The Electron Spin Resonance Spectra of the Radical Cations of Furans, Thiophenes, and Pyrroles in Liquid Solution

Alwyn G. Davies,* Luis Julia, and Safieh N. Yazdi
Chemistry Department, University College, London, 20 Gordon Street, London WC1H 0AJ, U.K.

The radical cations of various furans, thiophenes, and pyrroles have been generated in fluid solution and characterised by e.s.r. spectroscopy.

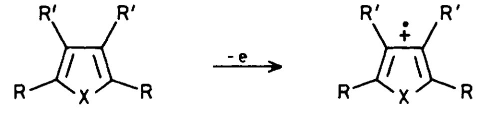
Our understanding of the chemistry of the radical cations of simple hydrocarbon π-systems is developing rapidly as a result of the application of new methods for generating these species under conditions where they can be studied in fluid solution by e.s.r. spectroscopy.[1] In particular, in the context of the present paper, we have shown that the radical cations (I$^{\cdot+}$) of various alkylcyclopentadienes can be identified when the parent hydrocarbons (I; X = CR''_2) are photolysed in trifluoroacetic acid solution.[2,3]

There is a lot of current interest in the radical cations of the corresponding heterocyclic systems (I$^{\cdot+}$; X = O, S, or NR'') because of their potential importance in electronic devices and as intermediates in heteroaromatic substitution reactions and in organic synthetic procedures. However, the e.s.r. spectra of these species have been observed previously only from the γ-radiolysis of solutions in frozen Freon matrices.[4,5] We report here the first observation of the high resolution e.s.r. spectra of these heterocyclopentadiene radical cations (I$^{\cdot+}$; X = O, S, or NR''_2) in liquid solution.

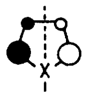
The reaction conditions and spectral parameters for representative examples are shown in Table 1, and a typical spectrum (that for tetramethylfuran) is shown in Figure 1.

The assignment of these spectra to the species (I$^{\cdot+}$) is confirmed by the fact that similar spectral parameters are observed when some of the precursors are subjected to the γ-radiolytic procedure,[4,5] which is known to be specific for the formation of the corresponding radical cations.[6,7]

In no case did we find evidence for the reaction of (I$^{\cdot+}$) with its precursor (I) to give the dimer radical cations (I$_2^{\cdot+}$) of either the type known for arenes (*e.g.* Me$_6$C$_6$),[8]† or for dialkyl



(I) (I$^{\cdot+}$)



(II)

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† Shiotani *et al.*[7] have reported the formation of the dimer radical cation of furan in a Freon matrix.

Table 1. E.s.r. spectra of furan, thiophene, pyrrole, and cyclopentadiene radical cations ($I^{\cdot +}$).

X	R	R′	Reagent[a]	T/K	a(R)/G[b]	a(R′)/G[b]	g
O	Me	H	A	262	16.6(6H)	3.6(2H)	2.0023[c]
O	Me	Me	B	261	16.2(6H)	3.8(6H)	2.0021
S	Me	H	C	291	17.0(6H)	3.1(2H)[d]	2.0023
S	Me	Me	A	263	16.0(6H)	3.3(6H)	2.0028
			C	291	16.0(6H)	3.3(6H)	2.0028
NH	Me	H	A	265	16.0(6H)	3.6(2H)[e]	2.0026[f]
NPr	Et	H	A	260	16.8(4H)	3.4(2H)[g]	2.0025
CH_2	Me	Me	B	263	15.2(6H)	4.0(6H)[h]	2.0026

[a] A: Photolysis in CF_3CO_2H containing $Hg(O_2CCF_3)_2$; B: photolysis in CF_3CO_2H; C: photolysis in conc. H_2SO_4. [b] 1 G = 10^{-4} T. [c] Ref. 5 reports a(6H) 16.9, a(2H) 4.3 G, g 2.003 at 100 K in cyclo-$C_6F_{11}CF_3$. [d] Ref. 4 reports a(6H) 18.1, a(2H) 3.5 G in $CFCl_3$. [e] a(N) 4.0, a(1H) 1.0 G. [f] Ref. 4 reports a(6H) 17.5, a(2H) 3.5, a(N) *ca.* 3 G, at 77 K in $CFCl_3$. [g] a(N) 4.3, $a(CH_2)$ 0.96 G. [h] a(2H) 1.4 G.

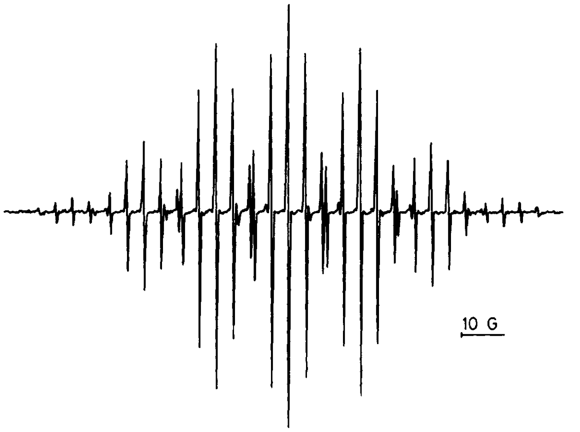

Figure 1. E.s.r. spectrum of the radical cation of tetramethylfuran (I, X = O, R = R′ = Me) in trifluoroacetic acid at 262 K.

sulphides (*e.g.* tetrahydrothiophene).[9] However, if the reaction conditions were varied from those specified in Table 1 different spectra could be observed. For example photolysis of 2,5-dimethylthiophene (I; X = S, R = Me, R′ = H) in trifluoroacetic acid showed a strong spectrum consisting of a septet of septets [a(6H) 4.80 and a(6H) 2.15 G], suggesting the formation of an unsymmetrical dimer, although the principal species that can be isolated from solution under these conditions is a trimer. These alternative reactions are being further investigated.

The similarity between the e.s.r. spectra of all these radical cations ($I^{\cdot +}$; X = O, S, NR″, or CR''_2) confirms, as Symons[4] and Shiotani[5] have pointed out, that the unpaired electron is in a molecular orbital ($^1a_2$) similar to that in the cyclopentadiene radical cations, with a node passing through the heteroatom as shown in (II).

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