EPR and ENDOR Study of the Formation of Pyrene and 1,2,3,6,7,8-Hexahydropyrene Cation Radicals in Solution

REIJO MÄKELÄ, MIKKO OKSANEN and MIKKO VUOLLE

Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä 10, Finland

EPR coupling constants have been measured for the pyrene cation radical generated by oxidation of pyrene with silver tetrafluoroborate, with trifluoroacetic acid as solvent, and with thallium(III) trifluoroacetate in the same solvent, and also by dissolving pyrene in deuterotrifluoroacetic acid or trifluoromethanesulfonic acid.

The cation radical of 1,2,3,6,7,8-hexahydropyrene has been prepared by thallium(III) trifluoroacetate oxidation with trifluoroacetic acid as solvent, and by silver tetrafluoroborate oxidation both in trifluoroacetic acid and in perfluoropropionic acid. The 1,2,3,6,7,8-hexahydropyrene cation radical has also been prepared by dissolving 1,2,3,6,7,8-hexahydropyrene in deuterosulfuric acid, fluorosulfuric acid and in a mixture of fluorosulfuric acid and sulfuryl chloride fluoride.

Interest in the reactions of radical cations has grown substantially in recent years, as radical cations are important intermediates in many organic processes.

Trifluoroacetic acid is often used as solvent in the oxidation of arenes and aromatic amines with lead(IV) acetate[1] and cobalt(IV) acetate.[2] The first EPR study of the cation radicals produced in oxidation of arenes using thallium(III) trifluoroacetate as oxidant and trifluoroacetic acid as solvent was made by Elson and Kochi.[3] We have used silver tetrafluoroborate as oxidant and trifluoroacetic acid as solvent to produce cation radicals in solution for EPR and ENDOR measurements. Well-resolved EPR spectra can also be obtained without thallium(III) trifluoroacetate by using strong acids such as

sulfuric acid,[4] trifluoroacetic acid,[5] trichloroacetic acid,[6] trifluoromethanesulfonic acid[7] and fluorosulfuric acid.[8]

In many organic syntheses thallium(III) trifluoroacetate is used as a one-electron oxidant and trifluoroacetic acid as solvent: for example in the allylation reaction of aromatic compounds[9] and in oxidative dehydrodimerization reactions to give symmetrical biaryls.[10] Often the exact structure of the reactive intermediate is unknown, or the mechanism of the oxidation reaction producing the cation radical is discussed in an incomplete way.

The aim of the present work was to study the reaction mechanism of oxidation with thallium(III) trifluoroacetate in trifluoroacetic acid, through reference to oxidation by other routes, and to find an optimum method of producing cation radicals in solution for ENDOR measurements.

EXPERIMENTAL

Chemicals. Pyrene (Fluka, *purissimum*) was used without further purification. 1,2,3,6,7,8-Hexahydropyrene (EGA-Chemie KG) was recrystallized twice from benzene and dried in a vacuum desiccator. Other chemicals were silver tetrafluoroborate (Fluka, anhydrous), fluorosulfuric acid (Fluka), perfluoropropionic acid (Fluka, *purum*), perfluoropropionic anhydride (Fluka, *pract.*), trichloroacetic acid (Merck, GR), deuterosulfuric acid (Merck, 96−98 %, deuteration degree not less than 99 %), deuterotrifluoroacetic acid (Merck, Uvasol), trifluoroacetic acid (Merck, Uvasol), trifluoroacetic anhydride (Fluka, *purum*), trifluoromethanesulfonic acid
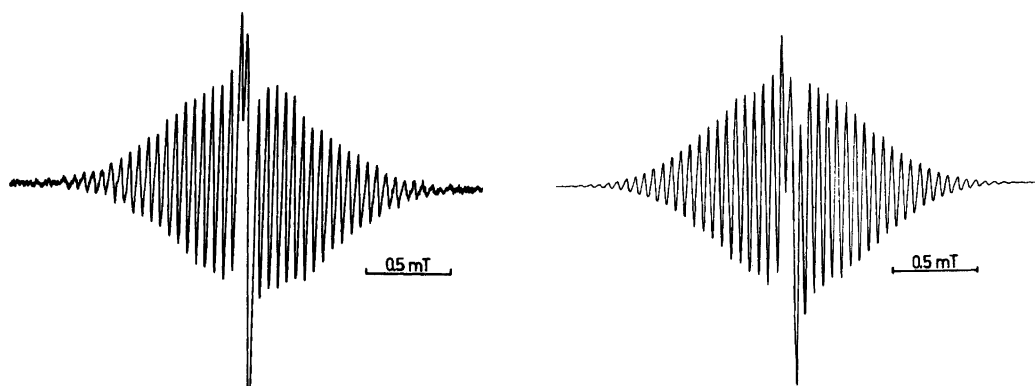
Fig. 1. (a) The EPR spectrum of pyrene dimer cation radical produced by oxidation with thallium(III) trifluoroacetate in trifluoroacetic acid. The spectrum was recorded at 259 K; (b) Simulated spectrum using the parameters given in Table 1.

(Fluka, *purum*) and sulfuryl chloride fluoride (Cationics Inc.).

Equipment. The EPR spectrometers were a Varian E-12 and a Varian E-9 with field-frequency lock, a Varian NMR gaussmeter E 500, a Varian variable temperature control unit, a Takeda Riken Industry Co. microwave counter TR 5211 D and an Apple II computer. ENDOR spectra were measured with a Bruker ENDOR B-EN 200 S connected to the Varian E-12.

The EPR spectra were simulated on a Varian 620/L computer and an Apple II. The ESREXN QCPE 209 modified by Dr. H. Joela, was run on a Univac 1100/11.

Methods. Pyrene. To a mixture of pyrene and silver tetrafluoroborate were added trifluoroacetic acid and a few drops of trifluoroacetic anhydride and the sample was sealed under high vacuum. The cation radicals were also prepared by dissolving pyrene in deuterotrifluoroacetic acid, fluorosulfuric acid or trifluoromethanesulfonic acid. These samples were likewise sealed under high vacuum.

1,2,3,6,7,8-Hexahydropyrene. To a mixture of 1,2,3,6,7,8-hexahydropyrene and silver tetrafluoroborate were added trifluoroacetic acid or perfluoropropionic acid and a few drops of the appropriate anhydride. The cation radicals were also prepared by dissolving 1,2,3,6,7,8-hexahydropyrene in fluorosulfuric acid, trifluoromethanesulfonic acid or in a mixture of fluorosulfuric acid and sulfuryl chloride fluoride. Samples were sealed under high vacuum, or when deuterosulfuric acid was used, without high vacuum. The cation radicals were likewise produced under high vacuum when 1,2,3,6,7,8-hexahydropyrene was dissolved in trifluoroacetic acid or deuterotrifluoroacetic acid and thallium(III) trifluoroacetate was added as oxidizing agent.

RESULTS AND DISCUSSION

Oxidation of pyrene with thallium(III) trifluoroacetate in trifluoroacetic and generated a

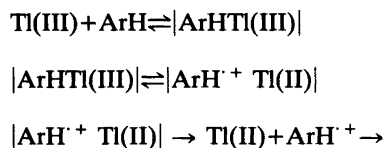*Table 1.* The coupling constants (mT) of pyrene cation radicals.

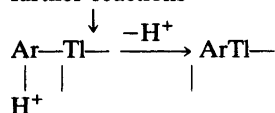| Pos.	Dimer SbCl$_5$[a]	Spectr. 1a	Spectr. 2a	Spectr. 3	INDO
1	0.266	0.269	0.547	0.546	−0.529
2	0.057	0.054	0.123	0.122	0.227
4	0.110	0.110	0.217	0.217	−0.200
g	2.00253	2.00253	2.00259	—	—
T	203	259	256	241	—

[a] Ref. 21.

dimer radical cation and the spectrum shown in Fig. 1a was observed. A simulation based on the parameters given in Table 1 is shown in Fig. 1b.

When pyrene was dissolved in trifluoroacetic acid or deuterotrifluoroacetic acid a spectrum was observed which was similar to that of Fig. 1a except that the prominent peak in the middle was absent.

Elson and Kochi[3] have proposed the mechanism given in Scheme 1 for oxdiation of arene (ArH) with thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA).

$$Tl(III) + ArH \rightleftharpoons |ArHTl(III)|$$

$$|ArHTl(III)| \rightleftharpoons |ArH^{\cdot\,+}\ Tl(II)|$$

$$|ArH^{\cdot\,+}\ Tl(II)| \rightarrow Tl(II) + ArH^{\cdot\,+} \rightarrow$$

further reactions

$$\text{Ar—Tl—} \xrightarrow{\ -H^+\ } \text{ArTl—}$$

Scheme 1.

The further reactions would include direct attachment to the anion and formation of the substituted product as in the case of anthracene,[11] or the dimerization of the radical cation as in the case of pyrene or the radical cation may interact with another molecule of the aromatic compound which leads to the formation of biphenyl derivatives.[12] The dimerization of radical cations is the result of π-electron interactions between the aromatic ring systems, which are oriented in a sandwich structure.[13] A solution of thallium(III) trifluoroacetate in trifluoroacetic acid constitutes a powerful reaction mixture for the direct thallation of aromatic compounds.[14] The reaction is generally complete within a few minutes at room temperature.

The prominent peak in the middle of the spectrum Fig. 1a has an intensity proportional to the amount of the thallium(III) trifluoroacetate and does not appear without thallium(III) trifluoroacetate and is thus generated by Tl(II). With CH_2Cl_2 as solvent and $SbCl_5$ as oxidant at 235 K Lewis and Singer[15] found that only some

of the pyrene dissolved and both the sharp peak due to solid and well-resolved EPR spectrum of the pyrene cation radical were observed. We have used a very low concentration of pyrene and the hydrocarbon was dissolved completely.

Because of the complexity of the EPR spectrum 1a we have tried repeatedly to record an ENDOR spectrum for the dimer cation radical, but without success. The ENDOR spectrum of the pyrene dimer cation radical was not detected because of the slight solubility of pyrene in trifluoroacetic acid at 263 K and the thallation of pyrene at higher temperature.

The first stage of the reaction of pyrene with trifluoroacetic acid is formation of the pyrene cation radical as outlined in Scheme 2.

$$ArH + 3CF_3COOH \rightarrow |ArH^{\cdot\,+} \cdots CF_3COO^-$$
$$(HOOCCF_3)_2| + H^+ \rightarrow \text{ further reactions}$$
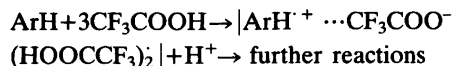
Scheme 2.

The electron-withdrawing groups that make trifluoroacetic acid a strong Brönsted acid also make it a good electron acceptor.[16] The existence of complexes containing two or more acid molecules has been demonstrated by IR spectroscopy.[17]

The fate of the radical cation formed via Scheme II is the formation of the dimer cation radical as in the case of pyrene. Alternatively the reaction pathway could involve direct attack by solvent molecule on the radical cation and formation of a substituted product. Dannenberg[18,19] has shown by MO calculations that for interactions of 1-methylethylium ion and benzenium ion with trifluoroacetic acid stabilization by the CF_3 group is the kinetically prefered process.

Oxidation of pyrene with silver tetrafluoroborate, with trifluoroacetic acid as solvent, leads to pyrene monomer cation radicals. The EPR spectrum is shown in Fig. 2a and a simulation based on the parameters given in Table 1 is shown in Fig. 2b. Silver(I) salts are commonly used for the oxidation of hydroquinones and aldehydes.[20] In the case of pyrene we suggest that the BF_4^- ion stabilizes the cation monomer radical. The π-electron interaction between aromatic ring systems is weak and the dimerization reaction does not take place.
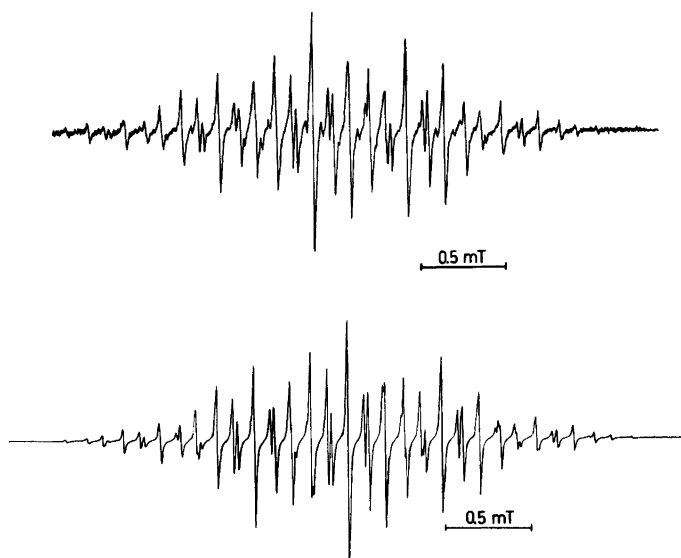
Fig. 2. (a) The EPR spectrum of pyrene monomer cation radical observed on oxidation of pyrene with AgBF$_4$ in trifluoroacetic acid at 256 K; (b) The simulated spectrum of the pyrene cation radical based on the parameters given in Table 1.

Howarth and Fraenkel[21] reported finding both the monomer and dimer cation radicals of pyrene but they did not report the *g* value of the pyrene monomer cation radical. We have measured a *g* value of 2.00259 for this radical and it is consistent with that of the anthracene cation radical in trifluoroacetic acid.[11]

Fig. 3 shows the ENDOR spectrum of the pyrene monomer cation radical produced by dissolving pyrene in trifluoromethanesulfonic acid: the optimum temperature for recording the ENDOR spectrum is 241 K. Trifluoromethanesulfonic acid has often been acclaimed as the strongest of all known monoprotic organic acids.[22] Trifluoromethanesulfonic acid has lower freezing point and viscocity than trifluoroacetic acid and is therefore a better solvent than trifluoroacetic acid for ENDOR measurements.

When 1,2,3,6,7,8-hexahydropyrene was oxidized with thallium(III) trifluoroacetate, with trifluoroacetic acid as solvent, the spectrum of 1,2,3,6,7,8-hexahydropyrene cation radical was recorded. With deuterotrifluoroacetic acid as solvent and thallium(III) trifluoroacetate as oxidizing agent a similar spectrum was obtained. Attempts to produce 1,2,3,6,7,8-hexahydropyrene cation radical by dissolving 1,2,3,6,7,8-hexahydropyrene in trifluoroacetic acid were

unsuccessful. Thus 1,2,3,6,7,8-hexahydropyrene cation radical does not form in trifluoroacetic acid in the absence of thallium(III) trifluoroacetate and use of deuterotrifluoroacetic acid instead of trifluoroacetic acid does not change the spectrum.

The mode of thallium(III) trifluoroacetate reactions with aromatic compounds is determined primarily by the oxidation potential of the substrate. Oxidation of 1,2,3,6,7,8-hexahydropyrene with thallium(III) trifluoroacetate in trifluoroacetic acid gives a cation radical without the inclusion of the substrate molecule in the coordination sphere of thallium (Scheme 3).
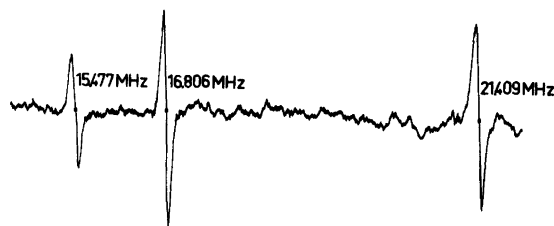

Fig. 3. The ENDOR spectrum of pyrene monomer cation radical produced by dissolving pyrene in trifluoromethanesulfonic acid. The spectrum was recorded at 241 K.
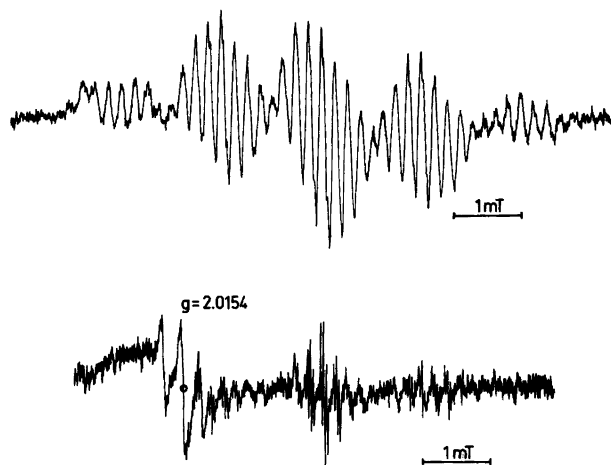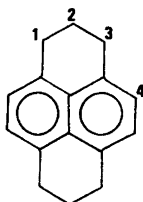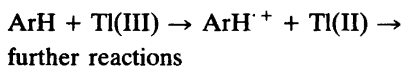
Fig. 4. (a) The experimental spectrum of 1,2,3,6,7,8-hexahydropyrene cation radical produced by dissolving 1,2,3,6,7,8-hexahydropyrene in FSO_3H. The spectrum was recorded at 190 K; (b) The spectrum of the same cation radical recorded at 229 K.

$ArH + Tl(III) \rightarrow ArH^{\cdot+} + Tl(II) \rightarrow$ further reactions

Scheme 3.

When 1,2,3,6,7,8-hexahydropyrene was dissolved in D_2SO_4 a spectrum of a cation radical was recorded and the coupling constants are shown in Table 2. In D_2SO_4 the ring protons of 1,2,3,6,7,8-hexahydropyrene have exchanged places with deuterons and the ratio 0.031/0.19 agrees with the theoretical value.

When 1,2,3,6,7,8-hexahydropyrene was dissolved in fluorosulfuric acid we got the spectrum shown in Fig. 4a. The same cation radical gave a weak ENDOR spectrum. As the temperature rose fluorosulfuric acid reacted with 1,2,3,6,7,8-hexahydropyrene and the spectrum shown in Fig. 4b with splitting 0.285 mT and the *g* value 2.0154 appeared. This *g* value is higher than that observed for aromatic cation radicals but similar to the *g* value of aromatic sulfinyl radicals.[23] The *g* value of the new radical suggests that it may be sulfur-centred.

Since H_2SO_4, D_2SO_4 or FSO_3H alone produce cation radicals from 1,2,3,6,7,8-hexahydropyrene

Table 2. The coupling constants of 1,2,3,6,7,8-hexahydropyrene cation radical.

Pos.	AgBF₄/TFA	D₂SO₄	SO₂ClF/FSO₃H	SO₂/BF₃[a]
1ax	1.470		1.474	1.460
1eq	0.365		0.360	0.378
2ax	0.039	0.037	0.042	0.040
2eq	0.039	0.037	0.042	0.040
4	0.031	0.190	0.192	0.190
g		—	2.00268	
T	313	254	168	178

[a] Ref. 26.

but trifluoroacetic acid does not, H_2SO_4 and FSO_3H must have a different mode of reaction. The first step in the reaction series is a fast protonation. Depending on temperature and the electron acceptor, sulfonation may occur simultaneously with oxidation as in the case of 1,2,3,6,7,8-hexahydropyrene (Fig. 4b). Lammertsma[24] has investigated the protonation reaction of 1,2,3,6,7,8-hexahydropyrene with FSO_3H at 193 K and concluded from NMR data that the stable protonated cation (position 4) is formed.

Reaction of 1,2,3,6,7,8-hexahydropyrene with silver tetrafluoroborate in perfluoropropionic acid yielded 1,2,3,6,7,8-hexahydropyrene cation radical and a spectrum similar to Fig. 4a was observed.

In Table 2 are shown the coupling constants of 1,2,3,6,7,8-hexahydropyrene cation radical produced by dissolving this compound in a mixture of fluorosulfuric acid and sulfuryl chloride fluoride.

The ENDOR spectrum can be scanned between 213 and 143 K using this solvent system,[25] which was the best ENDOR solvent system in the case of 1,2,3,6,7,8-hexahydropyrene.

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