Radical-Nucleophilic Substitution ($S_{RN}1$) Reactions: Electron Spin Resonance Studies of Electron-capture Processes. Part 4.[1] α-Substituted 2-Methyl-5-nitrofurans

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We have probed two steps postulated for the radical-nucleophilic substitution ($S_{RN}1$) mechanism for α-substituted 2-methyl-5-nitrofurans ($O_2NFurCH_2X$) by detecting the intermediates involved using e.s.r. spectroscopy. These two steps are the electron-capture by $O_2NFurCH_2X$ to form radical-anions, and their dissociation to yield the 5-nitrofurfuryl radical ($O_2NFur\dot{C}H_2$) and anion. A range of radical-anions $(O_2NFurCH_2X)^{-\bullet}$ with X = I, Br, SCN, SO_2Ph, and H have been unambiguously identified by e.s.r. spectroscopy and shown to be infinitely long-lived at low temperature. The results are compared with those obtained for intermediates in the $S_{RN}1$ reactions. Their relevance to the $S_{ET}2$ mechanism is also discussed.

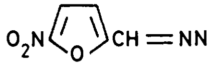
Study of the substitution reactions between nitronate anions and *p*-nitrobenzyl halides led to the first proposal of the $S_{RN}1$ mechanism.[2] The reactions of *p*-nitrobenzyl and *p*-nitrocumyl halides have since been central to the development of the $S_{RN}1$ and related mechanisms.[3] The $S_{RN}1$ mechanism was also observed in the reactions of α-substituted nitroalkanes[4] and aryl halides[5] which have also played a key role in $S_{RN}1$ chemistry.

While an increasing amount of evidence has been obtained to support the $S_{RN}1$ mechanism, difficulty has been experienced in detecting the reaction intermediates (radical-anions and radicals) using e.s.r. spectroscopy. Initial studies[6] with aryl halides using e.s.r. spectroscopy at low temperature in solid matrices identified the π* and σ* radical-anions of iodobenzene. Dissociation of the radical-anion $[(PhI)^{-\bullet}]$ to the phenyl radical and iodide anion was also observed. These studies therefore provided evidence for the first two steps in the aromatic $S_{RN}1$ mechanism[5] electron-capture by PhX to yield $(PhX)^{-\bullet}$ and dissociation of $(PhX)^{-\bullet}$ to $Ph^{\bullet}$ and X^-.

Studies with 2-substituted 2-nitropropanes[7] $[Me_2C(X)NO_2]$ and *p*-nitrobenzyl chloride and bromide[8] were also successful in detecting the corresponding intermediate radical-anions, providing evidence for the first step in the $S_{RN}1$ reactions of 2-substituted 2-nitropropanes and *p*-nitrobenzyl halides respectively. The free radicals ($Me_2\dot{C}NO_2$ and $Me_2\dot{C}X$), resulting from the dissociation of the radical-anions $Me_2C(X)\dot{N}O_2^-$ were also identified.[7] The 1-nitro-1-methylethyl radical ($Me_2\dot{C}NO_2$) was observed[9] to undergo reaction with new anions to form new radical-anions. The latter two observations provided evidence for the second and third steps of the $S_{RN}1$ mechanism for 2-substituted 2-nitropropanes.

Heterocyclic analogues of *p*-nitrobenzyl and *p*-nitrocumyl halides have also been shown to participate in $S_{RN}1$ reactions, *i.e.* the reactions between nitronate anions and 2-(1-methyl-1-nitroethyl)-5-nitrothiophene,[10] and 2-(chloromethyl)-*N*-methyl-5-nitroimidazole.[11]

An $S_{RN}1$ mechanism (Scheme 1; X = Br) had been proposed[12] for the reactions between various anions and 2-(bromomethyl)-5-nitrofuran, another mechanistic analogue. However, these were later shown[13] to occur by a non-chain mechanism, probably S_N2. Nevertheless, the reactions between the anion of 2-nitropropane ($Me_2CNO_2^-$) and α-substituted 2-methyl-5-nitrofurans (Scheme 1; X = I, Br, and $^+NEt_3I^-$, A^- = $Me_2CNO_2^-$) were shown to be light-catalysed and inhibited by the use of radical traps and strong electron-acceptors,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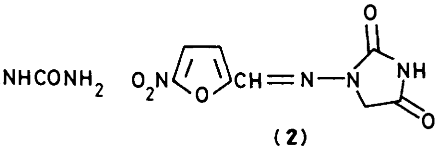
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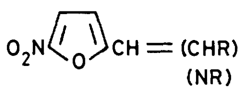
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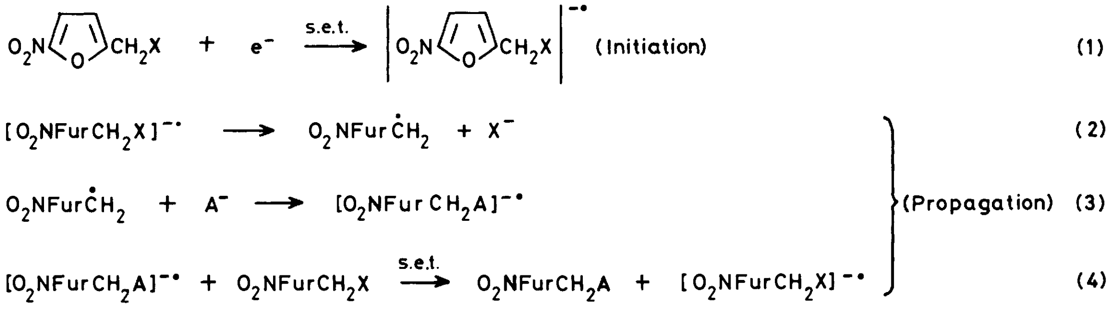
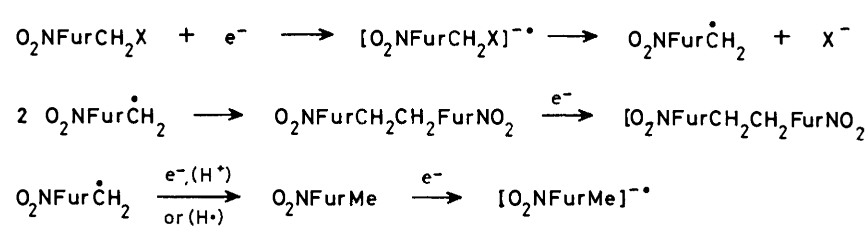


Scheme 1. $S_{RN}1$ Mechanism for the reaction between α-substituted 2-methyl-5-nitrofurans ($O_2NFurCH_2X$) and anions (A^-) (s.e.t. = single-electron-transfer)



Scheme 2. Proposed mechanism for the electrochemical reduction of $O_2NFurCH_2X$[18]

indicating an $S_{RN}1$ mechanism in this case, so there is a relatively subtle balance between the two mechanisms.[14]

5-Nitrofurans are important synthetic antibiotics[15] [*e.g.* nitrofurazone (**1**) and nitrofurantoin (**2**)] and all contain the 5-nitrofurfurylidene partial structure (**3**). While the complete mode of action of nitrofuran antibiotics is unknown, it has been shown that a reduction product interferes with DNA replication.[15] One of the possible active reduction products, the radical-anion, has been observed for several analogues using e.s.r. spectroscopy.[16]

α-Substituted 2-methyl-5-nitrofurans also exhibit good antimicrobial activity and have been shown to interfere with DNA replication.[17] Therefore a study of the radical-anions of these compounds is also of importance in relation to the possible mode of action of these compounds and to provide a useful comparison with the clinically used analogues.

An attempt to observe the nitrofuran radical-anions $(O_2NFurCH_2X)^{-\bullet}$, produced by electrochemical reduction of O_2FurCH_2X, using e.s.r. spectroscopy was unsuccessful, except for the radical-anions of 2-methyl-5-nitrofuran and 1,2-bis-(5-nitro-2-furyl)ethane ($O_2NFurCH_2CH_2FurNO_2$) (see Scheme 2).[18]

In this paper we report the detection of the radical-anions and radicals, resulting from electron-capture by $O_2NFurCH_2X$, using e.s.r. spectroscopy at low temperature. E.s.r. spectroscopy at low temperature of matrix-isolated radical-anions and radicals has previously been successfully used to obtain information regarding such unstable species.[19] The technique has the advantage that the first formed intermediates are often detectable, and that for strongly coupled nuclei anisotropic hyperfine coupling constants are obtained which lead to good estimates of spin densities. The disadvantage is that lines are broad and smaller hyperfine splittings are often not resolved. By using solvents such as CD_3OD and methyltetrahydrofuran (MeTHF), it has been established that the major reaction exhibited by dilute solutes is electron addition.[19] This low-temperature technique is fully described in the literature.[19]

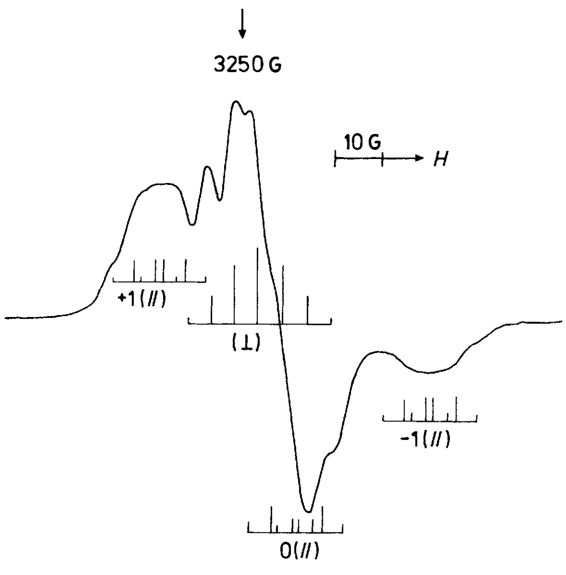


Figure 1. First-derivative X-band e.s.r. spectrum for a dilute solution of $O_2NFurMe$ in MeTHF after exposure to ^{60}Co γ-rays at 77 K, and annealing to remove solvent signals, assigned to the corresponding radical-anions

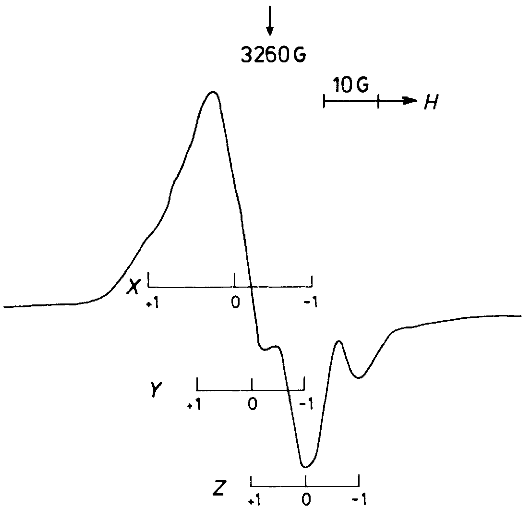


Figure 2. First-derivative X-band e.s.r. spectrum for a dilute solution of $O_2NFurCH_2I$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, and annealing to remove signals for the parent radical-anion, assigned to $O_2NFur\dot{C}H_2$ radicals. The lines give approximate positions for the proton *x*, *y*, and *z* features

Results and Discussion

Identification of Radical-Anions and Radicals.—As in our other studies of nitro derivatives, the parent radical-anions all display outer parallel features which provide unambiguous identification. By analogy with liquid-phase data[20] for the radical-anions of 5-nitrofuran and 2-methyl-5-nitrofuran, we expect to see extra splitting from one ring (α) proton (a_{iso} *ca.* 6 G) and, for the methyl derivative, splitting for three more protons (a_{iso} *ca.* 4 G). For the α-substituted 2-methyl-5-nitrofurans ($O_2NFurCH_2X$), coupling to the methylene protons will be a function of the orientation of the group relative to the ring, and hence cannot be readily predicted for the radical-anions.

As usual, the solid-state spectra comprise parallel and perpendicular (^{14}N) features (Figures 1—4 give some typical examples), and in only a few cases can the expected extra proton splittings be observed. For the thiocyanato derivative ($O_2NFurCH_2SCN$), a resonable fit can be obtained for one proton giving 6 G and two others giving *ca.* 3 G, but these values are only approximate. Some splitting was also observed for the methyl derivatives on annealing, but the data differed somewhat from those for the liquid phase.

However, coupling to bromine and iodine nuclei was clear (*e.g.* see Figure 3). Only the parallel (maximum) splitting was

E.s.r. parameters of radical-anions and radicals formed by electron-capture in the radiolysis of α-substituted 2-methyl-5-nitrofuran ($O_2NFurCH_2X$) solutions at 77 K

				A/G[a]			Orbital population (%)	
$O_2NFurCH_2X$	Solvent	Radical species	Nucleus	$A_{\parallel}$	$A_{\perp}$	A_{iso}	*s*	*p*
$O_2NFurCH_2I$	CD_3OD	$(O_2NFurCH_2I)^{-\bullet}$	^{14}N	*ca.* 25	0 ± 4	*ca.* 8		
			^{127}I	*ca.* 11	*ca.* 0	*ca.* 4		
		$O_2NFur\dot{C}H_2$[b]				*ca.* 8		
$O_2NFurCH_2Br$	CD_3OD	$(O_2NFurCH_2Br)^{-\bullet}$	^{14}N	25	0 ± 4			
	MeTHF		^{81}Br	*ca.* 13	*ca.* 0	*ca.* 4		
$O_2NFurCH_2SCN$	CD_3OD	$(O_2NFurCH_2SCN)^{-\bullet}$		Nothing clear				
	MeTHF	$(O_2NFurCH_2SCN)^{-\bullet}$[c]	^{14}N	*ca.* 27	0 ± 4	*ca.* 9		
$O_2NFurCH_2SO_2Ph$	CD_3OD	$(O_2NFurCH_2SO_2Ph)^{-\bullet}$[d]	^{14}N	28	0 ± 4	*ca.* 9		
	MeTHF	$(O_2NFurCH_2SO_2Ph)^{-\bullet}$[d]	^{14}N	27	*ca.* 4	*ca.* 11.7	2.1	46
$O_2NFurMe$[e]	CD_3OD	$(O_2NFurMe)^{-\bullet}$[f]	^{14}N	29	*ca.* 4.5	12.7	2.3	49
	METHF	$(O_2NFurMe)^{-\bullet}$[g]	^{14}N	28	5	12.7	2.3	46
	MeCN[h]		^{14}N			11.6	2.1	
$PhNO_2$		$Ph\dot{N}O_2^{-}$[i]	^{14}N	27.6	6.5	13.5	2.4	43

[a] G = 10^{-4} T. [b] This radical was obtained on annealing, 2-H = *ca.* 18(∥), *ca.* 11(⊥), 13 (*iso*) G, other = *ca.* 2.5 G (^1H + ^{14}N), $g_{\parallel}$ = *ca.* 2.002. [c] 1 H *ca.* 6 G, 2 H *ca.* 3 G. [d] The radical-anion is unstable on annealing. [e] No dissociation of the radical-anion on annealing. [f] Traces features due to NO_2 were detected. [g] A (3 H) *ca.* 5 G, A (1 H) *ca.* 7 G. [h] See ref. 20, 3-H 6.0, 4-H 0.8, 2-Me 4.0 G. [i] N. M. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc. A*, 1966, 448.

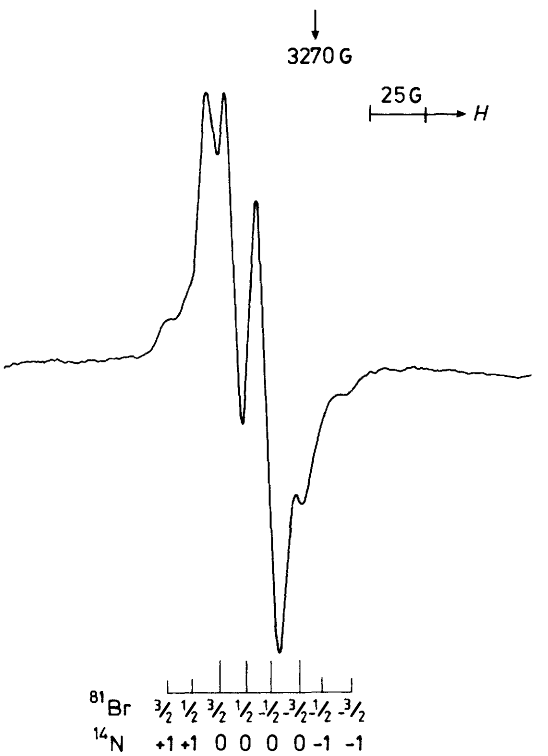


Figure 3. First-derivative X-band e.s.r. spectrum for a dilute solution of $O_2NFurCH_2Br$ in MeTHF after exposure to ^{60}Co γ-rays at 77 K, and annealing to remove solvent signals, showing features assigned to the corresponding radical-anions. The stick diagram only shows the outer M_I = ±1 (^{14}N) lines for clarity

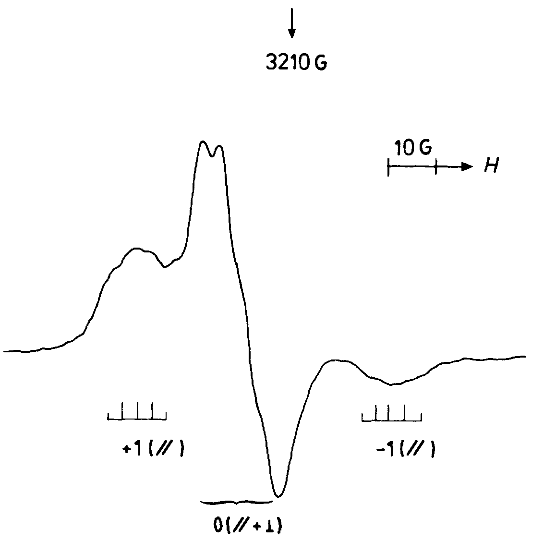


Figure 4. First-derivative X-band e.s.r. spectrum for a dilute solution of $O_2NFurCH_2SCN$ in MeTHF after exposure to ^{60}Co γ-rays at 77 K, and annealing to remove solvent signals, showing features assigned to the corresponding radical-anions

well defined, but the spectra suggest that, as with ^{14}N components, $A_{\perp}$ is small and unresolved.

Only in the case of the iodo derivative did the anion lose halide to give the expected radical ($O_2NFu\dot{C}H_2$) intermediate (Figure 2). The e.s.r. spectrum, although clearly due to this derivative, is difficult to interpret in detail, mainly because of the considerable *g*-anisotropy coupled with the anisotropic proton coupling. Our best fit gave the data included in the Table, which gives a_{iso} *ca.* 13 G for the methylene protons, with the normal anisotropy for such terminal methylene groups. Extra splittings are just resolved but we cannot distinguish between possible contributions for ^1H and ^{14}N.

Aspects of Structure.—In principle, from the isotropic and anisotropic ^{14}N coupling we can calculate approximate 2*s* and 2*p* spin densities.[21] In practice, since the perpendicular ^{14}N components were either unresolved or poorly defined, we have used the a_{iso} value reported for 2-methyl-5-nitrofuran in the liquid phase together with our $A_{\parallel}$ data to obtain a 2*s* population of 2.1% and a $2p_z$ population of *ca.* 49%. Thus, as with aromatic nitro-anions, and in contrast with the aliphatic derivatives, the $-NO_2$ moiety must be nearly planar. The total spin density on nitrogen is also similar to that for $Ph\dot{N}O_2^{-}$ and related anions (Table).

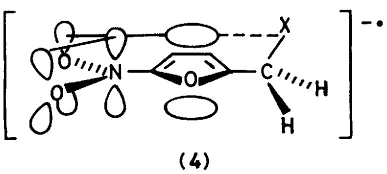
The coupling to bromine and iodine nuclei is small, as expected for these anions. However, it is significant, and implies that the halogen occupies an out-of-plane site, so that hyperconjugation can occur. Delocalisation as judged, approximately, from the magnitude of $A_{\parallel}$ is about half that found for the anions of *p*-nitrobenzyl bromide.[8] As we stressed for this anion,[8] the unpaired electron in $(O_2NFurCH_2X)^{-\bullet}$ which occupies a π^* molecular orbital is probably delocalised by overlap with (or donation into) the low-lying C–X σ^* orbital. The C–X σ orbital (bonding) will be at relatively lower energy and accordingly overlap will be less effective. This contrasts with the benzyl halide radical-cations[22] where the unpaired electron now occupies a π-orbital where overlap with (or donation from) the C–X σ-orbital is likely to be more effective than the σ^* orbital, again on the grounds of energy separation. This concept underlies the mechanism by which the C–X bond is broken during dissociation of the radical-anion to the corresponding radical and anion (X^-).

The results for the $O_2NFur\dot{C}H_2$ radical gives an approximate spin density on the methylene carbon of 0.56. This is slightly less than for benzyl radical [$A = (-)15.9$, giving *ca.* 0.69]. This almost certainly reflects delocalisation onto the nitro group, but unfortunately we have not been able to resolve the ^{14}N coupling.

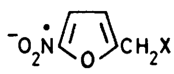
Dissociation of the Intermediate Radical-Anions.—The overlap between the C–I and C–Br σ^* orbitals and the NO_2–aromatic π^* orbitals is less with $O_2NFurCH_2X$ than with p-$NO_2C_6H_4CH_2X$ as judged from the e.s.r. data. This observation suggests that dissociation of $(O_2NFurCH_2X)^{-\bullet}$ radical-anions should be slower than for the *p*-nitrobenzyl analogues. The relative rate of dissociation of $(O_2NFurCH_2X)^{-\bullet}$ radical-anions is predicted to be I > Br > SCN > SO_2Ph by comparison with rate studies on the *p*-nitrobenzyl analogues.[23] Only the radical-anions of the iodo analogue dissociate to $O_2NFur\dot{C}H_2$ radicals and iodide anions in the temperature range of the study, which supports this order in a limited sense.

The limited data on the dissociation of the radical-anions of $O_2NFurCH_2X$ and p-$NO_2C_6H_4CH_2X$[24] precludes accurate comment on a comparison of their relative stabilities at this stage. However, the radical-anions of 2-halogeno-2-nitropropanes $[Me_2C(X)NO_2]^{-\bullet}$ clearly show considerable dissociation to the corresponding radicals ($Me_2\dot{C}NO_2$) and halide anions under analogous conditions, and are therefore clearly less stable than the $O_2NFurCH_2X$ and p-$NO_2C_6H_4CH_2X$ analogues.

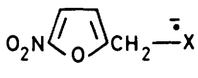
As stressed above, the results establish that there is considerable overlap between the C–X σ-orbitals and the NO_2–aromatic π^*-orbitals [see (**4**)]. We suggest that dissociation of the $(O_2NFurCH_2X)^{-\bullet}$ radical-anions proceeds by smooth reorganisation of the MOs to the required transition state for loss of X^-, and as we suggested[8] for the radical-anions of *p*-nitrobenzyl halides, it seems unreasonable to propose two separate π^* and σ^* structures (**5**) and (**6**) because they are, in effect, extreme valence-bond forms of the actual structure (**4**) (*cf.* ref. 23).



(**4**)



(**5**) π^*

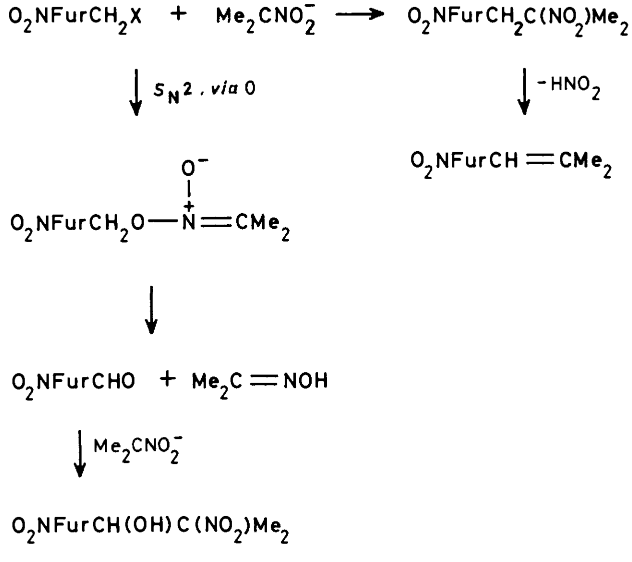


(**6**) σ^*

Furthermore, we suggest that the dissociation of the $(O_2NFurCH_2X)^{-\bullet}$ radical-anion proceeds to a planar intermediate $O_2NFur\dot{C}H_2$ radical and that planarity is smoothly achieved during the course of the dissociative process.

Anion Addition to $O_2NFur\dot{C}H_2$ *Radicals.*—Attempts to observe anion-addition to $O_2NFur\dot{C}H_2$ radicals [Scheme 1, equation (3)] in solid matrices by e.s.r. spectroscopy, as observed[9] for $Me_2\dot{C}NO_2$ radicals, were unsuccessful. Sodium benzenesulphinate was added to $O_2NFurCH_2I$ prior to irradiation and $(O_2NFurCH_2I)^{-\bullet}$ radical-anions and $O_2NFur\dot{C}H_2$ radicals were observed. However, as the e.s.r. signals due to the $O_2NFur\dot{C}H_2$ radical decreased, no e.s.r. signals were observed for the product of anion addition, $(O_2NFurCH_2SO_2Ph)^{-\bullet}$ This failure is possibly explained by the poor stability of $(O_2NFurCH_2SO_2Ph)^{-\bullet}$ radical-anions. No further study of anion addition was undertaken.

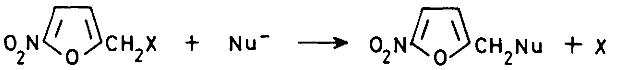
Correlation with Solution $S_{RN}1$ *Studies.*—Although the e.s.r. spectroscopic studies clearly indicate the feasibility of the formation of $(O_2NFurCH_2X)^{-\bullet}$ radical-anions, and $O_2NFur\dot{C}H_2$ radicals, as intermediates, they do not necessarily establish that they are obligatory intermediates in nucleophilic substitution reactions of $O_2NFurCH_2X$ derivatives. However, the results do show that the $S_{RN}1$ mechanism proposed[14] for the solution reaction between $Me_2CNO_2^-$ and $O_2NFurCH_2X$ (Scheme 1; X = I, Br, and $^+NEt_3I^-$, $A^- = Me_2CNO_2^-$) is indeed feasible. The above $S_{RN}1$ reaction occurs *via* the *C*-centre of the ambident $Me_2CNO_2^-$ anion (see Scheme 3).



Scheme 3. Reaction between α-substituted 2-methyl-5-nitrofurans ($O_2NFurCH_2X$) and the anion of 2-nitropropane

Products resulting from S_N2 attack *via* the *O*-centre of $Me_2CNO_2^-$ (see Scheme 3) were also identified.[14] This balance between $S_{RN}1$ and S_N2 was explained by suggesting that the $S_{RN}1$ mechanism is favoured for attack on the weakly nucleophilic and sterically hindered *C*-centre the S_N2 mechanism being favoured for reaction with the strongly nucleophilic and less hindered *O*-centre of the nitronate anion.[14] This useful difference of reactivity was first observed in the reactions between nitronates and *p*-nitrobenzyl halides,[2,3] allowing a clear distinction between the polar S_N2 mechanism and the electron-transfer $S_{RN}1$ mechanism.

Correlation with Non-chain Electron-transfer Reactions.—A large number of nucleophilic substitutions have been reported for $O_2NFurCH_2X$ derivatives [equation (5)].[12,25] Both S_N2[13,25] and $S_{RN}1$[12] mechanisms have been proposed for these substitution reactions. The reactions between $O_2NFurCH_2X$ (X = I and Br) and thiolates and sulphinates were not catalysed by light or inhibited by radical traps or strong electron-acceptors, thereby eliminating the radical-nucleophilic chain $S_{RN}1$ mechanism.[13] These results therefore suggest a polar S_N2 mechanism. The absence of single-electron-transfer (s.e.t.) is surprising because $O_2NFurCH_2X$ derivatives are clearly good electron-acceptors and the anions used, especially thiolates, are strong electron-donors. It has been suggested[13] that single-electron-transfer between thiolate anions and $O_2NFurCH_2X$ does occur and that a non-chain radical radical-anion nucleophilic substitution occurs. The $S_{ET}2$ (substitution, electron-transfer, bimolecular) mechanism initially proposed by Russell[26] was suggested as a possible mechanism for the reaction as shown in equation (6).



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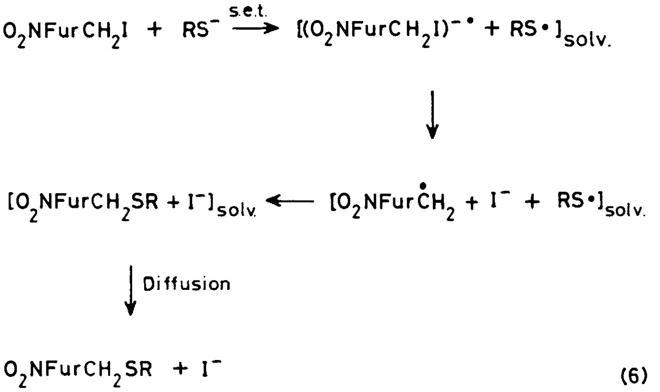

(6)

Our e.s.r. spectroscopic studies provide evidence that electron-capture by $O_2NFurCH_2X$ to form $(O_2NFurCH_2X)^{-\bullet}$ radical-anions and their dissociation to $O_2NFur\dot{C}H_2$ radicals are feasible steps in a $S_{ET}2$ mechanism. The observation[13] of strong red colours in the reactions between $O_2NFurCH_2X$ and thiolate anions, probably due to charge-transfer (c.t.) complexes, provides further evidence for the $S_{ET}2$ mechanism, although the formation of c.t. complexes does not necessarily indicate an electron-transfer step. In the analogous reaction between thiolate anions and p-$NO_2C_6H_4CH_2X$, inhibition was also not observed, but the intermediate radical-anions $(p\text{-}NO_2C_6H_4CH_2SR)^{-\bullet}$ were detected using e.s.r. spectroscopy.[27] Further studies are required to distinguish between S_N2 and $S_{ET}2$ mechanisms for the reactions between $O_2NFurCH_2X$ and thiolate anions.

In summary, e.s.r. spectroscopy has been used to identify a range of $(O_2NFurCH_2X)^{-\bullet}$ radical-anions and $O_2NFur\dot{C}H_2$ radicals. Hence, we have provided evidence for the first two steps of the $S_{RN}1$ [Scheme 1, equations (1) and (2)] and the first two steps of the $S_{ET}2$ [equation (6)] mechanisms for the nucleophilic substitution reactions of α-substituted 2-methyl-5-nitrofurans.

Experimental

E.s.r.—Degassed samples were irradiated as dilute solutions (*ca.* 1% v/v) in methanol (CD_3OD was used to avoid overlap with solvent radical features) or MeTHF. They were frozen as small beads in liquid nitrogen and irradiated at 77 K in a Vickrad ^{60}Co γ-ray source to doses of up to 1 Mrad. E.s.r. spectra were measured on a Varian E109 spectrometer. Samples were annealed to selected temperatures or until significant changes occurred in the e.s.r. spectra, and recooled to 77 K for study.

Materials.—5-Nitrofurfuryl nitrate was prepared by nitration of 2-furylmethanol with nitric acid and acetic anhydride.[25c] 2-(Bromomethyl)-5-nitrofuran,[25c] 5-nitrofurfuryl thiocyanate,[25c] and 2-(iodomethyl)-5-nitrofuran[25b] were prepared by reaction between 5-nitrofurfuryl nitrate and sodium bromide, thiocyanate, and iodide respectively, in acetone. Phenyl 5-nitrofurfuryl sulphone was prepared by reaction between 2-(bromomethyl)-5-nitrofuran and sodium benzenesulphinate in acetone.[25a] 2-Methyl-5-nitrofuran was prepared by reduction of 2-(iodomethyl)-5-nitrofuran with L-cysteine in aqueous methanol.[13] All materials had satisfactory spectral data and correct m.p.s.

Acknowledgements

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