ESR of the $.CD_3 \ldots I^-$ adduct in γ-irradiated $^{12}CD_3I$ and $^{13}CD_3I$ Crystals

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Z. Naturforsch. **39 a**, 1056 – 1060 (1984); received August 16, 1984

An alkyl radical-iodide anion adduct $.CD_3 \ldots I^-$ has been detected in γ-irradiated $^{12}CD_3I$ and $^{13}CD_3I$ by ESR measurements on single crystals at 77 K. The species has hyperfine couplings of $A_{\parallel} = 80 \cdot 9$ G, $A_{\perp} = 39$ G with ^{127}I and $A_{\parallel} = 80$ G, $A_{\perp} = 20$ G with ^{13}C. By comparison with INDO calculations it is concluded that the $.CD_3$ group is planar with the I^- ion at a distance of ca. 3 Å and located on the $.CD_3$ three-fold axis.

Introduction

Alkyl radical-halide ion adducts were first detected by Sprague and Williams in their studies of solutions of methyl bromide in methyl cyanide after γ-irradiation at 77 K [1]. Similar complexes were later reported by Mishra and Symons for several alkyl halides dissolved in CD_3CN after exposure to γ-rays at 77 K [2]. We have found that the adduct $.CD_3 \ldots I^-$ is stabilised in γ-irradiated CD_3I at 77 K. In this paper we investigate this species by ESR using single crystals of $^{12}CD_3I$ and $^{13}CD_3I$.

Experimental

The chemicals were $^{12}CH_3I$ of a claimed purity of 99% and $^{12}CD_3I$ of a claimed purity of 99.5% with a degree of deuteration of 99%. Both were supplied by Merck. A sample of $^{13}CD_3I$ with an isotopic purity of 99% ^{13}C and 98% D was obtained from Merck, Sharp and Dohme. The compounds were not further purified but after removal of the silver leaf stabilizer directly poured into the suprasil quartz tubes which were used for the ESR measurements. In order to avoid decomposition of the compounds after the removal of the stabilizer the sample preparation and handling were carried out in the dark. Single crystals of the compounds were grown in the tubes by a freezing method which has been described [3]. The melting point of $^{12}CH_3I$ is − 68 °C. A cryostat temperature of − 90 °C gave good crystals. Several crystals, of each compound, were grown. The crystal structure of methyliodide is not known and we did not determine the crystal orientation in the sample tube.

The samples were irradiated in a ^{60}Co AEC Gammacell 220 at a dose rate of 0.2 Mrad h^{-1} to a total dose of 0.8 Mrad. The irradiation temperature was 77 K. ESR measurements were done with a Varian E-9 spectrometer operated in the X-band. Measurement temperature was 77 K. The angular variation of the ESR spectra in three perpendicular planes were obtained by rotating the crystal about three axes perpendicular to the magnetic field.

Results

The samples were transparent after preparation but when they were put into liquid nitrogen a few cracks appeared. The ESR spectra were anisotropic on rotation which makes us believe that the samples are single crystals, and the different samples of methyliodide and deuteromethyliodide had the same respective spectra, which shows that the crystal growing was reproducible.

The ESR spectrum of γ-irradiated $^{12}CD_3I$ and $^{13}CD_3I$ changed irreversibly during a few days of storing in darkness at 77 K. We therefore investigated the samples of deuteromethyliodide immediately after irradiation as well as after about five days of ageing.

Single crystal data

In Fig. 1 a is shown an example of a spectrum of irradiated $^{12}CD_3I$ immediately after irradiation at 77 K. It consists of one single narrow line in the center flanked by six broader lines. Further out are

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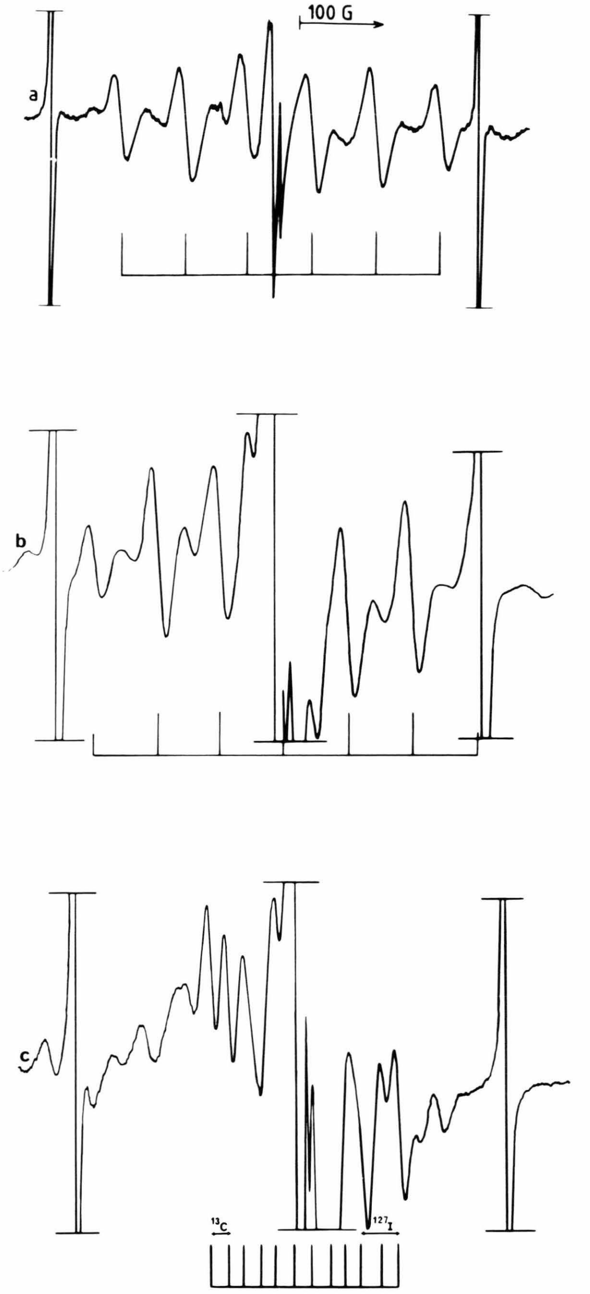


Fig. 1. Single crystal ESR spectra from $^{12}CD_3I$ recorded immediately after γ-irradiation at 77 K with the magnetic field perpendicular to the sample tube axis
a) $^{12}CD_3I$ sample oriented for maximum total width ($\theta = 0°$);
b) $^{13}CD_3I$ sample oriented for maximum total width ($\theta = 0°$);
c) $^{13}CD_3I$ sample oriented for minimum total width ($\theta = 90°$).
The stickplots correspond to the $.CD_3 \ldots I^-$ species discussed in the text.

two intense narrow lines separated by 505 G due to H atoms in the ESR quartz tube. The center line is attributed to a radiation damage center in the quartz. The six line component was anisotropic. Figure 1a corresponds to the orientation on rotation about the tube axis (z) where the total width of the six line component has a maximum. The six lines are attributed to hyperfine interaction with an ^{127}I nucleus ($I = 5/2$). The angular variation of the line positions on rotation around the sample tube axis is plotted in Figure 2. The next rotation axis (x) was chosen to coincide with the direction of the maximum width of the six line spectrum, shown in Fig. 1a. The angular variation of the line positions showed considerably less anisotropy than in Figure 2. The third axis of rotation (y) was chosen perpendicular to the first two axes. Two magnetic sites were observed in the spectra when the cyrstal was rotated about the x and y axes. The coupling tensors, derived from measurements in three orthogonal planes, [4] are collected in Table 1.

The ESR spectra of γ-irradiated $^{13}CD_3I$ were investigated in the same manner as described for $^{12}CD_3I$. The spectrum in Fig. 1b was obtained for the orientation giving the maximum total width

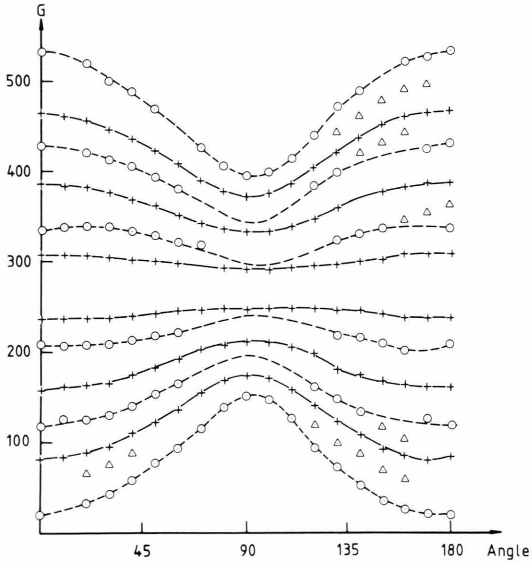


Fig. 2. Angular variation of the ESR line positions in a $^{12}CD_3I$ crystal immediately after irradiation at 77 K. The crystal was rotated about the sample tube axis. Full lines correspond to the $.CD_3 \ldots I^-$ species, dashed lines to a similar species present in a lower yield. Points marked by △ are not identified.

when the sample was rotated about the tube axis (z), and the crystal orientation is therefore nearly the same as in Figure 1a. The lines marked by the stick plot diagram are due to a species with hyperfine couplings to the ^{127}I and ^{13}C ($I = 1/2$) nuclei. At the particular orientation in Fig. 1b the ^{127}I and the ^{13}C hyperfine couplings are equal, so that a seven line spectrum is obtained for the species in $^{13}CD_3I$.

In the spectrum corresponding to the total minimum width in the xy-plane the ^{13}C and ^{127}I hyperfine splittings are unequal, $\mathbf{a}$ (^{13}C) = 20 G, $\mathbf{a}$ (^{127}I) = 39.5 G according to the stick plot analysis in Figure 1c. We did not manage to get detailed data in the xz and yz planes, due to the limited amount of the $^{13}CD_3I$ sample available. The ^{13}C coupling tensors in Table 1 were obtained by combining the single crystal data with those obtained from polycrystalline spectra, see below.

The species observed in $^{12}CD_3I$ disappeared when the crystals were aged at 77 K for a few days, giving the relatively simple six line spectrum with a high g-factor of $g = 2.028$ shown in Figure 3a. The species responsible for this spectrum obviously contains a ^{127}I nucleus giving rise to the hyperfine pattern. At most other orientations the spectra were more complex and an analysis was not under taken. A reasonable assignment is $.\,^{12}CD_2I$. A central line with an isotropic g-factor of $g = 2.0023$ can be partially resolved in 7 components, separated by 3.5 G, Figure 3b. It is assigned to the $.\,CD_3$ radical.

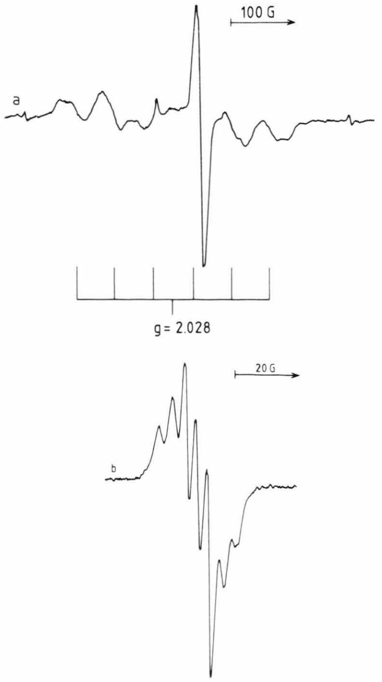


Fig. 3. Single crystal ESR spectra from CD_3I recorded 2 days after γ-irradiation at 77 K. The orientation is such as to give a maximum splitting in the plane perpendicular to the sample tube axis a) full spectrum and b) center part at higher resolution.

Single crystals of $^{12}CH_3I$ were also irradiated and measured at 77 K. No sign of the primary species observed in $^{12}CD_3I$ was detected. Such a species is obviously unstable in CH_3I at this temperature. An isotropic quartet of lines with $a_{\text{iso}} = 23$ G having a binomial intensity distribution was observed superimposed on a broad background. The quartet is assigned to the $.\,CH_3$ radical. The background spectrum was not analysed.

Polycrystalline data

A polycrystalline sample of freshly irradiated $^{12}CD_3I$ gave the spectrum shown in Figure 4a. The interpretation, indicated by the stick diagram under the spectrum in Fig. 4a is in agreement with the single crystal data. A calculation of the polycrystalline spectrum using the parameters of the species in Table 1 was also attempted. The computer program used is an extended version of that described previously [5] allowing for second order hyperfine shifts [6] and quadrupolar interactions. Best agreement with experiment was obtained by assuming axial symmetry with a small value of $Q_{\parallel} \leqq 2.5$ G. The calculated spectrum is shown in Figure 5b. There appears to be an additional weaker signal present in the experimental spectrum. Lines due to this species are also observed in the single crystal, see Figure 2. This spectrum has $A_{\parallel}$ (^{127}I) = 106 G, $|A_{\perp}(^{127}\text{I})| = 48$ G and a nearly isotopic g-factor according to the stick diagram above the spectrum in Figure 4a.

A polycrystalline sample of freshly irradiated $^{13}CD_3I$ was also recorded at 77 K and some simulations were undertaken in order to complement the single crystal data. Best agreement was obtained when the ^{13}C and ^{127}I hyperfine coupling tensors were taken to be axially symmetric with colinear principal axes. The parameters obtained for the ^{13}C hyperfine coupling are $A_{\parallel}(^{13}\text{C}) = 80$ G, $|A_{\perp}(^{13}\text{C})| = 20$ G, the latter value being deduced from the single crystal data. According to the simulations the value of $|A_{\perp}(^{13}\text{C})|$ is in the range 5 – 20 G.

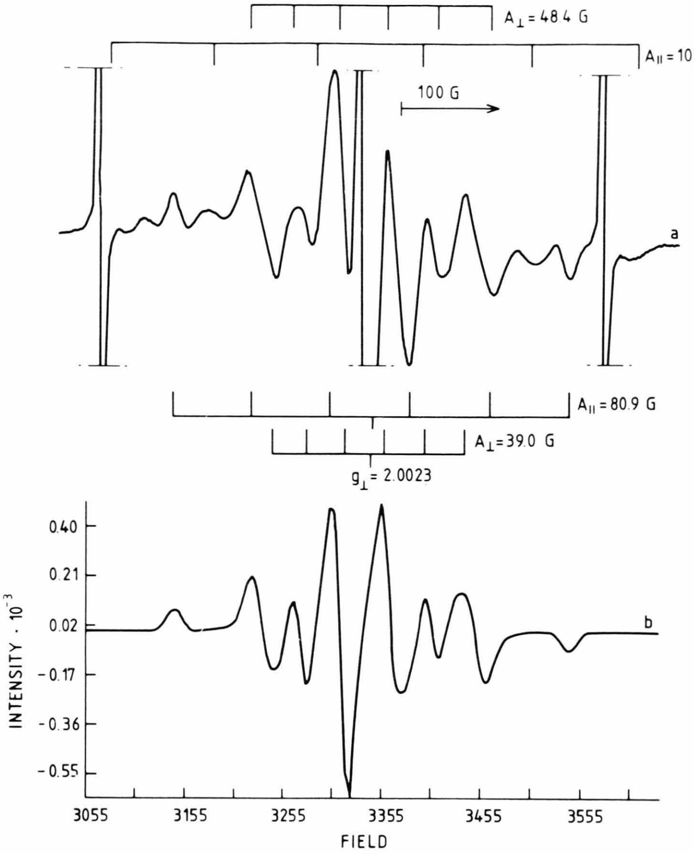


Fig. 4. a) Polycrystalline ESR spectra of $^{12}CD_3I$ immediately after γ-irradiation at 77 K. Parallel and perpendicular line positions for two types of $.CD_3 \ldots I^-$ species are indicated by stick plots. – b) Simulated spectrum using data for the major $.CD_3 \ldots I^-$ species.

Table 1. ESR data for the $.CD_3 \ldots I^-$ species in γ-irradiated CD_3I at 77 K. The g-factor is 2.0017–2.0023.

Nucleus	A_i (G)	Direction cosines with respect to		
		x	y	z
^{127}I	80.9	0.247	0.886	±0.392
	39.0			
	39.0			
^{13}C	$A_\parallel = 80$			
	$A_\perp = 20$			

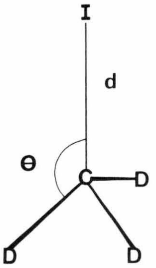
Radical Structure

The primary species observed in freshly irradiated $^{12}CD_3I$ and $^{13}CD_3I$ crystals has an almost isotropic g-factor close to the free electron value. The species was observed in different samples, i.e. in $^{12}CD_3I$ and $^{13}CD_3I$ with high purities from different suppliers indicating that the species is not due to an impurity. The elements of the iodine hyperfine coupling tensor are smaller than those found for genuine anions [7]. The quadrupole interaction is at least an order of magnitude smaller than in an α-iodine radical [8]. The value of $A_\parallel(^{13}C) = 80$ G is close to the splitting of $A_\parallel(^{13}C) = 82.7$ G in the methyl radical [9]. These observations suggest that the species observed is the adduct anion $.CD_3 \ldots I^-$. Such radical-halide anion adducts have been detected previously in γ-irradiated methyl bromide and iodide contained in a CD_3CN matrix [1, 2].

If one assumes that the $A_\parallel(^{13}C)$ and $A_\perp(^{13}C)$ couplings have the same (positive) sign then $A_{iso}(^{13}C) = 40$ G. The dipolar coupling becomes $2B(^{13}C) = 40$ G. These values are fairly close to the couplings $A_{iso}(^{13}C) = 38$ G, $2B(^{13}C) = 45$ G for the planar methyl radical [9]. The alternative assumption that $A_\parallel(^{13}C)$ and $A_\perp(^{13}C)$ have opposite signs results in values of $A_{iso}(^{13}C) = 13$ G, $2B(^{13}C) = 67$ G, which differ from the values to be expected for planar or pyramidal methyl radicals in a $.CD_3 \ldots I^-$ adduct (see below). We conclude that the parallel and perpendicular couplings have the same sign. The ^{127}I hyperfine coupling is, within experimental error, axially symmetric. If one assumes that the principal values of the ^{127}I couplings have the same sign, then $A_{iso}(^{127}I) = 53$ G, $2B(^{127}I) = 28$ G. The spin densities at the iodide ion were estimated as $\varrho_s(^{127}I) = 53/7294 = 0.007$ and $\varrho_p(^{127}I) = 28/453 = 0.062$ using the usual procedures [2]. These values are close to the halide spin densities in $.CH_3 \ldots Br^-$ and $.CH_3 \ldots I^-$ trapped in CD_3CN [2]. If $A_\parallel$ and $A_\perp$ have different signs then $\varrho_s(^{127}I) \leqq 0.001$, $\varrho_p(^{127}I) = 0.17$. It is difficult to account for a p orbital density of this magnitude without any significant s orbital spin density. We conclude that the principal values of the ^{127}I hyperfine coupling are of the same (positive) sign.

INDO Calculation

The spin densities and hyperfine coupling constants of the $.CD_3 \ldots I^-$ complex were investigated using a computer program developed by Oloff [10]. We assumed that I^- was located on the C_3 axis of the $.CD_3$ radical as indicated below



The parameters d and θ were varied while the C–D bond length was kept at 1.1 Å. An energy minimum was found for $d = 2.3$ Å, $\theta = 112°$ which corresponds to a genuine anion. The calculated values of A_{iso} (^{13}C) = 185 G and A_{iso} (^{127}I) = 310 G were much larger than the experimental couplings. No additional energy minimum was found for other (longer) distances d. On the other hand reasonable agreement between experimental and theoretical data was obtained for $d = 3.0$ Å and $\theta = 90°$, corresponding to a planar $.CD_3$ group. The calculated values were ϱ_p (^{13}C) = 0.93, ϱ_p (^{127}I) = 0.065, in good agreement with the experimental values ϱ_p (^{13}C) = 40/45 = 0.89, ϱ_p (^{127}I) = 0.062. We conclude that the iodide ion is at a distance of about 3 Å and that a probable geometry is as indicated above with $\theta = 90°$ (planar CD_3 group).

Discussion

The species $.CD_3 \ldots I^-$ is a product of anionic decomposition. It seems that the stabilisation is not caused by a real energy minimum for a certain $C \ldots I^-$ distance but is due to the cage effect which prevents a complete dissociation. This opinion is in agreement with the conclusion reached by Mishra and Symons for a similar complex in a CD_3CN matrix [2]. Their conclusion that the species is formed directly after electron capture with no resulting energy minimum for the parent CD_3I^- ion seems to be in contradiction with our INDO results. We cannot exclude that the adduct species is a secondary product and that the primary molecular anion might be detected under some circumstances.

Equal amounts of positively and negatively charged species must be formed by the action of the ionising radiation. We have not been able to characterize the cationic product completely. We conjecture that the molecular cation deprotonates to give the radical product $.CD_2I$, which is tentatively identified from the single crystal spectra of $^{12}CD_3I$ (Figure 3).

In conclusion we have obtained ESR evidence for an adduct ion $.CD_3 \ldots I^-$ formed by partial dissociation of the molecular ion. This type of adduct has been detected before [1, 2] but our study is the first on a ^{13}C labelled single crystal.

Acknowledgement

The work was supported by the Swedish Science Research Council.

[1] E. D. Sprague and Ff. Williams, J. Chem. Phys. **54**, 5425 (1971).
[2] S. P. Mishra and M. C. R. Symons, J. C. S. Perkin II **391** (1973).
[3] T. Dahlgren, T. Gillbro, G. Nilson, and A. Lund, J. Phys. E: Sci. Instr. **4**, 61 (1971).
[4] a) D. S. Schonland, Proc. Phys. Soc. London **73**, 788 (1959). – b) A. Lund and T. Vänngård, J. Chem. Phys. **42**, 2979 (1965).
[5] a) K. Å. Thuomas and A. Lund, J. Magn. Res. **22**, 315 (1976). – b) A. Lund, K. Å. Thuomas, and J. Maruani, J. Magn. Res. **30**, 505 (1978).
[6] O. Claesson and A. Lund, Research Report NFFL-24, The Studsvik Science Research Laboratory (1980).
[7] P. O. Samskog, L. D. Kispert, and B. Kalyanaraman, J. Chem. Soc. Faraday **2**, in press.
[8] J. Hüttermann, G. W. Neilson, and M. C. R. Symons, Mol. Phys. **32**, 269 (1976).
[9] Landolt-Börnstein, Zahlenwerte und Funktionen, Band 9, Magnetische Eigenschaften freier Radikale, Teil B, Springer-Verlag, Berlin 1977.
[10] H. Oloff, Thesis Regensburg 1981.