<sub>4</sub>CHO, 587-04-2; *p*-ClC<sub>6</sub>H<sub>4</sub>CHO, 104-88-1; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHO, 104-87-0; *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CHO, 123-11-5.

## Acetone Photophysics in Seeded Supersonic Molecular Beams

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The fluorescence decay characteristics of acetone- $h_6$  and acetone- $d_6$  upon excitation of the S<sub>1</sub>  $^1A_2$  state were studied in a supersonic molecular jet. It is shown that both internal conversion  $(S_1 - S_0)$  and intersystem crossing  $(S_1 - T_1)$  take place in the isolated molecule. At the origin, the rate of internal conversion is  $11.5 \times 10^5$  and  $2.3 \times 10^5$  s<sup>-1</sup> for acetone- $h_6$  and acetone- $d_6$ . respectively. The decay time of acetone increases gradually as the excitation frequency increases, due to better coupling with  $T_1$ . This trend reverses at an excess energy of about 2250 cm<sup>-1</sup>, where a very rapid decrease in the decay time as a function of energy is observed. The sudden change is ascribed to the onset of dissociation on the  $T_1$  surface, and a barrier of 93.5 kcal/mol (above the ground state) is found for this process. The results are consistent with a radiative lifetime of about 10  $\mu$ s for S<sub>1</sub>, as deduced from absorption measurements. The low fluorescence yield is accounted for, in the isolated molecule, by internal conversion or intersystem crossing. In bulk systems, these intramolecular processes alone do not account for the observed decay times, and collisional quenching must be taken into account.

#### Introduction

According to Calvert and Pitts' classic textbook,1 "the photochemistry of ketones is the most thoroughly studied of any class of compounds". This comment refers to the chemical events initiated by light absorption at the  $n\pi^*$  transition centered around 280 nm. Being the simplest ketone, acetone is probably the best studied molecule of this group. Some aspects of its photochemistry are well-established. The most important primary reaction is believed to be the homolytic cleavage to form an acetyl and methyl radical:

 $CH_3COCH_3 \rightarrow CH_3CO + CH_3$  $\Delta H^{\circ} = 81 \text{ kcal/mol} (1)$ 

The quantum yield has been carefully measured and is reported to rise with the temperature to a maximum of 100% at 130 °C in the gas phase.<sup>2</sup> The confidence level in these results is reflected by the fact that the system is often used as an actinometer in the UV. The triplet state is considered an important participant in this reaction, a feature common to all carbonyl compounds. The fluorescence quantum yields and lifetimes have been reported for both the gas<sup>3,4</sup> and the liquid<sup>4,5</sup> phases. The results have been interpreted as indicating very efficient intersystem crossing to  $T_1$ .

Nevertheless, many aspects of acetone photochemistry remain to be elucidated. Some important parameters need to be ex-

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perimentally measured, and discrepancies between different reports need to be settled. Thus, some of the rates and energy barriers relevant to the photochemistry of acetone, listed in a recent review,6 are admittedly estimates or guesses. A well-known anomaly is recorded in the literature concerning the radiative lifetime of acetone. Using integrated absorption measurements, one arrives at a lifetime of about 10  $\mu$ s,<sup>3,4,7</sup> while a determination based on the ratio of the measured lifetime to the measured quantum yield leads to  $1-2 \ \mu s.^{3,4,8}$ 

In recent years the photophysical properties of many isolated molecules have been extensively studied with pulsed lasers as light sources and molecular beams as a means to ensure collisionless conditions. In particular, considerable efforts were dedicated to the study of simple aldehydes,<sup>9-15</sup> leading to a much better understanding of the primary photochemical processes. The ab-

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