Formation of HO₂ Radicals from the 248 nm Two-Photon Excitation of Different Aromatic Hydrocarbons in the Presence of O₂

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ABSTRACT: The excitation energy dependence of HO₂ radical formation from the 248 nm irradiation of four different aromatic hydrocarbons (benzene, toluene, *o*-xylene, and mesitylene) in the presence of O₂ has been studied. HO₂ has been monitored at 6638.20 cm⁻¹ by cw-CRDS, and the formation of a short-lived, unidentified species, showing broad-band absorption around the HO₂ absorption line, has been observed. For all four hydrocarbons, the same HO₂ formation pattern has been observed: HO₂ is formed immediately on our time scale after the excitation pulse, followed by a formation of more HO₂ on a much longer time scale. Taking into account the absorption of the short-lived species, the yields of both types of HO₂ radicals are in agreement with a formation following 2-photon absorption by the aromatic hydrocarbons. The yields do not much depend on the nature of the aromatic hydrocarbon. For practical use in past and future experiments on



aromatic hydrocarbons, an empirical value is given, allowing the estimation of the total concentration of HO₂ radicals formed at 40 Torr He in the presence of around $[O_2] = 1 \times 10^{17} \text{cm}^{-3}$ as a function of the 248 nm excitation energy: $[HO_2]/[\text{aromatic hydrocarbon}] \approx 2 \times 10^{-6} \times E^2$ (with *E* in mJ cm⁻²).

INTRODUCTION

Aromatic hydrocarbons, in particular the so-called BTX (benzene, toluene, xylene), are an important class of volatile organic compounds emitted to the atmosphere from vehicle emissions, from various industrial processes, and from the use of organic solvents.¹ Their presence in the atmosphere was first detected by Lonneman et al.,² and a large number of laboratory, chamber, and field studies has been devoted to unraveling the oxidation mechanism of this class of hydrocarbons.³⁻¹⁰ Aromatic hydrocarbons also thought to contribute significantly to the photochemical formation of the tropospheric ozone even though the detailed mechanism of the tropospheric degradation of aromatic hydrocarbons is still controversially discussed.¹¹⁻¹⁴

Using the technique of laser photolysis coupled to a detection of HO_2 radicals by cw-CRDS we have shown in an earlier work that HO_2 radicals are formed after 248 nm irradiation of benzene in the presence of O_2 .¹⁵

 $C_6H_6 + h\nu_{248nm} + O_2 \rightarrow HO_2 + products$

From the rate of formation it could be concluded that the HO_2 radicals do not originate from a reaction of H-atoms with O_2 but must rather be the product of a very fast reaction of some kind of excited species with O_2 . Even though this finding had no direct impact on the tropospheric degradation of aromatic hydrocarbons, it was nevertheless interesting because 248 nm is a commonly used wavelength to initiate chemical reactions in laboratory studies. Hence, an unknown and unexpected side reaction such as the observed HO_2 formation can possibly influence the interpretation of experimental data

and leads to wrong conclusions. Following this discovery of the HO₂ formation, Kovacs and co-workers¹⁶ investigated the formation of H-atoms following the 248 nm irradiation of benzene and toluene and concluded that the observed H-atoms stem from a 2-photon process. They suggested that the HO_2 radicals observed in our experiments ¹⁵ might as well originate from a fast reaction of O2 with byproduct of the H-atoms, i.e from a 2-photon process. Following the publication of Kovacs and co-workers, we have reinvestigated the energy dependence of reaction 1 using higher excitation energies¹⁷ than in the earlier study, where experiments had been performed only at one low excitation energy (13 mJ cm^{-2}) .¹⁵ Doing so, we observed that with increasing excitation energy the formation of a secondary HO₂ becomes visible on a much longer time scale compared to the first, prompt HO₂. The rate of formation of this secondary HO₂ was strongly pressure dependent and in reasonable agreement with the rate constant for the reaction of H-atoms with O₂. The energy dependence of the yield of the first, prompt HO₂ radical showed a linear behavior, whereas the energy dependence of the yield of the secondary HO₂ radical was in agreement with a 2-photon process.

Following the work on benzene,¹⁷ we have continued to investigate the HO_2 formation yields of other aromatic

Special Issue: A. R. Ravishankara Festschrift

Received:November 30, 2011Revised:March 30, 2012Published:April 13, 2012



Figure 1. Schematic diagram of the experimental setup. APD = avalanche photodiode, DL = diode laser, OI = optical isolator, BS = beam splitter, AOM = acousto-optical modulator, M = mirror, and L = lens.

hydrocarbons (toluene, o-xylene, and mesitylene). During these experiments, a transient broad-band absorption following the photolysis pulse has been observed in the wavelength range used for the HO₂ dectection (around 1506 nm). This shortlived absorption had been overlooked during the earlier C₆H₆ experiments, because it is much less intense than for the alkylated aromatic hydrocarbons. Considering this transient absorption as a time-dependent baseline for the HO₂ measurements, it appears that both primary and secondary HO₂ radicals stem from 2-photon absorption. In this work we present the yield of HO₂ radical formation, obtained by taking into account the transient absorption, following 248 nm excitation for 4 different aromatic hydrocarbons: benzene, toluene, o-xylene, and mesitylene. The yield of HO₂ radicals has been parametrized to provide a simple tool for an estimation of the impact of this process in past or future laboratory studies.

EXPERIMENTAL SECTION

Laser photolysis coupled to the detection of HO_2 radicals by continuous wave cavity ring-down spectroscopy (cw-CRDS) has been used in the present work. The principle of this setup has been published earlier,^{18,19} and some very recent improvements on the data acquisition system can be found in Votava et al.²⁰ The setup consists of the photolysis cell, the photolysis laser, the cw-CRDS system, and the LIF system (which has not been used for this work). The photolysis reactor is a three axis stainless steel cell, internally coated with Teflon, with one long axis (78 cm) and two short axes. Photolysis is achieved along the longest axis using an excimer laser (Lambda Physik LPX 202i) operating at 248 nm and a repetition rate of 0.2 Hz. The cw-CRDS absorption path is installed at a small angle with respect to the photolysis path, leading to an overlap of 37 cm between photolyzed volume and cw-CRDS absorption path. A schematic view of the experimental setup is given in Figure 1.

cw-CRDS was used to monitor the time-resolved kinetics of HO₂ radicals. All HO₂ concentration—time profiles have been measured at peak of the most intense absorption line in the $2\nu_1$ band²¹ at 6638.20 cm⁻¹. Ring-down times were converted to HO₂ concentrations using the following equation:

$$[HO_2]_t = \frac{R_L}{c \times \sigma} \left(\frac{1}{\tau_t} - \frac{1}{\tau_0} \right)$$
(1)

where σ is the absorption cross section, R_L is the ratio between the cavity length L, i.e., the distance between the two cavity mirrors, and the length L_A over which the absorber is present (in our case the overlap of photolysis beam and absorption path), c is the speed of light, and τ_t and τ_0 are the ring-down times in the presence and absence of HO₂, respectively. Throughout the work we have used an absorption cross section of $\sigma_{6638.20 \text{cm}^{-1}} = 2.96 \times 10^{-19} \text{ cm}^{-2}$ for HO₂, additional broadening through added O₂ has not been taken into account, because it leads to a decrease of the absorption cross section of less than 2% for the highest O₂ concentration.^{22,23}

All experiments were carried out at 295 K. Pressure within the cell was kept constant by a pressure controller (Leybold MR16) and was monitored with a 0–1000 Torr Baratron (MKS). All experiments have been performed at total pressures of around 40 Torr Helium. Different gases were introduced to the reactor using calibrated mass flow controllers (Tylan FC260). Typical total gas flows were 300 cm³ min⁻¹, leading to a flow velocity of 3 cm/s within the reactor. Gases (He 6.0, O₂ 4.5: both Praxair) were used without further purification, aromatic hydrocarbons were prepared as diluted gas mixtures in

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glass balloons. Before introducing the hydrocarbons (all Aldrich with following purities: benzene >99%, toluene >99.5%, *o*-xylene and mesitylene >98%), the liquid reservoir was degassed by pump and freeze cycle.

RESULTS AND DISCUSSIONS

Correction of HO₂ **Concentration for Absorption by a Short-Lived Species.** Following our earlier work on the formation of HO₂ radicals after 248 nm excitation of benzene, we have performed additional experiments for a series of alkylated aromatic hydrocarbons: toluene, *o*-xylene, and mesitylene. Indeed, aromatic hydrocarbons present absorption features in the UV region, attributed to the S₁ \leftarrow S₀ electronic transition, reaching down to wavelengths below 248 nm for many of them. Absorption cross sections at 248 nm have been published for some aromatic hydrocarbons by Trost et al.²⁴ as well as more recently by Fally et al.,²⁵ and it can be noticed that the cross sections for the aromatic hydrocarbons investigated in this work are on the same order of magnitude: benzene, 2.3 × 10^{-19} cm²; toluene, 1.8×10^{-19} cm²; *o*-xylene, 3.3×10^{-19} cm²; mesitylene, 2.5×10^{-19} cm² (private communication U. Platt).

In the experiments with toluene, *o*-xylene, and mesitylene, curious and very different signals compared to the benzene experiments (Figures 2a) were observed at low photolysis energy: no secondary HO₂ was observed anymore, but the HO₂



Figure 2. (a) Plot of $[HO_2]$ against time at different energies. The open symbols and dashed lines represent the HO₂ concentrations profiles without baseline correction; full symbols and solid lines represent the HO₂ concentration profiles after the baseline correction. The benzene and O₂ concentrations used were 3.35×10^{15} and 1.0×10^{17} cm⁻³, respectively. The total pressure was 40 Torr He. (b) Laser energy dependence of HO₂ concentration obtained from the photolysis of a mixture of [*o*-xylene] = 3.0×10^{14} cm⁻³ and [O₂] = 9×10^{16} cm⁻³, showing an unusual behavior at the lower energies.

concentration decreased instead at low photolysis energies, as can be seen in Figure 2b for *o*-xylene, where this effect is particularly strong. It turned out that a short-lived species, absorbing around the HO₂ absorption line at 6638.20 cm⁻¹, is formed after 248 nm excitation of aromatic hydrocarbons, inducing thus an error in the calculation of the HO₂ concentration, as explained further down. Figure 3 illustrates for



Figure 3. Ring-down times obtained from the photolysis of [*o*-xylene] = 3.1×10^{14} cm⁻³ and $[O_2] = 1.0 \times 10^{17}$ cm⁻³, $E_{248nm} = 10$ (circles) and 35 (square) mJ cm⁻² at two different wavelengths: online (filled symbols, 6638.20 cm⁻¹) and offline (open symbols, 6638.30 cm⁻¹).

o-xylene the time-resolved evolution of the ring-down time at two different wavelengths: 6638.20 cm^{-1} (filled symbols, center of HO₂ absorption line) and 6638.30 cm^{-1} (open symbols, off any HO₂ absorption) for two different photolysis energies. Please note that the example in Figure 3 has been chosen for illustration and is one of the most extreme cases, the amplitude of the transient absorption was much less in most of the experiments. In our earlier work^{15,17} the ring-down times have been converted to HO₂ concentrations using eq 1, with τ_0 being the average of all ring-down times occurring before the photolysis pulse. However, the presence of a "time-resolved baseline" such as shown by the open symbols in Figure 3 does not allow for such a simple treatment of the raw data but needs to be taken into account for the conversion of individual ring-down times into HO₂ concentrations.

Therefore, we have first investigated if the transient absorption is due to a broad-band absorbing species or if the absorption is structured. In the first case, correction would be easy by measuring the baseline off any HO₂ absorption line; in the second case, i.e., a structured absorption spectrum of the transient species, the task would be much more difficult and unreliable. For this purpose, we have measured the absorption spectrum around the HO₂ absorption line in a similar way as recently explained in detail for the measurement of the HONO absorption spectrum:²⁶ the result is shown in Figure 4. Each data point in this spectrum is obtained from one time-resolved measurement such as shown in the inset: the data points of the upper line (a) represent the average of all ring-down times having occurred before the laser pulse, data points on the middle line (b) represent the average of all ring-down times having occurred at delays between 1 and 50 ms after the photolysis pulse, and data points on the lower line (c) are obtained by averaging all ring-down times having occurred at delays up to 1 ms after the photolysis pulse. The decay time of the unknown, absorbing species is short (less than 1 ms) compared to the



Wavenumber / cm⁻¹

Figure 4. Spectrum measured around the HO₂ absorption line: $[o-xylene] = 3.2 \times 10^{14} \text{ cm}^{-3}, [O_2] = 1.0 \times 10^{17} \text{ cm}^{-3}$, photolysis energy 30 mJ cm⁻². The inset shows an example (6638.43 cm⁻¹) of how the spectrum has been obtained from time-resolved measurements. (a) is the average of all ring-down times before the photolysis pulse, (b) is the average of ring-down times at delays 0-1 ms after photolysis pulse, (c) is the average of ring-down times at delays 1-50 ms, (d) = (c) - (b) (right-hand scale). The dashed, vertical line indicates the wavenumber, where background measurements have been performed for all offline measurements.

lifetime of HO₂ under our conditions (several 10 ms; Figure 2). Therefore, line (b) does not contain any absorption from the unknown species; only the HO₂ spectrum is obtained. The lower line (c) on the other hand contains the sum of the absorption both from the unknown species and from HO₂. The difference between lines (b) and (c) corresponds to the spectrum of the unidentified species and is shown as line (d) of the graph (right y-axis applies): it can be seen that the difference between both spectra is constant ($\approx 1.5 \ \mu s$) over the entire wavelength range, except for a slight maximum around the HO₂ absorption lines at 6638.11 and 6638.20 cm⁻¹. This is probably due to a slightly higher, average HO₂ concentration in the time window 0-1 ms compared to the HO₂ concentration in the time window 1-50 ms. From this result we have decided that it is reasonable to use the time-resolved evolution of the ring-down time, measured at 6638.30 cm⁻¹ (dashed, vertical line in Figure 4), as baseline for converting the ring-down times obtained at 6638.20 cm⁻¹ into HO₂ concentrations.

This baseline correction has been carried out by a Labview program as follows: offline signals such as shown in Figure 3 have been fitted to an exponential function:

$$\tau_t = \tau_{t=0} + (\tau_{t=\infty} - \tau_{t=0}) \times (1 - e^{-k \times t})$$
(2)

where k is the decay constant of the short-lived, absorbing species, $\tau_{t=0}$ is the ring-down time just after the photolysis pulse, $\tau_{t=\infty}$ is the ring-down time at very long delays (identical to the conventional τ_0 , i.e., the ring-down time just before the laser pulse). In practice, the value of $\tau_{t=\infty}$ has first been calculated from the average of all data points before the photolysis pulse and is then fixed as a constant in the baseline fit. In Figure 3 it can be seen that the ring-down times before the laser pulse are slightly lower for the online measurements compared to the offline measurements (0.05 μ s in the example of Figure 3). This shift is due to an absorption of the aromatic hydrocarbon, slightly different for the online and offline wavelengths: to correct for this absorption, the Labview program calculated this difference and deducted it from the $au_{t=\infty}$ value. These

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individual ring-down time au_0 for each individual ring-down event, to be used subsequently in eq 1. The impact on such a baseline correction on the HO₂ concentration-time profiles is shown in Figure 5 for o-xylene, using two different photolysis



Figure 5. HO₂ concentration time profiles from $[o-xylene] = 2.54 \times$ 10^{14} cm^{-3} , $[O_2] = 1.0 \times 10^{17} \text{ cm}^{-3}$ for two different photolysis energies. Open symbols are obtained by using constant τ_0 in eq 1; filled symbols are obtained by taking into account the absorption of the unknown species for the calculation of τ_0 using eq 2.

energies. The open symbols represent HO₂ concentrationtime profiles calculated the usual way, i.e., using the same τ_0 in eq 1 for all ring-down events (obtained from the average of all ring-down events before the photolysis pulse), whereas the HO₂ concentration-time profiles represented by the filled symbols have been obtained by calculating an individual τ_0 for each ring-down event. It can be seen that now the curious signal at low photolysis energy is not curious anymore but, rather, has the typical shape. Again, these two signals are extreme cases and have been chosen for illustration. In Figure 2a it can be seen that the effect is much smaller for benzene: open symbols and dashed lines show uncorrected HO₂ concentration-time profiles, filled symbols and full lines represent the baseline corrected profiles.

Energy Dependence of HO₂ Formation for Different Aromatic Hydrocarbons. Having realized that the absorption of the short-lived species has to be taken into account as "time-dependent baseline" and has thus an impact on the yield of the HO₂ formation, we have repeated all experiments, including benzene, now carefully measuring an offline signal before or after each online measurement. Though the impact was most important for o-xylene, it had also some consequences for the reinterpretation of the benzene experiments, already published recently.¹⁷ Systematic analysis of all baseline signals (see further down) showed that the intensity of the unknown absorption α , i.e., $(\tau_{t=\infty} - \tau_{t=0})$ in eq 2, rapidly approached saturation with increasing photolysis energy (see the small increase from 10 to 35 mJ cm^{-1} in Figure 3 and the dependence of α on photolysis energy, Figure 10). As a consequence, the baseline correction changes the HO₂ concentration (decreasing the initial and increasing the secondary) roughly by the same absolute number, independent of the photolysis energies. In Figure 6 are shown the results for the benzene experiment from Figure 2a with and without baseline correction: the HO₂ concentration-time profiles in Figure 2a have been fitted (dashed lines for uncorrected, full



Figure 6. Plot of $[HO_2]$ against photolysis energy with and without correction obtained for benzene. Experiments were carried out with $[C_6H_6] = 3.35 \times 10^{15} \text{ cm}^{-3}$ in the presence of $[O_2] = 1.0 \times 10^{17} \text{ cm}^{-3}$. Open symbols/dashed lines: without baseline correction. Filled symbols, full lines: with baseline correction. Error bars represent the statistical errors only (95% confidence interval).

lines for corrected profiles) to the following equation (for details see Jain et al.¹⁷):

$$[HO_2] = [HO_2]_{ini} \times e^{-k_{slow}t} + [HO_2]_{sec}$$
$$\times \frac{k_{fast}}{k_{slow} - k_{fast}} (e^{-k_{fast}t} - e^{-k_{slow}t})$$
(3)

From these fits, the initial, prompt HO₂ concentration $[HO_2]_{ini}$ can be obtained as the intercept whereas $[HO_2]_{sec}$ is the concentration of the HO₂ radicals, formed in a slow reaction on a longer time scale. Although the impact on the secondary HO_2 is very minor, the yield of the initial HO_2 radical experiences a fundamental change: without baseline correction, the increase of the yield with photolysis energy seems linear and is thus in agreement with a 1-photon process, whereas after baseline correction this yield is not anymore linear with energy. This energy dependence study has been extended to three other aromatic compounds: toluene, o-xylene, and mesitylene. The results for all hydrocarbons are in good agreement with a two photon processes being at the origin of both HO₂ radicals, initial and secondary: the results are summarized in Figure 7 with full lines showing a forced square-fit for the yields of both initial and secondary HO₂ to the equation:

$$[HO_2] = a \times E^2 \tag{4}$$

with *E* being the photolysis energy in mJ cm⁻².

Table 1 lists the parameters *a* from these fits for both the initial and secondary HO₂ yields for six different series of experiments. To compare the results by accounting for the different initial aromatic hydrocarbon concentration, the *a* values have been divided by this concentration. Except for the only series with a low O₂ concentration ($[O_2] = 1.12 \times 10^{16}$ cm⁻³), the HO₂ yields do not seem to be strongly dependent on the nature of the aromatic hydrocarbon. We propose for



Figure 7. Results of energy dependence studies of all four different aromatic compounds in a log–log plot. Full lines represent square dependence of HO₂ yields. Error bars in all figures represent the statistical errors only (95% confidence interval).

Table 1. Factor <i>a</i> from Eq 4 per Molecule of Aromatic Hydrocarbon for the Initial and Seco	ary HO ₂ "
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compound	initial HO ₂ $(a/[aromatic])/10^{-6}$	secondary HO_2 ($a/[aromatic])/10^{-6}$	no. of measurements	[aromatic]/10 ¹⁵ cm ⁻³	$[O_2]/10^{17} \text{ cm}^{-3}$
benzene	0.48 ± 0.05	1.3 ± 0.06	4	3.3	1.0
benzene	0.58 ± 0.06	1.8 ± 0.08	6	0.65	1.3
benzene	0.28 ± 0.03	0.73 ± 0.03	6	3.4	0.112
toluene	0.48 ± 0.05	2.0 ± 0.3	5	1.0	1.0
o-xylene	0.45 ± 0.07	2.0 ± 0.3	7	0.315	1.0
mesitylene	0.36 ± 0.05	1.3 ± 0.3	5	1.0	1.15
average	0.47	1.68			

^aValues have been obtained by fitting the experimental data to eq 4. Error represents 95% confidence interval.

practical purposes to estimate the concentration of HO_2 radicals, formed per molecule of aromatic hydrocarbon excited at 248 nm, for any aromatic hydrocarbon [A] using the average value of all series in Table 1 (except low O_2):

$$[HO_2]/[A] = ([HO_2]_{ini} + [HO_2]_{sec})/[A]$$

= (0.47 + 1.68) × 10⁻⁶ × E² ([5])

with *E* being the energy of the 248 nm laser pulse in mJ cm⁻². This empiric equation can be used to estimate the concentration of HO₂ radicals that has been generated in former experiments using the 248 nm photolysis of H₂O₂ as OH precursor for studying the OH-initiated degradation of aromatic hydrocarbons: Bohn and Zetzsch⁵ used a laser fluence of $E = 1.5 \text{ mJ cm}^{-2}$ and initial concentrations of $[C_6H_6] \approx 5 \times$ 10^{15} molecules cm⁻³, leading to the formation of unwanted [HO₂] = 2.9×10^{10} cm⁻³. To evaluate the possible impact on the reaction mechanism, this concentration needs be compared with the expected radical concentration from H₂O₂ photolysis: their typical [OH] concentration has been 1.7×10^{11} cm⁻³ obtained from the simultaneous photolysis of 5×10^{14} cm⁻³ H₂O₂ under the same conditions. Therefore, the unwanted HO₂ concentration is close to 20% of the total radical concentration. The situation is much worse for the experimental conditions used in the work of Johnson et al.,8 where much higher photolysis energies $(30-40 \text{ mJ cm}^{-2})$ were employed. The calculated unexpected $[HO_2]$ is 2 × 10¹³ and 3.5 × 10¹³ cm⁻³ for 30 and 40 mJ cm⁻², respectively, for their highest C₆H₆ concentration, to be compared to their typical initial OH concentration of 3.5×10^{13} and 4.6×10^{13} cm⁻³: under these conditions, the concentration of the parasite HO₂ radicals comes close to the concentration of the expected OH radicals. A similar situation can be found in the work of Johnson et al.⁶ on the measurement of the UV-absorption spectrum of methylsubstituted hydroxylcyclohexadienyl radicals. Taking into account the fact that each HO₂ radical is accompanied by at least one other radical, the concentration of unwanted (and unaccounted) radicals is higher than the known radical concentration.

It has already been stated in our earlier work¹⁷ that the decay rate of the HO₂ radicals depended on the photolysis energy, i.e., the absolute radical concentration. We have confirmed this behavior for all aromatic hydrocarbons, as can be seen in Figure 8: the exponential decay rates such as obtained from the fits to eq 3 over the first 5 ms are plotted against the sum of primary and secondary HO₂ radicals, serving as proxy for the accompanying RO₂ radicals. The obtained rate constants for benzene, toluene, and mesitylene are similar ((1.5 ± 0.1), (1.2 ± 0.2), and (2.3 ± 0.2) × 10⁻¹¹ cm³ s⁻¹), only the rate for



Figure 8. Decay rate k_{slow} of HO₂ radicals as a function of sum of $[HO_2]_{ini} + [HO_2]_{sec}$ for different aromatic compounds. Error bars represent the statistical errors only.

o-xylene is much faster: $(1.1 \pm 0.1) \times 10^{-10}$ cm³ s⁻¹, too fast for classical HO₂ + RO₂ reactions.

The origin of both types of HO₂ radicals is not clear. The prompt HO₂ is necessarily formed from a very fast reaction with O_{2} , because we are not able to resolve the increase of this prompt HO_2 on our time scale, even at the lowest O_2 concentrations. The origin of the secondary HO₂ has been investigated in some detail in our earlier work on benzene:¹⁷ we concluded that the reaction of H-atoms with O₂ is at least partly responsible, because we observed a strong pressure dependence of the rate of formation ((2.1 \pm 0.2) and (8.7 \pm 1.2) \times 10⁻¹⁴ cm³ s⁻¹ at 22 and 102 Torr, respectively). H-atoms had also been observed as product of 2-photon absorption by Kovacs et al.,¹⁶ however, at a very low yield not in line with our observations. In this study, we have measured the rate of formation as a function of the O2 concentration for different aromatic hydrocarbons at 40 Torr He. The obtained dependence of k_{fast} as a function of O₂ is shown in Figure 9: it can be seen that the formation rate for the secondary HO₂ radical is not dependent on the structure of the aromatic hydrocarbon. Also, the initial concentration or the photolysis energy does not have a noticeable impact on the formation rate. The rate constant, obtained from a linear regression to all data points, is $(4.7 \pm 0.4) \times 10^{-14}$ cm³ s⁻¹. Again, this rate is slightly higher than the expected value for the reaction of H-atoms with O₂ from literature data²⁷ but is in excellent agreement with the pressure-dependent rate from our earlier work (interpolation to 40 Torr of Jain et al.¹⁷ leads to 4.9×10^{-14} cm³ s⁻¹ prior to correction for the role of O_2 as a third body in the H + O_2 reaction; see ref 17 for details).



Figure 9. Dependence of kfast as obtained from eq 3 for different aromatic hydrocarbons. Total pressure was 40 Torr for all experiments.

The results from this work, now confirming two earlier aromatic hydrocarbon studies on the unexpected formation of HO₂ radicals after the 248 nm excitation of benzene,^{15,17} might have some impact on the decay kinetics measured in the abovementioned studies.^{4–8,28,29} This could especially have an impact on the determination of rate constants for radical–radical reactions such as the self-reaction of aromatic–OH adducts or the reaction of aromatic–OH adduct with HO₂ radicals. In his work on the formation of peroxy radicals from the toluene– OH adduct with O₂, Bohn⁴ had to consider a very fast rate constant of 1.8×10^{-10} cm³ s⁻¹ for the reaction of the toluene– OH adduct with HO₂ to correctly reproduce his experimental results. Therefore, the presence of even low, unaccounted concentrations of HO₂ radicals might have an impact on the observed decays and a re-evaluation of former experiments might be interesting.

Characterization of the Absorption from the Short-Lived Species. With the wish to better identify the unknown absorbing species, we have evaluated the two parameters, *k* and α , obtained from the baseline fits to eq 2, as a function of different parameters. The intensity α has been calculated using eq 1 with $\sigma = 1$, $\tau_t = (\tau_{t=\infty} - \tau_{t=0})$, and $\tau_0 = \tau_{t=\infty}$. In Figure 10 the intensity α (for comparison divided by the initial aromatic



Figure 10. Absorption of the unknown reactive intermediate absorption measured at 6638.30 cm⁻¹ (right *y*-axis) and decay rate of the unknown reactive intermediate (left *y*-axis) as a function of photolysis energy. Initial hydrocarbon concentrations: 0.3, 1.0, 1.0, and 3.2×10^{15} cm⁻³ for *o*-xylene, toluene, mesitylene, and benzene, respectively.

hydrocarbon concentration) is plotted as a function of the excitation energy for all four hydrocarbons. It can be seen what has already been mentioned earlier: the absorption is very strong for o-xylene, whereas it is minor for benzene. What can also be seen from Figure 10 is that the intensity rapidly saturates with increasing excitation energy, which has also been mentioned already and can be seen in Figure 3. From this behavior we suggest that the absorbing species originates from the absorption of one photon: the absorption cross section for the second photon at 248 nm is much higher than for the first photon;¹⁶ therefore, the reservoir of 1-photon excited aromatic hydrocarbons will be more and more depleted with increasing excitation energy. A simple model considering a sequential absorption of both photons and a $\sigma_{2\text{-photon}} = 2 \times 10^{-17} \text{ cm}^2$ shows that at 10 mJ cm⁻² 78% of the species having initially absorbed 1-photon are still available, whereas at 40 mJ cm⁻² this theoretical rate falls to 37%. This simple model thus reproduces very well the observations made in this study (Figure 10). In Figure 10 (upper part) it can be seen that the decay rate slightly increases with the photolysis energy, indicating a very fast reaction with other photolysis products: the rate constant of this reaction is close to collision frequency, when considering formation of one active species per absorbed photon. Figure 11 shows the dependence of α with the initial



Figure 11. Absorption of the unknown reactive intermediate absorption for toluene and *o*-xylene concentrations (right *y*-axis) and decay rate of the unknown reactive intermediate (left *y*-axis) as a function of initial concentration, photolysis energy was 35 and 62 mJ cm⁻² for *o*-xylene and toluene, respectively.

aromatic hydrocarbon concentration: a rapid saturation of the intensity is visible with increasing concentration, being visible already at the lowest hydrocarbon concentration (the signal decreases to zero very shortly after shutting off the hydrocarbon flow). Figure 11 shows in the upper part that the decay rate k increases linearly as a function of the aromatic hydrocarbon concentration: the rate constant for the quenching process, obtained for toluene and o-xylene is 4.6 and 7.2 \times 10^{-12} cm³ s⁻¹, respectively. These values are on the order of magnitude for the rate constant that has been found for the quenching of triplet benzene with ground state benzene:³⁰ 1.1×10^{-13} cm³ s⁻¹. In the same work, the decay of triplet benzene has been found to be 5×10^3 s⁻¹, the same order of magnitude as the decay rates found in this work for the unknown species. Figure 12 finally shows the evolution of α and k with O_2 : though the intensity increases linearly with O_2 , the decay rates do not depend on O_2 concentration. O_2 is



Figure 12. Absorption of the unknown reactive intermediate (6638.30 cm⁻¹) as a function of O₂ concentrations (left *y*-axis) and dependence of the decay rate of the unknown reactive intermediate (right *y*-axis) as a function of the O₂ concentration. Initial aromatic hydrocarbon concentrations were 0.2, 1, and 2.2 × 10¹⁵ cm⁻³ for *o*-xylene, toluene, and benzene, respectively.

known to be a good quencher for singlet benzene, leading to an increased yield in triplet benzene.³¹ The increase in intensity is therefore in agreement with triplet benzene being involved in the formation of the absorbing species. However, the quenching of triplet benzene with O_2 has been found³¹ to be 2.1×10^{-11} cm³ s⁻¹, which is not at all in agreement with the independence of the decay rate with O_2 : even under the lowest O_2 concentrations, the decay should already be 2×10^5 s⁻¹, around 100 times faster than our observation. Therefore, triplet benzene itself cannot be the absorbing species; it is, however, in line with our observations that triplet benzene is a precursor for the absorbing species: a possible candidate could be vibrationally excited benzene in the ground state obtained through quenching of the triplet state.

CONCLUSIONS

The energy-dependent study of the formation of HO₂ radicals after 248 nm irradiation of four different aromatic hydrocarbons in the presence of O₂ has revealed that the formation of the HO₂ radicals involves a two photon excitation processes. Our earlier work on HO₂ formation from excited benzene¹⁷ had to be revised in this study: the formation of an unknown, shortlived species, absorbing at the same wavelength than HO₂ has been taken into account as baseline for the calculation of HO₂ concentrations. The intensity as well as the decay time of the absorption of the unknown species has been analyzed to identify its nature. However, no explanation could be found that would explain all characteristics of this absorption. An empiric equation has been proposed to allow an estimation of the impact of this HO₂ formation for all aromatic hydrocarbons for past and future laboratory studies.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the CNRS through the French-German program "ATMOCHEM" and by the Nord-Pas de Calais region in the frame of the IRENI research program, by the French Research Ministry and by the European Fund for Regional Economic Development (FEDER). C.J. thanks the EU for financial support through project MEST-CT-2005-020659.

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