JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 549–552

Oxidation of cyclohexane to cyclohexanone via the electrochemical reduction of molecular oxygen: the HCl effect

R. TOMAT

Laboratorio di Polarografia ed Elettrochimica Preparativa del CNR, PO Box 1075, 35100 Padova, Italy

A. RIGO

Istituto di Chimica Fisica dell'Università di Venezia, Ca'Foscari, 30100 Venezia, Italy

Received 9 February 1979; in revised form 24 October 1979

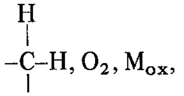
OH radicals, produced by the electrochemical reduction of solutions containing both oxygen and iron(III) oxidize cyclohexane to cyclohexanone in t-BuOH/H_2O/HCl media; in some experiments cyclohexanol was also produced. The use of a non-chloride medium or the use of Ti(III) instead of Fe(II) leads to a remarkable decrease in the yields. These results are interpreted by a mechanism involving the intermediate formation of Cl radicals.

---

1. Introduction

The production of cyclohexanone, an intermediate in the preparation of nylon 66, is a multistage process, usually carried out through the reduction of phenol to cyclohexanol followed by oxidation in the gas-phase. This paper reports an investigation of the one-step electrochemical oxidation of cyclohexane to cyclohexanone and is part of a study of the controlled oxidation of alkanes. The formation of a carbon–oxygen bond could be achieved by hydrogen abstraction to give a free radical and reaction of the radical with molecular oxygen.

OH radicals are suitable for the H abstraction process and they are generated at room temperature from H_2O_2 and a reducing metal ion, M_{red}, such as Fe(II), Ti(III) or Cu(I). In particular, the production of OH radicals via H_2O_2 and M_{red}, in the system



$$\begin{array}{l} \;\;H \\ \;\;| \\ -C-H,\ O_2,\ M_{ox}, \\ \;\;| \end{array}$$

(where M_{ox} is Fe(III), Ti(IV) or Cu(II)) by the cathodic reduction of M_{ox} and O_2 appears particularly promising for the controlled oxidation of C–H bonds. High selectivities and oxidation yields as high as 100% were obtained in the oxidation of methyl toluenes [1, 2]. In these electrochemical reactions a positive 'Cl^- effect' on the yields was observed [2].

2. Experimental

2.1. *Chemicals*

All the chemicals were reagent grade products. High-purity oxygen was employed to saturate the solutions. Water and mercury were twice distilled.

2.2. *Apparatus and procedure*

The experimental apparatus and instrumentation have already been described [1, 2]. Because of the very low solubility of cyclohexane in H_2O, t-butyl alcohol was used as a co-solvent. The electrolysis system composition was: t-butyl alcohol (15 cm^3), cyclohexane (10 cm^3), aqueous HCl 12 M (2 cm^3), to which various amounts of a concentrated $FeCl_3$ solution were added in such a way to prevent phase separation. The electrolyses were carried out at $P_{O_2} = 1$ atm and at a potential of -0.2 V versus SCE, a potential in the limiting current region for Fe(III) and O_2 reduction.

After electrolysis the reaction mixture was

0021–891X/80/040549–04$02.40/0

neutralized with sodium bicarbonate and analysed by GL chromatography, employing 1-hexanol as an external standard. The column (200 x 0.5 cm, 115° C) was packed with diethylene glycol succinate (LAC 728) on Chromosorb W (80–100 mesh), and N_2 was the carrier gas ($40\,cm^3\,min^{-1}$).

Retention times were: 1-hexanol (679 s), cyclohexanone (935 s), cyclohexanol (1067 s). The experimental results reported in the following section were, unless otherwise stated, obtained with the electrolyses carried out at 50° C.

3. Results and discussion

OH radicals were generated from H_2O_2 and M_{red} produced by a simultaneous cathodic reduction of molecular oxygen (2 electrons) and of M_{ox} (1 electron) according to the overall reaction:

$$H_2O_2 + M_{red} \xrightarrow{k_1} OH + OH^- + M_{ox} \qquad (1)$$

$$k_1 = 5 \times 10^2\,M^{-1}s^{-1}(M_{red} = Ti^{3+}[3])$$

$$k_1 = 60\,M^{-1}s^{-1}(M_{red} = Fe^{2+}[4])$$

The current yields were calculated on the basis of a consumption of $3\,F\,mol^{-1}$ of cyclohexane oxidized, since in these conditions 3 electrons are engaged in the generation of an OH radical from O_2 and M_{ox}. The results obtained in a series of preliminary runs are summarized in Table 1.

Table 1. Cyclohexanone yields in the electrochemical activation of cyclohexane at – 0.2 V *versus S.C.E.,* $M_{ox} = 2 \times 10^{-3}\,M$; $P_{O_2} = 1$ atm, *temperature:* 50° C.

Composition of the oxidation medium	M_{ox}	
	Fe(III)	*Ti(IV)*
(A) Cyclohexane; H_2O; 1 M $HClO_4$ (biphasic)	2%*	–
(B) Cyclohexane; H_2O (8%)‡; *t*-BuOH (55%)‡; 1 M $HClO_4$ (monophasic)	12%*	5%*
(C) Cyclohexane; H_2O (8%)‡; *t*-BuOH (55%)‡; 0.9 M HCl (monophasic)	48%†	20%*

* trace of cyclohexanol.
† cyclohexanol 6%.
‡ by volume.

3.1. *Reaction in the system cyclohexane–*H_2O*–*$HClO_4$

Only traces of cyclohexanone were detected in experiments carried out in these conditions in the presence of Fe(III) or of Ti(IV). This result, compared with the oxidation yields of about 60% obtained with methyl-substituted aromatic compounds [1, 2], could be ascribed to the lower reactivity of the OH radical towards the cyclohexane C–H bonds. In fact, from the data of Anbar *et al.* [5] it appears that the rate constant for reaction of aliphatic secondary C–H bonds with the OH radical, ($k = 3 \times 10^8\,M^{-1}s^{-1}$) is at least an order of magnitude lower than that of aromatic hydrocarbons. This lower reaction rate together with the poorer solubility in water of the cyclohexane [6], leads to wastage of the OH radicals in reactions such as

$$M_{red} + HO^{\cdot} \rightarrow M_{ox} + HO^- \qquad (2)$$

3.2. *Electrooxidation in the system cyclohexane–t-BuOH–*H_2O*–*$HClO_4$

The cyclohexane oxidation yields obtained in this system for different ratios of $[M_{ox}]/[O_2]$ were always lower than 12% with Fe(III) and 5% with Ti(IV). No marked increase was observed by substituting H_2SO_4 for $HClO_4$.

The high concentration of cyclohexane in the solution should make the ˙OH wastage by reaction 2 negligible. However, the *t*-BuOH, whose concentration is about twice that of the alkane, competes effectively with the cyclohexane for the OH radicals ($k_{t\text{-BuOH}+{}^{\cdot}OH} = 4.2 \times 10^8 M^{-1}s^{-1}$ [7]) with a consequent negative effect on the cyclohexanone yields.

The oxidation of the C–H bond to C=O should occur in at least three distinct and consecutive steps:

(I) H-abstraction by OH radicals:

$$C_6H_{12} + {}^{\cdot}OH \rightarrow {\cdot}C_6H_{11} + H_2O$$

(II) O_2 insertion

$${\cdot}C_6H_{11} + O_2 \rightarrow {\cdot}O_2C_6H_{11}$$

This reaction appears the most probable among the possible reactions of the cyclohexyl radical formed in step I because of the relatively high concentration of molecular oxygen (about 10^{-3} M) which is a very efficient trap of radicals.

(III) conversion of the cyclohexyl–oxygen adduct to cyclohexanone.

Some authors [8] have reported that at temperatures below 100° C aliphatic peroxy radicals undergo a rearrangement by a 1–3 hydrogen shift. Under the conditions of the electrolyses the product of the rearrangement, $C_6H_{10}OOH$, will react with Fe(II)

$$>\dot{C}\text{–OOH} + \text{Fe(II)} \rightarrow >C{=}O + \text{Fe(III)} + OH^-.$$

This hypothesis is difficult to prove experimentally, but can explain the ratio $[C_6H_{10}O]/[C_6H_{11}OH]$ ($\gg 1$) found in this study. The small yield of cyclohexanol, which is independent of $[O_2]/[\text{Fe(III)}]$ ratio, may be due to a parallel disproportionation of the peroxy radical [9]:

$$2\cdot O_2C_6H_{11} \rightarrow C_6H_{10}O + C_6H_{11}OH + O_2$$

3.3. *Electrooxidation in the system cyclohexane–t-BuOH–H$_2$O–HCl*

The use of HCl instead of $HClO_4$ or H_2SO_4 in the system B increases the cyclohexane oxidation yields by a factor of about 5. Thus in the presence of about 1 M HCl the cyclohexanone plus cyclohexanol current yield is higher than 50% when M_{ox} = Fe(III) and is about 20% when M_{ox} = Ti(IV) assuming again that 3e are involved for each cyclohexane C–H bond oxidized.

This dramatic increase of the yields can only be explained by direct involvement of a chlorine species in the reaction mechanism. At pH = O the reaction

$$^{\cdot}OH + HCl \rightarrow Cl^{\cdot} + H_2O \quad k = 4 \times 10^9\ M^{-1}s^{-1}\ [10]$$

is competitive with the reaction between *t*-BuOH and OH radicals. In fact, taking into account the relative concentrations and rate constants, about 70% of the generated OH radicals react with the HCl giving Cl atoms.

Since the reactivity of chlorine atoms towards an aliphatic C–H bond is almost two orders of magnitude higher than that of OH radicals [11] the H-abstraction from cyclohexane probably occurs mainly via Cl atoms

$$C_6H_{12} + Cl^{\cdot} \rightarrow \cdot C_6H_{11} + HCl.$$

As a consequence, the activation of cyclohexane is controlled by the relative reactivities of Cl atoms towards the cyclohexane and *t*-BuOH molecules, which were calculated to be approximately 4:1 by Huyser [12]. On this basis and taking into account the relative concentrations present in the electrolysis solution about 70% of the Cl atoms react with cyclohexane. Thus about one-half of the electrochemically generated OH radicals should react, via the Cl˙ atom, with the cyclohexane molecule and this estimate agrees quite well with the experimental results obtained with Fe(III), see Table 1. In particular, the plots of the cyclohexane oxidation yields versus Fe(III), at three different temperatures, show a maximum at a Fe(III) concentration of about 2×10^{-3} M, see Fig. 1, as was obtained for the methyl-substituted benzenes [1, 2]. This value corresponds to a comparable rate of H_2O_2 and Fe(II) generation, taking into account the O_2 solubility and the diffusion coefficient of Fe(III) and O_2. With an increase of HCl concentration from 0.2 to 1.2 M, the presence of 2×10^{-3} M Fe(III) gives rise to a monotonic increase in the cyclohexanone yield from 30% to 55%. The cyclohexanone yield versus the Ti(IV) concentration, reported in Fig. 2, shows a behaviour similar to that observed with Fe(III) (Fig. 1). This result indicates the general validity of the C–H bond activation reaction via an $O_2 \rightarrow H_2O_2 \xrightarrow{M_{red}} {}^{\cdot}OH \xrightarrow{HCl} Cl^{\cdot}$ mechanism.

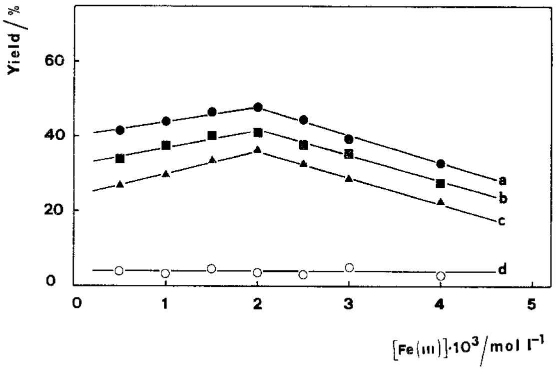


Fig. 1. Percentage current yields of cyclohexanone (curves: a, b, c) and cyclohexanol (d) against Fe(III) bulk concentration at various temperatures. 37% cyclohexane, 55% *t*-BuOH, 8% H_2O (by volume), 0.9 M HCl; total charge: 250 C. Temperature: (■) 30° C; (●) 50° C; (▲) 65° C. The cyclohexanol yields are independent of the temperature and therefore the mean values are reported.

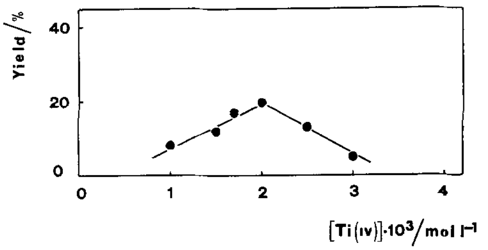


Fig. 2. Percentage current yields of cyclohexanone against Ti(IV) bulk concentration at 50° C. 37% cyclohexane, 55% *t*-BuOH, 8% H_2O (by volume), 0.9 M HCl; total charge; 250 C.

In addition to the higher reactivity of $Cl^{\cdot}$ compared to $^{\cdot}OH$ toward the C–H band, two possibilities should be considered to explain the 'Cl-effect':

(i) Cl^- ions form complexes with both Fe(II) and Fe(III) ions, with a consequent change of their redox potentials and of the kinetic rate constants;

(ii) Cl atoms are involved in many reactions with both Fe(II) and Cl^- ions [13].

The lower yields obtained with Ti(IV) could be ascribed to the much higher reactivity of the OH radicals towards Ti(III) [3].

In conclusion it appears that the selective oxidation of an aliphatic $-\overset{|}{\underset{|}{C}}-H$ bond to $>C{=}O$ group could be easily achieved by the electrochemical activation of molecular oxygen in the presence of the simultaneously electrogenerated Fe(II) or Ti(III). Furthermore, the massive increase of the yield in the presence of HCl calls for the involvement of the Cl atom in the functionalization of the aliphatic system.

Acknowledgement

We thank Mr R. Salmaso of the Italian National Research Council (CNR) for his helpful support in the experimental work.

References

[1] R. Tomat and A. Rigo, *J. Appl. Electrochem.* 6 (1976) 257.
[2] *Idem*, *ibid* 9 (1979) 301.
[3] V. Peruzzo and R. E. Hester, *Inorg. Chim. Acta* 20 (1976) 145.
[4] H. N. Po and N. Sutin, *Inorg. Chem.* 7 (1968) 621.
[5] M. Anbar, D. Meyerstein and P. Neta, *J. Chem. Soc.* (*B*) (1966) 742.
[6] A. N. Guser and E. Parnov, *Zh. Phys. Khim.* 37 (1963) 2763.
[7] G. Scholes, P. Shaw, R. L. Willson and M. Ebert, in 'Pulse radiolysis' (edited by J. H. Baxendale, M. Ebert, J. P. Keene and A. J. Swallow), Academic Press, New York (1965) p. 151.
[8] R. Kh. Freidlina, in 'Advances in free radical chemistry', Vol. I (edited by G. H. Williams) Logos Press, London (1965) ch. 6, p. 227.
[9] M. Simic and E. Hayon, *J. Phys. Chem.* 75 (1971) 1677.
[10] J. F. Ward and L. S. Myers, *Radiation Res.* 26 (1965) 483.
[11] A. F. Trotman-Dickenson, in 'Advances in free-radical chemistry', Vol. I (edited by G. H. Williams), Logos Press, London (1965) ch. 1, p. 11.
[12] E. S. Huyser, *ibid*, ch. 3, p. 92.
[13] G. G. Jayson, B. J. Parsons and A. J. Swallow, *J.C.S. Faraday I* 69 (1973) 1597.