Time-Resolved REMPI Detection of Methyl Radicals Generated in Laser-Induced Unimolecular Reactions

Ralf Fröchtenicht[†] and Matthias Hartmann*.[‡]

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073 Göttingen, Germany Received: June 5, 1995; In Final Form: August 14, 1995[®]

The specific rate constants for the photofragmentation of four substituted benzene molecules (ethylbenzene, *tert*-butylbenzene, toluene, benzotrifluoride) following pulsed laser excitation at $\lambda = 193$ nm were measured in a molecular beam experiment by monitoring the change of the intensity of the nascent products as a function of time delay between excitation and detection laser pulses. In the case of toluene (C₆H₅CH₃), ethylbenzene (C₆H₅CH₂CH₃), and *tert*-butylbenzene (C₆H₅C(CH₃)₃) a (3+1)REMPI process at $\lambda = 450.8$ nm was used to ionize the CH₃ products, which were detected in a time-of-flight mass spectrometer. Following dissociation of benzotrifluoride (C₆H₅CF₃) the trifluormethyl radical CF₃ was detected at $\lambda = 455$ nm. The measured specific rate constants can be modeled satisfactorily by using the SACM (statistic adiabatic channel model) statistical theory.

I. Introduction

Unimolecular reactions of polyatomic molecules are important intermediate steps in complex reaction processes.¹⁻⁴ Because of the large number of internal degrees of freedom associated with many molecules, an *ab-initio* theoretical treatment of the reaction dynamics often fails for these systems, while they are ideally suited for treatment by statistical models, which are usually successful. To test the accuracy of such calculations, experimental data are needed under well-defined conditions over an extended range of excitation energies.

The goal of the present work is to determine the specific rate constant k, which is the sum of the rate constants k_i for each reaction pathway of the investigated reaction, for a number of polyatomic molecules. This rate constant can be deduced from the temporal evolution of each of the products. We have studied the C-C bond fission of the substituted benzene molecules ethylbenzene, tert-butylbenzene, toluene, and benzotrifluoride following laser excitation at $\lambda = 193$ nm, yielding the methyl radical as one product (CF₃ in the case of benzotrifluoride, respectively). The reaction proceeds via fast internal conversion of the initial electronic excitation to highly vibrationally excited levels of the electronic ground state. Recently, a reaction pathway yielding H-atoms was observed for all four reaction systems.⁵ For tert-butylbenzene, phenyl and tert-butyl products were found.^{6,7} The different pathways, together with their reaction yields, are listed in Table 1.

The paper is organized as follows: the experimental setup is described first. In the following section the measurements of the specific rate constants of the unimolecular reactions are presented. The results are finally compared with experimental work of other groups and with calculations based on the SACM theory.

II. Experimental Technique

A. Experimental Set-Up. The molecular beam apparatus is described in detail in ref 8. Briefly, the molecular beam apparatus consists of two vacuum chambers. The molecules

are expanded with helium as a carrier gas (mixture 1:10) through a pulsed nozzle (General Valve, diameter 1 mm) into the first chamber. The gas lines and nozzle can be heated to 350–400 K to avoid condensation of the molecules entrained in the helium gas flow. After the nozzle expansion the molecules pass a 0.8mm diameter skimmer and reach the detection chamber, where they are detected in a two-stage Whiley–McLaren time-of-flight mass spectrometer (TOF-MS).⁹ A liquid nitrogen cold trap is used to freeze out effectively the background organic compounds in the detection chamber, resulting in a total pressure of 5 × 10^{-8} mbar without and 6 × 10^{-7} mbar with molecular beam.

The specific rate constant of the ethylbenzene photodissociation determined in this molecular beam experiment did not deviate from those measured recently with gas cell experiments.^{10–12} Therefore, we conclude that there is no evidence for vibrational cooling to low temperatures in the beam. Due to the lack of any precise knowledge, we assume that the internal energy of the vibrational excitation of the reactant molecules after the beam expansion almost corresponds to 300 K.

A pulsed excimer laser (Lambda Physik LPX 110), operating at 193 nm, excites the reactant molecules. The laser intensity is attenuated to less than 1 mJ/cm² in order to avoid multiphoton processes. Next, the focused (f = 50 mm) output of an excimer pumped dye laser (Lambda LPD3002) ionizes the reaction products after a given time delay. Dye laser pulse energies of about 20 mJ are used. The laser beams are directed through two MgF₂ windows into the apparatus and cross the molecular beam axis at 45° about 180 mm downstream the nozzle. A delay generator (time jitter ± 1 ns) is used to trigger the pulsed nozzle and the two lasers. The exact time delay between the laser pulses is measured with two photodiodes. In addition, the output of the laser diode for the dye laser is used to trigger a multichannel scaler (CMTE Fast TOF/MCS 7885). The signal pulses from the electron multiplier of the detector are counted and added time-resolved in the different channels of the scaler (dwell time down to 5 ns). For each time delay a complete mass spectrum is recorded.

The TOF-MS was operated both with and without space focus conditions.⁹ The former case with 70 V/cm for the first and 440 V/cm for the second acceleration stage allows the detection of ions generated by both the excimer laser and the dye laser. In the latter operation mode, the spatial extension of the

[†] Present address: BMW AG, D-80788 München, Germany. E-mail: froechtenicht.ralf@bmw.de.

[‡]E-mail: hartmann@msfdl.dnet.gwdg.de.

^{*} Abstract published in Advance ACS Abstracts, October 1, 1995.

 TABLE 1: Reaction Pathways of Ethylbenzene, tert-Butylbenzene, Toluene, and Benzotrifluoride

reactant		reaction pathway ^a		reaction yield ^{b,c}	ref
ethylbenzene	C ₆ H ₅ CH ₂ CH ₃	R _{ETB1}	$C_6H_5CH_2 + CH_3$	0.96 ± 0.04	13
-		R_{ETB2}	$C_8H_9 + H$	0.11 ± 0.04	5
tert-butylbenzene	$C_6H_5C(CH_3)_3$	R _{tBut1}	$C_6H_5C(CH_3)_2 + CH_3$	0.80 ± 0.05	6,7
-		R_{tBut2}	$C_6H_5 + C(CH_3)_3$	0.05 ± 0.02	6, 7
		R _{tBut3}	$C_{10}H_{13} + H$	0.13 ± 0.04	5
toluene	$C_6H_5CH_3$	R_{Tol1}	$C_6H_5CH_2 + H$	0.80 ± 0.05	32
		R _{Tol2}	$C_6H_5 + CH_3$	0.20 ± 0.05	10, 32
benzotrifluoride	$C_6H_5CF_3$	R_{BTF1}	$C_6H_5 + CF_3$	0.96 ± 0.04	6, 7
		R_{BTF2}	$C_7H_4F_3 + H$	$0.026^{+0.01}_{-0.005}$	5

^{*a*} R denotes the different pathways for the reaction of the corresponding molecule. ^{*b*} For an excitation wavelength of 193 nm. ^{*c*} Uncertainties $\pm 1\sigma$.



Figure 1. CH_3^+ yield as a function of the detection laser wavelength after exciting ethylbenzene at 193 nm. The variation of the laser power is shown in the lower part.

excitation laser ionization volume is no longer compensated. Hence the ions created by that laser show up only as a broad, unstructured background. The relative signal strengths of the ions generated by the probe laser are not affected, but their absolute values can be increased by operating the TOF-MS in single-stage mode with 450 V/cm acceleration field strength. Since only the ions generated by the probe laser were of interest, the kinetic measurements were performed without space focus conditions.

B. REMPI Detection of the Methyl/CF₃ Radical. In the past, different detection schemes like nonresonant one-photon ionization, ¹³ (1 + 1), ¹⁴ (2 + 1), ¹⁵⁻¹⁷ and (3 + 1)REMPI^{18,19} were employed to detect the methyl radical. In the present work we use a one-color (3 + 1)REMPI process, which was found experimentally to be more efficient than the one-color (2 + 1)-**REMPI** scheme. In Figure 1 the CH_3^+ signal is shown as a function of the laser wavelength around 450.8 nm. The neutral methyl radicals in the electronic ground state $2p^2A''_2$ are generated by photodissociating ethylbenzene at $\lambda = 193$ nm. The strong peak near 450.8 nm originates from methyl radicals in the vibrational ground state, corresponding to a 0_0^0 transition. The intermediate state populated by the first three photon transition is a $3d^2E''$ Rydberg state, ^{18,19} from which the methyl is ionized by a fourth photon. The smaller peak at 446 nm is due to vibrationally excited methyl radicals, which are generated in the photodissociation reaction. The strong shift in the transition frequency is due to the large difference between the methyl inversion frequencies (v_2) in the electronic ground state and the Rydberg state of $v_2 = 606.453$ cm⁻¹ and $v_2 = 1372$ cm⁻¹, respectively.^{20,21} For both bands, no rotational structure could be resolved. Very similar rotational envelopes were observed by ionizing methyl radicals from the photodissociation of toluene and tert-butylbenzene. This indicates similar rotational temperatures of the methyl products produced in the reaction. A detailed analysis of the rotational contour is not



Figure 2. Possible pathways in the pump-probe study of the reaction system AB, which finally yield A⁺. AB and AB^{*} denote the reactant before and after laser excitation, respectively. A labels the neutral product and A⁺ the ionic one. k(E) is the specific rate constant of the neutral photodissociation and $k_{ion,i}$ are the ones of ionic fragmentations.

yet possible due to the lack of rotational resolution and the unknown spectroscopic constants for the intermediate state.

Neutral CF₃ from the reaction of benzotrifluoride was detected at $\lambda = 455$ nm also by a (3 + 1)REMPI mechanism.²² The intermediate state belongs to a long vibrational progression along the ν_2 out-of-plane bending mode in a 4p Rydberg state.^{22,23} As for CH₃, no rotational analysis could be performed.

C. Evaluation of the Specific Rate Constant. Given a reaction with *j* reaction channels $AB \rightarrow A_i + B_i$, and rate constants k_i , the temporal behavior of the number density of the reactant, N_{AB} , is given by the specific rate constant $k := \sum_i k_i$:

$$N_{AB}(\Delta t) = N_{AB}(\Delta t = 0)e^{-k\Delta t}$$
(1)

The number densities of the products are

$$N_{A_i}(\Delta t) = N_{B_i}(\Delta t) = N_{AB}(\Delta t = 0)\frac{k_i}{k}(1 - e^{-k\Delta t})$$
(2)

Here, Δt denotes the time delay between excitation and detection.

Three major contributions affect the *measured* intensities, namely, (a) the fragmentation of nonresonantly generated ions onto the mass of the reaction product, (b) the time resolution of the laser system, and (c) the drift of neutral fragments out of the detection volume.

(a) Ionic Fragmentation. The excitation and the detection laser pulses can both create ions via nonresonant multiphoton ionization of the reactant molecules, which are detected at the same mass as the neutral fragments. In Figure 2 the possible pathways in the reaction system AB leading to A^+ ions are plotted. Only A^+ ions of channel II refer to the unimolecular reaction of interest, whereas the others result from fragmentation of AB⁺, which can be produced in a number of different ways, I2...I5. The ions formed by the excitation laser (I4) are suppressed in the single-stage operation mode of the TOF-MS (see above). For the following discussion it is assumed that the rate constant of the ionic fragmentation exceeds k: $k_{ion} \gg k$. The validity of this assumption was proven by the observation that the ion peaks were not asymmetrically broadened and did not depend on the acceleration voltages in the TOF-MS. With $k_{ion} \gg k$, process I3 leads to a stepwise decrease of the signal at $\Delta t = 0$, which stays constant for $\Delta t > 0$. In contrast, the A⁺ yield in process I2 is proportional to the number density of AB*, which decays with the rate constant k. Thus one gets two contributions for the signal intensity I_{A^+} , which vary with time delay: an increasing one according to I1 and a decreasing one according to I2. The time evolution of both is governed by k:

$$dI_{A^{-}}/dt = \alpha k_{i} N_{AB^{*}} - \beta k N_{AB^{*}}$$
(3)

$$\Rightarrow I_{A^{-}}(\Delta t) = N_{AB^{*}}(\Delta t = 0) \left[\beta + \frac{\alpha k_{i} - \beta k}{k} (1 - e^{-k\Delta t}) \right] \quad (4)$$

in which α and β are related to the probabilities for the ionization of a neutral product A and for the generation of A⁺ from AB^{*}, respectively. Equation 4 directly shows that the observed temporal behavior remains the same as without including fragmentation effects, which is equivalent to $\beta = 0$. The only differences are the constant offset for $\Delta t \ge 0$ and the reduced amplitude $(\alpha k_i - \beta k)/k$. If $\alpha k_i > \beta k$ the A⁺ signal increases for $\Delta t \ge 0$ and if $\alpha k_i < \beta k$ the A⁺ signal decreases.

The ionic fragmentation to A^+ after a coherent two-photon excitation process (I5) requires the temporal overlap of both laser pulses and is therefore only important for a time range ± 30 ns around $\Delta t = 0$ ns. In this case one would expect to see a Gaussian peak at $\Delta t = 0$ superimposed on the reaction kinetics. This was indeed observed for benzotrifluoride.

(b) Time Resolution of the Laser System. The temporal resolution is limited by the temporal pulse widths τ_L of the excitation and detection lasers of about 10 ns (FWHM) as well as by the temporal jitter between the laser pulses. If the time constant of the reaction, $\tau = 1/k$, is comparable with τ_L , the measured temporal evolution of the product signal $I_{\rm A}$ -(Δt), see eq 4, gives

$$I_{A^{-}}(\Delta t) \propto \int_{-\infty}^{\Delta t} R(s) [1 - e^{-k(\Delta t - s)}] \, ds \tag{5}$$

with $R(s) = \int_{-\infty}^{+\infty} I_{pump}(s + \tau)I_{probe}(\tau) d\tau$ being the crosscorrelation function of pump and probe laser pulses.^{8.24} Assuming Gaussian time profiles for both laser pulses leads to the following relation

$$I_{A^{-}}(\Delta t) = C + I^{\infty} \int_{-\infty}^{\Delta t} e^{-s^{2}/4\sigma^{2}} [1 - e^{-k(\Delta t - s)}] ds$$

= $C + I^{\infty} [\frac{1}{2} (\operatorname{erf}(\frac{\Delta t}{2\sigma}) + 1) - \frac{1}{2} e^{-k(\Delta t - \sigma^{2}k)} \times (\operatorname{erf}(\frac{\Delta t}{2\sigma} - \sigma k) + 1)]$ (6)

with $\sigma = \tau_L/(2\sqrt{2 \ln 2}) \approx 4$ ns being the standard deviation of the Gaussian function. The expression (6) is fitted numerically to the measured spectra by using a Levenberg-Marquardt algorithm.²⁵ The only fit parameter is k, whereas the constant background C and the signal amplitude I^{∞} can usually be determined from an averaging of the data.

(c) Drift of Reaction Products out of the Detection Volume. Another difficulty that is particularly important for slow reactions arises when the products that are generated in a reaction volume, which is defined by the overlap of the excitation laser and the molecular beam, move out of the



Figure 3. Ion yield (\oplus) as a function of the time delay between the excitation of ethylbenzene and the detection laser pulse (a) at mass 15 amu (CH₃⁺) and (b) at mass 13 amu (CH⁺). The solid line in (a) is the result of a fit according to eq 6.

detection laser volume. As soon as the motion of reaction products *out* of the detection volume exceeds the motion *into* it, the product density and consequently the number of detected ions decrease. This leads to the following expression for the ion yield, if one assumes that the excitation volume is a cylinder and the detection volume is a small sphere:

$$I_{A^{-}}(\Delta t) = C + I^{\infty} \left[(1 - e^{-k\Delta t}) - \int_{0}^{\infty} f(v) k \int_{R/v}^{\Delta t} e^{-k(\Delta t - t')} \sqrt{1 - \frac{R^{2}}{(vt')^{2}}} dt' dv \right]$$
(7)

in which f(v) describes the velocity distribution of the products and *R* the radius of the excitation laser.^{8,13} For the sake of simplicity we assume a Maxwellian velocity distribution with a characteristic temperature *T* to fit the data.

III. Results

A. Ethylbenzene. Mass spectra of ethylbenzene were recorded without space focus conditions for $\Delta t = -100$ to 700 ns in order to probe the temporal evolution of the product concentration.

In Figure 3 the signal of (a) CH_3^+ and (b) CH^+ is plotted as a function of Δt . CH_3^+ is the only ion in the mass spectrum that shows a significant dependence on time delay. For other ion masses like CH^+ (cf. Figure 3b) no such behavior could be observed. In the case of CH_3^+ , the initial rise can be fitted with an exponential according to eq 6, shown as a solid line. The explicit inclusion of the laser temporal widths was necessary since the reaction time is comparable to the laser pulse widths. The fit yields a value of $k = (2.2 \pm 0.3) \times 10^7 \text{ s}^{-1}$, while fitting a large number of measurements gives $k = (2.4 \pm 0.4) \times 10^7 \text{ s}^{-1}$.

B. *tert*-**Butylbenzene.** The intensity of (a) CH_3^+ and (b) C_2^+ versus time delay for the reaction of excited *tert*-butylbenzene is shown in Figure 4. Once again, the only prominent temporal increase is found on mass 15 amu, which is attributed to neutral methyl radicals generated in the photodissociation of *tert*-



Figure 4. Ion yield (\bullet) as a function of the time delay between the excitation of *tert*-butylbenzene and the detection laser pulse (a) at mass 15 amu (CH₃⁺) and (b) at mass 24 amu (C₂⁺). The solid line in (a) is the result of a fit according to eq 7.

butylbenzene. This identification is further supported by the signal dependence on the detection laser wavelength (not shown here).⁸ The constant background for $\Delta t < 0$ ns stems from fragmentative ionization of tert-butylbenzene in the dye laser focus (cf. I3 in Figure 2). For $\Delta t > 0$ ns the CH₃⁺ signal rises, reaches a maximum at about 1000 ns, and decreases again with increasing time delay. This signal decrease can be explained by motion of neutral product molecules out of the detection volume. This motion was taken into account by fitting the specific rate constant using eq 7. Here, the constant background C for $\Delta t < 0$ ns was determined from an averaging of the data. The specific rate constant k, the final ion yield I^{∞} , and the effective translational temperature T of the products were used as fit parameters. Since T was very sensitive to the radius R of the cylindrical excitation volume, which was difficult to determine precisely, no values of that parameter are given here. However, the results for fitting k did not depend on varying the value of R within reasonable limits. The result of the fit with a specific rate constant of $k = (4.1 \pm 0.4) \times 10^6 \text{ s}^{-1}$ is shown in Figure 4 as a solid line in addition to the measured data (\bullet) . The mean value of all measurements was found to be $k = (4.4 \pm 0.4) \times 10^6 \text{ s}^{-1}$.

The ion yields for most of the other observed fragments, namely, H⁺, C⁺, CH⁺, C₂H⁺, and C₂H⁺₂, do not show any temporal dependence. The exception is C⁺₂ (see Figure 4b), which shows a sudden increase, followed by a fairly constant signal for positive time delays. A possible explanation for this behavior is that excited *tert*-butylbenzene fragments to C⁺₂ in the dye laser focus more efficiently compared to *tert*-butylbenzene in the ground state (cf. I2/I3 in Figure 2). Note also that ionic fragmentation of product radicals (2-phenylisopropyl, phenyl, *tert*-butyl, or C₁₀H₁₃) could contribute to the signal at mass 24 amu.

C. Toluene. Again, only the CH_3^+ ions from the neutral methyl radical show a significant Δt dependence (Figure 5). In contrast to ethylbenzene and *tert*-butylbenzene, the CH_3^+ signal increases promptly within the time resolution given by the laser pulse profiles. This sudden rise can be explained by fragmenta-



Figure 5. CH_3^+ yield (\bullet) from the photodissociation of toluene as a function of the time delay between excitation and detection laser pulses. The solid line is the result of a fit according to eq 7. The dashed line takes into account the stepwise excitation process discussed in the text.

tion of vibrationally excited toluene in the electronic ground state, which produces CH_3^+ according to process I2 (cf. Figure 2):

$$C_7H_8 \xrightarrow{193nm} C_7H_8^* \xrightarrow{1C} C_7H_8^* * \xrightarrow{450.8nm} C_7H_8^+ \rightarrow CH_3^+ +$$

neutral fragments (8)

The cross section for this process, including 193-nm excitation, is obviously higher than for ground-state toluene being fragmented to CH_3^+ in the dye laser focus. The resulting component in the total signal decreases proportional to the decrease in the number density of excited toluene with the same rate constant k (cf. eq 4).

The portion of the CH_3^+ signal originating from neutral methyl radicals to the whole signal is quite small, so that the specific rate constant is more difficult to determine. However, it was possible to fit the data according to eq 7 by taking the initial rise directly from the data and fitting I^{∞} and k as well as the translational temperature T (cf. eq 7). The data in Figure 5 were fitted with a specific rate constant of $(2.5 \pm 0.2) \times 10^6$ s⁻¹, which was confirmed by further measurements.

D. Benzotrifluoride. Figure 6 summarizes the results of the photodissociation of benzotrifluoride. The time delay dependences of the ion yields on mass (a) 12 amu (C^+), (b) 24 amu (C_2^+) , (c) 31 amu (CF^+) , and (d) 69 amu (CF_3^+) are plotted. On each mass similar kinetics can be observed: the signal is constant for $\Delta t < -20$ ns, rises first, and decays within the temporal overlap of both laser pulses before reaching a constant signal level for $\Delta t > 50$ ns. The initial peak around 20 ns is due to a two-color ionization mechanism to which both laser pulses contribute (cf. I5 in Figure 2). To model this coherent process, a Gaussian curve with a peak halfwidth of 20 ns, which is approximately the sum of both laser pulse widths, was added to the function of eq 6. From a fit of k as well as the height of the Gaussian, specific rate constants of (a) $k = (8 \pm 3) \times 10^7 \text{ s}^{-1}$, (b) $k = (6 \pm 3) \times 10^7 \text{ s}^{-1}$, (c) $k = (7 \pm 3) \times 10^7 \text{ s}^{-1}$ \pm 3) × 10⁷ s⁻¹, and (d) $k = (7 \pm 3) \times 10^7$ s⁻¹ were determined, which agree satisfactorily with each other. The great error in the results for k is apparently due to (a) the influence of the two-color ionization peak and (b) to the fact that the kinetics is on the same time scale as the time resolution of the laser system. The response function of the laser system itself, which corresponds to $k = \infty$, is also shown in Figure 6d for comparison (- - -).

The precursor for CF^+ and CF_3^+ is probably the CF_3 radical, whereas C_2^+ could stem from the phenyl radical, which is



Figure 6. Ion yields (**•**) from the photodissociation of benzotrifluoride on mass (a) 12 amu (C⁻), (b) 24 amu (C⁻₂), (c) 31 amu (CF⁺), and (d) 69 amu (CF⁺₃) as a function of time delay between 193-nm excitation and 455-nm detection laser pulses. The solid lines are the results of fits according to eq 6. The dashed line in (d) indicates the response function of the laser system, which corresponds to $k = \infty$.

TABLE 2: Survey of the Results on the Specific RateConstants Using (3 + 1)REMPI Detection

reactant	E_{ex}^{a} cm ⁻¹	specific rate constant, s ⁻¹	detected product
ethylbenzene	52 960	$\begin{array}{c} (2.4 \pm 0.4) \times 10^{7} \\ (4.4 \pm 0.4) \times 10^{6} \\ (2.5 \pm 0.2) \times 10^{6} \\ (7 \pm 3) \times 10^{7} \end{array}$	CH ₃
<i>tert</i> -butylbenzene	53 580		CH ₃
toluene	52 730		CH ₃
benzotrifluoride	53 000		CF ₃

^a Sum of photon and presumed thermal energy.

nonresonantly ionized at $\lambda = 455$ nm. The kinetics observed for C⁺ can be caused by fragmentation of several products. The agreement of the *k*-values determined on different fragment masses implies that the process of fragmentation is much faster than the reaction of the neutral reactant and does not determine the time evolution of the ionic signals, which should otherwise show different kinetics.

The results for specific rate constants determined in this work are summarized in Table 2.

IV. Discussion and Conclusion

As demonstrated in Figure 7, the specific rate constants for the photodissociation of ethylbenzene determined in this work and those measured by other groups^{7,10-12} agree very well. The SACM calculation for ethylbenzene shown in this figure was performed by using a dissociation energy of $E_0 = 26910$ cm^{-1 26} and a correction factor of F = 0.67, which is independent of the excitation energy. Here and in the following, the SACM parameter α/β was set at a value of 0.5. The factor F is necessary to compensate for errors in the interpolation of the vibrational frequencies (for details of the calculations see refs 6 and 11). The parameters were chosen such that the measured *specific* rate constants as well as the *thermal* rate constants could be fitted simultaneously.^{8,11}

In addition the specific rate constants for the reaction of *tert*butylbenzene, determined in our group with two different



Figure 7. Experimental results of the specific rate constant for the unimolecular reactions of ethylbenzene and *tert*-butylbenzene from ref 5 (\blacksquare), ref 10 (\triangle), ref 11 (\bigcirc), ref 12 (\bigtriangledown) and from the present work (\bullet) are shown together with SACM calculations. For *tert*-butylbenzene the SACM calculations were performed for two dissociation energies of 24 000 cm⁻¹ (-) and 24 500 cm⁻¹ (-).

methods, namely, REMPI detection of methyl (this work) and hydrogen products,⁵ are also presented in Figure 7. As seen, they agree very well with each other, whereas another value for the rate constant, determined via UV absorption of an unknown reaction product,¹¹ differs by a factor of about 2. This discrepancy can be taken into account by changing E_0 from $24\ 000\ \text{cm}^{-1}$ (--) to $24\ 500\ \text{cm}^{-1}$ (--) in the SACM calculations. For the calculations only the reaction pathway R_{tBut1} to 2-phenylisopropyl and methyl was considered, which dominates the reaction at an excitation energy of 53 580 cm^{-1,6,7} Note, that it is not possible to reproduce the results of thermal experiments¹¹ using the above-derived specific rate constants with either $E_0 = 24\ 000\ cm^{-1}$ or $E_0 = 24\ 500\ cm^{-1}$. This might be due to the fact that we have neglected the two additional reaction channels R_{tBut2} to phenyl and *tert*-butyl and R_{tBut3} to C₁₀H₁₃ and H. The branching ratios of these channels are most likely functions of the excitation energy, but exact values for these ratios are presently only known for $E_{Ex} = 53580 \text{ cm}^{-1.5.6}$ and not for thermal excitation. Hence more conclusive statements have to wait for further thermal or laser-induced measurements of rate constants and branching ratios as a function of excitation energy.

The measured specific rate constants for the unimolecular reactions of toluene and benzotrifluoride are displayed in Figure 8 together with SACM calculations. The calculation for toluene only includes the reaction pathway R_{Tol1} to benzyl and H, the quantum yield of which was determined to be about 0.8.^{6,13} A dissociation energy of $E_0 = 31\ 0.80\ \text{cm}^{-126}$ and a correction factor of F = 2.7 were used. For comparison the experimental results of other groups^{11,27–31} are also presented. The calculated $k(E_{ex})$ values agree satisfactorily with all of the experimental data. For benzotrifluoride the SACM calculation was performed with a dissociation energy $E_0 = 36\ 000\ \text{cm}^{-1}$. This value is the same as that used for modeling the reaction pathway R_{Tol2} of toluene to phenyl and methyl. The $k(E_{ex})$ -dependence is in good agreement with the experimental results without using any correction factor.

In conclusion, we have measured and calculated specific rate constants for the unimolecular reactions of substituted benzenes. In the case of ethylbenzene and toluene the experimental values of $k(E_{ex})$, which are extracted from the temporal evolution of primary reaction products (methyl radicals), are in good agreement with those determined by other groups. Furthermore, these results can be modeled by using SACM theory. The



Figure 8. Experimental results of the specific rate constant for the unimolecular reactions of toluene and benzotrifluoride from ref 5 (**■**), refs 11 and 27 (O), ref 28 (\bigtriangledown), refs 29 and 30 (\Box), ref 31 (\triangle) and the present work (\bullet) are shown together with SACM calculations (-).

quantitative agreement between experiment and calculation is within a factor of 3, which is reasonable for reactions of such polyatomics. Experimental values for the dependence of the rate constant on excitation energy are available only for the reaction of toluene. It is gratifying to see that in this case very good agreement can be achieved.

For the photodissociation of tert-butylbenzene and benzotrifluoride, time-resolved detection of primary reaction products was demonstrated for the first time. In both cases statistical theory results in quantitative agreement with the experiment if one assumes reasonable values for the dissociation energy of the reactants. This strongly indicates that in both reactions a statistical randomization of the excitation energy takes place prior to the bond fission. The given interpretation is further supported by the small release of kinetic energy of the reaction products,^{5,6} which is typical for unimolecular reactions starting from highly vibrationally excited levels in the electronic ground state.

By measuring the specific rate constants as a function of the excitation energy for a set of molecules with similar reaction coordinates on the one hand and by improving the accuracy of molecular constants for theoretical calculations on the other hand, it should be possible to achieve even better agreement between experiment and theory, taking into account thermal reactions of the same species.

Acknowledgment. This work was initiated by stimulative and enlightning discussions with Peter Toennies. His support is gratefully acknowledged. We thank Susanne Lange, Thomas Rech, and Jürgen Troe, University of Göttingen, for providing

the SACM program as well as for many discussions and important suggestions and Horst-Günther Rubahn for carefully reading the manuscript and his valuable comments. Partial financial support was provided by the DFG Sonderforschungsbereich 93 "Photochemie mit Lasern".

References and Notes

(1) Ferguson, E. E.; Arnold, F. Acc. Chem. Res. 1981, 14, 327.

(2) Golden, D. M. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling; Eval. # 11; Nat. Aeron. Space Adm. Jet Prop. Lab.; Pasadena, 1994.

(3) Dove, J. E.; Warnatz, J. Ber. Bunsenges. Phys. Chem. 1993, 87, 1040.

(4) Schroeder, J.; Troe, J. Annu. Rev. Phys. Chem. 1987, 38, 163.

(5) Fröchtenicht, R.; Hartmann, M. To be submitted to Chem. Phys. Lett.

(6) Fröchtenicht, R. Untersuchung der Dynamik von laserinduzierten Reaktionen substituierter Benzole in Molekularstrahl; report 26/1992; Max-Planck-Institut für Strömungsforschung, Göttingen, 1992.

(7) Fröchtenicht, R. To be submitted to J. Phys. Chem.

(8) Hartmann, M. Untersuchung unimolekularer Zerfälle im Molekularstrahl mittels Multiphotonenionisation; report 103/1994; Max-Planck-Institut für Strömungsforschung, Göttingen, 1994.

(9) Wiley, W. C.; McLaren, I. C. Rev. Sci. Instrum. 1954, 26, 1150.

(10) Luther, K.; Troe, J.; Weitzel, K.-M. J. Phys. Chem. 1990, 94, 6317.

(11) Brand, U.; Hippler, H.; Lindemann, L.; Troe, J. J. Phys. Chem. 1990, 94, 6305

- (12) Nakashima, N.; Yoshihara, K. J. Phys. Chem. 1989, 93, 7763
- (13) Rech, Th. Ph.D. Thesis, University of Göttingen; Göttingen, 1992.

(14) Rottke, H.; Danon, J.; Zacharias, H.; Welge, K. H. J. Chem. Phys. 1982. 76. 2399.

- (15) Hudgens, J. W.; DiGiuseppe, T. G.; Lin, M. C. J. Chem. Phys. 1982. 76. 3338
- (16) Hudgens, J. W.; DiGiuseppe, T. G.; Lin, M. C. J. Chem. Phys. 1983, 79, 571.
- (17) Parker, D. H.; Chandler, D. W.; Janssen, M.; Wang, Z. W. J. Chem. Phys. 1989, 90, 60.
- (18) Hudgens, J. W.; DiGiuseppe, T. G.; Lin, M. C. Chem. Phys. Lett. 1981, 82, 267.
- (19) Hudgens, J. W.; DiGiuseppe, T. G.; Lin, M. C. J. Phys. Chem. 1982. 86. 36.
- (20) Hirota, E.; Yamada, C.; Kawaguchim, K. J. Chem. Phys. 1981, 75. 5256.
 - (21) DeFrees, D. J.; McLean, A. D. J. Chem. Phys. 1985, 82, 333.
- (22) Duignan, M. T.; Hudgens, J. W.; Wyatt, J. R. J. Phys. Chem. 1982, 86, 4156.
- (23) Washida, N.; Suto, M. J. Chem. Phys. 1983, 78, 1025.
- (24) Ionov, S.; Böhmer, E.; Wen, Y.; Segall, J.; Jaques, C.; Valachovic, L.; Wittig, C. J. Chem. Soc. Faraday Trans. 1993, 89, 1419.
 - (25) Marquardt, D. W. J. Soc. Ind. Appl. Math. 1963, 11, 431.
- (26) Hippler, H.; Troe, J. J. Phys. Chem. 1990, 94, 3803.
- (27) Hippler, H.; Schubert, V.; Troe, J.; Wendelken, H. J. Chem. Phys. Lett. 1981, 84, 253.
- (28) Kajii, Y.; Obi, K.; Tanaka, I.; Ikeda, N.; Nakashima, N.; Yoshihara, K. J. Chem. Phys. 1987, 86, 6115.
 - (29) Park, J.; Bersohn, R.; Oref, I. J. Chem. Phys. 1990, 93, 5700. (30) Tsukiyama, K.; Bersohn, R. J. Chem. Phys. 1987, 86, 745.
- (31) Shimada, T.; Ojima, Y.; Nakashima, N.; Izawa, Y.; Yamanaka, C. J. Phys. Chem. 1992, 96, 6298.
- (32) Fröchtenicht, R. J. Chem. Phys. 1995, 102, 4850.

JP951509X