June, 1985] *Bull. Chem. Soc. Jpn.*, *58*, *1717—1722 (1985)*

Anodic Oxidation of Cyclohexanone on Lead Dioxide Electrode in Aqueous Sulfuric Acid Solution

Atsutaka KUNAI,* Kazuhito HATOH, Yoshinobu HIRANO, Junji HARADA, and Kazuo SASAKI
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Shitami, Saijo-cho, Higashi-Hiroshima 724
(Received December 3, 1984)

The electrolytic behavior of cyclohexanone was examined by potentiometry with rotating disk electrode as well as by product analyses. The reaction was activation controlled and the reaction orders were first with respect to cyclohexanone and zero for proton. Cyclohexanone reacted by approximately 6 electrons to give adipic acid mainly which accumulated proportionally to the electricity consumed. Changes in temperature, proton concentration, and current density resulted in only minor effects on the reaction. In neutral solution, however, the oxidation was suppressed and oxygen evolution dominated. Other electrode materials such as Pt, graphite, RuO_2, and PtO_2 were inactive. The chemical oxidation with PbO_2 itself did not occur. From these facts, reaction mechanism was discussed.

It is well known that lead dioxide electrode is effective to the anodic oxidation of certain organic compounds. Especially, the oxidation of aromatic compounds, such as benzene, toluene, or phenol, with lead dioxide electrode leads to the formation of *p*-benzoquinone in good yields, and therefore, this reaction has been investigated by many workers from the industrial and mechanistic points of view.[1—13] The reason is, however, still left uncertain why PbO_2 electrode is actually effective to the oxidation of aromatic compounds.

This electrode is known to be active also to the oxidation of a certain alicyclic ketone such as cyclohexanone, but the formation of different products has been reported by Yokoyama,[14] Pyrrone,[15] and Sugawara and Sato.[16] At present time, no quantitative information is shown yet about the electrochemical behavior of PbO_2 electrode toward aliphatic ketones, in views of the special reactivity of this electrode, the product selectivity, or the reaction mechanism.

In this study, we should like to discuss in detail the basic behavior of PbO_2 in the presence of aliphatic ketones. For this purpose, cyclohexanone was chosen as the representative of the ketones and its oxidation behavior was compared with that of benzene. The main object was placed on studying the effectiveness of this particular electrode and evaluating the active species on PbO_2 as well as clarifying product selectivity.

Experimental

Cyclohexanone was reagent grade which was distilled and checked by GLC before use. All the other chemicals were analytical grade and were used as purchased.

All the electrochemical measurements were made using a Nichia Keiki NPG 1070E potentiostat. For preparative electrolysis, a Kikusui Denki PAD 110-1.5L regulated DC power supply was used. Proton concentration of the solutions was determined by a Toa Dempa MH-7B pH meter. All the potential values cited in this paper were those referred to Hg/Hg_2SO_4 electrode in 0.5 M[†] sulfuric acid. The reaction products were analyzed by Hitachi 665 high pressure liquid and 163 gas chromatographs.

The rotating disk electrode was prepared by filling a Pb rod of 5 mm in diameter into the center of a teflon holder, and the surface of the electrode was shaved planarly with a lathe and polished with cellulose fiber paper. The PbO_2 film was coated on the cleaned Pb surface by first stepping the electrode potential to 1.70 V for 25 min and to 1.10 V for another 20 min. The PbO_2 film was freshly prepared before each series of the experiments and the current values were determined after ten min of polarization.

For macro-scale electrolysis, a Pb plate of 5×6 cm in size was used as the anode which was pretreated before use in a similar manner as described above. An anolyte of 150 cm^3 in volume containing 0.34 M cyclohexanone was polarized under controlled current conditions in a divided cell. A small quantity of the sample was taken up in each interval and analyzed by HPLC using Merck Lichrosorb RP-18 (particle size 10 μm, 4×125 mm) as the column and a mixed solvent of acetonitrile (20%) and phosphate buffer solution of pH 3.5 (80%) as the eluent. The amounts were determined at 220 nm for adipic acid and at 280 nm for both cyclohexanone and 2-cyclohexenone.

For analysis of lactones, the electrolyzed solution was continuously extracted with ether and the concentrated extract was subjected to GLC analysis using PEG 20 M and KG 2 as columns and diethyl phthalate as the internal standard material. In some experiments, carboxylic acids were analyzed after the treatment with methanolic BF_3 solution. The products, 5-hexanolide, 4-hexanolide, and methyl esters of adipic, 5-oxohexanoic, glutaric, and succinic acids were isolated by preparative GLC and their spectrometric properties were compared with those of authentic samples.

Electrolyses were made also using other electrode materials, platinum, graphite, PtO_2, and RuO_2. The latter two electrodes were prepared by thermally depositing the metal oxide layer on Ti plates in the usual way.[17,18]

Results and Discussion

1. Current-potential Curves. Typical polarization curves obtained with the rotating disk electrode at 1500 rpm[††] are shown in Fig. 1. In 0.5 M sulfuric acid solution, an apparent Tafel slope of 125 mV was observed and the current was independent of rotating velocity. On addition of cyclohexanone, the anodic current increased in the wide range of the potential

---

[†] M=mol dm^{-3}.

[††] rpm=120 π rad s^{-1}.

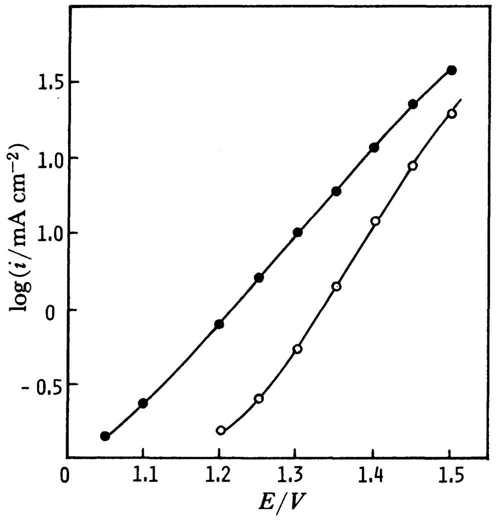

Fig. 1. Polarization curve for rotating PbO_2 electrode in 0.5 M H_2SO_4 (ω=1500 rpm), (○) in the absence and (●) in the presence of cyclohexanone (100 mM).

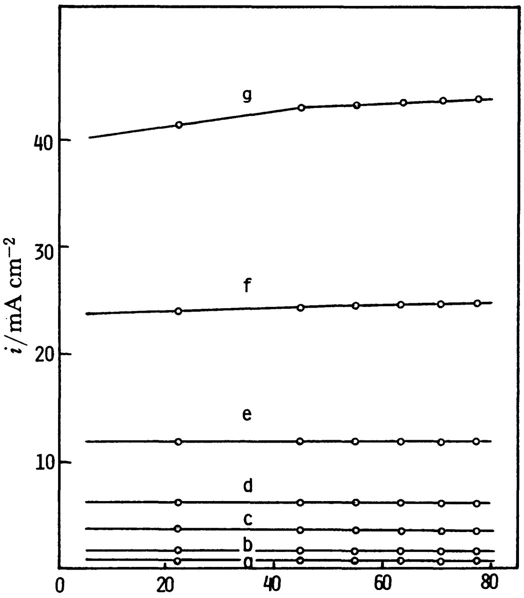

Fig. 2. Variation of total oxidation current as a function of $\omega^{1/2}$ at potentials of (a) 1.20, (b) 1.25, (c) 1.30, (d) 1.35, (e) 1.40, (f) 1.45, and (g) 1.50 V.

studied, and the Tafel region was observed in the potential range between 1.15 and 1.40 V.

The effect of rotating velocity on the current in the cyclohexanone solution is shown in Fig. 2. At the potential lower than 1.4 V, the anodic current was completely independent of rotating velocity. Although a slight influence of diffusion controlled process was observed at higher potential than 1.45 V, the oxidation of cyclohexanone on this electrode seemed to be essentially reaction controlled.

Figure 3 shows the effect of the concentration of cyclohexanone on the current at a rate of 1500 rpm. The plot of the currents against the concentrations within 200 mM exhibited a good linearity at each potential applied, 1.1, 1.2, 1.3, and 1.4 V, respectively. The extrapolated intercept of each line coincided with the value of the back ground current of the base solution. This indicates that there is no appreciable change in residual current even in the presence of high concentration of cyclohexanone. This is a marked difference from the case of benzene solution reported by Clarke *et al.*,[9] where oxygen evolution was substantially suppressed.

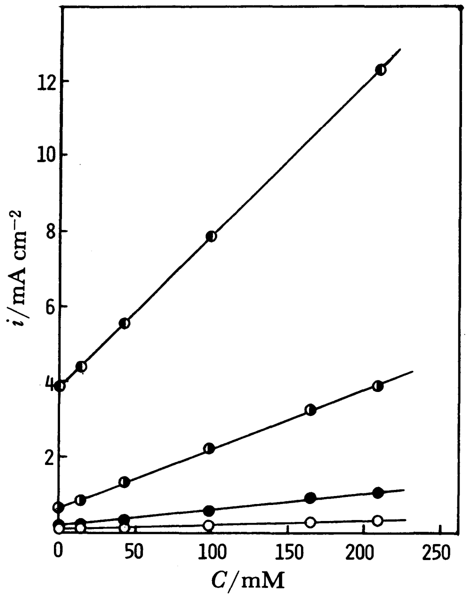

Fig. 3. Variation of total oxidation current as a function of cyclohexanone concentration, at potentials of (○) 1.10, (●) 1.20, (◑) 1.30, and (◐) 1.40 V (ω= 1500 rpm).

2. Reaction Order. The mass transport study (Fig. 2) and product analysis (section 3) clearly demonstrate that both diffusion and electrode potential little affect the reaction. The main reaction is the formation of adipic acid:

$$C_6H_{10}O + 3H_2O \longrightarrow C_6H_{10}O_4 + 6H^+ + 6e.$$

In general, activation controlled process can be expressed by the form of Eq. 1 for the anodic reaction:

$$i = nFk[C]^p\,[H^+]^q \exp(\alpha nFE/RT), \qquad (1)$$

where [C] is the concentration of cyclohexanone, E the electrode potential applied, and i the current. In this case, the current i should be the net oxidation current i_{net}, which is the difference between observed and residual currents. The reaction orders p with respect to cyclohexanone and q for proton should be, therefore, conveniently obtained from Eq. 2.

$$\log i_{net} = p\log[C] + q\log[H^+] + (\alpha nF/RT)E + \text{constant}. \qquad (2)$$

For the determination of p, i_{net} at 1500 rpm was plotted against log[C] in 0.5 M sulfuric acid solutions, where the concentration of proton was assumed to be constant (Fig. 4). The slopes of the log i_{net} *vs.* log[C] satis-

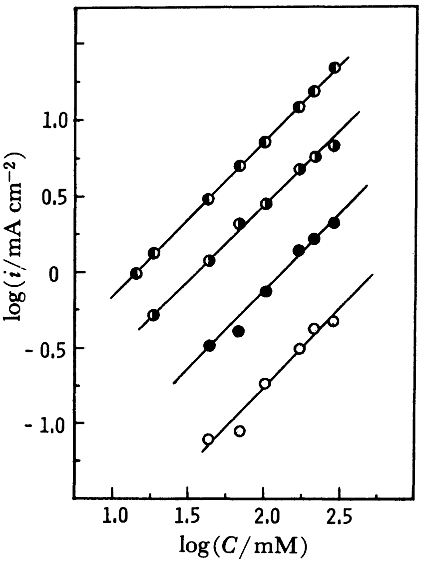

Fig. 4. Logarithmic plots of net oxidation current *vs.* cyclohexanone concentration obtained at potentials of (○) 1.10, (●) 1.20, (◑) 1.30, and (◐) 1.40 V (ω=1500 rpm).

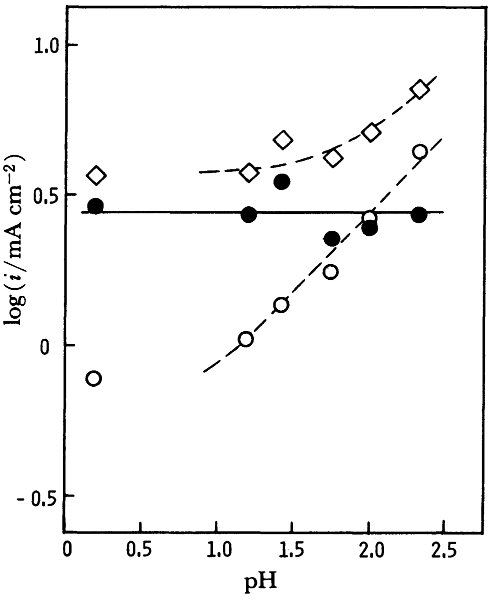

Fig. 5. Plot of oxidation currents *vs.* pH obtained in sulfate solutions (1.30 V, ω=1500 rpm).
Symbols stand for (○) residual current in base solution, (◇) total current of cyclohexanone solution (200 mM), and (●) net oxidation current.

fied good linearities and were exactly 1.0 at each potential applied, 1.1, 1.2, 1.3, and 1.4 V, respectively. This means that the oxidation of cyclohexanone is first order with respect to cyclohexanone.

For evaluating the participation of proton to the anodic process, we prepared a series of sulfate solutions within the pH range of 1 to 2.5, where the total concentration of the sulfate was adjusted to be 0.5 M.

We examined the relation of pH and logarithmic current of i_{net} under constant potential conditions, 1.3 V, where the concentration of cyclohexanone and the potential were kept unchanged. As shown in Fig. 5, the net oxidation current was unaffected by pH and the reaction order for proton was concluded to be zero.

3. Product Analysis. As a typical run, a solution of 0.34 M cyclohexanone in 0.5 M sulfuric acid was electrolyzed on PbO_2 anode under the constant current conditions (2 A dm^{-2}, 10 °C).

Product Isolation: The electrolyzed solution was extracted with ether. The concentrated extract was distilled *in vacuo*. The initial fraction consisted of mostly cyclohexanone recovered and the second fraction contained two products, 5-hexanolide (δ-lactone) and 4-hexanolide (γ-lactone), which were isolated by preparative GLC.

The nonvolatile residue showed strong IR absorption bands of carboxyl groups. Isolation of carboxylic acids was first tried by preparative LC (reverse phase), but complete identification was failed because of poor separation. The acids were, therefore, isolated as their methyl esters after the treatment with methanolic BF_3 solution. By preparative GLC, the esters of adipic, 5-oxohexanoic, glutaric, and succinic acids were isolated.

GLC Analysis: After passing 1.2 F mol^{-1} of the electricity,††† products were extracted with ether and analyzed by GLC. Taking an average over nine individual experiments, we estimated that the conversion rate of cyclohexanone was 155 mmol F^{-1} where approximately 6.5 electrons were necessary for a molecule that disappeared (Table 1). The chemical selectivity of δ- and γ-lactones were 25 and 4%, respectively. Traces of 2-cyclohexenone were detected.

In another run, the extract was esterified and analyzed by GLC (Table 2). The main product, adipic acid, was detected only in 7—8% of selectivity by this method because of, presumably, poor extraction efficiency of the dicarboxylic acids.

HPLC Analysis: The changes in concentration of cyclohexanone and carboxylic acids were monitored by reverse phase HPLC in the time course of the electrolysis. Cyclohexanone disappeared linearly at a rate of 150 mmol F^{-1} and, instead, a distinctive peak corresponding to adipic acid increased. The accumulation of this material was proportional to the quantities of electricity consumed. Supposing that this peak consisted of solely adipic acid, we obtained the accumulation rate to be 80.8 mmol F^{-1}. If this is the case, the chemical selectivity and the current efficiency for adipic acid reach to 54 and 49%, respectively. Other acids identified before seemed to be rather minor by HPLC analysis. The linear accumulation of adipic acid clearly shows that adipic acid is not formed by reoxidation of some solution phase products, such as lactones, but formed directly from cyclohexanone on the electrode.

These results were little affected by temperature, concentration of sulfuric acid, or current density which

---

††† F=96480 C.

Table 1. GLC analysis of lactones

Electricity	Cyclohexanone reacted		δ-Lactone		γ-Lactone		Total	
consumed	Amount	Conv.	Amount	Select.	Amount	Select.	Amount	Select.
F mol^{-1}	mmol F,$^{-1}$	%	mmol F,$^{-1}$	%	mmol F,$^{-1}$	%	mmol F,$^{-1}$	%
1.20	155	19	33.1	21	6.4	4	39.5	25

Solutions of 0.34 M cyclohexanone in 0.5 M sulfuric acid (100, 120, or 150 cm^3) were electrolyzed on the pretreated PbO_2 electrode. Average values over nine individual runs are shown in the Table.

Table 2. GLC analysis of carboxylic acids after esterification

Methyl ester[a]	Method A		Method B	
of acid	Amount/mmol F,$^{-1}$	Select./%	Amount/mmol F,$^{-1}$	Select./%
Adipic	10.3	6.9	11.3	7.6
Glutaric	6.6	4.4	6.1	4.1
Succinic	2.9	2.0	2.3	1.5
5-Oxohexanoic	9.2	6.2	7.6	4.9
Total	29.0	19.5	27.3	18.1

Solutions of 0.34 M cyclohexanone in aqueous sulfuric acid (150 cm^3) were electrolyzed until 1.5 F mol^{-1} of the electricity was consumed under the conditions of 10 °C in temp., 2.0 A dm^{-2} in current density, and 0.5 M in H_2SO_4 concentration.

a) Method A: Treated with methanolic BF_3 solution; Method B: Heated in methanol in the presence of H_2SO_4.

Table 3. Effects of electrolytic conditions on the formation of adipic acid

Run	Changes in conditions	Cyclohexanone reacted			Adipic acid		
		Amount	Conv.	n	Amount	Select.	Current efficiency
		mmol,	%,		mmol,	%,	%
1	Unchanged[a]	11.5	23	6.7	6.18	54	49
2	Temp 0 °C	12.0	24	6.4	6.24	52	49
3	Temp 20 °C	14.8	29	5.2	6.36	43	50
4	Acid 3 M	13.8	27	5.5	8.42	61	66
5	Acid 6 M	14.6	29	5.2	7.29	50	57
6	C.D. 1 A dm^{-2}	14.4	28	5.3	7.96	55	62
7	C.D. 4 A dm^{-2}	12.3	24	6.2	6.01	49	47
8	MeCN 2 v/v%	11.0	22	7.0	6.92	63	54
9	MeCN 50 v/v%	10.3	20	7.4	7.38	72	58

a) The standard conditions were the same as those described in Table 2.

Table 4. Effect of pH on the oxidation of cyclohexanone

Base solution	pH	Cyclohexanone	Adipic acid	δ-Lactone	γ-Lactone	Cyclohexenone
	(final)	reacted/mmol	mmol	mmol	mmol	mmol
0.5 M H_2SO_4	0.3	11.5	6.18	1.71	0.45	0.18
0.5 M NaH_2PO_4[a]	1.6	5.75	1.33	0.74	0.37	0.07
1.0 M NaH_2PO_4[a]	2.2	4.87	0.63	0.65	0.21	0.04
1.0 M NaH_2PO_4 −1.0 M K_2HPO_4[a]	5.3	1.45	Trace	Trace	Trace	Trace

Electrolytic conditions were the same as those described in Table 2.

a) The solution contains 0.1 M Na_2SO_4.

were changed in the range of 0—20 °C, 0.5—6.0 M, or 0.5—4.0 A dm^{-2}, respectively (Table 3).

Effect of pH: When the electrolyses were done in phosphate buffer solutions containing 0.1 M sodium sulfate, the oxidation of cyclohexanone also occurred. Its reactivity, however, markedly decreased with the increase of pH (Table 4). At higher pH's, the chemical selectivity and the current efficiency of adipic acid were considerably suppressed, but the chemical selectivity of lactones did not much changed.

Comparison of Electrode Materials: In order to evaluate the effectiveness of PbO_2 as the electrode material for the oxidation of cyclohexanone, we studied the behaviors of other electrode materials. The polarization curves obtained with the stationary Pt and graphite electrodes were compared in the absence and presence of cyclohexanone. On addition of cyclohexanone, the total currents were rather suppressed over the potential range measured.

The macro-scale electrolyses with these electrodes

TABLE 5. COMPARISON OF ELECTRODE MATERIALS

Electrode	Cyclohexanone reacted/mmol F^{-1}	Adipic acid mmol F^{-1}	δ-Lactone mmol F^{-1}	γ-Lactone mmol F^{-1}	Cyclohexenone mmol F^{-1}
PbO_2	150	81	22	5.9	2.4
Bare Pt	17.3	—	Trace	Trace	0.4
Graphite	40	8.9	Trace	Trace	1.2
PtO_2/Ti	10.7	—	—	—	0.4
RuO_2/Ti	17.4	—	—	—	—

Electrolytic conditions were the same as those described in Table 2.

were carried out under similar conditions as described before. The reactivity of cyclohexanone was, as expected by the polarization curves, extremely small and substantial oxygen evolution occurred. We also tried to use PtO_2 and RuO_2 electrodes, but cyclohexanone was not oxidized on these electrodes (Table 5).

4. Reaction Mechanism. First, we briefly summarize the results for the oxidation of cyclohexanone on PbO_2 electrode. As discussed in *product analysis* study, PbO_2 shows particularly high oxidation ability toward cyclohexanone, but other electrode materials, such as Pt, graphite, RuO_2, and PtO_2, are almost inactive. At lower pH's, cyclohexanone consumes *ca.* 6 electrons on PbO_2 to afford adipic acid with 50—65% of the current efficiencies. Other products, such as lower carboxylic acids and lactones, are minor. Such results are almost unchanged with the increase of the acid concentrations. Furthermore, adipic acid is formed as the primary electrode product on PbO_2 surface, where ε-lactone is not the intermediate. All of these facts have not been clarified in earlier reports.[14—16]

By examination of *current-potential curves*, it is also confirmed that the velocity of the reaction is affected only by the cyclohexanone concentrations obeying first order law, but not by mass transport and proton concentrations.

The effect of pH on the reaction seems, however, drastic at higher pH's. In neutral solutions, only the oxygen evolution occurs. These phenomena are undoubtedly due to the properties of PbO_2 itself and independent of organic substrates, because similar observations have been reported in the cases of benzene[9] and thiophen.[21] This means that the reaction is governed only by the active state of PbO_2, *i.e.* β-PbO_2 in acidic media, [19] but not by acid-catalyzed enol formation. We now consider the relation of the reaction and β-PbO_2 in detail.

Many reports have been published for β-PbO_2 in views of preparation, structure, and chemical properties. Beta-lead dioxide is formed in acidic media by either oxidation of Pb(II) ion or, more conveniently, anodization of Pb itself. This material is thermodynamically an unstable form of Pb(IV) and therefore highly active, which oxidizes even water slowly to leave Pb(II) and oxygen.[19,20]

Here it should be worth noting the work reported by Clarke *et al.*[9] who discussed the oxidation of benzene on PbO_2 electrode in detail. They excluded the possibilities of the direct electron transfer to the electrode[8] and the hydroxylation reaction with adsorbed atomic oxygen[2,3] because of, mainly, highly selective formation of *p*-benzoquinone at low electrode potentials as well as completely unsimilar reactivity of other electrode materials such as Pt and graphite. Instead, they proposed the homogeneous phase reaction between benzene and PbO_2 followed by the electrochemical regeneration of PbO_2, where the former step was rate determining and the concentration of PbO_2 was a potential dependent term. The evidence for this mechanism was the fact that *p*-benzoquinone and maleic acid were formed chemically by shaking the benzene emulsion in the presence of PbO_2 powder for 24 h.

Their assumption should be understood in the following aspects. Namely, PbO_2 is practically insoluble in moderately acidic solutions such as 0.5 M sulfuric acid. The solubility is reported as $\log[Pb^{4+}]=-8.26 -4pH$, if free from complexing agents.[20] Such a situation seems unfavorable to the homogeneous reaction proposed. Suppose that the homogeneous reaction with PbO_2 occurs, probably as a form of Pb^{4+} in the bulk solution, it might be expected that the subsequently formed low valent Pb, *i.e.*, hardly soluble $PbSO_4$, deposits into the solution in the course of the electrolysis. Such phenomena were, however, not found in our cases, the oxidation of cyclohexanone.

Another thinkable possibility is that the oxidation with Pb(IV) occurs only in the limited region of diffusion double layer and the low valent Pb does not diffuse away into the bulk solution. If this is the case, the surface of the electrode will be covered finally with the low valent Pb salt resulting in the marked decrease in the electrode potential unless the electrode is externally anodized.

Taking these mechanisms into consideration, we carried out additional experiments. A very thin layer of β-PbO_2 was electro-deposited on Pt surface (0.34 μmol cm^{-2}) and the chemical durability of this electrode was examined by measuring the change in the open circuit potentials both in the presence and absence of cyclohexanone. In typical runs, the potential of this electrode, *ca.* 900 mV, was unchanged in the base solution for 60 min and then felt down rapidly. When some depolarizing materials such as formaldehyde or phenol were present in the solution, the duration time of this electrode was definitely shortened. On addition of cyclohexanone, however, the duration time was not changed at all. These facts may indicate that the chemical oxidation in the above manner is, even if occurs, extremely slow compared to the oxidation of the solvent water itself, in the case of cyclohexanone.

From all of the experimental results, one should deduce a clear conclusion that cyclohexanone is oxidized directly on the electrode but not oxidized chemically in the manner of the mediation with the lead(IV)/lead(II) couple. The simplest explanation is, of course, the occurrence of the direct electron transfer to the electrode inducing the subsequent chemical and electrochemical reactions, in which the rate determining step is activation controlled. As a result, adipic acid is formed directly on the electrode surface. This mechanism seems to satisfy most experimental results except for the particular effectiveness of PbO_2 compared to other electrode materials.

Alternative explanation is the participation of a particular surface species formed on the PbO_2 electrode. Lead dioxide has a large oxygen overvoltage, which may cause the accumulation of precursors of O_2 evolution in high concentration. The probable candidate for the reactive species is adsorbed hydroxyl radical.[10,21] Hydroxyl radical is highly reactive and electrophilic species. For example, it adds to benzene (k=3.5×10^9 $M^{-1}s^{-1}$) to give hydroxycyclohexadienyl radical or abstracts α-hydrogen from acetone (k=6×10^7 $M^{-1}s^{-1}$).[22] If this is applicable to our case, the abstraction of hydrogen from cyclohexanone should be rate determining step. Once organic radicals are formed on the electrode surface, they are trapped immediately with another oxygen species and/or oxidized electrodically to give other organic species in turn, leading to the final formation of stable products, such as adipic acid.

In summary, we should point out again at the present time that the anodic oxidation of cyclohexanone on PbO_2 may be accounted for by direct electron-transfer mechanism or, alternatively, by the reaction of hydroxyl radical formed on the electrode surface.

References

1) A. Renard, *Compt. Rend.*, **91**, 175 (1880).

2) F. Fichter and R. Stocker, *Ber.*, **47**, 2012 (1914).

3) G. Miodon and A. Seyewitz, *Bull. Soc. Chim. Fr.*, *Ser. 4*, **33**, 449 (1923).

4) H. Inoue and M. Shikata, *Kogyo Kagaku Zasshi*, **24**, 567 (1921).

5) Y. Isomura, *Nippon Kagaku Kaishi*, **62**, 1167 (1941).

6) K. S. Udupa, G. S. Subramanian, and H. V. K. Udupa, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **9**, 45 (1961).

7) S. Itoh, K. Sasaki, Y. Murakami, and H. Shiba, *Denki Kagaku*, **40**, 733 (1972).

8) M. Fremery, H. Höver, and G. Schwarzlose, *Chem.-Ing.-Tech.*, **46**, 635 (1974).

9) J. S. Clarke, R. E. Ehigamusoe, and A. T. Kuhn, *J. Electroanal. Chem.*, **70**, 333 (1976).

10) J. G. Sunderland, *Electr. Counc. Res. Cent.*, [Memo], ECRC/M 1065 (1977); *Chem. Abstr.*, **87**, 124470u (1977).

11) G. C. Jones and D. A. Payne, U. S. Patent 3994788; *Chem. Abstr.*, **86**, 35759g (1977).

12) G. C. Jones and H. R. Meer, U. S. Patent 4035253; *Chem. Abstr.*, **87**, 75732v (1977).

13) C. Oleman, *AIChE Symp. Ser.*, **77**, [204] 264 (1981).

14) M. Yokoyama, *Bull. Chem. Soc. Jpn.*, **8**, 71 (1933).

15) F. Pirrone, *Gazz. Chim. Ital.*, **66**, 244 (1936).

16) M. Sugawara and M. Sato, *Denki Kagaku*, **43**, 407 (1975).

17) C. Iwakura, K. Fukuda, and H, Tamura, *Electrochim. Acta*, **21**, 501 (1976).

18) C. Iwakura, F. Goto, and H. Tamura, *Denki Kagaku*, **48**, 20 (1980).

19) P. Delahey, M. Pourbaix, and P. V. Rysselberghe, *J. Electrochem. Soc.*, **98**, 57 (1951).

20) M. Pourvaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, Oxford (1966), p. 485.

21) I. Izumi and I. Yamamoto, *Denki Kagaku*, **51**, 333 (1983).

22) K. U. Ingold, "Free Radicals," ed by J. K. Kochi, Weiley-Interscience, New York (1973), p. 37.