An Efficient Electrochemical Process for the Oxidation of Saturated Hydrocarbons: the Gif–Orsay System

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The selective oxidation of saturated hydrocarbons can be carried out using triplet oxygen, pyridine, trifluoroacetic acid, and an iron catalyst in an unicellular electrochemical cell (Gif–Orsay system), cyclododecane, adamantane, and cyclo-octane being oxidised in 17—30 mmolar amounts with improved coulombic yields of up to ~30% being attainable; oxidation of cyclohexane in 48 mmolar amounts gave cyclohexanone with some cyclohexanol in ~40% coulombic yield, and similar yields were obtained on a 140—167 mmolar scale (saturated solution of hydrocarbon) with addition of electron transfer reagents and enough water to give two layers (good stirring) and satisfactory conductivity.

In a previous communication,[1] we described our first results concerning an electrochemical modification of the Gif system[2] for the selective oxidation of unactivated C–H bonds of saturated hydrocarbons. We showed that saturated hydrocarbons [adamantane (**4**), cyclododecane (**1**), and *trans*-decalin] in a mixture of pyridine and trifluoroacetic acid under a stream of oxygen are oxidised at 20 °C at the *cathode* in a separated-compartment cell [cathode: mercury, anode: platinum; E −0.6 to −0.7 V *vs.* standard calomel electrode (S.C.E.); current density 7—14 mA/cm^2] in the presence of catalytic amounts of the iron cluster, $Fe_3O(OAc)_6Pyr._{3.5}$ (Pyr. = pyridine). Yields of oxidation products (~20%) and regioselectivity are close to those observed in our previous chemical system,[2] ketones always being the major products. These results demonstrated that a cathode can replace zinc powder as the electron source and encouraged us to study in more depth this new electrochemical approach. This electrochemical process had several defects which limited the efficiency of the reaction. (i) Because of the diffusion through the ceramic wall separating the cathodic and the anodic compartments some of the hydrocarbon and its oxidation products were found in the anolyte [$Et_4N^+ClO_4^-$ in dimethyl formamide (DMF)] and more seriously DMF and Et_4N^+-ClO_4^- partly diffused into the catholyte (pyridine, HOAc or CF_3CO_2H or α-picolinic acid). As blank experiments showed that DMF partly inhibits the oxidation, its diffusion could be prejudicial to success. (ii) The resistance imposed by the ceramic wall limited the current which could be applied without excessive heating and hence led to long reaction times. (iii) The basicity of the reaction medium increased as the electrolysis proceeded thus requiring a continuous adjustment by addition of more carboxylic acid to keep the acidity in the range pH 4.5—5.0. (iv) The coulombic yields were rather low (η ~15%) and moreover decreased after 1000—1500 C.

In this paper we report major improvements in this electrochemical oxidation of hydrocarbons. The observation that, in a one-compartment cell, the presence of trifluoroacetic acid (or tetrafluoroboric acid) in pyridine made the reaction mixture sufficiently conducting to allow the electrolysis to be performed under potentiostatic conditions led us to simplify the electrochemical system. This modification is not only convenient from the practical point of view but also solves most of the above mentioned problems. In the unicellular system the solution has lower resistance, so a higher current density (42 mA/cm^2 or even more) can be used and hence shorter reaction times are necessary. The difficulties associated with diffusion between the compartments are,

(1) + CF_3CO_2H + 2,2′-bipyridyl
4 mmol 26 mmol, 1 mmol
2 ml

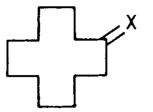
+ $Fe_3O(OAc)_6Pyr._3$ → **(2)** + **(3)**
25 μmol

Scheme 1. *Conditions*: O_2 stream, pyridine (30 ml), 20 °C (see Table 1).

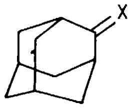
Table 1. Oxidation of cyclododecane (**1**) in the unicellular system under potentiostatic conditions [*E* −0.7 V (*vs.* S.C.E.), *i* ~ 15 mA/cm^2, anode: platinum, cathode: mercury]

	% Yield				
Q/C	(**2**)	(**3**)	Total yield, %	η[a]	Total (mmol)
200	—	2.30	2.30	18	0.09
500	—	6.05	6.05	19	0.24
1050	1.35	12.3	13.6	19	0.54
1500	1.50	12.7	14.2	14	0.57
2000	1.80	14.7	16.5	12	0.66
2500	2.35	16.6	18.9	11	0.76

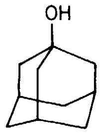
[a] The coulombic yield η is defined as: η = [(4*Nx* + 2*Ny*) 96.5 × 100]/Q_T, where *N* = mmoles of substrate, *x* = % of (**3**), *y* = % of (**2**) (% based on the substrate), Q_T = total electricity passed in C (1 Faraday = 96 500 C).



(1) X = H_2
(2) X = H, OH
(3) X = O



(4) X = H_2
(5) X = H, OH
(6) X = O



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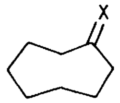
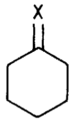
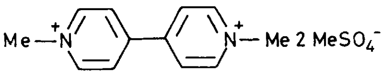


(8) X = H_2
(9) X = H, OH
(10) X = O



(11) X = H_2
(12) X = H, OH
(13) X = O



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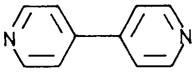

(15)

Table 2. Oxidation of cyclododecane (**1**), cyclo-octane (**8**), cyclohexane (**11**), and adamantane (**4**) in the unicellular system using a constant source (anode: platinum, cathode: mercury).

Substrate (mmol)	*i*/ (mA/cm^2)	*Q*[a]/C	Oxidised products (μmol)	Total (mmol)	η	C^2/C^3[c]
(**1**)[d] (20)	17	500	(**2**), 84; (**3**), 454	0.54	38	
		2000	(**2**), 284; (**3**), 1175	1.46	25	
		3000	(**2**), 430; (**3**), 1658	2.09	24	
		8800	(**2**), 582; (**3**), 2140	2.72	11	
(**4**) (17)	16	500	(**5**), 24; (**6**), 174; (**7**), 5	0.20	15	40
		1000	(**5**), 56; (**6**), 338; (**7**), 14	0.41	14	28
		3000	(**5**), 158; (**6**), 820; (**7**), 31	1.00	12	32
		3500	(**5**), 174; (**6**), 910; (**7**), 33	1.12	11	33
(**8**) (30)	14	500	(**9**) + (**10**), 500[b]	0.50	35	
		1000	(**9**) + (**10**), 900[b]	0.90	32	
		6250	(**9**) + (**10**), 4550[b]	4.55	26	
(**11**) (48)	17	500	(**12**), 45; (**13**), 535	0.58	43	
		1000	(**12**), 110; (**13**), 1190	1.30	48	
		2000	(**12**), 245; (**13**), 2200	2.45	45	
		8700	(**12**), 1050; (**13**), 7585	8.65	36	

[a] Aliquots were taken after passage of the quantity of electricity indicated and analysed by g.l.c. [b] Cyclo-octanone was the major product [(**10**)/(**9**) ~5]. [c] C^2/C^3 represents the relative ratio of attack at the secondary and tertiary positions, respectively; statistical attack would give C^2/C^3 = 3. [d] 1 ml of CF_3CO_2H was added after passage of 3000 C.

$$\text{Hydrocarbon} + \underset{\substack{39\text{ mmol,}\\ 3\text{ ml}}}{CF_3CO_2H} + \underset{25\ \mu\text{mol}}{Fe_3O(OAc)_6Pyr._3} \rightarrow \text{oxidised product}$$

Scheme 2. *Conditions*: O_2 stream, pyridine (30 ml), 20—30 °C (see Table 2).

of course, avoided. More interestingly, there is no need for correction of the acidity of the medium and the coulombic yield decreases more slowly than in the separated-compartment type cell. Oxidation of cyclododecane (**1**) is taken as an example (Table 1).

Examination by cyclic voltammetry showed that the most easily reducible species of the system was dioxygen, giving superoxide ($O_2^{\bullet -}$ and/or $HO_2^{\bullet}$) and then rapidly hydrogen peroxide, at the same potential (−0.6 V). Simple blank experiments made us consider that, as in the chemical system, the oxidant for the iron catalyst is not hydrogen peroxide (inactive in the oxidation process when generated *in situ* electrochemically), but superoxide. Starting from this observation we thought that, providing enough dioxygen was supplied to the system, the electrolysis could be carried out using only a very simple stabilised source of a constant current, the potential being 'self-adjusted' by the reduction of dioxygen. This prediction was confirmed by experiment (see below). We also found that the coulombic yield η was limited by the concentration of the substrate. The combination of these two factors, *i.e.* constant current source and high concentration of substrate, gave impressive results in terms of mmoles of oxidised products (Table 2) and, significantly, in terms of turnover for the catalyst.

In the case of cyclohexane (**11**), the substrate was introduced into the electrolysis cell at the beginning of the reaction and a constant flow of oxygen (3 ml/min) saturated with cyclohexane bubbled into the reaction mixture. The vapour phase containing cyclohexane and pyridine was trapped at the outlet of the vessel and analysed by g.l.c. No oxidation products were detected in this trap.

When an electron transfer reagent, more easily reduced at the cathode than dioxygen, such as Paraquat (**14**) or 4,4′-bipyridyl (**15**) (partly protonated in the medium) were used, under potentiostatic conditions (unicellular cell), coulombic yields as high as 49% were obtained (Table 3).

$$(\mathbf{11}) + \underset{\substack{39\text{ mmol,}\\ 3\text{ ml}}}{AcOH} + H_2O + \underset{25\ \mu\text{mol}}{Fe_3O(OAc)_6\,Pyr._{3.5}} \rightarrow (\mathbf{12}) + (\mathbf{13})$$

Scheme 3. *Conditions*: E −0.5 V *vs.* S.C.E., $i \sim 17$ mA/cm^2; 20 °C; Q_T 9400 C; pyridine (30 ml) (see Table 3).

Table 3. Oxidation of cyclohexane in the presence of electron transfer reagents (A).

(**11**), mmol	(A), mmol	H_2O,[a] mmol	(**12**), mmol	(**13**), mmol	η
140	(**14**) (1)	111	0.84	9.24	40
167	(**15**) (25)	22	1.42	11.2	49

[a] H_2O increases the conductivity and makes the reaction mixture inhomogeneous.

If it is now possible to understand the cathodic process readily [reduction of dioxygen to superoxide, possibly mediated by an electron transfer reagent, then oxidation of an iron(II) species by $O_2^{\bullet -}$ or $HO_2^{\bullet}$ to give an active iron catalyst able to react with the substrate and to lead to oxygenated products], the anodic process is less clear. We have, at present, good evidence (CO_2 evolution, isolation of trifluoromethylpyridines) that trifluoroacetic acid (or more probably trifluoroacetate ion) is partly oxidised in a Kolbé type reaction. Nevertheless, the coulombic yield determined for this latter reaction is only 10%, so another species (probably pyridine) is oxidised at the anode.

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