Low-temperature EPR study of radical cations of 2,5- and 2,3-dihydrofuran and their transformations in freon matrices

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Using low-temperature EPR spectroscopy, transformations of radical cations of 2,3- and 2,5-dihydrofuran (DHF) radiolytically generated in freon matrices ($CFCl_2CF_2Cl$ and CF_3CCl_3) were investigated. In addition, quantum chemical calculations were performed to obtain information on the electronic structure of the transient species observed. The radical cation 2,3-DHF$^{+\bullet}$ (a(H)/mT: 4.3(2H), 1.4(2H), 1.5(1H), 0.5(1H)) formed in frozen 2,3-DHF solutions is stable at 77 K. At higher temperatures it transforms into dihydrofuryl radical DHF$^{\bullet}$ (a(H)/mT: 3.6(2H), 1.3(2H), 0.2(1H)). The oxygen-centred radical cation 2,5-DHF$^{+\bullet}$ (a(H)/mT: 8.4(4H), 0.5(2H)) is rather unstable at 77 K and transforms *via* a first-order process (half life 2.3 or 4 min, according to the matrix type), which is apparently an intramolecular H-shift, into a transient distonic radical cation 2,4-DHF$^{+\bullet}$ (a(H)/mT: 3.9(2H), 4.0(1H), 3.6(1H), 2.3(1H), 0.02(1H)). The latter yields at higher temperatures again the DHF$^{\bullet}$ radical. Transformations of the DHF radical cations into the dihydrofuryl radical proceed most likely by ion–molecule reactions, when due to the softening of the matrix diffusion becomes possible. At high DHF concentrations the DHF$^{\bullet}$ radical is formed in the case of 2,5-DHF already during irradiation at 77 K and in the case of 2,3-DHF after warming to 95 K. This is explained by the presence of preformed DHF dimer agglomerates favouring deprotonation of the DHF cation (the attached DHF molecule acts as the proton acceptor). The most stable species, the dihydrofuryl radical, finally disappears by a simple bimolecular recombination reaction.

Introduction

Unsaturated cyclic ethers have been subject to investigations throughout the years with general interest in the formation and transformation of reactive intermediates.[1–11] Among these, 2,3-dihydrofuran (2,3-DHF) and 2,5-dihydrofuran (2,5-DHF) are involved in reactions which are currently under investigation from a more practical point of view.

The dehydrodimerization of 2,5-DHF photocatalyzed by ZnS is one of the rare examples when a new compound (dehydrodimer) was obtained by semiconductor photocatalysis on a preparative scale.[12] While colloidal systems are rather well understood, powder suspensions, which are more important for chemical synthesis, are still under investigation.[11] Some of the basic questions regarding the reactive surface sites and the redox mechanism involved are not answered yet. It is assumed that hole oxidation of the cyclic ether leads to radical cations and by subsequent deprotonation dihydrofuryl radicals are formed. These radicals should recombine yielding the dehydrodimer.

In the UV curing of recently developed electron-donor–acceptor systems, based on maleimide, maleic anhydride *etc.* as the acceptors, unsaturated ethers have received growing interest as donor components.[13] In the context of these investigations 2,3-DHF is of interest as a simple cyclic vinyl ether. It has been shown that the initiating step upon UV-irradiation is actually an electron transfer from the donor (*e.g.* vinyl ether, DHF) to the maleimide triplet, generating the maleimide anion and the ether radical cation.[14] Thus, the structure and fate of the ether radical cation are of great interest for understanding the mechanism of the alternating copolymerisation of electron-donor–acceptor systems.

Radical cations of 2,3- and 2,5-DHF have been postulated before,[3,11] however, direct information on their existence is only available from some gas-phase mass spectroscopic investigations.[10] This is even more surprising, as the technique of low-temperature EPR in a freon matrix is well established and has been used to study a variety of cyclic and aliphatic ether cations. Matrix radical cations, produced by γ-ray or electron irradiation, are able to transfer their positive charge to solutes with an ionisation potential (IP) lower than that of the matrix molecules (IP/eV: freons used: >11; 2,3-DHF: 8.5; 2,5-DHF: 9.14).[12,15] The free radicals formed by dissociative electron capture from matrix molecules show a broad EPR signal due to large anisotropy and do not interfere with spectra of solute species.

$CFCl_2CF_2Cl$ (F-113) and CF_3CCl_3 are often chosen as matrices because of their specific characteristics. F-113 (IP/eV = 11.99)[15] is considered to be a "soft" matrix above its phase-transition region around 110 K. When warming the samples to ~115 K, reorganisation of the matrix structure results in microcrystalline states of substrate similar to the liquid state.[16] Migration of molecules during and after the matrix phase transition makes ion–molecule reactions possible even at low solute concentration. Depending on the type and concentration of solute and sample preparation such reactions may take place well below 110 K. However, the matrix interaction with the solute is often strong and may lead to an anisotropic line broadening.[16]

CF_3CCl_3 (IP/eV = 11.78)[15] is considered to be more rigid, thus preventing solute diffusion below 145 K, but it contains cavities large enough to allow rearrangement reactions. Weaker matrix–solute interaction allows some rotation of solute radical ions, leading to much better resolved spectra.

The present study was aimed at the investigation of the formation and transformations of radical cations of DHFs in frozen freon matrices. It represents a part of our research on the role of radical cations of various monomers (*e.g.* vinyl ethers, acrylates, methacrylates) in the mechanisms of radiation-induced polymerization.[17,18]

Experimental

The EPR experiments were performed using a Bruker ESP 300e spectrometer (9.5 GHz, 100 kHz modulation) equipped with either a finger dewar (77 K) or a variable temperature control unit (ER 4121 VT, above 95 K). Spectra were recorded at a microwave power of 0.1 mW and a modulation amplitude of 0.05 mT. 2,5-DHF (Aldrich, 97%) and 2,3-DHF (Lancaster, 97%) were used as received. The dihydrofurans were dissolved at solute : solvent molar ratios typically from 1 : 1100 to 1 : 10 in 1,1,2-trifluorotrichloroethane (Merck, Uvasol 99.9%) or 1,1,1-trifluorotrichloroethane (Aldrich, 99%, purified by passing it through a column filled with neutral Al_2O_3). The solutions were carefully degassed by the freeze–thaw technique (10 cycles) and irradiated in the dark at 77 K with the 10 MeV electron beam of a LINAC (Elektronika U-003, Thorium, Moscow). A dose of ~10–15 kGy (irradiation time approx. 1 min) was sufficient to generate a well observable concentration of paramagnetic species. Irradiated samples were protected from light and the first spectrum was taken as soon as possible (within 2.5 min) after irradiation. EPR spectra were measured at 77 K usually up to 30 min (but in a few cases up to tens of hours) after irradiation and then in the temperature range of 95–150 K. The temperature was increased in 5 K steps and spectra were taken just after the temperature stabilised, as well as 2–10 min later, to check for slow transformations. In cases where changes in the EPR spectra were observed, the samples were cooled back to check for reversibility of these transformations.

Spectra simulations were performed using the WinSim software.[19]

Quantum chemical calculations

To gain information about the electronic structure of the transient species, the semiempirical PM3 method and two post-SCF (Self-Consistent Field) quantum chemical methods, namely *ab initio* Moller Plesset MP2/6-31G* and Density Functional Theory (DFT) B3LYP/6-31G*, were applied. Geometries and total energies † of the ground and transition states for the radical cations and radicals as well as total atomic spin densities and Mulliken charge distributions, commonly used in Molecular Orbital Theory, were calculated with Gaussian 94W and HyperChem 5.1. Using the optimised geometries, the hyperfine splitting constants for individual structures were computed with Gaussian as part of the population analysis. A survey of quantum chemical methods and guidelines regarding their use is given in Ref. 20.

Semiempirical PM3 structures and total atomic spin densities of the transients resemble those obtained from *ab initio* MP2 and DFT calculations. Regarding post-SCF methods, only the results of B3LYP/6-31G* calculations are presented in this report. MP2/6-31G* calculations generally provided qualitatively the same results, but B3LYP/6-31G* values were found to be in slightly better agreement with experimental data. Similar conclusions were obtained in a comparative study with a number of neutral radicals and radical ions including 2-methyldihydrofuran-4-yl radical.[21] Recently, the use of B3LYP has also been recommended for computation of splitting constants of larger systems, where application of somewhat more precise, but very time consuming QCISD (Quadratic Configuration Interaction, Single and Doubles) methods becomes impractical.[22]

Results and discussion

2,3-Dihydrofuran

The EPR spectrum recorded at 77 K in the dark in CF_3CCl_3 (Fig. 1(a)) consists of a triplet (a(2H) = 4.27 mT) of quartets (a(2H) ≈ a(1H) ≈ 1.4 mT) of doublets (a(H) = 0.53 mT) and is assigned to the radical cation **1** of 2,3-DHF. This assignment is strongly supported by the quantum chemical calculation of splitting constants performed on the B3YP/6-31G* level of DFT which agree very well with the values derived from the spectrum (hfs constants given in Table 1, calculated spin density distributions of cations and radicals summarised in Table 2). The same transient is observed in $CFCl_2CF_2Cl$ matrix (Fig. 1(*b*)) although the doublet is poorly resolved. At a low 2,3-DHF concentration, the 2,3-DHF$^{\bullet}$ is stable upon warming up to 145 K in CF_3CCl_3 and up to 95–100 K in F-113. Raising the temperature above these levels leads to an irreversible formation of a transient spectrum consisting of a triplet (a(2H) = 3.64 mT) of triplets (a(2H) = 1.34 mT) of doublets (a(H) = 0.21 mT) (Fig. 1(*c*) and Table 1). The splitting constants can be assigned to the dihydrofuryl radical **4** (DHF$^{\bullet}$), which has already been clearly identified by EPR.[1,3,4]

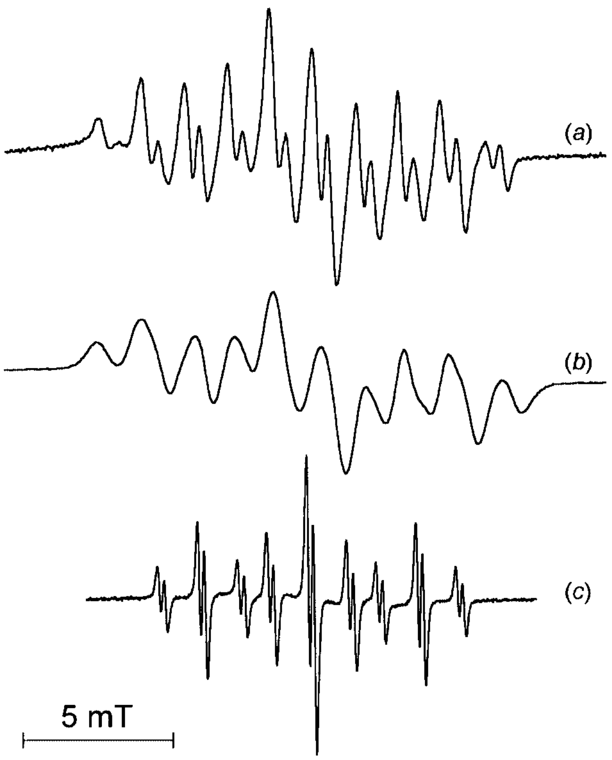

Fig. 1 EPR spectra of irradiated 2,3-DHF in freon matrix: (*a*) 1 : 90 dilution in CF_3CCl_3, 77 K (2,3-DHF$^{+\bullet}$); (*b*) 1 : 300 in F-113, 77 K (2,3-DHF$^{+\bullet}$); (*c*) 1 : 300 in F-113, 120 K (DHF$^{\bullet}$).

The decay of the DHF$^{\bullet}$ radical was studied in F-113 matrix in the temperature interval of 130–140 K. At these temperatures diffusion of solute radicals occurs and the decay is still slow enough to be followed. It can be seen from Fig. 2 that the DHF$^{\bullet}$ radicals decay in a second-order process by bimolecular recombination (without formation of other intermediates). As expected, the decay rate increases with increasing temperature.

2,5-Dihydrofuran

The EPR spectra recorded at solute-to-solvent molar ratios smaller than about 1 : 400 at 77 K, 2.5 min after the end of irradiation in the dark, correspond to two species (Fig. 3(*a*) and (*b*)). One of them shows a quintet with nearly binomial intensities and a large splitting constant of a(4H) = 8.4 mT. In CF_3CCl_3 matrix, due to better resolution of the spectra, an additional small splitting of each line into triplets (≈0.5 mT (2H)) is observable (Fig. 3(*b*)). The spectrum is assigned to the radical cation **2** of 2,5-DHF (2,5-DHF$^{+\bullet}$). Comparatively large splitting constants have been observed for radical cations of other cyclic and aliphatic ethers too (*e.g.* diethyl ether:[7] 6.8 mT (4H); tetrahydrofuran:[23] 8.9 mT (2H) and 4.0 mT (2H)) and have been assigned to the oxygen-centred radical cation. In

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† (Total energy is the sum of the electronic energy and nuclear repulsion energy of the molecule at the specified nuclear configuration.)

Table 1 Hfs splitting constants a(H) for species observed in 2,3-DHF solutions (lw = linewidth)

Species	Calc. method or Matrix, Temp.	lw/mT	a(H)/mT
2,3-DHF$^{+\bullet}$	B3YP/6-31G*		**4.18** (H:8,9), **1.56** (H:6,7), **1.50** (H:10), **0.38** (H:11)
	F-113 77 K	~0.55	**4.34** (2H), **1.46** (2H), **1.54** (1H), **0.47** (1H)
	CF_3CCl_3 77 K	~0.38	**4.27** (2H), **1.38** (2H), **1.44** (1H), **0.53** (1H)
DHF$^{\bullet}$	B3YP/6-31G*		**3.79** (H:6,7), **1.55** (H:8), **1.47** (H:10), **0.33** (H:9)
	F-113 120 K	~0.10	**3.64** (2H), **1.33** (2H), **0.2** (1H)
	CF_3CCl_3 150 K	~0.08	**3.64** (2H), **1.34** (2H), **0.2** (1H)

Table 2 B3YP/6-31G* calculated total energy E(DFT)/kJ mol^{-1} and spin density ρ at carbon and oxygen atoms as well as PM3 calculated total energy E(PM3)/kJ mol^{-1} of species under investigation. (In parentheses: energy differences with respect to the most stable species are given)

	2,3-DHF$^{+\bullet}$	2,5-DHF$^{+\bullet}$	2,4-DHF$^{+\bullet}$	DHF$^{\bullet}$	3-DHF$^{\bullet}$
ρ(O-1)	0.276	0.297	−0.003	0.101	0.089
ρ(C-2)	−0.006	−0.021	−0.076	−0.064	−0.041
ρ(C-3)	−0.037	0.197	1.021	0.611	0.077
ρ(C-4)	0.584	0.197	−0.076	−0.216	−0.082
ρ(C-5)	0.094	−0.021	0.001	0.524	0.878
E(PM3)	−82068	−81988	−82055	−81339	−81316
	(0)	(+80)	(+13)	(0)	(+23)
E(DFT)	−606023	−605935	−605947	−605108	−605058
	(0)	(+88)	(+76)	(0)	(+50)

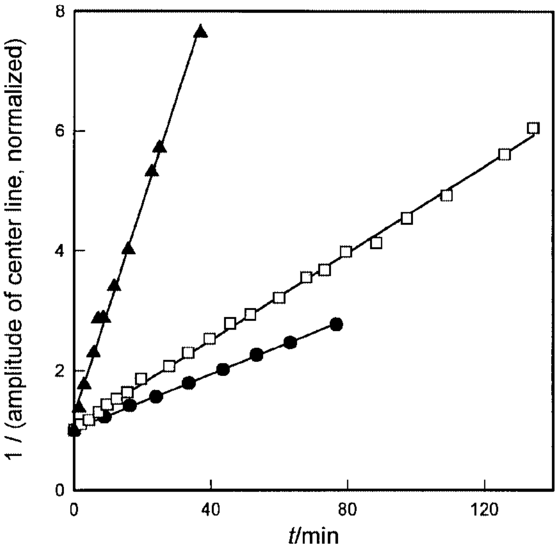


Fig. 2 Decay of the DHF$^{\bullet}$ at 130 K (●), 135 K (□) and 140 K (▲) in F-113 matrix.

addition, our assignment is strongly supported by the results of quantum chemical calculations, which agree well with the measured values (Table 3).

In both matrices the 2,5-DHF$^{+\bullet}$ decays rapidly by a first-order process (Fig. 4, the amplitude of the low-field line of the 2,5-DHF$^{+\bullet}$ spectrum was measured to follow the decay). The decay of the 2,5-DHF$^{\bullet}$ is accompanied by a change in colour from greenish to yellowish. The decay rate in F-113 is lower ($k = 0.17$ min^{-1}) than in CF_3CCl_3 ($k = 0.30$ min^{-1}), therefore the relative contribution of the 2,5-DHF$^{+\bullet}$ to the overall EPR-spectrum measured 2.5 min after the irradiation is higher in F-113 (*cf.* Fig. 3(*a*) and (*b*)). The decay rate does not change with increasing 2,5-DHF concentration. Fig. 4 shows that the overall spin concentration remains nearly constant during the decay of the 2,5-DHF$^{\bullet}$ *i.e.* a 1 : 1 transformation of the transient is observed.

It can be concluded that the 2,5-DHF$^{\bullet}$ is the primary species produced by charge transfer from the matrix and that it transforms quantitatively by a first-order process into the secondary species showing a doublet (a(H) = 2.27 mT) of nearly binomial quintets (a(4H) ≈ 3.6–3.9 mT) (Fig. 3(*c*)). This spectrum is assigned to a radical cation **3** (2,4-DHF$^{+\bullet}$) formed by intramolecular H-shift (see Fig. 7, reaction (3)).

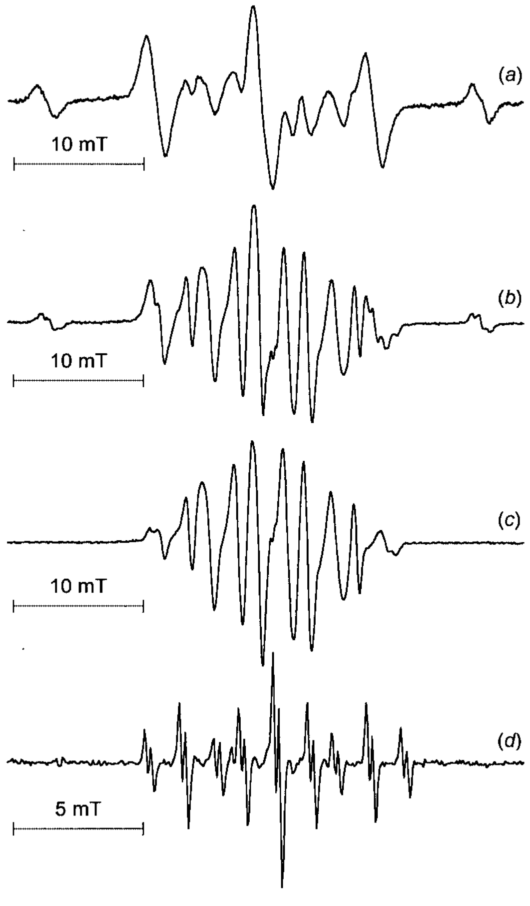


Fig. 3 EPR spectra of irradiated 2,5-DHF in freon matrix (dilution approx. 1 : 500): (*a*) F-113, 77 K, 2.5 min after irradiation; (*b*) CF_3CCl_3, 77 K, 2.5 min; (*c*) CF_3CCl_3, 77 K, 60 min; (*d*) CF_3CCl_3, 150 K.

The assignment is based on the following arguments: (i) the 2,5-DHF$^{+\bullet}$ transforms by a first-order process showing no dependence on solute concentration into the second species. Deprotonation can be ruled out because it would have taken

Table 3 Hfs splitting constants *a*(H) for species observed in 2,5-DHF solutions (lw = linewidth)

Species	Calc. method or Matrix, Temp.	lw/mT	*a*(H)/mT
2,5-DHF$^{+\bullet}$	B3YP/6-31G*		**7.93** (H:6,7,10,11), **0.52** (H:8,9)
	CF$_3$CCl$_3$ 77 K	~0.27	**8.40** (4H), **0.57** (2H)
	F-113 77 K	~0.55	**8.45** (4H), **0.71** (2H)
2,4-DHF$^{+\bullet}$	B3YP/6-31G*		**3.96** (H:6,7), **3.8** (H:9,10), **2.58** (H:8), **0.4** (H:11)
	CF$_3$CCl$_3$ 77 K	~0.4	**3.87** (2H), **4.0** (1H), **3.6** (1H), **2.27** (1H), **0.02** (1H)
	140 K	~0.17	**3.85** (2H), **3.82** (2H), **2.27** (1H), **0.03** (1H)
	F-113 77 K	~0.55	**3.86** (2H), **4.1** (1H), **3.5** (1H), **2.27** (1H), **0.31** (1H)
DHF$^\bullet$	B3YP/6-31G*		**3.79** (H:6,7), **1.55** (H:8), **1.47** (H:10), **0.33** (H:9)
	CF$_3$CCl$_3$ 95 K	~0.4	**3.33** (2H), **1.41** (1H), **1.38** (1H), **0.3** (1H)
	150 K	~0.2	**3.63** (2H), **1.34** (2H), **0.2** (1H)
	F-113 95 K	~0.5	**3.52** (2H), **1.36** (2H), **0.3** (1H)
	120 K	~0.15	**3.63** (2H), **1.32** (2H), **0.2** (1H)

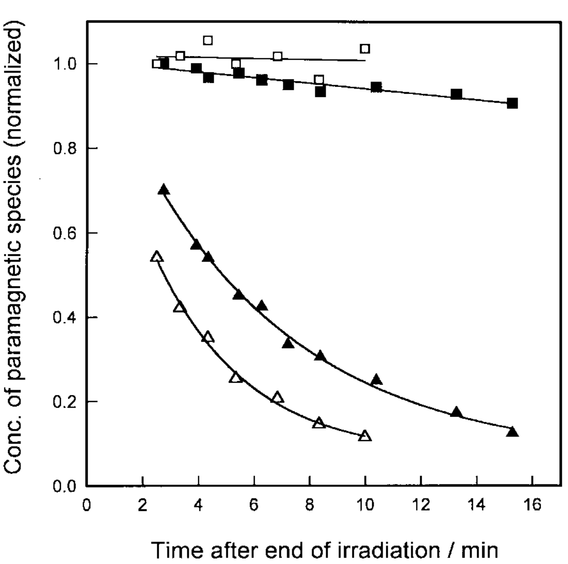


Fig. 4 Decay of 2,5-DHF$^{+\bullet}$ and time dependence of total spin concentration (integral) at 77 K in F-113: (▲) 2,5-DHF$^{+\bullet}$, (■) integral; and CF$_3$CCl$_3$: (△) 2,5-DHF$^{+\bullet}$, (□) integral. All data extrapolated and normalised at end of irradiation.

place most likely at the 2 or 5 position and would have led to the dihydrofuryl radical, with the spectrum shown in Fig. 1(*c*). (ii) The splitting constants measured (*cf.* Table 3) are typical for an α-proton (2.27 mT) and for magnetically nearly equal (symmetric) β-protons (approx. 3.9 mT) in a planar ring, and therefore agree with the suggested structure. (iii) In agreement with the observed values, the quantum chemical calculations predict splitting constants of 3.9 mT (2H), 3.8 mT (2H) and 2.6 mT (1H) for the 2,4-DHF$^{+\bullet}$ structure. In addition, the 2,4-DHF$^{+\bullet}$ is calculated to be more stable (B3YP/6-31*: 12 kJ mol^{-1}, PM3: 67 kJ mol^{-1}, *cf.* Table 2) than the 2,5-DHF$^{+\bullet}$, making the transformation favourable. The optical absorption spectra calculated show a strong line around 675 nm for the 2,5-DHF$^{+\bullet}$ but not for the 2,4-DHF$^{+\bullet}$, which complies with the observed colour change. The driving force for the 4,5-H-shift is probably the stabilisation of the cation radical by formation of a true distonic cation.

In CF$_3$CCl$_3$ matrix, this 2,4-DHF$^{+\bullet}$ is stable up to 140 K. A small reversible change of the linewidth from 0.4 mT (77 K) to 0.2 mT (140 K) is observed together with an equalisation of one set of splitting constants (3.6 mT (1H) and 4.0 mT (1H) at 77 K), to become 3.8 mT (2H) at 140 K. This effect is easily explained assuming that a true planar structure is present at higher temperatures only, due to motional averaging. At lower temperature a ring distortion with out-of-plane oxygen can occur, leading to a small tilt resulting in different splitting constants for the two β-protons at C-2. A similar but more pronounced effect is known for the tetrahydrofuran radical cation.[23] Raising the temperature to (or slightly above) the softening point of the matrix (145–150 K) the spectrum of the 2,4-DHF$^{+\bullet}$ disappears and the DHF$^\bullet$ is observed. The splitting constants (see Table 3) are exactly the same as found for the radical derived from deprotonation of the 2,3-DHF$^{+\bullet}$ (*cf.* Table 1).

In F-113 matrix, the 2,4-DHF$^{+\bullet}$ is stable at 77 K even for days (hfs-values in F-113 *cf.* Table 3). However, after raising the temperature to 95 K, contributions of the DHF$^\bullet$ are already obvious in the spectrum. The transformation continues slowly at this temperature, and is pronounced in the temperature range of 100–110 K. At low concentrations (<1:400, especially at 1:1100) small contributions of the 2,4-DHF$^{+\bullet}$ are present in the spectrum up to 130 K. Both the pronounced transformation in the range of ~100–110 K and the persistence of the 2,4-DHF$^{+\bullet}$ species in the spectrum up to 130 K (at low concentration) point strongly to an ion–molecule reaction. On the other hand, it is somewhat surprising that the transformation is observed already at 95 K as ion–molecule reactions usually do not take place at this temperature. One explanation may be that F-113 has no strict phase-transition point, but rather a transition region, which actually depends on the sample composition and preparation (fast or slow cooling, solute concentration and solubility at low temperature *etc.*).[16] Therefore, short-range diffusion especially of small cyclic molecules like DHF may be possible even at 95 K.

Effect of high solute concentration

The solute-to-solvent ratio was varied from 1:1100 up to 1:10, corresponding to a concentration range of 0.008 to 0.8 mol dm^{-3}.

With increasing concentration of 2,5-DHF (starting from a ratio of about 1:100) in both freons a third species appears with prevailing contribution to the overall EPR spectrum. At the same time, the relative concentration of the 2,5-DHF$^{+\bullet}$ measured 2.5 min after the irradiation decreases. Following the spectral changes with increasing solute concentration (Fig. 5) and comparing the additional features of the spectra with the transients identified so far, leads to the only possible conclusion that the third species is the DHF$^\bullet$ formed even at 77 K. (For clarity spectra are presented after decay of the 2,5-DHF$^{+\bullet}$and at 130 K. For justification, see below.) The decay of the remaining 2,5-DHF$^{+\bullet}$ at 77 K shows always the same decay rate independently of the solute concentration and leads again to the formation of the 2,4-DHF$^{+\bullet}$. Total spin concentration remains constant during this cation transformation as well as the relative spin concentrations of the DHF$^\bullet$ species, therefore it is evident that the DHF$^\bullet$ is produced only during irradiation. In CF$_3$CCl$_3$, upon warming to 130 K, the spectra become better resolved, but no further transformation is observed (*i.e.* the relative concentrations of the 2,4-DHF$^{+\bullet}$ and DHF$^\bullet$ do not change). The set of splitting constants derived for the DHF$^\bullet$

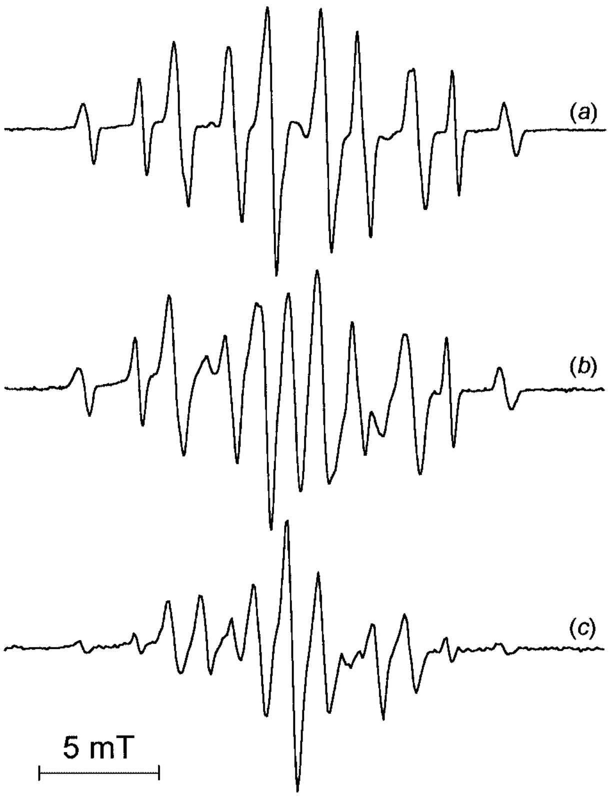


Fig. 5 EPR spectra of irradiated 2,5-DHF in CF_3CCl_3 matrix measured at 130–135 K. Solute-to-solvent ratio: 1 : 500 (*a*), 1 : 70 (*b*), 1 : 18 (*c*).

(*cf.* Table 3) changes slightly from 95 K to >135 K. This change is irreversible and may be due to some relaxation processes. In F-113 the behaviour is generally the same at 77 K; the transformation to the $DHF^•$ proceeds quickly after warming to 95 K and is complete at 110 K.

To explain the formation of the $DHF^•$ already at 77 K a closer look at the transformations at low concentrations is needed. Here the $DHF^•$ is formed most likely in an ion–molecule reaction, when diffusion in the matrices becomes possible (*i.e.* ~145 K in CF_3CCl_3 and 95–110 K in F-113). Therefore, the most probable reason for radical formation during irradiation at 77 K is the existence of "loosely associated DHF dimers", preformed on a statistical basis during the cooling process, being more likely at high concentrations. 2,5-$DHF^{+•}$ produced in such a "dimer agglomerate" would immediately deprotonate from the transition state because of loosely bonded protons, whereas non-associated 2,5-$DHF^{+•}$ still transform by H-shift into 2,4-$DHF^{+•}$.

In the case of 2,3-DHF, a high solute concentration has nearly no influence on the spectra recorded in F-113 at 77 and 95 K (*cf.* Fig. 6(*a*) and (*b*)). However, above a ratio of 1 : 20 and a temperature of 100 K a new four-line spectrum is observed (*cf.* Fig. 6(*c*)) before finally the $DHF^•$ appears above 105 K (*cf.* Fig. 6(*d*)). The four-line spectrum is best fitted with a doublet of doublets (3.07 mT (1H), 1.79 mT (1H), linewidth ≈ 0.9 mT). In CF_3CCl_3, up to a solute : solvent ratio of 1 : 50, the only significant observation is that the $DHF^•$ formation starts already at lower temperatures (*e.g.* about 130 K at 1 : 90 and 120 K at 1 : 55). At the highest concentration used (ratio of 1 : 17) the intensity of the 2,3-$DHF^{+•}$ spectrum at 77 K is decreased and the radical formation is observed already at ≥105 K. The spectra can no longer be satisfactorily fitted assuming 2,3-$DHF^{+•}$, $DHF^•$ and freon background only but the fit is essentially improved including the same transient with the four-line spectrum as found at high solute concentration in F-113 matrix.

Our explanation is based generally—as in the case of 2,5-DHF—on the formation of "dimers" at high solute concentration. In contrast to 2,5-$DHF^{+•}$ the 2,3-$DHF^{+•}$ is more stable (about 85 kJ mol^{-1} (PM3 and DF)) and therefore additional thermal energy (temperature increase) is needed for the ion–molecule reaction to occur in CF_3CCl_3 matrix. In F-113 matrix the spectrum transformation is observed in the same temperature interval in which the 2,4-$DHF^{+•}$ species converts into the $DHF^•$.

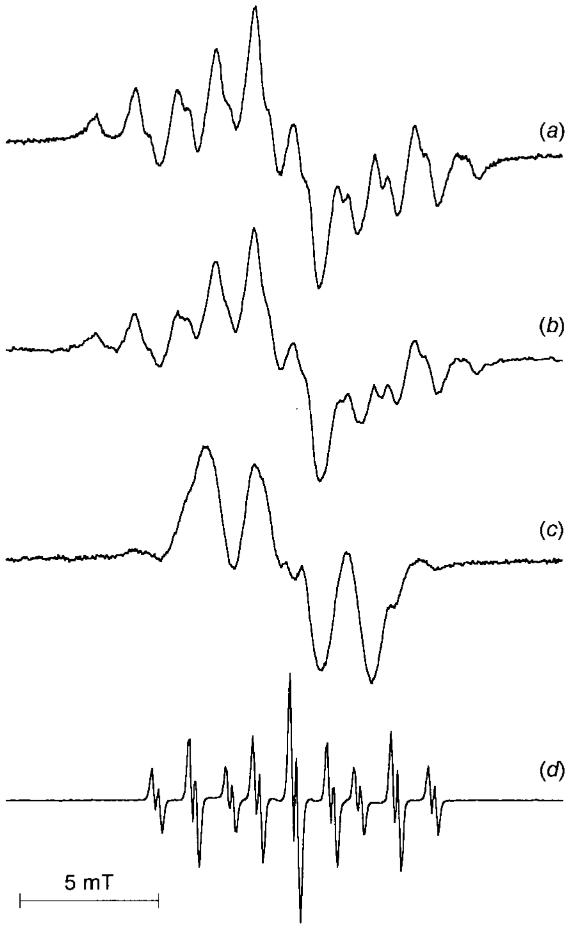


Fig. 6 EPR spectra of irradiated 2,3-DHF in F-113 matrix. Solute-to-solvent ratio and temperature: (*a*) 1 : 400, 95 K; (*b*) 1 : 20, 95 K; (*c*) 1 : 20, 100 K; (*d*) 1 : 20, 125 K.

The four-line spectrum is difficult to interpret, in particular the broad linewidth probably hides some additional smaller splittings, needed for a proper assignment. A suggestion to assign this spectrum to an intermediate dimer radical cation will be discussed in the next paragraph.

Discussion of possible reactions

It has been shown that all three cationic intermediates transform into $DHF^•$ radicals in an ion–molecule reaction either when matrix softening allows diffusion or when solute dimers are preformed at higher concentrations. It cannot be distinguished whether these radicals are formed by a deprotonation (neutral molecule acting as a proton acceptor) or by a hydrogen abstraction from the neutral molecule, as $DHF^•$ radicals formed in either of the reactions show the same EPR spectrum. However, some arguments in favour of one of both reactions can be drawn from the decay behaviour and from the quantum chemical calculations. The 2,5-$DHF^{•+}$ was found to be rather unstable even at 77 K. The quantum chemical calculations show that the spin density is delocalised and that the four protons in the neighbourhood of oxygen carry half of the positive excess charge. Therefore deprotonation seems to be very likely if a proton acceptor is available. (Otherwise the 2,5-$DHF^{+•}$ transforms by H-shift into the 2,4-$DHF^{+•}$.)

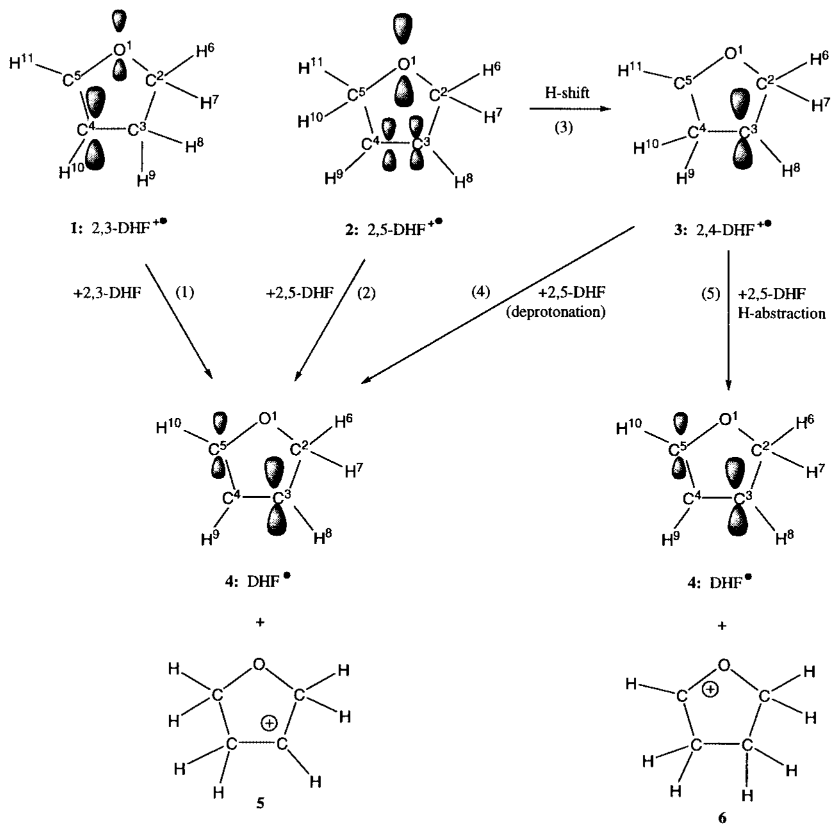
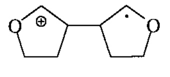


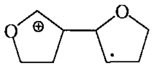
Fig. 7 Reaction scheme and numbering of atoms.

During the decay of 2,4-DHF$^{+•}$ the DHF$^•$ is evidently formed but both possible reactions—with a 2,5-DHF molecule—lead to different types of counter cations **5**, **6** (*cf.* Fig. 7, reactions (4) and (5)). The energy balance calculated for these reactions predicts hydrogen abstraction (reaction (5)) to be favoured over deprotonation (reaction (4)) by about 125 kJ mol^{-1}. Additionally, as the spin is nearly completely localised at C-3, hydrogen abstraction is the most likely reaction for this distonic cation radical of 2,4-DHF.

The 2,3-DHF$^{+•}$ has been calculated to be much more stable than the 2,5-DHF$^{+•}$. This agrees completely with the results of gas-phase mass spectroscopic investigations on the DHF cations.[10] The positive charge is mainly distributed over the conjugated π-systems of the vinyl group and oxygen. According to our experimental results in a freon matrix, ring-opening, suggested as one possible reaction path in the gas phase,[10] can be ruled out. The quantum chemical calculations also show that ring-opening is energetically unfavourable ($\Delta E = 108$ kJ mol^{-1}). The calculated charge distribution makes deprotonation less likely too, as none of the CH_2-groups carries significant positive charge. The spin density distribution given in Table 2 (60% of spin is localised at C-4) strongly suggests that the 2,3-DHF$^{+•}$ reacts preferably as a radical, *i.e.* hydrogen abstraction is more likely (at low solute concentration). The four-line spectrum observed at high 2,3-DHF concentrations is tentatively assigned to an intermediate dimer radical cation **7** formed by addition of the 2,3-DHF$^{+•}$ to the C-4 position of the other 2,3-DHF molecule.



7



8

The spin density in this distonic dimer radical cation is highly localised (60% (B3LYP/6-31G*)) at the C-5 position, therefore hfs-values corresponding to one α-proton and only one β-proton with a much larger splitting constant, are expected. Taking the reduced spin density at C-5 into account, the observed values of 1.79 mT (1H) and 3.07 mT (1H) agree well with our assignment. The second possible dimer **8** with a bond between C-4 and C-5 atoms of both molecules is energetically slightly less favourable (2.5 kJ mol^{-1}); hfs splittings due to one α-proton and three nearly equal β-protons would be expected, in disagreement with the observation. However, some minor contribution to the broad four-line spectrum cannot be excluded. The dimer cation radical **7** decays during temperature increase forming the DHF$^•$.

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