Absolute rate constants have recently been determined over the temperature range 296-473 K using a flash photolysis-resonance fluorescence technique. In all cases it was observed that for temperatures between ~ 325 and ~ 380 K the OH decays were nonexponential. For the temperature regions 380 K < T < 473 K and 296 K < T < 325 K the OH decays were exponential, with the rate constants at ~ 380 K being a factor of 4–12 lower than those at ~298 K. The observed behavior is explained by the occurrence of both OH radical addition to the aromatic ring and H atom abstraction at room temperature, while the abstraction reaction is the sole reaction observed above ~380 K due to the rapid decomposition of the OH–aromatic adduct within the time scale of the observations. In the temperature region where nonexponential decays are observed it is postulated that the OH–aromatic adduct, formed by OH radical addition to the ring, is decomposing back to reactants. The rate constants for the reaction of OH radicals with toluene-d₈ substantiates this reaction scheme, being within 5% of that for toluene at 298 K, but being a factor of ~2.5 lower at 423 K than that for toluene. The overall room temperature rate constants determined ranged from 1.20 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ for benzene to 6.24 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for 1,3,5-trimethylbenzene. Rate constants for both addition and abstraction for benzene, toluene, toluene-d₈, o-, m-, and p-xylene, and 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene are given. Heats of formation of the OH–aromatic adduct are derived, leading to a calculated stabilization energy of the OH–aromatic adduct (if a σ bonded moiety) of 16.5 ± 5 kcal mol⁻¹.

Introduction

The reactions of the hydroxyl radical with aromatic hydrocarbons are of fundamental interest as well as being of importance in chemical models of photochemical air pollution. Absolute rate constants have recently been determined at room temperature for the reaction of OH radicals with benzene and toluene and with a series of aromatic hydrocarbons using flash photolysis-resonance fluorescence techniques. In addition, rate constants for the reaction of OH radicals with aromatic hydrocarbons have been obtained from the initial rates of disappearance of the aromatic hydrocarbons relative to that of n-butane in an environmental chamber at 304–305 K.

However, rate constants for these reactions are not known as a function of temperature, nor are there direct product studies of the reaction of OH radicals with aromatic hydrocarbons. However, the rate constant data for benzene and toluene obtained by Davis, Bollinger, and Fischer indicated that at room temperature in the limiting high pressure region OH radical addition to the aromatic ring is at least as important a reaction pathway as that of abstraction.

In this work absolute rate constants for the reaction of OH radicals with a series of aromatic hydrocarbons have
been determined over the temperature range 296–473 K using a flash photolysis-resonance fluorescence technique.

Experimental Section

The apparatus and techniques used have been described previously, and hence only a brief summary will be given here. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H₂O at wavelengths longer than the LiF cutoff (≥1050 Å). OH radical concentrations were monitored as a function of time after the flash by resonance fluorescence using a cooled EMI 9659QA photomultiplier fitted with an interference filter transmitting the 3064-Å band of OH(A²Π, u” = 0 → X²Π, v” = 0). The intersection of the detection system aperture and the resonance radiation beam defined a fluorescence viewing zone at the center of the reaction vessel, whose cross section was ~2 cm in diameter. This region was well separated from the reaction vessel walls, thus minimizing wall losses of the OH radicals. The reaction cell was enclosed in a furnace which could be held constant to better than ±1 K over the temperature range 296–475 K. The gas temperature was measured by a chromel/alumel thermocouple mounted inside the reaction vessel.

The flash lamp was typically operated at discharge energies of 25–50 J per flash at repetition rates of one flash every 3 s. Signals were obtained by photon counting in conjunction with multichannel scaling. OH radical decay curves such as that shown in Figure 1 were accumulated from 20–1200 flashes, depending on the signal strengths. OH half-lives ranged from 1.54 to 161 ms, and the OH radical concentrations were followed over at least three half-lives. In all cases the flash duration was negligible in comparison to the OH radical half-lives encountered.

In order to avoid the accumulation of photoysis or reaction products, all experiments were carried out under flow conditions so that the gas mixture in the reaction vessel was replenished every few flashes. The partial pressure of H₂O in the reaction cell was ~0.02 Torr. Theargon and oxygen used had purity levels of ≥99.998 and ≥99.999%, respectively, according to the manufacturers. Gas chromatographic analyses of the aromatic hydrocarbons used showed them to have purity levels of ≥99.0%, except for m-xylene (98.6%) and 1,2,3-trimethylbenzene (97.6%). The impurities observed were other aromatic hydrocarbons, and for the xylenes and trimethylbenzenes were mainly their isomers. The toluene-d₈ had a stated D atom purity level of ≥99.9%.

A known fraction of the total flow was saturated with the aromatic vapor at 251–293 K, depending on the aromatic hydrocarbon used. Aromatic hydrocarbon partial pressures in this fraction of the total flow were determined by their ultraviolet absorption using a 9.0-cm pathlength cell and a Cary 15 spectrophotometer. The absorption cell was calibrated using known pressures of the aromatic hydrocarbons as measured by an MKS Baratron capacitance manometer. All flows were monitored by calibrated flowmeters and the gases were premixed before entering the reaction vessel.

Results

Under the conditions used, the aromatic hydrocarbon concentrations were in large excess of the initial OH radical concentrations (~10¹⁵ molecule cm⁻³). If the products of the reaction of OH radicals with the aromatic hydrocarbons are stable, or if they decompose to fragments other than OH radicals, then the OH concentration is given by

\[ -\frac{d[OH]}{dt} = (k₀ + k[aromatic])[OH] \]

and

\[ [OH]₀/[OH] = \frac{S₀}{S_r} = \exp[(k₀ + k[aromatic])(t - t₀)] \]

where [OH]₀ and [OH] are the concentrations of OH at times t₀ and t, respectively, S₀ and S_r are the corresponding resonance fluorescence intensities, k₀ is the first-order rate constant for removal of OH in the absence of added reactant (primarily attributed to diffusion out of the viewing zone and to reaction with impurities), and k is the rate constant for the reaction

OH + aromatic → products

However, if this reaction is reversible then, depending on the half-life of the product with respect to reformation of OH and the time scale that OH radicals are being observed over, the OH decays will no longer be exponential (vide infra).

OH radical decays were determined for the reaction of OH radicals with benzene, toluene, toluene-d₈, o-, m-, and p-xylene, and 1,2,3- and 1,2,4- and 1,3,5-trimethylbenzene over the temperature range 296–473 K at a total pressure of ~100 Torr of argon (total pressures up to 200 Torr of argon were used in the case of toluene). In all cases, as the temperature was increased from ~298 K the following characteristics were observed:

At room temperature (~298 K) the OH radical decays were exponential over at least three half-lives and the decay rates R, defined as \( R = (t - t₀)^{-1} \ln \frac{S₀}{S_r} \), were a linear function of the aromatic hydrocarbon concentration:

\[ R = k₀ + k[aromatic] \]

Similar behavior was observed up to ~325 K with the rate constant k changing only slightly with the increasing temperature.

For temperatures between ~325 and 380 K the OH decays were no longer exponential, with the decay rate decreasing with time after the flash (Figure 2). The rate constants k obtained at ~380 K from the initial OH decay rates were a factor of 4–12 lower than those at ~298 K.

For temperatures ≥380 K the OH decays were again exponential with a linear dependence of the decay rates on aromatic hydrocarbon concentration. The rate constants k obtained in this temperature regime generally
increased with temperature up to the highest temperatures used (420–470 K).

This behavior is illustrated by Figures 2 and 3. Figure 2 shows OH radical decays, plotted as ln [OH] against time, for a toluene concentration of $\sim 5 \times 10^{13}$ molecule cm$^{-3}$ at 297.9, 338.5, 354.2, and 424.4 K, while Figure 3 shows plots of the OH decay rate against toluene concentration for the temperatures 297.9 and 424.4 K.

Rate constants $k$ were determined as a function of temperature from either (a) the dependence of the OH radical decay rate on the aromatic hydrocarbon concentration, as shown in Figure 3 for toluene, or (b) a single OH decay rate $R$ at a known aromatic hydrocarbon concentration using eq III. The latter method obviously has a somewhat larger degree of uncertainty, partially associated with the estimation of the OH decay rate in the absence of reactant, $R = k_0$. However, for OH decay rates $\geq 200$ s$^{-1}$, any error associated with the estimation of $k_0$ (which was typically $\sim 10$–20 s$^{-1}$) was $\leq 5\%$. Values of $k_0$ were estimated using values obtained by method (a) for the same aromatic hydrocarbon at similar temperatures. The error limits given in Table I (see paragraph at end of

Figure 2. OH radical decays, plotted as ln [OH] against time after the flash, for the reaction of OH radicals with toluene at 297.9, 338.5, 354.2, and 424.4 K with $\sim 100$ Torr total pressure of argon diluent. Data points are plotted at every eleventh channel (100–or 200-ps channel widths). The toluene concentrations are: 297.9 K, $4.95 \times 10^{13}$ molecule cm$^{-3}$; 338.5 K, $4.68 \times 10^{13}$ molecule cm$^{-3}$; 354.2 K, $6.11 \times 10^{13}$ molecule cm$^{-3}$; 424.4 K, $5.22 \times 10^{13}$ molecule cm$^{-3}$.

Figure 3. Plots of the OH radical decay rate against aromatic hydrocarbon concentration for toluene at 297.9 and 424.4 K and for toluene-$d_6$ at 298.1 and 432.2 K. Total pressure $\sim 100$ Torr of argon.

Rate constants $k$ were determined as a function of temperature from either (a) the dependence of the OH radical decay rate on the aromatic hydrocarbon concentration, as shown in Figure 3 for toluene, or (b) a single OH decay rate $R$ at a known aromatic hydrocarbon concentration using eq III. The latter method obviously has a somewhat larger degree of uncertainty, partially associated with the estimation of the OH decay rate in the absence of reactant, $R = k_0$. However, for OH decay rates $\geq 200$ s$^{-1}$, any error associated with the estimation of $k_0$ (which was typically $\sim 10$–20 s$^{-1}$) was $\leq 5\%$. Values of $k_0$ were estimated using values obtained by method (a) for the same aromatic hydrocarbon at similar temperatures. The error limits given in Table I (see paragraph at end of
ations (1–7%) as well as the estimated accuracy limits of other parameters such as total pressure and the aromatic hydrocarbon concentrations in the reactant mixture. In all cases using method (a), the experimental decay rates in the range typically used for method (b) \((R \geq 200 \, \text{s}^{-1})\) were within 5% of those calculated from least-squares analysis of the data. Hence this spread is indicative of the random errors associated with method (b), and is included in the overall error limits for method (b) (Table I and Figures 4–7). For benzene at temperatures \(\geq 380 \, \text{K}\) the experimental conditions were limited by the low rate constants so that the OH decay rates were \(<100 \, \text{s}^{-1}\) and hence the error limits for benzene above \(\sim 380 \, \text{K}\) are much higher than those for the other aromatic hydrocarbons.

For the reaction of OH radicals with toluene, additional experiments were carried out to verify the observed behavior. A variation in the flash energy by a factor of 2 had no effect on the rate constants within the experimental errors, indicating that secondary reactions of the OH radicals with reaction products were negligible, as expected from the initial OH concentrations \((\sim 10^{11} \, \text{molecule/cm}^3)\) and the aromatic hydrocarbon concentrations used. Similarly, an increase in the total pressure (argon diluent) from 100 to 300 Torr at 325.3 and 378.4 K had no effect on the rate constants within the experimental errors (\(\pm 5–10\%\)) when the OH decay rates at 325.3 and 378.4 K were determined from the initial OH decays. Furthermore, the addition of 2.0 Torr of \(\text{O}_2\) at 397.4 K and 2.3 Torr of \(\text{O}_2\) at 352.6 K had no effect (within \(\pm 10–15\%\)) on the rate constants. In these cases the presence of \(\text{O}_2\) markedly reduced the OH resonance fluorescence signal, presumably due to quenching of the OH(\(A^22^+)\) state. Less extensive rate data for the reaction of OH radicals with toluene-\(d_8\) showed similar behavior. Thus the rate constant at room temperature was within 5% of that for toluene, while the rate constant determined for toluene-\(d_8\) at 432.2 K was a factor of 2.5 lower than that for toluene at 424.4 K. The rate constants obtained for toluene-\(d_8\) are given in Table I, while Figure 3 shows plots of the OH decay rate against toluene and toluene-\(d_8\) at room temperature and at \(\sim 428 \, \text{K}\).

Table I gives the rate constants obtained at the temperatures used for the aromatic hydrocarbons studied, while Figures 4–7 show the data plotted in Arrhenius form. The solid lines for \(\leq 325 \, \text{K}\) and for \(\geq 380 \, \text{K}\) were obtained from least-squares fitting of the data in these temperature regimes, while the dashed lines between these temperature regions merely reflect the trend of the data.

**Discussion**

From the initial OH radical concentrations and the aromatic hydrocarbon concentrations used, it can be estimated\(^1\) that errors in the measured rate constants due to reaction of OH radicals with reaction products would be typically \(<5–10\%\), using an assumed rate constant of \(10^{11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}\) for the reaction of OH radicals with all reaction products. This conclusion was substantiated by the fact that a variation of a factor of 2 in the flash energy had no effect, within the experimental errors, on the rate constants. Similarly, the reaction of OH radicals with reactant impurities can be calculated to cause errors in the measured rate constants of \(\leq 5\%\).

**Kinetics and Mechanism.** For the reactions of OH radicals with an aromatic hydrocarbon the initial reaction can be (using toluene as an example) either abstraction (reaction 1) or addition to the aromatic ring (reaction 2).

The rate constants \(k\) obtained for benzene and the substituted benzenes at temperatures of \(\sim 380–470 \, \text{K}\) indicate (see below) that at these temperatures H atom abstraction...
TABLE II: Comparison of the Room Temperature Rate Constants, \( k \), for the Reaction of OH Radicals with Aromatic Hydrocarbons from the Present Work with Literature Values

<table>
<thead>
<tr>
<th>Aromatic hydrocarbon</th>
<th>This work(^a)</th>
<th>Ref 4(^b)</th>
<th>Ref 5(^c)</th>
<th>Ref 6(^d)</th>
<th>Ref 3(^d)</th>
<th>Ref 14(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.20 ± 0.15</td>
<td>1.24 ± 0.12</td>
<td>&lt;0.8</td>
<td>1.59 ± 0.12</td>
<td>6.11 ± 0.40</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>6.40 ± 0.64</td>
<td>5.78 ± 0.58</td>
<td>4.2 ± 1.5</td>
<td>21.5 ± 4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene-(d_6)</td>
<td>6.13 ± 0.63</td>
<td>18.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(o)-Xylene</td>
<td>14.3 ± 1.5</td>
<td>15.8 ± 1.5</td>
<td>12.8 ± 3.8</td>
<td>12.3 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(m)-Xylene</td>
<td>24.0 ± 2.5</td>
<td>23.2 ± 1.7</td>
<td>23.5 ± 1.7</td>
<td>23.5 ± 1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(p)-Xylene</td>
<td>15.3 ± 1.7</td>
<td>12.2 ± 1.2</td>
<td>12.3 ± 2.5</td>
<td>12.3 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>33.3 ± 4.5</td>
<td>26.4 ± 2.6</td>
<td>23 ± 5</td>
<td>23 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>40.0 ± 4.5</td>
<td>33.5 ± 5.4</td>
<td>33 ± 5</td>
<td>33 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>62.4 ± 7.5</td>
<td>47.2 ± 4.8</td>
<td>51.5 ± 6.5</td>
<td>51.5 ± 6.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Total pressure 100 ± 2 Torr (Ar). \(b\) Total pressure >50 Torr (Ar). \(c\) Total pressure 1 atm of air at 304 ± 1 K (ref 5) or 305 ± 2 K (ref 6); rate constants placed on an absolute basis using a rate constant for \(OH + n\)-butane of \(3.0 × 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). \(d\) Total pressure 100 Torr (He). \(e\) Total pressure ~1 Torr (He), mixture of isomers.

\[ \text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5^- \]  
(1)

occurs mainly from the substituent \(\text{CH}_3\) groups rather than from the aromatic ring. Addition of the OH radical is shown for attack at the ortho position by analogy with the reaction of \(O(3P)\) atoms with aromatic hydrocarbons.\(^{11}\) Obviously addition of OH radicals may occur at any of the carbon atoms of the aromatic ring, forming a variety of OH–aromatic adducts which initially contain the excess energy due to the exothermicity of the reaction.

Such an energy-rich OH–aromatic adduct can either decompose or be stabilized, as was observed by Davis, Bollinger, and Fischer\(^c\) for benzene and toluene:

\[ \text{[C}_6\text{H}_6^+\text{OH]}^* \]  
(2)

A further reaction step is that the thermalized OH–aromatic adduct could unimolecularly decompose back to the reactants

\[ \text{[C}_6\text{H}_6^+\text{OH]}^* \rightarrow \text{C}_6\text{H}_5^+ + \text{OH} \]  
(3)

However, it is also possible that the initial reaction could involve the formation of a \(\pi\) complex, which could either decompose back to the reactants or evolve to a \(\sigma\) bonded OH–aromatic adduct such as shown above.

An analogous reaction system has been studied by Majer, Phillips, and Robb\(^2\) who investigated the reaction of \(\text{CF}_3\text{Cl}\) radicals with benzene. The \(\text{CF}_3\text{Cl}\)–benzene adduct was observed to decompose back to reactants above 373 K with an activation energy of 11.4 ± 0.8 kcal mol\(^{-1}\). While the activation energy for the addition of \(\text{CF}_3\text{Cl}\) radicals to benzene was determined to be 5.3 ± 0.4 kcal mol\(^{-1}\). Similar results were obtained for the reaction of \(\text{CF}_3\text{Cl}\) radicals with benzene-\(d_6\)\(^c\), for which an activation energy for the decomposition of the adduct of 10.7 ± 0.4 kcal mol\(^{-1}\) was obtained.

In a previous determination\(^4\) of the rate constants for the reaction of OH radicals with a series of aromatic hydrocarbons, it was observed that the rate constants for benzene and toluene were independent of the total pressure (argon diluent) over the ranges 50–600 and 100–620 Torr, respectively. This was in agreement with the data of Davis, Bollinger, and Fischer\(^c\) who observed a pressure dependence of \(k\) for benzene and toluene over the range 3–100 Torr of helium, but concluded from Lindemann plots that the rate constants measured at 100 Torr of helium were essentially the high pressure limiting values. Davis, Bollinger, and Fischer\(^d\) deduced from this pressure dependence that over half of the total reaction at room temperature proceeds via addition \((k_2 > k_1)\).

Table II compares the present room temperature rate constants \(k\) with literature values.\(^{2,4,14}\) It can be seen that the agreement with the literature data is generally good and that the present rate constants are in general agreement, within the experimental error limits, with those obtained previously\(^c\) in this laboratory. The agreement between the rate constants from this and the previous study\(^4\) for benzene, toluene, and \(o\)- and \(m\)-xylene is seen to be excellent. The present rate constants for \(p\)-xylene, 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene are, however, ∼20–30% higher than those determined previously,\(^4\) and this may reflect a systematic error in the previous calibration of the aromatic absorption, which was weak under the conditions used. The somewhat increased overall error limits quoted in the present work (10–14%) take into account more realistically the higher errors associated with such calibrations. However, the reproducibility of the data from the two studies is indicative of the likely overall error limits as the studies were performed independently, with complete recalibrations of flowmeters and the absorption cell–Cary 15 spectrophotometer combination.

The fact that the previous\(^4\) and present absolute rate constants \(k\) for the xylenes determined at ~100 Torr total pressure of argon are consistent with that obtained by Morris and Niki\(^2\) for a mixture of isomers at ~1 Torr total pressure of helium shows that \(k\) for the xylenes must be at, or close to, the limiting high pressure region at ~1 Torr total pressure. This is consistent with unimolecular theory which predicts that the falloff region should shift to lower total pressures as the complexity, or number of vibrational degrees of freedom, of the OH–aromatic adduct increases. As has been noted previously,\(^4\) the rate constants \(k\) at room temperature show the same trend with degree and position of alkylation as for \(O(3P)\) atom reaction,\(^3\) demonstrating the electrophilic character of the OH radical. This further suggests that at room temperature the major
reaction path is one of addition to the aromatic ring.

The lack of a dependence of $k$ for toluene on total pressure of argon over the range 100–200 Torr at 325.3, 378.4, and 424.4 K in the present work further indicates that the initially energy rich OH–toluene adduct is rapidly thermalized under these conditions.

The experimental results are thus consistent with the occurrence of reactions 1–3 with the OH–aromatic adducts being stable within the time frame of the OH radical observations (∼1–30 ms) at room temperature, and being unstable for temperatures ≥380 K. Hence at room temperature the measured rate constants are those for both addition and abstraction, $k = k_1 + k_2$ while at ≥380 K only $k_1$, the rate constant for abstraction, is measured. These conclusions are confirmed from the reaction of OH radicals with toluene-d$_6$: at room temperature the rate constant $k$ for toluene-d$_6$ is within 5% of that for toluene, while at 432 K the rate constant for toluene-d$_6$ is a factor of ∼2.5 lower than that for toluene. These observations are in accord with main OH radical addition to the aromatic ring at room temperature, as a small isotope effect is expected for addition (thus rate constants at room temperature for the reactions of OH radicals with propylene-d$_4$,14 of O$_3$ with ethylene-d$_4$,16 and propylene-d$_6$,17 and of O$_3$(P) atoms with acetylene-d$_2$,18 ethylene-d$_4$,19,20 iso- butene-d$_6$,21 and benzene-d$_5$ are all within ∼20% of those for the hydrogen isotope species). However, for abstraction a significant isotope effect is expected with the deuterium isotope reacting slower than the hydrogen isotope, as has been observed previously for the reaction of OH radicals with D$_4$ and DCI as compared to H$_2$ and HCl, respectively, and for the reaction of CH$_3$ radicals with toluene-d$_6$, toluene-d$_9$, benzene-d$_5$, and toluene-d$_{25}$.22

As the OH–aromatic adduct is deactivated to an essentially thermal energy population at the total pressures used in this study, then the rate constant $k_2$ is given by

$$k_2 = A_2 e^{-E_2/RT} \quad (IV)$$

With the present experimental technique OH radicals are monitored for ∼1–30 ms after the flash. Significant nonexponentiality of the OH decay curves was observed at temperatures from ∼325 to 380 K and hence the half-life of the OH–aromatic adduct must be of the order of ∼5–10 ms in this temperature range, corresponding to $k_2$ ∼ 100 s$^{-1}$ at 350 K. For $A_2 = 3 \times 10^{13}$ s$^{-1}$ (of the same order of magnitude as the $A$ factors for decomposition of the cyclohexadienyl$^{26}$ and methylcyclohexadienyl radicals$^{27}$) the activation energy for reaction $-2$ can be calculated to be $E_2 \approx 18$ kcal mol$^{-1}$. (Data for the individual aromatic hydrocarbons are given in Table V.) The initially formed OH–aromatic adduct will contain approximately this amount of excess energy and should thus be readily thermalized in a time scale shorter than 1–30 ms by ∼100 Torr of argon as argon has been shown to remove vibrational energy of the order of 1 kcal mol$^{-1}$ per collision with a number of photochemically and chemically activated molecules.28

From eq IV with $A_2 = 3 \times 10^{13}$ s$^{-1}$ and $E_2 = 18$ kcal mol$^{-1}$ the half-lives of the OH–aromatic adduct can be estimated to be 0.37 s at 298 K, 29 ms at 325 K, 0.52 ms at 380 K, and 0.16 ms at 400 K. These values of $A_2$ and $E_2$ thus give half-lives of the OH–aromatic adducts which are totally consistent with both the reaction scheme discussed above and the experimental observations. Thus the temperatures at which the appearance of nonexponential behavior in the OH radical decays will depend on the technique used and the observational time scale employed. For instance, if the OH radicals were observed over a time scale of ∼10–100 μs, as is typically the case with flash photolysis-resonance absorption systems (rather than over the time scale ∼1–30 ms used in the present work), then the low temperature onset of nonexponential behavior would move up from ∼325 to ∼400 K.

The rate constant data of Doyle et al.$^3$ and Lloyd et al.$^6$ are in good agreement with those obtained by the flash photolysis-resonance fluorescence technique$^{4,5}$ showing that the OH–aromatic adduct must react, presumably with O$_2$, NO, or NO$_2$, in their system before decomposition. However, the present lack of an effect of O$_2$ at 397.4 and 352.6 K allows an upper limit of 1 × 10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ to be set, at these temperatures, for the apparent rate constant for the reaction of O$_2$ with the OH–toluene adduct. However, the CH$_3$CHO(1OH)(O$_2$) radical may decompose at elevated temperatures which would give a low apparent rate constant for the addition of O$_2$ to the OH–toluene adduct.

Table III gives room temperature values of $k_1$, obtained by extrapolation of the data above ∼380 K, and the fraction of the reaction proceeding via H (or D) atom abstraction, $k_1/(k_1 + k_2)$, for the aromatic hydrocarbons studied. It can be seen that the amount of reaction at room temperature proceeding via abstraction is of the order of 2–20% depending on the individual hydrocarbon. The values of $k_1$ and $k_1/(k_1 + k_2)$ given for benzene are subject to large uncertainties, but the extrapolated value of $k_1 = (62^{+19}_{-29}) \times 10^{14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K can be compared with room temperature rate constants for the reaction of OH radicals with CH$_3$ and NH$_3$: of ∼8 × 10$^{-15}$–35 and ∼1.6 × 10$^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. CH$_3$ and NH$_3$ have C–H and N–H bond energies of 104 ± 1 and 110 ± 2 kcal mol$^{-1}$ respectively,42 compared to 110.2 ± 2.0 kcal mol$^{-1}$ for the C–H bond energy in benzene,42 and hence a rate constant $k_1$ of the magnitude observed is reasonably in line with the respective bond energies. For the alkylated benzenes, on the other hand, the rate constants $k_1$ at 298 K are much larger than $k_1$ for benzene, which is to be expected due to the lower C–H bond energies in the alkylated hydrocarbons. As noted above, the rate constants for $T > 380$ K increase with increasing temperature (Table I).

<table>
<thead>
<tr>
<th>Aromatic hydrocarbon</th>
<th>$10^{4}$k$_1$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>$k_1/(k_1 + k_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.06$^{+19}_{-29}$</td>
<td>0.05$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.0$^{+19}_{-29}$</td>
<td>0.16$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>Toluene-d$_6$</td>
<td>0.05$^{+0.04}_{-0.05}$</td>
<td>0.08$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>2.9$^{+19}_{-29}$</td>
<td>0.20$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>0.9$^{+19}_{-29}$</td>
<td>0.04$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>1.5$^{+19}_{-29}$</td>
<td>0.15$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>1,2,3-Trime-thylbenzene</td>
<td>1.2$^{+19}_{-29}$</td>
<td>0.20$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>1,2,4-Trime-thylbenzene</td>
<td>1.3$^{+19}_{-29}$</td>
<td>0.35$^{+0.04}_{-0.05}$</td>
</tr>
<tr>
<td>1,3,5-Trime-thylbenzene</td>
<td>1.3$^{+19}_{-29}$</td>
<td>0.03$^{+0.04}_{-0.05}$</td>
</tr>
</tbody>
</table>

* a Extrapolated from T ≥ 380 to 298 K using the Arrhenius lines in Figures 4–7 and given in Table IV.

* b Upper limit from the rate constants obtained at 432.2 and 298.1 K, as the rate constants for T > 380 K increase with increasing temperature (Table I).

Table IV gives the Arrhenius parameters for reactions 1 and 2 for the temperature ranges 298 K < T ≤ 325 K and T ≥ 380 K as determined from the data in Table I and

The Journal of Physical Chemistry, Vol. 81, No. 4, 1977
large error limits, except to point out that reaction 1 has 
dependence, as has been previously observed for the addition 
eventually zero or slightly negative temperature depen-
dashed lines of Figures 4-7. Calculated using $AH_f(0H)$ 
ortho to the substituent methyl groups, analogous to O(3P) atom  
trimethylbenzene, being similar for the three xylenes and for 
each region the error limits are large and extrapolation 
toluene, 1-methyl-2-hydroxy; o-xylene, 1,2-dimethyl-3-hydroxy; m-xylene, 
are zero $42$ and $E_2$ kcal mol$^{-1}$. $54$ Calculated using $AH_f$ (OH-aromatic 
Activity Energies for Reactions 2 and $-2$ and Heats of Formation $\Delta H_f$ for the OH-Aromatic and 
TABLE V: Activation Energies for Reactions 2 and and OH-aromatic adducts 
Aromatic hydrocarbon $E_2$, kcal mol$^{-1}$ $E_2$, kcal mol$^{-1}$ $E_1$, kcal mol$^{-1}$ $E_2$, kcal mol$^{-1}$ $E_1$, kcal mol$^{-1}$ $E_2$, kcal mol$^{-1}$ $E_2$, kcal mol$^{-1}$ 

<table>
<thead>
<tr>
<th>Aromatic hydrocarbon</th>
<th>$E_2$, kcal mol$^{-1}$</th>
<th>$E_2$, kcal mol$^{-1}$</th>
<th>$E_1$, kcal mol$^{-1}$</th>
<th>$E_2$, kcal mol$^{-1}$</th>
<th>$E_1$, kcal mol$^{-1}$</th>
<th>$E_2$, kcal mol$^{-1}$</th>
<th>$E_2$, kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>$0.9 \pm 0.1$</td>
<td>$19.82 \pm 0.12$</td>
<td>$11.95 \pm 0.15$</td>
<td>$10.5 \pm 3$</td>
<td>$1.8 \pm 2$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$-1.6 \pm 1$</td>
<td>$18.1 \pm 2$</td>
<td>$4.54 \pm 0.26$</td>
<td>$-6.1 \pm 4$</td>
<td>$-6.0 \pm 3$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>$-0.7 \pm 2$</td>
<td>$18.4 \pm 2$</td>
<td>$4.12 \pm 0.18$</td>
<td>$-5.4 \pm 4$</td>
<td>$-6.0 \pm 3$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>$-0.1 \pm 2$</td>
<td>$17.9 \pm 2$</td>
<td>$4.28 \pm 0.24$</td>
<td>$-6.5 \pm 3$</td>
<td>$-6.4 \pm 4$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>$-0.6 \pm 2$</td>
<td>$18.7 \pm 2$</td>
<td>$-2.29 \pm 0.30$</td>
<td>$-14.7 \pm 4$</td>
<td>$-15.1 \pm 4$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>$-2.3 \pm 2$</td>
<td>$18.6 \pm 2$</td>
<td>$-3.33 \pm 0.27$</td>
<td>$-14.8 \pm 4$</td>
<td>$-15.0 \pm 4$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>$-1.7 \pm 2$</td>
<td>$18.3 \pm 2$</td>
<td>$-3.84 \pm 0.34$</td>
<td>$-15.1 \pm 4$</td>
<td>$-14.7 \pm 4$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>$-1.7 \pm 2$</td>
<td>$18.1 \pm 2$</td>
<td>$-3.84 \pm 0.34$</td>
<td>$-15.1 \pm 4$</td>
<td>$-14.7 \pm 4$</td>
<td>$18.7 \pm 2$</td>
<td>$18.7 \pm 2$</td>
</tr>
</tbody>
</table>

$\Delta H_f$ (OH-aromatic adduct) = $AH_f$ (OH-aromatic) + $AH_f$ (OH) - ($E_1$ - $E_2$ - $RT$). Calculated from group additivity rules, using a stabilization en-
Figure 4-7. Because of the small temperature ranges in 
each region the error limits are large and extrapolation 
outside of the quoted temperature ranges will give large 
uncertainties in the values obtained. Discussion of the 
individual values of the preexponential factors and Ar-
henius activation energies has little merit in view of the 
large error limits, except to point out that reaction 1 has 
in all cases a positive activation energy of $\sim 0-4$ kcal mol$^{-1}$, 
while reaction 2 has, except in the case of benzene, an 
essentially zero or slightly negative temperature depend-
ence, as has been previously observed for the addition 
of O(3P)$^{49,50}$ and S(3P)$^{49-51}$ atoms, and OH radicals,$^{49-51}$ to 
dienes. It can also be seen from Table I and Figures 4-7 
that at $\sim 380-470$ K the values of $k_0$ obtained increase 
approximately linearly with the number of substituent 
methyl groups, being similar for the three xylenes and for 
the three trimethylbenzenes.

Thermochemistry. Knowing the activation energies for 
reactions 2 and $-2$, the heats of formation of the OH-
aroanic adducts can be obtained as$^{52}$

$$\Delta H_f(\text{OH-aromatic adduct}) = \Delta H_f(\text{OH-aromatic}) + \Delta H_f(\text{OH}) - \Delta H_2$$

where $\Delta H_2$ is the enthalpy of reaction 2 and

$$\Delta H_f(\text{OH-aromatic adduct}) = \Delta H_f(\text{OH-aromatic}) + \Delta H_f(\text{OH}) - \Delta H_2$$

where $\Delta E_2$ and $\Delta E_1$ are the activation energies for reactions $-2$ and 2, respectively. Except for benzene, the experi-
mental Arrhenius activation energies for reaction 2 are zero 
or negative. However, the observed Arrhenius activation 
energies are not necessarily equivalent to the activation 
energies $E_2$ for the addition reaction as the preexponential 
factors may be temperature dependent$^{49-51}$ and it is 
in fact likely that observed negative temperature depen-
dencies have a zero activation energy with a tem-
perature-dependent preexponential factor. In the absence 
of a knowledge of any temperature dependence of the 
preexponential factors for reaction 2 the activation energies 
$E_2$ have been set equal to the experimental Arrhenius 
activation energies for reaction 2.

Table V gives the Arrhenius activation energies $E_2$ and 
$E_1$ used, together with the experimental and calculated 
heats of formation $\Delta H_f$ of the OH-aromatic adduct. The 
calculated values of $\Delta H_f$ (OH-aromatic adduct) were 
obtained as follows (using II as an example): $\Delta H_f$ of I was 
calculated using group additivity rules,$^{52}$ and that for the 
radical II was derived from$^{27,52}$

$$\Delta H_f(\text{II}) = \Delta H_f(\text{I}) + D(\text{tertiary C-H}) - \Delta H_f(\text{H}) - SE$$

The Journal of Physical Chemistry, Vol. 81, No. 4, 1977
where $D(\text{tertiary C-H})$ is the tertiary C-H bond energy and $SE$ is the stabilization energy of radical II.

Table V shows that there is good agreement between calculated and experimental values of $\Delta H_f(\text{OH-aromatic adduct})$ within the experimental error limits of $\pm 3$ kcal mol$^{-1}$ using a best fit value of the stabilization energy of 16.5 kcal mol$^{-1}$. Furthermore, as also shown in Table V, the data of Majer, Phillips, and Robb$^{15}$ on the addition of CF$_2$Cl radicals to benzene ($E = 5.3 \pm 0.4$ kcal mol$^{-1}$) and the decomposition of the CF$_2$Cl-benzene adduct ($E = 11.4 \pm 0.8$ kcal mol$^{-1}$) at $\approx 273$ K leads to equally good agreement between calculated and experimental values of $\Delta H_f$ for the CF$_2$Cl-benzene radical using $SE = 16.5$ kcal mol$^{-1}$. Hence the present work leads to a stabilization energy for these substituted cyclohexadienyl radicals of 16.5 $\pm$ 5 kcal mol$^{-1}$ where the error limit includes the experimental error limits as well as an estimate of $\pm 2$ kcal mol$^{-1}$ for the calculated values of $\Delta H_f$ (OH-aromatic adduct).

This stabilization energy is very close to the value of 15.4 $\pm$ 1 kcal mol$^{-1}$ obtained for the pentadienyl radical by Egger and Benson.$^{54}$ However, James and Suart$^{30}$ reported a stabilization energy for the cyclohexadienyl radical of 25 kcal mol$^{-1}$ from a study of mutual interaction and thermal decomposition of cyclohexadienyl radicals, while Shaw, Cruickshank, and Benson$^{26}$ quote a value of 24.6 $\pm$ 0.7 kcal mol$^{-1}$. It has been suggested$^{26,34,35}$ that the temperature dependency of the association energy for CF$_2$Cl to benzene can be interpreted as a $\pi$ complex which could either dissociate back to the reactants or evolve to a more closely bonded $\sigma$ complex. If the addition of OH radicals to aromatic hydrocarbons proceeds via a $\pi$ complex formation

$$\text{OH + aromatic} \rightarrow \pi \text{complex}$$

$$\pi \text{complex} \rightarrow \text{OH + aromatic}$$

$$\rightarrow \sigma \text{-bonded adduct}$$

and if back dissociation to reactants is rapid at room temperature, the observed $\sim 18$ kcal mol$^{-1}$ activation energy for decomposition must refer to the $\sigma$-bonded complex. However, if $h_\pi > h_\sigma$, the observed activation energy of addition is given by $(E_a + E_p - E_\sigma)$ and would not refer to the reverse of reaction $-2$. However, if the 18 kcal mol$^{-1}$ decomposition activation energy refers to the $\pi$ complex, then both $h_\pi$ and $h_\sigma$ must be slow at room temperature and the activation energy of addition is given by $E_a$. In this case the $\pi$ complex would be a stable entity, (only some 5–10 kcal mol$^{-1}$ less stable than the $\sigma$-bonded adduct, calculated using a stabilization energy of the $\sigma$-bonded adduct of 25 kcal mol$^{-1}$).$^{26,55}$

Obviously, further work is needed to more precisely determine such stabilization energies, in view of the rather substantial uncertainties inherent in the present determinations.

Conclusions

The reaction of OH radicals with a series of aromatic hydrocarbons proceeds via two pathways: (a) abstraction of an H atom from the aromatic ring or (except for benzene) from the substituent CH$_3$ groups, and (b) addition to the aromatic ring to form an adduct which is readily thermalized at total pressures of $\sim 100$ Torr of argon but which can, in the absence of other competing reactions, decompose back to reactants at $\approx 2.25$ K in the time scale $\leq 30$ ms. For substituted benzenes, the rate constants extrapolated to room temperature for abstraction show (Table III) that abstraction occurs mainly from the CH$_3$ groups at room temperature but that abstraction from the ring becomes more important at elevated temperatures.

The present data enable an estimate of 16.5 $\pm$ 5 kcal mol$^{-1}$ to be made for the stabilization energy of the OH-aromatic (or CF$_2$Cl-benzene) adducts, which is lower than previously reported values of $\sim 25$ kcal mol$^{-1}$ but is close to the stabilization energy reported for the pentadienyl radical.$^{34}$ At room temperature under simulated atmospheric conditions the OH–aromatic adduct reacts further, presumably with O$_3$, NO, or NO$_2$, as shown by the good agreement between the rate constants obtained from relative rate studies in an environmental chamber$^{56}$ and those obtained by flash photolysis-resonance fluorescence.$^{54}$ However, at elevated temperatures (for instance, $\geq 400$ K) it appears that, unless the adduct can react further in $\leq 1$ ms, the reaction will proceed via abstraction on account of the short lifetime of the OH–aromatic adduct with respect to decomposition back to reactants.

Acknowledgment. The authors gratefully acknowledge the financial support of NSF Grants MPS73-08638-A03 and CHE 76-10447 and thank Dr. A. C. Lloyd and Dr. W. P. L. Carter for helpful discussions.

Supplementary Material Available: Table I containing rate constants obtained at the temperatures used for the aromatic hydrocarbons studied (6 pages). Ordering information is available on any current masthead page.

References and Notes


Radiolysis of Adenine in Dilute Neutral Aqueous Solution

George Gorin,* C. Lehman, C. A. Mannan, L. M. Raff, and S. E. Scheppel
Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074 (Received August 16, 1976)

Solutions of adenine, 0.2 to 2 mM, have been radiolyzed at constant dose rate in air-equilibrated and in oxygen-saturated phosphate buffer, pH 7. The radiochemical decomposition yield is 1.2 ± 0.1 molecules/(100 eV). The progress of the radiolysis was monitored by a highly specific colorimetric method for determining the adenine, and by measurements of the absorption spectrum at wavelengths between 290 and 220 nm. The results show that the radiolysis products absorb in the wavelength range investigated; this explains why previously reported values of $G$(-Ade), which had been calculated from the rate of decrease of the absorbance with dose, are lower than that reported here. The spectra are unusual in that isosbestic points develop at 280 and 238 nm and persist to >50% decomposition. Analysis by thin-layer chromatography and mass spectrometry shows that urea is one of the products, and it confirms the formation of 8-hydroxyadenine and of 4,6-diamino-5-formamidopyrimidine, which had been reported previously. None of these products interfere with the colorimetric determination of adenine.

Introduction

This investigation is one of a series aimed at elucidating the chemical reactions that take place when ionizing radiation interacts with living organisms. Our attention has been directed, in particular, to the bases which occur in DNA, inasmuch as this substance indubitably plays an important role in the development of radiation injuries. A previous paper describes our general approach and methods, and their application to the radiolysis of cytosine; here we report their extension to the radiolysis of adenine.

Adenine possesses an intense and fairly sharp absorption maximum at 260 nm, which decreases on irradiation. The change can be easily measured with relatively good accuracy, and such measurements thus provide a very convenient means of following the progress of the reaction. This approach was first utilized by Scholes et al. who came to the conclusion that the products of radiolysis did not absorb at 260 nm; on that basis they calculated the radiolytic decomposition yield, $G$(-Ade), to be 1.1 molecules/(100 eV). $G$ values ranging from 0.65 to 1.2 have been reported subsequently by other investigators. These results are inconsistent with the reports that some of the radiation products have a substantial absorbance at 260 nm. As we have shown in a previous paper, if the products have an appreciable absorbance and this fact is neglected in calculating the value of $G$ from spectrophotometric measurements, the result inevitably will be lower than the true value.

These considerations prompted us to reinvestigate the question, and to use a highly specific colorimetric method to determine the adenine. Moreover, we undertook to measure the complete spectrum of the irradiated solutions, not only the absorbance at the maximum. The results show that the radiolysis products do indeed absorb at 260 nm, so that the decrease in absorbance does not measure the amount of adenine decomposed.

The spectra of the irradiated solutions exhibit a rather strange and interesting feature, namely, two isosbestic points at 236 and 285 nm and persist to >50% decomposition. Analysis by thin-layer chromatography and mass spectrometry shows that urea is one of the products, and it confirms the formation of 8-hydroxyadenine and of 4,6-diamino-5-formamidopyrimidine, which had been reported previously. None of these products interfere with the colorimetric determination of adenine.

Experimental Section

Adenine (Sigma and Schwarz Biochemicals), [8-¹⁴C]-adenine (New England Nuclear), and isoguanine (Sigma) were commercial samples. 8-Hydroxyadenine and 4,6-diamino-5-formamidopyrimidine were synthesized. The solutions were prepared in 0.05 M phosphate buffer, pH 7.0. The radiation source was a ¹⁰⁰Co Gammapcell-200 (Atomic Energy of Canada); dose rates were 3300-2800 rad/min. The course of the radiolysis depended on the adenine/oxygen ratio. In air-equilibrated solutions, the