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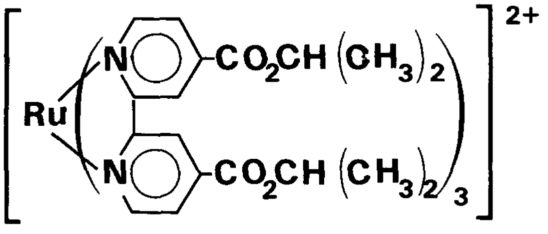
PHOTO-OXIDATION OF SOME CARBINOLS BY THE Ru(II) POLYPYRIDYL COMPLEX-ARYL DIAZONIUM SALT SYSTEM

Herminia Cano-Yelo and Alain Deronzier
Laboratoires de Chimie, Laboratoire d'Electrochimie Organique et Analytique (LA CNRS 321)
Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble,
85 X, F-38041 GRENOBLE CEDEX, France

Summary : The Ru(II) polypyridyl complex 2 effectively catalyzed the photo-oxidation by visible light of some carbinols to aldehydes in presence of a diazonium salt as quencher and a basic agent in acetonitrile.

We have recently [1,2] reported that aryl diazonium salts quench efficently the excited state of the polypyridyl ruthenium(II) complexes such as $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) and lead to the quantitative build up of the strong oxidizing species $Ru(bpy)_3^{3+}$ in acetonitrile. In this communication, we report the utilization of this system to photocatalyze the oxidation of some carbinols to their corresponding aldehydes by a photoredox cycle mechanism.

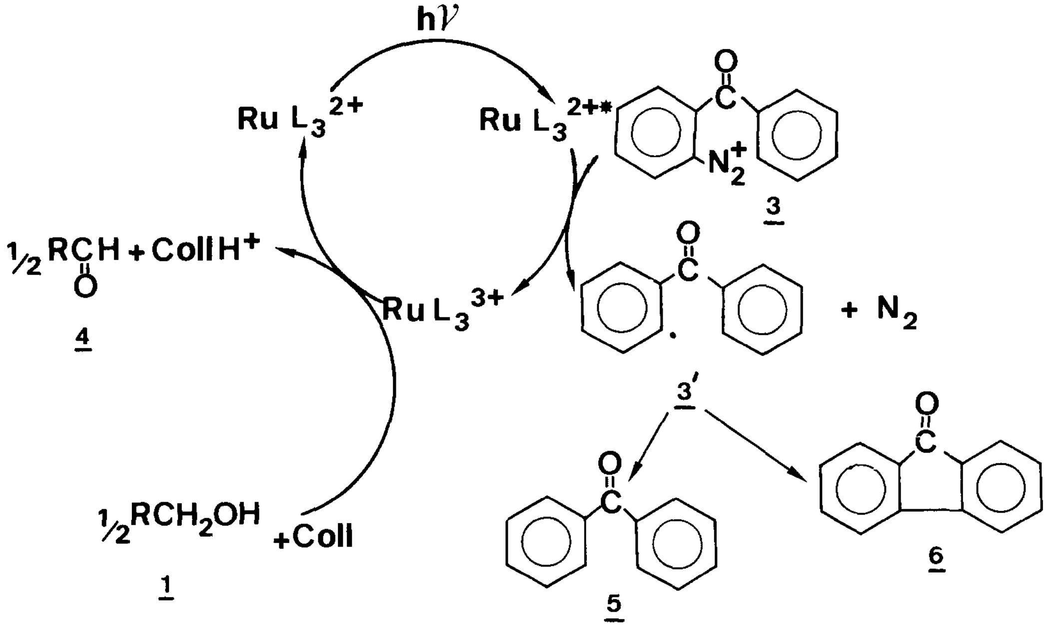
Irradiation with visible light (λ > 410 nm) of a solution of carbinols 1 a-e (5 x 10^{-3} M) in dry acetonitrile free of oxygen containing the complex [3] RuL_3^{2+} 2 (2-4 x 10^{-4} M), the diazonium salt of 2-aminobenzophenone 3 (1.5 x 10^{-2} M) as a quencher with a base like 2,4,6-trimethylpyridine (collidine;coll) induces the carbinol oxidation to the corresponding aldehydes 4 a-e. In the same reaction (eq. 1) the diazonium salt 3 is concomitantly reduced into benzophenone 5 and fluorenone 6.



2

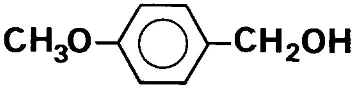
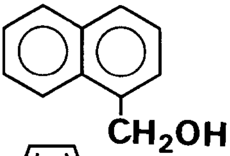
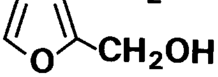
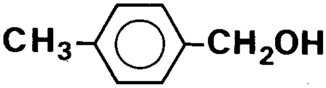
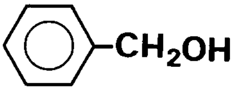
$$\underline{1}\text{ a-e} + \underline{3} \xrightarrow[\text{RuL}_3^{2+}\text{, coll.}]{h\nu} \underline{4}\text{ a-e} + \underline{5} + \underline{6} \qquad \text{(eq. 1)}$$

The progress of the photocatalyzed redox reaction (eq. 1) was followed during the irradiation by quantitative HPLC analysis (on a Waters radial pak μ Bondapak C_{18} cartridge, eluted with different mixtures of MeOH/H_2O). The redox reaction (eq. 1) does not occur in the dark or in the absence of RuL_3^{2+}. The following scheme represents the proposed mechanism of the photo-induced redox reaction :



The initial step consists of the quenching by an electron transfer of the excited state RuL_3^{2+*} by the diazonium salt 3. As for p-substituted benzene diazonium[1-2] the quenching operates at a diffusional rate ($kq = 2.5 \times 10^{10}\ M^{-1}s^{-1}$ determined by fluorescence measurements) and leads to the effective build up of the oxidized complex RuL_3^{3+} in the absence of carbinols. The rapid evolution of the aryl radical 3' issued from the reduction of 3 by RuL_3^{2+*} prevented the thermal back-reaction between RuL_3^{3+} and 3'. The radical 3' gives benzophenone and fluorenone (ratio ≃ 3:1). Benzophenone arises from 3' while fluorenone arises probably from cyclisation of 3' as in a Pschorr reaction[1]. We used 3 instead of the *p*-substituted benzene diazonium salt[2] for the easier HPLC analysis of the corresponding reduction products issued from 3. The photogenerated strong oxidizing species RuL_3^{3+} is able to oxidize carbinols (see Table for the half-wave potential of carbinols). As the carbinol oxidation to aldehyde requires two-electron and two-proton exchanges, the reaction is strongly improved by adding a base such as collidine. The Table gives the corresponding yields of aldehyde. In the absence of collidine, a markedly lower amount of aldehyde is observed (yield < 30 % with 1a and < 10% with 1b). In the table is shown that the yields of aldehyde depend of the half-wave oxidation potentials of the carbinols. Lower yields were obtained for the less oxidizable alcohols (1d,c). Increasing

Table

Alcohols	$E_{1/2}$ (V) (a)	Time of irradiation (mn) (b)	Yields of aldehydes, % (c)	Quantum yields (d)
1a, 	1.52	20	100	0.25
1b 	1.55	80	61	0.17
1c 	1.63	30	28	0.07
1d 	1.89	60	35	0.03
1e 	2.19	60	21	0.02

(a) From ref. 6, 7. The values reported in these references were *vs* the Ag/Ag^+ 10^{-1} M or Ag/Ag^+ 10^{-2} M reference electrode. The values cited later here have been respectively corrected by the addition of 0.30 V and 0.29 V, and are *vs* s.c.e.

(b) Time required to reach the maximum yield of aldehyde.

(c) Yields are determined by H.P.L.C. and are relative to the starting carbinols amounts. An identical quantity of collidine (1.5×10^{-2}M) was used.

(d) Quantum yields of aldehyde formation, determined by H.P.L.C.

the collidine amount induces an increase of yield for the more easily oxidizable carbinols ($E_{1/2}$ carbinol < $E_{1/2}$ $RuL_3^{2+/3+}$). For instance, the use of 3×10^{-2} M of collidine instead of 1.5×10^{-2} M increases the yield up to 90 % for **4b**. On the other hand, as collidine is itself oxidizable ($E_{pa} \simeq 2.0$ V *vs* s.c.e.) its concomitant oxidation [8] by RuL_3^{3+} can explain the low yield observed for carbinols having high oxidation potentials (**1** d-e). Consequently, the utilization of a larger amount of base does not increase the aldehyde yields for these alcohols. We are currently exploring the possibility of using the RuL_3^{2+}/diazonium system to photo-oxidize other kind of alcohols.

Aknowledgments :

We are thankful to Professor G. CAUQUIS for his interest in this work.

References and notes

1 H. Cano-Yelo and A. Deronzier, J. Chem. Soc., Perkin Trans. II, 1093 (1984).

2 H. Cano-Yelo and A. Deronzier, J. Chem. Soc., Faraday Trans I, in press.

3 RuL_3^{2+} is used in place of $Ru(bpy)_3^{2+}$ for the better oxidizing power of its oxidized form ($E_{1/2}$ $RuL_3^{3+/2+}$ = 1.59 V vs s.c.e. [4] in acetonitrile, while $E_{1/2}$ $Ru(bpy)_3^{3+/2+}$ = 1.35 V vs s.c.e. [5])

4 P.J. Delaive, J.T. Lee, H.W. Sprinschnik, H. Abruña, T.J. Meyer and D.G. Whitten, J. Amer. Chem. Soc., 99, 7094 (1977) and Adv. Chem. Ser., 168, 28 (1978).

5 N.E. Tokel-Takvoryan, R.E. Hemingway, and A.J. Bard, J. Amer. Chem. Soc., 95, 6582 (1973).

6 H. Lund, Acta Chem. Scand., 11, 491 (1957).

7 E.A. Mayeda, L.L. Miller, and J.F. Wolf, J. Amer. Chem. Soc., 94, 6812 (1972).

8 The final products from the collidine reduction are under investigation.

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