# 31. ESR. Study of an X-Irradiated Single Crystal of Methylene Diarsonic Acid

by **Michel Geoffroy** and **Antoine Llinares**

Département de Chimie Physique, Section de Chimie 30, quai E.-Ansermet, CH-1211 Genève 4

(7.X.80)

## *Summary*

X-Irradiation of single crystals of methylene diarsonic acid gives rise to a variety of radicals which have been identified by ESR. spectroscopy: $(OH)_2As(O)\dot{C}HAs(O)(OH)_2$, $^{-}O\dot{A}s(OH)_2CH_2As(O)(OH)_2$, $AsO_3^{--}$ and $(OH)\dot{A}s(O)CH_2As(O)(OH)_2$. The spin densities have been obtained from the $^{75}$As-hyperfine tensors. An additional species - probably a radical anion localized on a pentacoordinated arsenic - is also detected after annealing at room temperature. The radiation damage process is discussed.

**1. Introduction.** - ESR. studies of irradiated compounds have frequently been useful in explaining radical reaction mechanisms occurring when organic molecules are exposed to ionizing radiations. Carboxylic acids and amino acids have been intensively studied and for malonic acid different reaction steps have been determined [1-3].

The sensitivity of organic compounds to radiation can be considerably modified by the presence of a heteroatom. In previous investigations we have identified different paramagnetic species produced during X-irradiation of methylene diphosphonic acid [4] [5]. In the present study we report ESR. spectra obtained by X-irradiation of single crystals of $(OH)_2(O)As{-}CH_2{-}As(O)(OH)_2$. The determination of the $\bar{g}$ and $^{75}$As-hyperfine tensors ($^{75}$As: $I = 3/2$, natural abundance = 100%) enables us to identify four different paramagnetic species and to discuss the structure of two novel radicals: a 'phosphoranyl' type radical containing an As-atom in $\beta$-position and a C-centered radical containing two As-atoms in $\alpha$-positions. Furthermore, modifications of the spectra indicate that - at room temperature - radical reactions can give rise to a pentacoordinated arsenic radical anion.

**2. Experimental.** - Methylene diarsonic acid was synthesized following a published method [6]. Single crystals were obtained by very slow evaporation of a solution in water. These crystals were exposed to the radiation of a *Philips* tube PW 2184 (tungsten anticathode, 30 kV, 30 mA) at 77 K or at room temperature. They were then studied on a VARIAN E9 ESR spectrometer at 77 K or at 298 K. Further experimental details have been given elsewhere [7]. The spin densities are obtained by using the following atomic parameters: $^{75}As - A_{iso} = 14{,}660$ MHz [8] and $^{75}As - 2B_0$ (contribution of an electron in a 4p orbital) = 548 MHz [9]. The morphology of a crystal of $(HO)_2(O)AsCH_2As(O)(OH)_2$ is given on *Figure 1*

0018-019X/81/1/0329-09$01.00/0

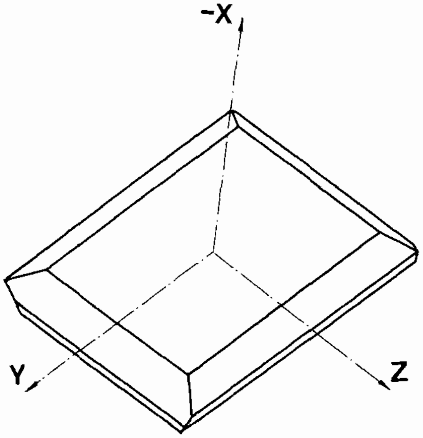


Fig. 1. *Single crystal of methylene diarsonic acid together with the ESR. reference axes*

together with the axes to which the ESR. tensors are referred. The crystallographic structure for $(OH)_2As(O)CH_2As(O)(OH)_2$ is unknown but that of $(OH)_2P(O)CH_2P(O)(OH)_2$ has been published [10].

**3. Results.** - In *Figure 2* we show an ESR. spectrum obtained at 77 K with a single crystal freshly irradiated at 298 K. Three sorts of signals are clearly observed: i) signals *A* due to a small coupling with two equivalent arsenic nuclei and to an additional coupling with a spin 1/2 nucleus; ii) signals *B* showing hyperfine interactions with two very different $^{75}$As-nuclei; iii) signals $C_1$, $C_2$ and $C_3$ due to a species exhibiting a large hyperfine interaction with a single As-nucleus.

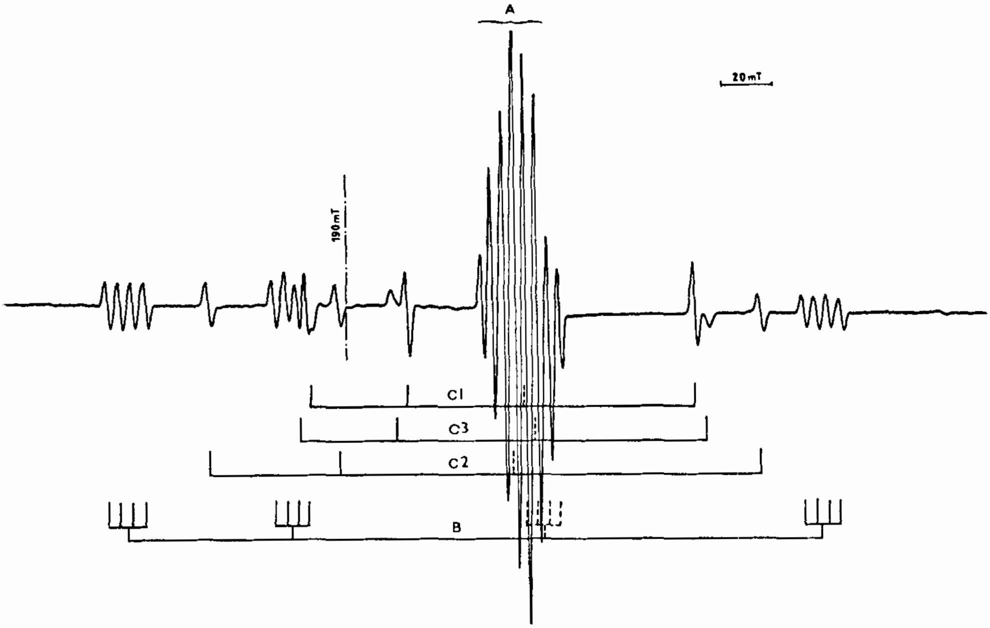


Fig. 2. *Example of an ESR. spectrum obtained at 77 K with a freshly irradiated single crystal of methylene diarsonic acid*

After annealing for two days at room temperature the two last sets of signals disappear and a fourth species appears (signals *D*). The spectrum due to this new radical is characterized by a considerable coupling to an $^{75}$As-nucleus (~4000 MHz), a small coupling with a second spin 3/2 nucleus is also observed. The corresponding spectrum is shown on *Figure 3*.

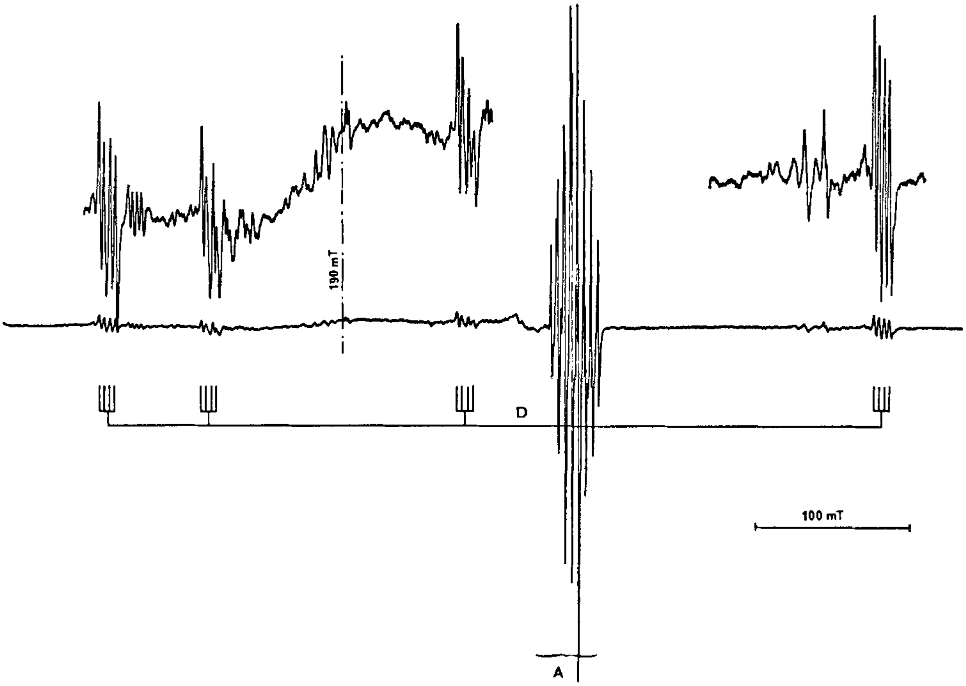
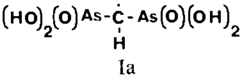
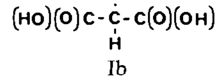


Fig. 3. *ESR. spectrum obtained with an irradiated crystal of methylene diarsonic acid after annealing at room temperature during two days*

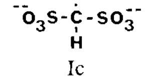
**4. Discussion.** - 4.1. *Identification and structure of the different radicals* - 4.1.1. *Radical centered on a C-atom.* This radical gives rise to a spectrum (signals *A*) whose analysis is illustrated in *Figure 4*. The unpaired electron interacts with two equivalent spin 3/2 nuclei and with a spin 1/2 nucleus. There is little doubt that this radical is produced by scission of a C, H-bond and corresponds to formula Ia.


$(HO)_2(O)As\text{-}\underset{H}{\dot{C}}\text{-}As(O)(OH)_2$

Ia


$(HO)(O)C\text{-}\underset{H}{\dot{C}}\text{-}C(O)(OH)$

Ib


$^{-}O_3S\text{-}\underset{H}{\dot{C}}\text{-}SO_3^{-}$

Ic

The *g* and the hyperfine tensors for radical Ia are given in *Table 1*. It is interesting to compare these parameters with those reported for the C-(Ib) and S-(Ic)analogues. The similarity between the H-coupling tensors for Ia, Ib and Ic indicates that the presence of two As-atoms does not modify appreciably the spin density on the central C-atom *(Table 2)*. This density, calculated by using the *McConnell* relation, is equal to 0.94±0.05 for the three species. This result shows

Table 1. *ESR. parameters for radicals trapped in an X-irradiated single crystal of methylene diarsonic acid*

| | Eigenvalues[a] | | Direction cosines[a] | | |
|---|---|---|---|---|---|
| | | | $\lambda$ | $\mu$ | $\nu$ |
| $(HO)_2(O)AsCHAs(O)(OH)_2$ (signals *A*) | | | | | |
| $\bar{g}$ | 2.003 | | 0.50 | 0.65 | 0.58 |
| | 2.002 | | −0.87 | 0.35 | 0.36 |
| | 1.998 | | 0.03 | −0.68 | 0.73 |
| $^1$H-$\bar{T}$(MHz) | 95.2 | | 0.99 | 0.07 | 0.14 |
| | 61.6 | | −0.14 | 0.82 | 0.56 |
| | 25.2 | | −0.08 | −0.57 | 0.82 |
| $^{75}$As-$\bar{T}$ (MHz) | 126.0 | | 0.99 | 0.05 | 0.12 |
| | 117.6 | | −0.12 | 0.68 | 0.76 |
| | 109.2 | | −0.05 | −0.73 | 0.68 |
| $(HO)_2\dot{A}s(O^-)CH_2As(O)(OH)_2$ (signals *B*) | | | | | |
| $\bar{g}$ | 2.006 | (2.006) | 0.06 ( 0.02) | −0.76 ( 0.75) | −0.65 ( 0.66) |
| | 1.998 | (2.000) | 0.80 (−0.72) | −0.37 (−0.45) | 0.47 ( 0.52) |
| | 1.994 | (1.994) | −0.60 ( 0.70) | −0.53 (−0.47) | 0.60 ( 0.54) |
| $^{75}$As-$\bar{T}$ (MHz) | 2775.0 | (2780.0) | 0.57 ( 0.56) | −0.41 ( 0.42) | 0.72 (−0.71) |
| | 2394.0 | (2394.0) | | | |
| | 2346.0 | (2335.0) | | | |
| $^{75}$As-$\bar{T}$ (MHz) | 168.0 | (176.0) | 0.40 ( 0.15) | 0.57 ( 0.56) | −0.72 ( 0.80) |
| | 145.0 | (142.0) | | | |
| | 131.0 | (134.0) | | | |
| $(HO)_2\dot{A}s{=}O$ (signals $C_1$) | | | | | |
| $\bar{g}$ | 2.011 | (2.012) | −0.05 ( 0.16) | −0.97 (−0.94) | 0.22 ( 0.29) |
| | 2.000 | (2.000) | 0.89 ( 0.92) | −0.06 ( 0.24) | −0.44 ( 0.31) |
| | 1.997 | (1.996) | 0.44 (−0.37) | 0.19 ( 0.22) | 0.88 ( 0.90) |
| $^{75}$As-$\bar{T}$ (MHz) | 1862.0 | (1862.0) | 0.05 ( 0.04) | 0.43 (−0.42) | 0.90 (−0.90) |
| | 1358.0 | (1355.0) | | | |
| | 1327.0 | (1330.0) | | | |
| $AsO_3^{--}$ (signals $C_2$) | | | | | |
| $\bar{g}$ | 2.004 | | 0.10 | −0.45 | 0.89 |
| | 2.000 | | 0.14 | −0.88 | −0.45 |
| | 1.997 | | 0.98 | 0.15 | 0.06 |
| $^{75}$As-$\bar{T}$ (MHz) | 2570.0 | | 0.01 | −0.97 | −0.25 |
| | 2046.0 | | | | |
| | 2030.0 | | | | |
| $(OH)\dot{A}s(O^{--})CH_2As(O)(OH)_2$ (signals $C_3$)[b] | | | | | |
| $\bar{g}$ | 2.010 | (2.011) | 0.20 (−0.20) | 0.96 ( 0.94) | 0.18 ( 0.25) |
| | 1.999 | (1.998) | −0.40 (−0.31) | −0.09 ( 0.23) | 0.91 (−0.92) |
| | 1.988 | (1.990) | 0.89 (−0.92) | −0.27 ( 0.20) | 0.37 ( 0.28) |
| $^{75}$As-$\bar{T}$ (MHz) | 2021.0 | (2004.0) | 0.07 ( 0.07) | 0.33 (−0.33) | −0.94 ( 0.94) |
| | 1528.0 | (1545.0) | | | |
| | 1444.0 | (1436.0) | | | |

---

[a] Data in parentheses correspond to other sites.

[b] Four additional sites are found for this radical, the corresponding data are close the values found for the four first sites.

Note: Except for radical *A* additional sites are obtained by permuting $\mu$ and $\nu$.

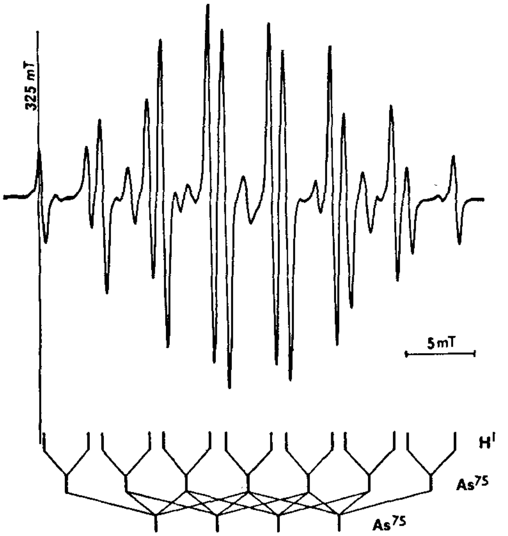


Fig. 4. *Central part of the ESR. spectrum (signals* A*) obtained with an X-irradiated single crystal of methylene diarsonic acid*

that the eventual participation of the arsenic 4-d orbitals does not lead to an important spin delocalization *via* a $p_\pi$-$d_\pi$, conjugation.

The large linewidth - due to the frequent overlap of the two crystallographic sites - together with the small anisotropy of the As-coupling makes the $^{75}$As-magnetic-hyperfine tensors less amenable to analysis. This experimental uncertainty is probably the cause of the equivalence of the two As-nuclei for whatever orientation of the magnetic field. Nevertheless it can be noticed that the spin populations calculated for the heteroatom are quite comparable for $(HO)_2(O)P\dot{C}H_2$ and $(HO)_2(O)As\dot{C}HAs(O)(OH)_2$ *(Table 2)*.

Table 2. *ESR. parameters and spin densities for some R–C(H)–R radicals*

| Radical | $H_\alpha$-coupling (G) | | | | Spin density on P/As[b]) | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | $\tau_x$ | $\tau_y$ | $\tau_z$ | $A_{iso}$ | $\rho_c$[a]) | $c_p^2$ | $c_s^2$ | |
| $[(OH)_2As(O)]_2\dot{C}H$ | 12.5 | 0.0 | −12.5 | −21.7 | 0.94 | 0.017 | 0.001 | c) |
| $OH{-}\overset{O}{\overset{\|}{P}}{-}\dot{C}H_2$ | 11.6 | 0.6 | −12.2 | −22.4 | 0.97 | 0.013 | 0.008 | [4] |
| $(SO_3^{--})_2\dot{C}H$ | 10.3 | 2 | −12.3 | −22.4 | 0.97 | | | [11] |
| $(COOH)_2\dot{C}H$ | 10.3 | 1.3 | −11.6 | −20.8 | 0.90 | | | [11] |

a) By using the *McConnell* equation $A_{iso} = -23\rho$ (Gauss).

b) By using the atomic parameters given in [8] [9].

c) This work.

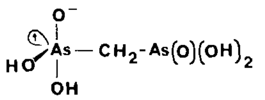
4.1.2. *Radicals centered on an As-atom.* - 4.1.2.1. *Radical centered on a tetra-coordinated As-atom.* Signals *B* are characterized by a strong coupling with an As-nucleus *(Table 1)*. The isotropic and anisotropic coupling constants show that 48% of the spin is localized in an arsenic-4p orbital while 17% is confined in an arsenic-4s orbital. The corresponding hybridization ratio and spin density (respectively $\lambda^2 = 2.8$ and $\Sigma = 0.65$) are quite consistent with a 'phosphoranyl type'

Table 3. *Spin densities for some arsoranyl and phosphoranyl radicals*

| | Spin densities on P/As | | | Hybridization ratio $\lambda^2$ | Ref. |
|---|---|---|---|---|---|
| | $c_p^2$ | $c_s^2$ | $\Sigma$ | | |
| $(HO)_2\dot{A}s(O^-)CH_2As(O)(OH)_2$ | 0.48 | 0.17 | 0.65 | 2.8 | [a] |
| $(CH_3)_2\dot{A}sO_2^{2-}$ | 0.46 | 0.18 | 0.64 | 2.5 | [13] |
| $Pr\dot{A}sO_3^{3-}$ | 0.58 | 0.23 | 0.81 | 2.5 | [12] |
| $(HO)_3\dot{P}CH_2P(O)(OH)_2$ | 0.60 | 0.19 | 0.79 | 3.1 | [5] |

[a] This work.

radical. Examples of parameters obtained with some phosphoranyl and arsoranyl radicals are given in *Table 3*. As we cannot detect any anisotropic hyperfine structure with a ligand it is impossible to determine the exact structure of this arsoranyl radical. The single additional parameter is the hyperfine tensor with a second As-nucleus. This coupling is essentially isotropic ($A_{iso} = 148$ MHz, $\tau_{\parallel} = 20$ MHz) and is in good accordance with a hyperconjugation mechanism. For some orientations an additional small splitting is observed, this further interaction probably arises from the methylene protons. Thus, we can identify the present radical as being $(OH)_2As(O)^- {-} CH_2 {-} As(O)(OH)_2$ for which II is a possible structure.



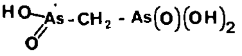
II

As indicated in *Table 1* there are four tensors which are assigned to this species; this is certainly due to the fact that in addition to two crystallographic sites there are two possibilities for a methylene diarsonic acid molecule to give rise to an arsoranyl radical. As shown from the crystallographic structure reported for $(HO)_2P(O){-}CH_2{-}P(O)(OH)_2$ [10] the two functional groups probably do not have a totally equivalent surrounding (role of hydrogen bonds) and the two resulting arsoranyl radicals can thus be differentiated.

4.1.2.2. *Radicals localized on a tricoordinated As-atom.* Four sites are obtained for the species corresponding to signals $C_1$. The scission of an As, C-bond is in good accordance with this observation and the parameters shown in *Table 1* agree well with those reported for $AsO_3^{--}$ (site 3) trapped in a single crystal of $KH_2AsO_4$, we think therefore that the present radical can be identified as being $^-O{-}As(OH)_2$.

The fact that only two sites are observed for signals $C_2$ suggests that the two $(HO)_2As(O)$ moieties give rise to a radical which can easily reorientate (*e.g.*: scission of hydrogen bonds) in order to occupy its most stable conformation. We tentatively identify this radical as being $AsO_3^{--}$. The parameters obtained for $AsO_3^{--}$ (site 1) trapped in a single crystal of $KH_2AsO_4$ are in good agreement with this suggestion.

The last species (signals $C_3$) can be identified with more certainty. Indeed for some orientations the splitting of the $C_3$ lines shows that these signals correspond to the overlap of two peaks. In the hypothesis that this splitting is not due to an additional hyperfine interaction we can conclude that eight sites are present for this radical. This indicates that each molecule can give rise to four paramagnetic fragments. There is little doubt that this radical results from the scission of one of the four As, O-bonds and that the signals $C_3$ are due to radical III.



III

Four tensors are given in *Table 1*; the four others - resulting from the splitting of the lines - have almost identical eigenvalues. The ESR. parameters for some arsonyl radicals are reported in *Table 4*; they very well agree with those found for radical $C_3$. Furthermore one can note that for irradiated methylene diarsonic acid the coupling with an As-atom in the $\beta$-position is detected for the arsoranyl radical while a similar $\beta$-coupling was observed for the phosphonyl radical in the case of $(OH)_2(O)PCH_2P(O)(OH)_2$ [5].

Table 4. *Spin densities for some $(HO)\dot{P}(O)-R$ and $(HO)\dot{A}s(O)-R$ radicals*

| | Spin densities on P/As | | | Hybridization ratio $\lambda^2$ | Ref. |
|---|---|---|---|---|---|
| | $c_p^2$ | $c_s^2$ | $\Sigma$ | | |
| $(HO)_2AsO$ (signals $C_1$) | 0.63 | 0.10 | 0.73 | 6.3 | [a] |
| $AsO_3^{--}$ (site 1/$KH_2AsO_4$) | 0.57 | 0.10 | 0.67 | 5.7 | [14] |
| $AsO_3^{--}$ (site 2/$KH_2AsO_4$) | 0.59 | 0.15 | 0.74 | 5.9 | [14] |
| $AsO_3^{--}$ (signals $C_2$) | 0.64 | 0.15 | 0.79 | 4.2 | [a] |
| $(HO)-\dot{A}s(O)-CH_2As(O)(OH)_2$ (signals $C_3$) | 0.62 | 0.11 | 0.73 | 5.6 | [a] |
| $Pr\dot{A}sO_2^-$ | 0.62 | 0.12 | 0.74 | 5.2 | [12] |
| $(HO)\dot{P}(O)-CH_2P(O)(OH)_2$ | 0.62 | 0.12 | 0.74 | 5.2 | [5] |

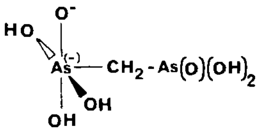
[a] This work.

4.1.2.3. *Radical localized on a pentacoordinated As-atom.* The unusual magnitude of the $^{75}$As coupling for radical *D* and the large anisotropy of this hyperfine interaction prevented us - for the moment - from determining the corresponding $\bar{g}$ and $^{75}$As-$\bar{T}$ tensors. Nevertheless some positions of the four main components of the spectrum (*e.g.*: $H_{m_I=3/2}=430$ G, $H_{m_I=1/2}=985$ G, $H_{m_I=-1/2}=2600$ G, $H_{m_I=-3/2}=5330$ G) indicates an arsenic coupling of ~4000 MHz. This value is similar to some constants reported for radicals localized on a pentacoordinated As-atom *(Table 5)*.

Table 5. *$^{75}$As-isotropic coupling for some radicals localized on a pentacoordinated As-atom*

| | $A_{iso}$ (MHz) | Ref. |
|---|---|---|
| $AsF_5^-$ | 5118 | [15] |
| $AsF_4O^{2-}_{apical}$ | 5193 | [16] |
| $AsF_4O^{2-}_{basal}$ | 4621 | [16] |

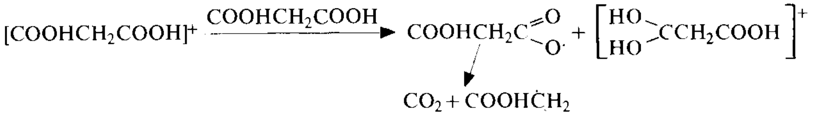
The observation of an additional coupling with an $^{75}$As-atom (T ~98 MHz) suggests the structure IV.



IV

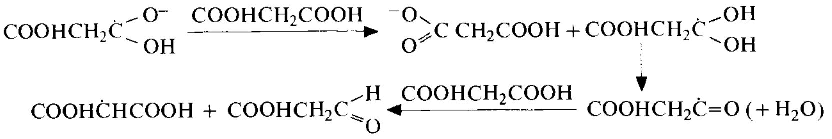
**4.2. The radiation damage process.** - For carboxylic acids it has been shown [1-2] that radiation damage results from the two following mechanisms:

i) reactions involving the formation of the cation:



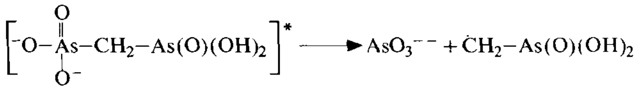
*(Reaction 1)*

ii) reactions involving the formation of the anion:



*(Reaction 2)*

In the present work the temperature dependance of the ESR. spectra only shows that all the species characterized in *Table 1* are present at 77 K and that the As-centered radicals progressively decrease between 77 K and 298 K. Nevertheless it can be seen that all radicals appearing in *reactions 2* have been identified in our study. Indeed $(OH)_2As(O){-}CH_2{-}\dot{A}s(OH)_3$, $(OH)_2As(O){-}CH_2{-}\dot{A}s(O)OH$ and $(OH)_2As(O){-}\dot{C}H{-}As(O)(OH)_2$ are respectively the arsenic analogues of $COOH{-}CH_2{-}\dot{C}(OH)_2$, $COOH{-}CH_2{-}\dot{C}{=}O$ and $COOH{-}\dot{C}H{-}COOH$. We did not detect $(OH)_2As(O){-}\dot{C}H_2$ which is probably the most stable radical produced after reaction of the cation *(reaction 1)*. However this fact does not necessarily imply that these reactions do not occur, the formation of $AsO_3^{--}$ also implies a homolytic scission of an As, C-bond *(reaction 3)* still, we could only observe the oxyanion radical.



*(Reaction 3)*

The fact that $(HO)_2P(O)\dot{C}H_2$ is the most abundant and the most stable radical produced when irradiating $(OH)_2P(O){-}CH_2{-}P(O)(OH)_2$ points out the crucial effect of the heteroatom on the radiation damage process.

Radical *D* is only observed when the irradiated crystal has been annealed during two days at room temperature; its formation coincides with the disappearance of the As-centered species. In the hypothesis of a radical anion centered on a pentacoordinated As-atom it is probable that this damage results from the addition of a hydroxyl anion onto the arsoranyl radical.

## REFERENCES

[1] *P.B. Ayscough & J.P. Oversby,* Trans. Faraday Soc. *67,* 1365 (1971).
[2] *B. Eda & M. Iwasaki,* J. Chem. Phys. *55,* 3442 (1971).
[3] *M. Kikuchi, N. Leray, J. Roncin & B. Joukoff,* Chem. Phys. *12,* 169 (1976).
[4] *M. Geoffroy, L. Ginet & E.A.C. Lucken,* Mol. Phys. *28,* 1289 (1974).
[5] *M. Geoffroy, L. Ginet & E.A.C. Lucken,* Mol. Phys. *31,* 745 (1976).
[6] *K. Sommer,* Z. Anorg. Allg. Chem. *377,* 120 (1970).
[7] *R. Franzi, M. Geoffroy, L. Ginet & N. Leray,* J. Phys. Chem. *83,* 2898 (1979).
[8] *J.R. Morton & K.F. Preston,* J. Magn. Reson. *30,* 577 (1978).
[9] *R.G. Barnes & W.V. Smith,* Phys. Rev. *93,* 95 (1954).
[10] *D. Delamatter, J.J. McCullough & C. Calvo,* J. Phys. Chem. *77,* 1146 (1973).
[11] *L. Bonazzola, C. Hesse-Bezot, N. Leray & J. Roncin,* J. Magn. Reson. *12,* 280 (1973).
[12] *A.R. Lyons & M.C.R. Symons,* J. Chem. Phys. *60,* 164 (1974).
[13] *M. Geoffroy & A. Llinares,* Helv. *62,* 1605 (1979).
[14] *J. Gaillard, O. Constantinescu & B. Lamotte,* J. Chem. Phys. *55,* 5447 (1971).
[15] *J.R. Morton, K.F. Preston & S.J. Strach,* J. Phys. Chem. *83,* 3418 (1979).
[16] *J.R. Morton, K.F. Preston & S.J. Strach,* J. Magn. Reson. *37,* 321 (1980).