PHOTOCHEMICAL HYDROGEN ATOM TRANSFER FROM ALDEHYDES TO BINUCLEAR PLATINUM(II)

Chi-Ming CHE [1a], *, Hoi-Lun KWONG [1a], Kar-Cheong CHO [1b], *
Pierre D. HARVEY [1c] and Harry B. GRAY [1c] *

Received 5 July 1988; accepted 6 August 1988

The phosphorescence of the triplet excited state ($^3Pt_2^*$) of a binuclear platinum(II) complex, $Pt_2(P_2O_5H_2)_4^{4-}$, is quenched by acetaldehyde and propionaldehyde with second-order rate constants of 5×10^5 and 2×10^5 M^{-1} s^{-1}, respectively, in methanol at room temperature. Flash photolysis experiments establish that the reaction of $^3Pt_2^*$ with RCHO occurs by hydrogen atom transfer, $^3Pt_2^* + RCHO \rightarrow Pt_2H + RCO$. The experiments also indicate that the Pt_2H intermediate reduces aldehydes to alcohols.

Recent experiments have established that a binuclear platinum(II) complex, $Pt_2(P_2O_5H_2)_4^{4-}(Pt_2)$, is a versatile photoredox agent [2–16]. It is of particular interest that the oxidation of an alcohol to an aldehyde or a ketone is photocatalyzed by Pt_2 [5,13]. The catalytic system is complicated when an aldehyde is formed, because aldehydes also react photochemically with Pt_2 [13,17]. We show here that the first step in the aldehyde reaction is hydrogen atom transfer to a triplet excited state, $^3Pt_2^*$, and that it is likely that the Pt_2H intermediate reduces the aldehyde to an alcohol.

In degassed methanol, the phosphorescence of $^3Pt_2^*$ is quenched by RCHO [18]. Analysis of room-temperature quenching data ($\tau_0/\tau = 1 + k_q\tau_0[RCHO]$; [RCHO], 0.1 to 0.5 M) gives second-order rate constants for the CH_3CHO (5×10^5) and CH_3CH_2CHO (2×10^5 M^{-1} s^{-1}) reactions. These rate constants are considerably higher than those obtained for methanol ($k_q < 10^4$ M^{-1} s^{-1}) [6,10]. Both electron-transfer (1) [19] and atom-transfer (2) pathways could contribute to the $^3Pt_2^*$ quenching:

$$^3Pt_2^* + RCHO \rightarrow Pt_2^+ + RCHO^- \tag{1}$$

$$^3Pt_2^* + RCHO \rightarrow Pt_2H + RCO. \tag{2}$$

Evidence for the Pt_2H intermediate in (2) has been obtained in flash photolysis

---

* Contribution from the Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, the Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, and No. 7775 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125

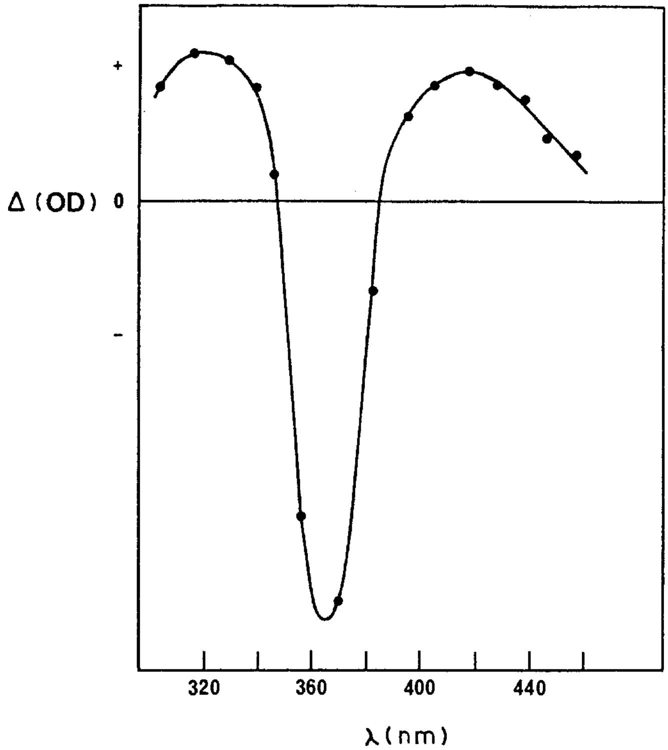

Fig. 1. Transient difference absorption spectrum recorded 10 μs after laser excitation (355 nm) of a degassed methanol solution of propionaldehyde (v/v 1/50) in the presence of Pt_2 (~ 5×10^{-5} M).

experiments. The transient difference absorption spectrum (fig. 1) generated 5 to 10 μs after laser excitation (355 nm) of a degassed methanol solution of Pt_2 and propionaldehyde (v/v, 1/50) is in qualitative agreement with the difference spectrum of Pt_2H and Pt_2 [3,6]. Thus a major pathway in the reaction of $^3Pt_2^*$ with propionaldehyde is H atom transfer, however, an electron-transfer contribution (1) to the quenching process cannot be ruled out, since Pt_2^+ also absorbs in the 300–340 nm region [15,20]. The prompt signal (fig. 1) rapidly decays by complex kinetics. When monitored at 390–420 nm, an approximate first-order decay that is independent of laser energy but proportional to the concentration of propionaldehyde is found. The difference absorption spectrum recorded 10 ms after the laser flash shows no new species that absorb in the 390–460 nm region. The result is consistent with a mechanism in which the photogenerated Pt_2H intermediate reacts with propionaldehyde (3),

$$Pt_2H + CH_3CH_2CHO \rightarrow Pt_2 + CH_3CH_2\dot{C}HOH \qquad (3)$$

Formation of the $CH_3CH_2\dot{C}HOH$ radical is consistent with the observation that propan-1-ol is obtained by broad-band irradiation ($\lambda > 320$ nm) of a degassed methanol or acetonitrile solution of propionaldehyde in the presence of Pt_2 for 6 h [21].

When the decay of the prompt transient absorption signal is monitored in the 300–400 nm region, a new species with a broad absorption band at 340–350 nm is observed 10 ms after the laser flash. This species exhibits an absorption spectrum that is typical of a $Pt_2(III)$ complex [17]. The kinetics for the formation of this new complex is complicated (neither first-order nor second-order kinetics was found); the complex could be produced from Pt_2^+ that is formed by electron-transfer quenching (Pt_2^+ rapidly disproportionates [20] into Pt_2 and Pt_2^{2+} in solution).

Acknowledgment

We thank Erica Harvey for helpful discussions. Support to CMC from the University of Hong Kong is acknowledged. HLK thanks the Croucher Foundation for a Croucher Studentship. PDH acknowledges the Government of Canada for a NSERC-NATO postdoctoral fellowship. Research at the California Institute of Technology was supported by the Sun Company and by National Science Foundation Grant CHE84-19828.

References and notes

[1] (a) University of Hong Kong. (b) The Chinese University of Hong Kong. (c) California Institute of Technology.
[2] C.-M. Che and W.-M. Lee, J. Chem. Soc., Chem. Commun. (1986) 512.
[3] C.-M. Che, W.-M. Lee, K.-C. Cho, P.D. Harvey and H.B. Gray, J. Phys. Chem., submitted for publication.
[4] C.-M. Che, K.-C. Cho, W.-S. Chan and H.B. Gray, Inorg. Chem. 25 (1986) 4906.
[5] D.M. Roundhill, J. Am. Chem. Soc. 107 (1985) 4354.
[6] D.M. Roundhill, S.J. Atherton and Z.-P. Shen, J. Am. Chem. Soc. 109 (1987) 6076.
[7] D.M. Roundhill and S.J. Atherton, Inorg. Chem. 25 (1986) 4071.
[8] D.M. Roundhill, Z.-P. Shen and S.J. Atherton, Inorg. Chem. 26 (1987) 3833.
[9] D.M. Roundhill, Z.-P. Shen, C. King and S.J. Atherton, J. Phys. Chem., in press.
[10] J.L. Marshall, A.E. Stiegman and H.B. Gray, in: *Excited States and Reactive Intermediates*, ed. A.B.P. Lever, ACS Symposium Series 307 (American Chemical Society, Washington, DC, 1986) pp. 166–176.
[11] A. Vlcek, Jr. and H.B. Gray, J. Am. Chem. Soc. 109 (1987) 286.
[12] A. Vlcek, Jr. and H.B. Gray, Inorg. Chem. 26 (1987) 1997.
[13] P.D. Harvey and H.B. Gray, Nouv. J. de Chim. 11 (1987) 595.
[14] C.-M. Che, L.G. Butler and H.B. Gray, J. Am. Chem. Soc. 103 (1981) 7796.
[15] J.R. Peterson and K. Kalyanasundaram, J. Phys. Chem. 89 (1985) 2486.
[16] D.M. Roundhill, H.B. Gray and C.-M. Che, Acc. Chem. Res., submitted for publication.
[17] Prolonged narrow-band irradiation (370 nm; 3 days; 55 ° C) of Pt_2 in neat ethanol produces H_2, CO, CH_4, and a diamagnetic diplatinum(III) complex that is photocatalytically inactive. {Photolysis of freeze-pump thaw degassed solutions was done using a 1000 W xenon lamp with selected Corning filters. Mass spectrometric analysis was performed with a DuPont 2-492 B

instrument. The photoreproduced Pt$_2$(III) complex is thermally unstable in solution. Its ^{31}P-NMR spectrum exhibits a sharp singlet at 31.6 ppm (phosphoric acid reference) and 2 satellites, $^1J_{\text{P-Pt}} = 2132$ MHz. Under high-resolution conditions, no further coupling is observed and the NMR signal indicates that the complex is symmetric. The UV spectrum of Pt$_2$(III) exhibits the following features: 350 (4000); 290 (12000), 260 (14000); 240 nm (ϵ 27000 M^{-1} cm^{-1})}. The same photoproducts also are found when acetaldehyde in acetonitrile is irradiated in the presence of Pt$_2$ at room temperature {17 h photolysis of 0.3 mL of CH_3CHO and 4.0 mL of CH_3CN with 1×10^{-4} M Pt$_2$ leads to complete conversion of Pt$_2$ to the Pt$_2$(III) complex}.

[18] There is no thermal reaction between RCHO ($R = CH_3$, C_2H_5) and Pt$_2$ at room temperature.

[19] P.D. Harvey and H.B. Gray, unpublished results.

[20] (a) C.-M. Che, H.B. Gray, S.J. Atherton and W.-M. Lee, J. Phys. Chem. 90 (1986) 6757;
(b) D.M. Roundhill and S.J. Atherton, J. Am. Chem. Soc. 108 (1986) 6829.

[21] Broad-band irradiation of propionaldehyde in methanol (v/v, 1:1, 10 mL) in the presence of Pt$_2$ (10–20 mg) was carried out with a 400 W high-pressure mercury short-arc lamp under degassed conditions at 25° C. The organic products were identified by GC-MS.