An NMR, ESR, ENDOR and TRIPLE Resonance Investigation of a Cation Radical Formed From 1,2,4,5-Tetramethoxybenzene

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Several methods have been established for preparing cation radicals from 1,2,4,5-tetramethoxybenzene that allow highly resolved ESR spectra to be recorded. Precise values of the hyperfine coupling constants for the aromatic and methoxy protons have been obtained; the values are 0.2268 ± 0.0004 and 0.0863 ± 0.0002 mT, respectively, with dichloromethane as solvent. No temperature dependence is evident. TRIPLE resonance experiments showed that both coupling constants have the same sign. NMR experiments provided contact shift and line broadening measurements; these proved that both the above constants are positive and led to a value of 3.1 (±0.3) × 10^8 M^{-1} s^{-1} at 23 °C for the rate constant for electron exchange between the cation radical and the parent compound.

INTRODUCTION

As part of a larger study[1] of radical cations formed from tocopherol model compounds, namely, the chromans, we selected the even simpler compound 1,2,4,5-tetramethoxybenzene for a detailed preliminary investigation. The objectives were: (i) to evaluate methods of generating the radical cations, (ii) to measure magnitudes and signs of hyperfine coupling constants, and (iii) to measure the rate of electron exchange between the radical cation and the parent compound. To achieve these aims we employed the techniques of electron spin resonance spectroscopy, electron nuclear double resonance, and nuclear magnetic resonance spectroscopy.

There have been several publications[2–5] on the ESR spectrum of the tetramethoxybenzene cation radical, but none of these have been high resolution studies as reported here. The resolution depends upon the method of radical generation, because effects from ion-pairing[6] with counter ions have to be minimized; we have found several methods of obtaining radical solutions which give well resolved ESR spectra.

EXPERIMENTAL

Methods of generating radical cations

The simplest satisfactory method of producing the cation radical is to add tetramethoxybenzene to a 1:3 v/v mixture of trifluoroacetic acid or trifluoromethanesulphonic acid[7] in dichloromethane.

Since strong acids (in the presence of oxygen) are useful reagents for producing cation radicals, we wished to check whether the proton plays an important part in the reaction. Hence, the radicals were prepared by (i) oxidation with a stable cation radical[8] and (ii) electrolysis. In the former method of generating the radical the parent compound was oxidized with tris(p-bromophenyl)amminium perchlorate or with the antimony hexachloride salt in dichloromethane. The antimony hexachloride counter ion associates with the tetramethoxybenzene cation radical and causes broadening of the ESR lines; however, the addition of silver perchlorate leads to precipitation of silver hexachloroantimonate and the ESR spectrum of the resulting solution shows sharp lines. In the second method, electrolysis was carried out in benzonitrile. First, a cyclic voltammogram was obtained using a silver/silver(I) reference electrode, a platinum foil secondary electrode and a platinum button-type working electrode. Solutions were prepared containing approximately 10^{-3} M tetramethoxybenzene and approximately 10^{-1} M of the supporting electrolyte, tetrabutylammonium perchlorate: the solution was purged with purified nitrogen and a nitrogen atmosphere was maintained during the electrolysis. The cyclic voltammogram comprised a peak at +0.24 V for the oxidation process and one at +0.19 V for reduction of the cationic species: the curve is completely reversible and is typical of a single step oxidation process. In order to obtain a sufficient concentration of radical for ESR examination, the solution was electrolysed with stirring at +0.28 V for 3 h and a sample was transferred to an ESR tube. The radical prepared in this way did not decay for several days and the spectrum comprised sharp lines.

Materials

1,2,4,5-Tetramethoxybenzene was prepared as described by Bennington, Morin and Clark:[9] our sample was kindly provided by Dr F. M. Dean.

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Tris(*p*-bromophenyl)amine was prepared by the method described by Walter *et al.*[10] and then converted to the ammonium hexachloroantimonate by dropwise addition of antimony pentachloride in dichloromethane: we were also given a sample of the cation radical salt by Dr F. M. Dean and Mr I. I. Abu-Abdoun.

The perchlorate was prepared by the method of Bell, Ledwith and Sherrington.[8]

BDH trifluoroacetic acid and Aristar dichloromethane were used without further purification. Benzonitrile was washed with aqueous alkali, dried and distilled.

Equipment

Hydrogen NMR spectra were obtained with a Varian HA-60 spectrometer (operating at 56.44 MHz) modified[11] with a crystal-controlled sweep oscillator to provide a sweep having a linearity of ±0.02%, which is far more precise than that of the original instrument. ESR spectra were recorded with a Varian E-4 X-band spectrometer. First-derivative spectra were digitized into about 5000 points on paper tape, then the data were processed to give second-derivative presentation and peak positions were measured automatically. The ENDOR measurements were made with a Bruker ER 200D spectrometer equipped with an ER 251 computer-controlled ENDOR/TRIPLE resonance system and with a 12 in magnet. Cyclic voltammetry experiments were carried out with the aid of a Chemical Electronics TR70/2a potentiostat fitted with a linear sweep generator.

All samples prepared for ESR or ENDOR examination were degassed thoroughly with several freeze/pump/thaw cycles.

RESULTS AND DISCUSSION

Electron spin resonance spectra

A typical first-derivative ESR spectrum of the 1,2,4,5-tetramethoxybenzene cation radical is shown in Fig. 1; an expanded spectrum is presented in Fig. 2. The spectrum shown in Fig. 1 is simple and comprises 13 lines from 12 equivalent methoxy protons, split further into 1:2:1 triplets by the two aromatic protons: the hyperfine splitting constants are listed in Table 1. The g-factor for the radical was found to be 2.00402: it was measured by using a capillary containing an aqueous solution of dipotassium nitrodisulphonate (Fremy's salt) which was taken to have a g-factor of 2.00552.[12] Our value agrees well with that of 2.00396 found by Sullivan and Brette[4] for the cation radical dissolved in nitromethane.

There are no gross changes observed in the ESR spectrum with change of temperature; however, it may be seen from Table 1 that small changes in the magnitude of the hyperfine splitting constants of the methoxy protons appear to take place. The temperature coefficients are -3×10^{-5} and $+5\times10^{-5}$ mT K^{-1} for the methoxy and aromatic protons, respectively. These values are in fair agreement with those already reported.[4,13,14] Although the significance of these temperature dependences has been discussed[4,14] in detail, it will be seen in the next section that some doubt is cast upon their existence.

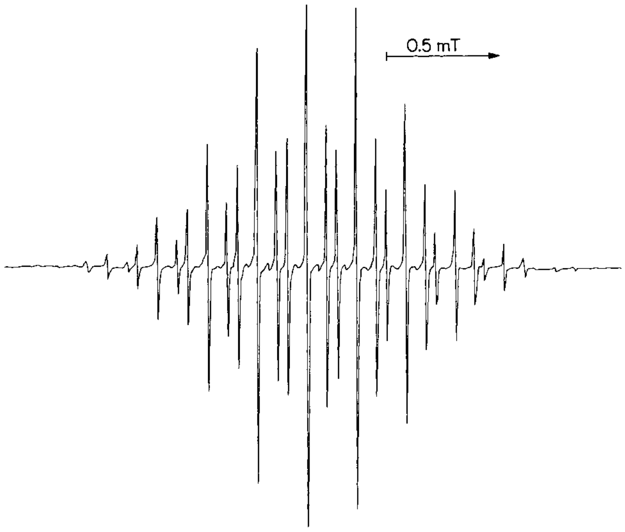

Figure 1. The first-derivative ESR spectrum of the 1,2,4,5-tetramethoxybenzene cation radical in dichloromethane containing trifluoroacetic acid at −13.8 °C.

Table 1 also shows that the hyperfine coupling constants have a small solvent dependence.

Vincow[15] has shown that a simple Hückel molecular orbital treatment can account for the magnitudes of the coupling constants for the cation radicals of both 1,2,4,5-tetramethoxybenzene and 1,2,4,5-tetramethylthiobenzene.

ENDOR and TRIPLE resonance

These experiments were undertaken in order to obtain greater precision in the hyperfine coupling constants

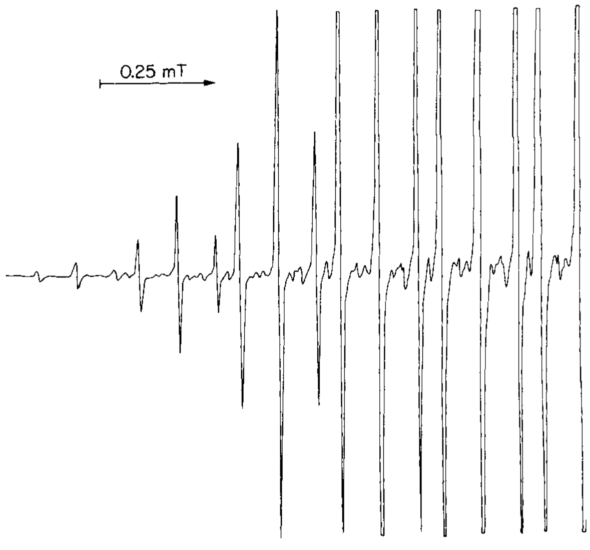

Figure 2. The low field half of the first-derivative ESR spectrum of the 1,2,4,5-tetramethoxybenzene cation radical in dichloromethane containing trifluoroacetic acid at −20 °C. The spectrum has been recorded at high gain in order to emphasize the low intensity bands.

Table 1. Hyperfine splitting constants obtained from the ESR spectrum of 1,2,4,5-tetramethoxybenzene cation radical

Solvent	Temperature (°C)	a^H_{OMe} (mT)	a^H_{Ar} (mT)
Dichloromethane	−66.0	0.225±0.002	0.0845±0.0007
	+19.8	0.2221±0.0009	0.0893±0.0008
Benzonitrile	+18.9	0.227±0.002	0.085±0.002
	+29.8	0.224±0.005	0.086±0.002
	+49.1	0.223±0.005	0.086±0.002
	+67.5	0.222±0.006	0.087±0.001

Table 2. Hyperfine splitting constants obtained from the ENDOR hydrogen spectrum of the 1,2,4,5-tetramethoxybenzene cation radical in dichloromethane

Temperature (°C)	a^H_{OMe} (mT)	a^H_{Ar} (mT)
−17	0.2268±0.0004	0.0863±0.0002
−33	0.2267±0.0007	0.086±0.001
−63	0.2268±0.0007	0.0855±0.004
−73	0.2268±0.0005	0.086±0.001

and to obtain their relative signs.[16] Figure 3 shows the ENDOR spectrum at −17 °C: similar spectra were obtained at different temperatures and the hyperfine coupling constants measured from them are given in Table 2. The precision obtained for these measurements is higher than has been achieved before for the radical under investigation, and there now appears to be no temperature dependence.

The TRIPLE resonance spectrum shows (Fig. 4) that the two coupling constants have the same sign.[16]

The ESR spectra shown in Figs. 1 and 2 contain some weak lines which cannot be accounted for by a simple spectral analysis, even when ^{13}C satellites are invoked. We attempted to assign these by means of the ENDOR technique. The data referred to so far were obtained by monitoring the centre line in the ESR spectrum. When the low intensity group of lines immediately to low fields of the centre line was monitored, an ENDOR spectrum was obtained which is completely different from that shown in Fig. 3: hydrogen hyperfine coupling constants of 0.310±0.001 and 0.1420±0.0007 mT were derived from this spectrum. These values correspond well with those reported[4] for the cation radical of 1,4-dihydroxy-2,5-di-*t*-butylbenzene, namely, 0.3062 and 0.1428 mT (although the parent compound is unlikely to be present as an impurity): there is also a small splitting of 0.0112 mT for this compound. However, a GLC/MS analysis of our sample did not reveal any impurities.

Study of the effect of the 1,2,4,5-tetramethoxybenzene radical cation on the NMR spectrum of 1,2,4,5-tetramethoxybenzene

The object of this part of our investigation was to obtain the absolute sign of the hyperfine coupling constants of the radical cation, and to determine the rate of electron exchange between the latter and the parent compound.

The 56.44 MHz ^1H NMR spectrum of tetramethoxybenzene is very simple and comprises two sharp lines of intensity ratio 1:6, having chemical shifts in deuterochloroform of 372.47 and 215.05 Hz, respectively, from TMS. In order to determine the sign of the coupling constants, the contact shifts were measured after addition of trifluoroacetic acid to generate the cation radical. A 1.6×10^{-1} M solution of tetramethoxybenzene was prepared in deuterochloroform containing TMS. A series of chemical shift measurements were made as trifluoroacetic acid was added successively in 0.5 μl increments to 0.3 ml of solution. When a total of 5 μl of acid had been added, corresponding to a concentration of 2.14×10^{-1} M acid, the spectral lines became too broad for reliable values of the contact shift to be measured. Measurement of the extent of line broadening allows the rate of electron exchange to be calculated, hence line widths were measured relative to dichloromethane. A small amount of the latter was present in the solution used:

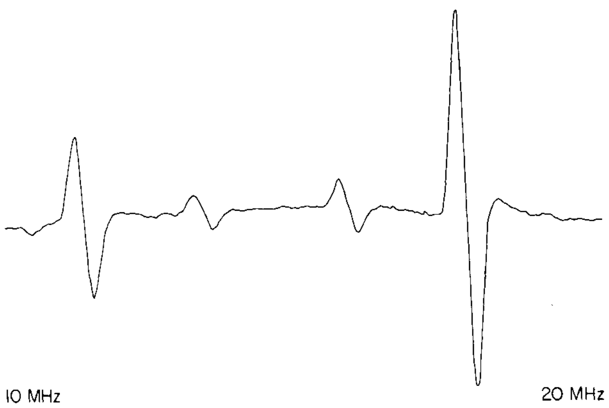

Figure 3. The hydrogen ENDOR spectrum of the 1,2,4,5-tetramethoxybenzene cation radical in dichloromethane containing trifluoroacetic acid at −17 °C. The spectrum runs from 10 to 20 MHz and is a composite of eight scans. The intense centre line of Fig. 1 was monitored.

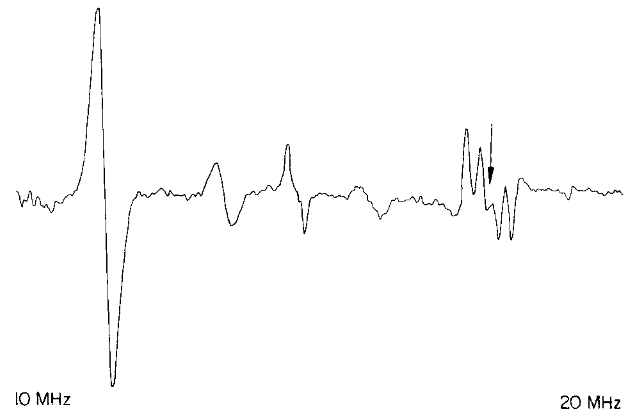

Figure 4. The hydrogen TRIPLE resonance spectrum of the 1,2,4,5-tetramethoxybenzene cation radical. Experimental conditions are as for Fig. 3. The pumped transition is marked with a vertical arrow: a pump frequency of 17.773 MHz was used. The centre line is an artefact.

Table 3. Contact shifts and line widths from NMR measurements at 23 °C

[CF$_3$COOH] (M)	Ring proton resonance (Hz) Downfield shifts from TMS	Contact shift	Line width[a] $\Delta\nu$	Methoxy proton resonance (Hz) Downfield shifts from TMS	Contact shift	Line width[a] $\Delta\nu$
0.0	372.47	0.00	0.00	215.05	0.00	0.00
2.173×10^{-2}	372.60	0.13 ± 0.02	0.54 ± 0.3	215.35	0.30 ± 0.02	4.07 ± 0.3
4.337×10^{-2}	372.74	0.27 ± 0.02	1.97 ± 0.3	215.70	0.65 ± 0.02	9.49 ± 0.4
6.496×10^{-2}	372.88	0.41 ± 0.02	3.59 ± 0.4	216.03	0.98 ± 0.02	17.2 ± 0.3
8.648×10^{-2}	373.02	0.55 ± 0.02	4.38 ± 0.6	216.35	1.30 ± 0.02	20.0 ± 0.8
10.78×10^{-2}	373.15	0.68 ± 0.02	5.43 ± 0.4	216.65	1.60 ± 0.02	23.5 ± 1.5
12.93×10^{-2}	373.25	0.78 ± 0.02	6.33 ± 0.6	216.95	1.90 ± 0.02	24.1 ± 2.2
15.06×10^{-2}	373.37	0.90 ± 0.02	6.87 ± 0.6	217.30	2.25 ± 0.02	23.3 ± 2.0
17.18×10^{-2}	373.47	1.00 ± 0.02	7.44 ± 0.6	217.60	2.55 ± 0.02	24.1 ± 4.0
19.30×10^{-2}	373.67	1.20 ± 0.2	10.7 ± 1.5	217.98	2.93 ± 0.1	31.1 ± 7.0
23.51×10^{-2}	373.76	1.29 ± 0.2	12.6 ± 4	218.83	3.78 ± 0.2	—

[a] This is the difference between the width of the tetramethoxybenzene line and that of the dichloromethane reference.

line width measurements required a reference line close to the aromatic and methoxy proton signals because expanded spectral sweeps were necessary in order to obtain good precision. At the higher trifluoroacetic concentrations additional peaks appeared close to the methoxy proton peak in the NMR spectra; these have been attributed to the formation of decomposition products of tetramethoxybenzene. Table 3 lists the data obtained from the contact shift and line width measurements. We have shown that the cation radical concentration is directly proportional to the concentration of trifluoroacetic acid: also, it can be seen from Table 3 that the contact shift is directly proportional to the acid concentration. Since both the ring proton and the methoxy proton signals move to low fields with increasing radical concentration it can be concluded that the signs of both the hyperfine coupling constants are positive from the expression[17]

$$\text{contact shift} = a^{\mathrm{H}} f_{\mathrm{p}} \frac{g_{\mathrm{e}}\beta_{\mathrm{e}}B}{4kT}$$

where f_p is the fraction of tetramethoxybenzene which is present as the cation radical. It is interesting to note that Sullivan and Brette,[4] from temperature dependence measurements, concluded that the aromatic proton hyperfine coupling constant is positive.

In calculating the rate of electron exchange between the cation radical and its parent, from the line width data of Table 3, we have followed the treatment of de Boer and Maclean.[17] They considered a variety of exchange rates, but we can identify the process occurring in this study as being of de Boer and Maclean's classification 'fast exchange of type 2'. We have reached this conclusion because: (a) the line broadening is proportional to the acid concentration; (b) the lines from the two types of proton are not broadened identically.

For these conditions the line width, $\Delta\nu$, is given by

$$\Delta\nu = f_{\mathrm{p}}\tau_{\mathrm{p}}(a^{\mathrm{H}})^2/4$$

where τ_p is the life time of the radical. In our experiments it was not possible to measure the very low radical concentrations (less than 10^{-6} M), hence, f_p was calculated from the contact shifts given in Table 3: these values are presented in Table 4 along with the values of τ_p calculated from the line width data. The rate of electron exchange, k_{ex}, can be calculated from

$$k_{\mathrm{ex}} = 1/\tau_{\mathrm{p}}[D]$$

where $[D]$ is the concentration of tetramethoxybenzene. The values obtained are given in Table 4. Both sets of τ_p and k_{ex} values for the aromatic and the methoxy protons are in reasonable agreement. However, the data for the methoxy protons are less reliable because their NMR lines were overlain with signals

Table 4. Electron exchange rate constants measured at 23 °C

$f_p\times10^5$	Ring proton analysis τ_p(s)	k_{ex}(M^{-1} s^{-1})	$f_p\times10^5$	Methoxy proton analysis τ_p(s)	k_{ex}(M^{-1} s^{-1})
7.3	1.81×10^{-8}	3.34×10^{8}	6.9	1.40×10^{-8}	4.35×10^{8}
11.0	2.17×10^{-8}	2.80×10^{8}	10.4	1.69×10^{-8}	3.62×10^{8}
14.8	1.96×10^{-8}	3.09×10^{8}	13.8	1.46×10^{-8}	4.12×10^{8}
18.3	1.97×10^{-8}	3.08×10^{8}	16.9	1.40×10^{-8}	4.33×10^{8}
21.0	2.01×10^{-8}	3.03×10^{8}	20.1	1.21×10^{-8}	5.00×10^{8}
24.3	1.89×10^{-8}	3.22×10^{8}	23.8	0.99×10^{-8}	6.13×10^{8}
26.9	1.85×10^{-8}	3.30×10^{8}	27.0	0.89×10^{-8}	6.76×10^{8}
32.3	2.20×10^{-8}	2.74×10^{8}	31.0	1.02×10^{-8}	6.00×10^{8}
Mean values	$1.9(\pm0.2)\times10^{-8}$ s	$3.1(\pm0.3)\times10^{8}$ M^{-1} s^{-1}	Mean values	$1.3(\pm0.4)\times10^{-8}$ s	$5.0(\pm1.0)\times10^{8}$ M^{-1} s^{-1}

from decomposition products. The value of k_{ex} ($3.0 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}$) is typical of the rate constants encountered for the exchange of an electron between a radical and its substrate.[18]

We are extending the work reported here to obtain the energetics for k_{ex} for tetramethoxybenzene and to carry out a similar set of measurements on the chromans.

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