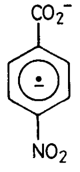
Production of Electron Spin Polarized Radical Anions in Solution

Keith A. McLauchlan and Andrew J. D. Ritchie

Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, U.K.

Emissively-polarized radical anions result on the photolysis of substituted benzenes in the presence of amines.

Photolysis of a wide range of substituted benzenes in the presence of aliphatic amines in a variety of solvents yields the corresponding radical anions. These have been observed directly as transient species using the time-integration spectroscopy (T.I.S.) technique of flash-photolysis e.s.r.,[1,2] with photolysis by excimer laser radiation at 308 nm. All the radicals exhibit chemically dynamic polarization (C.I.D.E.P.) due to the triplet mechanism (T.M.),[3] showing that they originate in the reactions of the triplet states of their precursors. This suggests that they are primary species formed by electron transfer from the amines; hydrogen transfer, followed by acid–base equilibration, is too slow to yield



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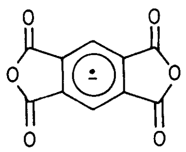

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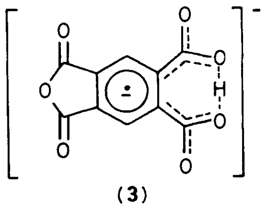

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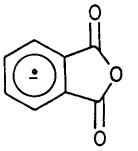

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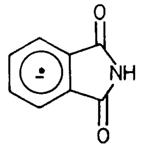

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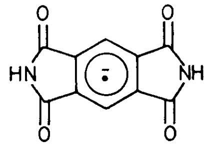

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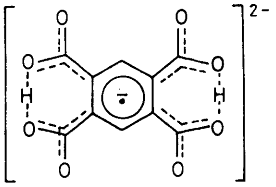

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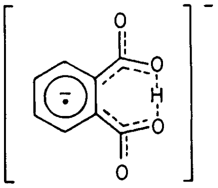

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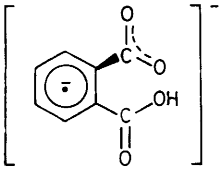

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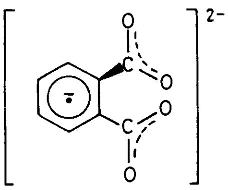

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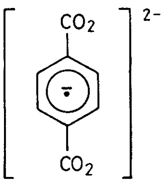

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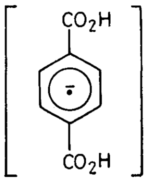

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effective T.M. polarization. The reaction may be represented as shown in equation (1) where the asterisk denotes an electron spin polarized molecule. The polarization in the triplet originates in spin-selective intersystem crossing from the excited singlet state of the precursor and is carried to the radicals by sufficiently-fast reaction; its occurrence enhances the e.s.r. signals above the levels exhibited by thermally-equilibrated radicals at similar concentrations. Some of the amines produced are recorded, together with their hyperfine coupling constants, in Table 1.

$$ {}^3\mathrm{M}^* + \text{amine} \rightarrow \mathrm{M}^{\cdot-*} + \text{amine}^{\cdot+*} \qquad (1) $$

In the solutions used (typically 1 : 3, triethylamine : methyl cyanide) the amine cations undergo rapid proton loss to form α-aminoalkyl radicals. Such neutral radicals have proved difficult to detect in e.s.r. studies since they normally undergo fast hydrogen-abstraction reactions to form enamines. However their lifetime may be enhanced by using a substrate more susceptible to charge-transfer from its excited state than it is to direct hydrogen abstraction from the ground state. This occurs with several of the carboxylic acids in Table 1 and we have reported the spectra of several α-aminoalkyl radicals recently.[4]

Figure 1 shows the spectrum of a typical species studied, the dianion of 4-nitrobenzoic acid formed by photolysis of the diamagnetic mono-anion, with the theoretical T.I.S. spectrum shown as an inset. The measured coupling constants agree well with the literature values.[5] The highest-field multiplet exhibits the line-broadening familiar in radicals with unpaired spin density on nitrogen atoms. The spin–spin relaxation time values used in the simulation were 0.2 μs for the low-field and centre lines, and 0.15 μs for the high-field ones. These values differ considerably in both absolute and relative sizes from those reported previously in other solutions.[5] A further example, that of the radical anion from benzene-1,2,4,5-diimide, is shown in Figure 2. Both of these spectra are displayed without field modulation and are in emission, as were all the spectra observed. This shows that in all of the substituted benzenes studied the reaction involved an over-populated upper Zeeman level of the reactive triplet state.

The use of a fast-observation technique disclosed a more complex chemistry for the radical anions created from carboxylic acids and anhydrides than had been recognised in their previous studies.[5—8] In the 1 : 3, amine : cyanide solution benzene-1,2,4,5-tetracarboxylic acid exists as the dianion which, on photolysis, yields the corresponding radical trianion. This undergoes electron exchange with the ground state dianion whilst, if diethylhydroxylamine is used as the quencher, proton exchange occurs between the trianion and its monoprotonated form. In all three compounds a hydrogen atom bridges the two carboxylate groups on each side of the molecule.

In a similar solution benzene-1,2-dicarboxylic acid exists as the mono-anion which, on photolysis at 220 K, yields the radical dianion; in both the carboxylate groups are bridged by a hydrogen atom. At higher temperatures the bridge breaks and two different radical dianions exist which are related as non-planar rotational isomers; their proportions vary with temperature. At room temperature both dicarboxylate groups become deprotonated and the radical observed is the non-planar trianion.

Photolysis of the ground state dianion of benzene-1,4-dicarboxylic acid yields the trianion which undergoes proton exchange with the mono-protonated radical dianion, which was not observed separately. In the presence of potassium hydroxide the proton exchange is suppressed and at temperatures of 260 K and below the radical produced changes to the diprotonated mono-anion; at intermediate temperatures this itself undergoes proton exchange with the radical dianion.

In the case of the anhydrides the radical observed depended upon the flow rate of the sample through the irradiation region, that is on the number of photolysis flashes experienced by a sample before its removal from the e.s.r. cavity. At high flow-rates and at concentrations >0.2 M the radical observed from benzene-1,2,4,5-dianhydride was the mono-anion, with both anhydride rings intact. At lower concentrations the radical observed was the radical dianion, with one of the anhydride rings broken and the carboxy groups bridged by a hydrogen atom. In these solutions, lowering the flow rate yielded the radical trianion, with bridging hydrogens on each side of the ring. Electron exchange processes were observed between both the mono-anion and the dianion with the parent molecule. Photolysis of benzene-1,2-anhydride produced the mono-anion only, and this was observed to undergo electron exchange with the anhydride molecule.

Table 1.

Parent compound	Radical anion	Coupling constants	References
4-Nitrobenzoic acid	**(1)**	11.8 G (N)	5
		3.28 G (2H)	
		1.09 G (2H)	
Benzene-1,2,4,5-dianhydride	**(2)**	0.69 G (2H)	7, 8, 10, 12
	(3)	0.53 G (2H)	7, 8, 10, 12
		0.12 G (1H)	
Benzene-1,2-anhydride	**(4)**	2.68 G (2,3H)^{c}	7, 8, 10
Benzene-1,2-imide	**(5)**	2.67 G (N)	
		0.44 G (NH)	7, 8, 12
		2.23 G (1,4H)	
		0.35 G (2,3H)	
Benzene-1,2,4,5-diimide	**(6)**	1.13 G (2N)	7, 8
		0.585 G (2H)	
Benzene-1,2,4,5-tetracarboxylic acid	**(7)**	1.03 G (2H)	4, 6, 9
		0.33 G (2H, CCOH)	
Benzene-1,2-dicarboxylic acid	**(8)**	3.23 G (2H)^{a}	9
		0.47 G (1H)	
	(9)	3.29 G (2H)^{b}	9
		0.375 G (2H)	
		3.10 G (2H)	
		0.375 G (2H)	
	(10)	3.09 G (2H)	
		0.345 G (1H)	6, 9
		0.29 G (1H)	
Benzene-1,4-dicarboxylic acid	**(11)**	1.54 G (4H)	6, 9
	(12)	1.57 G (4H)	6, 9
		0.3 G (2H)	

[a] Low temperature form ⩽220 K. [b] Two isomers 220—270 K. [c] 1,4H couplings unresolved.

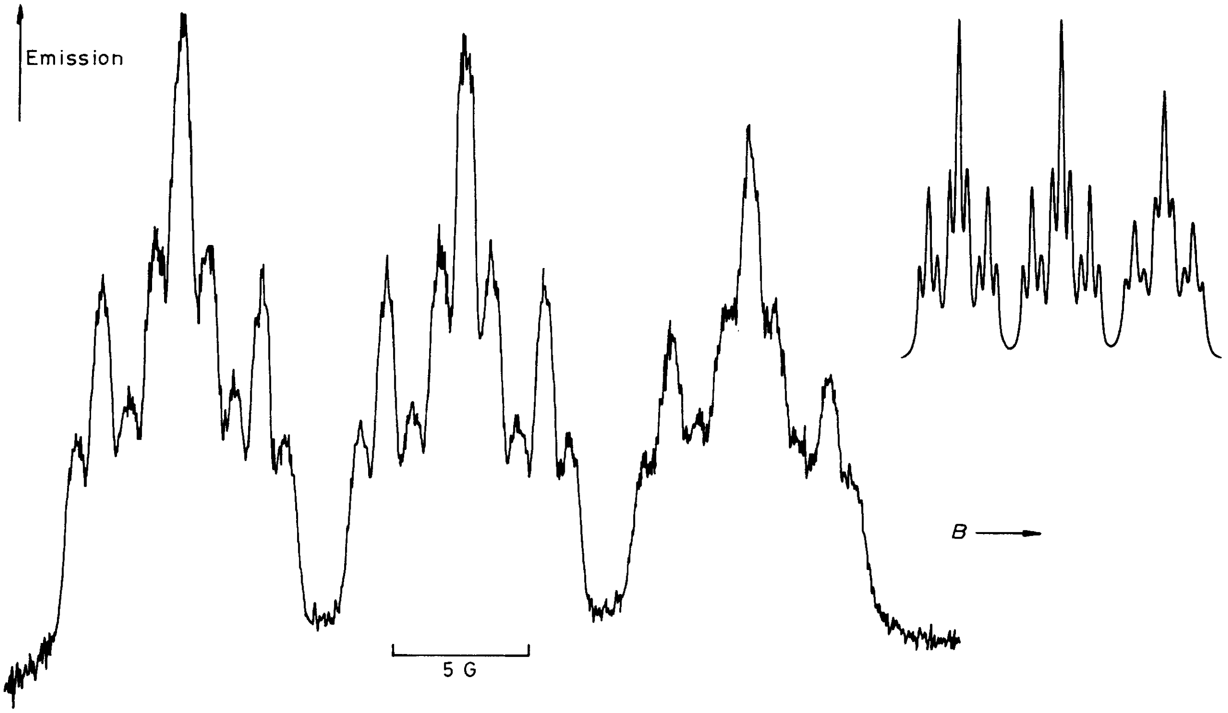

Figure 1. The e.s.r. spectrum of the dianion from 4-nitrobenzoic acid observed on photolysis of a 0.07 M solution in a 3 : 1 propan-2-ol : triethylamine mixture, with integration between 1.9 and 6.7 μs after the photolysis flash. A calculated spectrum is shown in the inset.

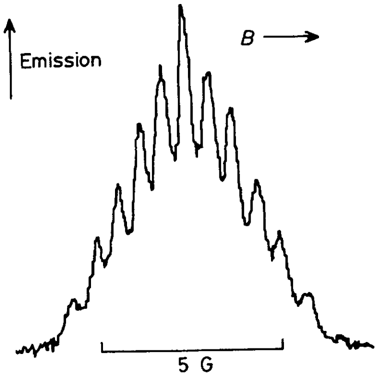

Figure 2. The e.s.r. spectrum of the mono-anion from benzene-1,2,4,5-diimide obtained on photolysis of a 0.05 M solution in a 4:1 propan-2-ol : triethylamine mixture, with integration between 1.7 and 6.3 μs after the photolysis flash.

Detailed descriptions and analyses of the exchange processes of polarized radicals emanating from aromatic acids and anhydrides have been published recently.[9,10] The imide analogues of the anhydrides displayed no such exchange effects.

The general method of preparation has also yielded the radical anions from a variety of nitrobenzenes, carbonyl compounds including the anion from isophthalaldehyde[11] (the first time it has been observed) and cyanobenzenes.

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