An Electron-transfer Induced Reaction Path Controlled by Ion-pair Formation: an ESR/ENDOR Study of Furan Carbaldehydes and their Reactivity

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When furan 2,5-dicarbaldehyde **1** is single-electron reduced to its radical anion $\mathbf{1}^{\cdot-}$ its readiness to couple to give dimer **2** depends upon the nature of the ion pair $\mathbf{1}^{\cdot-}/\mathrm{M}^+$ (M = Li, Na, K, Cs).

Electron transfer has been established as one of the key steps in a variety of chemical, biochemical and technical processes.[1] Starting with a ground-state diamagnetic donor (D) and acceptor (A), the primary intermediate formed is a radical ion pair [Scheme 1, eqn. (1)] independent of the initiation method for the single-electron transfer (SET). A special case exists, when the donor is an alkali metal M: because the ground state of an alkali atom is paramagnetic, the odd electron is transferred onto A and the counter-cation becomes diamagnetic [Scheme 1, eqn. (2)]. In solution, various stages of ion-pair formation[2] can be achieved, and the character and the amount of interactions between the solvent, the anion and the cation predetermine the further course of the reaction.

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{D}^{\cdot+} + \mathrm{A}^{\cdot-} \tag{1}$$

$$\mathrm{M} + \mathrm{A} \rightleftharpoons \mathrm{M}^{+} + \mathrm{A}^{\cdot-} \tag{2}$$

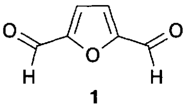
Scheme 1

According to eqn. (2) one distinct species is paramagnetic and can conveniently be studied by ESR spectroscopy.[3] A careful analysis of the hyperfine data not only sheds light on the structure of the radicals but also provides valuable information about ion-pairing phenomena.[4]

Here we present results which point to a systematic dependence of molecular reactivity upon the character of ion pairs formed after an SET reaction from an alkali metal to furan dicarbaldehyde **1**. Connected with our studies on ion pairs and redox chemistry of 2,5-disubstituted furans[5] we have been able to control the reactivity of the furan carbaldehydes by altering the solvents and the counterions.†

When **1** is SET reduced with alkali metals in solvents of high solvation power [1,2-dimethoxyethane-*N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylphosphoric acid triamide (DME–HMPA)], the ESR spectrum shown in Fig. 1 is detected (218–313 K). It consists of a 'triplet of triplets' and is in accord with intact $\mathbf{1}^{\cdot-}$ of C_{2v} symmetry. The two proton coupling constants, a_H, of 0.480 and 0.125 mT for two pairwise equivalent H-atoms are in perfect agreement with the Hückel (HMO) calculated values (0.48 and 0.13 mT, respectively; Table 1).

However, reduction of **1** in DME or THF leads to quite different results. An example is shown in Fig. 2. The ESR spectrum recorded after reaction of **1** with Cs metal in DME at 193 K has almost identical proton-hyperfine coupling constants as determined for $\mathbf{1}^{\cdot-}$ in DME–HMPA (Fig. 1) but an additional splitting caused by interaction with the ^{133}Cs nucleus [Table 1; Fig. 2(*a*)]. On warming (*ca.* 263 K) the ESR signal undergoes an irreversible change [Fig. 2(*b*)]. The a_H used for the simulation of this spectrum, determined by ENDOR spectroscopy (Table 2), do not correspond to $\mathbf{1}^{\cdot-}$. Analysis of the coupling constants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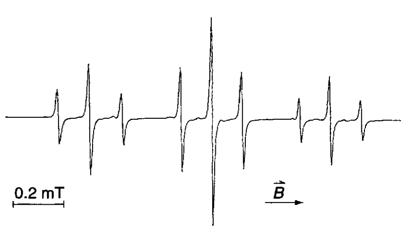

Fig. 1 ESR spectrum of $\mathbf{1}^{\cdot-}$ [solvent HMPA–DME (1 : 5), counterion K$^+$, 313 K]

Table 1 Experimental and calculated a_H values (mT) of $\mathbf{1}^{\cdot-}$

	Furan-ring protons (2 H)	Aldehyde protons (2 H)
Experiment[a]	0.480	0.125
Experiment[b]	0.484	0.126
HMO[c]	0.48	0.13

[a] Solvent HMPA–DME (1 : 5), counterion K$^+$, 218–313 K. [b] Solvent DME, counterion Cs$^+$ (a_Cs = 0.033 mT; 223 K). [c] Heteroatom parameters: $h_{\mathrm{O(C=O)}} = 1.2$, $h_{\mathrm{O(C-O-C)}} = 2.0$, $k_{\mathrm{C=O}} = 1.56$.[11]

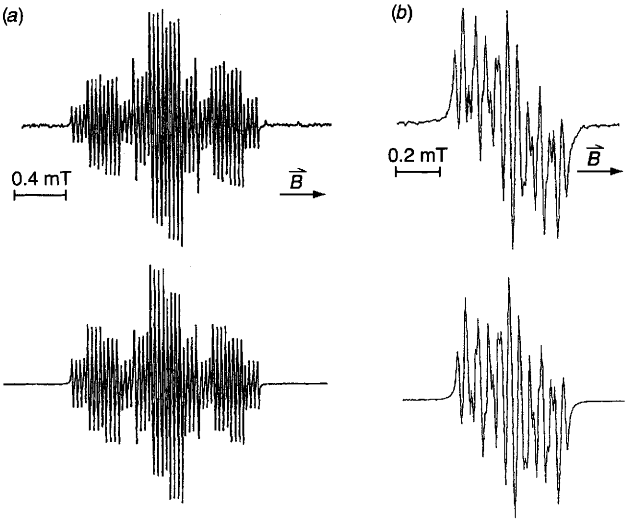

Fig. 2 (*a*) ESR spectrum of $\mathbf{1}^{\cdot-}/\mathrm{Cs}^+$ (solvent DME, 223 K); (*b*) ESR spectrum ascribed to $\mathbf{2}^{\cdot-}/\mathrm{Cs}^+$ detected upon warming to 305 K. The simulations are indicated below the experimental spectra.

Table 2 Experimental and calculated a_H values (mT) of $\mathbf{2}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$

	Position[a]	3,3′	4,4′	6,6′ (5,5′ for $\mathbf{4}^{\cdot-}$)
$\mathbf{2}^{\cdot-}$	Experiment[b]	0.141	0.040	0.058
	HMO[c]	0.14	0.04	0.07
$\mathbf{4}^{\cdot-}$	Experiment[d]	0.210	0.036	0.153
	Experiment[e]	0.210	0.037	0.149
	HMO[c]	0.26	0.08	0.24

[a] For numbering, see Fig. 3. [b] Solvent DME, counterion Cs$^+$ (a_Cs < 0.01 mT), 321 K (the hyperfine data represent the fast-exchange region of the ion pair $\mathrm{Cs}^+/\mathbf{2}^{\cdot-}$, at lower temperatures, the symmetry is diminished because of hindered rotation around the central C–C bond). [c] Heteroatom parameters: $h_{\mathrm{O(C=O)}} = 1.2$, $h_{\mathrm{O(C-O-C)}} = 2.0$, $k_{\mathrm{C=O}} = 1.56$.[11] [d] Solvent HMPA–DME (1 : 5), counterion K$^+$, 357 K. [e] See ref. 8.

and their multiplicities suggests the presence of $\mathbf{2}^{\cdot-}$ (Fig. 3), a 'dimer' of **1** as the species giving rise to the altered ESR spectrum [Fig. 2(*b*)]. As for $\mathbf{1}^{\cdot-}$, the agreement between the experimental and the calculated a_H values of $\mathbf{2}^{\cdot-}$ is excellent (Table 2).

Analogous behaviour was found for Li^+, Na^+ and K^+ as counterions (solvents DME, THF). The experimental observations indicate that: the 'harder' the counterion ($Li^+ > Na^+ > K^+ > Cs^+$) and the more the solvent promotes contact-ion pair formation (THF > DME), the 'sooner' the ESR spectrum ascribed to dimer $\mathbf{2}^{\cdot-}$ [Fig. 2(*b*)] is detected.

To inspect if such a dimerisation is a more general reaction pathway, we also investigated monoaldehyde **3**. The radical anion of **3** was reported only recently.[7]† It was generated by UV irradiation of furfuryl alcohol in alkaline solution since alkali metal reduction in ethereal solvents was unsuccessful.

Potassium metal reduction of **3** in DME–HMPA immediately yielded an intense ESR spectrum different to that of $\mathbf{3}^{\cdot-}$ (Fig. 4). The corresponding ENDOR spectrum indicated three proton coupling constants and the simulation of the ESR spectrum established that they are due to three pairs of equivalent protons (Table 2). The pairwise equivalency of the a_H values indicating twofold symmetry of the detected radical anion is not consistent with the molecular structure of $\mathbf{3}^{\cdot-}$. However, in analogy to $\mathbf{1}^{\cdot-}$, the ESR data reflect the radical anion of **4**, the dimer of **3**. Our parameters completely agree with those reported previously[8] (Table 2). Thus, also for **4** the same type of dimerisation as for $\mathbf{2}^{\cdot-}$ has been established.

At the moment we can only speculate about the mechanism underlying the coupling reaction. For $\mathbf{1}^{\cdot-}$, the evolution of the ESR spectrum of the dimeric species is observed under conditions which promote a close contact between the carbonyl O atom and the alkali metal cation. The observation that the coupling occurs without further contact of the reaction solution with the metal mirror and depends upon the concentration of the starting material is in accord with an attack of the nucleophilic radical-ion pair $\mathbf{1}^{\cdot-}/M^+$ onto the neutral **1** followed by the dehydrogenation. The counterbalance of the negative charge of $\mathbf{1}^{\cdot-}$ by M^+ promotes the radical reaction. The radical character of this reaction mechanism is substantiated by the observation that monoaldehyde $\mathbf{3}^{\cdot-}$ with a higher spin population at the carbonyl C atom 'couples' already in the strongly solvating HMPA–DME mixture with diminished assistance of the alkali metal counterion. This finding also rationalises that coupling of the 'dimer' $\mathbf{2}^{\cdot-}$ to a further neutral monomer **1** is impeded because of the diminished spin population at the carbaldehyde C atoms of $\mathbf{2}^{\cdot-}$.

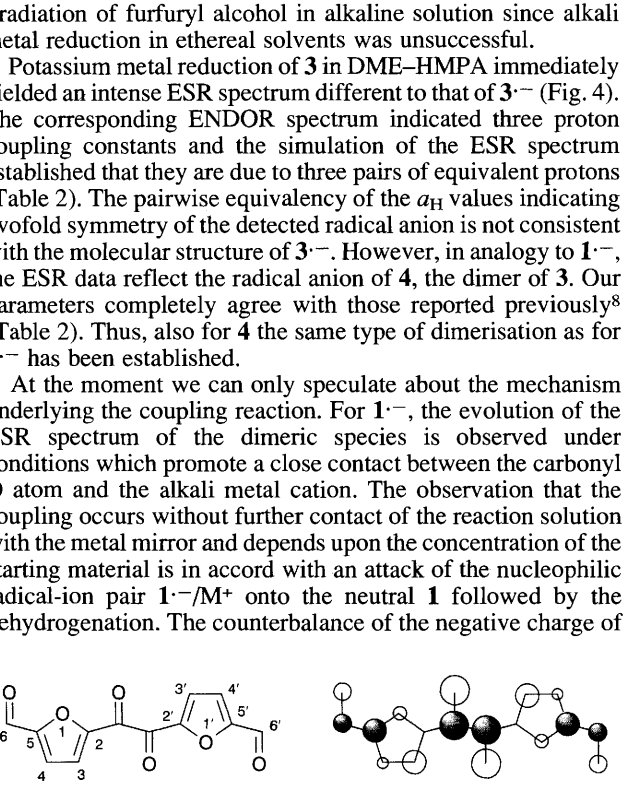

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Fig. 3 'Dimer' **2** and its LUMO (right; according to HMO calculations) representing the spin distribution in $\mathbf{2}^{\cdot-}$

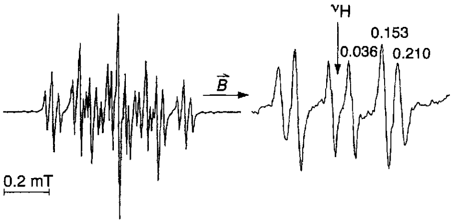
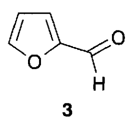


Fig. 4 ESR spectrum of $\mathbf{4}^{\cdot-}/K^+$ [solvent HMPA–DME (1 : 5) 357 K] and the corresponding ENDOR spectrum



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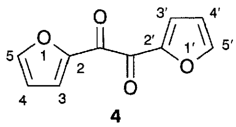

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A related pathway has also been proposed for the acyloin condensation.[9] Ion pairing also affects the reactivity of carbanions.[10] The electrostatic interactions between carbanions and their counterions are the same as for the radical anions. Therefore, our results should serve as guidelines for the characterisation of ion pairing phenomena of carbanions.

Kinetic studies of this reaction pathway and investigations of related aldehydes are under way.

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Footnote

† Interestingly the radical anion of the S-analogue, thiophene 2,5-dialdehyde has been known for several years,[6] but the radical anion of **1** has hitherto not been reported.

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