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REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

IV *. THE PHOTODECOMPOSITION IN SOLUTION

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Summary

The photolysis of platinum-cyclopropane compounds, $[X_2\overline{PtCH_2CH_2CH_2}\text{-}(L{-}L)]$[where X = Cl, Br and L—L = 2,2′-bipyridine, 1,10-phenanthroline] in solution at 25° C gives cyclopropane (plus a little propene) and $[X_2Pt(L{-}L)]$. The kinetics indicate that the C_3H_6moiety is ejected from the excited molecule in a single step.

Introduction

During an investigation of the homogeneous thermal decomposition of platinum-cyclopropane compounds with 2,2′-bipyridine or 1,10-phenanthroline ligands [1], it was observed that solutions left in the sunlight for some weeks became yellow, indicating reduction to platinum(II). Since there is very little information on the photolysis of organoplatinum compounds [2], we have studied the photoreduction of $[PtX_2(C_3H_6)(L{-}L)]$ (where X = Cl, Br; L—L = 2,2′-bipyridine, 1,10-phenanthroline) in solution. The nitrogen ligands were chosen (as for the thermal decomposition [1]) because the progress of the reaction can be followed simply by spectrophotometry.

Results and discussion

The trimethyleneplatinum(IV) compounds in solution in dichloromethane at 25° C decompose readily under the influence of UV radiation to give the corresponding platinum(II) compounds, with loss of the C_3H_6 moiety mainly

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[*] For Part III, see Ref. 1.

TABLE 1

FIRST ORDER RATE COEFFICIENTS FOR THE PHOTOLYSIS OF PLATINUM-CYCLOPROPANE COMPOUNDS $PtX_2(C_3H_6)(L—L)$

Temp. 25.0° C; incident radiation intensity, 2.29×10^{-6} einstein l^{-1} s^{-1}; initial concentration of platinum(IV) compound, 3.0×10^{-4} mol l^{-1}.

X	L—L [a]	Solvent		10^4 k_{obs}/s^{-1}
Cl	phen	CH_2Cl_2	—	5.9
Br	phen	CH_2Cl_2	—	7.3
Cl	bipy	CH_2Cl_2	—	3.8
Cl	phen	CH_2Cl_2	phen (3×10^{-3} *M*)	4.2
Br	phen	CH_2Cl_2	phen (3×10^{-3} *M*)	7.0
Cl	phen	DMSO	—	3.0
Cl	phen	DMSO	Me_4NCl (3×10^{-4} *M*)	1.3

[a] phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine.

in which the C_3H_6 moiety is ejected from the excited molecule. The rate of photolysis is:

$$-d[C]/dt = k_1[C]I_0 - k_2[C^*][S]$$

where C represents $[PtX_2(C_3H_6)(L—L)]$. Assuming a stationary concentration of C^*, we have:

$$k_1[C]I_0 = k_2[C^*][S] + k_3[C^*]$$

Thus:

$$-d[C]/dt = k_3[C^*] = k_1k_3[C]I_0/(k_2[S] + k_3)$$

in agreement with the first order kinetics, since [S] is a constant, and the experimental dependence of $k_{obs}\{= k_1k_3I_0/(k_2[S] + k_3)\}$ on I_0. Any variation of k_{obs} with the structure of C is then due to changes in k_1 and/or k_3 and the solvent effect due to the term $k_2[S]$.

The UV spectrum of $[PtCl_2(C_3H_6)(phen)]$ is almost identical with that of the phenanthroline itself and has a maximum absorption at 270 nm, with an extinction coefficient of about 2×10^4 l mol^{-1} cm^{-1}. This suggests that the nitrogen ligand absorbs the quantum of radiation giving rise to a $\pi - \pi^*$ transition and (unless collisional deactivation occurs) the energy is redistributed into the $PtCH_2CH_2CH_2$ moiety, cyclopropane being ejected. Photolysis of metal alkyls usually leads to homolysis of the M—C bond to give alkyl radicals [2]. The energy required actually to dissociate the two Pt—C bonds is only about 240 kJ mol^{-1} [3], compared to the quantum energy of 443 kJ mol^{-1} at 270 nm. However, the product analysis indicates that photolysis of the trimethyleneplatinum(IV) complexes does not give the free trimethylene diradical, since this would be expected to give more propene by rearrangement [4]. The data are consistent either with a concerted elimination of cyclopropane from the excited molecule, or with the initial fission of one platinum—carbon bond followed by rapid cyclization of the C_3H_6 moiety.

Experimental

The trimethyleneplatinum(IV) compounds were prepared as described earlier [1,3].

Product analysis

The photolysis was carried out in a special cell (see below) and the final solution degassed on a vacuum line, the volatile products being passed through a —78° C trap, to remove any CH_2Cl_2, and condensed in a second trap cooled in liquid nitrogen. This trap was isolated and allowed to warm to room temperature, and the cyclopropane and propene were estimated by GLC as described earlier [3]. The degassed solution was removed from the cell and allowed to evaporate. The complexes $[PtX_2(L—L)]$ remaining were identified by UV and IR spectra.

Kinetics

The solutions of the trimethyleneplatinum(IV) compounds were placed in a 1 cm UV spectrophotometer cell to which was attached a silica tube with a B10 socket at the end. The whole was stoppered and clamped in a thermostat with a quartz window. The cell was illuminated by the radiation from a mercury-arc lamp, being removed at suitable intervals from the thermostat to record the spectra of the solution using a Unicam SP800 spectrophotometer. The intensity of the radiation was determined at intervals by actinometry using potassium ferrioxalate [5].

References

1 F. Iwanciw, M.A. Quyser, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 113 (1976) 91.
2 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1970.
3 P.W. Hall, R.J. Puddephatt, K.R. Seddon and C.F.H. Tipper, J. Organometal. Chem., 81 (1974) 423.
4 R.G. Bergman in J.K. Kochi (Ed.), Free Radicals, Vol. 1, Wiley, New York, 1973, p. 191.
5 C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., A 235 (1956) 518.