Conversion of Hydroxycyclohexadienyl Radicals of Methylated Benzenes to Cation Radicals in Acid Media

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Formation of radical cations from the OH adducts of methylated benzenes in acidic aqueous solutions is demonstrated. The radical cation is formed as an intermediate species in the water elimination reaction in which the OH adduct is transformed into the corresponding methylbenzyl radical. The radical cations are also produced in neutral aqueous solution by reacting SO_4^- radical ions with the methylated benzenes. The cations have two absorption bands, an UV band, 280–300 nm, and a visible band, 430–470 nm, with extinction coefficient of about 6500 and 2000 M⁻¹ cm⁻¹, respectively. The formation of the radical cations from the OH adducts depends on the hydrogen ion concentration, $k_{OH adduct+H}^+ = (1.5 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The radical cations decay in acid solution exclusively into the corresponding methylbenzyl radicals.

Introduction

The hydroxyl radical is known to react with aromatic compounds preferentially in an addition reaction forming the corresponding hydroxycyclohexadienyl radical.¹ In our recent paper² we have shown that the OH adduct in some cases undergoes a dissociation reaction forming the radical cation. Previously both an uncatalyzed and an acid catalyzed water elimination reaction were reported from the OH adducts of phenols,³ hydroquinone,⁴ and methylated benzenes.⁵ Recently some papers appeared on the acid catalyzed formation of the radical cations of biphenyl⁶ and methoxylated benzenes⁷ and radical zwitterions from methoxylated benzoic acids.⁸ In a previous paper⁵ we reported the results from a pulse radiolysis study of the methylated benzenes in aqueous solution, and we tentatively assigned a transient species, appearing as an intermediate in the water elimination reaction in acid solution, in which the OH adduct is transformed into the corresponding methylbenzyl radical to the radical cation. The present report describes further experiments which confirm our previous assignment.

Experimental Section

The methylated benzenes of the highest available purity were obtained from Merck, BDH, Koch-Light, Fluka, and K & K, and used without further purification. The perchloric acid was reagent grade from G. F. Smith and the sodium hydroxide from Merck. The water was triply distilled and all glassware was preheated to 450 °C.

The pulse radiolysis system on the Linac was described previously^{5,9} and the setup on the 2.3-MeV Febetron was essentially the same except for a faster detection system. The doses were measured with the hexacyanoferrate(II) dosimeter¹⁰ using $g(e_{aq}^{-} + OH) = 5.25$ and $\epsilon(420 \text{ nm}) = 1000 \text{ M}^{-1} \text{ cm}^{-1}$.

Solutions of the liquid methylated benzenes were deaerated and saturated by bubbling gas through the solution with an excess of the methylated benzene in a 100-mL syringe. Solutions of the solid compounds were prepared in a 1-L flask by repeated evacuation and saturation with the appropriate gas. The pH was adjusted with perchloric acid or sodium hydroxide and was measured on a digital pH meter, Radiometer PHM52.

Results and Discussions

Spectrum in Acid Solution. Aqueous solutions saturated with various methylated benzenes in the pH range

0–7 were pulse radiolyzed. Solutions at pHs \geq 3 were N₂O saturated and at pHs <3 Ar or O₂ saturated. At high pH, the transient species are the hydroxycyclohexadienyl radical with the characteristic broad absorption band at 320–330 nm and a small yield of the methylbenzyl radical.^{1,5} As the pH is lowered, two new bands form, one below 300 nm, the other in the visible region at 430–470 nm. These bands decay simultaneously yielding a product which is identified as the corresponding methylbenzyl radical.⁵ These three spectra from *p*-xylene are shown in Figure 1.

In our previous paper⁵ the new spectrum was tentatively assigned to the radical cation. The intermediate species from isodurene existing between the hydroxycyclohexadienyl radical and the methylbenzyl radical spectrum is illustrated in Figure 2. At 331 nm the OH adduct absorption decays into the radical cation species absorbing at 465 nm, which successively decays into the methylbenzyl radical absorbing at 331 nm.

The decay of the OH adducts at 320-330 nm changes from a second-order reaction in neutral to pseudo-first order in acid solution. The rate of this pseudo-first-order decay is found to be linearly dependent on the hydrogen ion concentration and corresponds exactly to the buildup of the absorption at 450 nm. This behavior has also been found for the formation of radical cations of biphenvl.⁶ methoxylated benzenes,⁷ and methoxylated benzoic acids,⁸ where the OH adduct proves to be the precursor for the radical cation. A "clean" spectrum of the radical cations, without interference from the H adduct absorption, can be obtained in oxygen-saturated acid solution, since neither the absorption bands nor the kinetics of the radical cations are affected by oxygen. This spectrum can also be obtained at pH above 3 in N₂O-saturated solutions for the higher methylated compounds. In these cases the increase of the band height at 450 nm by a factor of 2 is demonstrated in N₂O-saturated solution compared to argonsaturated solutions. Moreover it was shown in our previous paper⁵ that the OH adduct is quantitatively converted into the methylbenzyl radical in acid solution. This justifies the use of the corrected yield of OH radicals in the calculation of the extinction coefficient of the new species. The correction applied to the OH radical yield is due to the small fraction entering the reaction of the direct H-atom abstraction.⁵ The extinction coefficients were then calculated from the absorptions in strong acid solution, pH 0-2, both in Ar and O_2 saturated, and the results are given in Table I.



Figure 1. Spectra of transient species in the acid-catalyzed water elimination reaction of *p*-xylene: (----) OH adduct; (-----) *p*-methylbenzyl radical.



Figure 2. Oscilloscopic traces of the transients in isodurene solution, pH 3.45: (a) 331 nm (absorption of the OH adduct and the trimethylbenzyl radical); (b) 455 nm (absorption of the radical cation). The time scale in both traces is 10 μ s per division.

The high acid concentration was used in order to obtain instantaneous conversion of the OH adduct, which is necessary to get a fully developed spectrum of the radical cation of the low methylated compounds because of the fast first-order decay of their radical cations, even though the extinction coefficient for o- and m-xylene may be too low. For the same reason we are not able to offer an extinction coefficient for the toluene radical cation, because the formation and decay rate in 1 M acid is of the same order of magnitude. However, the spectrum of the toluene radical cation can be observed in even stronger acid (2–5 M), but at these acid concentrations the primary yields are not well known. The ability to observe the spectrum in very strong acid is due to a general increase of the lifetime of the radical cations of the methylated benzenes

 TABLE I:
 Absorption Bands and Extinction Coefficients

 of the Radical Cations of Methylated Benzenes in
 Aqueous Solution

	λ _{max} , nm	ϵ, M^{-1}	
Taluana	005		
Toluene	200		
o Vulono	430	0000	
0-Aylene	290	6000	
37 1	430	2000	
<i>m</i> -Xylene	285	6300	
	450	2300	
<i>p</i> -Xylene	290	7000	
	435	2050	
Mesitylene	292	6600	
	475	2250	
Hemimillitene	290	6700	
	450	1950	
Pseudocumene	285	7000	
	445	2300	
Isodurene	290	6500	
	455	2200	
Prehnitene	300	7000	
	455	2000	
Durene	295	5000	
2010110	465	~1800	
Pentamethylbenzene	305	3750	
1 chrameonyiDenzene	475	~1500	
	-110	1000	

at acid concentrations above 0.5 M. This effect of acid concentration is not fully understood at the moment. For the high methylated benzenes the solubility is so low that the formation of the radical cation becomes controlled by the rate of reaction of the OH radicals with the substrate. This together with a fairly fast decay may result in a low value for the extinction coefficient for these compounds.

Formation of the New Transient Spectrum in Neutral Solution. Except for toluene and o- and m-xylene the radical cation can be observed in neutral solution by reacting SO_4^- radicals with the methylated benzenes. Persulfate is known to scavenge hydrated electrons with a rate constant of 1.1×10^{10} M⁻¹ s⁻¹, producing SO_4^- radicals,¹¹ while the OH radical reacts much slower with the persulfate, $k \leq 10^6$ M⁻¹ s⁻¹.¹ The sulfate radical reacts





with aromatic substrates yielding the radical cation^{7,12-16} in several cases. No addition products were detected.¹⁷

In an Ar-saturated neutral solution of methylated benzenes containing 5×10^{-3} M $S_2O_8^{2-}$, the transient spectrum consists of absorption bands at 420-470, 320-330, and 280-300 nm. The OH radicals produce the adduct with a band at 320–330 nm, and the SO_4^- radical is believed to produce the radical cation. When the OH adduct absorption is subtracted from the spectrum, the remaining absorption is identical with the spectrum found in oxygen-saturated acid solution. Moreover the extinction coefficient based on $G_{SO_4} = g_{e_{so}} = 2.7$ is identical with that obtained in acid solution, based on the corrected OH yield. A "clean" spectrum of the radical cation formed in the reaction with SO_4^- , free of the OH adduct absorption, may be obtained by scavenging the OH radicals by tert-butyl alcohol, since the SO_4^- radical reacts with the alcohol with a rate constant of $k = (9 \pm 1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$,¹⁸ while the OH radical reaction has a rate constant of $k = 5.2 \times 10^8$ M⁻¹ s⁻¹.¹ Using a concentration of *tert*-butyl alcohol two hundred times greater than the concentration of the methylated benzenes, more than 90% of the OH radicals are scavenged, while more than half of the SO_4^- radicals react with the methylated benzenes. The resulting spectrum at pH 8.2 is again identical with that obtained in acid solution. In Figure 3 the normalized spectrum of the *p*-xylene radical cation obtained in neutral solution containing *tert*-butyl alcohol and $S_2O_8^{2-}$ is compared with the spectrum observed in acid oxygen saturated solution.

The rate constants for the reaction of the SO_4^- radical with the various methylated benzenes were measured from the formation of the absorption band at 430 nm. These rate constants are generally three to five times lower than the rate constants for the OH radical reaction. The rate constants are all of the order of 1 to $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Some of the rates are rather difficult to determine accurately, however, because of the overlapping spectrum of the SO_4^- radical.

Assignment of the Transient Species. The assignment of the intermediate transient species to the radical cation is based on its identity with the species formed by the $SO_4^$ reaction and on the ionic strength dependency of the reaction of the species with ferrous and hydroxide ions. The reaction with Fe^{2+} was studied in N₂O-saturated sulfuric acid solution at pH 2.5–3.5. The ratio of the concentrations of the methylated benzene and the ferrous ions was adjusted so that most of the OH radicals react with the benzene. The pH was chosen as a compromise to avoid the H adduct formation and to obtain a fast transformation of the OH adduct into the radical cation. For this reaction is a reduction of the radical cation to the parent compound and an oxidation of ferrous to ferric ions.

$$(CH_3)_n \dot{C}_6 H_{6-n^{+}} + Fe^{2+} \rightarrow (CH_3)_n C_6 H_{6-n} + Fe^{3+}$$
 (1)

The rate constant was determined at different ferrous ion concentrations by following the decay of the radical cation at 460 nm and the formation of ferric ions at 302 nm.¹⁹ The rate of this reaction for pseudocumene and isodurene was $(6.0 \pm 1.0) \times 10^7$ M⁻¹ s⁻¹. For the ionic strength measurements the sulfuric acid was substituted by perchloric acid and the ionic strength of the solution was adjusted with NaClO₄. The rate was measured from the decay of the radical cation and the rate constant was calculated from the equation

$$k_{\rm m} = k_4 + k_1$$

where $k_{\rm m}$ is the measured first-order decay, k_4 the rate for the formation of the methylbenzyl radicals in acid solutions, and k_1 the rate constant for reaction 1. As was found for the anisole radical cation²⁰ the rate of reaction 1 is ionic strength dependent. Figure 4 shows the result for isodurene where the initial slope of the curve equals +2. This supports the conclusion that our species has a unit positive charge. k_4 proved to be independent of the salt concentration.

A second reaction supporting our assignment is the reaction with hydroxide ions yielding the OH adduct

$$(CH_3)_n \dot{C}_6 H_{6-n^+} + OH^- \rightarrow (CH_3)_n \dot{C}_6 H_{6-n} OH$$
(2)

This reaction was studied in argon-saturated solutions at pH 8–11 containing $S_2O_8^{2-}$. The radical cation was formed



Figure 4. The effect of ionic strength, μ , on the rate of the isodurene radical cation reactions: k, measured rate constant, k_0 , rate constant extrapolated to zero ionic strength: (X) reaction with Fe²⁺, pH 3.1; (O) decay into the trimethylbenzyl radical, pH 3.1; (Δ) reaction with OH⁻, pH 10.5.

from SO₄⁻ radicals and the OH radicals formed the OH adduct. At pH 7 the radical cation decays faster than in acid solutions, and it is concluded from the additional formation of OH adduct that a reaction with water (reverse of reaction 3) competes with the formation of methylbenzyl radicals (reaction 4). This reaction will be described in a successive paper.²¹ At higher pH the rate of the radical cation decay is proportional to the hydroxide ion concentration, and additional OH adduct is formed according to reaction 2 at the expense of methylbenzyl radicals. At pHs approaching 11 some minor part of the SO_4^- radicals contributes to the OH adduct formation directly through the reaction with hydroxide ions yielding OH radicals. The rate constant for this reaction is $7.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-115}$ and will be significant only with compounds of low solubility. However, this reaction has no influence on the determination of the rate constant of reaction 2, as this is measured from the decay of the radical cation. The rate constant for reaction 2 was calculated from an equation analogous to (A), but instead of using k_4 , which is considered to be pH independent, a rate constant as measured at pH 7 taking into account the reverse of reaction 3 is used, the reason being that reaction 2 is competing with reaction 4 as well as with the reverse of reaction 3. The rate constant for isodurene radical cation with OH^- (reaction 2) is 1.2 $\times 10^9$ M⁻¹ s⁻¹ and, as shown in Figure 4, the curve for the rate constant as function of ionic strength has a slope of -1 again suggesting a unit positive charge for the transient species.

The cationic behavior of the species is additionally demonstrated by its unreactivity with oxygen. The spectra obtained for the negative ions of benzene, toluene, and p-xylene by dissolution of alkali metals in organic systems show essentially the same absorption maxima as the

 TABLE II:
 Rate Constants for Reaction of OH Adducts

 of Methylated Benzenes with Hydrogen Ions

	$k_{OH adduct} + H^+ \times 10^{-9} M^{-1} s^{-1}$	
Toluene		
o-Xylene	>0.5	
<i>m</i> -Xylene		
<i>p</i> -Xylene	>0.5	
Mesitylene	>0.5	
Hemimillitene	1.4 ± 0.3	
Pseudocumene	1.5 ± 0.2	
Isodurene	1.0 ± 0.3	
Prehnitene	1.5 ± 0.2	
Durene	1.1 ± 0.2	
Pentamethylbenzene	1.5 ± 0.3	

corresponding radical cations which should be expected for a one electron deficient original compound.²² Furthermore the absorption energies of the toluene radical cation from the photodissociation spectra are 3.0 and 4.7 eV^{23} compared to our values 2.9 and 4.35 eV in the aqueous phase. Thus our assignment of the species to the radical cation seems justified.

The Reaction Mechanism in Acid Solution. The formation and decay of the radical cation in acid solution can be rationalized by the reactions:

$$(CH_3)_n \dot{C}_6 H_{6-n} OH + H^+ \rightarrow (CH_3)_n \dot{C}_6 H_{6-n}^+ + H_2 O$$
 (3)

$$(CH_3)_n C_6 H_{6-n}^* \to (CH_3)_{n-1} C_6 H_{6-n} CH_2 + H^*$$
 (4)

The dependency of the formation of the radical cation on the hydrogen ion concentration suggests a protonation of the OH adduct as the first step, followed by a rapid elimination of a water molecule. As we have not observed an absorption, which could be attributed to the protonated form of the OH adduct, the elimination reaction must then be very fast. An alternative mechanism could be an OH⁻ abstraction from the OH adduct caused by the high hydrogen ion concentration. In this case the adduct probably has to be in equilibrium with a charge-transfer complex. The OH⁻ elimination from OH adducts is suggested by Bansal and Henglein²⁴ in the cathodic process.

In the oxidation of benzene and its derivatives by the Fenton reagent and in related systems, 25,26 a reaction such as (3) involving the radical cation was suggested to explain the low yields of hydroxylated products in acid solution. Furthermore this reaction was postulated for the formation of radical cations from biphenyl⁶ and methoxylated benzenes⁷ and for the formation of zwitterions from methoxylated benzoic acids.⁸

Because of the complexity of the overall mechanism in the system, the formation of the radical cation from the OH adduct in acid solution is a combined effect of several reactions. The rate constant for reaction 3 cannot be accurately determined for the lower methylated compounds (one and two methyl groups) because of a fast decay of the radical cation and a back reaction with H_2O .²¹ We estimate a lower limit of $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for these compounds. For the slower decaying cations (three, four, and five methyl groups), the rate constant k(OH adduct+ H⁺) can be measured directly by the buildup of the positive ion transient as a function of the hydrogen ion concentration. The rate was found to be $k_3 = (1.5 \pm 0.5)$ $\times \, 10^9 \, M^{-1} \, {\rm s}^{-1}$ for all the compounds, and we assume that this value also is valid for the lower methylated benzenes (Table II). This rate constant agrees with values reported for methoxylated benzenes.⁷

Reaction 4, a proton splitting reaction, is the main path of the decay of the radical cations of the methylated benzenes in acid solution. It was found that the conversion Spectral Properties of MeOH-I2 and EtOH-I2 Complexes

of OH adducts to methylbenzyl radicals was quantitative.⁵ This reaction was not observed in the study of anisole,^{7,20} probably because its methyl group becomes more negative on ionization²⁷ contrary to the methylated benzene derivatives where the methyl group increases its positive charge. The fractional charge on the methyl group in toluene radical cation is calculated to be about 10% increasing to 20% for durene and pentamethylbenzene radical cations.²⁸

Neither a dimerization of the radical cations nor a reaction with the solute, as were found in the anisole system,²⁰ was observed for the methylated benzenes. This may be due to the short lifetime of the radical cations and the low solubility of the methylated benzenes.

The reverse of reaction 3 is being studied in neutral solution with the radical cations formed from SO_4^- , and the results will appear in a later paper.²¹

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The Spectral Properties of Methanol–lodine and Ethanol–lodine Complexes in *n*-Heptane Solution

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The iodine complexes of ethanol and methanol in *n*-heptane were studied by the constant activity method, and their UV and visible spectral characteristics were determined. With decreasing alcohol concentration, the blue-shifted iodine band maxima of both complexes shift to longer wavelengths, whereas their charge-transfer band maxima shift to shorter wavelengths. The value of the blue-shifted iodine band maximum extrapolated to zero alcohol concentration is $\simeq 475 \pm 5$ nm for each complex. This is an appreciably longer wavelength than previously reported for the alcohol-iodine system. The estimated charge-transfer band maxima for ethanol-iodine and methanol-iodine are $\simeq 225 \pm 5$ and $\simeq 223 \pm 5$ nm, respectively. A model based on the self-association of alcohol and preferential solvation of the complex is proposed to explain the concentration dependence of the bands. The iodine interacts with an alcohol aggregate, the donor strength of which increases with an increase in degree of aggregation.

Introduction

Diethyl sulfide, diethyl ether, methanol, and ethanol are classical examples of n-type electron donors which interact with an iodine molecule to form charge-transfer complexes. These have been studied in solution before.¹⁻⁶ Results for the equilibrium constants and heats of complexation show that diethyl sulfide is a stronger donor than the ether and alcohols, the latter two being comparable in strength. According to Mulliken's theory,⁷ the extent of the blue shift of the complexed iodine visible band should increase with increasing strength of the donor. Therefore, it would be expected that the blue-shifted (hereafter abbreviated by BS) iodine bands of the ether and alcohol complexes should appear in the same region of the spectrum but at

appreciably longer wavelength than that of the sulfide complex. The literature data are not in accord with expectation. The often quoted values for the BS iodine band maximum (λ^{BS}) for ethanol-iodine is 443 nm and for methanol-iodine is 440 nm, these being from the work of de Maine who used carbon tetrachloride as the solvent.⁵ Exactly, the same results were reported by Voigt⁸ for iodine in pure ethanol and in pure methanol. These maxima are rather close to that of 435 or 437 nm reported for the diethyl sulfide-iodine complex,^{1,2} but are quite far from the value of 470 nm obtained for the diethyl ether-iodine complex.

Another point to consider is the intensity of the BS iodine band when complexed with donors containing an