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THE PHOTOLYSIS OF METHYLPLATINUM(IV) COMPOUNDS

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Summary

The UV photolysis of three methylplatinum(IV) compounds has been studied with special emphasis on the products formed in the presence and absence of deuterium in the solvent. It is concluded that free radicals are formed and abstract hydrogen, or combine, in solvent cages or in the bulk of the solution.

Introduction

Interest is growing in the photolysis of transition metal alkyls and aryls [1], but little work with platinum compounds has been reported. We have studied the kinetics of the photodecomposition of trimethyleneplatinum(IV) compounds [2], and recently Van Leeuwen et al. [3] followed the photolysis of platinum(II) alkyls in $CDCl_3$ by proton magnetic resonance and observed chemically induced dynamic nuclear polarisation due to radical pairs formed. We have investigated the photolysis of the three methylplatinum(IV) compounds, $[PtIMePh_2(bipy)]$, $[PtI_2Me_3(bipy)]$ and $[PtIMe_2(bipy)]$ where Me = CH_3, Ph = C_6H_5 and bipy = 2,2'-bipyridine, concentrating on the products formed under various conditions in order to obtain information on the role of free radicals in the reactions.

Results and discussion

The bipyridine derivatives were chosen because the progress of the reaction in solution under UV irradiation could be followed by UV spectroscopy by monitoring the growth of the appropriate peak between 350 and 450 nm due to the (2,2'-bipyridine)platinum(II) product (see ref. 2). The photolyses were first order in the platinum compound, but, as mentioned above, interest was mainly

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TABLE 1

FIRST ORDER RATE COEFFICIENTS FOR, AND PRODUCTS OF, THE PHOTOLYSIS OF METHYLPLATINUM(IV) COMPOUNDS

Temp. 25°C; incident radiation intensity 1.0×10^{-6} einstein l^{-1} s^{-1}; initial concentration of Pt(IV) compound 3.0×10^{-4} mol l^{-1} for kinetics.

Compound [a]	Solvent [b]	$10^4\ k/s^{-1}$	Products [c]
[PtIMePh$_2$(bipy)	THF	1.20	
	DCB	4.82	
	CH_2Cl_2	1.88	CH_4, C_2H_6, $C_6H_5CH_3$, $(C_6H_5)_2$, [PtIPh(bipy)]
with 366 nm filter	CH_2Cl_2	0.72	
	CD_2Cl_2		C_6H_6, $C_6H_5CH_3$
	$CH_2Cl_2/C_6D_5CD_3$ (3/2, v/v)		C_6H_6, C_6H_5D
[PtIMePh$_2$(bipy)] + [PtIMe(4-$CH_3C_6H_4$)$_2$(bipy)] (1/1)	CH_2Cl_2		C_6H_6, $C_6H_5CH_3$, $(C_6H_5)_2$, $C_6H_4(CH_3)_2$, $(CH_3C_6H_4)_2$, $C_6H_5C_6H_4CH_3$
[PtIMe$_2$(bipy)]	CH_2Cl_2	2.96	CH_4, C_2H_6, [PtI$_2$(bipy)]
[PtIMe$_3$(bipy)]	CH_2Cl_2	1.91	CH_4, C_2H_4, [PtIMe(bipy)]
	CD_2Cl_2		CH_4, CH_3D, $C_2H_2D_2$ (methane/ethylene = 4)
	$CH_2Cl_2/C_6D_5CD_3$ (3/2 v/v)		CH_4, CH_3D, C_2H_4 (methane/ethylene = 10)
[PtI$(CD_3)_3$(bipy)]	CD_2Cl_2		CD_4, CD_3H, C_2D_4

[a] bipy = 2,2′-bipyridene. [b] THF = tetrahydrofuran; DCB = 1,2-dichlorobenzene. [c] Under some conditions, only certain products were analysed for.

directed towards the products. The results are summarised in Table 1.

The first order rate coefficients varied somewhat with solvent and with the nature of the platinum compound, but were of the same order as those for the photolysis of trimethyleneplatinum(IV) compounds [2]. Excluding radiation of wavelength less than 366 nm reduced the rate coefficient for the photolysis of [PtIMePh$_2$(bipy)] but only by a factor of 2.6.

Most of the organic products, e.g. CH_4, C_2H_6, C_6H_6, $C_6H_5CH_3$, could be formed either by intramolecular processes in the excited molecules or by processes involving free radicals produced in the primary photolytic steps. However, the detection of ethane and diphenyl in the products of photolysis of [PtIMePh$_2$(bipy)] and particularly of $C_6H_5C_6H_4CH_3$ from the mixture of [PtIMePh$_2$(bipy)] [PtIMe(4-MeC$_6$H$_4$)$_2$(bipy)], together with the deuterated products when the solvent contained deuterium (especially toluene-d_8, a good deuterium atom donor), shows that methyl and aryl radicals are formed and at least some escape from the solvent cages. The photolysis of [PtIMe$_3$(bipy)] by radiation of 366 nm wavelength initiated the polymerisation of methyl methacrylate, confirming that free radicals are formed from this methylplatinum(IV) compound.

The probable mechanism of the photolysis of the methylplatinum(IV) compounds can, therefore, be summarised as; [PtIMePh$_2$(bipy)] = I, [PtI$_2$Me$_2$(bipy)]

= II, $[PtIMe_3(bipy)]$ = III; $(\ )_s$ = solvent cage:

$$\mathrm{I, II, III} + h\nu \rightarrow \mathrm{I^*, II^*, III^*}$$

$$\begin{tikzcd}[column sep=small]
 & \mathrm{I}^* \arrow[r, "a"] \arrow[dr] & C_6H_5CH_3 + [PtIPh(bipy)] & \\
(CH_2Cl_2\ \text{solvent}) & & ([PtIPh(bipy)], CH_3^{\bullet}, C_6H_5^{\bullet})_s \arrow[r, "b"] \arrow[d] & CH_4, C_6H_6, C_6H_5CH_3 \\
 & & CH_3^{\bullet}, C_6H_5^{\bullet} \arrow[r] & CH_4, C_6H_6, C_2H_6, (C_6H_5)_2, C_6H_5CH_3
\end{tikzcd}$$

$$\begin{tikzcd}[column sep=small]
\mathrm{II}^* \arrow[r, "a"] \arrow[dr] & {[PtI_2(bipy)]} + C_2H_6 & \\
 & ([PtI_2(bipy)], 2\ CH_3^{\bullet})_s \arrow[r, "b"] \arrow[d] & CH_4, C_2H_6 \\
 & CH_3^{\bullet} \arrow[r] & CH_4, C_2H_6
\end{tikzcd}$$

$$\begin{tikzcd}[column sep=small]
\mathrm{III}^* \arrow[r] & ([PtIMe_2(bipy)], CH_3^{\bullet})_s \arrow[r, "c"] \arrow[d, "d"] & CH_4 + [PtIMe(CH_2)(bipy)] \arrow[d, "e", "CH_2Cl_2"'] \\
 & CH_4 + [PtIMe_2(bipy)] \arrow[d] & C_2H_4 + [PtIMe(bipy)] \\
CH_4 & CH_3^{\bullet} + [PtIMe(bipy)] \arrow[l] &
\end{tikzcd}$$

Some intramolecular decomposition (step a) probably occurs, as in the thermal decomposition of platinum(IV) alkyls and aryls [4], but it appears that most of the organic products are formed by hydrogen (or deuterium) abstraction by, or combination of, radicals either in solvent cages or in the bulk of the solution. The work of Van Leeuwen et al. [2] indicates that some production of radical pairs is likely. The formation, with CD_2Cl_2 as solvent, of C_6H_6 from I, of CH_4 from III, and especially of CD_3H from $[PtI(CD_3)_3(bipy)]$, suggests that radicals in the solvent cage may abstract hydrogen from the platinum fragment (steps b with I and II, and c and d with III), as well as from surrounding solvent molecules. Competition between steps c and d is indicated by the increase in methane/ethylene ratio when the solvent contains toluene. The formation of $C_2H_2D_2$ from the photolysis of III in CD_2Cl_2 suggests that a methylene platinum intermediate is formed and reacts with the solvent (step e).

Experimental

Literature methods were used to prepare the platinum compounds, $[PtIMePh_2(bipy)]$, $[PtIMe(4\text{-}MeC_6H_4)_2(bipy)]$, $[PtI_2Me_2(bipy)]$, $[PtIMe_3(bipy)]$ and $[PtI(CD_3)_3(bipy)]$ [5—7]. CD_2Cl_2 and $C_6D_5CD_3$ were obtained from the Aldrich Chemical Company.

Kinetics and product analyses

The kinetics were investigated as described previously [2]. If it was required to analyse the gaseous products, the B10 stopper (at the top of the photolysis cell) was replaced by a B10 cone to which was attached a tube ending in a vacuum-tight septum. At the end of the photolysis, samples were removed in a pressure-lock gas-syringe and analysed by GLC-mass spectrometry using a 9 ft. 12% squalane on Chromosorb P column at 30°C. The solvent vapour present did not interfere. Products liquid at room temperature were also analysed by GLC-mass spectrometry using a Micromass 12 mass spectrometer. After removing the final solution from the cell and allowing to evaporate to dryness, the solid products were identified by IR, UV and mass spectrometry by comparison with authentic materials.

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