CHEMISTRY LETTERS, pp. 755-758, 1974. Published by the Chemical Society of Japan

ESR STUDY OF HOT IONS, Ir(II) AND Ir(IV) IN γ-IRRADIATED Ir(III) COMPLEXES

Shizuo FUJIWARA, Tokuko WATANABE, and Takeko INOUE*
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113

ESR study of Ir hot ions produced in γ-irradiated Ir(III) complexes has been carried out. It has been found that Ir(II) hot ions take d^7 configuration of low spin state. The unpaired electron is localized in $d_{3z^2-r^2}$ orbital in the elongated octahedral structure. Ir(IV) hot ions are found to be formed in irradiated Ir(III) hexachloro complexes.

It has been well known that γ-irradiation of diamagnetic inorganic complexes causes the reduction or the oxidation of the central metal atoms in the complexes, forming paramagnetic species referred to as " hot ions ".1)2)3)

In this note, we report an evidence of the formation of Ir(II) and Ir(IV) hot ions in the γ-irradiated diamagnetic Ir(III) complexes.

Most of the Ir(III) complexes with d^6 configuration are known to take octahedral symmetry and to be in the low spin state because of the larger ΔE values of d-d splitting. We have found by this experiment that the central atom of Ir(III) complex is reduced by γ-irradiation, forming hot ion of d^7 low spin state, as well as d^5 ion in low spin state after oxidization.

ESR patterns of d^7 low spin state (S=1/2) may be interpreted in terms of the spin Hamiltonian of (1).

$$\mathcal{H} = \beta H\cdot\tilde{g}\cdot S + I\cdot\tilde{A}\cdot S \qquad (1)$$

The g values are calculated theoretically, to the first order as shown in Table 1.

Experimental g values for d^7 low spin state of Ir complex have been reported by Danon et al.4), in irradiation of $K_3[Ir(CN)_6]$-KCl system. While, the ESR spectra of d^5 low spin state, which are usually broadened because of the short relaxation time, have successfully studied with Ir(IV) hexachloro complexes at 4°K by Griffiths et al.5) By comparing the observed g values with those obtained by calculation and by literature, both the oxidation state and the spin state of Ir hot ions can be investigated.

Ir(III) complexes were prepared according to the literature6). The powdered sample was degassed in a quarz tube at 10^{-3}mmHg and sealed in vacuo. ^{60}Co-γ-ray irradiation was carried out at 77°K on a total dosage of 10^6 rad with the doserate of 5×10^4 rad/h. The ESR spectra were recorded at 77°K on a JEOL 3BSX spectrometer with 100 KHz field modulation. Among 15 complexes examined, 9 complexes gave ESR spectra due to Ir.

A typical ESR spectrum of Ir hot ion from $K_3[Ir(NO_2)_4Cl_2]$ is given in Fig.1,

which coexists with the doublet lines of H atom from glass wall. The spectrum consists of two main signals, one around 2 and the other at 2.431.
The former one is assigned to the signal due to the ligand NO_2 radical as it presents three hyperfine lines, and the latter to that of Ir complex, which has four hyperfine lines due to Ir nuclei of Ir^{191}(I=3/2, 38.5%) and Ir^{193}(I=3.2, 61.5%). Furthermore, it is observed that each of the four lines is split into 7 lines,

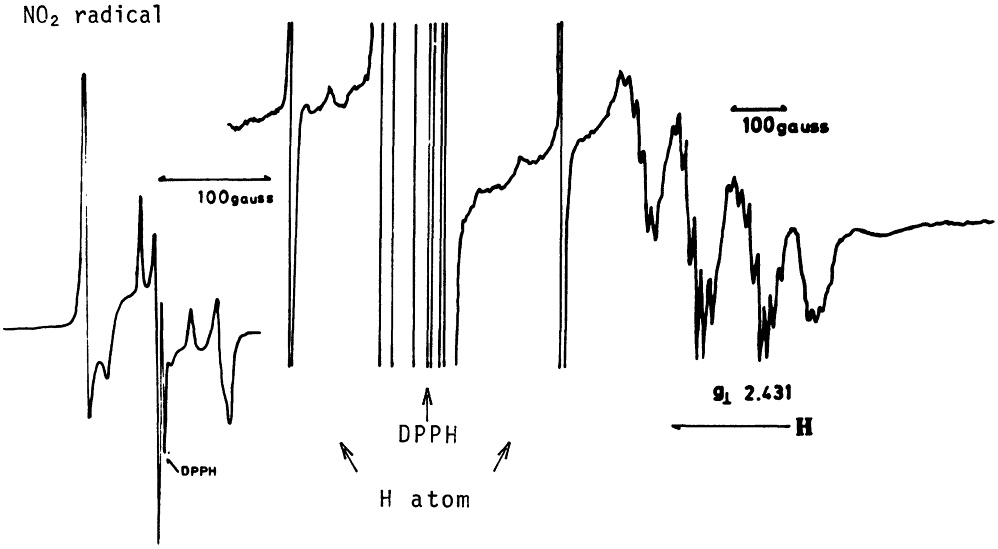

Fig. 1 ESR Spectrum of γ-Irradiated $K_3[Ir(NO_2)_4Cl_2]$

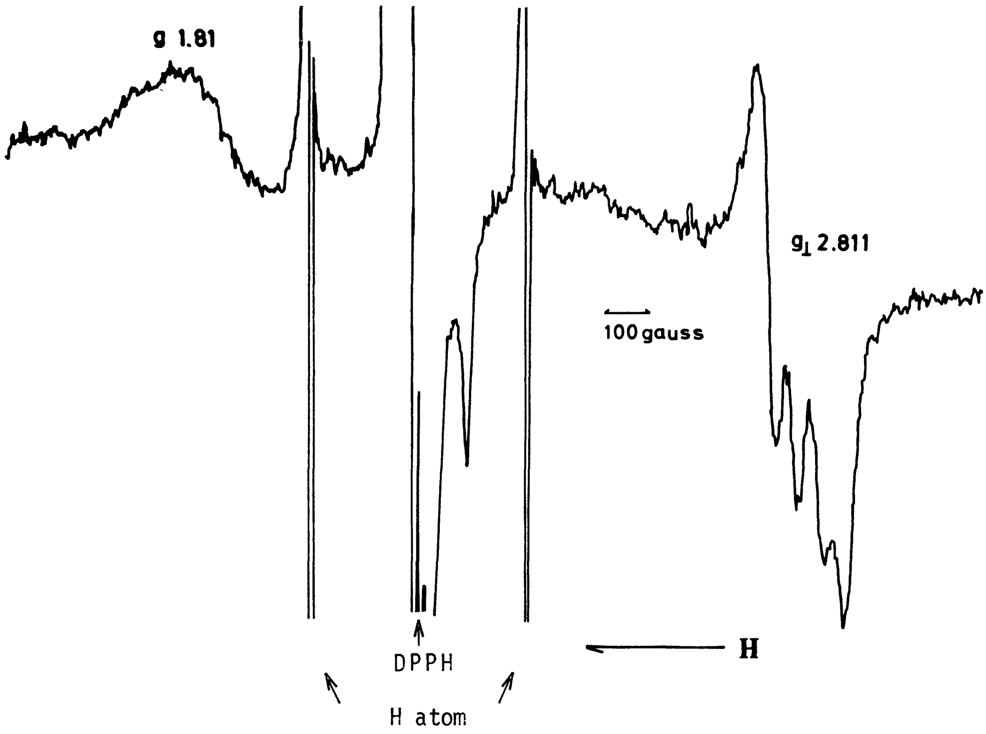

Fig. 2 ESR Spectrum of γ-Irradiated $Na_3[IrCl_6]$

indicating the interaction of the unpaired electron with the ligand Cl atoms bonded at the trans position of the octahedral complex. All other spectra of Ir hot ions, except those from $M_3[IrCl_6]$(M=Na or NH_4), consist of two kinds of signals that arise from the radicals of ligand which are observed at about 3300 gauss and from Ir complexes, whose g values are larger than 2. From the data shown in Table 1, it is concluded that all signals of Ir complex correspond to d^7 low spin state in which the unpaired electron is localized mainly in $d_{3z^2-r^2}$ orbital of the elongated octahedral symmetry. The $g_{\parallel}$ component, expected to be almost equal to 2, is not clearly observable as it is overlapped with the large signal of the ligand radical. In the case of $M_3[IrCl_6]$(M=Na or NH_4), an additional signal is observed at the higher magnetic field. The ESR spectrum of the irradiated $Na_3[IrCl_6]$ is as shown in Fig.2, which consists of three main signals, the first one at the lower field corresponding to the signal of Ir complex and the second at about 3300 gauss corresponding to that of the ligand Cl radical. The third one at the higher field

Table 1. The calculated g values for d^7 low spin state

5d orbital	$g_{\parallel}$	$g_{\perp}$	order	
$d_{x^2-y^2}$	$2(1+4\lambda/\Delta_1)$	$2(1+\lambda/\Delta_2)$	$g_{\parallel}>g_{\perp}>2$	$\Delta_1=\lvert E_{x^2-y^2}-E_{xy}\rvert$
d_{xz}	very large			$\Delta_2=\lvert E_{x^2-y^2}-E_{xz,yz}\rvert$
d_{yz}	very large			$\Delta_3=\lvert E_{3z^2-r^2}-E_{xy,yz}\rvert$
$d_{3z^2-r^2}$	2	$2(1+\lambda/\Delta_3)$	$g_{\perp}>g_{\parallel}=2$	$\Delta_4=\lvert E_{x^2-y^2}-E_{xz,yz}\rvert$
d_{xy}	$2(1-4\lambda/\Delta_1)$	$2(1+\lambda/\Delta_3)$	$g_{\perp}>2>g_{\parallel}$	

Table 2. The observed ESR parameters for d^7 low spin state

γ-irradiated complex	d^7 low spin state			d^5 low spin state
	$g_{\perp}$	A(Ir)	A(ligand) ($10^{-4}cm^{-1}$)	g
$Na_3[IrCl_6]$	2.811	67.5		1.81
$(NH_4)_3[IrCl_6]$	2.767	(64.5)		1.88
trans-$K[Ir(py)_2Cl_4]$	2.566	87.4	12(Cl)	
$[Ir(NH_3)_6]Cl_3$	2.566	106.7		
$[Ir(en)_3]I_3$*	2.631 2.491			
trans-$K_3[Ir(NO_2)_4Cl_2]$	2.431	118.5	15.9(Cl)	
cis-$[Ir(Et_2S)_3Cl_3]$	2.384			
cis-$[Ir(Et_3P)_3Cl_3]$	2.368	88.9		
trans-$[Ir(phen)_2Br_2]Br$	2.314		15(N)	
$K_3[Ir(CN)_6]$**	2.206	$CN_{ax.}$	$CN_{eq.}$	**Reference 4)
	g_x= 2.2110	A_x=+3.8	-0.2	
	g_y= 2.2026	A_y=+3.8	-0.2	
	g_z= 1.9665	A_z=+6.2	+2.3	

* g values correspond to two species.

exhibits a broad line, referring to the short relaxation time.

ESR parameters for Ir hot ions from various Ir(III) complexes are summarized in Table 2. The g values range from 2.811 for the irradiated $Na_3[IrCl_6]$ to 2.206 for the irradiated $K_3[Ir(CN)_6]$ and the g shift, $(g_{obs.}-g_e)$, follows the order of spectral series of ligand as seen following, which is consistent with the trend observed in the paramagnetic complexes of Ti^{3+} and Cu^{2+}.$^{7)}$

ESR spectra of Ir hot ions in the irradiated $Na_3[IrCl_6]$, $K[Ir(py)_2Cl_4]$, $[Ir(NH_3)_6]Cl_3$, $K_3[Ir(NO_2)_4Cl_2]$ and $[Ir(Et_3P)_3Cl_3]$, all have hyperfine structure of Ir nuclei. The hyperfine lines of irradiated $K_3[Ir(NO_2)_4Cl_2]$ and $K[Ir(py)_2Cl_4]$ are accompanied with the superhyperfine structure due to the ligand Cl atoms, while the spectrum of the irradiated $[Ir(phen)_2Br_2]Br$ has hyperfine lines which seem to arise from the ligand N atom. From the nature of A tensor, $A_\perp$ is expected to decrease as the covalency of the ligand increases. The observed $A_\perp$ is, however , in disagreement with the general cases. This may be partially interpreted in terms of the s character of the unpaired electron, however, more information for $A_\parallel$ seems necessary for further understanding. The signals of smaller g values, which are observed only with irradiated $M_3[IrCl_6]$ (M=Na or NH_4), seem to correspond to d^5 low spin state. This is consistent with the chemical nature of the ligand that stabilizes blth the higher and the lower valency state of the complex.

The following conclusion can be drawn from these experimental results.

1) It has been found that Ir(II) hot ions are mainly produced in γ-ray irradiation of Ir(III) complexes and that the unpaired electron is mainly localized in $d_{3z^2-r^2}$ orbital of the elongated octahedral structure in each Ir(II) hot ions, trapped in the lowest vacant orbital of Ir complex.

2) g factors for these Ir(II) hot ions vary with the ligand in such a way as g shift decreases in the order of $Cl>py\simeq NH_3\simeq en>NO_2>Et_2S>Et_3P>phen>CN$.

3) In addition to Ir(II) hot ions, Ir(IV) hot ions of d^5 low spin state are produced in irradiation of $M_3[IrCl_6]$.

Further study on Ir hot ions from various Ir(III) complexes is in progress.

The authors wish to thank Mr. Shingo Katsura of γ-ray irradiation center for experimental assistance and Mr. Masayuki Nakajima and Mr. Yoshinao Osawa for valuable assistance in the syntheses of Ir complexes. We thank also Dr. Jun-ichi Isoya and Mr. Chikara Amano for valuable discussions.

1) S. Fujiwara, T. Watanabe and H. Tadano, J. Coord. Chem., 1,195 (1971)
2) J. Isoya, Thesis, Univ. Tokyo (1974)
3) C. Amano and S. Fujiwara, Bull. Chem. Soc. Japan, 46, 1379 (1973)
4) N. Vugman, R. P. A. Muniz and J. Danon, J. Chem. Phys., 57, 1279 (1972)
5) J. H. E. Griffiths and J. Owen, Proc. Roy. Soc., A. 226, 96 (1954)
6) W. P. Griffith, The Chemistry of the Rarer Platinum Metals, Interscience, New York (1967)
7) I. Taminaga and S. Fujiwara,Spectroscopy Letters, 2(5), 127 (1969)

* On leave from Nara University of Education. Financial support from the Minstry of Education for this leave is acknowledged.

(Received April 25, 1974)