PERKIN 2

EPR study of methyl and ethyl acrylate radical cations and their transformations in low-temperature matrices

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Received (in Cambridge, UK) 19th June 2001, Accepted 14th January 2002
First published as an Advance Article on the web 11th February 2002

Using low-temperature EPR spectroscopy, transformations of radical cations of methyl (MeA) and ethyl acrylate (EtA) radiolytically generated in freon ($CFCl_2CF_2Cl$, CF_3CCl_3 and $CFCl_3$) and in argon matrices were investigated. The assignment of the EPR spectra was made with the help of partially deuterated acrylates, namely ethyl-d_2 (EtA-d_2) and ethyl-d_5 acrylates (EtA-d_5) and methyl-d_3 acrylate (MeA-d_3). In addition, quantum chemical calculations were performed to obtain information on the electronic structure, the hfs constants and energy levels of the transient species observed. The primary radical cations show broad singlet spectra ($\Delta H_{pp} \approx 1.4$ mT) and transform quickly by hydrogen transfer from the ester group to the carbonyl oxygen leading to distonic radical cations. This transformation can be observed directly at 77 K in the case of the MeA leading to $CH_2{=}CH{-}(COH)^+{-}OCH_2^{\bullet}$ ($a(2H_\alpha) = 2.24$ mT, first-order rate constant in CF_3CCl_3: 1 h^{-1}). The primary cation of EtA could be trapped below 40 K in a $CFCl_3$ matrix only. In all the freon matrices studied, the intramolecular rearrangement of this cation yields the $CH_2{=}CH{-}(COH)^+{-}OCH_2CH_2^{\bullet}$ terminal-type distonic radical cation. The conformation of the latter species in polycrystalline $CFCl_3$ and CF_3CCl_3 matrices corresponds to the calculated minimum close to the transition state geometry. In the case of CF_3CCl_3 matrix, warming the samples to temperatures above 130 K results in the simultaneous formation of two new species, which were assigned to six- and five-member ring structures (a(H)/mT: 2.36 (H_α), 5.13 ($H_{\beta1}$), 1.9 ($H_{\beta2}$) and 2.27 ($2H_\alpha$), 2.6 (H_β), respectively) formed by intramolecular cycloaddition of the terminal radical to the vinyl double bond. The formation of the propagating radical $-CH_2{-}CH^{\bullet}{-}R$ due to an ion-molecule reaction is observed in $CFCl_2CF_2Cl$ at temperatures above 98 K; this process was also detected in other freons under the conditions of matrix softening. The primary radical cation of EtA is not trapped in an argon matrix even at 16 K due to the realisation of the "high-energy" reaction paths yielding methyl radicals and, probably, rearrangement products.

Introduction

Acrylate monomers and oligomers are frequently used as main components in radiation and UV curable formulations. Most of the publications available are devoted to the study of the free radical polymerisation kinetics, especially after photo-initiation (see *e.g.* proceedings of RadTech conferences[1,2]). On the other hand, in the case of electron-irradiated acrylates, it was shown that short-lived ionic species precede the formation of different types of primary and secondary radicals capable of initiating polymerisation and forming reactive sites for cross-linking (see Mehnert *et al.*[3] and references therein). Pulse radiolysis was applied to study spectroscopic and kinetic properties of short-lived radical ions and radicals and to investigate the mechanism of electron beam curing.[4,5] Acrylate radical cations were identified in irradiated neat acrylates together with other ionic and radical species. To avoid complication by superposition of time profiles and transient optical absorption spectra in neat acrylates, the properties and kinetics of acrylate radical cations were investigated in *n*-butyl chloride solutions, where solute radical cations are formed by positive charge transfer from the solvent primary cations. The transient optical spectra of acrylate radical cations were found to be broad and unspecific[5] and do not give direct structural information.

Low-temperature, solid state EPR has been very successfully applied to structural studies of organic radical cations produced by γ-ray or fast electron irradiation of dilute solutions of the parent molecule in freon matrices.[6,7] Using this technique made it possible to characterise the radical cations of a large number of unsaturated compounds including some typical vinyl monomers.[8–10] As a rule, the isolated radical cations of simple vinyl compounds are stable enough at 77 K, and the structural interpretation of their EPR spectra is quite straightforward. However, the spectra observed for methyl acrylate irradiated in freon matrices[8,9,11] were not assigned convincingly. On the other hand, formation and reactions of the radical cations produced from saturated esters (mainly, formates and acetates) have been investigated extensively in freon matrices.[12–17] The primary radical cations of these esters were found to be extremely unstable even at low temperatures (below 77 K). All the ester radical cations studied undergo intramolecular rearrangement (H shift) to yield the corresponding distonic species; in certain cases this rearrangement may be followed by further secondary reactions.[12,17] From a rough structural point of view one may consider the acrylate molecules as consisting of two fragments with rather close ionisation potentials (*i.e.*, vinyl moiety and ester moiety). For this reason, elucidation of actual structure and reactivity of the acrylate radical cations is of specific chemical interest.

An important feature of the freon matrix studies is related to specific matrix effect on the stability and reactions of the trapped radical cations. The variations in the observed reactivity of the radical cations in different freons results, most probably, from the variations in matrix microstructure and

DOI: 10.1039/b105384c

thermal behaviour. In particular, in the cases of polycrystalline $CFCl_3$ and CF_3CCl_3 matrices, the diffusion-controlled bimolecular reaction of the trapped radical cations normally do not occur up to relatively high temperatures (140–150 K), whereas intramolecular rearrangement and fragmentation processes can be observed in the same temperature region.[6,18] On the other hand, the radical cations trapped in a $CFCl_2CF_2Cl$ matrix typically undergo ion–molecule reactions upon warming the samples to 100–110 K because of an increase in molecular diffusion mobility near the matrix softening point.[18,19] Thus, comparative studies of the behaviour of particular radical cations in different freon matrices are especially useful since they may provide important mechanistic clues.

In addition to common freon matrix experiments using the frozen solution samples, recently we applied a more rigorous matrix isolation procedure based on deposition technique to characterise some medium-size organic radical cations and their transformations in freon and solid rare gas matrices.[20,21] In the present work this approach was used as a supplementary method in order to get more details on the effects of matrix and temperature on the stability of the ethyl acrylate radical cation. Although a large series of mono- and difunctional acrylates has been investigated, we present here the results on MeA and EtA only, because both these acrylates show well-resolved EPR spectra and they are of key importance in understanding the matrix dependent transformations of the other acrylate radical cations.

Experimental

Ethyl acrylate (EtA, Merck, > 99%), methyl acrylate (MeA, Aldrich, 99%), 1,1,2-trifluorotrichloroethane (Freon-113, Merck, Uvasol 99.9%), trichlorofluoromethane (Khimprom, Volgograd, Russia, 99.95%) and high purity argon (> 99.99%) were used as received. 1,1,1-Trifluorotrichloroethane (Aldrich, 99%) was purified by passing it through a column filled with neutral Al_2O_3. Partially deuterated acrylates were synthesized according to standard procedures from acrylic acid (Fluka, ≥ 99%) and methanol-d_3, ethanol-d_2 and ethanol-d_5 (DeuChem GmbH, >99%), respectively, and were purified by distillation. The second of 3 fractions was used in the experiments. The purity was checked by GC to be >99%.

The EPR experiments in $CFCl_2CF_2Cl$ and CF_3CCl_3 matrices were performed at IOM (Leipzig) 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 100 μW and a modulation amplitude of 0.05 mT. The acrylates were dissolved in freons at solute : solvent molar ratios of typically 1 : 200 (1 : 1600 to 1 : 9 in special cases). The solutions were carefully degassed by 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 *ca.* 1 min) was sufficient to generate an easily observed concentration of paramagnetic species. Irradiated samples were protected from light and the first spectrum was taken as soon as possible (within 2–3 min) after irradiation. EPR spectra were measured at 77 K usually up to 30 min after irradiation and then in the temperature range of 95–150 K (further details have been described recently[10]).

Different procedures were used in the experiments with $CFCl_3$ and argon matrices carried out at the Karpov Institute (Moscow). The samples were obtained from gaseous mixtures of known composition. In the case of irradiation at 77 K, the mixtures of $CFCl_3$ and ethyl acrylate were condensed into cooled SK-4B glass ampoules, which gave no appreciable EPR signal upon irradiation, and sealed under vacuum. The ampoules with solutions prepared in this way were kept at room temperature and frozen rapidly in liquid nitrogen before irradiation. The samples were irradiated with ^{60}Co γ-rays at 77 K using a K-120000 unit. The total absorbed dose was *ca.* 10 kGy (irradiation time 40 min). The EPR spectra of irradiated samples were measured approximately 1 h after irradiation at 77 K and in the temperature range of 100–150 K.

A custom-made continuous-flow helium cryostat with vacuum resonator cavity designed at the Karpov Institute of Physical Chemistry was used for the EPR studies of samples irradiated at 16 K. The samples were obtained by slow controlled deposition of the gaseous mixtures through a needle valve onto the cooled sapphire rod inserted into the resonator cavity. The deposition temperature was 45–50 K (in the case of a $CFCl_3$ matrix) or 18–20 K (in the case of an argon matrix); typical deposition time was 1 to 2 h. After the deposition was complete, the samples were cooled down to 16 K and irradiated with fast electrons using an EG-2.5 Van de Graaf accelerator (electron energy of *ca.* 1.2 MeV) to a total absorbed dose of 20 kGy. Other details of the cryostat and experimental technique used are described elsewhere.[20,21]

At the Karpov Institute (Moscow), the EPR spectra were measured using an X-band spectrometer (9.4 GHz, 100 kHz modulation) manufactured by SPIN (St. Petersburg, Russia), operated under control of a PC-based system. The microwave power level was kept low in order to avoid the saturation of the EPR signal, especially at the lowest temperature (typically, 5–10 μW for measurements at 16–60 K, and 50–100 μW for measurements at 77 K and higher temperatures).

Spectra simulations were performed using the WinSim software[22] and the SimFonia program from BRUKER.

Quantum chemical calculations

Quantum chemical calculations were done using the density functional theory (DFT) hybrid B3LYP[23,24] method with standard 6-31G(d) basis set (Gaussian 98 progam,[25] Rev. A9). The equilibrium geometries and transition structures were optimised completely without any restriction; then the energy of the systems, the electronic structures, the atomic spin densities, and the Mulliken atomic charge distributions for the neutral radicals and the radical cations were calculated. The calculation of the hyperfine structures (hfs) is helpful for the identification of the transients.[10,26] The isotropic hyperfine coupling constants were calculated as part of the population analysis with the B3LYP/6-31G(d) method. To test the solvent effect (freon, relative permittivity ε = 2.4) on atomic spin and Mulliken charge distribution, the calculations with the geometry optimisation in dielectric continuum were also made using the Onsager model (Dipole & Sphere) implemented in the Gaussian 98 program. The results show only a relatively small solvent effect on the geometrical parameters, the spin and charge distributions in comparison with vacuum. This is not surprising as the investigated systems have relatively small dipole moments.

Calculation of symmetry and energy levels of the singlet state of molecules was performed using HF/6-31G(d) on DFT/B3LYP geometries, as HF is known to reproduce these values better than DFT.[27]

Results and discussion

Methyl acrylate in freon matrix, irradiated at 77 K

EPR spectra of frozen solutions of methyl acrylate in Freon-113 irradiated at 77 K are shown in Fig. 1(*a*)–(*d*). The spectrum recorded immediately (approx. 3 min, Fig. 1(*a*)) after irradiation at 77 K reveals an unresolved singlet with an approximate overall peak-to-peak linewidth of 1.4 mT. While keeping the sample at 77 K in the dark for a longer time, an irreversible transformation into a binomial triplet (a(2H) = 2.27 mT, linewidth ≈ 0.7 mT) is observed. The new lines become visible *ca.* 20 min after irradiation and the transformation is completed

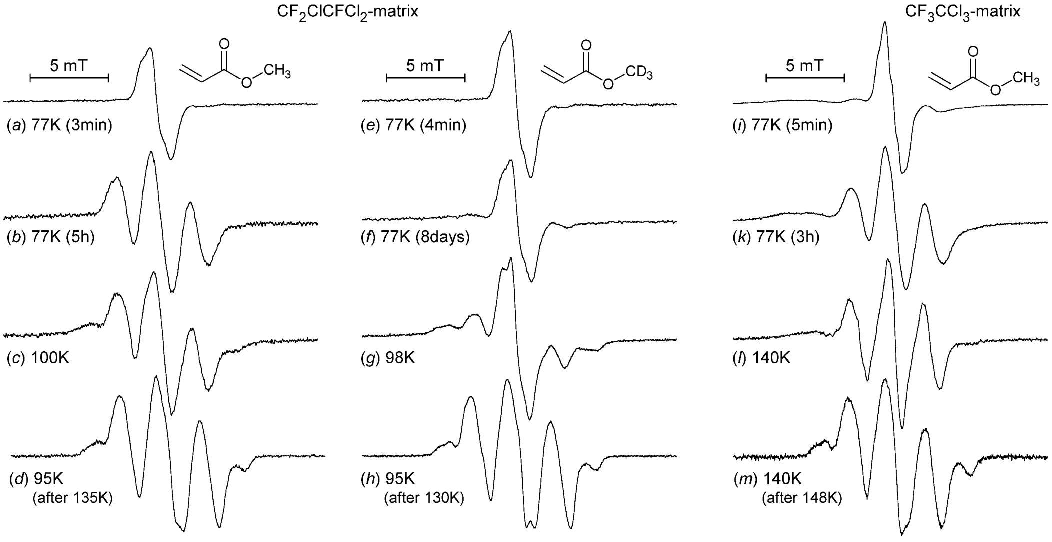


Fig. 1 EPR spectra of frozen solutions of methyl acrylate in freon matrices. (*a*)–(*d*) methyl acrylate in $CFCl_2CF_2Cl$ (1 : 410); (*e*)–(*h*) methyl-d_3 acrylate in $CFCl_2CF_2Cl$ (1 : 440) and (*i*)–(*m*) methyl acrylate in CF_3CCl_3 (~1 : 100) Solutions were irradiated at 77 K and measured at the temperatures indicated and at the time after the end of irradiation given in parentheses for 77 K spectra. Spectra (*d*), (*h*) and (*m*) are recorded after short annealing to the temperatures given in parentheses.

~5 h later (Fig. 1(*b*)). The transformation rate constant of ~0.47 h^{-1} does not change significantly (<5%) in the concentration range of 1 : 1680 to 1 : 170 (Fig. 2) and the overall spin concentration remains nearly constant. Illumination with visible light increased significantly the rate of transformation. A similar behaviour is observed at 77 K in CF_3CCl_3 matrix (Fig. 1 (*i*),(*k*)). Here, the transformation to the triplet (a(2H) = 2.24 mT) proceeds faster with a rate constant of ~1 h^{-1} and the spectra are slightly better resolved due to a smaller natural linewidth in this matrix. In Freon-113 the triplet seems to be stable when the samples are warmed to 95 K, but already at 98–100 K new sidebands appear in the spectrum with an overall splitting of ~9 mT (Fig. 1(*c*)). Further warming to 120–130 K leads to a final five-line spectrum with slightly improved resolution (Fig. 1(*d*)), which is stable upon cooling down. In CF_3CCl_3 the triplet is stable upon warming up to 140 K (Fig. 1(*l*)). Only after annealing the sample for a short time at 148 K (which is above the phase transition point of this matrix at 145 K) is the formation of the five-line spectrum observed (Fig. 1(*m*)).

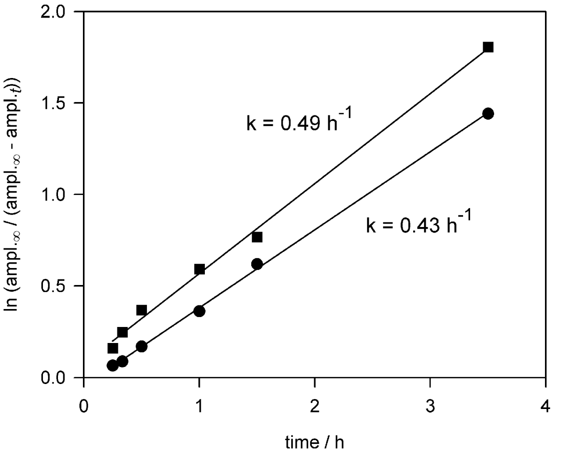
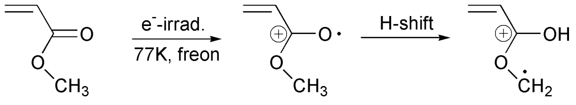


Fig. 2 Transformation of the primary radical cation of methyl acrylate in $CF_2ClCFCl_2$ at 77 K. Kinetics determined from the amplitude of the outer triplet lines. The total spin concentration remains nearly constant during the time followed. Molar ratios of methyl acrylate : freon are 1 : 1680 (●) and 1 : 170 (■).

There is only a few data available in the literature, which may contribute to the discussion of the observed spectra. Triplet spectra with coupling constants of ~2.5 mT have already been measured after γ-irradiation of a frozen MeA/CF_3CCl_3 solution,[8,9] but no singlet was observed. A tentative assignment of the triplet spectrum to the primary radical cation of MeA, assuming spin density is localised at the vinyl group, was rejected later,[11] when the authors reported a primary singlet spectrum after X-ray irradiation of a frozen MeA/CF_3CCl_3 solution. This singlet transformed into the triplet upon photobleaching. In the light of our results it is most likely that Tabata and Lund failed to observe the initial singlet in the case of γ-irradiation because the transformation had already had time to proceed during the irradiation (usually up to hours to apply a similar dose). The singlet spectrum can be reasonably well assigned to the primary radical cation **1a**, bearing the largest spin density at the carbonyl oxygen (detailed structure of this species will be discussed later).



1a **2a**

The triplet spectrum needs further discussion. The interpretation of the triplet as due to some "intermediates" appearing in the transformation from radical ion to polymer radicals[11] has to be rejected and the triplet should be assigned to the rearranged (distonic) cation **2a** (which was explicitly excluded by Tabata *et al.*[11]) for the following reasons: (i) the transformation observed at 77 K in the dark is of first order and the rate constant does not depend on the MeA concentration (Fig. 2), as expected for a unimolecular rearrangement reaction; (ii) the triplet is stable up to 140 K in a CF_3CCl_3 matrix; in this matrix ion–molecule reactions usually do not occur below 145 K, which is certainly true for the very low solute concentration of 1 : 1680 used; (iii) hydrogen atom migration to the carbonyl oxygen was—after a very controversial discussion—finally accepted (*cf.* ref. 15 and references therein) to explain a similar triplet spectrum found for the methyl formate radical cation. In this case hydrogen migration proceeds even at temperatures as low as 10 K.[15] It is very likely that we observe an analogous rearrangement reaction. The rate of transformations differ in both matrices roughly by a factor of 2, which may be explained by a stronger interaction with the matrix known for Freon-113, stabilizing the primary radical cation. Nearly the same factor of 2 has been observed recently for a hydrogen shift in case of the 2,5-dihydrofuran radical cation in both matrices.[10]

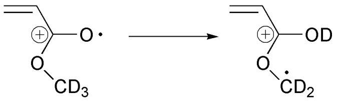
The appearance of the five-line spectrum at temperatures above 145 K in CF_3CCl_3 points to a species formed in an ion–molecule reaction because such reactions are usually not observed in this matrix below 145 K. Such interpretation is in line with the observation of the five-line spectrum in Freon-113 at much lower temperatures, as this matrix is commonly used to study ion–molecule reactions at temperatures around 105–110 K. Similar five-line spectra have been observed during photopolymerisation of MeA in the frozen state (170 K) and were explained by overlapping spectra of two conformers[28] of the propagating radical **8**. The same propagating radical is obviously formed in our experiments. It should be noted, that it is surprising to see first indications for such an ion–molecule reaction at temperatures as low as 98 K in the present case, but the same behaviour is found for EtA (see later).

$$-CH_2-\dot{C}H-COOR$$

8

To assist the assignments made so far, MeA with a deuterated methyl ester group (MeA-d_3) was synthesised. EPR spectra of frozen solutions of MeA-d_3 in Freon-113 irradiated at 77 K are shown in Fig. 1(*e*)–(*h*). The spectrum recorded immediately after irradiation at 77 K reveals an unresolved singlet (ΔH_{pp} = 1.33 mT, (Fig. 1(*e*)) as in the case of non-deuterated MeA (Fig. 1(*a*)). Keeping the sample at 77 K in the dark, even after 8 days only a slight broadening of the singlet is observed Fig. 1(*f*). Warming the sample to 98 K leads to the appearance of an additional species (five lines, *cf.* (Fig. 1(*g*)), with an overall splitting comparable to the separation of the outer lines in the case of non-deuterated MeA (Fig. 1(*c*) and (*d*)). Upon further warming to 130 K the contribution due to the singlet completely disappears and the remaining five-line spectrum is the same as in the case of MeA (compare (Fig. 1(*h*) with (*d*) and (*m*)).

The experiments with MeA-d_3 clearly support the idea that the transformation from singlet to triplet in the case of MeA is connected with a radical resulting from the methyl ester group, because no triplet is formed for MeA-d_3. There are two possible explanations for the singlet in the case of MeA-d_3: it can be either due to the primary radical cation **1b** or the rearranged species **2b** where the splitting due to the two α-deuterons is not resolved.



1b **2b**

To differentiate between both possibilities it is worth recalling the rather large deuterium isotope effect reported for methyl formate in the $CFCl_3$-matrix.[29] In this matrix the primary cations are stabilised by formation of strong complexes with solvent molecules. For non-deuterated methyl formate these complexes are destroyed upon temperature increase to 110 K or photo-illumination under formation of the H-transfer radical $H(COH)^+OCH_2^{\bullet}$, but in the case of methyl-d_3 formate the complexes are stable to temperatures near the melting point of the matrix (~150 K). We may therefore assume that the D-migration for MeA-d_3 would proceed at higher temperatures or with a much lower rate (in comparison with H-migration for MeA) only, and that the singlet observed at 77 K even after days (Fig. 1(*f*)) is due to the primary cation **1b** of MeA-d_3 stabilised by the isotope effect. Note that the shape of the singlet does not change at all within 8 days and is still the same as the singlet for MeA (Fig. 1(*a*)).

The final five-line spectrum for both MeA and MeA-d_3 (Fig. 1(*d*)) and (*h*)) supports the assignment to the propagating radical **8** as the deuterated side group would have no influence on the observed splitting. A detailed discussion of the five-line spectrum is beyond the scope of our paper and we refer to the paper by Sugiyama.[28]

Ethyl acrylate in $CFCl_3$ matrix, irradiated at 77 K

EPR spectra of frozen solutions of ethyl acrylate in $CFCl_3$ irradiated at 77 K are shown in Fig. 3. The spectra can be generally analysed as triplets of doublets with the hyperfine coupling constants of *a*(2H) = 2.25 mT and *a*(1H) ≈ 1.6 mT. The spectrum recorded at 77 K is somewhat distorted, so its shape cannot be reproduced adequately by isotropic simulations. Most probably, the spectrum is affected by incomplete averaging of anisotropic coupling due to slow tumbling. Warming the sample to 110–130 K results in reversible line broadening, whereas the signal shape becomes more isotropic and can be fitted well enough by a simple simulation as shown in Fig. 3(*c*). The spectrum exhibits a significant change at the temperatures above 140 K to yield a triplet of triplets with a_1(2H) = 2.25 mT and a_2(2H) = 0.95 mT. Although the transformation is accompanied by some decay of the observed radicals at high temperatures, qualitatively it is still reversible. It is worthwhile noting that rather similar spectra were observed previously for ethyl formate irradiated in the same freon matrix.[13,15,29,30] Early interpretations of the latter spectra were conflicting; however, on the basis of experiments with specifically deuterated esters, finally they were assigned to the rearranged distonic radical cations $H(COH)^+OCH_2CH_2^{\bullet}$ resulting from intramolecular H transfer from the methyl group to the carbonyl oxygen.[15,29] As this transfer occurs from the

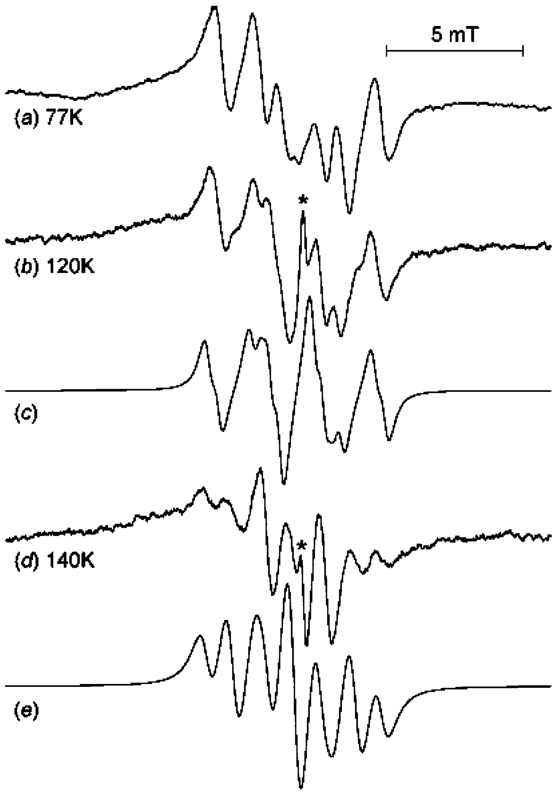
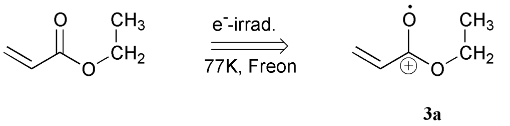
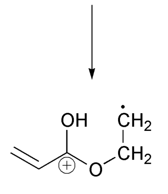


Fig. 3 EPR spectra of a frozen solution (1 : 250) of ethyl acrylate in $CFCl_3$ irradiated at 77 K and measured at the temperatures indicated (*a*), (*b*) and (*d*); (*c*) and (*e*) simulated spectra. The hfc parameters used in the simulation for: (*c*) a_1(2H) = 2.25 mT; a_2(1H) = 1.6 mT and for (*e*): a_1(2H) = 2.25 mT; a_2(2H) = 0.95 mT. A sharp feature marked with asterisks results from the quartz Dewar insert.



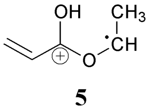


4a

ethyl moiety of the ester molecule, it is quite logical to make similar assignments for ethyl acrylate (structure **4a**).†

In this case, the coupling of 2.25 mT is due to two α-protons, whereas the coupling of *ca.* 1.6 mT results from a single β-proton, and the other β-proton does not yield observable hyperfine coupling. Taking into account the so-called "$\cos^2\theta$ rule", such a situation can be rationalized in terms of a conformation corresponding to the dihedral angles between the C–H_β bonds and unpaired electron orbital axes of $\theta_1 \approx 50°$ and $\theta_2 \approx -70°$. If the former proton is responsible for a 1.6 mT coupling, the latter one should have a coupling constant of *ca.* 0.4 mT, which cannot be resolved under the conditions of this experiment. The two β-protons become equivalent at high temperatures (above 140 K) yielding the hyperfine splitting of *ca.* 0.95 mT observed in the spectra. Note that this splitting most probably results from rapid interconversion between two equivalent conformers and not from formation of a "rigid" structure with $\theta_1 = \theta_2 = 60°$ since in the latter case one should expect irreversible relaxation to a more stable state. One can see that interconversion is actually induced by relatively small torsional oscillations. The dynamic nature of the effect is well illustrated by the temperature dependence of the spectrum, which exhibits first significant line broadening at elevated temperatures and then reveals dynamic equivalence of the two protons, when the frequency of oscillations becomes high enough on the EPR timescale. In the case of ethyl formate, the barrier for such interconversion was estimated to be as low as 7 kJ mol^{-1},[29] which is qualitatively consistent with the observed thermal behaviour. At first glance, the *Bρ* value derived from the conformational analysis ("$\cos^2\theta$ rule") appears to be unexpectedly low (*ca.* 3.9 mT); nevertheless it is virtually the same as in the case of the radical produced from ethyl formate. Considerable reduction of the apparent *Bρ* value observed for some terminal alkyl radicals was explained by dynamic effects.[31]

It should be noted, that a distonic secondary $R(COH)^+$-$OCH^{\bullet}CH_3$ type radical cation (structure **5**), formed by H-shift from the methylene group, would be in disagreement with the observed experimental spectrum. Such a radical cation is expected to show nearly a quintet pattern due to one α-proton (~2.2 mT) and three β-protons of the methyl group having coupling constants of approximately 2.5 mT.



5

Our assignment is supported by the experiments with partially deuterated ethyl-d_2 acrylate (see below). The fact that the distonic radical cation **5**, which would be thermodynamically more stable than **4** (*cf.* Table 1), is obviously not formed, will be dicussed later (see the section on Structure and stability of primary cations).

Ethyl acrylate in $CFCl_3$ matrix, irradiated at 16 K

EPR spectra obtained after irradiation of a deposited $CFCl_3$ matrix containing ethyl acrylate at 16 K (Fig. 4) show remarkable differences from those recorded after irradiation of polycrystalline samples (frozen solutions) at 77 K. The spectrum recorded immediately after irradiation at 16 K (Fig. 4(*a*)) reveals an unresolved singlet signal with a total linewidth of *ca.* 1.4 mT superimposed with a broad multiplet (presumably, quintet). The spectrum does not change upon warming the sample to 30 K; however, annealing at 40 K results in considerable irreversible loss of the singlet signal, whereas the multiplet becomes more prominent as shown in Fig. 4(*b*). Detailed consideration reveals that the multiplet is not a true quintet, since the lines are not equidistant, and, probably it does not belong to a single species. The singlet is not observed at the temperatures above 70 K. Further warming of the sample results in spectral changes, which become reversible after first warming to 130–140 K. The spectrum recorded at 140 K looks like a rather broad quintet of nearly equidistant lines with the splitting of *ca.* 2.2–2.3 mT (Fig. 4(*c*)). Annealing is accompanied by a certain loss of paramagnetic species; nevertheless, it is difficult to obtain quantitative data because of the presence of a broad background signal. The singlet signal was not observed upon irradiation of ethyl acrylate in any freon matrix at 77 K; however, as shown in the previous chapter, a similar singlet was recorded for methyl acrylate in a CF_3CCl_3 matrix. Note that in the case of methyl acrylate the singlet signal was found to be unstable even at 77 K. Following the considerations made for MeA we tentatively assign the singlet to the primary radical cation of ethyl acrylate (structure **3a**). Further detailed considerations of structure and reactivity of this species will be addressed later.

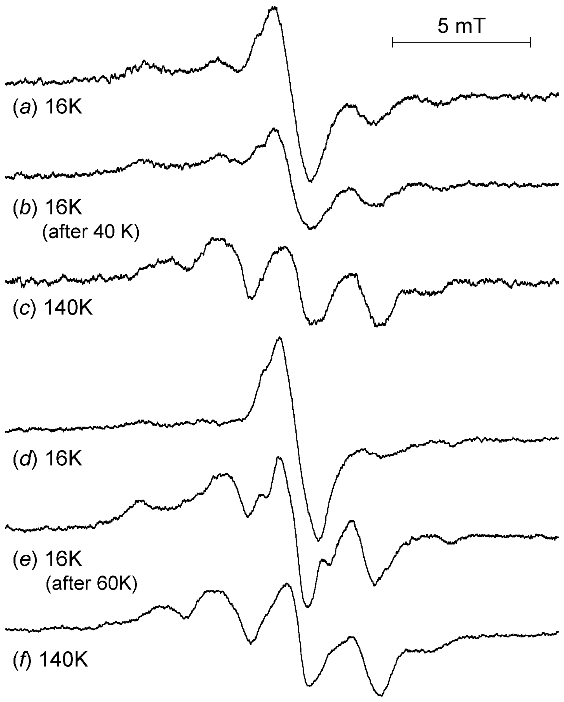


Fig. 4 EPR spectra of solid deposited mixtures of ((*a*)–(*c*)) ethyl acrylate–$CFCl_3$ (1 : 200) and ((*d*)–(*f*)) ethyl-d_2 acrylate–$CFCl_3$ (1 : 500) irradiated with fast electrons at 16 K and measured at the temperatures indicated.

The more stable multiplet signal should be assigned to an alkyl-type radical in view of its characteristic proton couplings. In principle, this may result from a rearrangement product (distonic radical cation of $RCH_2CH_2^{\bullet}$ type) or propagating radical. Regarding the former species, we should note that the total spread of the spectrum observed at and above 40 K is

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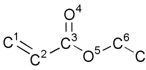
† Bold characters **a**, **b** and **c** denote species derived from ethyl, ethyl-d_5 and ethyl-d_2 acrylates, respectively.

Table 1 Quantum chemical calculation (DFT/B3LYP) of spin density distribution ρ, dihedral angles θ_i and total energies ΔE for species under investigation. **3**⟶**4** denotes transition state for the H-transfer

			Ethyl acrylate							
	Methyl acrylate				Conformer of **4**					
	**1**	**2**	**3**	**3**⟶**4**	1	2	3	**5**	**6**	**7**
$\rho(C^1)$	0.282	0.100	0.288	−0.007	0.014	0.003	0.000	0.279	0.045	1.067
$\rho(C^2)$	0.159	−0.049	0.199	0.058	−0.005	0.003	0.000	−0.132	0.761	−0.064
$\rho(C^3)$	−0.048	0.131	−0.054	−0.039	0.001	0.004	−0.001	0.243	0.047	0.053
$\rho(O^4)$	0.623	0.049	0.572	0.681	−0.001	0.001	0.000	0.056	0.077	0.003
$\rho(O^5)$	−0.001	−0.050	0.006	0.025	0.043	0.063	0.001	−0.087	0.112	0.001
$\rho(C^6)$	0.001	0.919	0.002	−0.009	−0.021	−0.002	−0.075	0.686	−0.004	0.007
$\rho(C^7)$	—	—	0.000	0.269	1.027	1.009	1.088	−0.052	0.008	0.020
$(\theta_1/\theta_2)/°$				37/83[a]	39/86	60/68	28/28			
ΔE/kJ mol^{-1}[b]	0	−27.8	0	+37.6	+16.3	−5.44	+2.1	−29.3	−131.3	−79.03

[a] Dihedral angles for transition state are given with respect to the corresponding C–H bond of the transferred H-atom. [b] Relative to primary cation **1** and **3**, respectively.

substantially larger in comparison with that observed in a polycrystalline $CFCl_3$ matrix at 77 K. Thus, if the spectrum recorded in the deposited matrix also belongs to the same radical, the conformation of the radical should be quite different. However, as the lines are broad enough, and actual hyperfine structure is not well defined, we cannot exclude contributions from other species or different configurations of this radical. The spectral pattern observed at 140 K is rather close to the spectrum of the propagating radical, which has a similar structure as in the case of MeA (see above); alternatively, it could be assigned to the $RCH_2CH_2^{\bullet}$ type radical undergoing free rotation.

In order to get more clarity, we have studied a specifically deuterated ethyl-d_2 acrylate (EtA-d_2) irradiated in the deposited $CFCl_3$ matrix under the same conditions. As shown in Fig. 4(*d*), the EPR spectrum obtained at the lowest temperature (16 K) shows a dominating contribution from the singlet signal with the same linewidth as in the case of non-deuterated EtA. On the basis of arguments considered above, it is quite reasonable to ascribe this signal to the primary radical cation **3c** of EAc-d_2 (as expected, deuteration in the ethyl moiety has virtually no effect on the hyperfine structure of this species). Additionally, close inspection also reveals a weak and broad additional multiplet signal with nearly the same total spread as for non-deuterated EtA. Decay of the singlet signal also starts at *ca.* 40 K being nearly complete at 60–70 K. Although detailed kinetic studies were not made, it seems there is no substantial isotopic effect in the decay reaction. The EPR spectrum recorded after annealing at 60 K is shown in Fig. 4(*e*). The most prominent new features appearing in the spectrum are two rather intense lines positioned at ±2.3 mT from the central component, which becomes narrower and reveals side splittings (probably, due to a residual broad singlet). The outermost lines present in the spectrum shown in Fig. 4(*e*) can be hardly attributed to the same species, because their thermal behaviour is substantially different. Indeed, the intensity of the high-field line changes only slightly after annealing at 60 K. The low-field line exhibits a more definite increase; however, at the same time, its shape reveals marked anisotropy, which may imply contribution from a matrix radical coming from some other process. Thus, comparison of the spectra shown in Fig. 4(*d*) and (*e*) shows that the main new species resulting from annealing the sample in this temperature region is characterised by a nearly binomial triplet pattern with the splitting of *ca.* 2.3 mT. Most reasonably, such a signal should be assigned to the $–OCD_2CH_2^{\bullet}$ type distonic radical cation **4c** resulting from intramolecular H-shift similar to that discussed above for the non-deuterated ester. Further warming the sample up to 110–140 K results finally in a quintet spectral pattern shown in Fig. 4(*f*), which is rather similar to the spectrum observed in the case of non-deuterated ester at the same temperature. This similarity strongly suggests that in both cases the observed hyperfine structure results from the acrylic moiety, so the spectrum should be ascribed to the propagating radical rather than to the distonic radical cation produced by H-shift.

As a whole, we may summarize that the radical cations of EtA and EtA-d_2 can be trapped in the deposited $CFCl_3$ matrix irradiated at 16 K. These species decay at 40–60 K for both esters. In the case of non-deuterated EtA, the interpretation of the EPR spectra observed after complete decay of the primary cations is not fully clear; however, for the deuterated ester, we have a definite indication of the intermediate formation of the terminal type distonic radical cation of the $–OCD_2CH_2^{\bullet}$ structure. Further chemical transformations occurring mainly above 100 K result in the formation of propagating radicals due to secondary reactions with neutral acrylate molecules. At first glance, the formation of the propagating radicals in a $CFCl_3$ matrix seems to be rather surprising since we did not observe formation of these species in the case of samples irradiated at 77 K, even after warming up to 150 K (see the previous section). Furthermore, it is well known that the bimolecular reactions of the radical cations normally do not occur in the $CFCl_3$ matrix up to the temperatures close to the matrix mp (162 K). However, we should note that all the previous observations (including our results for EtA in $CFCl_3$ irradiated at 77 K) were related to the *polycrystalline samples* obtained from liquid solutions, while the matrix deposited from the gas phase at 16 K should be a glassy medium (probably, somewhat similar to the $CF_2ClCFCl_2$ matrix). As reported previously,[18] the difference in the reaction mechanisms for the radical cations in various freon matrices are determined mainly by the variations in matrix microstructure and phase state rather than by variations in the molecular structure of freons, which are chemically very similar to each other. It is also possible that a certain contribution from the propagating radicals in the deposited matrix occurs even at the lowest temperature, immediately after irradiation (a broad and weak multiplet signal observed for both non-deuterated and deuterated ester). If it is the case, these radicals most probably result from the pre-existing dimers. Unfortunately, the spectra of non-deuterated species observed at the intermediate temperatures are complicated and poorly resolved, so it is rather difficult to determine the contribution from different species and, in particular, to assign the conformation of the distonic terminal-type radical cation.

Ethyl acrylate in CF_3CCl_3 matrix, irradiated at 77 K

Irradiation of a dilute (1 : 900) frozen solution of ethyl acrylate in a CF_3CCl_3 matrix at 77 K results in the EPR spectra shown in Fig. 5. Variations in the acrylate concentration (up to 1 : 180) had little effect on the spectra except for appearance of some weak and broad extra lines at higher concentrations. One can see that the total spread and roughly quartet pattern of the spectrum recorded at 77–95 K (Fig. 5(*a*)) is close to that observed in the case of a $CFCl_3$ matrix irradiated under the same conditions. A broadened spectral envelope can be reproduced well by isotropic simulation with the parameters used for the radical observed in a $CFCl_3$ matrix. This similarity suggests strongly that the main species is the same, *i.e.* the rearranged distonic radical cation **4a** of $RCH_2CH_2^{\bullet}$ type resulting from intramolecular H transfer. Furthermore, as the total spread of the spectrum is quite characteristic of the specific configuration of β-protons yielding nearly minimum sum of the corresponding coupling constants, we may conclude that the conformations of this radical in the two freon matrices are more or less similar. However, in comparison with the spectra presented in Fig. 3, the EPR spectrum obtained in the CF_3CCl_3 matrix exhibits a well-defined sub-structure, which is quite prominent due to relatively small linewidths in the latter case. The presence of this sub-structure clearly indicates the occurrence of additional protons with hyperfine coupling constants of *ca.* 0.5 mT. An unequivocal detailed assignment is not straightforward because of insufficient resolution and marked lineshape anisotropy. A rough isotropic simulation was done with the assumption of $a(2H_\alpha)$ = 2.25 mT, $a(1H_\beta)$ = 1.7 mT and two additional proton couplings of 0.45 mT, as shown in Fig. 5(*b*). One of these couplings should be ascribed to the β-proton with a smaller hfc constant that corresponds to the dihedral angle of $\theta \approx -70°$ (this coupling constant is to be compared with the value of 0.4 mT reported for ethyl formate[13,29]). The other relatively small coupling may be associated with the OH proton in the rearranged distonic radical cation. The appearance of such significant coupling in the case of OH proton can be explained if one takes into account the specific configuration of the distonic radical resulting from a cyclic transition state precursor. Evidence for OH proton coupling of roughly the same value was reported by Iwasaki *et al.*[14] for the rearranged distonic radical cation resulting from intramolecular H transfer in methyl formate radical cation; however, there was no direct confirmation of this observation for ethyl formate.

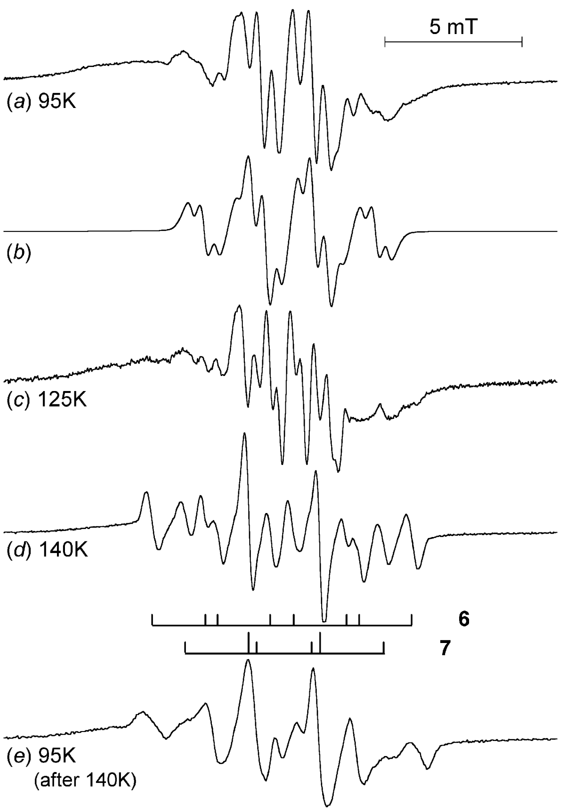
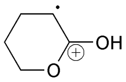


Fig. 5 EPR spectra ((*a*), (*c*)–(*e*)) of a frozen solution (1 : 900) of ethyl acrylate in CF_3CCl_3 irradiated at 77 K and measured at the temperatures indicated. Simulation (*b*) performed with the following hfc parameters: a_1(2H) = 2.25 mT, a_2(1H) = 1.7 mT und a_3(2H) = 0.45 mT. Stick diagrams are given to show the assignment. Note: changes from (*a*) to (*c*) are completely reversible.

Warming the sample up to 100–125 K results in reversible changes of the spectrum (Fig. 5(*c*)). The intensity and linewidth for some components exhibit marked alterations. Such behaviour should be ascribed to dynamic effects, which may involve both torsional oscillations of β-protons (similar to those described above for a $CFCl_3$ matrix) and radical tumbling averaging an anisotropic part of α-proton coupling. Warming the sample up to higher temperatures brings about irreversible spectral changes. The transformation proceeds very slowly at 130 K, but at 140 K it is completed after a few hours without significant loss of spin concentration (Fig. 5(*d*)). A detailed analysis of the resulting spectrum (including the dependence of individual lines upon microwave saturation) and comparison with the results for deuterated EtA (see following paragraph) let us distinguish two different species. The one species (stick diagram marked **6** in Fig. 5), being firstly apparent from its outermost lines separated by *ca.* 9.5 mT, is nicely reproduced from a set of three different protons with coupling constants of 5.13, 2.36 and 1.9 mT. As we will discuss later, this set of coupling constants arises from a cyclic structure, produced by addition of the terminal radical site to the vinyl group.



6a

Structure **6a** agrees well with the assignment of the coupling constants to one α-proton (2.36 mT) and two β-protons. The values of 5.13 and 1.9 mT correspond to dihedral angles of ~15°/45° with a *Bρ* value of ~5.2 mT.

The second species (stick diagram marked **7** in Fig. 5) shows roughly a quartet structure with two equal coupling constants of ~2.27 mT and one slightly larger value of ~2.6 mT. The assignment of this species is not so unambiguous and therefore we refer to the following section and the discussion of secondary species for further consideration.

Deuterated ethyl acrylates in CF_3CCl_3 matrix, irradiated at 77 K

In order to prove the formation of a secondary radical cation of the $-OCH_2CH_2^{\bullet}$ type partially deuterated acrylates, namely ethyl-d_2 and ethyl-d_5 acrylates (EtA-d_2 and EtA-d_5), were investigated. EPR spectra of irradiated frozen solutions of EtA-d_5 in CF_3CCl_3 matrix (1 : 570) are shown in Fig. 6. An unresolved spectrum is observed at low temperatures (77–110 K, Fig. 6(*a*)). This could be either due to the primary radical cation with spin localization at the carbonyl oxygen (stabilized due to an isotopic effect in intramolecular D/H-transfer) or the rearranged distonic cation with a $-OCD_2CD_2^{\bullet}$ radical structure, which also yields a poorly resolved spectral pattern because of the small D-couplings. In contrast to the case of MeA we favour the assignment of the singlet to the distonic radical cation structure **4b**, in complete analogy to ethyl-d_3 acetate $CH_3C(=O)OCH_2CD_3$, where an efficient D-transfer occurred at 77 K and the $CH_3(COD)^+OCH_2CD_2^{\bullet}$ terminal radical was observed.[15]

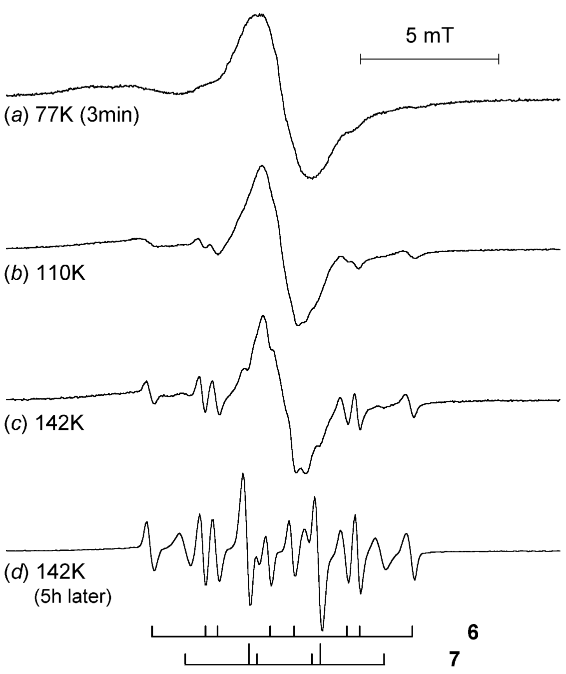
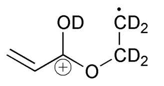


Fig. 6 EPR spectra of a frozen solution (1 : 570) of ethyl-d$_5$ acrylate in CF_3CCl_3 irradiated at 77 K and measured at the temperatures indicated. Stick diagrams are given to show the assignment (see text).



4b

Increasing the temperature to ≥110 K leads to the irreversible formation of a new species yielding a spectrum with the same overall splitting of 9.5 mT as observed in the case of non-deuterated EtA. After warming the sample to 142 K, the outer line groups of this species are well resolved and coupling constants of 5.14, 2.37 and 1.86 mT (exactly the same set as for EtA) can already be derived. The central part is still overlapped with a contribution of the previous singlet structure. The existence of this singlet at such high temperatures is another argument for its tentative assignment to the rearranged deuterated distonic cation **4b** (additionally, the width of this singlet corresponds well to the width calculated from the gyromagnetic ratio and the set of splitting constants of the non-deuterated $-OCH_2CH_2^{\bullet}$ species **4a**). Note that at this stage it is difficult to recognize a contribution of the species showing the quartet spectrum as in the case of EtA (main lines are at the same position as the outer "features" of the singlet). However, when keeping the sample for several hours at 142 K the central singlet disappears completely and again a (nearly) quartet spectrum with coupling constants of 2.13 mT (2H) and 2.6 mT (1H) is observed.

The EPR spectra recorded at 77–95 K for an irradiated frozen solution of EtA-d$_2$ in CF_3CCl_3 (Fig. 7(*a*)) reveals generally a triplet structure ($a(2H) \approx 2.23$ mT) with nearly binomial intensities. Such a triplet is expected for the rearranged distonic radical cation **4c** with the $-OCD_2CH_2^{\bullet}$ structure having two α-protons, the splitting of the two deuterons in β-position being poorly resolved. In fact, the central line of the spectrum exhibits an additional substructure, which may indicate the occurrence of small couplings of 0.3 to 0.5 mT due to OH proton (see above) and at least one deuteron; however, the actual pattern is not identified clearly because of insufficient resolution.

During temperature increases this triplet is stable up to 130 K (Fig. 7(*b*)); only the small additional splittings present at low temperatures disappear reversibly, probably due to dynamic effects. Annealing the sample at temperatures >130 K leads to the irreversible formation of a spectrum similar to those observed for EtA and EtA-d$_5$ (compare Fig. 7(*c*) with Fig. 5(*d*) and Fig. 6(*d*)). The two sets of coupling constants (5.06, 2.38 and 1.89 mT for one species and 2.28 mT (2H), 2.55 mT (1H) for the other, respectively) are again very close to the values obtained for EtA and EtA-d$_5$ (*cf.* Table 2).

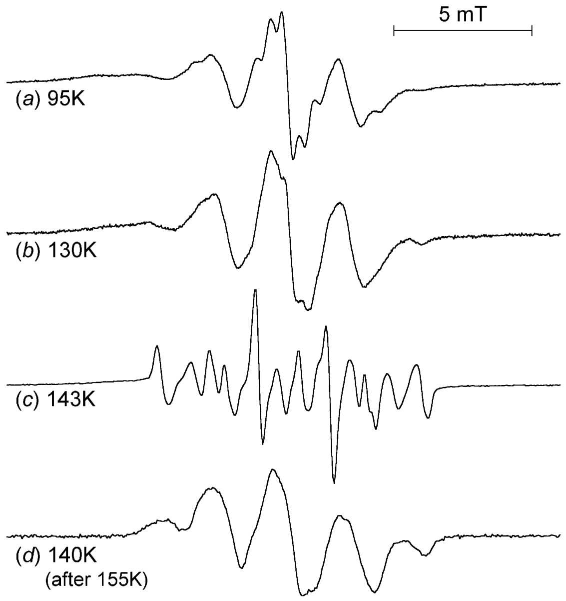
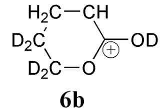
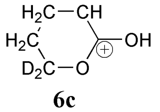


Fig. 7 EPR spectra of a frozen solution (1 : 110) of ethyl-d$_2$ acrylate in CF_3CCl_3 irradiated at 77 K and measured at the temperatures indicated; (*d*) was measured after short annealing at 155 K.

The transformation for all three ethyl acrylates proceeds at comparable temperatures and rates. At 142 K it is completed after 6–8 hours and no further changes in the EPR spectra are observed. The transformation follows first-order kinetics with rate constants of about 1 h^{-1} and 0.5 h^{-1} for the formation of **6** and **7** (see stick diagrams in Fig. 5), respectively. At the end the concentration ratio of both species is approximately 1 : 1 for all three EtA's. Apparently, the observation of the same EPR pattern for EtA, EtA-d$_5$ and EtA-d$_2$ in CF_3CCl_3 at 130–143 K strongly supports the idea of radical transfer to the vinyl group, as this is the only site of the deuterated and non-deuterated EtA molecules having 3 protons which are needed for both **6** and **7** to yield the observed spectra. A "normal" addition to the vinyl double bond of another molecule can be ruled out, because (i) the transformation is observed at low solute concentrations (down to 1 : 900) and it proceeds (though slowly) at temperatures as low as 130 K—under such conditions ion–molecule reactions in CF_3CCl_3 are unlikely; (ii) the transformation is of first order and is observed in the CF_3CCl_3 matrix only, pointing to an intramolecular rearrangement; (iii) a bimolecular addition reaction would lead to a propagating radical; such radicals were characterized in a number of studies dealing with the polymerisation of different acrylates[28,32] to have coupling constants of ~2.8 mT ($H_{\beta1}$), ≤1 mT ($H_{\beta2}$) and 1.8–2.2 mT (H_α) differing quite significantly from our case. Therefore, we assign the spectra with the set of coupling constants of ~5.1, 2.38 and 1.89 mT to the cyclic radical cations **6a** (EtA) and its deuterated analogues **6b** and **6c** produced by cycloaddition of the deuterated distonic terminal radical cations **4** to the double bond.



6b



6c

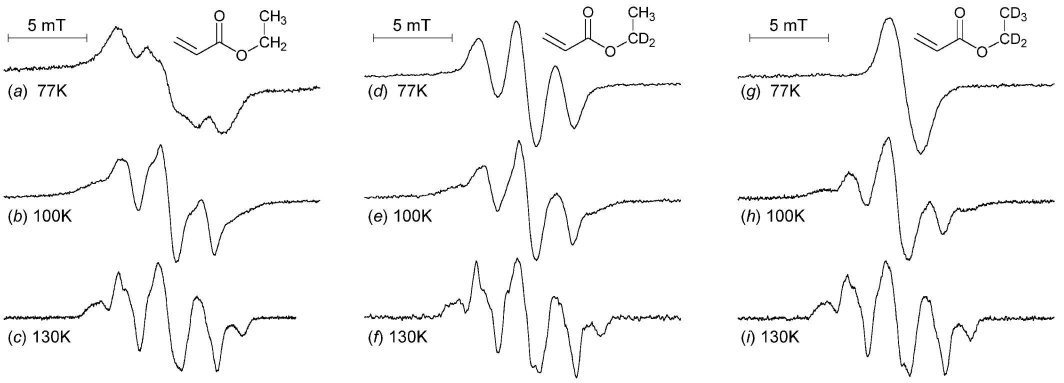
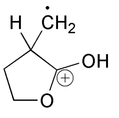


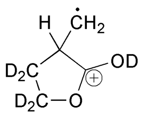
Fig. 8 EPR spectra of frozen solutions of ethyl acrylates in $CFCl_2CF_2Cl$ irradiated at 77 K and measured at the temperatures indicated: (*a*)–(*c*) ethyl acrylate (1 : 500); (*d*)–(*f*) ethyl-d_2 acrylate (1 : 270) and (*g*)–(*i*) ethyl-d_5 acrylate (1 : 390).

One can see easily that all isomers yield the same EPR pattern as the splittings due to the protons or deuterons in the γ-position are too small to be resolved in freon matrices.

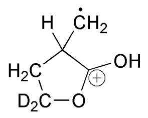
Following the general argument given above, the quartet appearing concomitantly to the disappearance of the remaining contributions of the rearranged distonic radical cation, is assigned to another cyclic structure **7**, produced by addition of the terminal radical **4** to the vinyl double bond at the =CH– position.



7a



7b



7c

Structure **7** agrees well with the assignment of the coupling constants to two α-protons (a(2H) = 2.28 mT) and one β-proton (and non-distinguishable H/D γ-splittings). The value of 2.6 mT for the β-proton may be either explained by a torsion of the radical site with a resulting dihedral angle of *ca.* 45° or by a nearly complete rotation of the $–CH_2$ group yielding an average value of 2.6 mT. Further discussion regarding the assignment and geometrical structure and the slight difference in thermal behaviour between **6** and **7** is given later.

It should be mentioned, that annealing the samples for a short time (3 min) at 155 K (well above the phase transition point of this matrix at 145 K), results in the formation of a similar five-line spectrum as in the case of MeA and MeA-d_3 (Fig. 1(*d*), (*h*), (*m*)). For comparison, the spectrum of EtA-d_2 measured at 140 K after annealing at 155 K is given (Fig. 7(*d*)); exactly the same spectra were recorded for EtA and EtA-d_5 under those conditions.

Ethyl acrylates in $CFCl_2CF_2Cl$ matrix, irradiated at 77 K

EPR spectra of frozen solutions of the three EtA's in Freon-113 irradiated at 77 K are summarised in Fig. 8. The spectra measured in the temperature range 77–95 K are more or less similar to those observed in the CF_3CCl_3 matrix. EtA-d_5 shows the same broad unresolved singlet with an overall linewidth of 1 mT and EtA-d_2 yields a triplet with binomial intensities and coupling constants of ~2.35 mT (2H) (no substructure is found because the natural linewidth in Freon-113 is too large to observe a splitting below 0.5 mT). At first sight, the spectrum of EtA (Fig. 8(*a*), the same spectrum is observed in a concentration range of 1 : 400 to 1 : 100) seems to differ more significantly from the spectrum in the CF_3CCl_3-matrix (*cf.* Fig. 5(*a*)), however, it is also roughly a four-line spectrum with a comparable overall splitting. Note that the linewidths of the spectra observed in a glassy Freon-113 are typically larger than in the polycrystalline freon matrices discussed above. These spectra can be assigned reasonably to the rearranged distonic radical cations **4**.

Already at 98–100 K a new species appears in the spectra, which is quite clearly seen in the case of EtA-d_5 (Fig. 8(*h*)). In the case of EtA and EtA-d_2 the new species is mainly indicated by its outermost features separated by ~9 mT (Fig. 8(*b*) and (*e*), respectively), whereas the inner lines are overlapping with precursor lines with a similar splitting pattern. At 130 K all three isomers yield the same five-line spectrum, identical to the final spectrum in the case of MeA (Fig. 1(*d*), (*h*) and (*m*)) and the spectrum observed for EtA in CF_3CCl_3 matrix after annealing the samples for a short time above the phase transition point of this matrix (Fig. 7(*d*)). Additionally, such five-line spectra were found to be typical of the propagating radicals in frozen MeA.[28] It is therefore reasonable to make a similar assignment in the case of EtA. The first indication of the ion–molecule reaction in the $CFCl_2CF_2Cl$ matrix at temperatures as low as 98 K is a little bit surprising, as such reactions are typically observed at temperatures around and above 105–110 K,[18,19] but our experimental finding seems to be characteristic of acrylate radical cations; it was also observed for other acrylates with longer side chains (data not presented here).

Ethyl acrylate in argon matrix in the presence of CF_3CCl_3, irradiated at 16 K

The EPR spectrum of an irradiated argon matrix containing ethyl acrylate and $CFCl_3$ (Fig. 9(*a*)) exhibits a superposition of a relatively sharp quartet with the coupling constant of a(3H) = 2.3 mT and a broad, poorly resolved multiplet signal, which is somewhat similar to that observed in a deposited $CFCl_3$ matrix irradiated at 16 K. The former signal (quartet) is quite characteristic of methyl radicals, which result most probably from the fragmentation of the primary radical cations. Formation of methyl radicals upon irradiation of different aliphatic molecules containing alkyl groups (alkanes, ethers) in an argon matrix was observed previously.[21,33]

This result was attributed to the fragmentation of the primary radical cations due to high exothermicity of the positive hole transfer (large excess energy) in the case of argon (the IP "gap" between argon and guest molecule exceeds 5 eV). In most cases, the fragmentation results in preferential formation of methyl radicals, independent of alkyl chain length. The broad multiplet signal is, most probably, due to alkyl-type radicals; however, detailed structure of the spectrum is not clear.

In the case of EtA-d_2 (Fig. 9(*b*)), the quartet signal from methyl radicals is again quite prominent. In fact, the corresponding lines are even sharper; such a difference may imply that in the case of non-deuterated ester, the components from methyl radicals overlap with broader lines from other species, which are not observed for EtA-d_2. The weak outermost lines in the spectrum shown in Fig. 9(*b*) separated by 15.7 mT are due

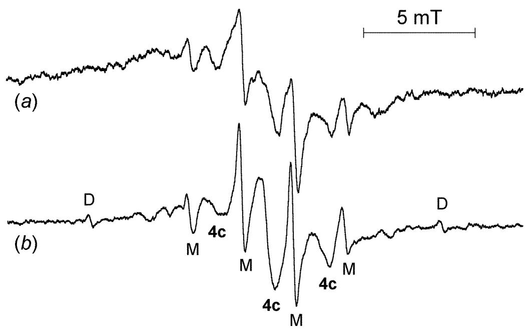


Fig. 9 EPR spectra of a solid deposited mixture ethyl acrylate/argon/ CF_3CCl_3 (molar ratio 1 : 1000 : 2) irradiated with fast electrons and measured at 16 K: (*a*) ethyl acrylate and (*b*) ethyl-d_2 acrylate. The symbols **M** and **D** denote the lines due to methyl radicals and trapped D atoms, respectively; the components assigned tentatively to rearranged distonic radical cation **4c** are also marked (see text for details).

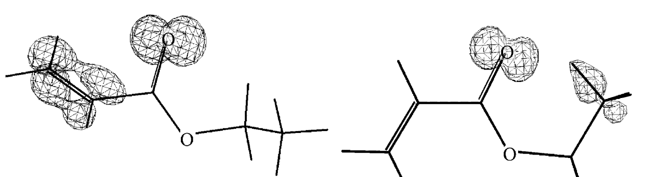
to trapped deuterium atoms (the separation is equal to 2*a*(D) since the line corresponding to $M_I = 0$ is hidden by an intense central component of the main signal). ‡ The central component of the spectrum is defined better in the case of partially deuterated ester. Nevertheless, this line cannot be attributed to the primary unstable radical cation since the observed linewidth of *ca.* 0.7 mT is only one half of that recorded in $CFCl_3$ and expected theoretically for the envelope resulting from unresolved hyperfine coupling in the radical cation (see below). The occurrence of anisotropic components positioned at ±(2.3–2.4) mT from the central line bears an indication of a triplet signal, which can be ascribed tentatively to the $–OCD_2CH_2^{\bullet}$ type distonic radical cation **4c** resulting from the rearrangement observed in all other matrices. Evidence for rearrangement of the primary radical cations occurring in argon immediately after irradiation was reported for several hydrocarbon cations.[34] Such a process (not observed in freons) was also ascribed to the effect of excess energy mentioned above. However, we should note that the spectrum recorded in argon contains also a number of additional weak lines, which cannot be assigned definitely. One cannot exclude the occurrence of some side fragmentation processes, which cannot be characterised in detail on the basis of available data. Warming the sample to 30–38 K results in gradual decay of methyl radicals, whereas the changes in other signals are not well defined.

In summary, we failed to obtain any evidence for trapping of the primary EtA radical cations in the argon matrix after irradiation at 16 K. Instead, we have detected the products of fragmentation and, most probably, of rearrangement, which indicate definitely the significance of "high-energy" reaction paths invoked in several previous studies of aliphatic cations produced in argon.[21,33,34]

Structure and stability of the primary radical cations of acrylates

As was shown in the previous section, in the cases of both methyl and ethyl acrylate, the primary unstable paramagnetic intermediates are characterised by unresolved relatively broad singlet EPR spectra with the observed peak-to-peak linewidth of *ca.* 1.4 mT. This singlet disappears at 77 K for methyl acrylate, or even at lower temperatures for ethyl acrylate, giving rise to multiplet signals, which can be ascribed definitely to alkyl-type radicals (in fact, distonic radical cations). Thus, from a phenomenological point of view, the unstable singlet signal should be assigned to the primary acrylate radical cation. The absence of resolved hyperfine structure implies small proton hyperfine coupling constants in this species (not larger than 0.5–0.6 mT). The quantum chemical calculations for methyl acrylate and ethyl acrylate radical cations provide an unequivocal support to this qualitative reasoning (Table 1, species **1** and **3**). Indeed, according to calculations, the maximum spin density ($\rho \approx 0.6$) is located at the carbonyl oxygen atom. The calculated coupling constants for vinyl group protons do not exceed 0.5 mT, whereas the hyperfine coupling with the protons of alkyl groups adjacent to ether oxygen are negligible. The simulation using hyperfine parameters listed in Table 2 makes it possible to reproduce the experimental spectrum envelope, if the component linewidth is assumed to be *ca.* ~0.5 mT.

At this point, it is of interest to compare the experimental spin density distribution in acrylate radical cations with those expected for unstable radical cations of saturated esters (formates and acetates). The earlier assignment of the latter species as π-type cations[12,14] has proved to be unreasonable in view of later arguments provided by Rideout and Symons.[15] Their interpretation suggests the n_σ-type SOMO with the spin density localised largely at the carbonyl oxygen atom. Nevertheless, there are no direct experimental or calculational data describing actual structure of the n_σ saturated ester radical cations in terms of spin populations and the corresponding hyperfine coupling parameters. For this reason, we have carried out the quantum chemical calculations for simple formates and acetates. Saturated ester molecules exhibit nearly degenerate n_σ(O) and π(OCO) orbitals; however, at the appropriate level of theory (HF/6-31G(d)//B3LYP/6-31G(d)), the separation between these orbitals ΔE is ≈0.3 eV, and the n_σ(O) orbital is clearly identified as HOMO. Ionisation from this orbital leads to the radical-cation structure with the unpaired electron localised at the carbonyl oxygen atom (*ca.* 95%). As mentioned above, the calculations of acrylate radical cations also reveal the largest spin density at the carbonyl oxygen atom, which may be the reason for a certain similarity in the chemical behaviour of all the ester radical cations. The main difference between saturated esters and acrylates results from the occurrence of one higher molecular orbital ($\Delta E \approx 1.5$ eV with respect to the n_σ(O) and π(OCO) orbitals), that is, a π-type HOMO comprising carbonyl and vinyl groups. Ionisation from this orbital leads to a SOMO of the radical cation, still delocalised over both groups, but being mainly n-type on carbonyl oxygen (Fig. 10).



3 **3→4**

Fig. 10 Calculated geometry and spin density distribution of the primary ethyl acrylate radical cation **3** and the transition state **3⟶4** for H-transfer.

In fact, the calculations reveal significant spin density on the vinyl group in the acrylate radical cations (the sum of spin densities at C^1 and C^2 is larger than 0.4). It is worthwhile noting that the experimental EPR spectra of the primary acrylate cations show small anisotropy in the *g*-factor, and the effective *g*-value is rather close to g_e, which is more consistent with a partially delocalised structure than with fully localised n_σ(O) state. The dramatic effect of the double bond on the SOMO nature was observed in the studies of vinyl ether radical cations[35,36] which show very low spin density at the oxygen atom (in sharp contrast with saturated ether cations). This

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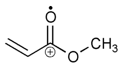
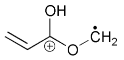
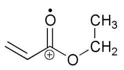
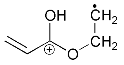
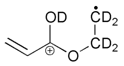
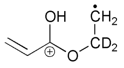
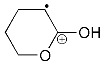
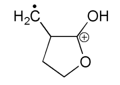
‡ The signals of trapped H atoms (sharp doublets separated by *ca.* 51 mT) are also well observed in both EtA and EtA-d_2, if the spectra are recorded in a wider magnetic field scale; however the relative yields of trapped H (D) atoms are anyway minor (less than 5% of the total amount of paramagnetic species).

Table 2 Hfs splitting constants *a*(H) measured in low-temperature matrices and calculated by B3LYP/6-31G(d) theory

	Species	*Calculation* or matrix	*T* /K	*a*(H)/mT
1a		*B3LYP/6-31G(d)*		***0.5***, ***0.44*** *(2H(CH$_2$=));* ***0.5*** *(H(=CH–))*
		CF$_3$CCl$_3$	77	Singlet: ΔH_{pp} = **1.1** mT
		CFCl$_2$CF$_2$Cl	77	Singlet: ΔH_{pp} = **1.4** mT
				(**1b** singlet: ΔH_{pp} = **1.3** mT)
2a		*B3LYP/6-31G(d)*		***2.47*** *(2H$_\alpha$)*
		CF$_3$CCl$_3$	77	**2.24** (2H)
			140	**2.25** (2H)
		CFCl$_2$CF$_2$Cl	77	**2.27** (2H)
3a		*B3LYP/6-31G(d)*		***0.38***, ***0.44*** *(2H(CH$_2$=));* ***0.6*** *(H(*=CH–))
		CFCl$_3$	16	Singlet: ΔH_{pp} = **1.4** mT
				(**3c** singlet: ΔH_{pp} = **1.4** mT)
4a		*B3LYP/6-31G(d)*		*Conformer 1*: ***2.36*** *(2H$_\alpha$),* ***2.84*** *(H$_{\beta 1}$),* ***0.10*** *(H$_{\beta 2}$)*
				Conformer 3: ***2.58*** *(2H$_\alpha$),* ***3.87*** *(H$_{\beta 1}$),* ***3.92*** *(H$_{\beta 2}$)*
				Conformer 2: ***2.38*** *(2H$_\alpha$),* ***0.83*** *(H$_{\beta 1}$),* ***0.34*** *(H$_{\beta 2}$)*
		CFCl$_3$	77	**2.25** (2H$_\alpha$), ~**1.6** (1H$_\beta$)
			140	**2.25** (2H$_\alpha$), **0.95** (2H$_\beta$)
		CF$_3$CCl$_3$	95	**2.25** (2H$_\alpha$), **1.7** (1H$_\beta$), **0.45** (2H)
		CFCl$_2$CF$_2$Cl	77	Poorly resolved
4b		CF$_3$CCl$_3$	77	Singlet: ΔH_{pp} = **1.8** mT
		CFCl$_2$CF$_2$Cl	77	Singlet: ΔH_{pp} = **2.0** mT
4c		CF$_3$CCl$_3$	77	**2.23** (2H$_\alpha$)
		CFCl$_2$CF$_2$Cl	77	**2.35** (2H$_\alpha$)
6		*B3LYP/6-31G(d)*		***1.88*** (*H$_{\beta 1}$*), ***5.07*** (*H$_{\beta 2}$*), ***2.36*** (*H$_\alpha$*)
		CF$_3$CCl$_3$	140	**6a** EtA: **1.90** (H$_{\beta 1}$), **5.13** (H$_{\beta 2}$), **2.36** (H$_\alpha$)
		CF$_3$CCl$_3$	140	**6b** EtA-d$_2$: **1.89** (H$_{\beta 1}$), **5.06** (H$_{\beta 2}$), **2.38** (H$_\alpha$)
		CF$_3$CCl$_3$	140	**6c** EtA-d$_5$: **1.88** (H$_{\beta 1}$), **5.14** (H$_{\beta 2}$), **2.37** (H$_\alpha$)
7		*B3LYP/6-31G(d)*		***2.47*** *(2H$_\alpha$),* ***1.13*** *(H$_\beta$)*
		CF$_3$CCl$_3$	140	**7a** EtA: **2.27** (2H$_\alpha$), **2.60** (H$_\beta$)
		CF$_3$CCl$_3$	140	**7d** EtA-d$_2$: **2.28** (2H$_\alpha$), **2.55** (H$_\beta$)
		CF$_3$CCl$_3$	140	**7c** EtA-d$_5$: **2.21** (2H$_\alpha$), **2.59** (H$_\beta$)

difference in electronic structure may be the key in understanding different stability of the primary radical cations of saturated esters and acrylates. Indeed, the radical cations of formates and acetates have a highly localised radical site (like alkoxy-type radicals), which makes them very reactive toward the intramolecular hydrogen atom abstraction ("H-shift"). As a result, the isolated primary radical cations of saturated esters were not observed in the freon matrices even at very low temperatures. Meanwhile, delocalisation of spin density in the case of acrylates implies reduced reactivity of these species in hydrogen abstraction reactions, in particular, in the intramolecular "H-shift", so the primary radical cations of acrylates are somewhat stabilised and can be trapped in freon matrices, at least, at low temperatures.

Anyway, the primary acrylate radical cations proved to yield the corresponding distonic species *via* intramolecular H transfer occurring at 77 K for methyl acrylate or even at lower temperatures for ethyl acrylate. As mentioned above, a similar type of rearrangement was reported for saturated ester radical cations. The experiments with deuterium labelled compounds provide clear evidence that in the case of ethyl acrylate hydrogen transfer occurs from the terminal methyl group rather than from the methylene fragment (see Scheme 1). According to calculations (Table 1, species **4** and **5**), both rearrangements are possible, and the product **5** resulting from H transfer from the methylene group is even more stable. § This result implies kinetic control of the reaction path, that is, selection of the reaction channel is determined by the transition state structure. Indeed, the rearrangement observed in the experiment (H transfer from terminal methyl group) occurs *via* a six-member cyclic transition state, which is typically the most favourable transition state geometry. An alternative reaction path (H transfer from methylene group) implies a five-member cyclic transition state, which appears to be less favourable in terms of higher energy profile of the reaction. The calculated barriers are 37.6 and 50.2 kJ mol^{-1} for the six-member and five-member transition states, respectively.¶ (Note: in the case of partially deuterated ethyl-d$_3$ formate the –OCH$_2$CD$_2^{\bullet}$ radical was formed at 77 K in a CFCl$_3$ matrix.[29] Usually a strong deuterium isotope effect would be expected to reduce the transfer probability. The fact that D-transfer from the terminal –CD$_3$ group is still completely favoured over H-transfer from the methylene group, highlights the large effect of transition state

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§ Most probably, the rearrangements under consideration in solid matrices are much more favourable than it could be expected from the "gas-phase" calculations since strong solvation of the localised cationic site in the resulting distonic species may bring about large additional stabilisation (see *e.g.*, ref. 37 and 38).

¶ It should be understood clearly that these estimates are merely qualitative since they do not take into account the medium effects, which could be very important for the reaction barriers in solid matrices.

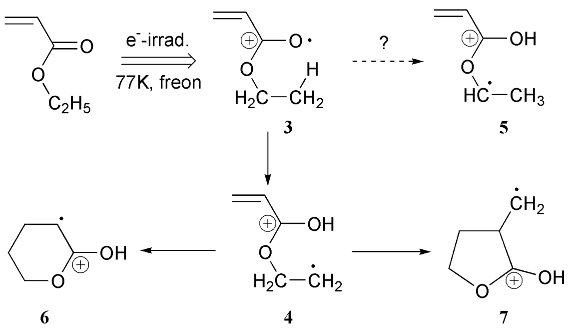
geometry control.) Further support for the concept of transition state control comes from the comparison of decay kinetics for ethyl acrylate and methyl acrylate radical cations. In the latter case, the reaction definitely proceeds *via* a five-member ring transition state (this is the only possible way). As expected, the calculated barrier of the H-transfer reaction for the methyl acrylate cation is higher (57.6 kJ mol^{-1}). The experimental results indicate clearly that the rearrangement of methyl acrylate cation is much slower and occurs at higher temperature, which is in accord with the above consideration.

Regarding the elementary mechanism of intramolecular H-transfer, it is worthwhile noting that the estimated barrier height values are too high to explain the occurrence of a fully classical pathway at very low temperatures (40–77 K). In fact, the stable conformer of the primary cation lies rather far from transition state geometry, so the first step should be rotation to achieve favourable intramolecular arrangement. It is not clear in detail how this process occurs inside the matrix cage. Nevertheless, the involvement of H tunnelling appears to be highly probable at the final stage. The possibility of a tunnelling mechanism was discussed for intramolecular H transfer in saturated ester radical cations.[15] From this point of view, it would be of interest to follow the isotopic effect in the rearrangement reaction since the tunnelling processes are characterised by large isotopic effects. Unfortunately, it is not easy to get unequivocal proof of the isotopic effect from the available data, because both the primary radical cations and rearranged deuterated radicals yield poorly resolved spectra due to small deuteron coupling constants. Most reasonably, the reaction can be represented as a combination of classical (temperature-dependent) and tunnelling steps; however, it is not possible to make definite conclusion at present.

The results obtained in this work provide further evidence for strong preference of a specific conformation for the rearranged distonic radical cations of the type **4** produced from ethyl esters. This conformation characterised by $\theta_1 \approx 50°$ and $\theta_2 \approx 70°$ is common for the species produced from ethyl acrylate and ethyl formate. The quantum chemical calculations (Tables 1 and 2) actually fail to reproduce experimental hyperfine coupling constants for the β-protons of species **4**. This may rather reflect a general problem of correct theoretical description of the spin density distribution in this type of distonic radical cations. A similar discrepancy is found comparing measured and calculated values in the case of ethyl formate: $H_{\beta1,\beta2} \approx 1.6/0.4$ mT,[13] and 0.57/0.27 mT (this work), respectively. However, if we take into account only the geometry of the rearranged species **4**, we can note that the calculated conformer 2 (the most stable conformer) is relatively close to the experimentally observed species in terms of dihedral angles; in this case the calculated H_β coupling constants for both, the acrylate and the formate, have to be scaled by a factor of *ca.* 2 to fit the experimental values

Two other calculated conformers (1 and 3) correspond to dihedral angles of $\theta_1 \approx 40°/\theta_2 \approx 85°$ and $\theta_1 \approx \theta_2 \approx 30°$, respectively. The former relatively unstable minimum (if it does exist) is rather close to conformer 2 and can be converted to it by some 20° rotation around the C–C bond. Conformer 3 is a planar, linear extended radical with two equivalent β-protons; in fact, such a conformation is adopted by the neutral radical $HCOOCH_2CH_2^•$ resulting from dissociative electron capture by chlorinated ethyl formate.[15] Concerning the reasons for complete preference of conformer 2 for the rearranged distonic species produced from ethyl acrylate (as well as from ethyl formate) primary radical cations, one may consider the rearrangement reaction pathway and transition state geometry.

Indeed, one can see that the transition state geometry (*cf.* Fig. 10 and Table 1) is very close to conformer 1. Thus, it is reasonable to suggest that the resulting radical first adopts the transition state configuration, which is followed by relatively small (possibly matrix assisted) rotation to yield a stable conformation 2 observed in the experiment. We should note that an intuitive explanation of this kind was proposed tentatively for the case of ethyl formate;[15] now it seems to be supported by quantum chemical consideration, at least at qualitative level.



Scheme 1

Secondary transformations—discussion of cyclic structures

Clear evidence for the formation of cyclic structures due to an intramolecular radical site attack of **4** at the vinyl double bond is found in the CF_3CCl_3 matrix. Other possible reaction channels had to be ruled out by the arguments given before which are valid for both observed spectra (*cf.* spectrum Fig. 5(*d*) and stick diagrams **6** and **7**).

The assignment made for **6** on the basis of the experimental facts, especially from comparison of the different deuterations, is strongly supported by our quantum chemical calculations. The six-member ring is slightly distorted leading to dihedral angles of ~15° and 45° for the β-protons and corresponding coupling constants of 5.07 and 1.88 mT (DFT), respectively. The calculated coupling constants agree very well with the experimental values (*cf.* Table 2). The energy barrier for the formation of the six-member ring is estimated to be about 49 kJ mol^{-1}, which is of the same order as the barrier for the primary H-shift, but the stabilising energy is rather large (−131 kJ mol^{-1}).

The assignment of the quartet spectrum to **7** is not so straightforward and deserves more discussion, especially for the β-proton coupling. Following the argument regarding radical transfer to the vinyl group (the only fragment which has three protons for deuterated as well as non-deuterated EtA's) by an intramolecular rearrangement reaction there is only one possibility open, namely addition of the terminal radical site to the vinyl group in the =CH– position. The quantum chemical calculations for this type of cycloaddition show a similar barrier height of 45 kJ mol^{-1} and a stabilising energy of −79 kJ mol^{-1} which is somewhat smaller as for the formation of **6** but still quite large. Structure **7** has two α-protons accounting for the splitting of 2.25 mT observed and one β-proton, whose coupling constant depends on its dihedral angle with the π-orbital. The experimental value of 2.6 mT can be explained either by a dihedral angle of approximately 45° or by nearly complete free rotation of the methylene group. The first assumption is hardly supported by the quantum chemical DFT calculations: the π-orbital is nearly perpendicular to the C–H_β bond (a dihedral angle of 77° is calculated; the use of the larger basis set 6–311+G(2d,p) results even in a value of 87°) and the corresponding coupling constant should be very small. Therefore one would have to assume further matrix assisted rotation to explain the experimental data. The second assumption of nearly complete free rotation of the $–CH_2^•$ group can easily yield the observed (averaged) value of 2.6 mT, but the question has to be addressed, whether such a free rotation is possible. The quantum chemical calculations give a bond length between the ring and the methylene group (1.494 Å) which is significantly longer than the $–CH_2–CH_2^•$ bond in **4** (1.467 Å) and closer to the length of a standard single bond (1.523 Å). Additionally, the rotational barrier of the $–CH_2^•$ group in **7** (4.2 kJ mol^{-1}) is much lower than in **4** (9.2 kJ mol^{-1}) and comparable to the rotational barrier of a terminal methyl group (~4 kJ mol^{-1}), which is known to rotate freely even at 77 K. An experimental argument in favour of free rotation can be derived from the microwave saturation studies, which revealed that the lines assigned to species **7** exhibited virtually no saturation even at high microwave power. In general, such behaviour is characteristic of a "pending" or free rotating radical site in view of short spin–lattice relaxation time (it is worthwhile noting that the lines attributed to species **6** show definite saturation under the same conditions). Following these arguments we prefer to explain the observed β-proton coupling of 2.6 mT on the basis of nearly free rotation of the $-CH_2^{\bullet}$ group of **7**, although the other assumption of a matrix assisted torsion cannot be ruled out completely on the basis of the experimental data.

The rate constants for the formation of **6** and **7** (1 h^{-1} and 0.5 h^{-1}, respectively, at 142 K) differ roughly by a factor of 2. A tentative explanation of this fact may be drawn from the calculated stabilising energies, the stabilisation for **7** being by a factor of 0.6 smaller than for **6** (at similar barrier heights). It is a little bit surprising, however, that at the end of the transformation both species are present at a relative concentration of roughly 1 : 1 (2 : 1 expected from the ratio of rate constants). Although it is difficult to compare the kinetic data exactly because of slightly different sample "histories" (preparation, irradiation, heating regime *etc.*), the observed rate constants and the final concentration ratio of species **6** and **7** agree for the three different ethyl acrylates.

Conclusions

The results obtained show that ionisation of simple acrylates in solid media is followed by diverse chemical transformations, which are essentially controlled by the matrix environment. The primary unstable radical cations can be trapped in frozen freon matrices at 77 K (for methyl acrylate) or below 40 K (for ethyl acrylate). In both cases, the first reaction step is an intramolecular rearrangement (H-shift) yielding the terminal-type distonic radical cations. Further fate of these species is affected crucially by the matrix properties. In the case of glassy matrices ("soft media" in terms of bimolecular processes), intermolecular reactions resulting in formation of propagating radicals readily occur even at rather low temperature (near 100 K). It seems quite logical that these two steps (intramolecular H-shift followed by intermolecular radical addition) should be of common significance for ionised acrylates in neat liquids and liquid solutions. However, in the case of "rigid" polycrystalline matrices with relatively large cavities, the secondary distonic radical cations of ethyl acrylate may undergo intramolecular addition to a vinyl double bond resulting in the formation of six-member or five-member cyclic species. In particular, this reaction path can be realised for acrylate molecules embedded in a specific constrained environment, *e.g.*, in microporous media.

In principle, similar-type consideration can be applied to longer-chain acrylates. However, the length and conformation of alkyl chains may affect strongly the kinetics of the primary H-shift and secondary ring formation, because both processes are controlled by the transition state geometry. Thus, it is of interest to follow the fate of radical cations of a series of higher acrylates in a systematic way. Another extension of the present studies implies investigation of the effect of substitution at a vinyl double bond on the structure and reactivity of unsaturated ester radical cations (the simplest and, probably, the most important example is represented by methacrylates). The work in both areas is in progress now.

Acknowledgements

The work in Moscow was supported in part by the Russian Foundation for Basic Research (project no. 00-03-32041).

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