ESR of Cation Radicals of Vinyl Monomers in a CF_3CCl_3 Matrix

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Molecular cations of the vinyl monomers acrolein, methylacrylate and methylmetacrylate have been prepared by irradiation at 77 K of the monomers contained in a CF_3CCl_3 matrix. The ions have been studied by ESR. The effect of photobleaching has been investigated.

Introduction

It has been known for some time that halogenated compounds form suitable matrices to trap molecular cations of several types of organic solutes [1 – 3] when the mixture is irradiated at 77 K. It is not until recently, however, that matrices suitable for ESR detection of the cations have been devised [4]. The most commonly used matrix is $CFCl_3$. We have found another matrix, 1,1,1-trifluoro-trichloroethane, to be suitable for the study of the structure and the photoinduced decomposition of several cations of n- and c-alkanes and methyl-substituted benzenes [5 – 7]. In this work we have used the same CF_3CCl_3 matrix for a similar study of cations of some vinyl monomers. The results are concerned with the structure of the cations of acrolein, methylmetacrylate and methylacrylate as revealed by ESR spectroscopy and to some extent with the structure of the species formed upon photoillumination. The results are new in the respect that cations of vinyl monomers have not been previously detected in ESR studies. The observation is important because these cations have been considered as initiators of polymerisation in these systems.

The identification of the cation of acrolein has been supported in this work by theoretical calculations and by comparison with experimental data for other radical cations of aldehydes. In the case of methylmetacrylate and methylacrylate the identification was less obvious, because cations of related substances have not been identified and because the spin density was localised to the vinyl group contrary to the case of acrolein and also to the prediction of molecular orbital calculations. We have therefore tried to elucidate the structure by observing how the ESR spectra are affected by replacing the ester methyl with other alkyl groups.

Experimental

Methylmetacrylate (99%) (MMA), methylacrylate (99.5%) (MA) and acrolein (pract) were purchased from Fluka. A sample of methylmetacrylate deuterated at the ester methyl group (MMA-d_3) was synthetized according to a method described by Nagai et al. [8]. Samples of several alkyl methacrylates (alkyl = ethyl, isopropyl or n-butyl) were synthetized analogously. The samples were distilled previous to use. 1,1,1-trifluorotrichloroethane from Aldrich was used as a matrix. Samples for ESR measurements were prepared on a vacuum line. A small amount (~ 0.1 – 0.3 mole %) of the monomer to be investigated was added to the CF_3CCl_3 solution contained in a 4 mm Suprasil sample tube. The solution was degassed, sealed under vacuum and irradiated with ^{60}Co γ rays to a dose of 0.3 Mrad. The ESR measurements were made with a Varian E9 spectrometer at temperatures between 77 and 142 K. The irradiations and the measurements were made in the dark in order to avoid irreversible changes in the spectra caused by illumination with visible light (see below).

Results

ESR spectra of samples containing acrolein, MMA, MMA-d_3 or MA changed relatively little,

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Table 1. Summary of ESR data for monomers contained in the CF_3CCl_3 matrix after γ-irradiation at 77 K. 1) and 2) are two radical components.

Monomer	T (K)	Condition	g	Hyperfine coupling
Methylmetacrylate	77	Dark	2.0030	$a = 15.5$ G (4H)
Methylmetacrylate	140	Dark	2.0030	$a = 15.5$ G (4H)
Methylmetacrylate-d_3	140	Dark	2.0030	$a = 15.5$ G (4H)
Methylmetacrylate	140	Photobleached	2.0040	$a_1 = 23.0$ G (4H) $a_2 = 3.5$ G (3H)
Methylmetacrylate-d_3	140	Photobleached	2.0040	$a = 23.0$ G (4H)
i-propylmetacrylate	140	Photobleached	2.0040	$a = 23.0$ G (4H)
n-butylmetacrylate	140	Photobleached	2.0040	1) $a = 23.0$ G (4H) 2) $a = 20.0$ G (6H)
Methylacrylate	140	Dark	2.0029	$a = 25$ G (2H)
Methylacrylate	140	Photobleached	2.0041	complex
Acrolein	140	Dark	2.0072	$a = 125$ G (1H)

and reversibly within the temperature interval 77 – 142 K. Photobleaching at 77 K induced irreversible spectral changes. The ESR data obtained are summarized in Table 1. Below follows a detailed account of results and interpretations for each monomer.

Acrolein

A sample containing acrolein gave rise to a large doublet splitting of 125 G, Figure 1. A triplet substructure is evident in the spectrum. The spectrum changed irreversibly by photobleaching during one minute with visible light. It has not been possible to analyse the resulting spectrum.

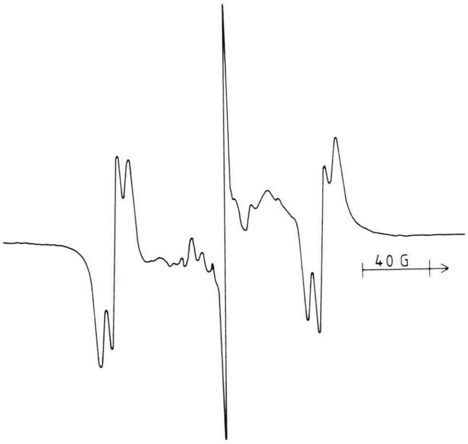


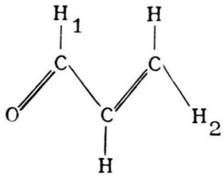
Fig. 1. First derivative ESR spectrum at 142 K of 0.3 mole% acrolein in a CF_3CCl_3 matrix irradiated at 77 K.

The acrolein molecule is assumed to be planar. The highest occupied molecular orbital is of σ symmetry (13 A′ in the notation of [9]). According to the molecular orbital drawings by Jorgensen and Salem [9] this orbital is centred on the aldehyde group, primarily on the oxygen. An analogous structure has recently been proposed for the acetaldehyde cation [10].

According to our data the spin density on the hydrogen is $125/505 = 0.25$. The g-factor of $g = 2.0072$ is too high for a carbon-centred radical, implying that the unpaired spin is to some extent on the oxygen with its higher spin-orbit coupling. These observations suggest that the acrolein cation has a σ-structure with the unpaired spin density confined to the aldehyde group.

Symons and Boon [10] have suggested that the hyperfine splitting in the acetaldehyde cation has a relatively large anisotropic component of $2\,B = 11$ G for an axially symmetric tensor. We have calculated the magnitude of the anisotropic couplings using a computer program developed by Edlund [11]. In this program the dipolar integrals are evaluated analytically using the unrestricted Hartree-Fock wave function from an INDO calculation on the acrolein cation. According to these calculations the dipolar coupling is fairly small, Table 2. This result was expected because of the large distance between the oxygen which carries the largest portion of the spin density and the aldehyde hydrogen. It is doubtful if the splitting of each main line that we do observe is to be attributed to hyperfine coupling anisotropy. According to our INDO calculation the substructure

Table 2. Calculated values of isotropic (a) and dipolar (B_i, $i = 1, 2, 3$) hyperfine couplings in the acrolein cation by INDO theory. x is along the C=O bond, and z is perpendicular to the molecular plane.

Geometry	Nucleus	a G	B_i G	Direction cosines		
				x	y	z
	H_1	73.8	4.4	0.9967	−0.0814	0
			−1.5	–	–	1.0
			−2.9	−0.0814	−0.9967	0
	H_2	4.9	0.7	0.9897	−0.1431	0
			−0.2	–	–	1.0
			−0.5	−0.1431	−0.9897	0

can also arise by the interaction with the vinyl hydrogens.

Methylacrylate (MA)

A sample containing MA gave rise to a triplet spectrum with $a = 25$ G when recorded at 140 K, Figure 2. The g-factor is $g = 2.0029$, suggesting that the spin density in this case is not on an oxygen atom. At 77 K the resolution was considerably lower, indicative of a broadening due to hyperfine coupling anisotropy. Possible assignments of the spectrum in Fig. 2 will be discussed together with the interpretations of the spectra obtained from MMA, see below. After photobleaching with visible light for a few seconds the ESR spectrum in Fig. 2 changed irreversibly. A similar change was observed and investigated in more detail in the case of MMA discussed below.

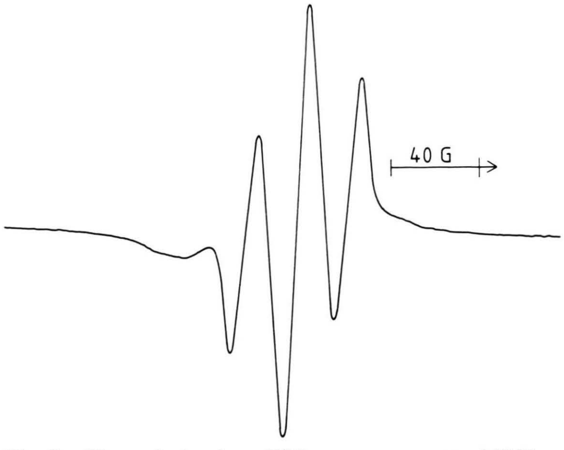


Fig. 2. First derivative ESR spectrum at 142 K of 0.3 mole% methylacrylate in a CF_3CCl_3 matrix irradiated at 77 K.

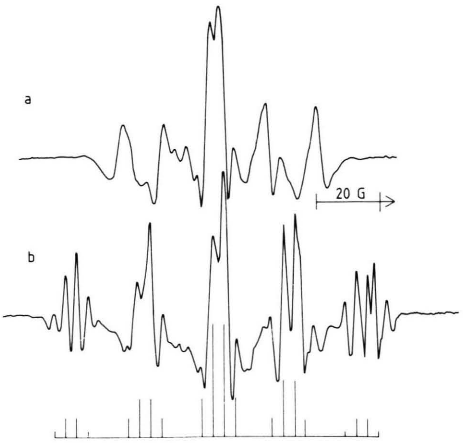


Fig. 3. Second derivative ESR spectra at 142 K of 0.3 mole% methylmetacrylate in a CF_3CCl_3 matrix irradiated at 77 K a) before and b) after photobleaching with visible light.

Methylmetacrylate (MMA)

The second derivative ESR spectrum obtained at 77 K in the dark was a quintet of lines split by $a = 15.5$ G as shown in Figure 3a. The spectrum obtained from the MMA-d_3 sample was almost identical to that in Figure 3a. Thus, there is no significant spin density on the ester methyl group in this case.

After photobleaching with visible light for a few seconds the ESR spectrum changed drastically; compare the second derivative spectra in Figure 3. The spectrum after photobleaching is a main quintet with $a = 23.0$ G with an additional substructure, Figure 3b. In order to elucidate the origin of the substructure in the photobleached sample experiments with MMA-d_3 and methacrylates with different alkyl groups were performed.

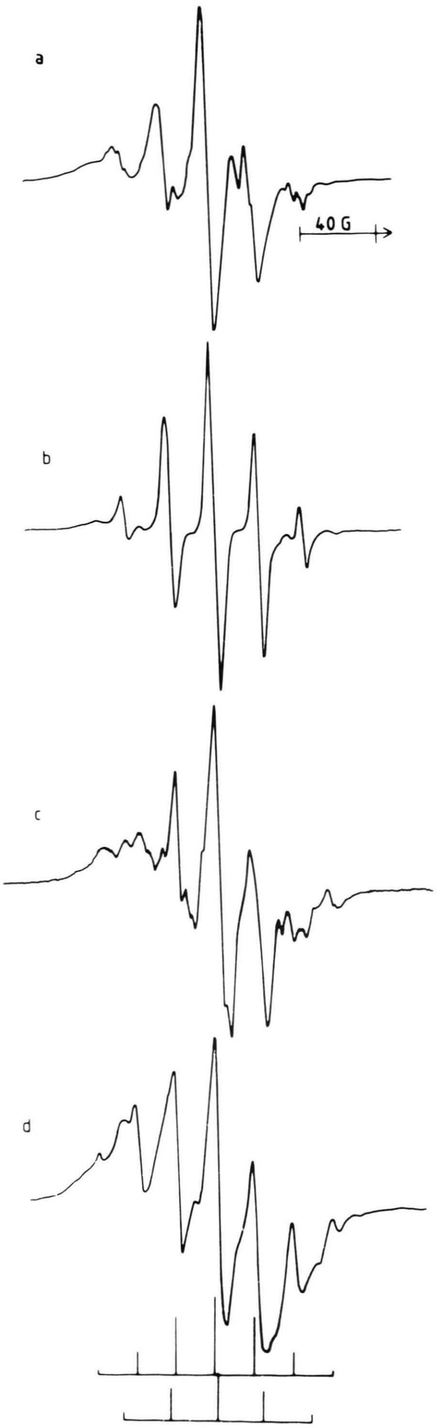


Fig. 4. First derivative ESR spectra at 142 K of metacrylate solutes in a CF_3CCl_3 matrix irradiated at 77 K after photobleaching with visible light. a) solute = methyl metacrylate; b) solute = methylmetacrylate-d_3; c) solute = isopropylmetacrylate; d) solute = *n*-butylmetacrylate.

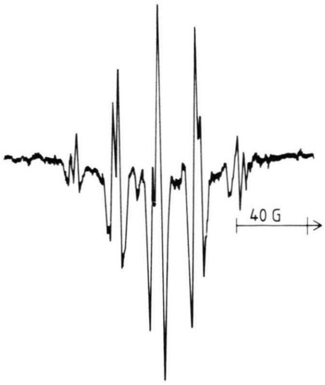


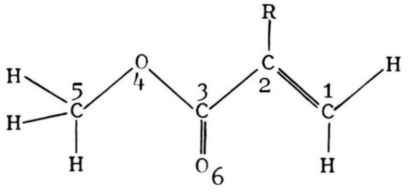
Fig. 5. Second derivative ESR spectrum at 142 K of isopropylmetacrylate in a CF_3CCl_3 matrix irradiated at 77 K. The sample was warmed to 180 K before the recording.

First derivative ESR spectra of samples containing MMA, MMA-d_3, *i*-propylmetacrylate and *n*-butylmetacrylate recorded after photobleaching are compared in Figure 4a–d. The MMA-d_3 sample is seen to produce the same main five line spectrum as in the case of ordinary MMA. The additional substructure, which is visible in the sample containing MMA, was absent, however, compare Fig. 4a and b. This shows that the substructure in this case originates from the ester alkyl group. This structure, $a_{CH_3} = 3.5$ G, was resolved into a quartet of lines in the second derivative spectrum, see stick diagram below Figure 3b. The spectra from the samples containing isopropylacrylate and *n*-butylmetacrylate, are shown in Fig. 4c and d. We suggest that a five line spectrum with $a = 23$ G gives rise to the broad lines and shoulders indicated by the stick diagram below Fig. 4d, and that a septet spectrum with a splitting of $a = 21.0$ G is superimposed. The spectrum from the sample containing *i*-propylmetacrylate in Fig. 4c, can be similarly explained.

In an attempt to support this suggestion the photobleached sample containing *i*-propylmetacrylate was warmed to 180 K and then recooled to 142 K. By this treatment the quintet structure became very clear as is seen in Figure 5. The five lines are separated by $a_1 = 23.5$ G. An additional doublet splitting of $a_2 = 3.5$ G is most clearly seen on the extreme lines in Figure 5. A similar observation was made with a sample containing ethylmetacrylate. In this case the quintet splitting was $a_1 = 22.5$ G. A weaker septet with $a = 20.5$ G was also observed.

Structure of primary species of MMA and MA

The spectra obtained in the dark have $g = 2.003$, characteristic of a carbon-centred radical. As mentioned previously, there is no hyperfine coupling with the protons of the ester methyl group in the case of MMA. These two facts indicate that the unpaired spin density is localised on the vinyl group. One possible assignment is that the spectra in Fig. 2 and Fig. 3a are due to the MA and MMA cations, respectively. The MA molecule is planar apart for the methyl group [12] and the same is probably true for the metacrylate, $R = H$(MA), $R = CH_3$(MMA)



This suggests the possibility of a π-electron structure for the cations of MA and MMA. The magnitude of the triplet splitting, $a = 25$ G, indicates that the spin density is localised on the C_1 atom in the case of MA. The quintet spectrum with $a = 15$ G in the case of MMA can be explained with accidental equal couplings of the H atoms on C_1 and two out-of-plane H atoms in the CH_3 group, the remaining (in plane) H atom coupling being unresolved. The spin density is thus delocalised over the vinyl group.

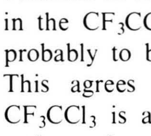
The assignment was tested by performing an INDO calculation on the MA cation with the geometry of the parent molecule [12]. According to this calculation the unpaired spin density was mainly localised on O_6 in a 2 p orbital in the molecular plane and perpendicular to the $C_3{=}O_6$ bond. The calculated proton hyperfine couplings were small ($\leqq 3$ G). A positive g-factor shift is expected for an oxygen centred cation radical, compare the case of acrolein. This was not observed experimentally. Thus, the INDO calculation is not in agreement with the interpretation that the MA and MMA cations have a π-electron structure suggested above. This forces us to consider alternative assignments of the spectra in Figs. 2 and 3a.

Abstraction of an H atom from C_5 would give an alkyl radical centred at C_5 with a triplet spectrum as observed for MA. Alkyl radicals are as a rule not easily photobleached, however, as we observed experimentally, for the species in MA. Vinyl radicals obtained by abstraction of an H atom from C_1 or C_2 would probably give a spectrum with two inequivalent proton couplings [13] rather than a triplet as observed. A radical obtained by addition of an H atom to the vinyl group would give an alkyl radical with couplings to four H atoms. A secondary radical obtained by addition of a precursor radical to the vinyl group of another MA molecule would probably not be sensitive to photobleaching as observed. In the case of MMA a radical obtained by abstraction of an H atom from the α-methyl group (= R) would give an allyl type radical with a quintet structure similar to that observed. The radical would probably not be easily photobleached, however, contrary to the observation illustrated in Figure 3. Other possibilities analogous to those discussed above for MA have been considered unlikely.

The conclusion is that the alternative assignments discussed above are less probable and the spectra obtained in the dark from MA and MMA contained in the CF_3CCl_3 matrix, Figs. 2 and 3a, are more probably to be assigned to the molecular cations. This agrees with the previous experience that CF_3CCl_3 is an efficient matrix to trap molecular cations of organic compounds [5–7]. It is known that the INDO method sometimes predicts a wrong ground state of radicals, see for example [14]. A definite assignment in the case of MMA and MA seems to require ESR studies of substances specifically deuterated in the vinyl group and also more accurate molecular orbital calculations.

Photoinduced reactions

Two interpretations of the spectra obtained by photobleaching samples containing MMA will be suggested. According to the first, the five line spectrum with $a = 23$ G observed in the diagram shown in Fig. 3b is due to the propagating radical



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CCOOCH_3}{\overset{|}{\underset{|}{C}}}}\cdot$$

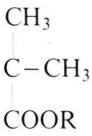
. This interpretation implies that a polymerization is initiated, probably cationically, under the influence of illumination. As is well known [15], a nine line spectrum is expected for this radical, but only five lines with a separation of 25 G are sharp. There are some difficulties with this interpretation, however. Thus the substructure seen in Fig. 3b is difficult to reconcile with the propagating radical. The effect of deuteration illustrated in Figs. 4a and b unambigously demonstrates that the substructure originates from the ester group. Such a substructure from a distant group has not been observed previously in the propagating radical. It has been observed in ESR spectra of radicals formed by radical addition to MMA in a flow system, however [16].

Another dfficulty with the propagating radical hypothesis is that the MMA molecules are present at low concentration in the CF_3CCl_3 matrix. If the molecules are well dispersed the reaction between a cation and one or several MMA molecules to form the propagating radical should not occur easily in the rigid CF_3CCl_3 matrix, contrary to observation. These facts have lead us to consider an alternative interpretation. According to the second interpretation a radical cation is present also after photobleaching. It may be formed from the primary species either by an isomerisation reaction or merely by a change in the conformation. The spin density in radical cations is often delocalised, and a small splitting from the ester hydrogen atoms is not unreasonable. There are, however, problems also with this interpretation. Thus, the isomeric structure or the conformation of the MMA cation after photobleaching is not clear. Another difficulty with the cation hypothesis is that the quintet spectrum with $a = 23$ G could be observed after warming to 180 K, Figure 5. In our previous experiments [5–7] with organic solutes in CF_3CCl_3 it appeared that the matrix looses the ability to trap cations above 142 K. It seems that experiments with MMA deuterated at the α-methyl group would be helpful for an unambigous assignment of the spectrum obtained after photobleaching.

The sensitivity to photobleaching decreased depending on the size of the substituent alkyl ester group in the order

$$CH_3 > CD_3 > C_2H_5 \gtrsim i\text{-}C_3H_7 \gtrsim n\text{-}C_4H_9 .$$

Thus, with CD_3 as the ester group, a few minutes photobleaching was required to completely transform the spectrum to the 23 G quintet. This effect is to be expected if any of the two interpretations is correct.

The spectrum of the sample containing n-butylmetacrylate seems to contain two components after photobleaching. The first is the five line spectrum just discussed, the other is the sharp septet spectrum marked in Figure 4d. A septet spectrum would be obtained from the secondary species of the type  $\cdot\underset{\displaystyle COOR}{\overset{\displaystyle CH_3}{C}}-CH_3$ derived, formally, by hydrogen atom addition to the vinyl group. The reason for the sharp lines is that the methyl splitting is usually isotropic, so that broadening due to anisotropy does not occur. The measured hyperfine coupling $a = 23.0$ G agrees with the value obtained in a pure MMA single crystal [17].

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