$$k_{s}(0) = -\frac{d}{dt} \ln S(t)|_{t=0} = -\dot{S}(0)$$
 (A.1)

To evaluate the derivative  $\dot{S}(0)$ , we use the short-time expansion of the solvation TCF

$$S(t) = 1 + \dot{S}(0) + \mathcal{O}(t^2)$$
 (A.2)

The Laplace transformation of (A.2),  $\hat{S}(p) = \int_0^{\infty} dt \exp(-pt)S(t)$ , has the form<sup>34</sup>

$$\lim_{p \to \infty} \hat{S}(p) = \frac{1}{p} + \frac{\dot{S}(0)}{p^2} + \mathcal{O}\left(\frac{1}{p^3}\right)$$

As a result, the initial solvation rate can be expressed in terms of the admittance of the system, resulting in (3.8). Expressing  $\hat{S}(p)$  in the form

$$\hat{S}(p) = [\hat{\chi}(p) - \hat{\chi}(0)] / p[\hat{\chi}(\infty) - \hat{\chi}(0)]$$
(A.3)

where  $\hat{\chi}(\mathbf{p})$  is the complex admittance of the system,  $k_s(0)$  assumes the form

$$k_{s}(0) = -\lim_{p \to \infty} p[p\hat{S}(p) - 1] = -\lim_{p \to \infty} p\frac{[\hat{\chi}(p) - \hat{\chi}(\infty)]}{[\hat{\chi}(0) - \chi(\infty)]}$$
(A.4)

We now evaluate the initial solvation rate explicitly for the dipole and for the ion.

A. Dipole Solvation. We have shown that in this case  $\hat{\chi}(p) \propto \hat{\xi}(p)$ , where<sup>34,35</sup>

$$\hat{\xi}(p) = \frac{1}{2} \left\{ 1 - \frac{9}{\hat{h}(p) + 4} \right\}$$
 (A.5)

with

$$\hat{h}(p) = [\hat{f}(p)]^{1/3} + [\hat{f}(p)]^{-1/3}$$
 (A.6)

$$\hat{f}(p) = \hat{g}(p) - ([\hat{g}(p)]^2 - 1)^{1/2}$$
 (A.7)

$$\hat{g}(p) = 1 + 54[\epsilon(p)]^{1/2}$$
 (A.8)

Substitution of (A.5) gives for the initial dipole solvation rate

$$k_{s}^{(\text{dip})}(0) = \frac{[\hat{h}(0) + 4]}{[\hat{h}(\infty) + 4][\hat{h}(\infty) - \hat{h}(0)]} \lim_{p \to \infty} p[\hat{h}(\infty) - \hat{h}(p)]$$
(A.9)

For most of the applications, the  $\hat{h}(p)$  function can be approximated by

$$\hat{h}(p) \simeq 4.7622[\hat{\epsilon}(p)]^{1/6}$$
 (A.10)

leading to the final expression for the initial dipole solvation rate

$$k_{\rm s}^{\rm (dip)}(0) \simeq \frac{1}{\tau_{\rm L}} \frac{[4.76\epsilon_{\rm s}^{1/6} + 4]}{6[(\epsilon_{\rm s}/\epsilon_{\rm w})^{1/6} - 1][4.76\epsilon_{\rm w}^{1/6} + 4]}$$
 (A.11)

B. Ion Solvation. In this case the MSA admittance is given by  $^{35}$ 

$$\hat{\chi}(\mathbf{p}) \propto \frac{[1-1/\hat{\epsilon}(\mathbf{p})]}{1+\hat{\Delta}(\mathbf{p})}$$
 (A.12)

where the dynamic correction factor,  $\hat{\Delta}(p)$ , can be approximated by

$$\hat{\Delta}(p) \simeq 3(r_{\rm s}/R_{\rm i})[4.76[\hat{\epsilon}(p)]^{1/6} - 2]^{-1}$$
 (A.13)

where  $r_s$  and  $R_i$  are the solvent and the ion radius, respectively. Combining (A.15), (A.12), and (A.13), we derive the final result for the initial ion solvation rate in the case of the Debye solvent:

$$k_{\rm s}^{\rm ion}(0) \simeq \frac{1}{\tau_{\rm L}} \frac{[1 + \Delta(0)]}{[1 + \hat{\Delta}(\infty)]} \frac{A}{B}$$
 (A.14)

where

$$A \equiv (\epsilon_{s} - \epsilon_{\infty})[1 + \hat{\Delta}(\infty)] + C\epsilon_{\infty}(\epsilon_{\infty} - 1)$$

$$B = (\epsilon_{s} - \epsilon_{\infty}) + \epsilon_{s}\hat{\Delta}(0)(1 - \epsilon_{\infty}) + \epsilon_{\omega}\hat{\Delta}(\infty)(\epsilon_{s} - 1)$$

$$C = \frac{2.3811\epsilon_{\infty}^{1/6}(\epsilon_{s}/\epsilon_{\infty} - 1)}{(4.7622\epsilon_{\infty}^{1/6} - 2)^{2}}(r_{s}/R)$$
(A.15)

# Temperature Dependence of the Rate Constants for Reactions of the Sulfate Radical, $SO_4^-$ , with Anions

Robert E. Huie\* and Carol L. Clifton

Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 (Received: February 22, 1990; In Final Form: June 11, 1990)

Rate constants have been measured as a function of temperature over the range 10-60 °C for the reactions of the sulfate radical, SO<sub>4</sub><sup>-</sup>, with azide, chloride, cyanate, cyanide, acetate, and carbonate anions. Room-temperature rate constants ranged from about  $5 \times 10^6$  to  $5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. The variation of the rate constant with substrate depended mainly on the Arrhenius preexponential factor and less on the activation energy. For the reaction of SO<sub>4</sub><sup>-</sup> with Cl<sup>-</sup>, the dependence of the rate constant on ionic strength was determined to be in agreement with the theoretical prediction.

#### Introduction

There have been a large number of rate constant measurements on the reactions of small inorganic free radicals in aqueous solutions,<sup>1</sup> almost all of which have been carried out only at room temperature. The change in a rate constant with temperature can provide a significant amount of information about the nature of the reaction. For example, abstraction reactions typically exhibit a systematic variation of the temperature dependence (the activation energy) with the bond strength of the atom being removed. Addition reactions may have a more complicated relationship of the rate constant with temperature, particularly if the reaction involves reversible complex formation. In electron-transfer reactions, the temperature dependence is expected to be related both to the free energy difference between reactants and products and to the solvent reorganization energy.

Information on the variation of the rate constant with temperature is needed both for an improved basic understanding of these reactions and because kinetic data on elementary reactions

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are used to understand complex systems where temperature and ionic strength excursions are important. In a study of the hightemperature radiolysis of water,<sup>2</sup> for example, the experimental results were computer modeled, but very few of the elementary reactions had actually been measured at other than room temperature. In general, it was assumed in the model calculations that fast reactions  $(k > 10^9 \text{ M}^{-1} \text{ s}^{-1})$  have a temperature dependence or activation energy of 12.5 kJ mol<sup>-1</sup> (corresponding to the temperature dependence of diffusion) and that slower reactions have an activation energy of 19 kJ mol<sup>-1</sup>. In a modeling study of cloudwater chemistry,<sup>3</sup> the activation energy was estimated by assuming an Arrhenius preexponential factor of  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for reactions with room-temperature rate constants less than 7  $\times 10^7$  M<sup>-1</sup> s<sup>-1</sup>. For reactions with higher room-temperature rate constants, the activation energy was assumed to be 12.5 kJ mol<sup>-1</sup>. As we will show in this work, these approaches, while quite reasonable, are unlikely to give correct results.

In the present study, we focus on the temperature dependence of a particular group of reactions: the reactions of the sulfate radical,  $SO_4$ , with monoanions. These reactions are most typically expected to proceed by electron transfer, but in some cases it is also possible that  $SO_4^-$  might react by addition to the anion. In an earlier work<sup>4,5</sup> we investigated the hydrogen abstraction reactions of SO<sub>4</sub><sup>-</sup>. We found that the rate constants increased as the C-H bond strength decreased and that this increase was due to a decrease in the activation energy for the reaction.

SO<sub>4</sub><sup>-</sup> is well established as a strong one-electron oxidant.<sup>6</sup> Although its reduction potential has not been determined directly, Stanbury<sup>7</sup> has calculated a value of 2.43 V for the  $SO_4^{-}/SO_4^{-2}$ couple from a consideration of persulfate decomposition results and the rate constant for the recombination of the radical. This value is also supported by other experimental information cited in that review.

For this study, we have chosen a series of anions,  $HCO_3^{-}$ ,  $CH_3CO_2^-$ ,  $OCN^-$ ,  $CN^-$ ,  $Cl^-$ , and  $N_3^-$ , whose reactions with  $SO_4^$ have reported<sup>1</sup> rate constants at room temperature that range from about  $4 \times 10^6$  to  $3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. We have measured rate constants for all of the reactions as a function of temperature and have investigated the effect of ionic strength on the reaction of SO<sub>4</sub><sup>-</sup> with Cl<sup>-</sup>.

#### Experimental Section<sup>8</sup>

The SO<sub>4</sub><sup>-</sup> radical was produced by the laser-flash photolysis of sodium persulfate solutions:9,10

$$S_2 O_8^{2-} + h\nu \rightarrow 2SO_4^{-} \tag{1}$$

A Lambda Physik EMG 201 MSC excimer laser, operating mostly at 248 nm (KrF) and occasionally at 193 nm (ArF), was used to irradiate the central 2.5 cm of a 4-cm-long reaction cell constructed of 1-cm<sup>2</sup> quartz tubing with 1/16-in.-thick optical-grade quartz windows fused to the ends. The reaction mixture was flowed through the reaction cell to replenish the solution between laser pulses. The temperature of the reaction mixture was controlled by flowing the solution through a 1-m-long water-jacketed capillary tube before reaching the cell. The temperature was measured by a copper-constantan thermocouple located in the liquid stream immediately after the cell.



Figure 1. Decay of the absorption at 450 nm after the flash photolysis of 0.5 mM  $Na_2S_2O_8$  in the presence of (a) 1.0 mM CH<sub>3</sub>COONa, (b) 1.0 mM NaCN. In (a) the time base is  $600-\mu s$  full scale; in (b) it is  $20-\mu s$ full scale. The second and third vertical lines locate the region over which the data are fitted; the first vertical line is the chosen t = 0. The line through the data is the linear least-squares fit.

The reaction was monitored by focusing the light from a 300-W xenon arc lamp through the cell and into the entrance slit of a Kratos monochromator. A shutter and optical filter were located between the lamp and the cell to minimize photolysis of the sample by the analysis light. Before the flash, the optical signal was measured by a sample-and-hold circuit, and the change in absorption after the laser flash determined with a differential amplifier. Kinetic curves were recorded on a Tektronix 7612D transient analyzer and transferred to a PC Designs CV-386 computer. The optical train, the electronics and the experimental procedure have been described in detail previously.<sup>4</sup> At a typical laser energy, the concentration of  $SO_4^-$  radicals produced by the flash was about 20  $\mu$ M.

The sulfate radical has a broad optical absorption with a maximum at 450 nm. The product of the molar absorptivity and the quantum yield for the production of  $SO_4^-$  from the photolysis of  $S_2O_4^{2-}$  at 266 nm has been determined recently<sup>11</sup> to be 2770  $\pm$  280 M<sup>-1</sup> cm<sup>-1</sup>. Assuming a quantum yield of 2, this results in  $\epsilon = 1385 \text{ M}^{-1} \text{ cm}^{-1}$ . This value is similar to the pulse radiolysis result<sup>12</sup> of  $\epsilon = 1100 \text{ M}^{-1} \text{ cm}^{-1}$ . We have made use of the absorption at 450 nm to monitor the loss of  $SO_4^-$  in most of these studies but have also employed other wavelengths when preferable (to avoid overlap with product absorption) or have used the absorption of the product radical. The results from multiple runs were averaged before undergoing linear least-squares analysis. Sample curves are presented in Figure 1.

The second-order rate constants were fit to the Arrhenius expression  $k = Ae^{-E/RT}$ , by a weighted least-squares routine, ARRH,<sup>13</sup> and were weighted by the reciprocal of the squares of the standard errors derived from the second-order fits. The error limits reported with the Arrhenius parameters are the standard errors from the least-squares fit.

House-deionized water was further purified by a Gelman Water-I system.  $Na_2S_2O_8$ ,  $NaN_3$ , and NaCNO were from

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Figure 2. First-order rate constants for the reaction of  $SO_4^-$  with  $CH_3CO_2^-$  as a function of the acetate concentration. The squares are the uncorrected decay rates; the diamonds are the data corrected for ionic strength.

Aldrich, NaCl and NaHCO<sub>3</sub> from Fisher,  $Na_2C_2O_4$  from Mallinckrodt, NaCN from B&A (Allied), and LiClO<sub>4</sub> from GFS.

#### Results

Second-order rate constants for the reactions of  $SO_4^-$  with a number of substrates were determined by measuring the first-order rate constants for the decay of  $SO_4^-$  or the appearance of a product radical in the presence of various amounts of added substrate. Typically, the solution consisted of 0.5 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and amounts of added substrate ranging up to 15 mM, depending upon the reaction rate constant. Because all of the added reactants were salts, the ionic strength of the solution changed upon each addition. In some cases, we have adjusted the ionic strength with added LiClO<sub>4</sub> to a constant value; in some others, we have added excess LiClO<sub>4</sub> so that the variation in ionic strength is small compared to the total. In most cases, however, we have chosen to correct for the influence of the change in ionic strength on the rate constant by use of the equation<sup>14</sup>

$$\log k_0 = \log (k) - 2z_a z_b [A\mu^{1/2} / (1 + \mu^{1/2})]$$
(I)

where k is the measured rate constant,  $k_0$  is the rate constant at zero ionic strength, z is the species charge,  $\mu$  is the ionic strength, and A is a collection of physical constants that is a function of temperature.<sup>15</sup> The first-order rate constant was corrected at each concentration of added reactant, and a new rate constant derived. An example of second-order plots with corrected and uncorrected first-order rate constants is given in Figure 2. We have investigated the reactions of SO<sub>4</sub><sup>-</sup> with Cl<sup>-</sup> as a function of added LiClO<sub>4</sub> to confirm the validity of this approach.

We have studied the reactions of  $SO_4^-$  with a number of anions, chosen to span a wide range of reactivity at room temperature.<sup>1</sup> We have found that some of the anions investigated can undergo photoionization, even at 248 nm. This results in an optical absorption due to the hydrated electron, which rapidly decays by self-reaction, reaction with H<sup>+</sup>, and reaction with  $S_2O_8^{2-}$ . In these cases, care was taken to begin the kinetic analysis after the decay of this initial absorption. In addition to the hydrated electron, photolysis results in the formation of a free radical. The extent of photolysis of the reactant was always small compared to the photolysis is typically the same as produced in the reaction of  $SO_4^$ with the substrate and since these reactions are irreversible under our conditions, this leads to no complications in the kinetic analysis.

In the course of this work, we have also investigated the selfreactions of  $Cl_2^-$  and  $CO_3^-$ , which are formed in the reactions of  $SO_4^-$  with  $Cl^-$  and  $HCO_3^-$ , respectively.



Figure 3. Ionic strength dependence of the rate constant for the reaction of  $SO_4^-$  with  $Cl^-$ .

TABLE I: Rate Constants for the Reaction of SO4- with Cl-

		•	
 <i>T</i> , °C	k, M <sup>-1</sup> s <sup>-1</sup>	$k(\mu=0), M^{-1} s^{-1}$	
11.4	$2.76 \times 10^{8}$	$2.57 \times 10^{8}$	
24.3	$2.71 \times 10^{8}$	$2.42 \times 10^{8}$	
24.3		$2.76 \times 10^{8}$ <sup>a</sup>	
35.0	$2.74 \times 10^{8}$	$2.42 \times 10^{8}$	

"From the ionic strength data, Table II.

TABLE II: Rate Constants for the Reaction of  $SO_4^-$  with Cl<sup>-</sup> as a Function of Ionic Strength at 24.3 °C

ionic strength, M	k, M <sup>-1</sup> s <sup>-1</sup>	ionic strength, M	k, M <sup>-1</sup> s <sup>-1</sup>
0.0025ª	$3.02 \times 10^{8}$	0.2	5.35 × 10 <sup>8</sup>
0.15	$4.28 \times 10^{8}$	0.4	6.18 × 10 <sup>8</sup>
0.1	$4.71 \times 10^{8}$		

" Ionic strength not controlled.

Chloride Reaction. The reaction of  $SO_4^-$  with  $Cl^-$  resulted in the production of a strongly absorbing species with a maximum absorption at 360 nm, which is characteristic of the  $Cl_2^-$  radical. This radical arises from the reactions

$$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl$$
 (2)

$$Cl + Cl^- \rightarrow Cl_2^-$$
 (3)

The reduction potential for the Cl/Cl<sup>-</sup> couple is 2.41 V, close to that estimated for  $SO_4^0/SO_4^{2-}$ , while that for  $Cl_2^-/2Cl^-$  is 2.09 V.<sup>7</sup> The rate constant for the reaction of the chlorine atom with the chloride ion is<sup>16</sup> 8 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, and since there is no sulfate present in the reaction mixture before photolysis, the reaction should be essentially irreversible. Although the formation of  $Cl_2^-$  is fast, it is not instantaneous at the Cl<sup>-</sup> concentrations used. Therefore, we have monitored the decay of SO<sub>4</sub><sup>-</sup> at 500 nm, rather than 450 nm, to avoid any contribution to the absorption decay from the tail of the  $Cl_2^-$  spectrum.

We have measured second-order rate constants for the disappearance of  $SO_4^-$  at ionic strengths ranging from approximately 2.5 mM (no added LiClO<sub>4</sub>) to 400 mM. The results are plotted according to eq I in Figure 3. The line is a least-squares fit and has a slope of 0.96, close to the theoretical slope of 1.0.

We have summarized our results on the reaction of  $SO_4^-$  with Cl<sup>-</sup> in Tables I and II. Both the measured rate constants and those corrected for ionic strength are included. Rate constants were determined over the temperature range 11-35 °C. Within experimental error, there was no change in the measured rate constant over this temperature interval, and an average value of  $k_0 = (2.47 \pm 0.09) \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> was derived (excluding the result extrapolated from high ionic strength), where the error limit is the standard deviation.

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TABLE III: Rate Constants for the Self-Reaction of Cl2

ionic strength, m	Cl⁻, mM	k, M <sup>-1</sup> s <sup>-1</sup>	$k(\mu=0), M^{-1} s^{-1}$
0.0024	0.94	$1.85 \times 10^{9}$	$1.66 \times 10^{9}$
0.0029	1.37	$1.50 \times 10^{9}$	$1.33 \times 10^{9}$
0.016	0.5	$2.25 \times 10^{9}$	$1.73 \times 10^{9}$
0.1	1.34	$2.11 \times 10^{9}$	$1.21 \times 10^{9}$
0.2	0.5	$2.65 \times 10^{9}$	$1.29 \times 10^{9}$
0.2	1.0	$2.24 \times 10^{9}$	$1.09 \times 10^{9}$
0.2	1.5	$2.12 \times 10^{9}$	$1.03 \times 10^{9}$
0.4	0.5	$3.43 \times 10^{9}$	$1.39 \times 10^{9}$
0.4	0.8	$2.57 \times 10^{9}$	$1.04 \times 10^{9}$

TABLE IV: Rate Constants for the Reaction of SO<sub>4</sub><sup>-</sup> with CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>

			-
 <i>T</i> , °C	k, M <sup>-1</sup> s <sup>-1</sup>	$k(\mu=0), M^{-1} s^{-1}$	
8.5	$4.37 \times 10^{6}$	$3.41 \times 10^{6}$	
15.2	$4.69 \times 10^{9}$	$3.64 \times 10^{9}$	
25.0	$5.06 \times 10^{6}$	$3.93 \times 10^{6}$	
33.7	$6.48 \times 10^{6}$	$4.94 \times 10^{6}$	
44.6	$6.95 \times 10^{6}$	$5.23 \times 10^{6}$	
63.0	$8.48 \times 10^{6}$	$6.28 \times 10^{6}$	

There have been several previous determinations of the rate constant for this reaction at room temperature, three by pulse radiolysis<sup>17-19</sup> and two by laser-flash photolysis.<sup>20,21</sup> The rate constants reported range from  $1.3 \times 10^8$  to  $3.1 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>, in good agreement with the value determined here.

In the course of this work, we have also measured rate constants for the disproportionation of Cl2<sup>-</sup> at various values of the ionic strength by following the decay of the absorption at 340 nm:

$$Cl_2^- + Cl_2^- \rightarrow Cl_2 + 2Cl^- \tag{4}$$

The results are summarized in Table III. There appears to be a slight decrease in the rate constant as the chloride ion concentration is increased. Assuming an absorptivity of<sup>22</sup> 8800 M<sup>-1</sup> cm<sup>-1</sup>, we obtain an average  $k = 1.3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, corrected to zero ionic strength. This is in reasonable agreement with most of the many other determinations of this rate constant,<sup>1</sup> when those values are also corrected for ionic strength. In a very recent laser-flash photolysis study,<sup>21</sup> the decay of Cl<sub>2</sub><sup>-</sup> was reported to follow both first- and second-order kinetics, with a value of 0.7  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for the second-order component. We observed no deviation in our second-order fits due to a first-order component. as we did in our study of the self-reaction of  $SO_4^{-9}$ 

Acetate Reaction. The reaction of  $SO_4^-$  with  $CH_3CO_2^-$  has been observed to yield  $CH_3$  by the reactions<sup>6,23</sup>

$$\mathrm{SO}_4^- + \mathrm{CH}_3\mathrm{CO}_2^- \to \mathrm{SO}_4^{2-} + \mathrm{CH}_3\mathrm{CO}_2 \tag{5}$$

$$CH_3CO_2 \rightarrow CH_3 + CO_2$$
 (6)

The hydrogen abstraction channel

$$SO_4^- + CH_3CO_2^- \rightarrow CH_2CO_2^- + HSO_4^-$$
 (7)

appears to be unimportant for the anion. In the present study, all of the rate measurements were carried out at near neutral pH (6.6-7.2) so that little CH<sub>3</sub>COOH was present. We are not aware of a reported reduction potential for the  $CH_3CO_2/CH_3CO_2^{-1}$ couple.

The results for the reaction of  $SO_4^-$  with  $CH_3CO_2^-$  over the temperature range 8.5-63 °C are presented in Table IV and plotted in Figure 4. A least-squares fit of the data to the Arrhenius expression resulted in  $k_0 = (2.57 \pm 1.49) \times 10^8 \exp(-10.1)$  $\pm$  1.4 kJ mol<sup>-1</sup>/RT) M<sup>-1</sup> s<sup>-1</sup>.

There have been two previous determinations of the rate con-





Figure 4. Temperature dependence of the rate constants for the reactions of  $SO_4^-$  with several monoanions.

TABLE V: Rate Constants for the Reaction of SO4 with HCO3

<i>T</i> , °C	k, M <sup>-1</sup> s <sup>-1</sup>	$k(\mu=0), M^{-1} s^{-1}$	
13.1	2.81 × 10 <sup>6</sup>	$2.16 \times 10^{6}$	
22.7	$3.33 \times 10^{6}$	$2.52 \times 10^{6}$	
22.9	$3.53 \times 10^{6}$	$2.80 \times 10^{6}$	
33.1	$4.51 \times 10^{6}$	$3.42 \times 10^{6}$	
43.1	$5.25 \times 10^{6}$	$3.85 \times 10^{6}$	
57.0	$7.60 \times 10^{6}$	$5.68 \times 10^{6}$	

stant for the reaction of  $SO_4^-$  with  $CH_3CO_2^-$ . Chawla and Fessenden<sup>6</sup> obtained a rate constant of  $5.0 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$  by pulse radiolysis, slightly higher than the room-temperature value obtained here. In a laser-flash photolysis study, Wine et al.<sup>20</sup> reported a value of  $3.7 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>, corrected to zero ionic strength, almost identical with our room-temperature value.

Bicarbonate Reaction. The reaction of  $SO_4^-$  with  $HCO_3^-$  has been shown to yield a product with an ESR spectrum the same as found for the  $CO_3^-$  radical in the solid.<sup>6</sup> Although the reaction could proceed by hydrogen abstraction, it is most likely an electron-transfer reaction:

$$SO_4^- + HCO_3^- \rightarrow SO_4^{2-} + HCO_3$$
 (8)

$$HCO_{3} \rightleftharpoons H^{+} + CO_{3}^{-} \tag{9}$$

The reduction potential for the  $CO_3^-/CO_3^{2-}$  couple was estimated to be 1.5 V;<sup>7</sup> in this laboratory, a value of 1.59 V was determined recently.<sup>24</sup> The  $pK_a$  values for the equilibria

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{10}$$

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$
(11)

are 10.33 and 6.35.25 The carbonate radical has been reported to have a  $pK_a$  of between 7.0 and 8.2.<sup>26</sup> We have carried out our kinetic measurements around pH 8 (7.8-8.2). From the equation F =

$$E_0 + 0.059 \log \{ (K_{10}K_{11} + K_{11}[H^+] + [H^+]^2) / (K_9 + [H^+]) \}$$
(II)

and assuming that  $pK_9$  is 7.6, we calculate that the reduction potential for HCO<sub>3</sub><sup>-</sup> at pH 8 is 1.72. Therefore the electrontransfer reaction of  $SO_4^-$  with  $HCO_3^-$  is about 0.7 V exothermic.

We have measured rate constants for the reaction of  $SO_4^-$  with  $HCO_3^-$  over the temperature range 13-57 °C (Table V); a least-squares fit to the Arrhenius expression gives  $k_0 = (3.11 \pm$ 1.47 × 10<sup>9</sup> exp(-17.4 ± 1.2 kJ mol<sup>-1</sup>/RT) M<sup>-1</sup> s<sup>-1</sup>.

In the course of these studies, we have also investigated the self-reaction of  $CO_3^-$  by following the decay of the absorption at

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Figure 5. Absorption spectrum of the product formed in the reaction of  $SO_4^-$  with OCN<sup>-</sup>. Flash photolysis at 248 nm of an air-saturated solution of 0.5 mM  $Na_2S_2O_8$  and 0.5 mM NaOCN.

600 nm due to  $CO_3^-$ . We have not carried out any experiments with added LiClO<sub>4</sub>, but the second-order rate constants did not show any clear variation with NaHCO<sub>3</sub> concentration. Values of  $k/\epsilon$  of 1570 cm s<sup>-1</sup> at 13.1 °C, 1445 cm s<sup>-1</sup> at 23.2 °C, and 1230 cm s<sup>-1</sup> at 43.1 °C were obtained. Eriksen et al.<sup>26</sup> also reported that the reaction had a negative temperature dependence but did not report a rate constant. If we assume that the absorptivity of HCO<sub>3</sub>/CO<sub>3</sub><sup>-</sup> at pH 8 is about 1500 M<sup>-1</sup> cm<sup>-1</sup> (about midway between those measured at pH 7.4 and 11.4), then we obtain a rate constant of  $2.2 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> at 23.2 °C. This is 2-10 times lower than other values that have been reported,<sup>1</sup> most of which were obtained at high pH and ionic strength.

Cyanate Reaction. The reduction potential for the couple OCN/OCN<sup>-</sup> was estimated by Stanbury<sup>7</sup> to be 2.66 V, higher than the value for the SO<sub>4</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> couple. A high value for this couple is consistent with the observation that OH adds to OCN<sup>-</sup> instead of reacting by electron transfer, but it appears to be higher than would be expected on the basis of the room-temperature rate constant for the reaction of SO<sub>4</sub><sup>-</sup> with OCN<sup>-</sup>, which was reported to be<sup>27</sup> ~5 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>.

The reaction of  $SO_4^-$  with OCN<sup>-</sup> results in a slowly decaying product with an absorption spectrum (Figure 5) of shape identical with that found in the reaction of OH with OCN<sup>-,28</sup> By comparison with the  $SO_4^-$  absorption at 450 nm, we estimate the absorptivity to be  $\epsilon = 360 \text{ M}^{-1} \text{ cm}^{-1}$ , much less than the 970 M<sup>-1</sup> cm<sup>-1</sup> obtained from the OH reaction. The product in the reaction of OH with OCN<sup>-</sup> results from the addition of OH to cyanate with subsequent rearrangement and reaction with further OCN<sup>-,28</sup>

$$OH + OCN^{-} \rightarrow N = C(OH)O^{-} \rightarrow NHCO_{2}^{-}$$
 (12)

$$NHCO_2^- + OCN^- \rightleftharpoons ^-O_2CN(H)NCO^-$$
(13)

In the reaction of OCN<sup>-</sup> with  $SO_4^-$ , the initial step could be electron transfer, followed by hydration of the product radical. But the high reduction potential estimated for the OCN/OCN<sup>-</sup> suggests that the reaction involves the addition of  $SO_4^-$  to OCN<sup>-</sup>, with subsequent hydration and loss of  $SO_4^{-2-}$ :

$$SO_4^- + OCN^- \rightarrow -SO_4OCN^-$$
 (14a)

$$SO_4OCN^- + H_2O \rightarrow SO_4^{2-} + H^+ + N = C(OH)O^-$$
 (14b)

The higher absorptivity obtained in the OH reaction is then due to the much higher (0.25 M) concentration of OCN<sup>-</sup> used in that study, which shifts the equilibrium (reaction 13) to the right.

We have measured rate constants for this reaction over the temperature range 9-66 °C. The results are presented in Table VI and in Figure 4. A fit to the data, extrapolated to zero ionic strength, yields the expression  $k_0 = (2.94 \pm 1.08) \times 10^8 \exp(-2.1 \pm 0.9 \text{ kJ mol}^{-1}/RT) \text{ M}^{-1} \text{ s}^{-1}$ . Rate constants were also determined

TABLE VI: Rate Constants for the Reaction of SO<sub>4</sub><sup>-</sup> with OCN<sup>-</sup>

<i>T</i> , °C	k, M <sup>-1</sup> s <sup>-1</sup>	$k(\mu=0), M^{-1} s^{-1}$
9.0	$1.43 \times 10^{8}$	$1.23 \times 10^{8}$
24.6	$1.40 \times 10^{8}$	$1.19 \times 10^{8}$
29.7	$1.42 \times 10^{8}$	$1.25 \times 10^{8}$
37.1	$1.60 \times 10^{8}$	$1.39 \times 10^{8}$
57.5	$1.63 \times 10^{8}$	$1.41 \times 10^{8}$
66.4	$1.53 \times 10^{8}$	$1.31 \times 10^{8}$
	$\mu = 0.1  \mathrm{M}$	
13.0	$1.76 \times 10^{8}$	$1.03 \times 10^{8}$
47.0	$2.24 \times 10^{8}$	$1.24 \times 10^{8}$

TABLE VII: Rate Constants for the Reaction of SO<sub>4</sub><sup>-</sup> with CN<sup>-</sup>

<i>T</i> , °C	k, M <sup>-1</sup> s <sup>-1</sup>	$k(\mu=0), M^{-1} s^{-1}$
10.5	$2.74 \times 10^{8}$	$2.54 \times 10^{8}$
12.1	$2.55 \times 10^{8}$	$2.25 \times 10^{8}$ a
24.3	$2.60 \times 10^{8}$	$2.35 \times 10^{8}$
43.7	$2.05 \times 10^{8}$	$1.84 \times 10^{8}$
63.8	$1.68 \times 10^{8}$	$1.48 \times 10^{8}$
	$\mu = 0.1  \mathrm{M}$	
13.0	$4.23 \times 10^{8}$	$2.46 \times 10^{8}$
24.3	$3.03 \times 10^{8}$	$1.71 \times 10^{8}$
47.0	$3.31 \times 10^{8}$	$1.82 \times 10^{8}$

<sup>a</sup> pH 10.

TABLE VIII: Rate Constants for the Reaction of  $SO_4^-$  with  $N_3^-$ 

<i>T</i> , °C	$k, M^{-1} s^{-1}$	$k(\mu=0), M^{-1} s^{-1}$
8.7	$2.04 \times 10^{9}$	$1.86 \times 10^{9}$
24.4	$2.52 \times 10^{9}$	$2.29 \times 10^{9}$
39.9	$3.09 \times 10^{9}$	$2.84 \times 10^{9}$
58.0	$3.89 \times 10^{9}$	$3.50 \times 10^{9}$

at 13 and 47 °C with 0.1 M LiClO<sub>4</sub> added. These results extrapolate to rate constants 10-20% lower than those measured at low ionic strength, which is a quite reasonable agreement.

Cyanide Reaction. There have been two studies of the reaction of  $SO_4^-$  with  $CN^-$  by ESR. Chawla and Fessenden<sup>6</sup> found evidence for two adducts in the presence of the spin trap  $CH_2^-NO_2^-$ , due to both  $CONH_2$  and CN. Rehorek and Janzen,<sup>29</sup> with *N*phenyl *tert*-butyl nitrone as a spin trap, apparently found evidence for the protonated adduct of  $SO_4^-$  and  $CN^-$  in an acetonitrile/ water (6:1) solution. They suggest that the lifetime of the adduct in pure water is too short to allow it to be trapped and it decomposes to  $CONH_2$  or  $HOCN^-$ , depending on pH. They reported no evidence for either CN or  $(CN)_2^-$  formation.

In this work, we have found that the  $SO_4^-$  radical reacts with  $CN^{-}$  to produce a product with an absorption maximum around 260 nm. We derive  $\epsilon = 1450 \text{ M}^{-1} \text{ cm}^{-1}$  at pH 10 for this product by comparison with the initial absorption of  $SO_4^-$  at 450 nm. The buildup of the product absorption is not exactly coincident with the decay of the absorption at 450 nm (Figure 6). At higher CN<sup>-</sup> concentrations, where the decay of  $SO_4^-$  is fast, there is a "foot" in the buildup at 260 nm, indicating a reaction that has at least two steps. At 290 nm, where both  $SO_4^-$  and the product absorb, the absorption first decreases and then increases. These results are consistent with either the addition of  $SO_4^-$  to the C=N triple bond, with the subsequent formation of CONH<sub>2</sub>, or the oxidation of  $CN^-$  or HCN by  $SO_4^-$  to form the CN radical, with subsequent hydration to  $CONH_2$ . The absorption at 260 nm results from the buildup of  $CONH_2$ . The very high potential, estimated<sup>7</sup> to be 2.59 V, for the CN/CN<sup>-</sup> couple supports the addition mechanism over the electron-transfer mechanism.

Apparent rate constants for the reaction of  $SO_4^-$  with  $CN^-$  have been determined over the temperature range 10-64 °C by measuring the first-order rate constant for the decay of the absorption at 450 nm as a function of added NaCN. Frequently, the intercept of these plots was less than zero, particularly at the higher temperatures. The apparent rate constant was found to decrease with temperature; a fit to the Arrhenius equation gave  $k_0 = (1.41 \pm 1.14) \times 10^7 \exp(6.8 \pm 2.0 \text{ kJ mol}^{-1}/RT) \text{ M}^{-1} \text{ s}^{-1}$ .

<sup>(27)</sup> Chawla, O. P. Ph.D. Thesis, Carnegie-Mellon University, Aug 6, 1973.

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<sup>(29)</sup> Rehorek, D.; Janzen, E. G. Z. Chem. 1985, 25, 451.



 $\begin{array}{c} \begin{array}{c} \begin{array}{c} 400\\ \text{K1} = 229943 \end{array} \overset{8}{\text{SD} = 3422} \overset{400}{\text{ABS}(0) = 3.7990-04} \overset{800}{\text{ABS}(1MP) = 1.6690-02} \end{array} \overset{1600}{\text{Z000}} \end{array} \overset{2000}{\text{Figure 6.}} \\ \hline \\ \begin{array}{c} \text{Figure 6.} \\ \text{Decay of absorption at 450 nm (a) and buildup in absorption at 260 nm (b) due to the reaction of SO_4^- with CN^-. Flash photolysis at 248 nm of air-saturated solution of 0.5 mM Na_2S_2O_8 and 1.25 mM NaCN. \end{array}$ 

Rate constants measured in the presence of  $0.1 \text{ M LiClO}_4$  gave values, when extrapolated to zero ionic strength, close to those measured at low ionic strength. Most measurements were made at near neutral pH; measurements made at pH 10 produced very similar results. At room temperature, our rate constant is about 4 times lower than the approximate value reported by Chawla.<sup>27</sup>

Azide Reaction. The reduction potential for the N<sub>3</sub>/N<sub>3</sub><sup>-</sup> couple is 1.33 V,<sup>7</sup> considerably lower than the potential of the SO<sub>4</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> couple. The reaction of SO<sub>4</sub><sup>-</sup> with N<sub>3</sub><sup>-</sup> was monitored by following the decay of the SO<sub>4</sub><sup>-</sup> absorption at 450 nm. Rate constants were determined over the temperature range 9–58 °C, and a leastsquares fit gave  $k_0 = (1.32 \pm 0.08) \times 10^{11} \exp(-10.0 \pm 1.6 \text{ kJ} \text{ mol}^{-1}/RT) \text{ M}^{-1} \text{ s}^{-1}$ . This expression gives a room-temperature rate constant very close to that reported previously.<sup>30</sup>

The reaction of  $SO_4^-$  with  $N_3^-$  is sufficiently fast that it is likely to be at least partly limited by the rate at which the reactants can diffuse toward each other. The diffusion-controlled rate constant for ions can be calculated by using the equation developed by Debye:<sup>31</sup>

$$k_0 = f/4(2 + r_1/r_2 + r_2/r_1)8kT/3\eta$$
(III)

where

$$f = b/(e^b - 1) \tag{IV}$$

$$b = (z_1 z_2 \epsilon^2 / DkT)(2/r_1 + r_2)$$
 (V)

We have assumed that  $r_1 = r_2$  in our calculations and have taken values of the dielectric constant, *D*, and the viscosity,  $\eta$ , from *Lange's.*<sup>25</sup> If we take the 8.7 °C rate constant to be diffusion controlled, then we calculate that the effective radii of the ions are equal to about 0.45 nm. Smaller radii give diffusion-controlled rate constants lower than actually measured. An Arrhenius plot of the diffusion-controlled rate constant for 0.45 nm shows clear curvature, but a linear fit from 10 to 60 °C gives a preexponential factor of  $3.6 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$  and an activation energy of 17.5 kJ mol<sup>-1</sup>, both considerably higher than those measured for the SO<sub>4</sub><sup>-</sup> + N<sub>3</sub><sup>-</sup> reaction. The preexponential factor and the activation energy increase as the radii are increased, the latter more slowly than the former.

TABLE IX: Arrhenius Parameters for the Reactions of  $SO_4^-$  with Monoanions

anion	A, M <sup>-1</sup> s <sup>-1</sup>	E, kJ mol <sup>-1</sup>	k(298 K)
N <sub>3</sub> <sup>-</sup> Cl <sup>-</sup> CN <sup>-</sup> OCN <sup>-</sup> CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	$\begin{array}{c} (1.32 \pm 0.08) \times 10^{11} \\ (2.47 \pm 0.09) \times 10^8 \\ (1.41 \pm 1.41) \times 10^7 \\ (2.94 \pm 1.08) \times 10^8 \\ (2.57 \pm 1.49) \times 10^8 \end{array}$	$10.0 \pm 1.6 \\ 0 \\ -6.8 \pm 2.0 \\ 2.1 \pm 0.9 \\ 10.1 \pm 1.4$	$\begin{array}{c} 2.35 \times 10^9 \\ 2.54 \times 10^8 \\ 2.21 \times 10^8 \\ 1.27 \times 10^8 \\ 4.29 \times 10^6 \end{array}$
HCO3-	$(3.11 \pm 1.47) \times 10^9$	$17.4 \pm 1.2$	$2.80 \times 10^{6}$

We can correct for diffusion control by use of the equation

$$1/k_{act} = 1/k_{calc} - 1/k_{dif}$$
(VI)

If we assume 0.45-nm radii, we find that our calculated values for  $k_{act}$  decrease strongly with temperature, leading to an apparent negative activation energy of -19.6 kJ mol<sup>-1</sup>. With 0.6-nm radii,  $k_{act}$  has essentially no temperature dependence and a preexponential factor of about  $3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. For these small anions a much larger radius is not likely, suggesting that the reaction of SO<sub>4</sub><sup>-</sup> with N<sub>3</sub><sup>-</sup> actually has little or no activation energy after correction for diffusion.

#### Discussion

The reactions of  $SO_4^-$  with  $Cl^-$ ,  $N_3^-$ ,  $CH_3CO_2^-$ , and  $HCO_3^$ appear to result in an electron transfer to the radical, possibly involving short-lived adducts; the reactions of  $SO_4^-$  with  $CN^-$  and  $OCN^-$  most likely proceed by an addition mechanism, with subsequent transformation of the adducts. The kinetic results for the reactions of  $SO_4^-$  with these anions are summarized in Table IX. The activation energy ranges from -6.8 kJ mol<sup>-1</sup> for  $CN^-$ , where the reaction is almost certainly an addition reaction complicated by subsequent hydration, to 17.4 kJ mol<sup>-1</sup> for  $HCO_3^-$ . There is no apparent correlation between the values of the preexponential factor and the activation energy.

If we accept the diffusion-corrected preexponential factor for the azide reaction, all of these reactions have A factors less than about  $3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, well below the collision frequency. This, along with the low activation energies for these reactions, suggests that the reactions involve the reversible formation of a transient intermediate:

$$\mathbf{R} + \mathbf{S} \rightleftharpoons \mathbf{RS} \tag{15}$$

$$RS \rightarrow R^- + S^+ \text{ (or P)} \tag{16}$$

If a steady-state in RS is assumed, the observed rate constant will be given by

$$-d \ln [R]/dt = k_{obs} = k_{15}k_{16}[S]/(k_{-15} + k_{16}) \quad (VII)$$

If  $k_{16} \gg k_{-15}$ , the reaction will behave as a simple bimolecular reaction. If, however,  $k_{-15}$  is important, it can dramatically affect the kinetics, particularly the temperature dependence. We would expect that when the reactant couples have reduction potentials similar to those of  $SO_4^-/SO_4^{2-}$ , as with  $Cl/Cl^-$ ,  $OCN/OCN^-$ , and  $CN/CN^-$ , the electron-transfer step is much more likely to be slow enough for the dissociation step to become important. This then leads to the low, or negative, activation energies found for those reactions and to their low preexponential factors. In some cases, the direct electron-transfer step may not take place at all. For example, the reaction of  $SO_4^-$  with  $Cl^-$  might involve the reaction of the complex with a second  $Cl^-$ :

$$SO_4^- + Cl^- \rightleftharpoons (SO_4^-)(Cl^-)$$
 (17)

$$(\mathrm{SO}_4^{-})(\mathrm{Cl}^{-}) + \mathrm{Cl}^{-} \rightarrow \mathrm{SO}_4^{2-} + \mathrm{Cl}_2^{-}$$
(18)

There are few studies of the temperature dependence of other free radical reactions with which we can compare these results. Elliot and Simsons<sup>32</sup> have measured rate constants for some hydrogen abstraction and electron-transfer reactions of the OH radical. For the alcohols 2-propanol and *tert*-butyl alcohol the preexponential factors were well below the collision rate and the activation energy decreased with decreasing C-H bond strength, analogous to what we observed for SO<sub>4</sub><sup>-</sup> abstraction reactions.<sup>5</sup> The electron-transfer reactions, however, were very fast ( $k \sim 10^{10}$ 

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 $M^{-1}$  s<sup>-1</sup>), and the Arrhenius parameters were similar to those that would be expected for diffusion-controlled reactions.

There has been a report<sup>33</sup> on the temperature dependence of the reactions of OH with  $HCO_3^-$  and  $CO_3^{2-}$ . These reactions have very similar activation energies (21.2 and 23.6 kJ mol<sup>-1</sup>, respectively), and the rate constants are below the diffusion-controlled region. The difference in reactivity between HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> appears to be due to the preexponential factors, which differ by a factor of 100 (6  $\times$  10<sup>12</sup> and 6  $\times$  10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively). These results are similar to our observation that the rate constants of the  $SO_4^-$  reactions appear to be controlled more by the preex-

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ponential factors than by the activation energies.

Finally, there has been a recent report on the reduction of oxidized dithiothreitol by several reducing radicals.<sup>34</sup> They observed that the reactivity was not determined by the reduction potential, that the Arrhenius plots showed distinct curvature, and, in one case, that there was a plateau in the second-order plot. These observations were also explained as due to the formation of an intermediate complex before the electron transfer.

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## Tandem Time of Flight Techniques and Multiphoton Mass Spectrometry: The Ladder Switching in Benzene

### U. Boesl,\* R. Weinkauf, K. Walter, C. Weickhardt, and E. W. Schlag

Institut für Theoretische und Physikalische Chemie, Technische Universität München, Lichtenbergstrasse 4, 8046 Garching, Federal Republic of Germany (Received: June 5, 1990)

The stepwise multiphoton ionization and fragmentation of benzene could be followed employing our new laser tandem mass spectrometer, a combination of a new, high-resolution, short, linear time-of-flight instrument with a reflectron time-of-flight analyzer. The fragmentation tree proposed in a previous theoretical paper of our group was largely verified; also some new details were discovered. Obviously, ladder switching is operative throughout this process. We discuss some generalizations to multiphoton ionization of polyatomic organic molecules.

#### I. Introduction

Resonantly enhanced multiphoton ionization as a useful ionization technique in mass spectrometry of polyatomic molecules is now known since 1978.<sup>1</sup> Multiphoton ionization with tunable lasers provides special information due to its many different features such as very soft ionization,<sup>2,3</sup> species-selective ionization,<sup>4</sup> tunable degree of fragmentation,<sup>3,5</sup> and a large yield of metastable molecular ions.6

In particular, the high degree of fragmentation possible with multiphoton absorption was one of the first astonishing effects in the early studies of multiphoton ionization of molecules. This behavior has been explained by several models.8-11 The "ladder-switching" model<sup>5,7,12</sup> has been proposed and proved by

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1.

previous work of our group to be the most important mechanism for fragmentation during multiphoton excitation of polyatomic organic molecules when employing conventional laser sources (with pulse lengths in the nanosecond range and laser intensities below  $10 \, \mathrm{GW/cm^2}$ ). In this model multiphoton absorption within one ion species (molecular or fragment ion) is interrupted as soon as a dissociation threshold is exceeded. The absorption of photons is then "switched" over to the absorption ladder of its fragment ion

In this work, we investigate the fragmentation behavior of multiphoton ionization by a new technique of laser tandem mass spectrometry<sup>13</sup> employing a unique TOF/TOF technique. This permits mass spectra due to secondary excitation to be recorded as well as metastable mass spectra for each molecular or fragment ion formed in the ion source. Therefore, we are now able to follow step by step the mechanism of the ladder-switching and analyze the whole fragmentation tree in detail. As an example, we chose benzene. For this molecule we already made a theoretical prediction of its multiphoton-induced fragmentation tree in an earlier publication.12

Tandem mass spectrometry experiments with lasers have been performed recently including those by our group directly in the ion source,<sup>5</sup> by Lineberger and co-workers in the field-free drift region,<sup>14</sup> and by Duncan and co-workers in the ion mirror of a reflectron.<sup>15</sup> In our new method, primary as well as secondary mass resolution has been improved considerably over the resolution of earlier experiments. Our new setup includes a double timeof-flight technique. Time-of-flight techniques are distinguished by their high transmission and nowadays also by their good mass resolution.<sup>16-18</sup> The single stages of our instrument are (a) a

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