Preliminary examination of an electrochemical process for converting olefins to ketones

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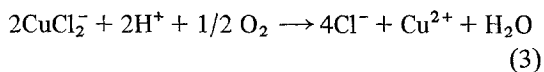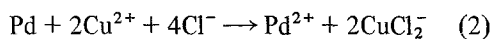
Olefins higher than 3-C were converted to ketones using aqueous chloropalladate ion as oxidant. The chloride ion content of the solution was kept at very low levels relative to normal usage to increase significantly the reaction rates of these higher olefins. The reduced palladium was reoxidized electrochemically using the ferric/ferrous couple as the transfer agent. Using cyclopentene as a model compound the ionic strength, the acidity, the concentration of palladium, the means of extracting product and the means of adding olefin were all adjusted as to achieve about 70% current selectivity with minimal palladium inventory. There were indications of even better behaviour with several open chain ketones.

1. Introduction

This paper discusses a means of converting olefins higher in molecular weight than ethylene into the corresponding ketones via an electrochemical version of the Wacker process. In the latter process [1–3], the olefin, ethylene or sometimes propylene, is bubbled through an aqueous solution of palladium chloride where it is converted to the corresponding carbonyl compound, acetaldehyde or acetone in these cases. With no oxidant present, palladium metal would eventually precipitate out.

$$Pd^{2+} + C_2H_4 + H_2O \longrightarrow Pd + CH_3CHO + 2H^+$$
$$(1)$$
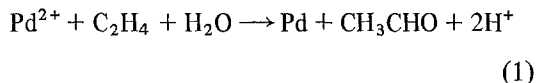
However, cupric chloride and hydrochloric acid are also present in the solution to reoxidize the reduced palladium and form the dichlorocuprate (I) anion. An excess of hydrochloric acid is required to render the cuprous complex thermodynamically stable. In the absence of excess chloride, cuprous ion would dismutate to copper metal and cupric ion. Finally, the cupric ion is regenerated by blowing air or oxygen through the mixture so that

$$Pd + 2Cu^{2+} + 4Cl^- \longrightarrow Pd^{2+} + 2CuCl_2^- \quad (2)$$
$$2CuCl_2^- + 2H^+ + 1/2 O_2 \longrightarrow 4Cl^- + Cu^{2+} + H_2O$$
$$(3)$$

The net result is that olefin plus oxygen yield carbonyl, and all other reagents are recycled.

Kinetic and mechanistic work on the process [4–7] reveals that the chemical Wacker process runs despite the fact that the chloride required to stabilize the cuprous ion is a strong inhibitor for the reaction. There are at least two steps in the mechanism where it has been postulated that chloride ion inhibits. One is in the formation of a palladium olefin complex ion:

$$(4)$$
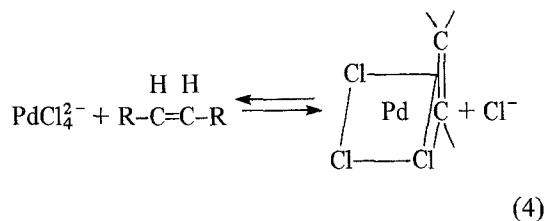
Actually, this soluble ion is postulated by analogy with the platinum analogue, Zeise's salt, $KPtCl_3C_2H_4$. The solid palladium compounds that have actually been isolated are neutral dimers of the apparent structure given below [8].
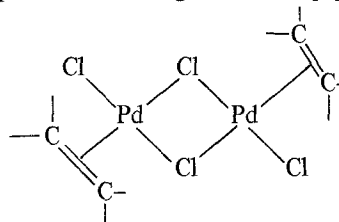
Kinetic and isotopic data suggest that after the complex forms, the next step involves reaction with water to produce an aqua complex which ionizes to a hydroxy complex releasing more chloride and hydrogen ions:

$$[PdCl_3 \text{ olefin}]^- + H_2O \rightleftharpoons [PdCl_2OH \text{ olefin}]^-$$
$$+ H^+ + Cl^- \qquad (5)$$
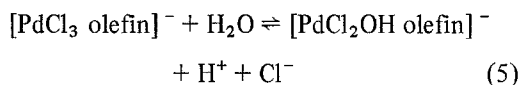
In the absence of excess chloride, the same complex may be arrived at by the reaction of an aqua complex of $PdCl_2OH(H_2O)^-$ with an olefin molecule.

At this point, a relatively slow rearrangement of the complex occurs whose details are in doubt. A good discussion of the mechanism is given by Aguilo [9]. There may be a shift of the OH group from a *trans*- to a *cis*-position relative to the olefin. Then, the complexed olefin is apparently attacked at one end of the double bond by the neighbouring OH group causing the organic ligand to shift from π-bonding to σ-bonding to the palladium. A hydride is shifted from the attacked carbon to its neighbour, and a molecule of the carbonyl compound splits off the complex. The palladium is left in a reduced form, possibly as a hydride (postulated by Halpern [10]) which soon decomposes to the metal:
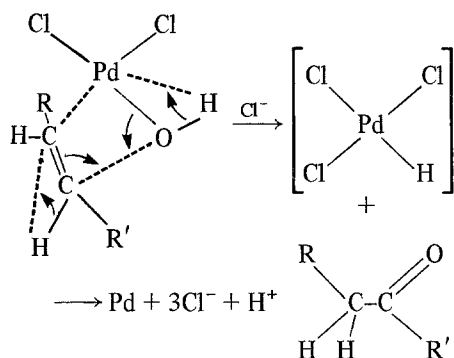
The most certain step in the above scheme is the shift of the hydrogen. Radiotracer studies have confirmed that the hydrogens on the carbon α to the carbonyl come from the olefin and not from the solvent. The hydride shift is not involved in the rate determining step, however, based on the lack of a kinetic isotope effect with C_2D_4. The reaction shows 'carbonium ion character' in that the Markonikov product is obtained. That is, ketones are formed from α-olefins in great

preference to aldehydes. It is possible that the Pd–C σ-bond is partially ionic, leaving a slightly positively charged carbon. The effect of hydrocarbon structure on reaction rate is small, so that a free carbonium ion is probably not involved in the rate determing step.

In any case, the important mechanistic point for the purposes of this work is that the reaction is sharply inhibited by chloride ion. The original workers [4] give an empirical rate expression for the ethylene reaction as:

$$\text{Rate} = \frac{a\,[H^+]\,[Cl^-]}{b + [H^+]^2\,[Cl^-]^3} \qquad (7)$$

where the bracketed terms appear to signify the total solution contents. This expression shows the initial rise of rate at low chloride contents and the subsequent decline in rate with the square of the chloride content at higher concentrations. A similar relationship was shown for *n*-butene in 1972 [11].

Another rate study by Henry [5] gives:

$$-\frac{d[C_2H_4]}{dt} = \frac{k\,K_1\,[PdCl_4^{2-}]\,[C_2H_4]}{[Cl^-]^2\,[H^+]} \qquad (8)$$

where $K_1 = [PdCl_3C_2H_4^-]\,[Cl^-]/([PdCl_4^{2-}]\,[C_2H_4])$ an equilibrium constant.

The bracketed terms indicate the concentrations of the actual species. This expression is not suitable for systems containing less than 3–4 moles of total chloride per palladium, but again shows the sharp inhibiting effect of chloride at higher concentrations.

Nevertheless, the Wacker process runs at ratios of chloride to palladium of 200 to 400, in order to stabilize the cuprous ion regenerant. Apparently, ethylene is so reactive that it can withstand this impediment; however, reactivity drops with olefin size as given by the data of Henry at 25° C (Table 1). This is one of the
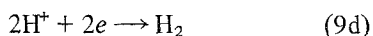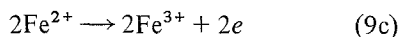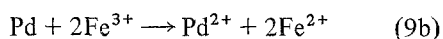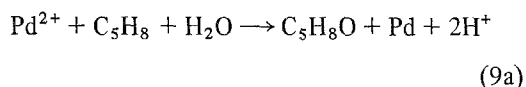
Table 1. Literature data: palladium–olefin reaction rates

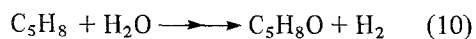| Olefin	Product $k\,K_1$ ($\times 10^5$)
Ethylene	353
Propylene	94
cis-2-Butene	30
trans-2-Butene	34

reasons that this process has not been applied to the oxidation of higher olefins to the corresponding ketones.

A second inherent drawback associated with the use of air oxidation in acidic copper halide solutions is the formation of chlorinated by-products. Except for its palladium content the solution used for air regeneration in the Wacker process has the same ingredients as those used in the Kellogg olefin–oxyhydrochlorination process [12]. The by-products are apparently troublesome to remove, as indicated by the issue of various patents concerned with their separation [13].

In this paper, we consider an electrochemical process that permits the reaction to be run in the absence of excess chloride and oxygen. The reduced palladium, in whatever form it exists before it precipitates (shown above as $PdCl_3H^{2-}$), is reacted with an oxidant not requiring chloride for stability, such as ferric ion. The resulting ferrous ion is reoxidized electrochemically at an anode inserted in the aqueous phase. At the cathode conditions are arranged so that hydrogen is liberated. The complete scheme is:

$$Pd^{2+} + C_5H_8 + H_2O \longrightarrow C_5H_8O + Pd + 2H^+$$

$$(9a)$$

$$Pd + 2Fe^{3+} \longrightarrow Pd^{2+} + 2Fe^{2+} \qquad (9b)$$

$$2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e \qquad (9c)$$

$$2H^+ + 2e \longrightarrow H_2 \qquad (9d)$$

The overall reaction is:

$$C_5H_8 + H_2O \longrightarrow C_5H_8O + H_2 \qquad (10)$$

All other reagents recycle. This idea was actually suggested in 1967 by researchers at Hoechst [14]. The patent was apparently never implemented commercially, perhaps because it advocated total elimination of chloride ion, and might, therefore, have been inoperable.

The aim of this experimental programme was to determine whether such a scheme was feasible: whether the product could be isolated in high yield, whether the palladium inventory could be kept economically low and whether the palladium could be successfully recycled, and so on. The olefin chosen for the model study was cyclopentene, though others were subsequently examined.

2. Experimental details

The investigation was carried out in a simple glass apparatus, which was gradually modified and enlarged with other glass ancillaries as the variables were analysed and the process took shape. The basic cells consisted of a jacketed anode compartment connected via a glass frit to a side arm containing the cathode. The cathode was a platinum wire used for hydrogen evolution. The anode compartments were of 250 or 500 cm^3 capacity. A 5 cm × 5 cm gold-plated tantalum screen served as the anode for most of the experiments, although a 5 cm^2 platinum screen was used in preliminary runs. The cell was also equipped with a gold wire probe and a reference electrode containing a gold wire, immersed in an equimolar mixture of ferrous and ferric perchlorates in 0.3 M perchloric acid. This was used to monitor the potential of the ferrous–ferric couple during measurements of the rate of reaction or during regenerations.

Operating temperatures ranged from 35 to 85° C. The olefin was either introduced as a gas from an auxiliary boiler or used as liquid floating on top of the aqueous layer.

The electrolyte used was 0.3 N perchloric acid containing varying concentrations of ferric and ferrous perchlorate. The latter were either purchased or prepared by dissolving high purity iron in more concentrated perchloric acid to form the ferrous salt and treating with dilute hydrogen peroxide to form the ferric salt. It was subsequently found that during this iron dissolution step some reduction of perchlorate to chloride occurred to the extent of 0.05–0.15 moles of Cl^- per mole of Fe^{2+}. Since the concentration of iron ions in solution eventually preferred was 0.2 M, an added chloride ion concentration of approximately 0.02 M was always present. Fortunately, this concentration kept the reaction rates close to the maximum value.

In later experiments, the glass apparatus was expanded to permit solvent extraction of the cyclopentanone product. Solvents were employed in a unit comprising a boiler, which sent the extractant vapours through a fractionating column to a condenser, from which the liquid was allowed to flow down to a dip leg to the bottom of the electrolyte chamber. Solvent collected atop the
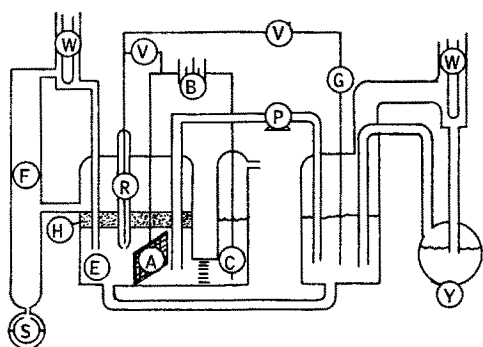
Fig. 1. Glass pilot unit for electrolytic cyclopentanone production. A – anode; B – power supply; C – cathode; E – electrolyte; F – fractionating column; G – gold wire probe; H – hydrocarbon layer; P – circulating pump; R – reference electrode; S – extractant boiler; V – voltmeter; W – water cooled condenser; Y – cyclopentene boiler.

electrolyte and overflowed through a side arm to the middle of the fractionating column, and was recycled.

The total 'pilot unit' now contained two main vessels, a reactor and a regenerator/extractor, as shown in Fig. 1. The continuous extractor described above is shown on the left in the figure, using 2-methylpentane as the extractant. The extractant passed through the left hand vessel containing electrolyte (HClO$_4$, Fe^{2+} and Fe^{3+} perchlorates and PdCl$_2$). The electrochemical regeneration of ferric ion was also carried out in this vessel by means of a gold-plated tantalum screen anode and a platinum wire cathode in a chamber isolated by a coarse glass frit. Gaseous cyclopentane was fed from a second boiler with a liquid return line, into the reactor vessel. Electrolyte was circulated between the two vessels by means of a Teflon pump and return line of glass

with polypropylene fittings. Power was supplied by a d.c. galvanostat. The voltages in both cells were read vs a 1/1 ferric/ferrous electrode. The circulation rate was maintained rapid enough so that the difference in voltage between the two reactors corresponded to a difference in ferric ion concentration of no more than 2% of the total iron concentration.

Approximately 40 runs were made from which the data shown in the following section was taken.

During measurement of the rates of the reaction of the olefin with palladous ion, no electrochemical regeneration was carried out; the effect of the reaction was simply to reduce the ferric ion to the ferrous ion. The fraction of the total iron present as ferric, f, at any time was calculated from the voltage, E, between the gold wire and the reference electrode using a modifed form of the Nernst equation,

$$f = \frac{1}{1 + 10^{-E/K}} \qquad (11)$$

where the constant, K, was determined empirically using solutions containing known Fe$^{(III)}$/Fe$^{(II)}$ ratios at various temperatures.

A good example of a rate plot thus determined is given in Fig. 2. From the slope of the plot and the total iron concentration, the rate of the reaction was calculated. It could be expressed in terms of current by multiplication by Faraday's number, and further normalized to current per gram of palladium for comparison with other runs.

In one case, the rate calculated from the open circuit potential drop was verified approximately by determining the regeneration current necessary to hold the solution potential constant (see Table 2).
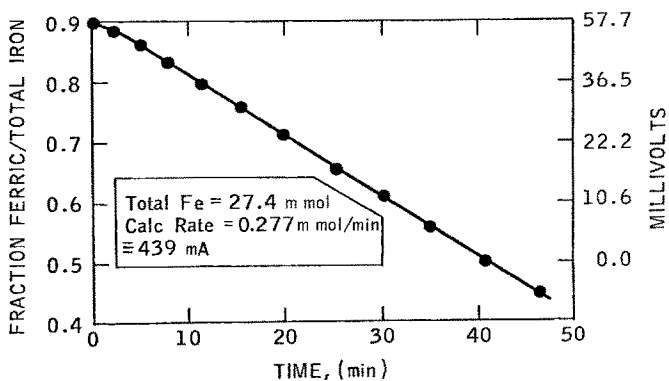

Total Fe = 27.4 m mol
Calc Rate = 0.277 m mol/min
≡ 439 mA

Fig. 2. Pd^{2+} – cyclopentene reaction rate plot. 55° C, gas feed.

*Table 2. Agreement between oxidation rate and regeneration current**

Current calculations from dE/dt (mA)	Current to hold voltage constant (mA)
278	250

* 35° C, 0.5 M total Fe, liquid cyclopentene feed

Routine analysis for cyclopentanone was carried out by extracting the electrolyte with ethyl ether, evaporating some of the ether through a fractionating column and examining the residue in a gas–liquid chromatograph using one or more internal standards. The gas chromatographs showed a clean base line, indicating greater than 99% purity for the product in the extract. In one case, the product was isolated as the 2,4-dinitrophenylhydrazone and proved to have the same melting point and mixed melting point as a sample of authentic cyclopentanone 2,4-dinitrophenylhydrazone.

3. Experimental results and discussion

3.1. Acid concentration

The acid concentration for the majority of the study was chosen on the basis of its effect on the solubility of $PdCl_2$ and on the electrical conductivity. The experimental results are shown in Fig. 3. It will be seen that the solubility of $PdCl_2$ decreases with acid concentration. To permit the maximum variance in palladium concentration while maintaining reasonable electrolyte conductivity, a concentration of 0.3 M $HClO_4$ was chosen. However, because of the high reaction rates ultimately obtained, lower palladium concentrations could have been tolerated and higher acidity would have been desirable. This would have improved conductivity, reduced concentration polarization in the cathode chamber and, according to Equation 7, would have accelerated the reaction at low chloride concentrations.

3.2. Verification of rate advantage

In a few preliminary experiments performed at 35° C with liquid cyclopentene with various electrolytes, it was verified that the perchlorate electrolyte did indeed provide a large rate advantage over electrolytes containing substantial amounts of chloride as shown in Table 3.

It will be seen that the rates are of the order of sixty times as great in the perchlorate solution as in the others and that the difference is not due to the presence of perchlorate, but the absence of chloride.
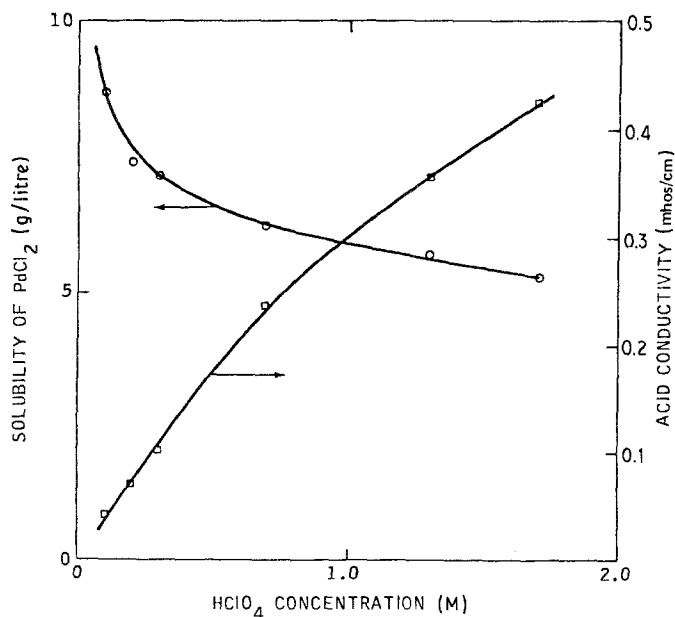

Fig. 3. The effect of $HClO_4$ concentration on conductivity and $PdCl_2$ solubility.

Table 3. $PdCl_2$–cyclopentene reaction rates in various electrolytes[*]

Electrolyte	Average rate (mA g^{-1} Pd)
1.3 N HCl	11
0.5 N HCl, 0.7 N $HClO_4$, 0.4 M $FeCl_3$	10
1.3 N HCl, 0.2 M $CuCl_2$	5
0.3 M $HClO_4$	640, 610

[*] 35° C, liquid cyclopentene, 0.042 M $PdCl_2$.

3.3. Effects of ionic strength and chloride content

Early attempts to use the ferric/ferrous redox couple at initial ferric concentrations of 0.6 M led to precipitate formation in the solution after the cyclopentene was introduced. This precipitation slowly generated palladium black, if wet with dilute perchloric acid or dissolved in aqueous acetone. Based on literature reports of the isolation of such complexes, it was probably the $(PdCl_2$ olefin$)_2$ dimer referred to in the Introduction. It is interesting that this complex could be dissolved in 1.3 N hydrochloric acid, where it yielded no palladium precipitate in 24 h, again attesting to the inhibitory properties of chloride ion. The material was not isolated in a pure enough form to be analysed, however.

Reducing the ferric ion concentration prevented the precipitation of the complex. Apparently, the palladium–cyclopentene complex, with its high hydrocarbon content, and therefore borderline solubility in water, was salted out by the high ionic strength provided by the ferric ion. (A solution of 0.6 M in ferric perchlorate contributes $1/2 (0.6 \times 9) + 3 \times 0.6 = 3.6$ mol 1^{-1} to the ionic strength.) Reducing the iron concentration and thereby the ionic strength, avoided precipitate formation and also increased the rate of the reaction somewhat (Table 4).

The effects of additions of chloride ion to the solutions were found to be small initially and increasingly negative (see Table 5), indicating that the chloride content was near the maximum predicted by Smidt's rate equation (Equation 1).

3.4. Diffusion limitation

Under conditions of reduced ferric and chloride contents, the factor having the largest effect on the reaction rate was the mode of feeding the olefin. Admitting it as gas bubbles gave a higher rate than simply stirring the liquid cyclopentene. Adding a mechanical mixer along with the gas feed increased the rate further, and finally sparging the olefin as a fine foam gave the highest rates obtained; in the order of 100 A g^{-1} (Table 6) as contrasted to the values of 600 mA g^{-1} in Table 5. The practical significance of this is that the palladium inventory required for commercial production becomes minimal at the highest rates. For example, at 100 A g^{-1} an inventory of 5700 g Pd is adequate for a production rate of ten million pounds of cyclopentanone per year at 70% selectivity. The investment cost of palladium should, therefore, amount to well under one cent per pound of ketone produced. The range of values shown in Table 6 is partially due to other variables studied, namely temperature and concentration, and partly due to the experimental variability connected with a diffusion limited reaction. These data indicate that the reaction itself is very fast and that the rate is limited only by the diffusion of the olefin into the liquid phase or by diffusion of the olefin complex from the edge of the bubbles into the bulk. The temperature dependence under these conditions was very low, and the reproducibility was not good ($\pm$ 10%) again as might be expected for a diffusion limitation (Table 7).

Table 4. Effect of ionic strength on reaction rate

Fe ion concentration (mol l^{-1})	Ionic strength (mol l^{-1})	Average reaction rate[*] (mA g^{-1} Pd)
0.6	4.0–4.3[†]	250[‡]
0.5	3.5	510
0.3	2.35	530
0.2	1.3, 1.5	630

[*] At 35° C with liquid cyclopentene feed; 0.3 M $HClO_4$
[†] Ionic strength varies slightly with ferric/ferrous ratio.
[‡] Turbidity noted; results occasionally erratic due to precipitate formation.

Table 5. Effect of added chloride on reaction rate

Moles HCl added per mole Pd^{2+}*	Average reaction rate $(mA\ g^{-1}\ Pd)$†
0	630
2	550
4	320
1.3–1.7 N Cl^- solns	10‡

* Above the chloride normally present as $PdCl_2$ and as contaminant in ferric perchlorate
† Liquid cyclopentene feed, 35° C, 0.042 M $PdCl_2$, 0.2 M Fe ions
‡ From Table 2

Table 6. Diffusion limitation of palladium cyclopentene reaction

Cyclopentene fed as	Reaction rate range $(A\ g^{-1}\ Pd)$
Liquid	0.2–0.7
Gas bubbles	1.5–6
Gas bubbles + vibro mix	15–27
Fine gas sparge	23–161

Table 7. Temperature dependence of palladium–cyclopentene reaction

Temperature (° C)	Rate $(A\ g^{-1}\ Pd)$
48	1.8
55	1.9, 1.5
70	2.3
85	2.5

It is interesting that changes in palladous ion concentration produced nearly proportionate changes in reaction rate, thus giving little change in activity per gram of palladium, at conditions of poor mass transport. Where olefin contact is better and the rates are higher, it is advantageous to use lower concentrations of palladium dichloride for the reaction rate tends to reach a limit at high palladium concentrations (Table 8).

In any case, the rates are high enough that the palladium inventory is no problem.

3.5. Product yield and stability

The yields of ketone varied from 25 to 74%, based on the total current passed and/or oxidant reduced, due to slow further reactions of the cyclopentanone in the electrolyte. Where the rates were low and the runs took 4–5 h to complete, current selectivities were only about 30%.

But where continuous extraction was carried out or the rate was high and runs short, current selectivities of 70% were observed (Table 9).

The rates of oxidation of the ketone were measured in separate experiments simply by adding it to the electrolyte containing the palladium chloride, perchloric acid and ferric perchlorate, and measuring the rate of ferric reduction from the open circuit voltage decline. The rates were not constant in a single run, but appeared to increase with time, as if the initially formed products were more reactive than the starting ketone. At a given conversion level, the rates were fairly sensitive to temperature, as shown in Table 10.

Table 8. Effect of palladium concentration on reaction rate

Mode of cyclopentene feed	Palladium content		Reaction rate*	
	$(g\ l^{-1})$	(Total g)	(mA)	$(A\ g^{-1}\ Pd)$
Liquid	2.27	0.30	194	0.65
	0.91	0.12	82	0.68
Gas bubbles	2.25	0.30	⎰570	⎰1.9
			⎱440	⎱1.46
	0.80	0.30†	1230(440)	4.1
	0.40	0.15†	820(290)	5.5
Gas sparge	2.26	0.30	7040	23
	0.36	0.048	⎰3000	63
			⎱7740	161

* Based on change in voltage with time.
† Greater total volume account for high rates for these two cases. Rates in parentheses are corrected back from 375 to 133 cm^3.

Table 9. Cyclopentene yields improved by short runs or continous extraction

Feed mode	Temperature (°C)	Run time (min)	Continuous extraction solvent	Current selectivity to ketone (%)
Liquid	35	255, 330	None	27, 30
Liquid	35	240	Cyclopentene	73
Gas	55	40, 50	None	74, 68
Gas	55	560	2-methylpentane	67

Not all the oxidation was caused by the palladium. At 70° C, the oxidation rate due to ferric alone in the absence of palladium was one fourth that of the oxidation rate of the total system. In the absence of ferric ion palladous ion oxidized cyclopentanone readily, as evidenced by a rapid drop in potential and precipitation of palladium metal. No rate data were taken under the latter conditions, however.

The ketone oxidation reaction probably does not go to a single intermediate, but appears to proceed largely to CO_2. In a long term run with an excess of oxidants, the reaction rate declined with time until eventually 20 equivs of oxidant were consumed per mole of ketone. Complete conversion to CO_2 would require 26 equivs per mole. In a subsequent run, considerable CO_2 was trapped in an Ascarite tube, though the results were not quantitative. This result is favourable, for it means that the current used in oxidizing ketone corresponds to very little wasted ketone. A current selectivity of 70% corresponds to a product selecitivty of 98%, assuming the side oxidation proceeds all the way to CO_2.

Due to the complexity of the ketone side reactions, the above data may be used only as a rough index of the rate of product loss via side

reactions. Using the maximum rate of ketone oxidation at 55° C, and the observed rate of olefin oxidation, one calculates current selectivities to product which are higher than those actually observed. Thus, the yields must also be lowered by acid catalysed condensation reactions and physical losses, not detected by this method. In any case, the need for continuous extraction to reduce the concentration of ketone in the electrolyte at any time, is clearly indicated.

The susceptibility to further oxidation is unusually severe for cyclopentanone and not typical of open chain ketones as will be discussed later.

3.6. Continuous extraction

To operate for long periods of time with product removal the continuous extraction set up described in Section 2 (Fig. 1) was used. The requirements for the extraction solvent proved to be quite stringent. Cyclopentene itself extracted the ketone from the aqueous phase quite efficiently and was at the same time the fed olefin. However, as has been discussed, rates of reaction were very low unless the olefin was fed as a gas, which made it impossible to use pure cyclopentene as extract-

Table 10. Effect of temperature and conversion level on cyclopentanone oxidation rate

Temperature (°C)	Concentration*		Extent of reaction (electrons/molecule)[†]	Oxidation rate[‡] (mA/g ketone per g Pd per l)
	Pd	Ketone		
55	1.1	28	0–0.13	22
55	2.2	13.3	0.35–0.65	64
70 [§]	2.2	13.3	0–0.09	80
70 [§]	2.2	13.3	0.35–0.80	272
70	2.2	0.79	0.5–6.5	415

* Iron content 0.18 mol l⁻¹, perchloric acid 0.3 mol l⁻¹
[†] In the range where the oxidation rate was measured
[‡] Based on total ketone added initially
[§] A single run with rates measured in two regions

Table 11. Distribution of cyclopentanone between hydrocarbons and aqueous acid

Hydrocarbon	Concentration ratio hydrocarbon/acid*
Cyclopentene	1.70
Cyclohexane	0.77†
2-methylpentane	0.52

* 0.3 N $HClO_4$
† Acid contained iron salts and palladium chloride

Table 12. Constancy of reaction date with time in continuous unit

Time period (min)	Rate (A)*
0–54	0.93
(no current)	
54–264	1.15
264–374	1.11
Overall	1.12†

* Based on coulombs passed, corrected for changes in ferric concentration derived from reference electrode potential measurement.
† 374 min at 1.12 A corresponds to 92.5 regenerations of 0.15 g Pd in the system. Rate = 7.5 A g^{-1} Pd

ant. Furthermore, the cyclopentene–palladium complex was soluble to a small extent in cyclopentene, so that in long runs black palladium was visible in the solvent boiler.

It was possible to operate at 55° C with liquid cyclopentene (b.p. = 44° C) with a mixed extractant containing cyclopentene plus a higher boiling liquid such as benzene or cyclohexane. However, the organic layer tended to be rich in cyclopentene and the palladium complex was again extracted.

Finally, it was realized that the extractant would have to be a saturated hydrocarbon and that the cyclopentene gas would have to be fed in a separate vessel so that it would not accumulate in the extractant stream. Since the reaction is diffusion limited, the amount of olefin dissolved in the electrolyte and thereby able to reach the extractant would be negligible.

Cyclohexane and 2-methylpentane were tried. Their ability to extract cyclopentanone from aqueous acid into a hydrocarbon layer was inferior to that of cyclopentene, but still tolerable (Table 11).

The methylpentane was finally selected as best since its lower boiling point, 60° C (cf. 81° C for cyclohexane), reduced the rate of evaporation of the product (b.p. = 131° C) from the extractant boiler. Its use completely eliminated the palladium extraction problem. The rate of accumulation of ketone in the boiler was measured by gas chromatography relative to internal standards which had been placed in the boiler at the start of the experiments. In trial extraction experiments, the contacting efficiency was calculated to be about one quarter to one third of that if saturation were always complete. This, coupled with the limited solvent recycle rates and the low distribution constant, caused the extraction half-life to be estimated at about 2 h. Thus, in continuous runs the product concentration in the electrolyte built up slowly until the rate of extraction matched the rate of production of cyclopentanone. Product accumulation in the solvent boiler lagged considerably behind its production and continued after the reaction stopped. All of this could be improved in a larger plant of pilot unit, and the yields thereby increased.

The longest run in the apparatus of Fig. 1 lasted for over six hours on feed, during which time the reaction continued at a higher and fairly constant rate and the palladium was calculated to have been regenerated over 90 times, as shown in Table 12. The rate of product accumulation in the extractant boiler lagged considerably behind the calculated rate of product generation (assuming 100% current selectivity) as shown in Fig. 4. The final yield, including material later extracted from the electrolyte with ether, was 67% of that calculated from the current passed and ferric ion reduced. The slope of the product accumulation curve of Fig. 4 never approached this value, indicating that the extraction was so poor that a steady-state was never reached during the six hours of ketone production. In addition, later work with normal pentanones and hexanones indicated that despite their high boiling points (131° C for cyclopentanone) these intermediate ketones have an appreciable vapour pressure at 55° C and might accumulate in the feed reboiler. No analysis of the boiler contents was made, however. In view of all the above, the current selectivity of 67% represents a minimal value which should easily be surpassed with other ketones or in more industrially configured apparatuses.
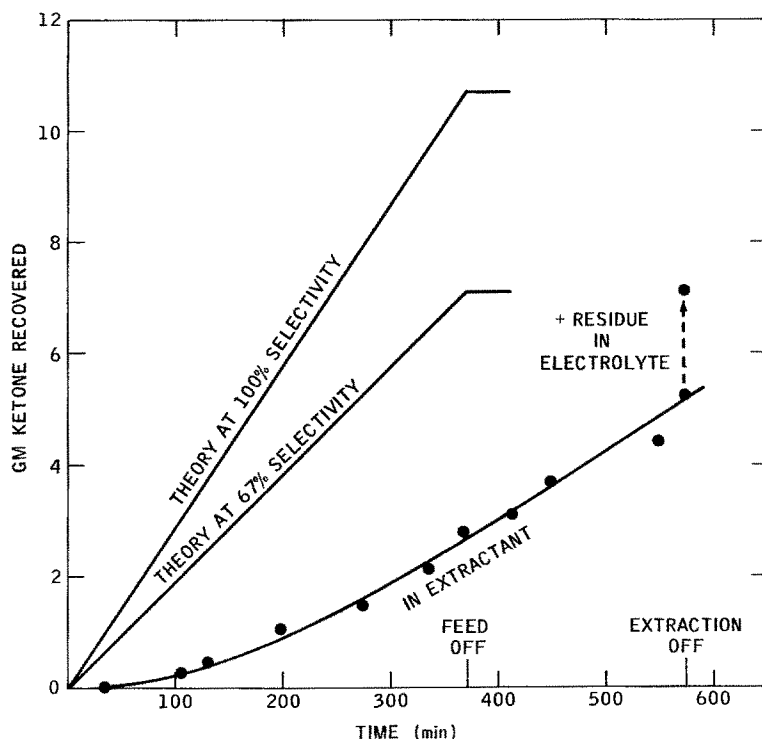
Fig. 4. Cyclopentanone production with continuous extraction.

3.7. Cell voltage requirements

In the apparatus of Fig. 1, a glass frit was used to isolate the cathode chamber and the cell voltages increased with time, reaching 25 V or more. The major cause of this was the development of acid concentration gradients across the frit. Because the anion transference number was finite, the discharge of the hydrogen ions caused the acid concentration in the cathode chamber to drop toward zero. Addition of small amounts of perchloric acid to the cathode chamber caused drastic drops in cell voltage. This problem was accentuated by the small area of the frit relative to the anode; current densities through the frit reached the order of 500 mA cm^{-2}.

In a practical system, a plate-and-frame type of regeneration cell might be envisaged using a cation-exchange membrane as separator. The palladium existing in anionic form would presumably be excluded from the cathode chamber, while the greater concentration and mobility of the hydrogen ion would keep the flux of Fe^{3+} and Fe^{2+} to a small percentage of the total current. Back diffusion of ferrous ion from the cathode chamber would keep the iron content of

the system in balance at steady-state. Since the area of the membrane would be equal to that of the anode, more reasonable current densities, in the range of 100–200 mA cm^{-2}, would be required across the membrane. With partial occupancy of the membrane sites by polyvalent Fe^{2+} and Fe^{3+} ions, a voltage drop of the order of 1.0 V might be expected. However, a proton transference number of about 1.0 would maintain high conductivity in the liquid on both sides of the membrane giving resistance losses of say 0.2 V. This coupled with anode and cathode voltage losses of 0.3 and 0.2 V respectively, plus a theoretical cell voltage of 0.8 V, gives a total cell voltage of about 2.5 V. This corresponds to 1.6 Wh kg^{-1}, at 100% efficiency or about 2.2 Wh kg^{-1} at 70% coulombic efficiency.

3.8. Process operability with other ketones

The possibility of manufacturing other ketones by this electrochemical process was examined briefly. It was first of all verified that open chain ketones are at least an order of magnitude more stable to oxidation than cyclopentanone in the acidic palladous–ferric solution (Table 13). The

Table 13. Stability of ketones in process electrolyte

Ketone	Oxidation rate (mA g^{-1} ketone per g Pd per litre)
Cyclopentanone	22.2
Pentanone-2	1.8
Pentanone-3	2.3
Acetone	Negligibly low

* 1.1 g Pd per litre, 0.18 M Fe, ~ 95% Fe^{3+}, 0.3 M HClO$_4$, 55° C, ~ 25 g ketone per litre, low conversion (~ 0.1 electrons per molecule)

results suggest that yields should be higher and the necessity for continuous extraction is less for ketones other than cyclopentanone from the standpoint of oxidation stability alone. Of course, the possibility of acid catalysed condensations, not measured by the above procedure, still makes continuous extraction mandatory.

The yields and reaction rates with open chain olefins were of the same order of magnitude as cyclopentene (Table 14). This was determined in batch experiments run without continuous liquid extraction, using only the two right-hand vessels in Fig. 1. Most of the product ketone was found in the olefin boiler due to the exceptionally high activity coefficients of C$_5$ and C$_6$ ketones in aqueous solutions. Thus, the product was being removed continuously. The isomer distributions shown in the last column verify that terminal olefins form essentially no aldehydes, that double bonds do not migrate in this process and that internal olefins form the two possible ketones in approximately the manner expected from the carbonium ion character of the reaction. In the case of pentene-2 a more sensitive chromatograph was used, and a number of minor peaks were

found. Their total area amounted to less than 1% of the major product peaks, however.

The reaction was also carried out on the branched olefin, 2-methyl butene-2, a likely contaminant of cyclopentene. Gas–liquid chromatography on the resultant extract showed at least six different products in comparable amounts, whose identity was not further investigated. Smidt [3] also indicated that olefins bearing no hydrogen on one of the double-bonded carbons react slowly, undergoing hydration, other oxidations and rearrangements, and later, cleavage. Isobutylene, for example, yielded tertiary butanol along with acetone, isobutyraldehyde, α-methyl acrolein and methyl ethyl ketone. Branched olefins are best eliminated from the feed stream.

4. Conclusion

This electrochemical chloropalladate process looks promising for small plants converting C4 and higher linear olefins to the corresponding ketones, cases where the corresponding air oxidation process has not been commercialized. The advantage of the electrochemical process lies in its avoidance of excess chloride, which leads to slow rates and chlorinated by-products. The process has been demonstrated in a continuous laboratory unit with good current selectivities and maintenance of high catalyst activity. The process cost remains to be investigated. It is known that the palladium inventory can be very low, but the electrode cost and the materials of construction have not been determined. The details of product recovery via extraction or stripping would have to be worked out for each olefin one desires to oxidize. Further studies would also have to be carried out to choose

*Table 14. Performance of olefins in electrochemical ketone process**

Olefin	Temperature (° C)	Rate[†] (A g^{-1} Pd)	Yield (%)	Pentanone-2[‡] (%)
Pentene-2 [§]	55	4.1, 3.4	51, 65	57, 54
Pentene-1	55	2.2	71	99 +
Hexene-1	74	1.7	57	–
Typical cyclopentene	55	2–8	70	–

* 0.2 M Fe^{3+}, 1.1 g Pd per litre, bubbled gas feed
† From voltage–time trace
‡ Determined using 300 ft squalane capillary GC column at 40° C
§ Mixture of *cis*- and *trans*-isomer

the optimum acid type and concentration based on considerations of safety and total cell voltage drop. Presumably, dilute sulphuric acid could replace the perchloric acid used in this study. Cells would have to be designed to optimize the current densities for ferrous oxidation, to reduce the cathodic reduction of ferric ion and to minimize the voltage drop. None of these problems appear to present any great difficulties.

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