Inorganica Chimica Acta, 83 (1984) L7–L8

Spin Trapping of Chlorine Atoms Produced by Photolysis of Hexachloroplatinate(IV) in Solution

DETLEF REHOREK*, COIT M. DUBOSE and EDWARD G. JANZEN**

Department of Chemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph, Ont. N1G 2W1, Canada

Received October 4, 1983

The photosensitivity of the hexachloroplatinate (IV) ion, $PtCl_6^{-2}$, has been known for more than a century [1] and has attracted widespread interest among photochemists [2]. Recent low-temperature ESR studies [3, 4] which provided evidence for the formation of Pt(III) intermediates, and the detection of $Cl_2{\cdot}^-$ radicals by flash-photolysis [5] suggest a primary reaction as given in eqn. 1:

$$PtCl_6^{-2} \xrightarrow{h\nu} PtCl_5^{-2} + Cl\cdot \qquad (1)$$

However no chlorine atoms have been detected by low-temperature ESR during the photolysis of $PtCl_6^{-2}$. Since it is known that hydroxyl radicals may oxidize chloride ion to give chlorine atoms [6] reactions 2–4 cannot be entirely ruled out:

$$PtCl_6^{-2} \xrightarrow[H_2O]{h\nu} PtCl_6^{-3} + HO\cdot + H^+ \qquad (2)$$

$$PtCl_6^{-3} \rightleftharpoons PtCl_5^{-2} + Cl^- \qquad (3)$$

$$Cl^- + HO\cdot \longrightarrow Cl\cdot + HO^- \qquad (4)$$

In order to distinguish between these possibilities ESR spin trapping experiments were performed. The results obtained appear to provide unambiguous evidence for the formation of chlorine atoms in the primary step of the photolysis of hexachloroplatinate (IV) ions in both acetonitrile and aqueous solutions.

The experimental procedures were similar to those published elsewhere [7]. Phenyl N-tert-butyl nitrone (PBN) and 2,4,6-trimethoxyphenyl N-tert-butyl nitrone ($(MO)_3PBN$) were used as spin traps [8]. Deaerated solutions were irradiated at room temperature with a 200W Hg/Xe lamp fitted with a 310 nm cut-off filter. The ESR spectra were recorded with a Varian E-104 EPR spectrometer.

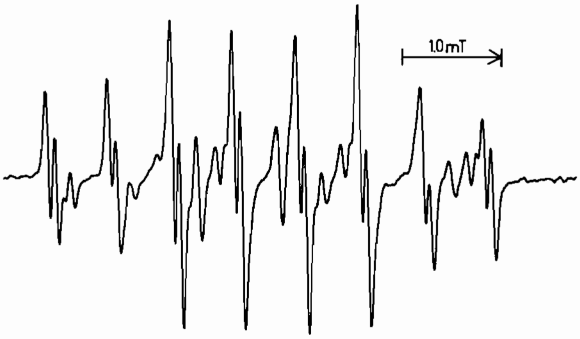
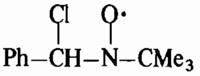


Fig. 1. ESR Spectrum of the chlorine atom adduct of phenyl N-tert-butyl nitrone.

Figure 1 shows the spectrum obtained during the photolysis of Na_2PtCl_2 in acetonitrile. This spectrum can be unambiguously assigned to the chlorine spin adduct of PBN, I [9].

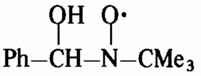


$Ph{-}CH(Cl){-}N(O\cdot){-}CMe_3$

I

$A_N = 1.270$ mT
$A_N = 0.089$ mT

$A_{Cl\text{-}35} = 0.620$ mT
$A_{Cl\text{-}37} = 0.512$ mT
(in acetonitrile)



$Ph{-}CH(OH){-}N(O\cdot){-}CMe_3$

II

$A_N = 1.546$ mT
$A_\beta^H = 0.272$ mT
(in water)

The same adduct was observed over the entire range of spin trap concentration used ($\sim 0.5\ M < [PBN] < 0.01\ M$) indicating only one radical being formed. This strongly supports the mechanistic proposals in the literature [3, 4] as shown in eqn. 1.

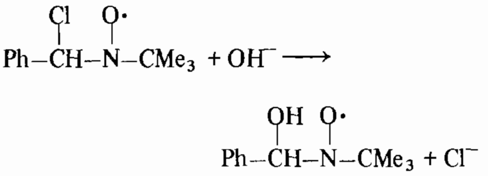
In contrast to the above results, no chlorine spin adduct could be detected in aqueous solution. Instead the ESR signals due to α-hydroxy benzyl N-tert-butyl aminoxyl (II) and tert-butyl aminoxyl ($a_N = 1.458\ a^H = 1.390$ mT) were observed. The latter is a common oxidation product of tert-butyl hydroxylamine formed in the hydrolysis of PBN. The hydroxyl adduct of PBN, II, may be generated by either the hydrolysis of the chlorine adduct, I, or by addition of hydroxyl radicals to PBN:

---

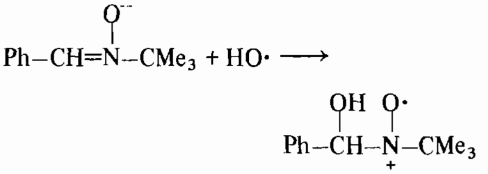
[*] On sabbatical leave from Sektion Chemie der Karl-Marx-Universität, Leipzig, DDR.

[**] Author to whom correspondence should be addressed.

0020-1693/84/$3.00

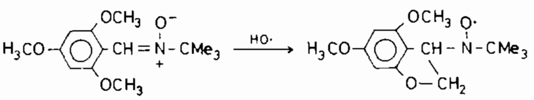


$$\text{Ph}-\overset{\text{Cl}}{\overset{|}{\text{CH}}}-\overset{\text{O}\cdot}{\overset{|}{\text{N}}}-\text{CMe}_3 + \text{OH}^- \longrightarrow \text{Ph}-\overset{\text{OH}}{\overset{|}{\text{CH}}}-\overset{\text{O}\cdot}{\overset{|}{\text{N}}}-\text{CMe}_3 + \text{Cl}^- \quad (5)$$



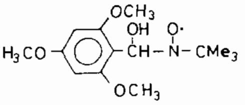
$$\text{Ph}-\text{CH}=\overset{\text{O}^-}{\overset{|}{\text{N}}}-\text{CMe}_3 + \text{HO}\cdot \longrightarrow \text{Ph}-\overset{\text{OH}}{\overset{|}{\text{CH}}}-\underset{+}{\overset{\text{O}\cdot}{\overset{|}{\text{N}}}}-\text{CMe}_3 \quad (6)$$

The use of $(MO)_3PBN$ as a spin trap provides a way to distinguish between these two reactions since for hydroxyl radicals (only) an aminoxyl resulting from intramolecular spin trapping is formed [9]:



(7)

When Na_2PtCl_6 was irradiated under the same conditions with $(MO)_3PBN$ a weak signal assigned to the hydroxyl adduct of $(MO)_3PBN$ together with the signal of tert-butyl aminoxyl were seen. The spectrum due to III was not observed.



(8)

$a_N = 1.621$ mT

$a_\beta^H = 0.885$ mT

(in water)

Thus it is possible to conclude that no free hydroxyl radicals are produced in the photolysis of Na_2PtCl_6. Instead chlorine atoms are formed in both acetonitrile and water. In the latter case the chlorine atom adducts of both PBN and $(MO)_3PBN$ hydrolyse to the hydroxyl adducts.

Acknowledgement

This work is being supported by the Natural Sciences and Engineering Research Council of Canada. Grateful acknowledgement is hereby made.

References

1 J. Herschel, *Phil. Mag.*, *1*, 58 (1832).

2 For reviews on Pt(IV) photochemistry see *e.g.*: V. Balzani and V. Carassitti, 'Photochemistry of Coordination Compounds', Academic Press, London-New York, 1970, p. 257;
P. C. Ford, R. E. Hintze and J. D. Petersen, In: 'Concepts of Inorganic Photochemistry', A. W. Adamson and P. D. Fleischauer, eds., John Wiley & Sons, New York-London-Sydney-Toronto, 1975, p. 203.

3 G. A. Shagisultanova, *Koord. Khim.*, *7*, 1527 (1981).

4 N. R. Pinskii, I. V. Voyakin, I. I. Blinov and G. A. Shagisultanova, *zh. Prikl. Khim.*, *51*, 235 (1978).

5 R. C. Wright and G. S. Lawrence, *J. Chem. Soc., Chem. Commun.*, 132 (1972).

6 J. W. Hunt, R. K. Wolff and S. G. Chenery, In: 'Fast Processes in Radiation Chemistry and Biology', G. E. Adams, E. M. Fielden and B. D. Micheal, eds., John Wiley and Sons, 1975, p. 109, and references therein.

7 For reviews on spin trapping, see *e.g.*:
(a) E. G. Janzen, *Acc. Chem. Res.*, *4*, 31 (1971).
(b) M. J. Perkins, *Adv. Phys. Org. Chem.*, *17*, 1 (1980).
(c) V. E. Zubarev, V. N. Belevskij and L. T. Bungaenko, *Usp. Khim.*, *48*, 1361 (1978).
(d) R. Kh. Freidlina, I. I. Kandror and R. G. Gasanov, *Usp. Khim.*, *47*, 508 (1978).
(e) D. Rehorek and H. Hennig, *Can. J. Chem.*, *60*, 1565 (1982).

8 E. G. Janzen and C. M. DuBose, to be submitted.

9 E. G. Janzen, H. J. Stronks, D. E. Nutter, E. R. Davis, H. N. Blount, J. L. Poyer and P. B. McCay, *Can. J. Chem.*, *58*, 1596 (1980).