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ELECTROCATALYTIC OXIDATION OF OLEFINES AND KETONES BASED ON A $Ru^{IV}=O/Ru^{II}-H_2O$ SYSTEM.

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Abstract: An electrocatalytic procedure is described for the oxidation of cyclohexene, safrole, isosafrole, isophorone, deoxybenzoin and acetophenone using the Ru^{IV} oxidant $[Ru^{IV}(trpy)(bpy)O]^{2+}$. The relative reactivities of the substrates are presented.

Polypyridyl complexes of ruthenium have a rich synthetic[1] and redox chemistry[2]. Complexes of Ru(II) which contain at least one aquo ligand can be oxidized to the corresponding oxo complexes of Ru(IV)[2]. The importance of the oxo group is that it can act as a site acceptor for a proton in the oxidation of a suitable substrate.

It has been shown that the Ru(IV) complex $[Ru^{IV}(trpy)(bpy)O]^{2+}$(trpy=2,2',2''- terpyridine; bpy=2,2'-bipyridine) acts as a catalyst for the electrocatalytic oxidation of alcohols, aldehydes, cyclic ketones, and C-H bonds adjacent to olefinic or aromatic groups[3]. In this system, the Ru^{IV}=O complex oxidizes the substrate being itself reduced to the Ru(II) complex, $[Ru^{II}(trpy)(bpy)(H_2O)]^{2+}$. The latter complex is continuously reoxidized to Ru^{IV}=O at an electrode. In this way the polypyridyl system remains unaltered and the only changes ocurring are at the active oxo-water groups. The proposed mechanistic pathway is equivalent to hydride transfer as in the oxidation of isopropanol[4] and of 4-alkyl-benzoic acids[5] (alkyl= methyl, ethyl, isopropyl).

We report here the results obtained for the electrocatalytic oxidation of cyclohexene, safrole, isosafrole, acetophenone, deoxybenzoin and isophorone. These olefines and ketones were carefully chosen on the basis of their structures and their relative reactivities have been analysed. Isophorone has a particular interest because one of its oxidation products is 4-oxo-isophorone[6], a very important synthon for the synthesis of many sesquiterpenoids.

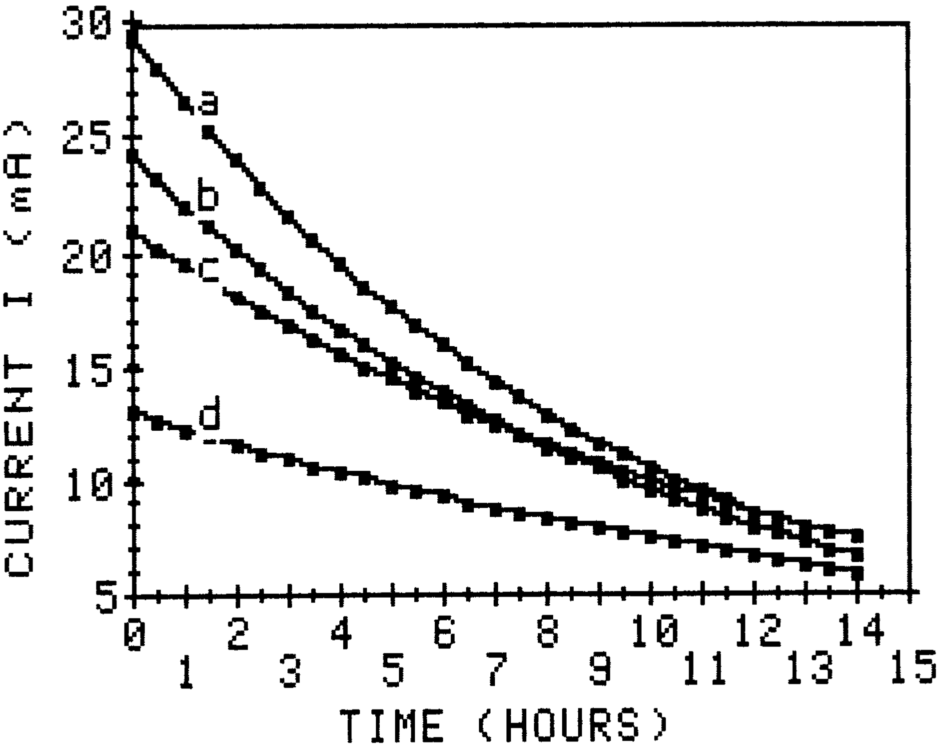
In the coulometric experiments reported here, the electrochemical cell had two compartments containing a platinum gauze working electrode and a platinum plate auxiliary electrode , connected to platinum wires. The reference electrode was a saturated calomel electrode (SCE). The electrolyses were performed at room temperature and at the fixed applied potential of 0.8V vs. SCE. This is sufficient to generate the Ru(IV) oxidant, $[Ru(trpy)(bpy)O]^{2+}$ from $[Ru(trpy)(bpy)(H_2O)]^{2+}$. The current was registered on a Y-T recorder. A constant pH of 6.8 was maintained by using 0.25 M 1:1 phosphate buffer. The buffer components also served as electrolytes. Whenever the substrates were poorly soluble in water, tert- butanol was used as co-solvent in amounts just necessary to solubilize them. The substrates and the co-solvent are unreactive under experimental conditions, i.e., under a potential of 0.8 V vs. SCE the currents were in the microampere range. In the experiments the concentration of $[Ru(trpy)(bpy)(H_2O)]^{2+}$ in the cell was 2.9 mM, the concentration of the substrate was 15 fold the concentration of the complex and the total volume of the electrolysis solution ranged between 30-34 ml.

In a typical experiment, a solution containing the buffer components and the ruthenium (II) complex was placed in the cell. A potential of 0.8 V was applied across the cell until the current fell to the order of microamperes. The substrate and the tert-butanol were then added all at once, under strong stirring. This led to catalytic currents in the milliampere range. The current change with time was recorded. The electrolysis was continued for a period long enough to obtain sufficient product for analysis and to evaluate the possibility of using this process as an alternative method in the synthesis of organic compounds. The product was extracted with a 9:1 diethyl ether: methylene chloride mixture, purified by preparative silica gel column or plate and analysed by conventional IR, UV-VIS, ^{1}H NMR, and MS methods (the isophorone oxidation products were analysed by GLC).

The results of the electrocatalytic oxidations are summarized in Table 1. By knowing the amount of Coulombs used in the oxidations, one can stop the process at any time in order to get selective oxidations based on the amount of Coulombs calculated for 4 or 6 electrons oxidations (to ketone or aldehyde or to acid, respectively) and on kinetic factors.

Figure 1

Plot of Current vs.Time*Obtained for the Oxidation of Olefines and Ketones

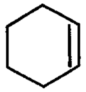
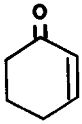
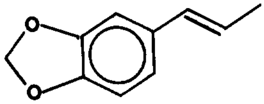
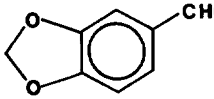
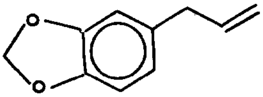
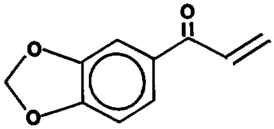
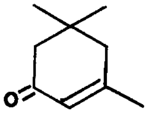
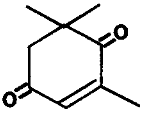
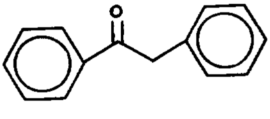
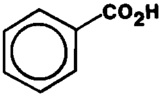
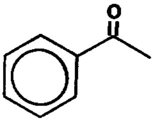
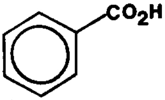


a= cyclohexene, b= isosafrole, c= safrole, d= isophorone

* Curve obtained by exponential regression.

Table 1

Results of Electrocatalytic Oxidation Based on [Ru(trpy)(bpy)O]$^{2+}$ [A]

Substrates (Conc.mM)	% V/V co-solvent	Products (% yield)[B]
 cyclohexene (44.8)	32.3	 2-cycloexen-1-one (47.6)
 isosafrole (44.4)	32.3	 piperonal (48.9)
 safrole (44.8)	32.3	 vinyl-(3,4-methylenedioxo)-phenyl-ketone (65.1)[7]
 isophorone (44.2)	17.7	 4-oxo-isophorone (14.0)[C] + unidentified products
 deoxybenzoin (29.9)[D]	30.0	 benzoic acid (59.4)
 acetophenone (44.2)	14.7	 benzoic acid (72.6)

[A] At room temperature, pH 6.8 (0.25M 1:1 phosphate buffer) and 2.9mM in catalyst unless otherwise noted.

[B] Analyses by: IR, ^{1}H NMR, and MS.

[C] Identification and yield calculation by comparative GLC with synthetized[6] authentic sample.

[D] Catalyst concentration 2.0 mM.

The observed current is proportional to the rate of the process[8]. The intensive stirring of the electrolized solution ensures that the chemical reaction takes place homogeneously in the bulk of the solution and not just in the immediate vicinity of the electrode surface[9]. The current-time curve reflects the rate-limiting formation of electron-deficient carbon in the transition state, which corresponds to hydride transfer $(-2e^-,-H^+)$[4,5]. The electron deficient carbon is stabilized by the adjacent double bond in the olefinic substrates and destabilized by adjacent carbonyl groups. In fact, it can be noticed in Figure 1 that the reactivity order is cyclohexene > isosafrole > safrole > isophorone. Deoxybenzoin and acetophenone have the lowest reactivities (lowest initial currents and highest half-lives); their experimental data don't fit exponential regression curves, probably due to kinetic complications. The isophorone, a ketone which has allylic positions, has an intermediate level of reactivity.

On the basis of differences among those reactivities and controlling the amount of Coulombs passed through the solution it was possible to obtain 2-cyclohexen-1-one as the only product of the oxidation of cyclohexene (47.6% yield of purified product), while in an uncontrolled process 2-cyclohexen-1-one (~15% yield), hydroquinone and other unidentified products were obtained[3a].

This work shows, then, an alternative method of oxidation of C-H bonds adjacent to unsaturated systems giving products of potential synthetic interest, as well as the possibility of indirectly estimating the relative reactivities of some substrates, which allows obtaining functional group specificity for complex molecules selective oxidations.

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References and Notes

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7. ^{1} NMR (60MHz, CCl_4, TMS) δ , 7.40 (d, 1H, 8Hz), 7.07 (d, 1H, 8Hz), 7.10- 6.95 (m, 1H), 6.88 (s, 1H), 6.80-6.48 (dd, 2H), and 6.02 (s, 2H). IR(KBr), cm^{-1}, 3090, 1670, 1620, 1605, 1255, 1115, 1100, and 1035. MS (m/e) 176 (35.1), 149 (100.0), 121 (42.9), 55 (13.0).
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