ESR of Cation Radicals of Methyl-substituted Benzenes in a CF_3CCl_3 Matrix

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A new matrix, 1,1,1-trifluorotrichloroethane, CF_3CCl_3, has been employed in radiation chemistry studies to stabilise positive ions. As a test, positive ions of benzene, toluene, orto-, meta- and paraxylene and biphenyl have been generated by γ-irradiation of the solutes contained in the CF_3CCl_3 matrix at 77 K. The ions have been investigated by ESR, and hyperfine couplings have been obtained. The data complement and correct the splitting values obtained previously in the adsorbed state.

Introduction

Some time ago we showed that cations of 1,3-butadiene could be stabilised in a CCl_4 matrix after γ-irradiation [1], but is is not until recently that other halogenated compounds capable of stabilising hydrocarbon and other organic radical cations have been found. Among the matrices, Freons like $CFCl_3$, and related compounds have found wide usage [2]. In a search for a matrix suitable for studying the structure and the degradation of cations of cyclo- and normal alkanes by means of ESR spectroscopy we found that 1,1,1-trifluorotrichloroethane had several advantages. Thus, radical cations are stably trapped up to a phase transition temperature of 142 K, permitting observation of ESR cation spectra over a wide temperature range. The spectral resolution is comparable to or even better than that afforded by other matrices. Another advantage is the suitability of the matrix for optical bleaching experiments. The matrix has recently been employed in connection with optical studies [3], but as far as we know the application to ESR is new. In this context it is important to know under what conditions molecular cations become stabilised and to what extent the ESR spectra of these cations are affected by the matrix. In order to elucidate these questions we have studied several aromatic compounds for which cations had either been prepared previously or whose ESR spectra could easily and confidently be predicted from simple molecular orbital theory.

Experimental

CF_3CCl_3 of 98% purity was purchased from Aldrich. The following additives of purum grade (AB Kebo, Sweden) were used: benzene, toluene, ***o***-, ***p***- and ***m***-xylene, naphthalene, anthracene, phenanthrene and biphenyl. Frozen solutions containing 0.3 mol% of solute were prepared in Suprasil ESR tubes and degassed on a vacuum line. The samples were irradiated at 77 K using a $^{60}Co\ \gamma$ source for 2–3 h to a total dose of $\leqq 0.5$ Mrad. The ESR measurements were made with a Varian E-9 spectrometer equipped with a variable temperature control unit at temperatures between 77–142 K. Photobleaching was made with a Varian Xe lamp using colored glass filters from Oriel.

Results

The pure CF_3CCl_3 matrix, when irradiated and measured at 77 K, gave rise to a broad ESR spectrum of low amplitude. The amplitude remained low up to $T = 142$ K, at which temperature an irreversible spectral change occurred. A very intense spectrum appeared. The spectrum shown in Fig. 1 a may be interpreted as arising from the radical $CF_3\dot{C}Cl_2$ having $g = 2.0085$, $a_F = 17.9$ G (3 F) and $a_{Cl} = 4.1$ G (2 Cl) as is evident by the simulation in Figure 1 b. At $T \geqq 142$ K the matrix also loses its ability to trap solute cations. The negative charge which might be trapped as the anion $[CF_3CCl_3]^-$ is probably released as Cl^-, and a neutralization process between Cl^- and the cation can take place. In general one expects the following sequence of reactions to occur [2]

$$2\,MCl \overset{\gamma}{\rightsquigarrow} [MCl]^+ + [MCl]^- , \qquad (1)$$

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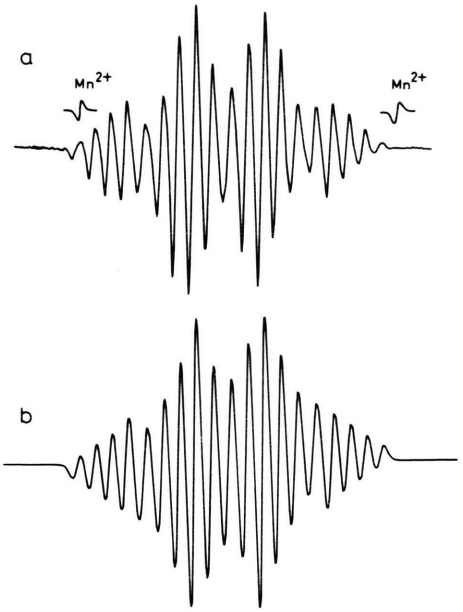


Fig. 1. a) First derivative ESR spectrum of CF_3CCl_3 after irradiating with γ-rays at 77 K and subsequent warming to 170 K. b) Simulation of a) with $a_F = 17.9$ G, $a_{Cl} = 4.1$ G for the species $CF_3\dot{C}Cl_2$.

$$[MCl]^+ + S \rightarrow MCl + S^+ , \tag{2}$$

$$[MCl]^- \xrightarrow{\Delta H} \dot{M} + Cl^- , \tag{3}$$

$$S^+ + Cl^- \rightarrow \text{products} . \tag{4}$$

$[MCl]^+$ is mobile even at 77 K so that solute cations S^+ are formed by charge transfer. $[MCl]^-$ is immobile at 77 K so that recombination cannot occur. At higher temperature (142 K) $[MCl]^-$ decomposes and a neutralization (4) can occur.

Table 1. ESR parameters for substituted benzene cations in CF_3CCl_3 at 140 K. $\Delta B_{1/2}$ is the full width at half height of a Gaussian line. Calculated values are obtained from $a = Q\,\varrho$, $Q_{CH_3} = 52.2$, $Q_H = 2.74$.

Compound	a_{CH_3}(G)		a_H(G)		$\Delta B_{1/2}$
	exp.	calc.	exp.	calc.	
benzene	–	–	4.4 (1–6)	4.6	1.85
toluene	20.0	18.6	12.5 (4)	10.5	5.0
o-xylene	13.2	15.3	5.5 (3,4)	6.4	3.75
m-xylene	12.0	11.5	8.5 (2,4)	8.7	3.75
p-xylene	18.3	18.0	3.0 (2,3,5,6)	1.5	2.1

Substituted benzenes

Irradiation of samples containing benzene, toluene, ortho-, meta- and para-xylene all gave ESR spectra centred at $g = 2.0033 \pm 0.0003$. The ESR parameters are collected in Table 1. The spectra can be assigned to the molecular cations in all cases on the basis of previous data and on the predictions by simple molecular orbital theory as discussed below.

The hyperfine coupling of the benzene cation, which has been previously observed in the adsorbed state [4], and in a frozen sulfuric acid solution [5] with a hyperfine splitting of $a = 4.4$ G, agrees with the coupling observed here. The reported hyperfine couplings of the toluene cation [6] $a_{CH_3} = 18$ G, $a_4 = 11.8$ G are also in reasonable accord with the values obtained here. The linewidth of this ion is larger than for the other substituted benzene cations. This might be due to an unresolved hyperfine structure anisotropy as discussed below. The coupling constants obtained here were obtained by adjusting the parameters until the experimental and simulated spectra agreed as closely as possible. The agreement obtained is illustrated by the spectra shown in Figure 2.

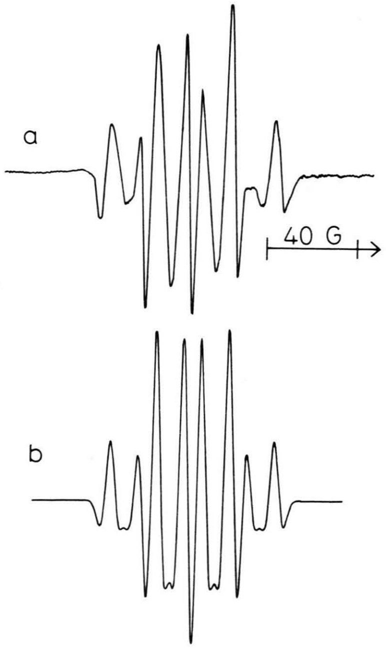


Fig. 2. Second derivative ESR spectra of the toluene cation in CF_3CCl_3 at 140 K. a) Experimental spectrum; b) Simulated spectrum with $a_{CH_3} = 20.0$ G, $a_4 = 12.5$ G and $\Delta B_{1/2} = 5.0$ G (linewidth of Gaussian profile at half height).

The cation radical spectra of the xylenes obtained previously on silica gel [7], are quite similar to those obtained here, but the hyperfine couplings differ somewhat. Thus, the reported values of the methyl group splittings of $a = 14.5$ G (p-xylene$^+$) and $a = 11.0$ G (m- and o-xylene$^+$) are smaller than those obtained here. The differences are probably caused by difficulties in the assignment of coupling constants and not by a real difference in splitting values. It is known that anisotropic interactions often result in a complicated line shape in the adsorbed state, and a careful analysis is required [4]. We believe that the couplings obtained here are more accurate than the values obtained previously, because of less disturbance due to anisotropies. However, some complications which might be attributed to hyperfine coupling anisotropy are noted in the ESR spectra of the o-xylene and p-xylene cations. In the former case (Fig. 3a and b) a simulation gives the correct line positions, but wrong intensities. In the latter case a simulation with isotropic couplings does not reproduce the spectrum (Fig. 4) very well.

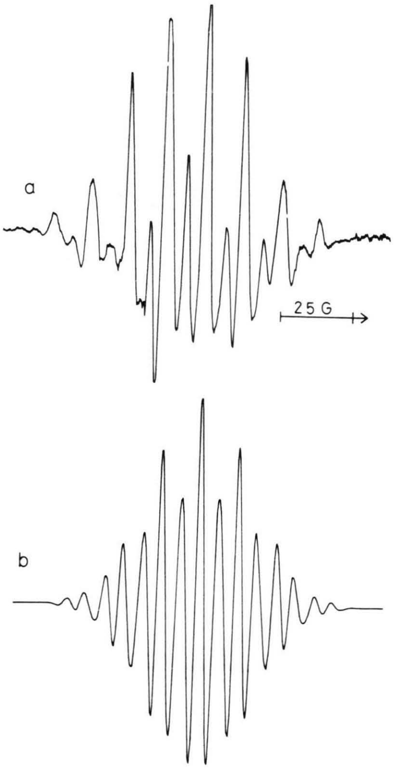


Fig. 3. Second derivative ESR spectra of the o-xylene cation in CF_3CCl_3 at 140 K. a) Experimental spectrum; b) Simulated spectrum with $a_{CH_3} = 13.2$ G, $a_3 = a_4 = 5.5$ G, and $\Delta B_{1/2} = 3.75$ G.

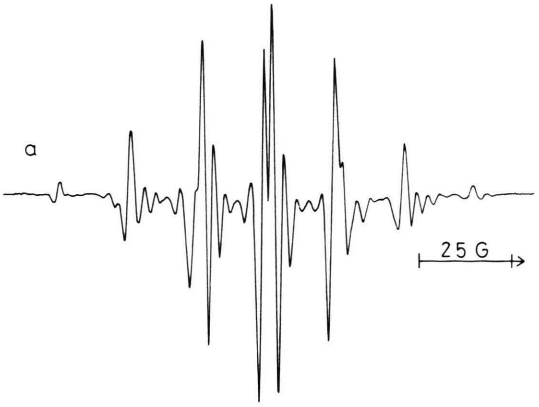


Fig. 4. Second derivative ESR spectrum of the p-xylene cation in CF_3CCl_3 at 140 K.

Molecular orbital calculations

The spin densities obtained from simple Hückel theory, and from the modified theory of McLachlan [8] given in Table 2 correlate fairly well with the experimental coupling constants. Best agreement between experimental splittings and calculated π-electron spin densities was obtained by choosing $Q_H = 27.4$ G and $Q_{CH_3} = 52.2$ G in the relation $a = Q \cdot \varrho$, where ϱ is the spin density calculated by McLachlans method on the carbon atom adjacent to the H atom or the CH_3 group. The calculated and experimental splittings are compared in Table 1. A less satisfactory correlation is obtained with Hückel spin densities and $Q_H = 35.7$ G and $Q_{CH_3} = 44$ G used previously [6, 9]. It is clear, however, that the observed couplings can be rationalized in terms of simple molecular orbital theory for the proposed cations, thus supporting the assignments.

Other aromatic compounds

Irradiation of samples containing naphthalene, anthracene, phenanthrene and biphenyl all gave spectra containing an odd number of lines, of which 5 could be resolved. The data are summarized in Table 3.

The hyperfine coupling data of the cations of naphthalene, anthracene and phenantrene are known from the solution. According to the comparison

Table 2. π-electron spin densities in substituted benzene radical cations calculated by the Hückel (HMO) and McLachlan (McL) methods with hyperconjugation. 7 and 9 stand for the C atom spin density and 8 and 10 for the H_3 group orbital spin density in the CH_3 group.

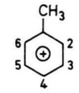
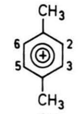
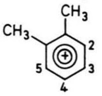
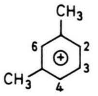
		π-electron spin density at position									
		1	2	3	4	5	6	7	8	9	10
	HMO	0.303	0.103	0.065	0.308	0.065	0.103	0.013	0.0402		
	McL	0.357	0.084	0.020	0.383	0.020	0.084	0.007	0.0446		
	HMO	0.287	0.084	0.084	0.287	0.084	0.084	0.010	0.0355	0.010	0.0355
	McL	0.345	0.055	0.055	0.345	0.055	0.055	0.004	0.0399	0.004	0.0399
	HMO	0.251	0.033	0.204	0.204	0.003	0.251	0.010	0.0319	0.010	0.0319
	McL	0.293	− 0.063	0.231	0.231	− 0.063	0.293	0.005	0.0353	0.005	0.0353
	HMO	0.205	0.260	0.000	0.260	0.205	0.000	0.008	0.0264	0.008	0.0264
	McL	0.220	0.317	− 0.079	0.317	0.220	− 0.059	0.004	0.0279	0.004	0.0279

Table 3. ESR parameters for species observed from irradiated aromatic compounds in CF_3CCl_3 at 140 K, compared with literature data for the molecular cations. n denotes the number of H atoms, a their hyperfine coupling and $\Delta B_{1/2}$ the line width.

Compound	Cation data			Literature data		
	n	a(G)	$\Delta B_{1/2}$(G)	a_1 (G)	a_2(G)	a_3(G)
biphenyl	4	3.43	2.5			
naphthalene	4	7.6	4.0	5.54 (4 H)	2.06 (4 H)	
anthracene	4	6.25	4.0	6.53 (2 H)	3.08 (4 H)	1.38 (4 H)
phenantrene	4	5.2	4.5	4.43 (2 H)	3.71 (2 H)	2.88 (2 H)

Table 4. Dipolar proton hyperfine couplings B_1, B_2 and B_3 and direction cosines calculated from π-electron spin densities in Table 2. a) One of 6 equivalent H's. x is perpendicular to the ring plane and z is along the C-H and the C-CH_3 bonds, respectively.

Ion	H atom	a (G)	B_i (G)	Direction cosines with respect to		
				x	y	z
benzene$^+$	1[a]	−4.4	$B_1 = -2.85$	0	1	0
			$B_2 = -0.75$	1	0	0
			$B_3 = 3.6$	0	0	1
toluene$^+$	4	−12.5	$B_1 = -6.0$	0	1	0
			$B_2 = 0.1$	1	0	0
			$B_3 = 5.9$	0	0	1

made in Table 3 none of the species observed in the CF_3CCl_3 matrix is due to the molecular cation. It may be noted that unusually high solute concentrations (0.5 mol%) had to be used to obtain the spectra. Aromatic cations easily form singly charged dimers [10], but the observed spectra cannot be assigned to this type of species. At present we cannot offer a suitable explanation of the spectra from samples containing naphthalene, anthracene of phenanthrene.

The spectrum of a sample containing biphenyl has an odd number of lines split by 3.35 G, Figure 5. The ESR spectrum of the biphenyl cation has not been reported in the liquid state. The 4,4-dimethylbiphenyl ion has $a_{CH_3} = 8.80$ G, and $a_2 = 2.65$ G [11]. An ESR spectrum of the biphenyl cation in the adsorbed state [12] has been analyzed to have $a_4 = 6.5$ G (2H) and $a_2 = 2.8$ G (4H). On the basis of these data we assign the spectrum in Fig. 5 to the biphenyl cation having coupling constants of $a_4 = 6.7$ G, $a_2 = 3.35$ G.

Line shapes

The line widths vary depending on the solute, see Table I. It is reasonable to ascribe these effects to unresolved hyperfine structure and to anisotropic interactions. The g anisotropy has been measured previously in the case of the benzene cation and was found to be small [4]. The anisotropic hyperfine interaction is, however, significant for a rigid aromatic ion [13]. We have calculated the dipolar couplings for the substituted benzene cations, and some results are summarized in Table IV. In these calculations the dipolar contribution from the π-electron spin density at each carbon atom is taken into account and the contributions are added together to a resulting coupling tensor [6]. As can be seen from Table 4 the dipolar coupling tensor of H_4 is large in the toluene cation which also has an ESR spectrum with large linewidth. In general the anisotropic couplings are not clearly resolved in the ESR spectra in the CF_3CCl_3 matrix in contrast to the situation in the adsorbed state [4]. One possible exception is the spectrum of the p-xylene cation at 140 K which cannot be well reproduced using isotropic couplings. The spectrum is characteristic of the ion and not influenced by matrix effects since a similar spectrum was obtained on silica gel [7]. No interpretation in terms of anisotropic couplings is possible by simple inspection, and simulations of powder line shapes are probably the only means to analyze this spectrum. Such simulations are very time consuming, however [4, 13], and have not been attempted.

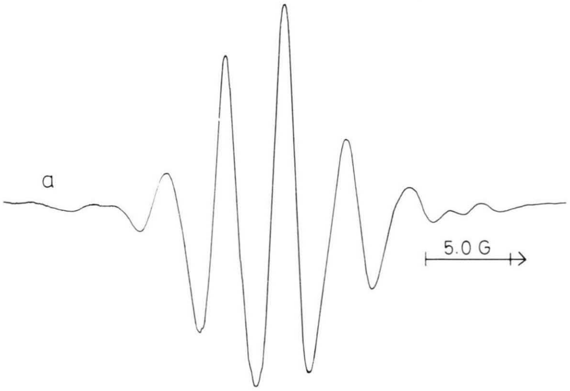


Fig. 5. Second derivative ESR spectrum of the species assigned to the biphenyl cation in CF_3CCl_3 at 140 K.

Discussion

Molecular cations of substituted benzene can be stabilized in the CF_3CCl_3 matrix. The hyperfine couplings correlate well with calculated spin densities, indicating that the spectra of the cations observed are not strongly affected by the matrix. The linewidth varies, however, depending on the solute, and the width can be correlated with the calculated anisotropy of the hyperfine coupling. This shows that the anisotropy is not averaged out by molecular tumbling in the CF_3CCl_3 matrix and has to be taken into account in a rigorous analysis of the ESR spectra. Molecular cations of condensed aromatics cannot be stabilized in the CF_3CCl_3 matrix. The ionization potentials of condensed aromatics are lower than the ionization potential of benzene. This shows that factors other than the ionization potential are essential for cations to become stabilised, but the nature of these factors could not be elucidated. It is clear, however, that one cannot always assume that observed ESR spectra can be assigned to the radical cations of the solute.

The ESR parameters of the substituted benzene cations are probably the most accurate obtained hitherto. As a by-product the ESR parameters of the radical species $CF_3\dot{C}Cl_2$ formed by the decomposition of the CF_3CCl_3 matrix have been obtained.

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