Heteroatom Chemistry
Volume 15, Number 2, 2004

# EPR-Investigations of Radicals Derived from Diethyl Iodomethylphosphonate in Solid and Liquid State

Tomasz Białas, Aldona Szadowiak, and Piotr Bałczewski

*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Łódź, Sienkiewicza 112, Poland*

*Received 7 August 2003; revised 25 September 2003*

ABSTRACT: *A selective homolysis of the C—I bond in diethyl iodomethylphosphonate to give the diethoxyphosphorylmethyl radical $(EtO)_2P(O)CH_2\cdot$ was observed in EPR spectra upon $\gamma$-irradiation and UV–vis photolysis. Analysis of stability of this radical was also investigated to show disappearance of EPR signals above 170–190 K. An attempt to observe this radical during the reaction with AIBN as an initiator failed.* Heteroatom Chem 15:127–130, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10225

## INTRODUCTION

In the course of our recent studies [1–4] on the radically initiated addition reaction of iodoalkylphosphonates **3** to alkenes and alkynes **6**, we have recently focused on mechanistic aspects of the iodine atom transfer reaction. The mechanism is shown in Scheme 1.

So far, our mechanistic conclusions were based on identification of the stable final and intermediate products **4, 8**, and **10** [1,4]. In this paper, we tried to observe unstable radical species that take part in the discussed reaction, using the EPR technique.

During continuous photolysis of pure diethyl iodomethylphosphonate **3** ($R^1 = H$) in liquid nitrogen without a solvent we observed a spectrum of the radical **5** ($R^1 = H$). We also $\gamma$-irradiated a sample of the frozen benzene solution of **3** at 77 K. In that case we observed the disappearance of radicals **5** at gradually rising the temperature to about 200 K. Besides, we tried to obtain radical **5, 7**, and **9** at standard addition reaction conditions using d,d′-azoisobutyronitrile (AIBN) as an initiator.

## EXPERIMENTAL

EPR spectra were recorded using a Bruker ER 200D-SRC spectrometer (working in X band at a frequency of 9.4 GHz) coupled with a computer system ESP 3220-200 SH.

### *Preparation of Samples Containing* **3** *for the UV-vis Irradiation*

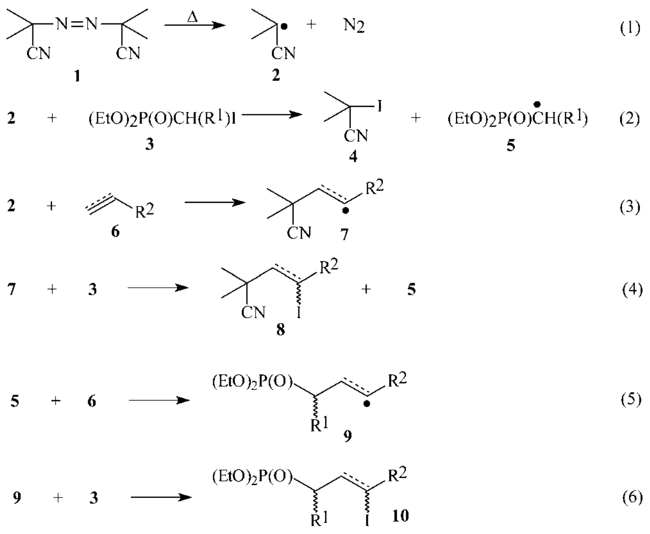
The diethyl iodomethylphosphonate **3** was synthesized according to a procedure described [2]. Samples containing **3** were prepared by dropping the pure **3** to liquid nitrogen using a thin pipette. Small spherical samples of the frozen compound were plunged in the liquid nitrogen placed in the Dewar's flask. Irradiation was carried out continuously using a mercury lamp HBO 200 W/2. This lamp generates a 280–600 nm light band with a maximum power at 365 nm.

---

This work is dedicated to the memory of the past Prof. A. Płonka.

*Correspondence to:* P. Bałczewski; e-mail: pbalczew@bilbo.cbmm.lodz.pl.

Contract grant sponsor: State Committee for Scientific Research.
Contract grant number: 7 T09A 139 21.



**SCHEME 1** A postulated mechanism of the reaction of AIBN, alkene (or alkyne), and diethyl iodoalkylphosphonate in a refluxing benzene solution. $R^1$: H, Me; $R^2$: $n$-$C_4H_9$, $n$-$C_5H_{11}$, $n$-$C_{14}H_{29}$.

## *Preparation of Samples Containing* **3** *for γ-Irradiation*

A sample of **3** (10 mg, 0.036 mmol) was dissolved in benzene (1 ml, $c = 0.036$ mol/l). Then, spherical samples of the frozen solution were formed using an analogous procedure as described above. The so formed spherical samples were ground in a mortar. The resulting powder was put into a thin glass tube sealed with a teflon strip at the bottom and filled with liquid nitrogen. The tube was filled with the powdered substance to a height of 1.5 cm. Next, the glass tube was sealed with the teflon strip at the top. Then, the tube with the substance was put into a test tube placed centrally in a Dewar's flask filled with liquid nitrogen. The sample prepared in this way was irradiated with the $^{60}$Co source (the dose rate—about 4.7 kGy/h). Samples for $\gamma$-irradiation of pure benzene were prepared using the similar method.

All samples were $\gamma$-irradiated for 1 h. When irradiation was completed, the irradiated powdered sample was put into a measurement tube (up to a height of about 1 cm). These samples were not drawn from liquid nitrogen during all described manipulations. Subsequently, the measurement tube was put into the Dewar's flask filled with liquid nitrogen.

## *A Procedure for the Controlled Heating of the Frozen γ-Irradiated Samples*

A device for heating of frozen samples above 77 K was constructed in the EPR laboratory of the Institute of Applied Radiation Chemistry at the Technical University of Łódź. It enables a continuous flow of nitrogen to the Dewar's insert, heaters, and a temperature regulator ITC 4 constructed by Oxford Instruments Ltd. The measurement tube with the sample was placed directly in the Dewar's insert. Velocities of the flow of nitrogen fumes could be adjusted manually by means of an autotransformer which controlled the first heater placed in a reservoir with liquid nitrogen. A second heater was put into the Dewar's insert and was controlled automatically by the temperature regulator. This allowed temperature maintainance with an accuracy of ±1 K.

The process of heating was effected according to the following procedure: first, a desired temperature was attained in the Dewar's insert, next the measurement tube (with the frozen benzene solution of **3**) was placed in it for 3 min. Then, the sample was put again into a cavity of the spectrometer. Adjusted temperatures: 110, 120, 130, 150, 170, and 190 K.

## *RESULTS AND DISCUSSION*

Analysis of EPR spectra of the phosphonate **3** ($R^1$ = H) photolyzed for 50 min (Fig. 1) or $\gamma$-irradiated (Fig. 2), revealed a signal attributed to the radical **5** ($R^1$ = H) formed from **3** via homolysis of the C—I bond. The EPR signal is split into a multiplet showing five lines in a 1:2:2:2:1 ratio caused by partially overlapping signals of a doublet ($A_{\mathrm{iso}}(^{31}P) = 44$ G) of triplets ($A_{\mathrm{iso}}(^{1}H) = 22$ G).

These values were similar to those reported for **5** in liquid state, $A(^{1}H) = 22$ G, $A(^{31}P) = 42.7$ G [5], and to those found for the structurally similar $(HO)_2P(O)CH_2\cdot$ radical in solid state, $A(^{1}H) = 21.5$ G and $A(^{31}P) = 41.5$ G [6]. A mean value of the $g$-factor equalled 2.0028 based on an EPR measurement with a $Cr^{3+}$ reference, for which $g_{Cr} = 1.9796$ [7]. Accurate

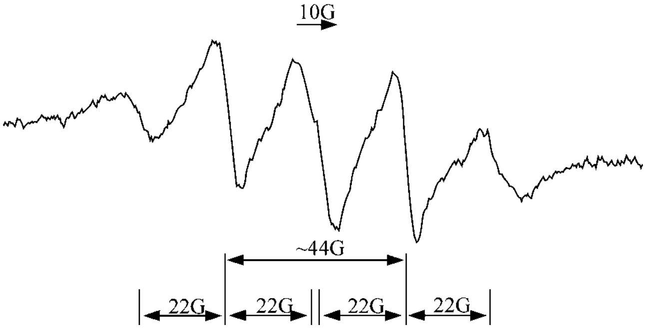


**FIGURE 1** A spectrum obtained upon UV-vis irradiation of the frozen sample of **3** in liquid nitrogen with the hyperfine splittings of **3** visualized.

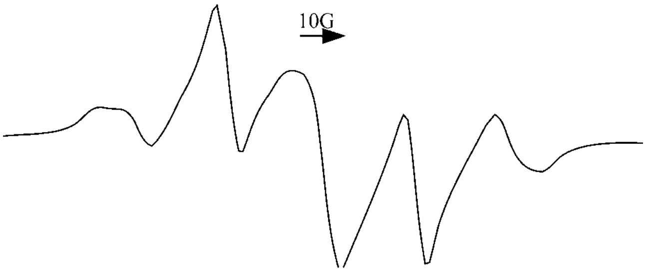


FIGURE 2 A spectrum obtained upon $\gamma$-irradiation of the sample frozen in liquid nitrogen.

values of the $g$-factor and hyperfine coupling constants were impossible to find due to broadening and irregularity of the peaks. Another reason is that both $g$ and $A$ values are tensors, generally consisting of three components each, that in our case may impose over lines from other tensors. In case of many organic radicals frozen in the carbohydrate matrices at 77 K, anisotropic components of the $A$ tensor for protons connected to the radical carbon centre are $-11, 0, +11$, and typical lines widths are in a 10–15 G range [8]. In our case, these values are of the same order of magnitude (about 10 G).

The $g$ value of the radical **5** found by us is similar to that reported for liquid state, but with lower accuracy. For the radical $(HO)_2P(O)CH_2\cdot$ derived from methylene diphosphonic acid, Geoffroy et al. [6] found $g_{av} = 2.0025$ (an average value of anisotropic components of the $g$-factor) in crystalline state at room temperature.

Based on the above findings one can conclude that the radical **5** is the main radical formed under $\gamma$-irradiation. This contrasts to previous work in which $\gamma$-irradiation of trimethylphosphine oxide [9] and dialkyl phosphonates [10] gave many different paramagnetic species that indicated breaking P—O, C—O bonds and C—H bonds in alkoxyl groups. A key reason of the selectivity in our case is undoubtedly a presence of a relatively weak C—I. An influence of a scavenging effect of benzene for free electrons generated during ionization and the benzene ability to dissipate an excitation energy of **3** cannot be excluded. Indeed $\gamma$-irradiation of pure benzene gave only a weak signal of much lesser intensity than intensity of **5**.

Next, we examined stability of radicals **5** as a function of temperature. Rising the temperature caused fast vanishing of these radicals. Just after 3 min at 110 K one could observe a decrease of intensities of EPR signals due to **5** (see Fig. 3). After heating the sample for further 3 min to 170–190 K all EPR signals disappeared.

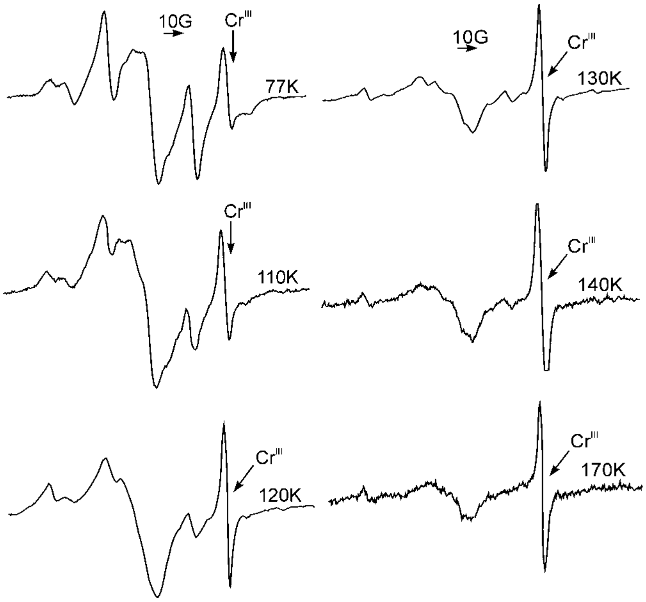


FIGURE 3 Spectra of the sample frozen in liquid nitrogen after heating up to 110, 120, 130, 140, and 170 K. A spectrum recorded at 77 K presented as a reference.

The possible recombination mechanisms involve a reverse reaction to the homolysis of the C—I bond, i.e. formation of the substrate **3** or dimerization of radicals [5,11].

It is also worth noticing that complete vanishing of the radicals at 190 K contrasts with the work [5], in which Baban and Roberts obtained a spectrum of the radical **5** in a liquid state at 236 K but in that case the radical **5** was generated under different reaction conditions, i.e. via continuous photolysis of a photoinitiator directly in a spectrometer cavity.

Attempts to generate radicals **5, 7**, and **9** in a chemical way using AIBN, **3**, and 1-hexene carried out in refluxing benzene failed.

Failure to observe radicals generated in a chemical way was a bit surprising and could be explained in the following way: (a) It is possible, that under the experimental conditions steady state concentration of the formed radicals were so low that it was below a sensitivity of the spectrometer (for a sample of $c = 0.1$ mol/dm$^3$, $10^{-8}$ mol/dm$^3$, or $10^{-12}$ moles of spins in the sample), (b) In the refluxing solution concentration of radicals are sufficient to the measure but their lifetime was so short that they recombined before the sample was frozen.

## *ACKNOWLEDGMENTS*

We are grateful to Prof. A. Płonka (Technical University of Łódź, Electron Spin Resonance Laboratory) for starting MSc thesis (T. Białas) in his team, part of which is the present work. We would also like to thank Prof. E. Szajdzińska-Piętek for enabling the continuation of this work and valuable discussions, Dr. H. Żegota for the laboratory equipment, and Miss J. Staluszka (MSc) for continuous assistance and helpful discussions.

## REFERENCES

[1] Bałczewski, P.; Białas, T.; Mikołajczyk, M. Tetrahedron Lett 2000, 41, 3687.

[2] Bałczewski, P.; Pietrzykowski, W. M. Tetrahedron 1997, 53, 7291.

[3] Bałczewski, P.; Pietrzykowski, W. M. Tetrahedron 1996, 52, 13681.

[4] Bałczewski, P.; Mikołajczyk, M. New J Chem 2001, 25, 659.

[5] Baban, J. A.; Roberts, B. P. Chem Commun 1979, 8, 373.

[6] Geoffroy, M.; Ginet, L.; Lucken, E. A. C. Mol Phys 1974, 28, 1289.

[7] Staluszka, J. MSc thesis, Technical University of Łódź, 2000.

[8] Ayscough, P. B. Electron Spin Resonance in Chemistry; Methuen & Co Ltd.: London, 1967; pp. 324–332.

[9] Begum, A.; Symons, M. C. R. J Chem Soc, Faraday Trans 2 1973, 69(1), 43.

[10] Huai-Iu, S.; Zhi-Zhong, W.; Yao-Huan, C.; Yong-Hai, H.; Qi-Zhong, W.; Jin-Tai, C.; Ren-Zhong, L. Radiat Phys Chem 1989, 33, 585.

[11] Baban, J. A.; Roberts, B. P. J Chem Soc, Faraday Trans 2 1981, 1, 161.