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## Formation and reactions of radical cations of substituted benzenes in aqueous media. A pulse radiolysis study

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<p><b>Title and author(s)</b></p> <p>Formation and Reactions of Radical Cations of Substituted Benzenes in Aqueous Media. A Pulse Radiolysis Study.</p> <p>Jerzy Holcman</p>	<p><b>Date</b> August 1977</p>
<p>74 pages + tables + illustrations</p>	<p><b>Department or group</b></p> <p>Accelerator</p>
<p><b>Abstract</b></p> <p>Radical cations of anisole, methylated benzenes, ethylbenzene, isopropylbenzene, tert-butylbenzene and N,N-dimethylaniline were studied in aqueous media by pulse radiolytic technique. Absorption spectra and reaction kinetics of the radical cations were recorded.</p> <p>The radical cations are formed from the corresponding OH adducts by elimination of OH<sup>-</sup> either by a simple dissociation or by an acid catalyzed reaction.</p> <p>The rate constants of the formation of the radical cations and their reactions with water, OH<sup>-</sup> and Fe<sup>2+</sup> or the reaction of a proton loss were measured.</p> <p>The rate constants for reaction with water and OH<sup>-</sup> together with the rate constant for the dissociation of the OH adducts are correlated with the ionization potential of the parent compound. These correlations offer a possibility of predicting the acid-base properties of radical cations of substituted benzenes, or estimation of their ionization potential.</p>	<p><b>Group's own registration number(s)</b></p>
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### Forord

Denne rapport er udført som led i de betingelser, der skal opfyldes ved erhvervelsen af den tekniske licentiatgrad på Danmarks tekniske Højskole.

Projektet er udført under Institutet for Organisk Kemi med professor, dr. phil. Chr. Pedersen som faglærer. Arbejdet er imidlertid foregået i Acceleratorafdelingen, Forsøgsanlæg Rise, med afdelingsleder, civ.ing. K. Sehested som medfaglærer. Ligeledes er den finansielle støtte til projektet ydet af Forsøgsanlæg Rise.

Rapporten er skrevet på engelsk, fordi hovedparten af resultaterne allerede er publiceret eller indgivet til publikation i The Journal of Physical Chemistry.



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## 1. INTRODUCTION

This report describes the results of a pulse radiolytic study of formation and reactions of radical cations of substituted benzenes in aqueous media.

On radical hydroxylation of aromatic compounds, the hydroxyl radical adds very rapidly to the aromatic ring with a rate constant  $10^9 - 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  (1), forming the corresponding hydroxycyclohexadienyl radical (OH adduct) as an intermediate species. This radical will under further oxidation give a hydroxylated derivative.

For the OH adducts of phenols, anilines and methylated benzenes intramolecular water elimination, which can be acid and base catalyzed, is described in the literature (2,3,4). These reactions decrease considerably the yield of hydroxylated products.

An investigation of the water elimination reaction from OH adducts of methylated benzenes undertaken by Sehested et al. at Riss's Accelerator Department has shown that this reaction is a two step process with the radical cation as an intermediate species.

The aim of the reported work is:

- a) to study the water elimination reaction for several substituted benzenes in order to explain the role of the radical cation and the influence of different substituents on the mechanism of this reaction;
- b) to study formation and reactions of the radical cations of substituted benzenes, their optical spectra and acid-base properties in aqueous media.

The results reported were obtained by pulse radiolytic technique mainly by using the optical detection system (kinetic spectrophotometry) at Riss's Accelerator Department.

This report is submitted to the Danish Technical University (Danmarks tekniske Højskole) in partial fulfilment of the requirements for the degree of lic.tech. (Ph.D.).

With some minor changes parts of this report have already been published or submitted for publication. The work was performed during the period 1st March 1975 - 1st September 1977.



## 2. RADIATION CHEMISTRY OF WATER AND AQUEOUS SOLUTIONS

### 2.1. General

Radiation chemistry is usually defined as a study of chemical effects caused by the absorption of ionizing radiation in a system.

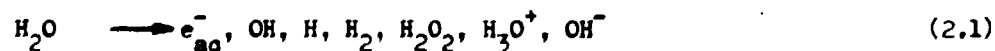
The sources of radiation can be generally divided into two groups, isotope sources - those employing natural or artificial radioactive isotopes- and machine sources those employing some form of particle accelerator. From all possible sources of ionizing radiation cobalt-60 gamma sources and electron accelerators are by far the most common and almost exclusively used in radiation research as well as in industrial applications.

Until recently radiation chemistry according to its definition has been mainly concerned with investigating the chemical reactions taking place in irradiated solutions in order to understand the primary processes. However, many of the irradiated systems are now reasonably well understood, and recent applications of radiation techniques to biochemistry, biology, inorganic chemistry, polymer and physical organic chemistry have shown that these techniques can be considered as important advanced tools for research in other fields than radiation chemistry.

Among other systems water and aqueous solutions occupy a very special position in radiation chemistry. Due to its relative simplicity and relevance to radiation biology, the aqueous system has been the most intensively studied solvent system in radiation chemistry in qualitative and quantitative as well as in theoretical aspects. As a result of thorough study, main features of the water radiolysis are now firmly established, and the aqueous system is considered the best understood solvent system from a radiation chemical point of view.

### 2.2. Radiolysis of Water. Qualitative Aspects

After about  $10^{-9}$  sec after the passage of high energy radiation the radiation induced decomposition of water can be qualitatively radicalized according to eq. (2.1).



These products are often referred to as the "primary products" or "primary species" and are found homogeneously distributed in irradiated water irrespectively of the type and energy of radiation.

The primary products are not necessarily the very first entities formed but rather the earliest which are readily accessible chemically.

In absorption of high energy radiation, energy packets of million electron volts are broken in packets of several orders of magnitude lower energy. This energy is deposited in form of ionized and excited molecules and atoms. These are grouped in zones of different size, energy content, number and identity of species in a non uniform distribution along the track of the ionizing particle. These zones although classified and more specifically characterized can for simplicity be referred to as the "spurs". An essential feature of spurs is a relatively high concentration of free radicals (of the order of 0.1 M), which results in an enhancement of radical-radical reactions before the radicals have diffused into the bulk of the solution. Their concentration is lower by many orders of magnitude in the bulk and a reaction with a solute is therefore greatly enhanced.

The Hydrated Electron,  $e_{aq}^-$

The hydrated electron can be considered as an electron trapped by orientated water-molecule dipoles in its vicinity. It has a broad optical absorption with a maximum at 720 nm,  $\epsilon = 1.58 \times 10^4 \text{ M cm}^{-1}$ , and the mean radius of charge distribution is about 0.25 - 0.3 nm. The hydrated electron is a very powerful reducing agent; its standard redox potential is about 2.7 V.

In pure water hydrated electrons react with each other yielding hydrogen



They react very slowly with water



On the other hand the hydrated electrons react often very rapidly with solutes or impurities present in the water



Thus the lifetime of the hydrated electron in water can be used as a water purity criterion.

The Hydrogen Atom, H

Hydrated electrons react readily with hydrogen ions present in the solution yielding H atoms



Reaction (2.5) shows that the hydrogen atom can be considered as an acid and

the hydrated electron as its conjugated base. Their interconversion is possible by reactions (2.5) and (2.6).



The pK is 9.7.

The H atom although weaker than  $\text{e}_{\text{aq}}^-$  is still a potent reducing agent with redox potential of 2.31 V. Both  $\text{e}_{\text{aq}}^-$  and H are important in the pH range 4-11. In most radiolytic studies  $\text{e}_{\text{aq}}^-$  is the only reducing radical above pH 13 and H atoms below pH 2.

#### The Hydroxyl Radical, OH

The hydroxyl radical is a powerful oxidizing agent; its redox potential is - 2.8 V in acid solution. It behaves like a weak acid undergoing ionic dissociation in strongly basic solution



The pK for this equilibrium is  $11.9 \pm 0.2$ .

In absence of solutes the OH radical reacts with the reducing radical reforming water or with another OH radical yielding hydrogen peroxide.



### 2.3. Radiolysis of Water. Quantitative Aspects

The radiation chemical yield is almost universally expressed as the "G-value".

The G-value is defined as the number of molecules, atoms, radicals or ions formed or destroyed by 100 eV (16 aJ) of energy absorbed in the system. Thus a material balance of the water radiolysis can be written as

$$G_{(-\text{H}_2\text{O})} = 2G_{\text{H}_2} + G_{\text{H}} + G_{\text{e}_{\text{aq}}^-} = 2G_{\text{H}_2\text{O}_2} + G_{\text{OH}} \quad (2.9)$$

Having in mind that the "primary" products are not the very first species formed and that the chemical yields of the short-lived and very reactive species like H,  $\text{e}_{\text{aq}}^-$  or OH cannot be determined directly, it is obvious that the G-values of the primary products must be understood as a working definition and can be measured or used in a restricted range of solute concentrations. This range is restricted by three factors:

- a) Direct Effect. The concentration of the solute must be so low that

the effect of a direct energy absorption by the solute can be neglected.

- b) Spur Reactions. The effect of the solute on spur reactions must be negligible.
- c) Concurrent Reactions. The concentration of the solute must be high enough to prohibit concurrent reactions of the primary species.

A cumbersome analysis of the yield of radiolytic products in a number of studied systems has led to generally accepted G-values of the primary products of the water radiolysis.

At low solute concentrations the generally accepted G-values are 2.7 for OH, 0.6 for H, 2.7 for  $e_{aq}^-$ , 0.7 for  $H_2O_2$  and 0.4 for  $H_2$  in neutral water. As an effect of acid-base equilibria the primary yields from water are pH dependent. The nature and yields of the primary species, that would be expected to react with  $10^{-3}$  M solute at various pH's are shown in Fig. 2.1.

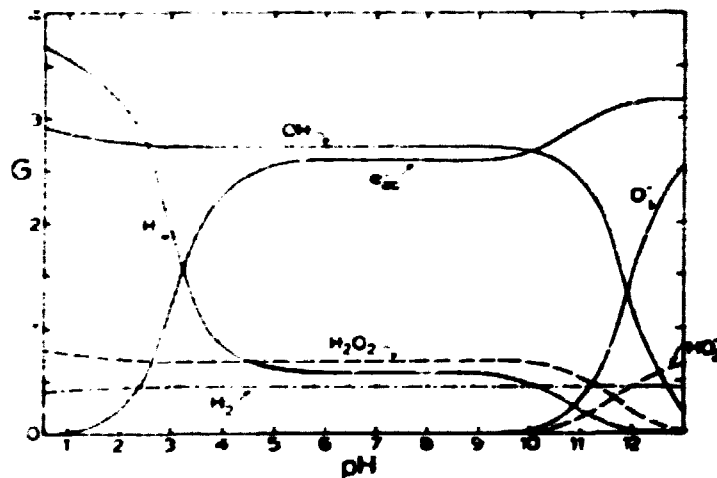


Fig. 2.1. The nature and yields of primary species of water radiolysis at different pH's.

General References to Chapter 2.

J.W.T. Spinks and R.J. Woods, "An Introduction to Radiation Chemistry". Wiley, New York and London 1976.

I.G. Draganić and Z.D. Draganić, "The Radiation Chemistry of Water". Academic Press, New York and London 1971.

### 3. PULSE RADIOLYSIS

The pulse radiolytic technique is based on a pulsed source of ionizing radiation usually an electron accelerator which is able to irradiate a sample with an "instantaneous" pulse. The radiation intensity should be high enough to produce easily detectable concentrations of transient species. A schematic diagram of a typical pulse radiolysis set-up is shown in Fig. 3.1.

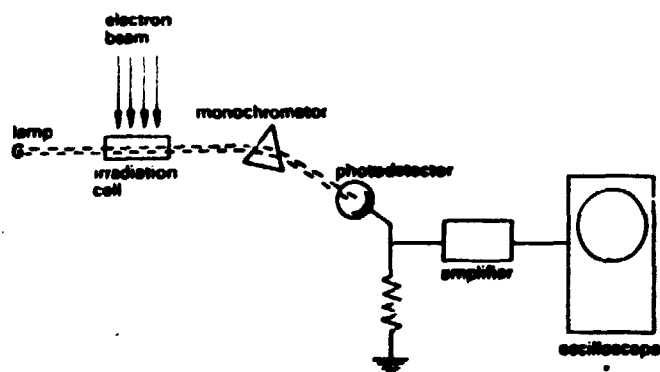


Fig. 3.1. A schematic diagram of a typical pulse radiolysis set-up.

A short pulse of electrons is delivered to the irradiation cell which serves simultaneously as a spectrophotometric cell. The light from a continuous or pulsed light source passes through the solution being irradiated and then through a monochromator to select the chosen wavelength. The monochromated light is collected in a photodetector usually a photomultiplier tube. The photomultiplier tube converts the light intensity into an electric signal which after amplification is finally displayed on an oscilloscope with a fast time sweep. The trace is either photographed or stored. An idealized oscilloscopic trace is shown in Fig. 3.2. In the region AB the intensity level of light passing through unirradiated solution is recorded. In BC the electron pulse is being delivered. Pulse parameters like pulse energy, duration and electron energy can usually be adjusted to meet optimal conditions for the experiment. High energy electrons travelling through matter cause light emission named Čerenkov emission. Čerenkov light especially in the ultraviolet region may cause temporary overload of the photodetector. At longer wavelength Čerenkov light is not observed.

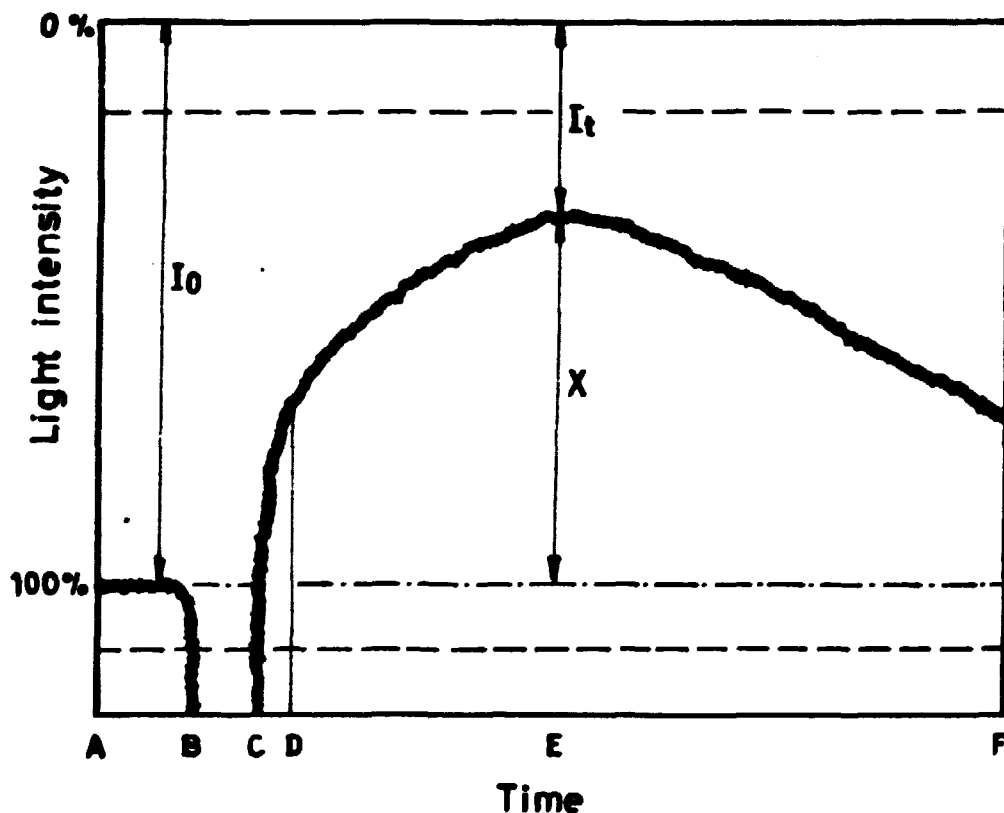


Fig. 3.2. An idealized oscilloscopic trace obtained by pulse radiolysis for a given wavelength.

--- area usually displayed on the oscilloscope

- - base line (100% intensity)

AB - light intensity before the electron pulse (100%)

BC - Čerenkov radiation overloading the photodetector caused by the electron pulse

CD - recovery of the photodetector

DE - formation of a transient species by radical solute reaction

EF - decay of the transient species

After the recovery of the photodetector, CD, a formation of a transient species, DE, or a decay of the primary radicals may be observed. Later on the decay of the transient, EF, or permanent absorption due to stable products is detected. By choice of conditions, it is possible to enhance or eliminate

various sections of the idealized trace, and obtain optimum conditions for a measurement of a particular effect.

From Fig. 3.2 transient optical density,  $D_t$ , can be calculated at any given time after the pulse as

$$D_t = \log_{10} (I_o/I_t) \quad (3.1)$$

$I_o$  - the light intensity measured before the pulse (AB) (usually measured in mV)

$I_t$  - the light intensity at time t, obtained by subtracting of X (in mV) from  $I_o$

$$D_t = \log_{10} [I_o/(I_o - X)] \quad (3.2)$$

An absorption spectrum is obtained by measurements at discrete wavelengths.

From the shape of the optical trace an absolute rate constant can be calculated. For pure first order reactions and for radical-solute reactions where pseudo first-order conditions can be met by adjusting the solute concentration, no further information is required. In case of a radical-radical reaction, however, the molar extinction coefficient of the transient species is required. The extinction coefficients can be calculated from primary radical yields and dose absorbed in the sample.

In radiation dosimetry primary standards are set up by calorimetric measurements. In practice, however, chemical dosimeter, namely the Fricke dosimeter based on the oxidation of ferrous to ferric in aqueous solution, has become a standard secondary dosimeter. The formation of ferric ions can be measured spectrophotometrically. The disadvantage of the Fricke dosimeter for pulse radiolysis lies in the need for the source of analyzing light stable for a period of many seconds - the period for completion of reactions in the dosimeter. Thus other secondary dosimeters are used where completion of reactions is obtained immediately or at very short time after the pulse such as the  $N_2O$  saturated  $10^{-3}$  M  $[Fe(CN)_6]^{4-}$ .

The optical detection system is not the only system which can be used in pulse radiolysis. Detection techniques like conductometry, polarography, electron spin resonance, light emission, etc. are used. Optical absorption spectroscopy, however, has proved to be the most versatile method and the "pulse radiolysis" refers usually to pulse radiolysis with this particular detection system.

General References to Chapter 3.

M.S. Matheson and L.M. Dorfman, "Pulse Radiolysis".  
The M.I.T. Press, Cambridge Mass., 1964.

L.M. Dorfman in "Investigation of Rates and Mechanisms of Reactions".  
Part II 3rd. Edition, G.G. Hammes Ed., Wiley, New York 1974.

4. RADICAL CATIONS OF AROMATIC COMPOUNDS IN SOLUTIONS

Radical cations are usually generated by reactions resulting in the overall removal of an electron from a neutral, electron paired molecule. Thus they have both a positive charge and an unpaired electron. Cation radicals of molecules and molecular fragments are easily formed and studied in the mass spectrometer. In the solution, however, their occurrence is usually due to the electron transfer reactions or acid-base properties of uncharged free radicals.

The ability of a neutral molecule to give up an electron is governed by the energy of the highest occupied molecular orbital (HOMO) which can be estimated experimentally by measuring the gas phase ionization potential.

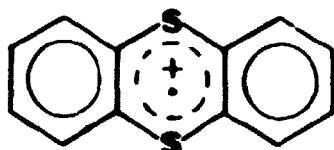
In solution the energetic effect of a solvation has to be taken into account.

Molecules containing  $\pi$  electrons and/or "lone pair" heteroatoms as O, N, and S are particularly prone to give up an electron.

Radical cations are usually very reactive species. Their stability in solution is rather complicated and difficult to study due to a variety of reaction pathways in which they disappear also influenced by the complexity of solvent effects. A pure solution of radical cations cannot be obtained, not even of those isolated in form of radical-cation salts. Generally, however, steric and conformational factors play an important role. Compounds of relatively low ionization potentials containing  $\pi$  systems able to delocalize the charge and unpaired electron are expected to give stable radical cations. The best known radical cations are those of aromatic and heteroaromatic compounds.

The stability of radical cations in solutions varies from perfectly stable radical cations like for example those from thianthrene [1] and Würster cations [2] which can be kept in solution for weeks,





[1]



[2]

to short-lived cations which cannot be detected directly even employing the fastest detection techniques known.

Radical cations have been exhaustively studied by electron spin resonance spectroscopy. However, chemical reactions of cation radicals have not until recently received much attention. Due to growing interest in organic oxidation processes and a vigorous development of organic electrochemistry the interest in the chemistry of radical cations drastically expanded.

Radical cations in solution are formed by chemical oxidation with agents like Brønsted acids, Lewis acids, halogens or metal salts, via a dissociation of the charge-transfer complexes, by anodic oxidation or by physical means like photoionization and radiolysis.

From a kinetical point of view the stability of radical cations in solution is governed by reactions like fragmentation, disproportionation, radical-radical and radical-parent molecule dimerizations, and radical cation-solvent reactions. Thus kinetical parameters of these reactions are often crucial for the study of radical cation chemistry.

#### General References to Chapter 4.

E.T. Kaiser, L. Kevan Eds, "Radical Ions".  
Wiley Intersciences, New York 1968.

A.J. Bard, A. Ledwith, and H.J. Shine, "Formation, Properties and Reactions of Cation Radicals in Solution". In "Advances in Physical Chemistry", Vol. 13.  
V. Gold and D. Bethell Eds. p. 155 ff.

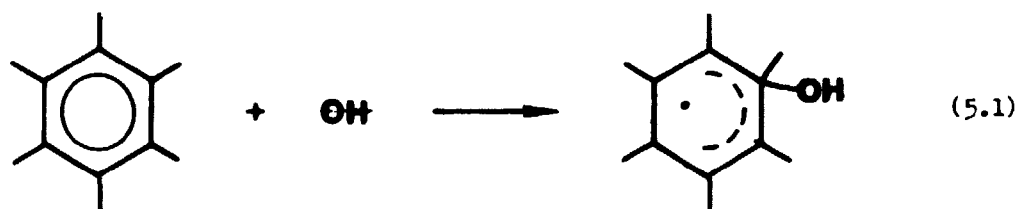
## 5. RESULTS AND DISCUSSION

### 5.1. General Introduction

Pulse radiolysis of aqueous solutions has been successfully used in the study of radical anions of aromatic compounds<sup>5)</sup>.

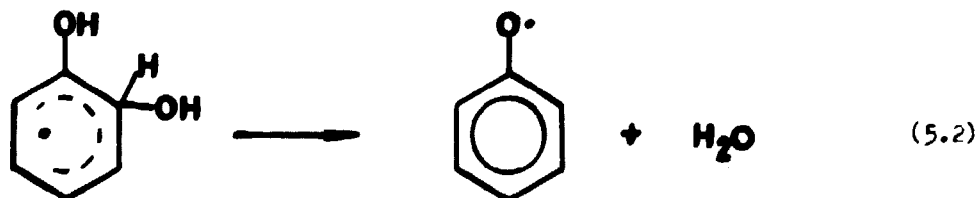
Radical anions are readily formed by addition of the hydrated electron, which is an exclusive way of reaction of this species with a solute<sup>7)</sup>. In contrast to radical anions it is usually much more difficult to generate radical cations, and until recently no information of their role in pulse radiolysis of aqueous solutions was available in the literature.

The oxidizing counterpart of  $e_{aq}^-$ , the hydroxyl radical, OH, is known to react with aromatic compounds forming the "OH adduct", e.g. the corresponding hydroxycyclohexadienyl radical whereas reactions with substituents have been generally considered negligible<sup>1)</sup>.

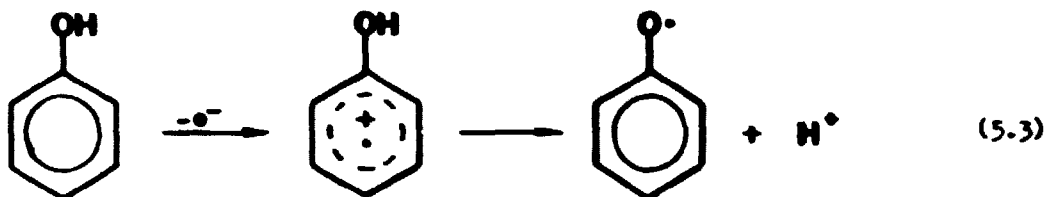


Reactions of aromatic compounds with OH radicals were studied by radiolytic methods as well as with Fenton reagent ( $Fe^{2+}/H_2O_2$ ) and with related systems where the OH radical is the main oxidizing species<sup>7)</sup>. Besides a certain preparative interest of the metal-ion catalyzed reactions of hydrogen peroxide<sup>8)</sup>, the reaction of OH radicals with organic compounds recently received much attention due to the widely suggested role of the OH radicals in biological systems.

The aromatic OH adduct formed in a pulse radiolytic experiment decays usually in a bimolecular radical-radical reaction or is oxidized to a phenol by oxidants present in the solution. The OH adduct may also eliminate a water molecule, which was known for phenolic compounds for a long time<sup>9,10)</sup>.

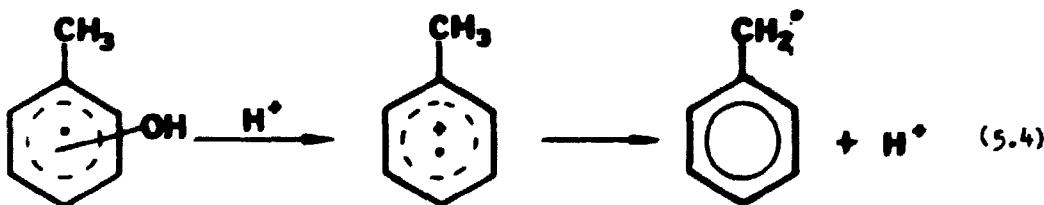


This reaction was found to be acid and base catalyzed and yields the phenoxy radical which is also a product of anodic oxidation of phenols. Its formation via a radical cation is suggested<sup>11)</sup>



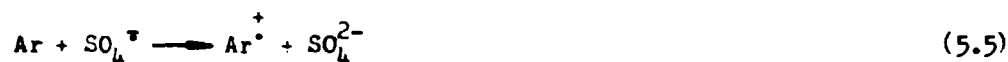
More recently an acid catalyzed water elimination from the OH adducts of aniline<sup>12)</sup>, toluene<sup>13)</sup>, and methylated benzenes<sup>14)</sup> has been demonstrated. These findings are in excellent agreement with studies of aromatic compounds in metal-ion-hydrogen peroxide systems, where water elimination and other heterolytic fragmentation processes were inferred from the product composition<sup>4)</sup>. More recently direct electron transfer from phenyl-substituted alcohols and ethers to the OH radical was suggested on the basis of a comparison of peroxydisulphate-metal-ion and Fenton reagent oxidation<sup>15)</sup>. This hypothesis, however, is in contradiction with results obtained hitherto by pulse radiolysis.

In the study of OH adducts of methylated benzenes, Sehested et al.<sup>3)</sup> have shown that acid catalyzed water elimination is a two-step process. The intermediate between the hydroxycyclohexadienyl radical and the benzyl radical was tentatively assigned to the corresponding radical cation, eq. 5.4<sup>3)</sup>.



The last step in eq. 5.4 is known from studies of metal-ion oxidations, e.g. cobalt (III) acetate in acetic acid<sup>16)</sup>.

An electron transfer mechanism has been suggested for the reaction of aromatic compounds with the sulphate radical anion  $\text{SO}_4^{\cdot -}$  (17,18) and later on supported by pulse radiolytic investigations (19,20,21,22).



The sulphate radical anion is easily obtained in pulse radiolysis in a reaction of solvated electrons with persulphate (23,24).



Another procedure which leads to an electron transfer from aromatic compounds in water solutions is their reaction with radiolytically generated ions like  $\text{Tl}^{2+}$  and  $\text{Ag}^{2+}$  (25).



Reactions 5.4, 5.5, and 5.7 offer a possibility of generating and studying aromatic radical cations in aqueous media in the wide pH range.

## 5.2. Experimental

**Materials.** The organic compounds were obtained from Merck, BDH, Fluka, Koch Light, K & K, and Fisher and were of purest available quality and used without further purification. Very sparingly soluble compounds were washed several times with tripple distilled water in order to remove soluble impurities. The perchloric acid was reagent grade from G.F. Smith, and sodium hydroxide, sulphuric acid, potassium peroxide, potassium ferrocyanide and ferrous sulphate were analytical grades from Merck and sodium perchlorate Analar R from BDH. Argon and oxygen were obtained from Dansk Ilt & Brintfabrik A/S, and nitrous oxide from AGA A/S and were used as received.

Ion-exchanged water was purified by tripple distillation in an oxygen stream; first from alkaline permanganate, then from acid dichromate, and finally without any additives. Each distillation being done through a column packed with glass rings.

**Preparation of Solutions.** Aqueous solutions were deaerated and saturated with the appropriate gas by bubbling the gas through the solution in a 100 cc glass syringe. Volatile organic compounds are added in surplus in order to obtain saturated solutions. Since the syringes are calibrated, solutions may be added or removed in precise amounts in order to obtain appropriate dilutions (Fig. 5.1)

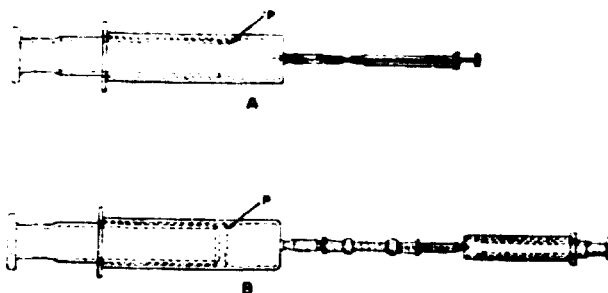


Fig. 5.1. Syringes for sample preparation and dilution.

The pH of the solutions was adjusted with perchloric acid or sodium hydroxide and was measured on a Radiometer digital pH-meter, PHM 52. The organic solute concentration was measured on the Cary 16 absorption spectrophotometer.

Pulse Radiolytic Cell. The irradiation cell constitutes a 2.5 cm long cylinder 2 cm in diameter with two quartz windows and two capillaries for refilling. The cell is irradiated through the window provided with a mirror. The analytical light enters the cell through the other window, is reflected in the mirror and exits through the same window. Thus the light path is 5 cm. The cell and refilling system is shown schematically in Fig. 5.2. The refilling system is automatic and remote controlled. It is based on the syringe driving mechanism and two one-way magnetic valves.

To empty the cell, valve 1 and 2 are opened. Under pressure of helium entering through valve 1, the solution in the system (with exception of branch A) is exhausted. After a preset time interval valve 2 is closed and the syringe driving mechanism delivers a certain amount of the solution to the irradiation cell. Valve 1 is then closed and the solution in the cell can be irradiated. When exchanging syringes a microswitch in the syringe driving mechanism closes valve 1 as well.

Irradiation. Pulse radiolysis was carried out on the Rise Linac set-up. The essential features are the Linac (linear accelerator) delivering 0.1 - 4  $\mu$ sec single pulses of 10 MeV electrons with maximum peak current of 1.1 A, the source of analytical light an Osram XBO 450 W xenon lamp, which can be used in pulsed operation, a Zeiss MM 12 double quartz prism monochromator, an EMI 9558 Q photomultiplier, and a Tektronix 555 double beam oscilloscope. The traces on the oscilloscope screen corresponding to the transient absorption changes were photographed with a Polaroid camera. The time resolution

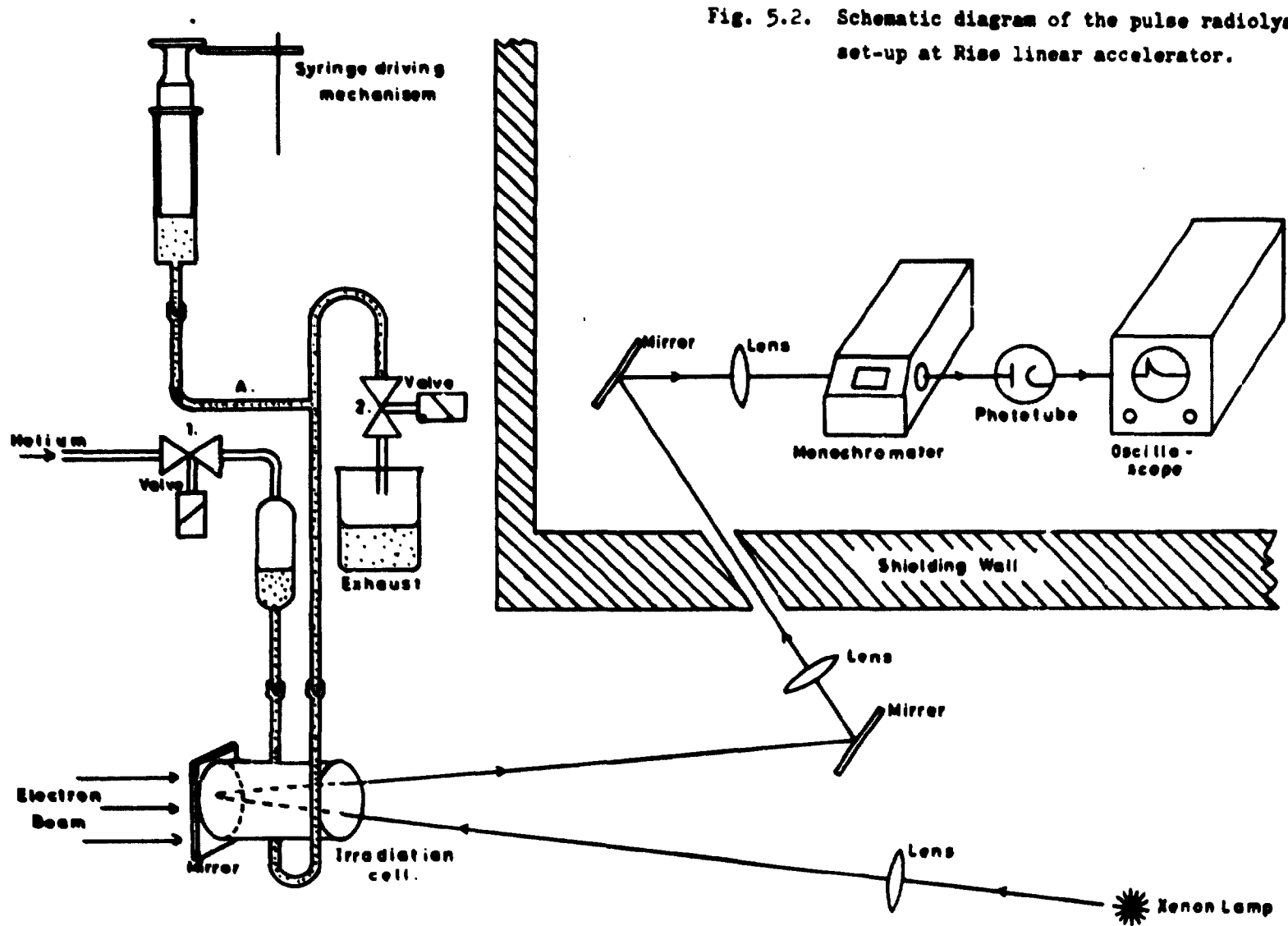


Fig. 5.2. Schematic diagram of the pulse radiolysis set-up at Rise linear accelerator.

of the Linac set-up is about 1  $\mu$ sec. In some experiments the set-up on the 2.3 MeV electron accelerator (Febetron) was used. The Febetron delivers single pulses of 2.3 MeV electrons of 20 nsec duration, and the detection system is 5 - 10 times faster than that of the Linac. The transient absorption signal is sampled and stored as a digital information by the transient recorder Bio-mation Model 8100 and processed further by the PDP-8/1 computer.

Dosimetri. The absolute dose was measured with the hexacyanoferrate (II) dosimeter<sup>26)</sup> by measuring optical density after pulse radiolysis of  $10^{-3}$  M hexacyanoferrate,  $N_2O$  saturated neutral aqueous solution using  $G(e_{aq}^- + OH) = 5.25$  and  $\epsilon_{(420\text{ nm})} = 1000\text{ M}^{-1}\text{ cm}^{-1}$ .

The current induced in a coil surrounding the electron beam was used as relative dosimetry<sup>27)</sup>.

#### 5.2.1. Manipulation of Primary Radicals. Radical Scavengers.

As it was pointed out in section 2.2. radiolysis of water leads to the formation of three primary radicals:  $e_{aq}^-$ , H, and OH. Thus, the manipulation of primary radicals is crucial for resolving the system from the quantitative as well as the qualitative point of view. This is achieved by the use of "radical scavengers" by which conversion of one primary radical into another or separation of one reaction from others can be accomplished.

A radical scavenger can be defined as a solute which added deliberately will react preferentially with radicals at the expense of the normal radical reactions.

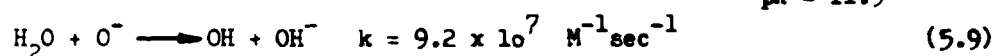
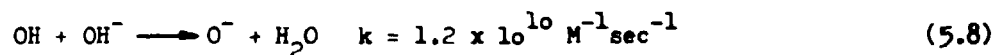
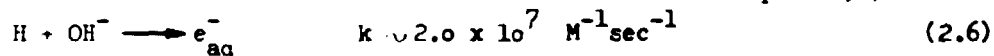
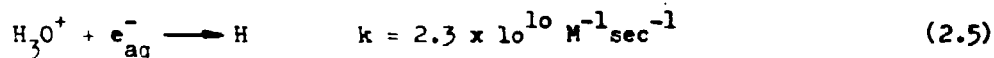
A good radical scavenger is expected to be:

- selective - reactive towards a particular radical or radicals while non-reactive towards the others,
- effective - high rate constant of the reaction between the scavenger and the scavenged radical will allow total scavenging using moderate concentrations of the former. This will leave spur processes undisturbed,
- neutral in relation to the studied subject - neither the presence of the scavenger nor the products of its reaction may interfere with the subject under study.

There is a number of scavengers used in radiation chemistry of aqueous systems; only those, however, used in the work reported will be described below.

Interconversion of Primary Radicals due to their Acid-base Properties.

In section 2.2. interconversion of primary radicals due to their acid-base properties was mentioned. This can be interpreted as a scavenging of corresponding primary radicals by  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$ .

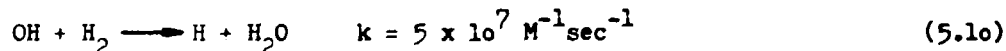


pK = 9.7

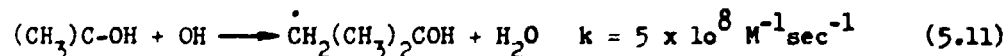
pK = 11.9

Of special importance to this work is the conversion of OH radicals into  $\text{O}^-$  since the oxide radical reacts in a different way with aromatic compounds than the OH radical.

The Hydroxyl Radical, OH. Conversion of OH into H (or  $e_{\text{aq}}^-$  in alkaline solution, eq. 2.6) can be accomplished out by the reaction with hydrogen, eq. 5.10.

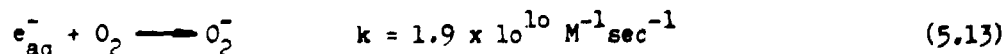
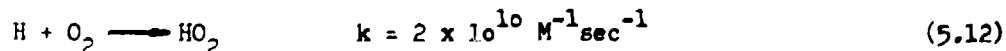


However, due to a low rate constant and low solubility of  $\text{H}_2$  ( $\sim 10^{-3}$  M) the utility of this reaction is limited. A more common way of eliminating OH radicals in order to study reactions of H and  $e_{\text{aq}}^-$  is to scavenge the OH radicals with t-butyl alcohol.



The radical formed is relatively inert and has a weak absorption in the UV part of the spectrum. H and  $e_{\text{aq}}^-$  are much less reactive with t-butanol,  $k_{\text{H}} = 8 \times 10^4 \text{ M}^{-1}\text{sec}^{-1}$  and  $k_{e_{\text{aq}}^-} < 10^4 \text{ M}^{-1}\text{sec}^{-1}$ . Thus H and  $e_{\text{aq}}^-$  are left to react with other solutes even at fairly high t-butanol concentrations.

Oxygen Saturation. Saturation of the solution with oxygen converts H and  $e_{\text{aq}}^-$  into  $\text{HO}_2$  and  $\text{O}_2^-$  radicals respectively, while the OH radical does not react with  $\text{O}_2$ .

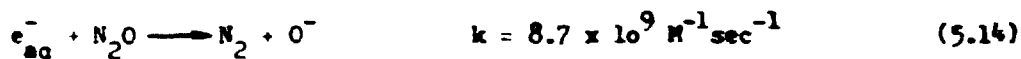




The hydroperoxyl radical,  $\text{HO}_2$ , and its base form ( $\text{pK} = 4.8$ ) the superoxide ion,  $\text{O}_2^-$ , are known to be quite unreactive towards organic compounds.

A serious disadvantage in using oxygen as a radical scavenger is a high reactivity towards secondary radicals. It appears, however, that aromatic radical cations are less reactive towards oxygen.

Nitrous Oxide,  $\text{N}_2\text{O}$ . Nitrous oxide is a key scavenger for radiolytic studies of OH radical reactions. It scavenges efficiently hydrated electrons



which converts the system almost completely into a one radical system. The only remaining primary radical besides OH is the H atom,  $G = 0.6$  thus  $[\text{OH}]/[\text{H}] \approx 10$  since  $G_{\text{OH}} = 5.6$  in  $\text{N}_2\text{O}$  saturated water.

Nitrous oxide is fairly soluble in water ( $2 \times 10^{-2} \text{ M}$ ) and is practically inert towards OH and H ( $k_{\text{H}} + \text{N}_2\text{O} < 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ ). The  $\text{N}_2\text{O}$  saturated system has been widely used in pulse radiolysis for measurement of rate constants of OH radicals with variety of compounds.

#### 5.2.2. Transient Conductivity Measurements

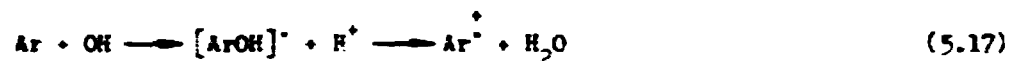
Irradiation of water introduces a change in electrical conductivity of the solution due to the formation of the primary products  $e_{\text{aq}}^- \lambda = 190 \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ,  $\text{H}_3\text{O}^+ \lambda_{18} = 314 \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$  and  $\text{OH}^- \lambda = 172 \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ . The pulse conductivity technique in connection with pulse irradiation was developed about a decade ago and has been applied to the study of primary processes in water radiolysis. Until recently this technique has not received much attention. Due to the recent interest in chemistry of radical ions, the transient conductivity detection became widely used as a supplementary technique in pulse radiolysis and several technical refinements have been introduced.

Radiolysis of  $\text{N}_2\text{O}$  saturated water after the acid-base equilibrium has been attained can be rationalized according to eq. (5.15) (H formation being neglected)



As it appears no essential change in electrical conductivity can be expected in such a system. However, formation of the radical cation in the reaction

of OH radicals with an aromatic solute either dissociative (5.16) or acid catalyzed (5.17)



will result in a net change of conductivity of the solution. In the first case (5.16) the change is due to the formation of a pair of ions and in the second (5.17) due to the substitution of extremely mobile  $\text{H}_3\text{O}^+$  by less motile radical cations. The mobility of radical cations can be measured in case of known stoichiometry or assumed to be identical to the mobility of cations of similar radius. This is much lower than the mobility of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  thus the observed change in conductivity is substantially due to introduction of  $\text{OH}^-$  or removal of  $\text{H}_3\text{O}^+$ . The uncertainty in equivalent conductance for the radical cation has a minor influence on the uncertainty of the overall measurement. In the course of the reported work it appeared necessary to supply the optical measurements with transient conductivity measurements. Generally two methods of transient conductivity measurement are used in connection with pulsed sources of ionizing radiation; the DC method where the DC pulse is used to polarize electrodes in the conductivity cell and the AC method where the electrodes are polarized by high frequency (usually of the order of 10 MHz) alternated voltage.

An interimistic set-up for measuring transient conductivity by the DC method in connection with the existing transient signal detection system at Rise's Linac was built. Besides some noise problems which prohibited measurements of conductivity signals up to 12  $\mu\text{sec}$  after the radiation pulse the equipment proved to give reliable results. These were in good agreement with the results obtained with the set-up at the Department of Nuclear Chemistry of the Royal Institute of Technology, Stockholm<sup>2d)</sup>, where part of the conductivity results were obtained.

A permanent set-up for transient conductivity measurements which allows simultaneous optical detection is now under construction.

#### General References to Chapter 5.

K.-D. Asmus, "Application of conductivity techniques in pulse radiolysis", in "Fast Processes in Radiation Chemistry and Biology", G.E. Adams, E.M. Fielden and B.D. Michael, Eds., Wiley 1975, pp. 40-59 and references cited therein.

### 5.3. Anisole Radical Cation Reactions in Aqueous Solution<sup>⑥</sup>

When Sehested et al.<sup>3)</sup> identified an intermediate species in the water molecule elimination from the OH adducts of methylated benzenes as the corresponding radical cation, little was known about the properties of aromatic radical cations in aqueous medium, and their formation from the corresponding OH adducts was hardly established.

As a pulse radiolytic study of radical cations of methylated benzenes is somewhat difficult due to the complexity of reactions, relatively short life time of radical cations, the presence of species with overlapping spectra, and the need for higher acid concentrations it turned out to be advantageous to study a related, but more stable radical cation first. Since methoxy substituted aromatic compounds are known to give relatively stable radical cations<sup>29)</sup> under anodic oxidation, anisole was chosen as a model compound.

The absorption band of the OH adduct was found at  $\lambda_{\max} = 320 \text{ nm}$  (Fig. 5.3.) with the extinction coefficient  $\epsilon_{320} = 3400 \text{ M}^{-1} \text{ cm}^{-1}$  and the decay rate constant for the bimolecular reaction  $2k = 1.4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ .

The H adduct absorbs at the same wavelength with  $\epsilon_{320} = 4000 \text{ M}^{-1} \text{ cm}^{-1}$  and the decay rate constant  $2k = 3.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . When going from neutral or slightly alkaline to acidic solution (pH 0 - 3), new absorption bands appear at  $\lambda_{\max} = 280$  and  $430 \text{ nm}$ , while the  $320 \text{ nm}$  band can be totally removed by oxygen saturation (Fig. 5.3.). On the assumption that the OH radical is a precursor for the  $280$  and  $430 \text{ nm}$  absorption, the extinction coefficients are  $\epsilon_{280} = 7400 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{430} = 3200 \text{ M}^{-1} \text{ cm}^{-1}$ . The same two bands although absent in neutral solution were observed at pH 6 - 10, Ar saturated, when  $(2 - 10) \times 10^{-3} \text{ M}$   $\text{K}_2\text{S}_2\text{O}_8$  were added. These bands are formed in the reaction of anisole with  $\text{SO}_4^{\cdot -}$  formed in the reaction of solvated electrons with persulphate. Extinction coefficients for the  $280$  and  $430 \text{ nm}$  bands based on the yield of solvated electrons are identical with those obtained from acid experiments. These data are in good agreement with results of O'Neill et al.<sup>21)</sup> which were published during the course of this work.

These authors assign the absorption at  $280$  and  $480 \text{ nm}$  to the anisole radical cation. This assignment is in agreement with our results and is additionally confirmed by the unreactivity of the species with oxygen and its reactions with  $\text{Fe}^{2+}$  and  $\text{OH}^-$ .

Oxygen saturation of acid solution of anisole removes the H adduct absorption band by scavenging the H atoms forming  $\text{HO}_2$ , but has no influence on the decay kinetics of the  $280$  and  $430 \text{ nm}$  bands, which is characteristic for cationic behaviour<sup>30,31)</sup>.

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<sup>⑥</sup>Published in J. Phys. Chem. 80, 163 (1976).

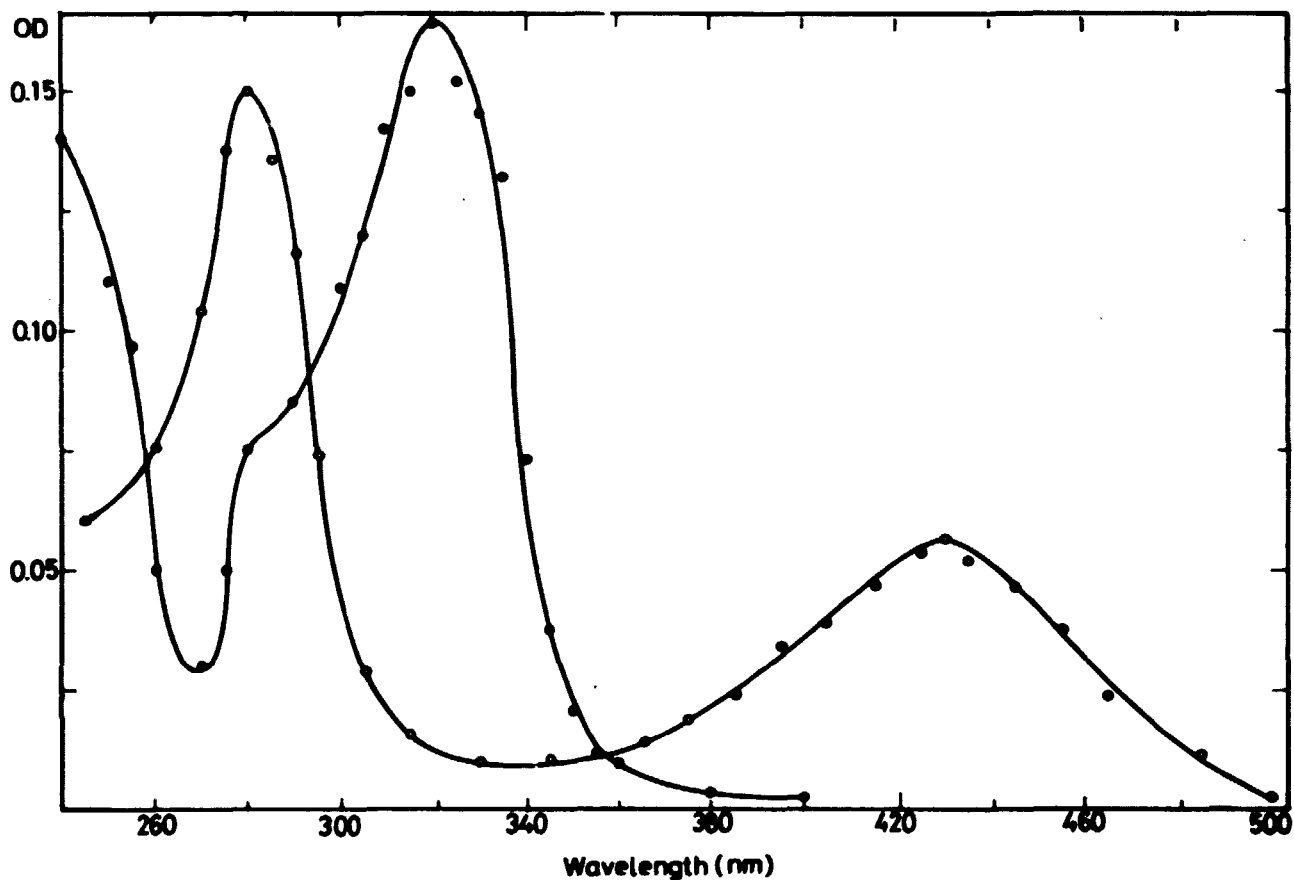
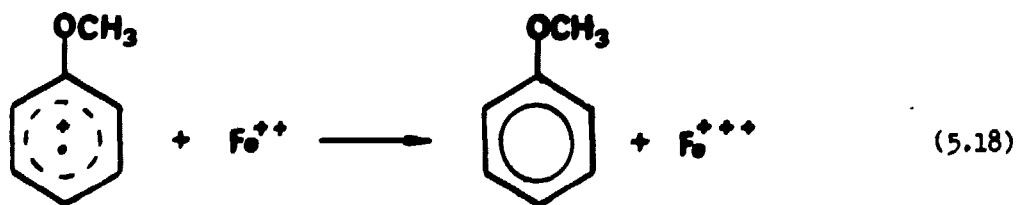


Fig. 5.3. Spectra obtained 1  $\mu$ sec after the electron pulse.

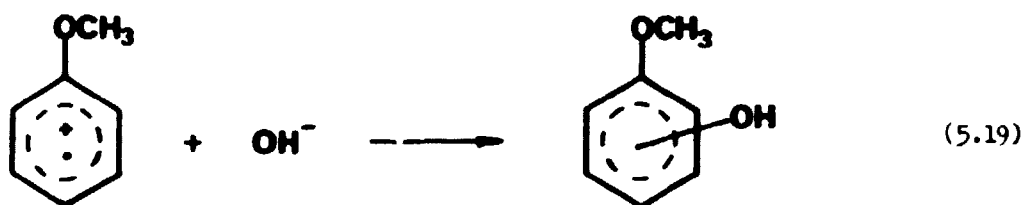
- $3 \times 10^{-4}$  M anisole, pH 8.7,  $N_2O$  saturated, dose 1.5 krad
- $3 \times 10^{-4}$  M anisole, pH 0 ( $HClO_4$ ),  $O_2$  saturated, dose 1.3 krad

The radical cation reacts with ferrous ion (eq. 5.18) with a rate constant  $k_{18} = 6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  at pH 1.0.

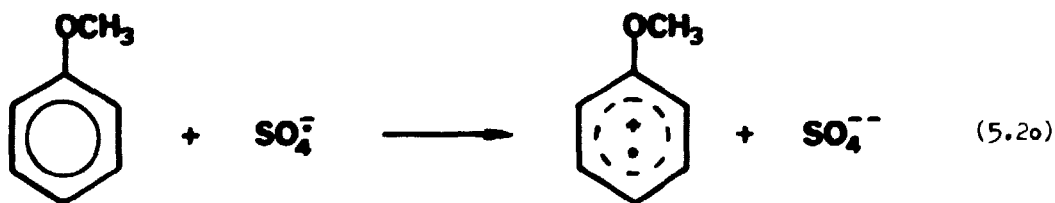


Formation of ferric ions in reaction (5.18) was confirmed by the build-up of its absorption at 320 nm<sup>32)</sup> in the presence of sulphuric acid.

In the Fenton reagent system Jefcoate and Norman<sup>33)</sup> found a drastic decrease in the yield of hydroxylated anisoles (the yield decreases from 14.6 to 0.018) when going from pH 3.6 to 0.8. This is to be expected as the OH adduct in strong acid solution is converted into the radical cation and the reaction of the radical cation with ferrous regenerates the parent molecule, so that the net reaction in the system is the oxidation of the ferrous ions. In alkaline solution (pH 8 - 11) containing  $5 \times 10^{-3}$  M  $K_2S_2O_8$  the anisole radical cation reacts with  $OH^-$  (eq. 5.19)



forming the OH adduct with a rate constant  $k_{19} = (1.0 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . The  $SO_4^{\cdot-}$  radicals reacts with anisole forming the radical cation (eq. 5.20)



with a rate constant  $k_{20} = 4.9 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  (21). Even at pH 11 with  $10^{-4}$  M anisole about 90% of the  $SO_4^{\cdot-}$  radicals will react with the substrate and not with  $OH^-$  to form OH radicals ( $k_{SO_4^{\cdot-} + OH^-} = 6.5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>24)</sup>. The rate constant for reaction (5.19) was determined by the decay rate of the radical cation at 430 nm as a function of the  $OH^-$  concentration. The product of reaction (5.19), the OH adduct, was identified by the build up of a spectrum similar to and with the same extinction coefficient as that measured in  $N_2O$  saturated solution for the OH adduct.

The kinetics of reactions (5.18) and (5.19) are ionic strength dependent and the plot  $\log k/k_0$  vs  $\mu^{1/2}/(\mu^{1/2} + 1)$  (Fig. 5.4.)

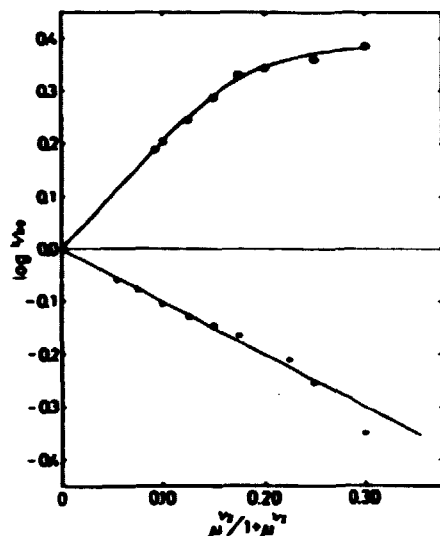
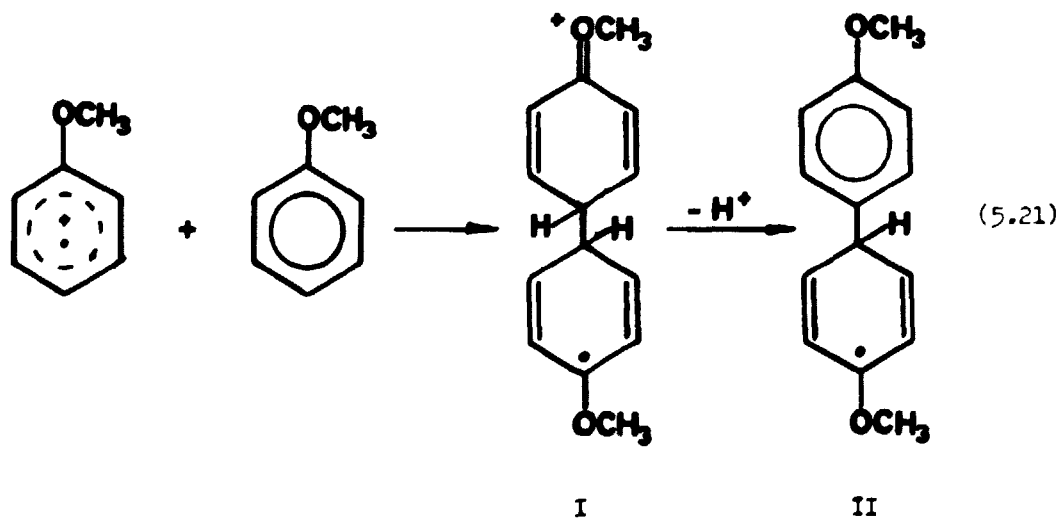


Fig. 5.4. The effect of ionic strength,  $\mu$ , on the rate of anisole radical reactions:

O, reaction with  $\text{Fe}^{2+}$ , eq 5.18

●, reaction with  $\text{OH}^-$ , eq 5.19

is consistent with the species having a unit positive charge. In a saturated anisole solution ( $1.4 \times 10^{-2}$  M) the anisole radical cation reacts with the solute, (eq. 5.21) (eq. 1 in ref. 21).



The rate constant for this reaction measured in acid solution (pH 0 - 2) is  $k_3 = 1 \times 10^7 \text{ M}^{-1}\text{sec}^{-1}$ . The product of this reaction has absorption bands at 380 - 420 nm (Fig. 5.5.)  $\lambda_{\text{max}} = 405 \text{ nm}$  and  $\epsilon_{405} = 2500 \text{ M}^{-1}\text{cm}^{-1}$ . The product decays in a second order reaction with a rate constant  $2k = 2 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$ .

The absorption at 380 - 420 nm can be ascribed to the species II on the basis of its second order decay and the similarity to the absorption spectrum of the biphenyl H adduct<sup>30)</sup>.

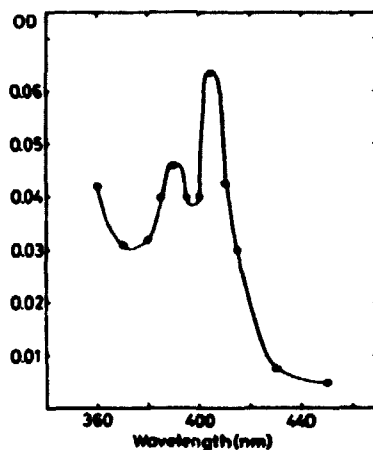


Fig. 5.5. Transient absorption spectra of the product from the reaction of the anisole radical cation with the solute molecule, eq. 5.20

An indication of the formation of such dimeric products is found in the nitro-methane-borontrifluoride system, where Allara et al.<sup>34)</sup> concluded that the dimeric radical cation is derived from a reaction of the monomeric radical cation and the substrate. They observed the same E.S.R. spectrum for the radical cation for anisole and 4,4'-dimethoxybiphenyl and found that the latter compound was a product of the reaction of the anisole.

An electrophilic attack by the radical cation on the electron-rich parent compound molecule seems to be an important ability of radical cations of aromatic compounds<sup>35)</sup>. It was observed in anodic oxidation of mesitylene<sup>36)</sup> and suggested as an important process in oxidative substitution of arenes by cobalt (III)<sup>37)</sup>. However, it was not observed for radical cations of methylated benzenes<sup>31)</sup>, but conditions with low solubility of the substrates and low stability of the corresponding radical cations are unfavorable in the water system. A fast reaction with the solute confirms the assignment of the radical cation to a monomer species. As pointed out by O'Neill et al.<sup>21)</sup> the anisole radical cation in dilute anisole solution ( $10^{-4} \text{ M}$ ) decays in a second order reaction

with a rate constant in neutral solution  $2k = 1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . The kinetic of this reaction was found strongly dependent on pH, which qualitatively may be explained essentially as an ionic strength effect. The rate constant measured at pH 0 and 1 is  $2k = 1.2 \times 10^{10}$  and  $4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  respectively. The determination was made with and without oxygen which had only a minor influence on the rate, but from the higher yield of the product in oxygen saturated solutions it can be estimated that the H adduct reacts with the radical cation at the rate corresponding to the rate given for the OH adduct<sup>21)</sup>. The product of the bimolecular reaction has a broad, weak absorption in the region of 660 - 850 nm with  $\lambda_{\text{max}} = 810 \text{ nm}$  and  $\epsilon_{810} \approx 300 \text{ M}^{-1} \text{ cm}^{-1}$  taking the yield of the product equal to half of the anisole radical cation yield. The absorption at  $\lambda_{\text{max}} = 810 \text{ nm}$  decays by first order with a half life 90  $\mu\text{sec}$ . This first-order decay may correspond to the deprotonation reaction that is considered to be a step leading to a biphenylic product. It was found that 2,2', 5,5' tetramethoxydiphenyl was a product of 1,4 dimethoxybenzene radical cation<sup>38)</sup>. In the case of methylated benzenes the main decay path for radical cations is the proton split off from the methyl group leading to the benzyl radical<sup>31)</sup>. As O'Neill et al.<sup>21)</sup> we find no indication of a proton loss from the methyl group in the anisole and higher methoxylated benzenes. A pH independent first-order decay of the radical cation was not observed. This is in good agreement with the molecular orbital calculations<sup>39)</sup>, which show the increase of a negative charge on the methyl group under ionization of anisole, whereas the methyl group of toluene becomes more positive.

Concerning the formation of radical cations from hydroxycyclohexadienyl radicals, O'Neill et al.<sup>21)</sup> assume that the rate of H atom abstraction from substituents by the OH radical is two order of magnitude lower than the rate of addition. This assumption does not apply in the case of methylated benzenes<sup>3)</sup>, where for toluene the rate for the direct H abstraction is only about one order of magnitude lower than the rate of addition. Furthermore, this rate is proportional to the number of methyl substituents which yields an appreciable amount of directly formed methylbenzyl radicals from the higher methylated benzenes.

With 0.6 M NaOH,  $\text{N}_2\text{O}$  saturated solution of anisole a transient with a peak at 280 nm has been observed. This absorption can be ascribed to the phenoxy-methyl radical, as  $\text{O}^-$  is known to abstract an H atom from the methyl group rather than add to the ring<sup>4,40)</sup>. The spectrum of the OH adduct in neutral solution has a shoulder in this region (Fig. 5.3), which could be characteristic of the OH adduct spectrum, but may as well be explained by an absorption due to



a second radical, the phenoxymethyl radical. Further support for a direct H-abstraction reaction by OH radicals is the slightly lower yield of the radical cation in acid solution (5 - 10% lower) as compared to the yield in neutral solution. The yields of the primary radicals, OH in acid and  $e_{aq}^-$  ( $SO_4^-$ ) in neutral solution, are about equal, which indicates that a small fraction of OH radicals reacts in another reaction. This conclusion is made on the assumption of a complete conversion of the OH adduct into the radical cation, which is the case for the methylated benzenes<sup>31)</sup>. The transient spectrum obtained with 1,3,5-trimethoxybenzene both in neutral  $N_2O$  saturated and at pH 1 in argon-saturated solution shows a peak at 260 nm that can be ascribed to the product of direct H atom abstraction from the methyl group. Additionally, phenol is recognized as a product of  $\gamma$ -radiolysis<sup>41)</sup> and in Fenton reagent hydroxylation of anisole<sup>33)</sup>. In the latter case, the phenol yield is independent of pH in contrast to the yield of methoxyphenols and constitutes about 7% of the yield of methoxyphenols at pH 3.6. Thus, the H atom abstraction from the methyl group can be considered to be a possible source of phenol. This point can be important to the explanation of the lower yields of radical cations obtained in acid solution in relation to the OH radical yield. However, it does not seem to explain some very low yields 45 - 60% obtained by O'Neill et al.<sup>21)</sup> for compounds substituted with several methoxy groups.

#### 5.4. Conversion of hydroxycyclohexadienyl radicals of methylated benzenes to cation radicals in acid media<sup>6)</sup>

K. Sehested et al.<sup>3)</sup> reported results from a pulse radiolytic study of the methylated benzenes in aqueous solution and 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 via the radical cation. This chapter describes further experiments, which confirm the previous assignment.

Spectrum in acid solution. Aqueous solutions saturated with various methylated benzenes in the pH range 0-7 were pulse radiolysed. Solutions at pH's  $\geq 3$  were  $N_2O$ -saturated and at pH's  $< 3$  Ar- or  $O_2$ -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<sup>1,3)</sup>. 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<sup>3)</sup>. These three spectra from p-xylene are shown in Fig. 5.6.

<sup>6)</sup>Published in J. Phys. Chem., 81, 1363 (1977).

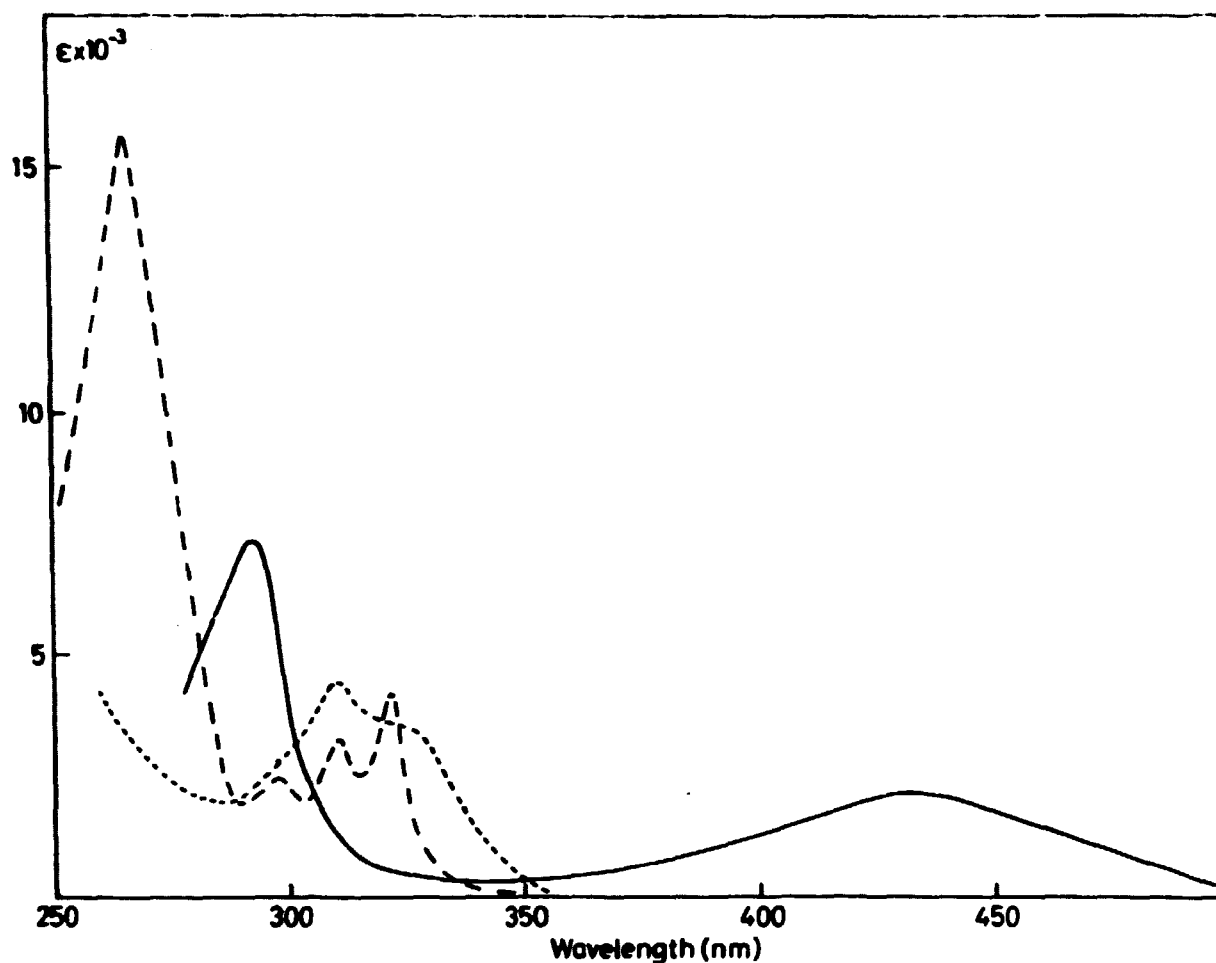


Fig. 5.6. Spectra of transient species in the acid catalyzed water elimination reaction of p-xylene:

- ..... OH adduct
- radical cation
- p-methylbenzyl radical.

Previously, the new spectrum was tentatively assigned to the radical cation<sup>3)</sup>. The intermediate species from isodurene existing between the hydroxycyclohexadienyl radical and the methylbenzyl radical spectrum is illustrated in Fig. 5.7. 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.

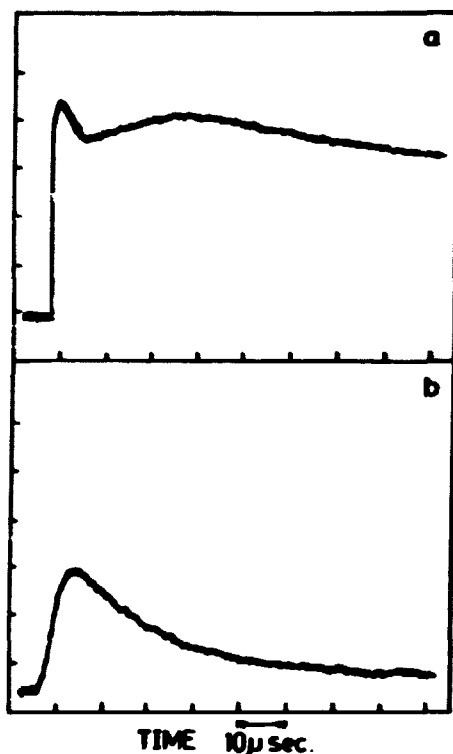


Fig. 5.7. Oscilloscopic traces of the transients in isodurene solution, pH 3.45.

a) 331 nm (absorption of the OH adduct and the trimethylbenzyl radical)

b) 455 nm (absorption of the radical cation)

Time scale in both pictures, 10  $\mu$ sec per division.

The decay of the OH adducts at 320 - 330 nm changes from a second order reaction in neutral to a 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 build up of the absorption at 450 nm. This behavior has also been found for the formation of radical cations of biphenyl<sup>30)</sup>, methoxylated benzenes<sup>21,45)</sup>, and methoxylated benzoic acids<sup>42)</sup>, 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 N<sub>2</sub>O-saturated sol-

utions for the higher methylated compounds. In these cases the increase of the band height at 450 nm by a factor of two is demonstrated in  $N_2O$ -saturated solution compared to Argon-saturated solutions. Moreover it was shown<sup>3)</sup> 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<sup>3)</sup>. 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 5.1.

Table 5.1. Absorption Bands and Extinction Coefficients of the Radical Cations of Methylated Benzenes in Aqueous Solution.

	$\lambda_{max}$ nm	$\epsilon$ $M^{-1}cm^{-1}$
toluene	285 430	- -
o-xylene	290 430	6000 2000
m-xylene	285 450	6300 2300
p-xylene	290 435	7000 2050
mesitylene	292 475	6600 2250
hemimellitene	290 450	6700 1950
pseudocumene	285 445	7000 2300
isodurene	290 455	6500 2200
prehnitene	300 455	7000 2000
durene	295 465	5000 ~1800
pentamethylbenzene	305 475	3750 ~1500

The high acid concentration was used in order to obtain instantaneous conversion of the OH adduct, which is necessary to get a full 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 it is not possible 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 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, o- and m-xylene the radical cation can be observed in neutral solution by reacting  $\text{SO}_4^-$  radicals with the methylated benzenes. Persulphate is known to scavenge hydrated electrons with a rate constant of  $1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ , producing  $\text{SO}_4^-$  radicals<sup>43)</sup>, while the OH radical reacts much slower with the persulphate,  $k \leq 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  1). The sulphate radical reacts with aromatic substrates yielding the radical cation<sup>15,17-19,21,44)</sup> in several cases. No addition products were detected<sup>20)</sup>.

In an Ar-saturated neutral solution of methylated benzenes containing  $5 \times 10^{-3} \text{ M S}_2\text{O}_8^{2-}$ , the transient spectrum consists of absorption bands at 420 - 470 nm, 320 - 330 nm and at 280 - 300 nm. The OH radicals produce the adduct with a band at 320 - 330 nm, and the  $\text{SO}_4^-$  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  $G_{\text{SO}_4^-} = G_{e^-} = 2.7$  is identical to that obtained in acid solution, based on the corrected OH yield. A "clean" spectrum of the radical cation formed in the reaction with  $\text{SO}_4^-$ , free of the OH adduct absorption, may be obtained by scavenging the OH radicals by tert-butyl alcohol, since the  $\text{SO}_4^-$  radical reacts with the alcohol with a rate constant of  $k = (9 \pm 1) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$  24), while the OH radical reaction has a rate constant of  $k = 5.2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  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  $\text{SO}_4^-$  radicals react with the methylated benzenes. The resulting spectrum at pH 8.2 is again identical to that obtained in acid solution. In Fig. 5.8 the normalized spectrum of the p-xylene radical cation obtained in neutral solution containing tert-butyl alcohol and  $\text{S}_2\text{O}_8^{2-}$  is compared with the spectrum observed in acid oxygen saturated solution.

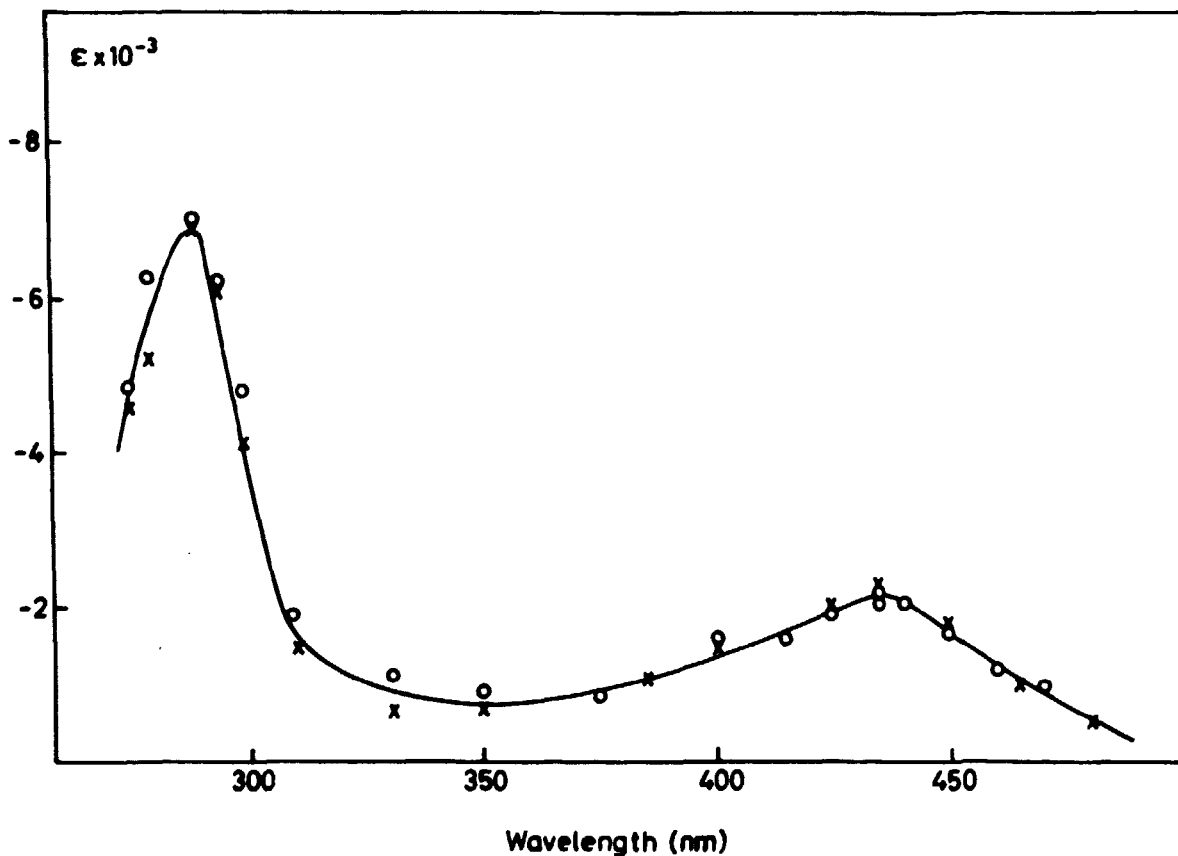


Fig. 5.8. Spectrum of the p-xylene radical cation in aqueous solution:

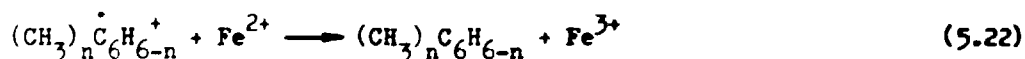
X -  $\text{O}_2$ -saturated with 1 M  $\text{HClO}_4$ ;

O - Ar-saturated at pH 8.2, containing  $5 \times 10^{-3}$  M  $\text{S}_2\text{O}_8^{2-}$  and 0.4 M tert-butyl alcohol; normalized at 435 nm.

The rate constants for the reaction of the  $\text{SO}_4^-$  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  $2 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$ . Some of the rates are rather difficult to determine accurately, however, because of the overlapping spectrum of the  $\text{SO}_4^-$  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  $\text{SO}_4^-$  reaction and on the ionic strength dependency of the reaction of the species with ferrous and hydroxide ions. The reaction with  $\text{Fe}^{2+}$  was studied in  $\text{N}_2\text{O}$ -saturated sulphuric acid solution at pH 2.5 - 3.5. The ratio of the concentrations of the methylated benzenes 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 reason only tri- and tetramethylbenzenes were used. The reaction is a reduction of the radical cation to the parent compound and an oxydation of ferrous to ferric ions.



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<sup>32)</sup>. The rate of this reaction for pseudocumene and isodurene was  $(6.0 \pm 1.0) \times 10^7 \text{ M}^{-1}\text{sec}^{-1}$ . For the ionic strength measurements the sulphuric acid was substituted by perchloric acid and the ionic strength of the solution was adjusted with  $\text{NaClO}_4$ . The rate was measured from the decay of the radical cation and the rate constant was calculated from the equation

$$k_m = k_{22} + k_{25} \quad (A)$$

where  $k_m$  is the measured first order decay,  $k_{25}$  the rate for the formation of the methylbenzyl radicals in acid solution, and  $k_{22}$  the rate constant for reaction (5.22). As was found for the anisole radical cation<sup>45)</sup> the rate of reaction (5.22) is ionic strength dependent. Fig. 5.9 shows the result for isodurene where the initial slope of the curve equals +2.

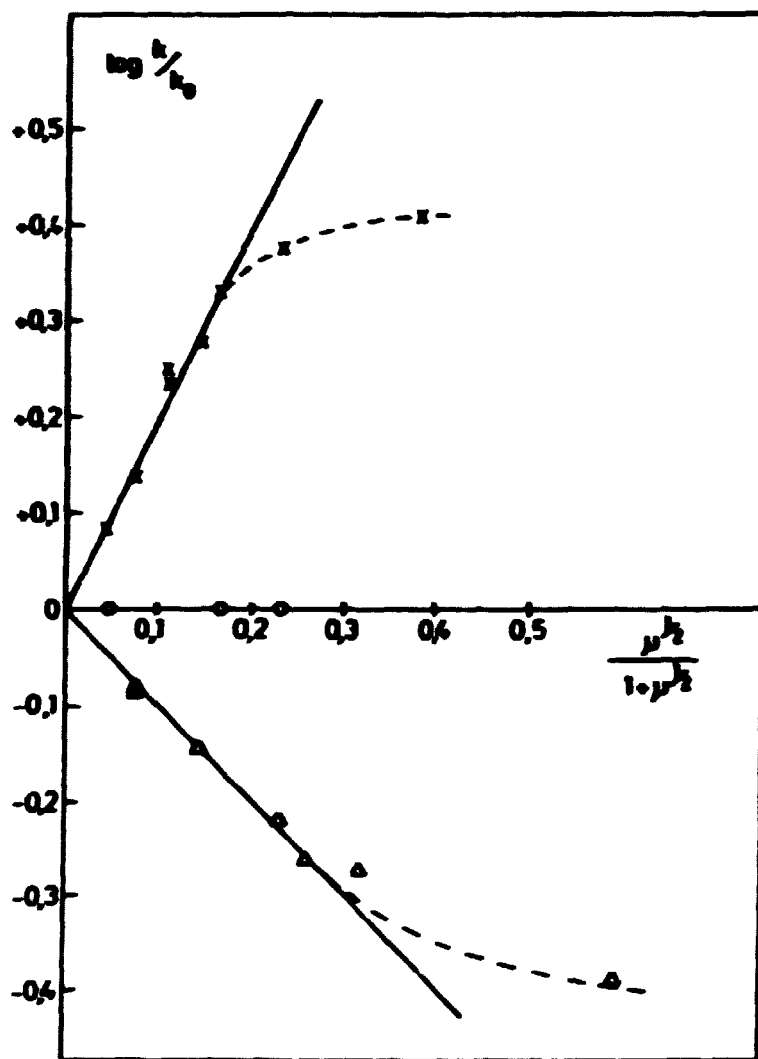


Fig. 5.9. The effect of ionic strength,  $\mu$ , on the rate of the isodurene radical cation reactions.  $k$ , measured rate constant,  $k_0$  rate constant extrapolated to zero ionic strength:

X - reaction with  $\text{Fe}^{2+}$ , pH 3.1;

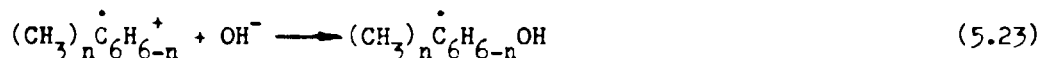
O - formation of the trimethylbenzyl radical, pH 3.1;

Δ - reaction with  $\text{OH}^-$ , pH 10.5.

This supports the conclusion, that our species has a unit positive charge.  $k_{25}$  proved to be independent of the salt concentration.



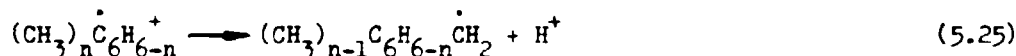
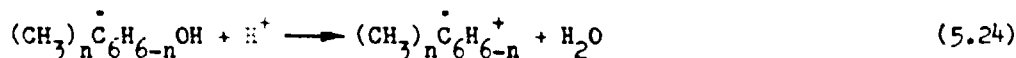
A second reaction supporting our assignment is the reaction with hydroxide ions yielding the OH adduct



This reaction was studied in argon-saturated solutions at pH 8 - 11 containing  $\text{S}_2\text{O}_8^{2-}$ . The radical cation was formed from  $\text{SO}_4^-$  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 (5.24)) compete with the formation of methylbenzyl radicals (reaction (5.25)). This reaction will be described in the successive chapter<sup>46)</sup>. 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 (5.23) on the expense of methylbenzyl radicals. At pH's approaching 11 some minor part of the  $\text{SO}_4^-$  radicals contributes to the OH adduct formation directly through the reaction with hydroxide ions yielding OH radicals. The rate constant for this reaction is  $7.3 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ <sup>19)</sup> 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 (5.23), as this is measured from the decay of the radical cation. The rate constant for reaction (5.23) was calculated from an equation analogous to (A), but instead of using  $k_{25}$ , which is considered to be pH independent, a rate constant as measured at pH 7 taking into account the reverse reaction of (5.24) is used, the reason being that reaction (5.23) is competing with reaction (5.25) as well as with the reverse reaction to (5.24). The rate constant for isodurene radical cation with  $\text{OH}^-$  (reaction (5.23)) is  $1.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  and, as shown in Fig. 5.9, 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 corresponding radical cations which should be expected for a one electron deficient original compound<sup>47)</sup>. Furthermore the absorption energies of the toluene radical cation from the photodissociation spectra are 3.0 and 4.7 eV<sup>48)</sup> compared to our values 2.9 and 4.35 eV in the aqueous phase. Thus the 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:



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. Since an absorption, which could be attributed to the protonated form of the OH adduct, was not observed, the elimination reaction must then be very fast. An alternative mechanism could be an OH<sup>-</sup> 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<sup>-</sup> elimination from OH adducts is suggested by Bansal and Henglein<sup>49)</sup> in the cathodic process.

In the oxydation of benzene and its derivatives by the Fenton reagent and in related systems<sup>33,50)</sup>, a reaction like (5.24) 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 biphenyl<sup>30)</sup> and methoxylated benzenes<sup>21)</sup> and for the formation of zwitterions from methoxylated benzoic acids<sup>42)</sup>.

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 (5.24) can not 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<sub>2</sub>O<sup>46)</sup>. A lower limit of  $5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  for these compounds is estimated. For the slower decaying cation (three, four and five methyl groups), the rate constant  $k(\text{OH adduct} + \text{H}^+)$ , reaction (5.24), can be measured directly by the build-up of the positive ion transient as a function of the hydrogen ion concentration. The rate was found to be  $k_{24} = (1.5 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  for all the compounds, and we assume that this value also is valid for the lower methylated benzenes (Table 5.2). This rate constant agrees with values reported for methoxylated benzenes<sup>21)</sup>.

Table 5.2. Rate Constants for Reaction of OH Adducts of Methylated Benzenes with Hydrogen Ions.

	$k_{\text{OH adduct} + \text{H}^+}$ $\times 10^{-9} \text{ M}^{-1} \text{ sec}^{-1}$	(5.24)
toluene	-	
o-xylene	>0.5	
m-xylene	-	
p-xylene	>0.5	
mesitylene	>0.5	
hemimillitene	$1.4 \pm 0.3$	
pseudocumene	$1.5 \pm 0.2$	
isodurene	$1.0 \pm 0.3$	
prehnitene	$1.5 \pm 0.2$	
durene	$1.1 \pm 0.2$	
pentamethylbenzene	$1.5 \pm 0.3$	

Reaction (5.25), 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 of OH adducts to methylbenzyl radicals was quantitative<sup>3)</sup>. This reaction was not observed in the study of anisole<sup>21,45)</sup>, probably because its methyl group becomes more negative on ionization<sup>33)</sup> 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<sup>51)</sup>.

Neither a dimerization of the radical cations nor a reaction with the solute, as were found in the anisole system<sup>45)</sup>, 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.

#### 5.5. Reactions of the Radical Cations of Methylated Benzene Derivatives in Aqueous Solution<sup>6)</sup>

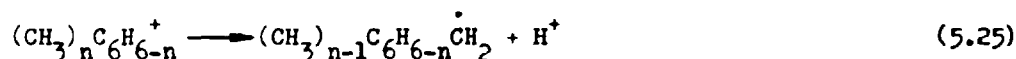
In the previous chapter the OH radical induced formation of radical cations of methylated benzenes in aqueous acidic media and neutral solution is described. The precursor of the radical cation in acid media is the OH adduct, whereas the cation is formed directly in a reaction with  $\text{SO}_4^{\cdot -}$  radical anions in neutral sol-

<sup>6)</sup>Submitted for publication in J. Phys. Chem.

ution. The dependency of ionic strength of some reactions of radical cations demonstrated the unit positive charge of the species.

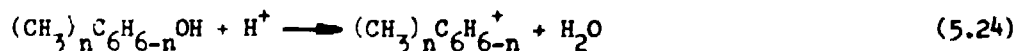
This chapter describes the proton splitting reaction and the reactions with water and hydroxide ions. Some considerations of the reverse reactions are also included.

Acid solution. The radical cations decay in acid solution by first-order kinetics independent of solute and acid concentration up to 0.5 M acid. The product of the decay is exclusively the corresponding methylbenzyl radical.



In acid solution all the OH radicals yield the methylbenzyl radicals, mainly through the conversion of the OH adduct via the radical cation, but with a small contribution from the direct attack on a methyl group<sup>3)</sup>.

The rate constant for this conversion was previously determined by measuring the rate of the formation of the methylbenzyl radicals<sup>3)</sup> as the existence of the radical cation as an intermediate species was not established yet. The formation of the radical cation from the OH adduct was demonstrated<sup>52)</sup> to be a result of the reaction of the hydroxycyclohexadienyl radicals with hydrogen ions.



The rate constant for this reaction is  $(1.5 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  irrespective of the compound. The appearance of the radical cation in acid media, however, is governed by the rate of a reaction, in which the radical cation reacts with water yielding the OH adduct (reverse of reaction (5.24)).

The rate constants for the decay of the radical cations in reaction (5.25) were determined in  $10^{-3}$  to 1 M  $\text{HClO}_4$ , Ar or  $\text{O}_2$  saturated solution.

**Table 5.3. Rate Constant for the Methylated Benzene Radical Cation Reactions in Aqueous Solution**

	Proton splitting reaction, $k_{25} \text{ sec}^{-1}$	Methylbenzyl radical % (see text)	Reaction with $\text{H}_2\text{O}$ , $k_{-24} \text{ M}^{-1} \text{ sec}^{-1}$	Reaction with $\text{OH}^-$ , $k_{26} \text{ M}^{-1} \text{ sec}^{-1}$
toluene	$1.0 \pm 0.5 \times 10^7$	< 5	$> 2 \times 10^7$	-
o-xylene	$2.0 \pm 0.5 \times 10^6$	$\sim 10$	$8 \pm 4 \times 10^5$	-
m-xylene	$2.0 \pm 0.5 \times 10^6$	$\leq 5$	$1.5 \pm 0.5 \times 10^6$	-
p-xylene	$1.4 \pm 0.2 \times 10^6$	$\sim 10$	$5.0 \pm 2.0 \times 10^5$	-
mesitylene	$1.5 \pm 0.2 \times 10^6$	$\leq 5$	$1.0 \pm 0.5 \times 10^6$	-
hemimillitene	$1.5 \pm 0.3 \times 10^6$	40	$5.0 \pm 2.0 \times 10^4$	$\sim 1 \times 10^{10}$
pseudocumene	$2.0 \pm 0.2 \times 10^5$	60	$3.0 \pm 1.0 \times 10^3$	$3.5 \pm 0.5 \times 10^9$
isodurene	$1.0 \pm 0.2 \times 10^5$	65	$1.0 \pm 0.3 \times 10^3$	$1.2 \pm 0.2 \times 10^9$
prehnitene	$2.5 \pm 0.2 \times 10^5$	$\sim 90$	$4 \pm 2 \times 10^2$	$6.0 \pm 1.0 \times 10^8$
durene	$2.7 \pm 0.5 \times 10^4$	$\geq 95$	$6 \pm 2$	$1.5 \pm 0.3 \times 10^8$
pentamethylbenzene	$1.6 \pm 0.3 \times 10^4$	> 95	< 4	$1.0 \pm 0.2 \times 10^8$

These rate constants (Table 5.3) agree with those measured for the build-up of the methylbenzyl radicals ( $k_2$  in ref. 3) for compounds substituted with three or less methyl groups. For the higher methylated benzenes (four or five methyl groups) the rate of the decay of the cation is slower than the previously measured rate of build-up of the methylbenzyl radicals. This overestimation of the build-up rate may be due to the low rate of the reaction of the solute with the primary radicals because of the low solubility of the compounds together with a fairly high direct formation, up to 30%, of the corresponding methylbenzyl radicals. The rate constants for the proton splitting reaction (5.25) varies three orders of magnitude from one to five methyl-substituents.

As the Hammett substituent constants for most of these compounds are not available, the rate constants,  $k_{25}$ , are correlated with the adiabatic ionization potential of the parent compounds (Fig. 5.10). The ionization potential is primarily determined by the energy of the highest occupied molecular orbital and Rao<sup>53)</sup> has shown a linear relationship between the IP and the Hammett substituent constants for disubstituted benzenes, where only little or no steric effects due to substituents are operative. No appreciable steric effect is expected from the methyl groups in the studied compounds thus the substituent effect is primarily of electronic nature.

At even higher acid concentrations, 1 to 8 M  $\text{HClO}_4$ , the  $k_{25}$ 's become successively lower, e.g. the rate for p-xylene radical cation is lowered by an order of magnitude in going from 1 to 5 M acid. Accordingly an attempt was made to detect the reverse reaction (-5.25), i.e. a protonation of the methylbenzyl radical. It was not possible to observe this reaction up to 5 M acid neither with methylbenzyl radicals produced by an H atom reaction with some methylbenzylchloride compounds nor in the case where the direct formation of methylbenzyl radicals exceed 25% (high methylated compounds).

Neutral solution. As mentioned earlier<sup>52)</sup> the radical cations decay faster in neutral than in acid solution. Contrary to acid media, where the cations decay exclusively into the methylbenzyl radicals, the decay in neutral solution yields the OH adduct and the methylbenzyl radical. The rates of decay are independent of solute concentrations, which excludes a reaction with the parent hydrocarbon as is the case with anisole<sup>45)</sup>. There is no indications of a radical-radical dimerization since the decay is strictly first-order, independent of dose rate.

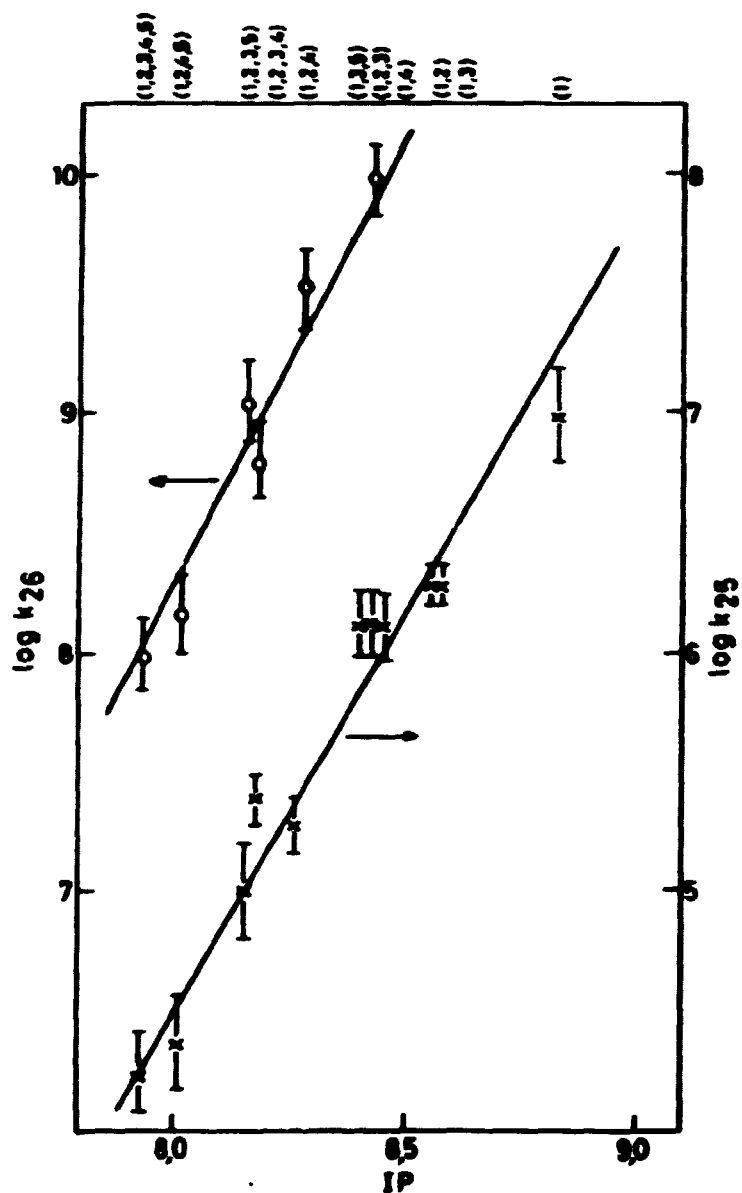
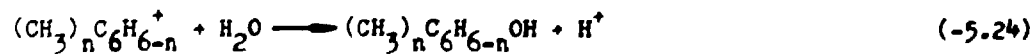


Fig. 5.10. Rate constants of the reactions (5.25) -x- and (5.26) -o- as function of the ionization potential of the parent compounds.

These results are ascribed to a reaction of radical cations with water in competition with the proton splitting reaction, reaction (5.25)



This reaction is analogous to that proposed for other aromatic radical cations<sup>54)</sup>. Reaction (-5.24) is the reverse of reaction (5.24). It was studied in electron irradiated Ar-saturated neutral solution containing persulfate by producing the radical cations in a reaction of  $SO_4^-$  radicals with the substrate. From the radical cation decay data  $k_{-24}$  can be derived under the assumption that  $k_{25}$  is the same in neutral as in moderate acid solution. Only the  $k_{-24}$ 's for the higher methylated compounds ( $n \geq 3$ ) can be determined in this way, as the decay of the lower methylated compounds ( $n = 1$  or  $2$ ) is either too fast to be measured (toluene and m-xylene) or the cation radical spectrum overlaps the original spectrum of the  $SO_4^-$  anion radical ( $\lambda_{max} = 450$  nm), which prohibits a meaningful determination of the radical cation decay (o-xylene and mesitylene).

An independent way of determining the rate of reaction (-5.24) is to measure the distribution of the OH adduct and the methylbenzyl radical formed from the radical cation. This was done by analyzing the spectrum from 240 nm to 340 nm in an Ar-saturated solution containing  $5 \times 10^{-3}$  M  $S_2O_8^{2-}$  and comparing this with the spectrum in  $N_2O$ -saturated. Using the extinction coefficients for the OH adduct (at 320 - 330 nm) and the methylbenzyl radical (at 250 - 270 nm and 320 - 330 nm) and taking into account the amount of directly formed methylbenzyl radicals<sup>3)</sup>, the yields of the methylbenzyl radical produced from the decay of the radical cations were calculated. These yields are given as percentage of the total radical cation yields in Table 5.3. From the distribution of the OH adduct and the methylbenzyl radical and from the observed decay rate of the radical cation,  $k_{25}$  and  $k_{-24}$  can be calculated. The results confirm the assumption that the rate constants of reaction (5.25) are unchanged in acid and neutral solutions. Furthermore  $k_{-24}$  from the two sets of experiments agree. The mean values are shown in Table 5.3. These rate constants decrease by seven order of magnitude as the number of methyl groups increases from one to five. This trend is consistent with the high rate of the hydrolysis reaction reported for the benzene radical cation<sup>22)</sup>.  $k_{-24}$  shows a good correlation with the ionization potential of the parent compound (Fig. 5.11).



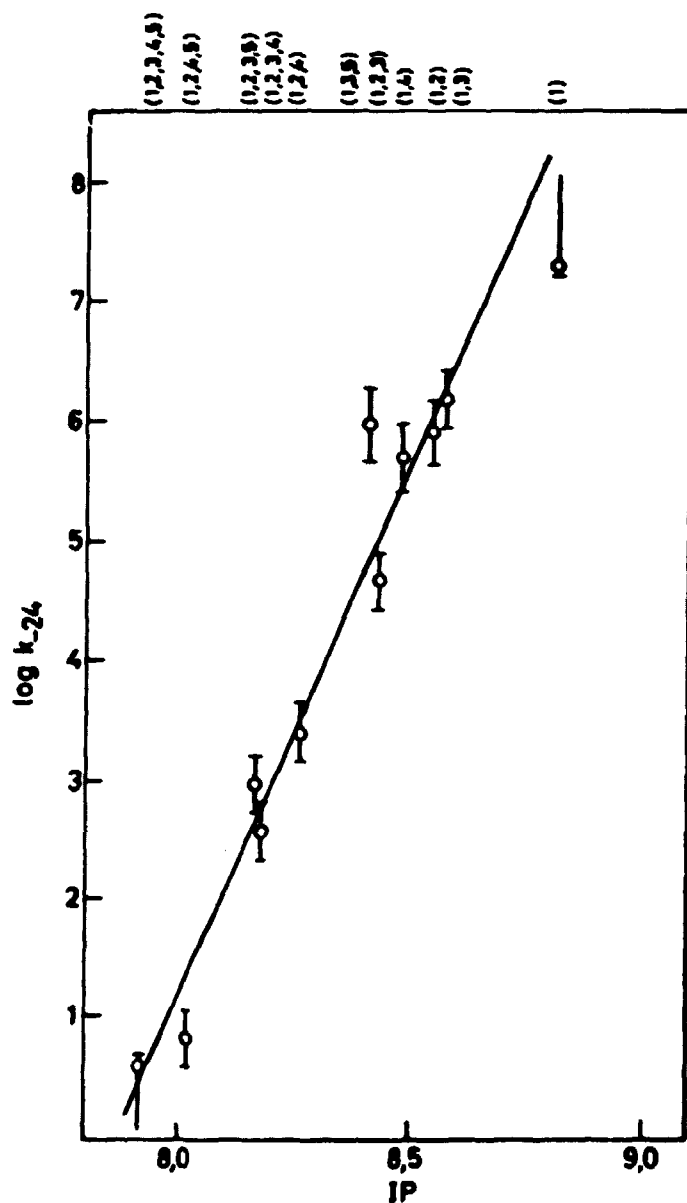
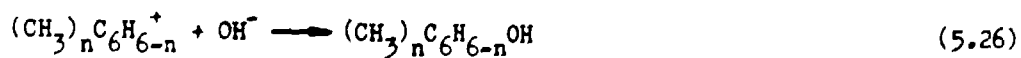


Fig. 5.11. Rate constants of the reaction (-5.24) as function of the ionization potential of the parent compounds.

Alkaline solution. In alkaline solution the radical cation reacts with hydroxide ions forming the OH adduct:



As a consequence of fast reaction (-5.24) with water only the methylated benzenes with  $n \geq 3$  can be studied with respect to reaction (5.26). With compounds

of  $n < 3$ ,  $k_{-24}$  is  $10^7$  or higher (Table 5.3) and we are unable to establish a competition between reaction (-5.24) and (5.26), because the decay of the radical cation is either too fast or mixed with the  $SO_4^-$  decay (see neutral solution), and the product in both cases is the OH adduct. Another limitation is that production of the radical cation from  $SO_4^-$  is not feasible above  $pH \approx 12$ , as the rate constant for the reaction  $SO_4^- + OH^- \rightarrow SO_4^{2-} + OH$  is  $7.3 \times 10^7 M^{-1} sec^{-1}$  (19). On the other hand, if reaction (5.25) and (-5.24) are competing, which means that an appreciable amount of methylbenzyl radicals are formed ( $n \geq 3$ ), a competition with reaction (5.26) in the pH region 8 - 12 can be established.

The radical cation was produced in an electron irradiated Ar-saturated alkaline solution containing  $S_2O_8^{2-}$  and  $k_{26}$  was calculated from the decrease in half-life of the radical cation over the pH range 8 - 12. As an example the half-life versus pH for isodurene radical cation is shown in Fig. 5.12.

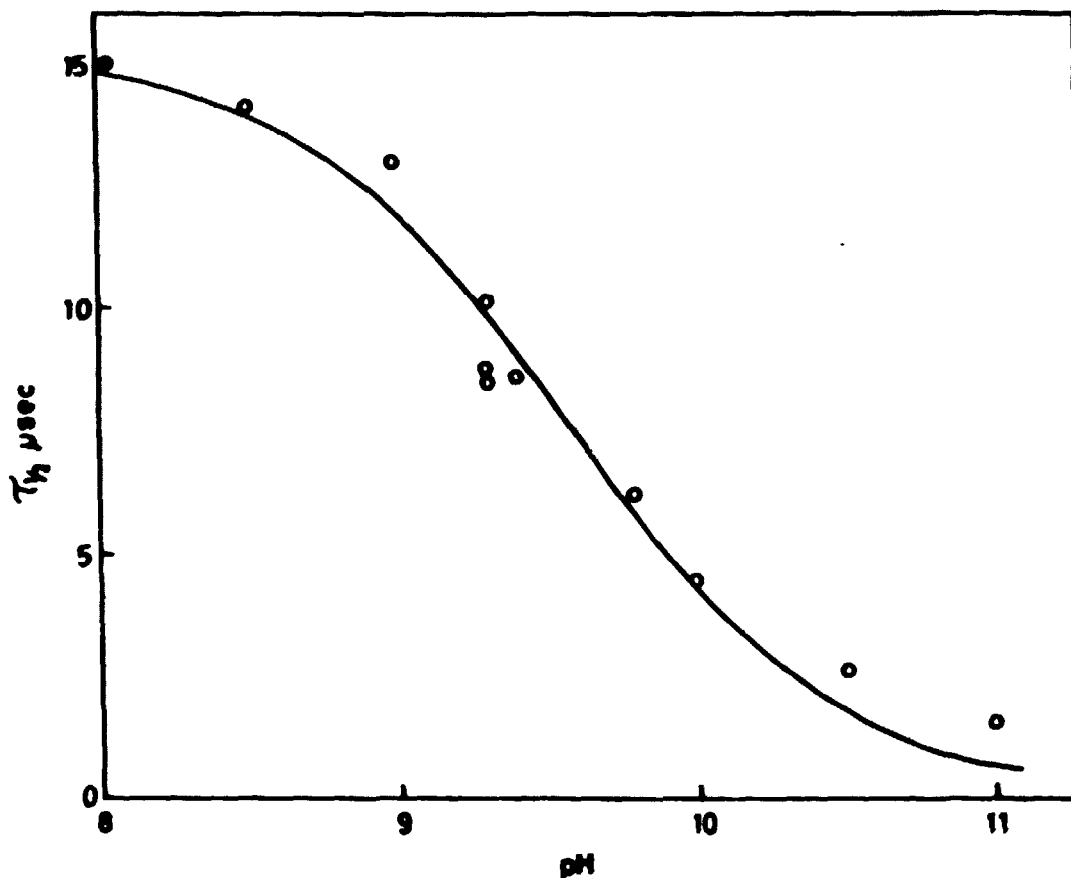


Fig. 5.12. The half-life of the first order decay of the radical cation of isodurene (1,2,3,5) as function of pH. The solid line is calculated as  $1.2 \times 10^9 M^{-1} sec^{-1}$  for reaction (5.26).

The rate constants in Table 5.3 are determined by this method but checked by the method of determining the yield of methylbenzyl radicals formed. This is done by recording the resulting spectra as previously in neutral solution and from this yield,  $k_{25}$  and  $k_{-24}$ , the rate of reaction (5.26) is derived. These rates agree with those measured from the kinetics. Also in case of reaction (5.26) the rate constants can be correlated with the ionization potential of the parent compound (Fig. 5.10).

The reverse reaction of (5.26), a dissociation of the OH adduct, was not observed directly, but its existence for several of the compounds ( $n > 3$ ) is strongly suggested from a previous study on the formation of the methylated benzyl radicals in acid solution<sup>3)</sup>. The flat portion of the growth curve at pH's 3 - 5 indicates the formation of the methylbenzyl radicals from an uncatalyzed reaction like (-5.26) followed by reaction (5.25). This type of reaction, (-5.26), proceeds with DMA<sup>55)</sup> and is discussed in more detail in a later chapter concerning the uncatalyzed water elimination reactions<sup>56)</sup>.  $k_{-26}$  for methylated benzenes are generally small ( $< 10^4$ ) and can be measured in only a few cases ( $n = 4$  or  $5$ ), but some upper limit estimates were made before ( $k_1$  in Table IV ref. 3). Reaction (-5.24) must be slow compared to reaction (5.25) in order to obtain reliable values.

#### 5.6. Radical Cations of tert-Butylbenzene, Isopropylbenzene and Ethylbenzene<sup>•</sup>

The lack of a proton splitting reaction from the anisole radical cation may lead to the supposition that only protons from the  $\alpha$ -position can be lost. It is therefore of interest to investigate the radical cations of compounds with  $\beta$ -positioned H atoms, such as the homologs tert-butyl-, isopropyl- and ethylbenzene. It turned out that this study requires very high acid concentrations (2-8 M acid), thus a quantitative interpretation of the results is difficult since the G-values of the primary radicals are not well known at these acid concentrations.

Tert-Butylbenzene. The absorption spectrum obtained in neutral  $N_2O$  saturated solution of tert-butylbenzene is shown in Fig. 5.13.

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<sup>•</sup>This subject is under current investigation at Risø's Accelerator Department. Some of the results and conclusions may therefore be considered as preliminary only.

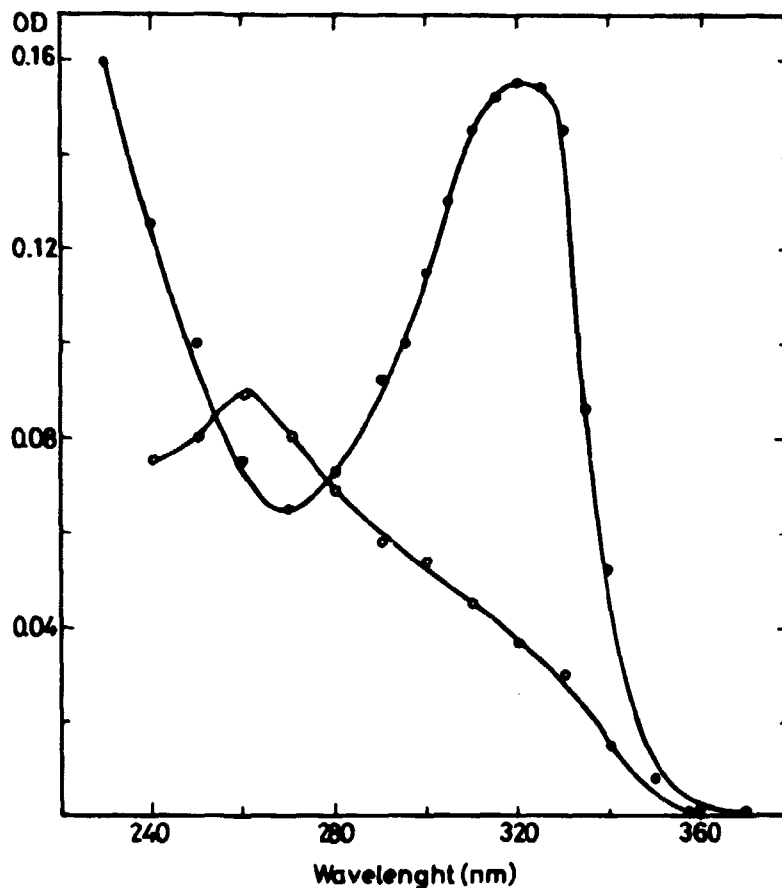


Fig. 5.13. Absorption spectra obtained in saturated tert-butylbenzene solution saturated with  $N_2O$  after the 1  $\mu$ sec, 1.6 krad electron pulse.  
 ● pH 7, ○ pH 13.8

The absorption maximum at 320 nm is assigned to the OH adduct in agreement with the absorption of OH adducts observed for methylated benzenes<sup>3)</sup>. The extinction coefficient calculated for the total yield of OH radicals,  $G = 5.4$ , is  $\epsilon_{320} = 3200 \text{ M}^{-1} \text{ cm}^{-1}$ , which is somewhat lower than that for methylated benzenes. This value may be too low due to a partial direct abstraction of methylic hydrogen. A meaningful correction, however, like the one applied for methylated benzenes<sup>3)</sup>, is in this case prohibited by the weak absorption of the methylic radical.

The spectrum obtained in 0.6 N NaOH,  $N_2O$  saturated solution has an extinction coefficient  $\epsilon_{260} = 1600 \text{ M}^{-1} \text{ cm}^{-1}$  (Fig. 5.13).  $O^-$  reacts with tert-butylbenzene by abstracting an H atom from one of the methyl groups form-

ing a substituted methyl radical. The results are in contrast to the high extinction coefficients obtained for the methyl substituted benzyl radicals ( $\epsilon_{\text{max}} > 10^4$ )<sup>3)</sup>, but agree with the results obtained under the same conditions with anisole<sup>45)</sup>. The conclusion is that the abstraction of  $\alpha$ -hydrogen results in a radical of much stronger absorption than in the case of  $\beta$ -hydrogen abstraction, where the radical site is separated from the aromatic ring.

Going from  $\text{N}_2\text{O}$  saturated neutral to acid solution the spectrum does not change except for a gradual lowering of the extinction at 320 nm. This can be interpreted as a formation of the methylic radical on the expense of the OH adduct as a result of an acid catalyzed water elimination from the OH adduct.

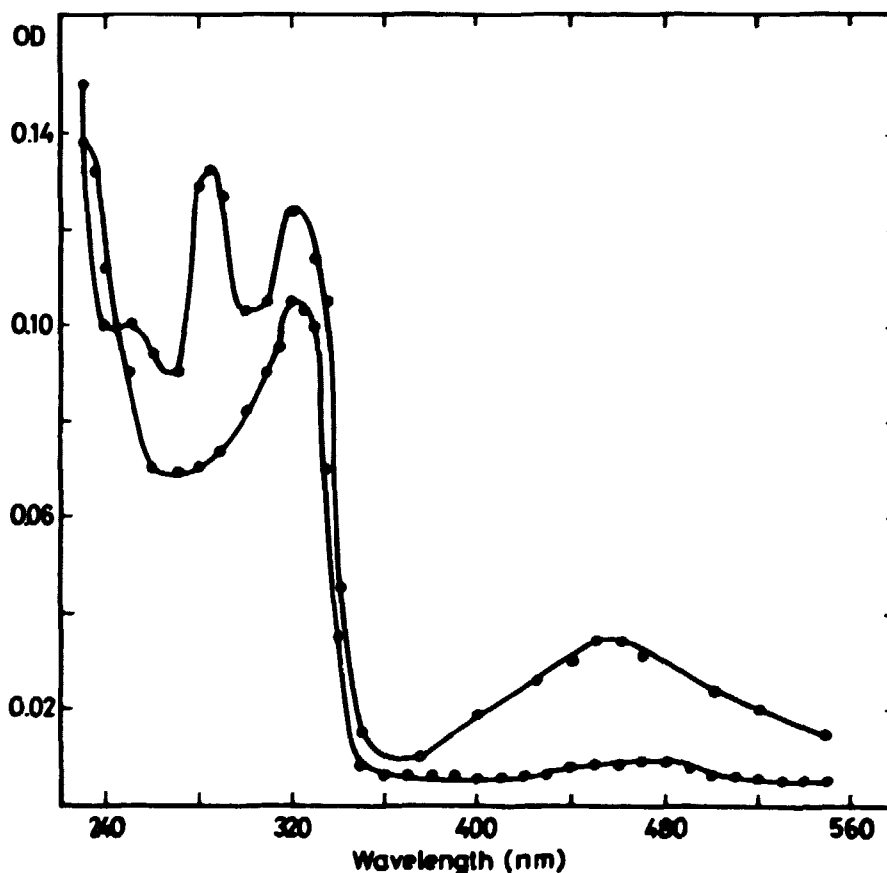


Fig. 5.14. Absorption spectra obtained in saturated tert-butylbenzene solution, Ar saturated, after the 1  $\mu$ sec, 1.6 krad electron pulse.  
● 1 M  $\text{HClO}_4$ , ○ 2 M  $\text{HClO}_4$ .

Since this radical has a lower extinction coefficient than the OH adduct in the recorded spectral range, and since the H adduct has the same absorption and approximately the same extinction as the OH adduct, no other changes are to be expected.

In 1 M HClO<sub>4</sub> solution a weak absorption maximum in the range 420-520 nm can be observed and in 2 M acid new absorption bands at 285 and 455 nm appear (Fig. 5.14). The absorption at 320 nm is now slightly higher, which can be attributed to additional absorption from the tail of the 285 nm peak. The absorptions at 285 and 455 nm are assigned to the tert-butylbenzene radical cation. A first order decay with  $k = 1.0 \times 10^5 \text{ sec}^{-1}$  was observed both at 285 and 455 nm. This decay is ascribed to the loss of a methylic proton. The possibility of radical cation-solute dimerization analogous to that observed for anisole is excluded on the basis of the lack of a transient corresponding to the product of this reaction. This dimerization has been observed in oxidation of tert-butylbenzene with Co(III) trifluoroacetate in trifluoroacetic acid giving a transient blue solution<sup>37)</sup>. The product of the dimerization was also observed for anisole<sup>45)</sup>. If the decay of the radical cation was ascribed to a dimerization this would result in a second order rate constant of  $5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  which is much higher than that of anisole ( $1 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>45)</sup>. Further experiments are going on in order to confirm this conclusion.

Isopropylbenzene (Cumene) and Ethylbenzene. Transient absorption spectra obtained after pulse radiolysis of isopropylbenzene and ethylbenzene in 0.6 M NaOH, N<sub>2</sub>O saturated solution, are shown in Fig. 5.15. The spectra are similar to those obtained for methylated benzyl radicals, and the extinction coefficients  $\epsilon_{265} = 16.000$  for isopropylbenzene and  $\epsilon_{258} = 17.000$  for ethylbenzene are of the same order of magnitude<sup>3)</sup>. This indicates a formation of an  $\alpha$ -hydrogen deficient radical. In neutral N<sub>2</sub>O saturated solution absorptions at 265 nm for isopropylbenzene and 258 nm for ethylbenzene were observed together with the absorptions of the OH adduct at 320 and 318 nm respectively. Using the extinction coefficients from alkaline solution result in a direct H abstraction of 15-25% for the two compounds. These figures are substantially higher than that of direct H abstraction obtained from methylated benzenes ( $\approx 6\%$  per methyl group)<sup>3)</sup>. This may well indicate a higher reactivity of the  $\alpha$ -hydrogen towards OH radicals.

In acid solutions (pH 3-0) the ultraviolet bands are growing in on the expense of the OH adducts. As for methylated benzenes this is interpreted as an acid catalyzed water elimination reaction. The bands, however, have a

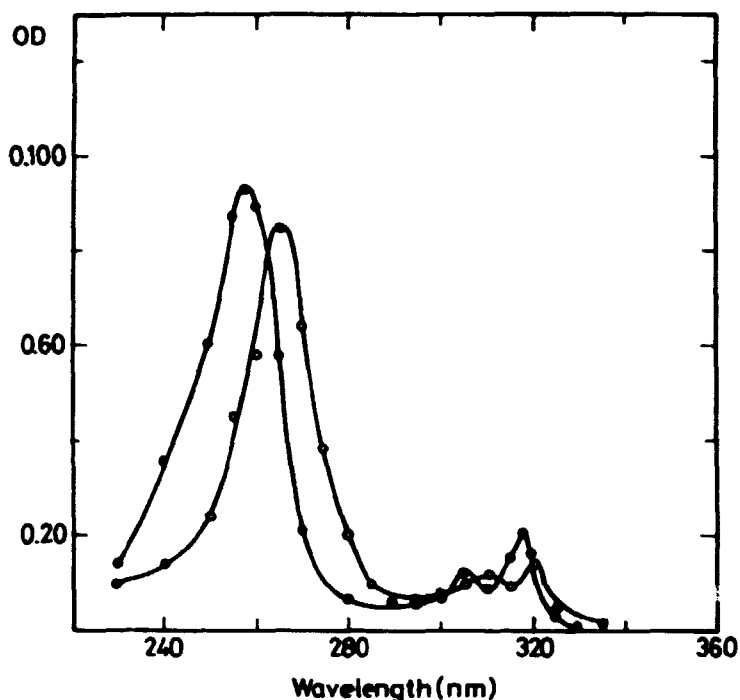


Fig. 5.15. Transient absorption spectra obtained after pulse radiolysis of 0.6 N NaOH, N<sub>2</sub>O saturated solution, pulse 1  $\mu$ sec, dosis 1.6 krad.  
● ethylbenzene, ○ cumene.

20% higher extinction coefficient in 1 M acid than that found in alkaline solution. This may be explained either by partial formation of  $\beta$ -hydrogen deficient radicals in alkaline solution, which if formed in acid solution undergo rearrangement, or by exclusive formation of  $\alpha$ -hydrogen deficient radicals from the water elimination reaction.

In acid concentrations up to 5 M, only the bands attributable to the product of H abstraction and the H adduct are observed. At higher acid concentrations (8 M) a broad band at 450 nm and a second one at about 280 nm appears for both compounds. These bands are similar to those obtained for the radical cations of methylated benzenes<sup>52)</sup> and tert-butylbenzene, and are consequently assigned to the radical cations of isopropyl- and ethylbenzene. The two bands decay with first-order kinetics. The rate constants of the decay together with that of the toluene radical cation in 8 M HClO<sub>4</sub> measured at the visible band are given in Table 5.4.

Table 5.4. Rate Constants for Decay of Radical Cations in 2 and 8 M HClO<sub>4</sub>

Compound	IP [eV]	k [sec <sup>-1</sup> ]	[HClO <sub>4</sub> ]
toluene	8.82	3.5 x 10 <sup>6</sup>	2 M
		1 x 10 <sup>5</sup>	8 M
ethylbenzene	8.75	3.5 x 10 <sup>5</sup>	8 M
isopropylbenzene	8.69	6 x 10 <sup>5</sup>	8 M
tert-butylbenzene	8.68	1 x 10 <sup>5</sup>	2 M

The decay of the radical cations does not follow the pattern of the ionization potential dependence as was found for the methylated benzenes<sup>46)</sup>. On the contrary the rate constant increases with decreasing ionization potential. The rate constant for the proton attack on the OH adducts of aromatic compounds was found to be of the order of 10<sup>9</sup> M<sup>-1</sup> sec<sup>-1</sup> (21,42,46) and the appearance rate of the UV band of the hydrogen deficient radicals of isopropyl- and ethyl benzene at pH 3 - 0 agree with these findings, indicating that the lifetime of the corresponding radical cations are very short. The observations of the radical cations of toluene<sup>52)</sup>, ethyl-, isopropyl- and tert-butyl benzenes are possible only because of the previously mentioned decrease in the rate constant of the proton splitting reaction<sup>46)</sup> caused by very high acid concentrations. As the nature of this acid effect is not yet known, it is unclear whether it is of linear nature. Experiments with persulphate in neutral solution show formation of the H deficient radical with a yield 40-60% of the radical cation yield for both compounds. Using a rate constant of reaction (-5.24) for isopropyl- and ethyl benzene taken from the correlation in Fig. 5.11, the rate constant for a proton loss from their radical cations would be one or two orders of magnitude higher than that of toluene. Thus, the results in Table 5.4 do not necessarily represent the ratio between the decay rate of the radical cations in dilute acidic media. The individual relation between the rate constants in Table 5.4, however, is probably qualitative correct. Thus the conclusion is made that the rate of the proton splitting reaction is governed by the reactivity of H atoms of the substituents.

5.7. Dissociation of the OH Adduct of N,N-Dimethylaniline in Aqueous Solution<sup>⊙</sup>

Acid catalyzed removal of OH<sup>-</sup> from the aromatic OH adduct has been reported

<sup>⊙</sup> Accepted for publication in J. Phys. Chem. (December 1977 issue)



recently for several compounds and is described in previous chapters<sup>21,30,42,45,52</sup>. Rao and Hayon<sup>57</sup> reported the formation of radical cations of several aromatic diamines and diphenylamine as a product of a one electron oxidation by OH radicals.

The authors suggest a two step mechanism



where the second step is an uncatalyzed dissociation of the OH adduct to hydroxide and the radical cation.

The present chapter describes the results from a pulse radiolytic study of the reaction of OH radicals with N,N-dimethylaniline (DMA) in aqueous solution and gives evidence for the mechanism suggested by Rao and Hayon<sup>57</sup>.

Transient spectra obtained immediately after pulse radiolysis of  $2.4 \times 10^{-4}$  M DMA in N<sub>2</sub>O saturated water solution at pH 9 with a 1 μsec pulse of 1.2 krad (Fig. 5.16) show absorption bands at 330 and 465 nm in agreement with Christensen<sup>12</sup>.

The spectra are identical within experimental error in the pH range 6 to 11 and for DMA concentrations from  $2.4 \times 10^{-2}$  M to  $2.4 \times 10^{-4}$  M. The band below 300 nm was obtained in  $5 \times 10^{-5}$  M DMA solution at pH 9.2, normalized by the ratio of the 465 nm absorption and corrected for DMA depletion. The rate constant of the OH reaction with DMA was measured to  $(1.4 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  in good agreement with reported value<sup>12</sup>.

The maximum at 330 nm is assigned to the product of methylic hydrogen abstraction, i.e. the N-methylanilinomethyl radical, on the basis of the transient spectrum obtained in  $5 \times 10^{-4}$  M solution of DMA in N<sub>2</sub>O saturated 0.6 N NaOH (Fig. 5.17). The only primary radical reaction with DMA in this solution is the O<sup>-</sup>, which is known to abstract H from the methyl groups rather than add to the ring<sup>3,40</sup>. An alternative reaction of O<sup>-</sup> with DMA would be an electron transfer reaction as reported for the phenoxide ion and suggested for aniline by Neta and Schuler<sup>58</sup>. In this case a radical cation would be produced, probably followed by a reaction reverse to (5.28) yielding the OH adduct. As the observed spectrum is quite different from the well established radical cation spectrum<sup>12-14</sup> and from the spectrum, which is assigned to the OH adduct (see later), thus this kind of reaction can be excluded in the case of DMA. The ratio of the 330 and the 465 nm absorptions, which is constant for pH's between 6 and 11, starts to increase at pH above 11.5. The extinction coefficient for the N-methylanilinomethyl radical based on its absorption in N<sub>2</sub>O

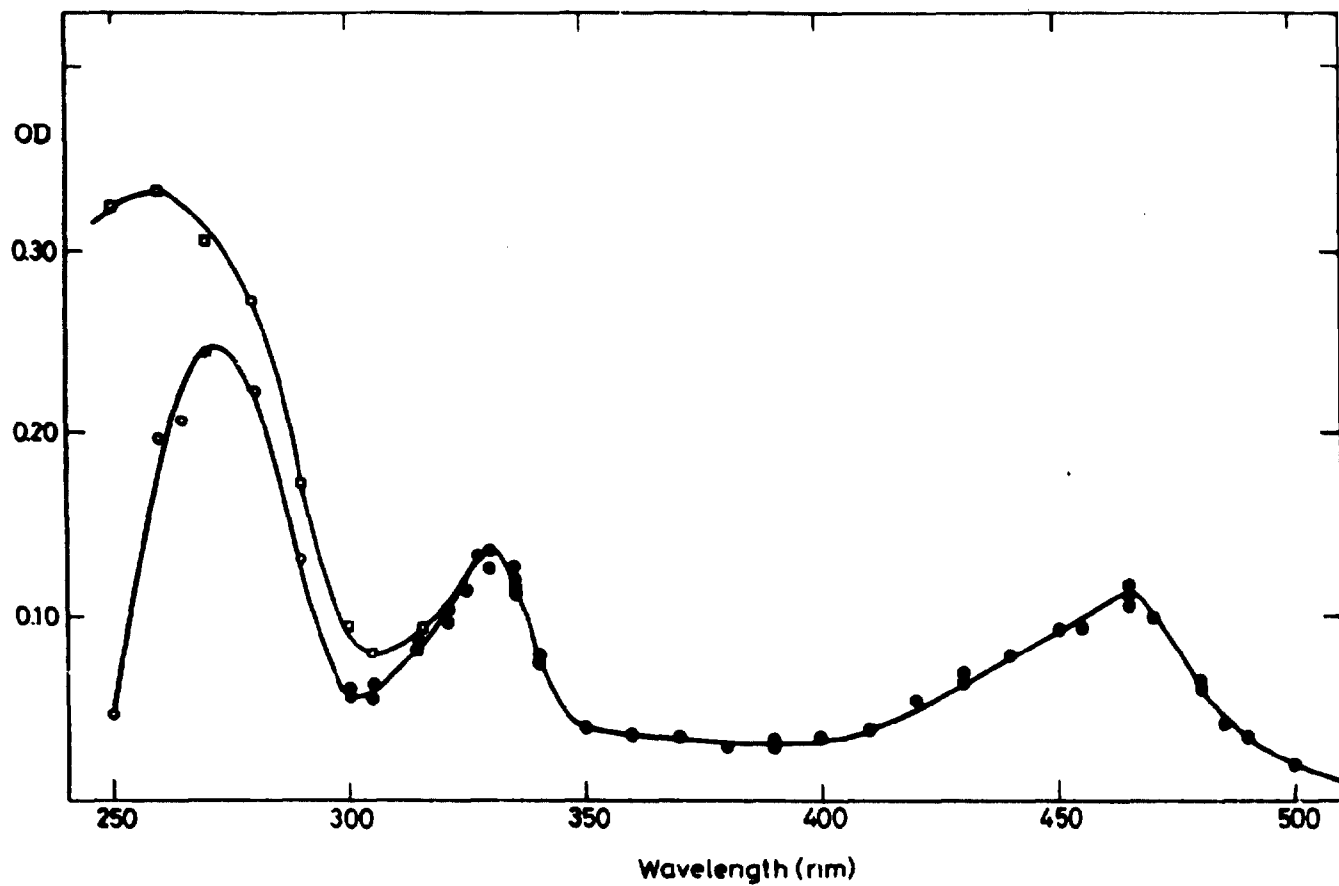


Fig. 5.16 The transient absorption spectrum obtained after 1  $\mu$ sec in  $N_2O$  saturated solution:  
 ● , DMA  $2.4 \times 10^{-4}$  M, pH 9.0, dose 1.22 krad. ○ , DMA  $5 \times 10^{-5}$  M, pH 9.2,  
 normalized spectrum. ◻ , the spectrum corrected for DMA depletion.

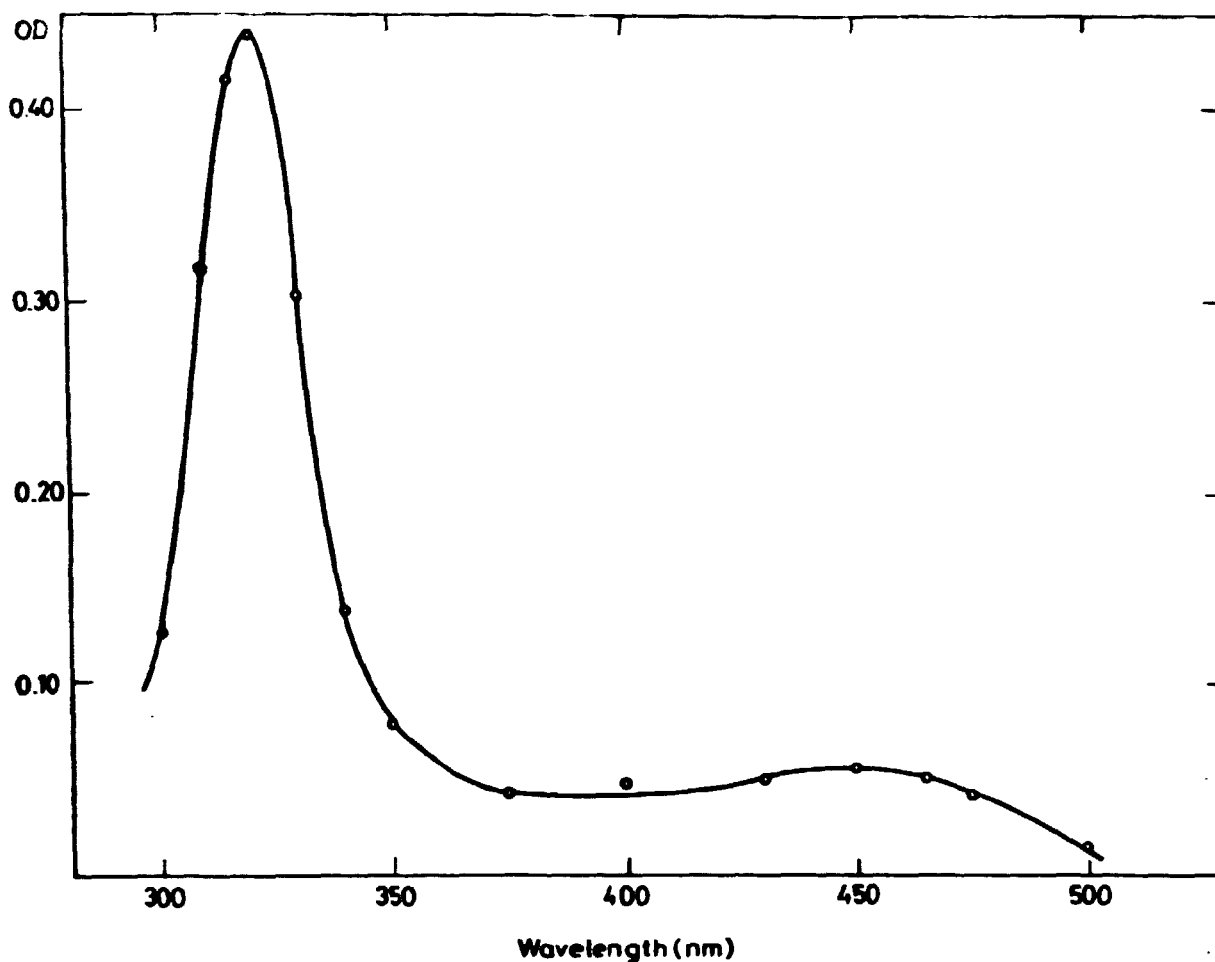


Fig. 5.17. The transient absorption spectrum obtained after 1  $\mu$ sec in 0.6 N NaOH,  $N_2O$  saturated  $5 \times 10^{-4}$  M DMA solution: dose 1.22 krad.

saturated 0.6 N NaOH and  $G_{O^-} = 6.5$  is  $\epsilon_{330} = 10\,500 \pm 500 \text{ M}^{-1}\text{cm}^{-1}$  and  $\epsilon_{450} = 1400 \pm 100 \text{ M}^{-1}\text{cm}^{-1}$ .

The 465 nm peak is assigned to the radical cation of N,N-dimethylaniline. The 465 nm band was previously assigned to the DMA radical cation<sup>12-14)</sup> in organic solvent, and in water applying flash photolysis or electrochemical methods.

The assignment is experimentally supported by conductometric pulse radiolysis, where a conductivity signal is observed which decays at the same rate as the optical absorption at 465 nm. Furthermore, a comparison of the transient spectrum obtained in  $N_2O$  saturated solution with that obtained in argon saturated with  $K_2S_2O_8$  added (rapid mixing technique) as an electron scavenger supports this conclusion (Fig. 5.18).

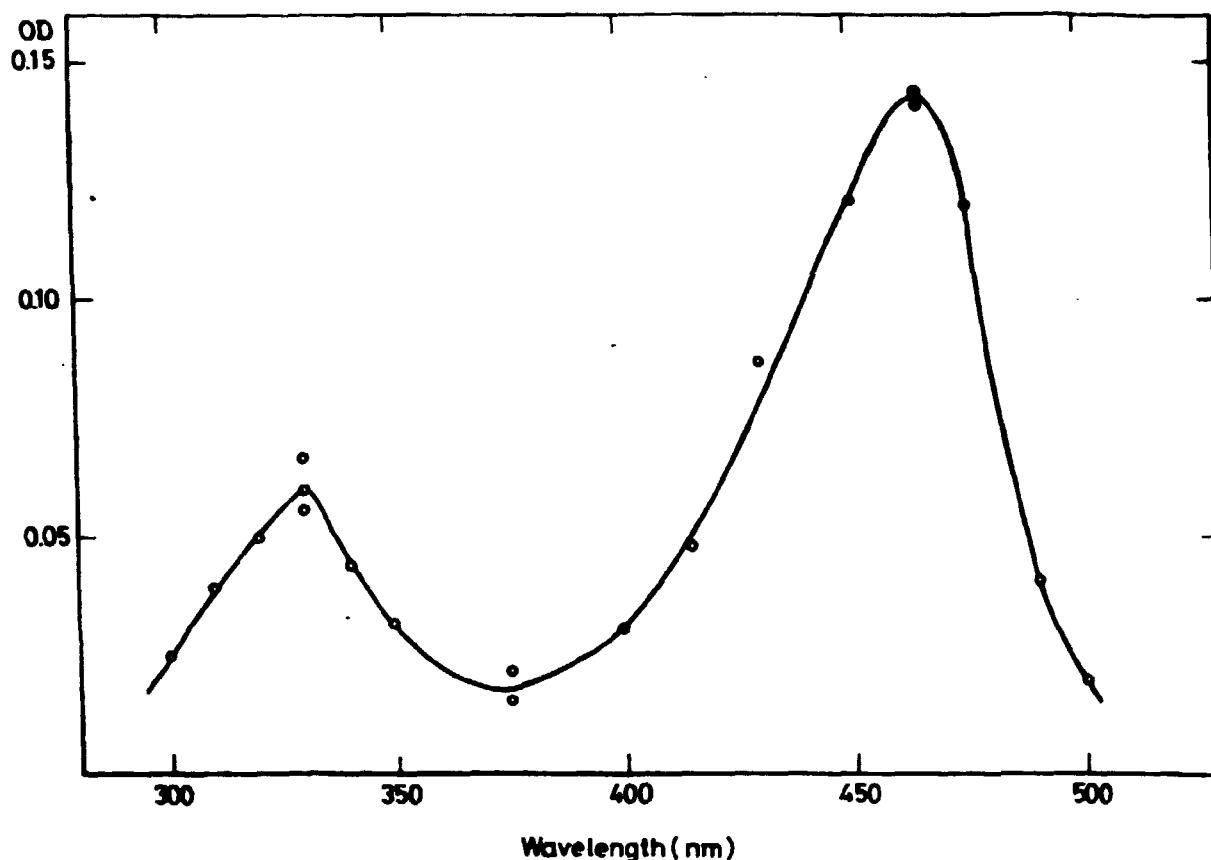


Fig. 5.18. The transient spectrum obtained after 1  $\mu\text{sec}$  in Ar saturated  $2.4 \times 10^{-4}$  M solution with  $2 \times 10^{-3}$  M  $\text{S}_2\text{O}_8^{2-}$  after 1  $\mu\text{sec}$  pulse: dose 1.22 krad.

The hydrated electron reacts readily with persulphate ( $k = 1.1 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$ ) to produce sulphate radical anion,  $\text{SO}_4^{\cdot -}$  (23,24). The  $\text{SO}_4^{\cdot -}$  radical anion is known to react with aromatic solutes by a direct oxidative electron transfer (18,20,21,31,45,62) forming corresponding radical cations or other oxidation products.

On the basis of the extinction coefficients obtained in alkaline solution for the product of direct abstraction of methylic hydrogen ( $\epsilon_{330} = 10\,500 \text{ M}^{-1}\text{cm}^{-1}$  and  $\epsilon_{465} = 1400 \text{ M}^{-1}\text{cm}^{-1}$ ), the fraction of OH radicals entering this reaction in neutral solution can be calculated. In terms of G-values this fraction is 1.9 and 0.9 in  $\text{N}_2\text{O}$  saturated and Ar saturated solution containing  $\text{S}_2\text{O}_8^{2-}$  respectively. Assuming that  $\text{SO}_4^{\cdot -}$  ( $G_{\text{SO}_4^{\cdot -}} = G_{e_{\text{aq}}^-} = 2.7$ ) reacts quantitatively with

DMA to form the radical cation and that the remaining fraction of OH radicals also yields the radical cation with absorption at 465 nm, the extinction coefficient for the radical cation at 465 nm in the two solutions can be calculated to  $4650 \text{ M}^{-1} \text{ cm}^{-1}$  and  $4400 \text{ M}^{-1} \text{ cm}^{-1}$  respectively. The extinction coefficients are corrected for the small absorption at 465 nm due to the N-methylanilinomethyl radical. The excellent agreement between the absorptions in the two experiments justifies our assumptions and shows a 1:2 ratio between the direct H abstraction from the two methyl groups and the radical cation formation. This is additionally confirmed by the transient conductivity measurement which for  $2 \times 10^{-3} \text{ M}$  DMA at pH = 9.0,  $\text{N}_2\text{O}$  saturated solution gives  $G = 3.4 \pm 0.4$  ( $\sim 65\%$  of  $G(\text{OH})$ ) for the radical cation. The conductivity detection system was calibrated with  $\text{CCl}_4$  in neutral aqueous deaerated solution taking  $G = 3.1$ <sup>63)</sup>. The result is comparable with the 1:1 ratio between formation of the anilino and the cyclohexadienyl radical in the reaction of OH radicals with aniline suggested by Christensen<sup>12)</sup> on the basis of the final product composition. The absorption below 300 nm consists of a second absorption band of the DMA radical cation corresponding to the 270 nm band obtained by Christensen<sup>12)</sup> in  $\text{N}_2\text{O}$  saturated acidic DMA solution and a third band of the N-methylanilinomethyl radical.

The H adduct of DMA in neutral solution formed by the H atoms ( $G_{\text{H}} = 0.6$ ) was observed at 380 nm in  $\text{N}_2\text{O}$  saturated solution with t-butyl alcohol to scavenge the OH radicals in agreement with Zador et al.<sup>61)</sup>, who assign the 370 nm absorption observed in pulse radiolysis of cyclohexane solutions of DMA to the corresponding cyclohexadienyl radical. The apparent lack of the OH adduct of DMA, which according to the correlation given by Chutny<sup>64)</sup> should be expected to have an absorption about 380 nm, led to experiments with a shortened time scale. In a solution saturated with  $\text{N}_2\text{O}$  ( $2 \times 10^{-2} \text{ M}$ ) and DMA ( $\sim 2.4 \times 10^{-2} \text{ M}$ ) at pH 9, all the hydrated electrons are scavenged by the  $\text{N}_2\text{O}$ , as an upper limit for the rate constant of the reaction of  $e_{\text{aq}}^-$  with DMA was found to be  $10^7 \text{ M}^{-1} \text{ sec}^{-1}$ . The absorption spectrum in this solution irradiated with a 20 nsec electron pulse undergoes a drastic change during the first 500 nsec. In the region 350 - 400 nm an intermediate species decays fast in a first order process with a rate constant  $k = (7 \pm 2) \times 10^6 \text{ sec}^{-1}$ . A corresponding build up at 465 nm is observed (Fig. 5.19 inset).

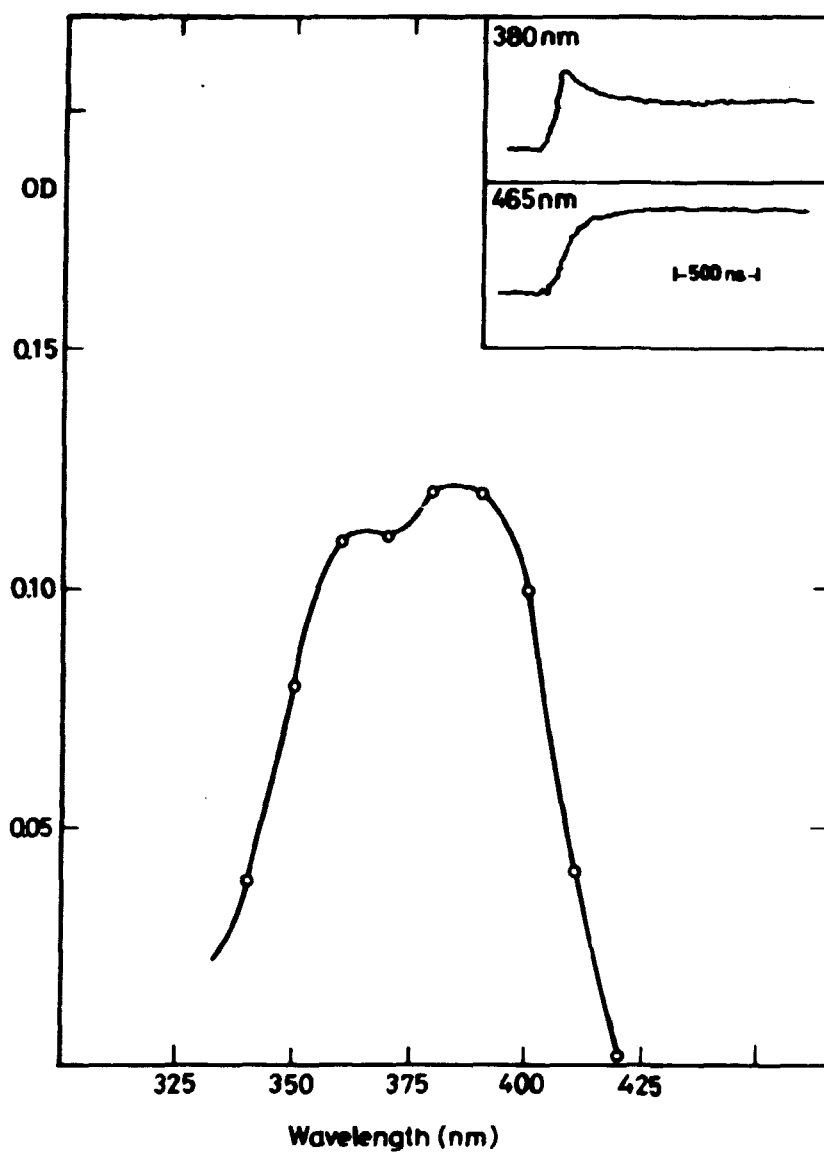
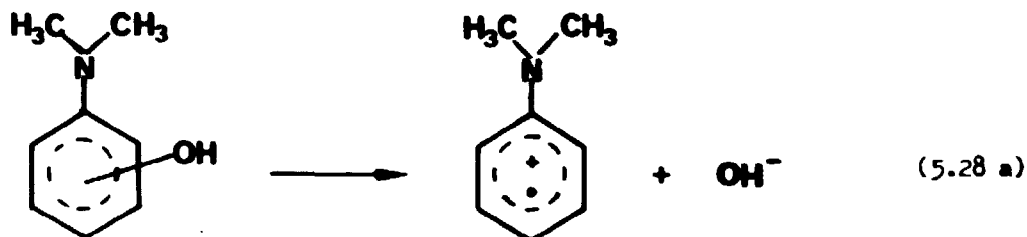


Fig. 5.19. The absorption spectrum of the DMA OH adduct. Insets show changes in optical absorption signals at 380 and 465 nm in the first microsecond after a 20 nsec pulse.

The difference between the spectra obtained 100 nsec and 800 nsec after the pulse yields a spectrum with a maximum about 380 nm (Fig. 5.19). This spectrum is assigned to the genuine OH adduct of DMA. The rate of the first order decay at 380 nm is not affected by a five fold decrease in solute concentration in the pH region 6-11. We postulate that the OH radical reacts with DMA to

form the OH adduct which subsequently dissociates according to eq. (5.28 a)



A reaction analogical to (5.28 a) has been reported recently for methoxy-substituted benzoic acids<sup>42)</sup>.

The extinction coefficient of the OH adduct is estimated to be  $\epsilon_{380} = 6500 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$ , although the available time resolution is not good enough to trace the species from the beginning.

The spectral characteristics of radicals formed in reaction of OH radicals with DMA are given in Table 5.5.

Table 5.5. Spectral Characteristic of the Radicals formed in the Reaction of the OH Radicals with DMA.

Radical	$\lambda_{\text{max}}$ [nm]	$\epsilon \text{ M}^{-1} \text{ cm}^{-1}$
$[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2]\text{H}$	380	-
$[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2]\text{OH}$	380	$6.500 \pm 1000$
	< 270	-
	330	$10.500 \pm 500$
	450	$1.400 \pm 100$
$[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2]^+$	270	-
	465	$4.500 \pm 400$

Since no influence of pH on the formation and decay of the radical cation of DMA up to pH = 11.5 was observed, the rate of the reverse reaction (5.28),  $k_{28a}$ , will be low.

The first order rate constant for the dissociation of the OH adduct of DMA,  $k_{28a} = (17 \pm 2) \times 10^6 \text{ sec}^{-1}$ , is about two orders of magnitude higher than those given for aromatic diamines by Rao and Hayon<sup>57)</sup>. This difference can hardly be expected as the formation of radical cations of tetramethylphenylenediamine (TMPD) and phenylenediamine (PD) should be energetically more favourable because of a lower ionization potential than DMA and formation of highly symmetrical radical cations.

The absorption spectra assigned to the OH adducts by these authors possess essentially the same maxima as the spectra of the corresponding radical cations with extinction coefficients of the same order of magnitude (Table II in ref. 57). This similarity is rather unusual for TMPD and N,N-dimethylphenylenediamine as the spectra of the radical cations of other substituted benzenes usually are well separated from those of the corresponding OH adducts and shifted substantially to the red<sup>12,21,40,52)</sup>. Rao and Hayon assign the spectrum obtained immediately after the pulse in  $\text{N}_2\text{O}$  saturated solution to the OH adduct. This is obviously an insufficient basis for the assignment in cases where reaction (5.28) is to be expected. In addition our conductivity measurements at pH = 8-10 in  $\text{N}_2\text{O}$  saturated solutions of TMPD and PD show a conductivity signal within 1  $\mu\text{sec}$  (time resolution of the equipment) with  $G \approx 4.2$  for the radical cations. For these reasons the initial absorption spectrum is assigned to the radical cation rather than to the genuine OH adduct. Thus the first order changes in the absorbance  $k \approx 10^5 \text{ sec}^{-1}$  observed by Rao and Hayon could not be ascribed to the dissociation reaction of the OH adduct (eq. 28). At the moment, however, a conclusive explanation for these changes cannot be offered. A tentative explanation is a reaction due to the product of the direct H abstraction from the methyl group. In 0.6 N NaOH,  $\text{N}_2\text{O}$  saturated TMPD solution, a first order change with the rate constant  $k = 10^5 \text{ sec}^{-1}$  from a spectrum similar to that obtained with DMA under the same conditions, into a spectrum similar to that of the radical cation of TMPD was observed. Another explanation could be a reaction with the buffer used by Rao and Hayon in neutral solution, as we are not able to reproduce the first order reaction in unbuffered neutral PD solutions. An additional complication which may be expected for para-phenylenediamines is the possibility of an ipso substitution in analogy with methoxylated benzenes and benzoic acids as reported by P. O'Neill et al.<sup>65)</sup>, because amino and dimethylamino groups are even stronger ortho-para-directing substituents than the methoxy group.

On assigning the OH adduct spectra, Rao and Hayon<sup>57)</sup> do not take into account the possibility of a direct formation of radical cations via an elec-



tron transfer from the amines to the OH radicals; nevertheless they point out that this possibility cannot be excluded on basis of their results.

It seems likely, however, that this possibility can be excluded as it requires the electron transfer step prior to hydration of the ions formed, which with the OH radical gas phase electron affinity of about  $2 \text{ eV}^{1)}$  and the lowest known ionization potential of organic compound  $5.4 \text{ eV}^{66)}$  would be energetically unfavorable.

#### 5.8. The Relation Between the Ionization Potential of Substituted Benzenes and the Acid-base Behaviour of their OH Adducts

OH adducts of aromatic compounds of relatively high ionization potentials (IP) like benzene, nitrobenzene and benzonitrile decay even in highly acidic media in a bimolecular radical-radical reaction forming corresponding hydroxy-derivatives.

For several compounds of lower ionization potentials like phenol, hydroquinone and aniline, acid catalyzed intramolecular water elimination has been demonstrated<sup>2)</sup>.

Recently acid catalyzed elimination of  $\text{OH}^-$  from the OH adducts leading to the formation of the corresponding radical cation (eq. 5.29) was demonstrated for biphenyl<sup>30)</sup>, naphthalene<sup>67)</sup>, methoxylated benzenes and methoxybenzoic acids<sup>21,42)</sup> and proved to be the first step in the acid catalyzed water elimination from the OH adduct of methylated benzenes<sup>52)</sup>.

For compounds of even lower ionization potential e.g. N-substituted phenylenediamines<sup>57)</sup> and N,N-dimethylaniline<sup>55)</sup> the uncatalyzed dissociation of the OH adduct (eq. 5.28) was reported.

On the other hand formation of the OH adduct from the radical cation in neutral and alkaline solution has been demonstrated<sup>45,46,52)</sup> (eq. 5.30 and 5.31).



The acid-base behaviour described by equations (5.28 - 5.31) is formally analogous to that observed for carbonium ion - carbinol equilibria or the covalent hydroxide adducts of quaternary nitrogen heteroaromatic cations which are usually described as "pseudobases". In analogy the OH adduct can be considered as a pseudobase of the corresponding radical cation.

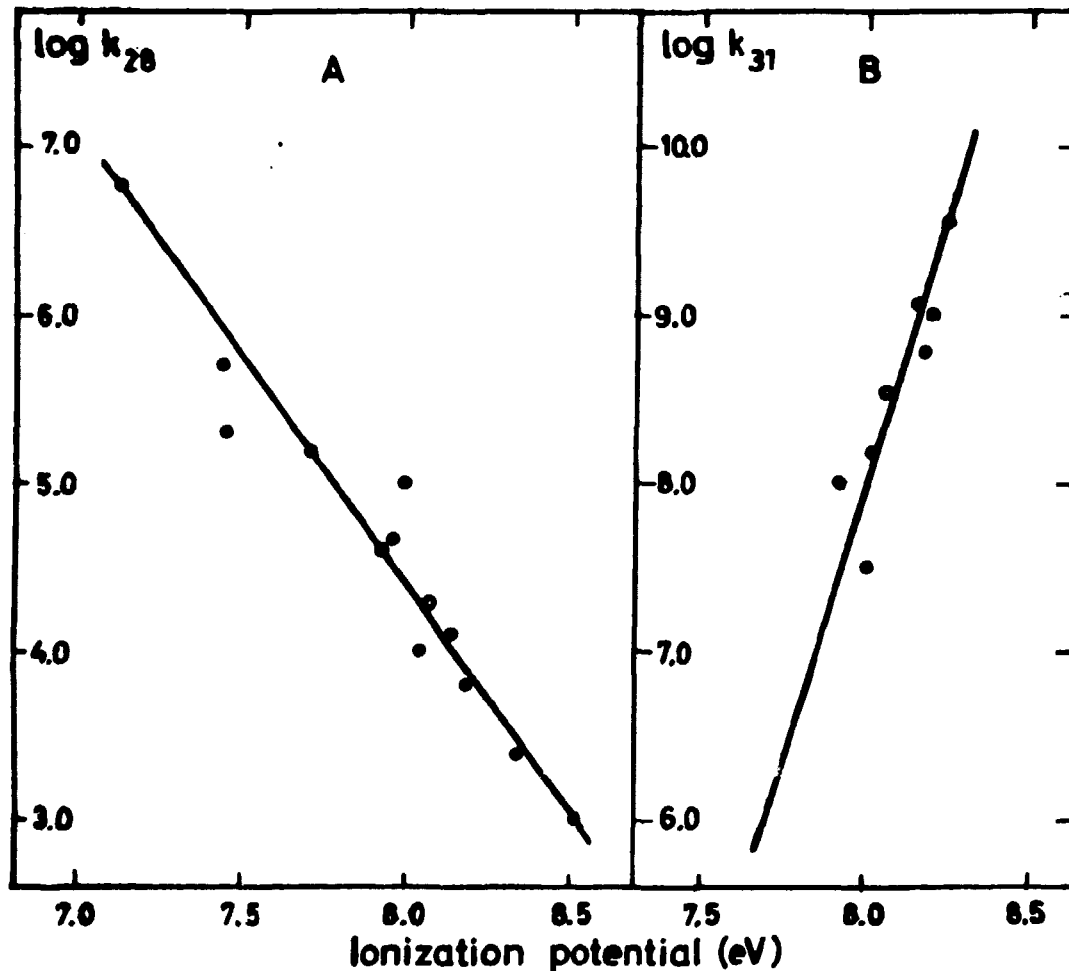


Fig. 5.20 Dependence of log k for reaction 5.28 - A and 5.31 - B on the ionization potential of the parent compounds.

This chapter gives a correlation between the rate constant for reaction (5.28) and (5.31) and the ionization potentials of several substituted benzenes. The correlation is shown in Fig. (5.20). The data used for the correlation are given in Table 5.6. The rate constants for reaction (5.28) were measured from the first order decay of the corresponding OH adducts for anisidine, p-N,N-dimethylaminobenzonitrile, 1,3,5-trimethoxybenzene and o-toluidine. For aniline, phenol, hydroquinone and p-cresol the rate constant for the uncatalyzed water elimination, e.g. formation of anilino<sup>12)</sup> and phenoxy radicals<sup>9,10)</sup>, was taken as rate constant for reaction (5.28). This is based on the assumption that reaction (5.28) is the first and rate controlling step

Table 5.6. Rate Constants for Reactions (5.28) and (5.31)

No.	Compound	$k_{28} \text{ sec}^{-1}$	$\lambda$ a)	b)	$k_{31} \text{ M}^{-1} \text{ sec}^{-1}$	$\lambda$ a)	b)	Ionization Potential eV
		$\text{AOH}^+ \rightarrow \text{A}^+ + \text{OH}^-$	nm	ref	$\text{A}^+ + \text{OH}^- \rightarrow \text{AOH}^+$	nm	ref	
1.	N,N-dimethylaniline	$6 \times 10^6$	380	•	-	-	-	7.17
2.	p-anisidine	$5 \times 10^5$	365	•	-	-	-	7.44
3.	p-N,N-dimethylamino-benzonitrile	$1 \times 10^5$	445	•	$3 \times 10^7$	550	•	7.99
4.	1,3,5-trimethoxybenzene	$2 \times 10^4$	340	•	$3.5 \times 10^8$	580	•	-
5.	aniline	$1.5 \times 10^5$	-	12	-	-	-	7.70
6.	anisole	-	-	-	$1 \times 10^9$	-	chap. 5.4	8.20
7.	phenol	$1 \times 10^3$	-	9	-	-	-	8.51
8.	p-cresol	$2.4 \times 10^3$	-	9	-	-	-	8.34
9.	hydroquinone	$4.6 \times 10^4$	-	10	-	-	-	7.95
10.	o-toluidine	$2.0 \times 10^5$	350	•	-	-	-	7.45
11.	1,2,3,5-tetramethylbenzene	$1.3 \times 10^4$	-	3	$1.2 \times 10^9$	-	chap. 5.5	8.15
12.	1,2,3,4-tetramethylbenzene	$5 \times 10^3$	-	3	$6.0 \times 10^8$	-		8.18
13.	1,2,4,5-tetramethylbenzene	$1 \times 10^4$	-	3	$1.5 \times 10^8$	-		8.03
14.	pentamethylbenzene	$4 \times 10^4$	-	3	$1.0 \times 10^8$	-		7.92
15.	1,2,4-trimethylbenzene	-	-	-	$3.5 \times 10^9$	-		8.24

• this work

a) wavelength at which rate constants were measured.

b) references.

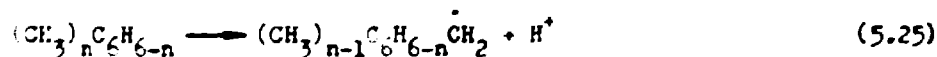
in the uncatalyzed water elimination from the OH adducts of hydroxyaromatic compounds, which is strongly indicated by the following:

- a) the  $SO_4^{\cdot-}$  radicals from radical cations of several aromatic compounds<sup>21, 31, 45, 62, 67</sup>, which can be observed in the time scale available in the pulse radiolysis. The phenoxy radical, however, was found to be the product of the reaction of  $SO_4^{\cdot-}$  radicals with phenolic compounds, but a very rapid proton loss from the radical cation (eq. 5.32) was suggested as a step in this reaction<sup>26</sup>.



- b) Phenoxy radical is formed under the photolytic electron ejection from phenolic compounds in flash photolysis of aqueous solution<sup>68</sup>.
- c) The formation of radical cations via protonation of several phenoxy radicals was demonstrated in highly acidic solutions with pKa varying from -2.0 for phenol to -0.8 for hydroquinone<sup>69</sup>. As proton reactions are usually diffusion controlled, high acidic values of pKa indicate that the reaction (5.32) must be very rapid which in turn means that reaction (5.28) can be extremely difficult to demonstrate experimentally with phenolic compounds.

For the methylated benzenes the rate constant for uncatalyzed formation of the corresponding benzyl radical from the OH adduct<sup>3)</sup> was taken as the rate constant for reaction (5.28) on the assumption that this reaction is the rate controlling step since the proton loss from the corresponding radical cation (eq. 5.25)



is at least one order of magnitude higher<sup>46)</sup>. The rate constant of the OH adduct decay for methylated benzenes can only be estimated from the formation of the corresponding benzyl radicals because of the overlap of the second absorption maximum of the benzyl radical and the absorption maximum of the OH adduct<sup>3)</sup>. Pentamethylbenzene, durene, isodurene and prehnitene for which the rate constants of reaction (5.25) are most reliable, are included.

The correlation of the rate constants of reaction (5.31) (Table 5.6, Fig. 5.21) contains data obtained for methylated benzenes<sup>46)</sup> in addition to data for p-N,N-dimethylaminobenzonitrile, anisole and 1,3,5-trimethoxybenzene. In the case of sym-trimethoxybenzene the ionization potential is not available.

However, when a straight line is drawn through the points in Fig. 5.20A and 5.20B, the ionization potential of 1,3,5-trimethoxybenzene can be estimated from the intercept of the rate constants for reactions (5.28) and (5.31), to be 8.03 eV and 8.09 eV respectively. The kinetic data for 1,3,5-trimethoxybenzene are therefore plotted at IP 8.06 in the figures (open circles). The rate constants for reaction (5.31) were measured in argon saturated alkaline solution with  $2.5 \times 10^{-3}$  M persulphate added.

The rate constants of reaction (5.31) can be obtained for only a few compounds due to the following limitations:

- a) The solute must compete for  $\text{SO}_4^{\cdot -}$  radicals with  $\text{OH}^-$  ( $k_{\text{OH}^-} + \text{SO}_4^{\cdot -} = 7.3 \times 10^7 \text{ M}^{-1} \text{sec}^{-1}$ ,<sup>19</sup>).
- b) The radical cation formed must be fairly stable in respect to other reactions, if reaction (5.31) should be detectable.
- c) The condition  $k_{28} < k_{31} [\text{OH}^-]$  must be fulfilled.
- d) The solute must be relatively stable in the presence of  $\text{S}_2\text{O}_8^{2-}$  which itself is a strong oxidizing agent.

The presented correlations are considered as a working hypothesis which allows for a prediction of the rate constants of the reactions (5.28) and (5.31). For example in the case of N,N-dimethylaniline, the radical cation is formed according to eq. (5.28) in  $\text{N}_2\text{O}$  saturated alkaline solution up to pH 11.5<sup>55</sup>), where the OH radicals start to convert into  $\text{O}^-$  radicals by the equilibrium reaction (2.7). This behaviour is in agreement with a very low rate constant of reaction (5.31) for N,N-dimethylaniline which may be obtained from an extrapolation of the straight line in Fig. 5.20B. The rate constant is estimated to  $1 \times 10^3 \text{ M}^{-1} \text{sec}^{-1}$  at an IP of 7.12 eV.

The correlations also support the conclusions made in chapter 5.7, that Rao and Hayon<sup>57</sup>) by assigning the first order changes in extinction for p-phenylenediamines to reaction (5.28) are in error as the ionization potentials for these compounds are between 6.18 and 6.8 eV.

For the analogical reactions of quinolinium and isoquinolinium cations a correlation with the Hammett substituent function was obtained<sup>70</sup>). Since a radical cation of approximately the same radius and  $\text{OH}^-$  are formed from the OH adducts, a linear relationship between the free energy of activation and the ionization potential can presumably be expected. These correlations are therefore considered as a special case of a free energy relationship.

## CONCLUSION

The formation of radical cations of substituted benzenes from the corresponding OH adducts has been demonstrated. This reaction is important in free radical hydroxylation reactions especially in acid solutions.

On the basis of the results obtained, a two step mechanism of the water elimination reaction from aromatic OH adducts is demonstrated. The first step is a formation of a radical cation and the second a loss of a proton.

The stability of the radical cations of substituted benzenes was found to increase with decreasing ionization potential of the parent compound; however, it also depends on the ability of the substituents to give up a proton.

The acid-base properties of the radical cations have been demonstrated. A correlation between the rate constants determining the acid-base behaviour of the radical cations and the ionization potential of the parent compound is shown.

The formation of OH adducts in the reaction of the radical cations with  $\text{OH}^-$  has been proved. This result, however, is quite astonishing in the case of methylated benzenes, because these radical cations are very prone to give up a proton.

The activation energy of this reaction as well as of other reactions of radical cations is now being studied at Risø Accelerator Department, and will presumably provide more information about the nature of this reaction.

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REFERENCES

- 1) L.M. Dorfman and G.E. Adams, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 46 (1973).
- 2) for review see P. Neta, Advances in Physical Organic Chemistry 12, 283 pp., 1976.
- 3) K. Sehested, H. Corfitzen, H.C. Christensen and E.J. Hart, J. Phys. Chem., 79, 310 (1975).
- 4) D.C. Nonhebel and J.C. Walton, "Free-Radical Chemistry" (Cambridge 1974), 487 pp. and references therein.
- 5) L.M. Dorfman, Accounts Chem. Res. 3, 224 (1970).
- 6) E.J. Hart and M. Anbar, "The Hydrated Electron", Wiley Interscience, New York, 1970.
- 7) C. Walling, Accounts Chem. Res. 8, 125 (1975).
- 8) G. Sosnovsky and D.J. Rawlinson, "Organic Peroxides", Wiley Interscience, New York 1971, Vol. II, 269 pp.
- 9) E.J. Land and M. Ebert, Trans. Faraday Soc., 63, 1181 (1967).
- 10) G.E. Adams and B.D. Michael, Trans. Faraday Soc., 63, 1171 (1967).
- 11) A. Ronlan and V.D. Parker, J. Chem. Soc. C, 3214 (1971).
- 12) H.C. Christensen, Int. J. Radiat. Phys. Chem., 4, 311 (1972).
- 13) H.C. Christensen, K. Sehested and E.J. Hart, J. Phys. Chem., 77, 983 (1973).
- 14) K. Sehested and H.C. Christensen, Symposium on Radiation Chemistry of Aqueous Systems, Moscow 1973, p. 34.
- 15) M.E. Snook and G.A. Hamilton, J. Amer. Chem. Soc., 96, 860 (1974).
- 16) E.J. Heiba, R.M. Dessau and W.J. Koehl Jr., J. Amer. Chem. Soc. 91, 6830 (1969).
- 17) J.K. Kochi in "Free Radicals". J.K. Kochi, Editor, Wiley Interscience, New York 1973, Vol. II, 673 pp.
- 18) C. Walling and D.M. Camaioni, J. Amer. Chem. Soc., 97, 1063 (1975).
- 19) O.P. Chawla and R.W. Fessenden, J. Phys. Chem., 79, 2693 (1975).



- 20) K. Bansal and R.W. Fessenden, *Radiat. Res.*, 67, 1 (1976).
- 21) P. O'Neill, S. Steenken and D. Schulte-Frohlinde, *J. Phys. Chem.*, 79, 2773 (1975).
- 22) P. Neta et al., *J. Amer. Chem. Soc.*, 99, 163 (1977).
- 23) W. Roebke, M. Renz and A. Henglein, *Int. J. Radiat. Phys. Chem.*, 1, 29 (1969).
- 24) E. Hayon, A. Treinin and J. Wilf, *J. Amer. Chem. Soc.*, 94, 47 (1972).
- 25) P. O'Neill, S. Steenken and D. Schulte-Frohlinde, *Angew. Chem., Int. Ed. Engl.* 14, 430 (1975).
- 26) H. Rabani and M.S. Matheson, *J. Phys. Chem.*, 70, 761 (1966).
- 27) A. Miller, *Nucl. Instr. and Meth.*, 114, 189 (1974).
- 28) T.E. Eriksen, *Chemica Scripta*, 7, 193 (1975).
- 29) V.D. Parker in "Organic Electrochemistry". M.M. Baizer, Ed., Marcel Dekker, New York 1973, p. 539, p. 545.
- 30) K. Sehested and E.J. Hart, *J. Phys. Chem.*, 79, 1639 (1975).
- 31) K. Sehested, J. Holcman and E.J. Hart, *J. Phys. Chem.*, 81 (14) 1363 (1977)(chapter 5.4 of this report).
- 32) K. Sehested, E. Bjergbakke, O. Lang Rasmussen and H. Fricke, *J. Chem. Phys.* 51, 3159 (1969).
- 33) C.R.E. Jefcoate and R.O.C. Norman, *J. Chem. Soc. B*, 48 (1968).
- 34) D.L. Allara, B.C. Gilbert and R.O.C. Norman, *Chem. Commun.* 319 (1965).
- 35) A.J. Bard, A. Ledwith and H.J. Shine in "Advances in Physical Organic Chemistry". V. Gold and D. Bethell, Eds., Academic Press, London 1976, pp. 210.
- 36) L. Ebersson in "Organic Electrochemistry". M.M. Baizer, Ed., Marcel Dekker, New York 1973, p. 462.
- 37) J.K. Kochi, R.T. Tang and T. Bernath, *J. Amer. Chem. Soc.*, 95, 7114 (1973).
- 38) A. Nishinaga, H. Hayashi and T. Matsura, *Bull. Chem. Soc. Jpn.*, 47, 1813 (1974).
- 39) B. Cantone, F. Grasso and S. Pignataro, *Mol. Phys.* 11, 221 (1966).

- 40) P. Neta, M.Z. Hoffman and M. Simic, *J. Phys. Chem.*, 76, 847 (1972),  
and P. Neta and R.H. Schuler, *Radiat. Res.*, 62, 233 (1975).
- 41) J.H. Fendler and G.L. Gasowski, *J. Org. Chem.*, 33, 2755 (1968).
- 42) P. O'Neill, S. Steenken and D. Schulte-Frohlinde, *J. Phys. Chem.*, 81,  
31 (1977).
- 43) M. Anbar, M. Rambenek and A.B. Ross, *Nat. Stand. Ref. Data Ser., Nat.*  
*Bur. Stand., No. 43* (1973).
- 44) H. Zemel and R.W. Schuler, *J. Phys. Chem.*, 79, 1419 (1975).
- 45) J. Holcman and K. Sehested, *J. Phys. Chem.*, 80, 1642 (1976)  
(chapter 5.3. of this report).
- 46) K. Sehested and J. Holcman, submitted for publication in *J. Phys.*  
*Chem.* (chapter 5.5 of this report).
- 47) C.N.R. Rao, V. Kalyanaraman and M.V. George, "Electronic Spectra of  
Radical Ions", in *Appl. Spec. Revs.*, 3, 153 (1970).
- 48) R.C. Dunbar, *Chem. Phys. Lett.*, 32, 508 (1975).
- 49) K.M. Bansal and A. Henglein, *J. Phys. Chem.*, 78, 160 (1974).
- 50) C. Walling and R.A. Johnson, *J. Amer. Chem. Soc.*, 97, 363 (1975).
- 51) A.B. King, *J. Chem. Phys.*, 47, 2701 (1967).
- 52) K. Sehested, International Conference on Radiation Chemistry, July  
7-9, 1975, Argonne National Laboratory, U.S.A., and ref. 31.
- 53) C.N.R. Rao, *Tetrahedron*, 32, 1561 (1976).
- 54) R.O.C. Norman, P.M. Storey and P.R. West, *J. Chem. Soc. B*, 1087  
(1970); C. Walling and D.M. Camaioni, *J. Amer. Chem. Soc.*, 97,  
1603 (1975); S. Steenken, P.O'Neill and D. Schulte-Frohlinde, *J.*  
*Phys. Chem.*, Vol. 81, No. 1, 26 (1977); M.K. Eberhardt, *J. Org.*  
*Chem.*, Vol. 42, No. 5, 832 (1977).
- 55) J. Holcman and K. Sehested, *J. Phys. Chem.* (1977) December issue.  
(chapter 5.7 of this report).
- 56) J. Holcman and K. Sehested, to be published (chapter 5.8 of this  
report).
- 57) P.S. Rao and E. Hayon, *J. Phys. Chem.*, 79, 1063 (1975).

- 55) P. Neta and K.H. Schuler, *J. Amer. Chem. Soc.*, 97, 918 (1975).
- 56) A. Habersbergova, I. Janovsky and J. Těplý, *Radiation Res. Rev.*, 1, 153 (1968), and A. Habersbergova, J. Těplý and P. Kourim, *Radiation Res. Rev.*, 4, 155 (1971).
- 57) J. Wheeler and R.F. Nelson, *J. Phys. Chem.*, 77, 1490 (1973).
- 58) E. Zador, J.M. Warman and A. Hummel, *J. Chem. Soc. Faraday Trans. I*, 72, 1368 (1976).
- 59) S. Steenken, P. O'Neill and D. Schulte-Frohlinde, *J. Phys. Chem.*, 81, 16 (1977).
- 60) T.E. Eriksen, private communication, and ref. 28.
- 61) B. Chutny, *Nature*, 213, 593 (1967).
- 62) P. O'Neill, D. Schulte-Frohlinde and S. Steenken, *Faraday Discussion*, 63, in press.
- 63) Y. Nakato, T. Chiyoda and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, 47, 3001 (1974).
- 64) N. Zevos and K. Sehested, submitted to *J. Amer. Chem. Soc.*
- 65) E.J. Land, G. Porter and E. Strachan, *Trans. Faraday Soc.*, 57, 1855 (1961); G. Dobson and L.J. Grossweiner, *Trans. Faraday Soc.*, 61, 708 (1965); J. Feitelson and E. Hayon, *J. Phys. Chem.*, 77, 10 (1973).
- 66) W.T. Dixon and D. Murphy, *Faraday Trans. II*, 72, 1222 (1976).
- 67) J.W. Hunting and D.J. Norris, *J. Amer. Chem. Soc.*, 99, 1189 (1977).