

Effect of Cation on the Quantum Efficiency and the Photoreaction Pathways of $[\text{W}(\text{CO})_5\text{X}]^-$ Anions

By R. MARC DAHLGREN and JEFFREY I. ZINK*

(Department of Chemistry, University of California, Los Angeles, California 90024)

Summary The quantum efficiencies and product distributions for ligand photosubstitution and co-ordinated ligand phototransformation reactions of anionic $[\text{W}(\text{CO})_5\text{X}]^-$ ($\text{X} = \text{Br}$, NCO , or N_3) in CHCl_3 vary by $>300\%$ when the cation is changed in the series Li^+ , AsPh_4^+ , PPN^+ , and NEt_4^+ [$\text{PPN} = \mu$ -nitrido-bis(triphenylphosphorus)].

In the course of investigating the photochemistry of a series of anionic monosubstituted derivatives of tungsten hexacarbonyl $[\text{W}(\text{CO})_5\text{X}]^-$ ($\text{X} = \text{Br}$, NCO , or N_3) in the low dielectric solvent CHCl_3 , we have observed that both the efficiency of the photochemical transformation and the nature of the photoproducts depend significantly on the cation used to isolate the starting tungsten complex.¹ Because photochemical procedures are routinely employed in the synthesis of novel metal carbonyl derivatives² and in the production of co-ordinatively unsaturated species capable of applications in catalysis,³ counterion influences on the photochemistry of metal carbonyl ions,⁴ especially in low dielectric media, must be recognized and considered as a critical factor in the design of synthetic routes or in mechanistic studies. In this communication we report the magnitude of the cation's effect on the photochemistry of $[\text{W}(\text{CO})_5\text{X}]^-$ anions.

The quantum efficiencies of the photochemical reactions of $[\text{W}(\text{CO})_5\text{Br}]^-$ vary by $>300\%$ when the Li^+ ,[†] $[\text{NEt}_4]^+$,[‡] and $[\text{AsPh}_4]^+$,[§] salts are irradiated in their lowest energy

[†] $\text{Li}^+[\text{W}(\text{CO})_5\text{Br}]^-$ was prepared by treating photochemically produced $[\text{W}(\text{CO})_5]\cdot\text{thf}$ ($\text{thf} = \text{tetrahydrofuran}$) with LiBr followed by chromatography on a silica gel column with hexane as eluant.

[‡] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 1963, 2068; satisfactory C and H analyses were obtained.

[§] The $[\text{AsPh}_4]^+$ complex was obtained by precipitation with the addition of water from an EtOH solution containing equimolar portions of $\text{Li}[\text{W}(\text{CO})_5\text{Br}]$ and $\text{AsPh}_4\text{Cl}\cdot\text{H}_2\text{O}$.

[¶] (a) $[\text{W}(\text{CO})_5\text{NCO}][\text{AsPh}_4]$ was synthesized as in H. Werner, W. Beck, and H. Engelmann, *Inorg. Chim. Acta*, 1969, **3**, 331; satisfactory C, H, and N analyses were obtained. (b) $[\text{W}(\text{CO})_5\text{NCO}][\text{PPN}]$ was prepared by refluxing $[\text{W}(\text{CO})_5\text{N}_3][\text{PPN}]$ in EtOH saturated with CO and precipitation by addition of water; found for $\text{C}_{42}\text{H}_{30}\text{N}_2\text{O}_8\text{P}_2\text{W}$: C, 54.60; H, 3.36; N, 3.27; W, 20.06; calc. C, 55.77; H, 3.35; N, 3.10; W, 20.33%.

TABLE
Influence of cation on the quantum yields of $[\text{W}(\text{CO})_5\text{X}]^-$ phototransformations^a

$[\text{W}(\text{CO})_5\text{X}]^-$ X	Cation	$\Phi(\text{dis.})^b$	$\Phi[\text{W}(\text{CO})_6]^c$
Br	Li^+	0.094	0.094
Br	$[\text{NEt}_4]^+$	0.0034	0.0034
Br	$[\text{AsPh}_4]^+$	0.014	0.002
NCO	$[\text{PPN}]^+$	0.009	0.009
NCO	$[\text{AsPh}_4]^+$	—	0.0
N_3	$[\text{PPN}]^+$	0.027	0.027
N_3	$[\text{AsPh}_4]^+$	0.071	0.0

^a Photolysed at 436 nm, at 280 K in CO -saturated CHCl_3 .
^b Disappearance quantum yield for $[\text{W}(\text{CO})_5\text{X}]^-$ anions. ^c Formation quantum yield for $[\text{W}(\text{CO})_6]$. ^d Sum of production of both $[\text{W}(\text{CO})_6]$ and $[\text{W}(\text{CO})_5\text{NCO}]^-$.

absorption feature at 436 nm (Table). Quantum yields for the disappearance of starting material were calculated from the decrease in the intensity of the 410 nm absorption band of $[\text{W}(\text{CO})_5\text{X}]^-$ and $[\text{W}(\text{CO})_6]$ formation yields were obtained by monitoring the appearance of the $T_{1u}[\text{W}(\text{CO})_6]$ vibration at 1985 cm^{-1} in the i.r. spectrum using a Beer's Law plot and a calculation procedure reported previously.⁵

The cation affects the quantum efficiency not only of ligand photosubstitution as in the $[\text{W}(\text{CO})_5\text{X}]^-$ ($\text{X} = \text{Br}$ or NCO) systems, but also of the photoreactions of a co-ordinated ligand in the conversion of the co-ordinated azide into co-ordinated isocyanate. Whereas $[\text{W}(\text{CO})_5\text{NCO}]^-$ and $[\text{W}(\text{CO})_6]$ are produced when the PPN^+ salt of

$[\text{W}(\text{CO})_5\text{N}_3]^{--}$ is photolysed, the quantum yield for production of both of these materials is zero when the AsPh_4^+ salt of the azide is used. Similarly the quantum yield of formation of $[\text{W}(\text{CO})_6]$ is substantially reduced in both the bromide and isocyanate systems when the AsPh_4^+ salt is utilized.

The dominant photoproduct in those studies where the AsPh_4^+ cation is present is a white precipitate containing both W and As but no carbonyl groups. This product is the end result of a complex chain of secondary thermal reactions and was not characterized further. When solutions containing both $[\text{AsPh}_4]^+$ and $[\text{NEt}_4]^+$ ions were photolysed, a 4:1 or a 63:1 molar ratio of NEt_4Br to $[\text{W}(\text{CO})_5\text{Br}][\text{AsPh}_4]$ caused the disappearance quantum yield of $[\text{W}(\text{CO})_5\text{Br}]^-$ to decrease to 0.0055 which is intermediate between the quantum yields for the pure $[\text{AsPh}_4]^+$ and $[\text{NEt}_4]^+$ salts. There is no simple functional dependence of the yields for the mixed cation systems on either the relative concentration ratio of the two cations present or on the concentration of added Br^- . The reaction with $[\text{AsPh}_4]^+$ can be initiated thermally by addition of benzoyl peroxide suggesting a radical mechanism.

No change in the energy of the low lying electronic states is observed when the cations are changed. The energies of the luminescences in low temperature (77 K) 4:1 EtOH-MeOH glasses are also cation invariant. Furthermore,

within experimental error, the i.r. spectrum of the carbonyl and internal unique ligand vibrational energies in CHCl_3 solutions are unaffected by changes in the cations $\{\nu(\text{CO}) (\pm 1.5 \text{ cm}^{-1})$ in CHCl_3 for the Li^+ , $[\text{NEt}_4]^+$, and $[\text{AsPh}_4]^+$ salts of $[\text{W}(\text{CO})_5\text{Br}]^-$: 2071, 1844, and 1924 cm^{-1} ; for the $[\text{PPN}]^+$ and $[\text{AsPh}_4]^+$ salts of $[\text{W}(\text{CO})_5\text{NCO}]^-$: 2069, 1843, 1921, and 2236 (NCO) cm^{-1} ; and for the $[\text{PPN}]^+$ and $[\text{AsPh}_4]^+$ salts of $[\text{W}(\text{CO})_5\text{N}_3]^-$: 2084, 1849, 1922, and 2048 (N_3) cm^{-1}).

The previously reported counterion effects on the photochemistry of metal complexes were small and were attributed to ion pairing in aqueous media.⁶ In solvents with low dielectric constants (CHCl_3 , $\epsilon = 4.7$), the results reported here illustrate the large counterion influences on both the quantum efficiency and photoproduct distribution of ligand photosubstitution and co-ordinated ligand photochemistry. In particular, the $[\text{AsPh}_4]^+$ cation may introduce complexities when a radical-like excited state occurs.

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** $[\text{W}(\text{CO})_5\text{N}_3][\text{AsPh}_4]$ was synthesized as in footnote ¶ (a); found for $\text{C}_{29}\text{H}_{20}\text{AsN}_3\text{O}_5\text{W}$: C, 46.22; H, 2.57; W, 24.80; N, 4.89; calc. C, 46.78; H, 2.70; W, 24.24; N, 5.61%. $[\text{W}(\text{CO})_5\text{N}_3][\text{PPN}]$ was prepared by the reaction of $(\text{PPN})\text{N}_3$ with photochemically produced $[\text{W}(\text{CO})_5]\cdot\text{thf}$. The product was precipitated from ethyl acetate by addition of pentane. The i.r. spectrum corresponded exactly to that of $[\text{W}(\text{CO})_5\text{N}_3][\text{AsPh}_4]$ [$\nu(\text{CO})$ 2084, 2048 (N_3), 1922 (s), and 1850 cm^{-1}].

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