

Anodic Oxidation of 1,3-Cyclohexanedione to 1,2,3-Cyclohexanetrione

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1,3-cyclohexanedione can be electrochemically oxidized in aqueous sulfuric acid at platinum to the 1,2,3-cyclohexanetrione. Yields of about 76% and current efficiencies up to 54% were found.

1,2,3-cyclohexanetrione (2) can be synthesized in multistep chemical syntheses.¹⁾ We report on a simple one step electrosynthesis of this product at a Pt-anode, starting from 1,3-cyclohexanedione (1). Chemical oxidation of ketones leads very often to products of C-C-cleavage.²⁾ However the cleavage of the C-C-bond can be omitted under special conditions. Two possibilities arise, leading to products of greater preparative interest: 1) insertion of oxygen according to the Baeyer-Villiger oxidation. 2) oxidation of adjacent CH₂-groups.

Specific oxidants are peroxo mono sulfuric acid,³⁾ Mn⁺⁺⁺, and SeO₂.⁴⁾ Anodic oxidation at conventional anodes displays a behaviour in analogy to this. At PbO₂ anodes, cyclohexanone and acetylacetone⁵⁾ as well as 1,3-cyclohexanedione⁶⁾ yield mainly the products of a cleavage of the C-C-bond. In the case of platinum anodes, the open chained β -diketone tends to fragmentation,⁵⁾ while the 1,3-cyclohexanedione retains mainly the six-membered ring.⁶⁾ We report on our effort to optimize this electrosynthesis of great preparative interest.

Electrolytes were prepared from triple distilled water, anal. grade 97% H₂SO₄ (Merck) and 1,3-cyclohexanedione 1, 96% from Merck. The following anode materials were used: a) Bright Pt-sheet, thickness 0.1 mm and b) Pb/PbO₂, made from 1 mm lead sheet.⁶⁾ The pretreatment of the electrodes is described elsewhere.⁷⁾ Two types of cells were employed. In the quasidivided cell, two wire counter electrodes with small surface areas were located on both sides of the sheet anode, A = 50 cm².^{7,8)} A divided plate and frame cell, A = 100 cm², with an anolyte loop, equipped with a centrifugal pump was also used. A cation exchange membrane (type SELEMION CTM of ASAHI GLASS company) was employed. The catholyte was 0.05 M H₂SO₄. The electrolyte volumes were 200 ml and 500 ml, respectively. Electrolysis was performed at constant current density. After the passage of 4 F/mol, the batch experiment was stopped. Analysis was due to HPLC (UV/VIS detection) directly in the electrolyte. H₂SO₄ (pH 1.7) was used as the eluent.⁹⁾ The UV-detection wave length was 220 nm. Typical retention times were: 1,2,3-cyclohexanetrione-

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hydrate **2** : 4.1 min; possible intermediate, α -oxo-adipic acid **4** : 9.4 min; glutaric acid **3** : 12.9 - 13.6 min; 1,3-cyclohexanedione **1** : 34.8 min; 1-hydroxy[1,1'-bicyclohexyl]-2,2', 6,6'-tetrone **5** : 100 min. These values were confirmed by authentic compounds.

The preparation of the 1,2,3-cyclohexanetrionehydrate reference sample was performed according to the method of Schank and Lick,¹⁾ treating phenyliodonium-1,3-cyclohexanedione-enolate, dissolved in CH_2Cl_2 , at -60°C with an equimolar amount of ozone. The product was identified as the 1,2,3-cyclohexanetrionemonohydrate by ^1H NMR and mass-spectroscopy. **2** is present in the enolic form.

In a typical electrochemical run, 1.12 g (10 mmol) **1** were dissolved in 200 ml 1 M H_2SO_4 . The electrolysis was carried out in a quasidivided cell at a constant current density of 10 mA cm^{-2} , corresponding to $I = 0.5 \text{ A}$. After 2 hours and 8.7 minutes, i.e. after passage of 4 F/mol, the electrolysis was stopped.

The results of the preparative runs are compiled in Table 1. **2** could be obtained with material yields (with respect to converted starting material **1**) up to 76% and current efficiencies up to 54%. The main electrochemical side reaction is due to oxygen evolution. Temperatures below room temperature (14°C) were found to be beneficial. Low current densities are superior over elevated ones with regard to CE. This is clear from a comparison of entries 3 and 5. The improvement at low current densities is even more pronounced for 1 M HClO_4 as electrolyte, cf. entries 7 and 8. A comparison of entries 1 and 3 or 2 and 4 shows, that higher sulfuric acid concentrations raise the yields for **2** appreciably, while the substitution of H_2SO_4 by HClO_4 has no great effect at low cur-

Table 1. Anodic oxidation of **1** in aqueous acids at bright Pt (only No. 9: PbO_2) with current conversions of 4 F mol^{-1} **1** (theoretical charge), except No. 2 (12 F mol^{-1}), Temperature about 14°C , MY = material yield, CE = current efficiency

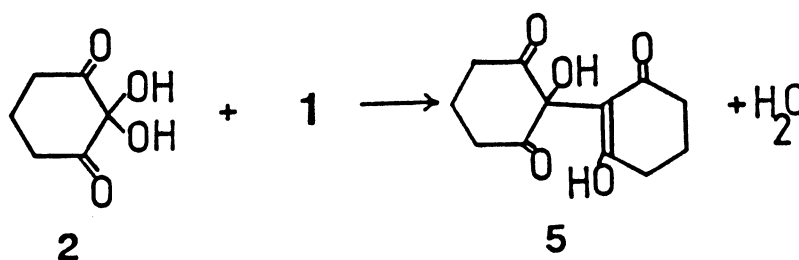
Entry	Type of cell	Electrolyte	c(1)/M	j/ mA cm^{-2}	Cyclohexanetrione 2		Glutaric acid 3	
					MY/%	CE/%	MY/%	CE/%
1	quasi divid.	0.05 M H_2SO_4	0.05	30	64	32	4	4
2	plate & frame	0.05 M H_2SO_4	0.5	30	37	12	10	3
3	quasi divid.	1 M H_2SO_4	0.05	10	72	52	7	10
4	plate & frame	1 M H_2SO_4	0.05	10	69	54	11	18
5	quasi divid.	1 M H_2SO_4	0.05	30	76	35	9	8
6	quasi divid.	1 M H_2SO_4	0.5	30	64	32	13	12
7	quasi divid.	1 M HClO_4	0.05	10	68	52	8	12
8	quasi divid.	1 M HClO_4	0.05	30	6	3	28	29
9	quasi divid.	1 M H_2SO_4	0.05	30	23	9	57	34

rent densities. Similar results are obtained with the plate and frame-cell, as a comparison of entries 3 and 4 clearly demonstrates. Optimum results were obtained with bright platinum as an anode, whereas PbO_2 predominantly generates the follow up product, glutaric acid 3, cf. runs 5 and 9. The stability of the triketone 2 against the strongly oxidizing PbO_2 seems to be low. This confirms the mechanism of heterogeneous redox catalysis,¹⁰⁾ which was proposed by us for the anodic oxidation of 1 to glutaric acid at PbO_2 anodes.⁶⁾

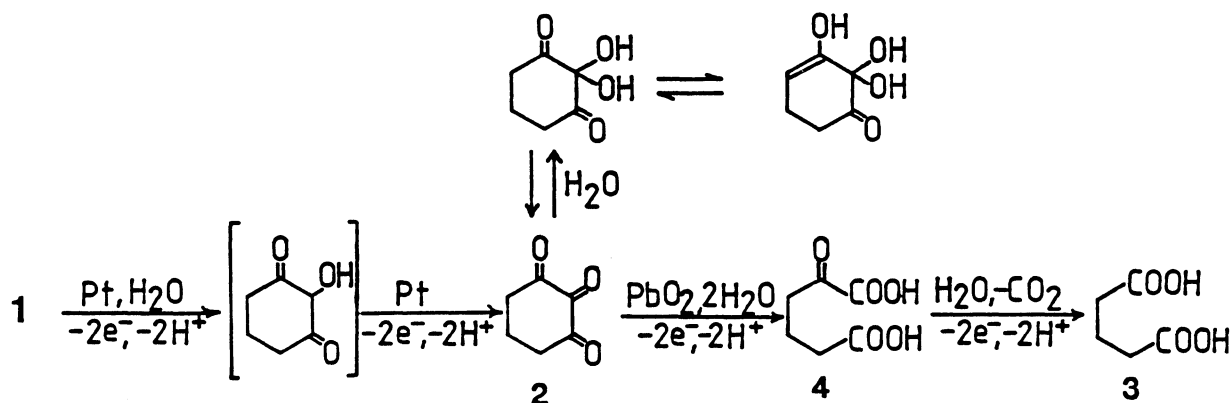
Minimization of the sulfuric acid concentration is regarded to be useful, in view of isolation of the extremely water soluble cyclohexanetrionehydrate. It requires removal of the electrolyte after neutralization. A large salt ballast should be avoided. However, attempts to work up by this method were unsuccessful. Therefore, the isolated product from the experiment No. 2 in Table 1 with a nearly complete conversion of 1 contained only 10% of the original amount of 2. Most of it had reacted to products showing a large retention time in HPLC, and 10% had converted to pyrogallol. As an alternative, 2, as the bis-(2,4-dinitrophenylhydrazone) derivative,¹¹⁾ was isolated by precipitation directly from the electrolyte in 83.7% yield, as related to the 2-content determined by HPLC. Mp. 230 °C, decomposition. Elemental analysis, Found: C, 43.55; H, 3.02; N, 21.27%, Calcd: C, 44.44; H, 2.88; N, 23.05%. Starting from chemically prep'd. 2: C, 43.64; H, 2.90; N, 22.73%.

As the kinetic curves (a plot of mole numbers vs. time) in the case of platinum point out, 2 accumulates early, whereas the formation of 3, as the final oxidation product is rather retarded at the initial stage. A third product exhibits typical intermediate behaviour. The maximum is at 16 F/mol. Presumably it is the precursor for glutaric acid, α -oxo-adipic acid 4.

Kinetic curves for PbO_2 anode reveal,⁶⁾ that in this case 2 only plays the role of a minor side product, and 3 is formed from the beginning. The concentration of the above mentioned α -oxo-adipic acid 4 as second intermediate already reaches the five fold value of that in the case of platinum. At about 6 F/mol after storage of the electrolyte following electrolysis at platinum anodes at room temperature, the appearance of chemically follow-up products was observed. Besides pyrogallol, some of them are assumed to be dihydrated species.¹⁾ A further compound could be identified as 1-hydroxy[1,1'-bicyclohexyl]-2,2',6,6'-tetrone 5, generated by a nucleophilic addition reaction between 1 and 2.¹¹⁾ A rapid in situ utilization of the product 2 is therefore advisable.



In conclusion, the anodic oxidation of **1** at platinum leads in a straightforward way to **2**. The intermediate diketoalcohol could not be analyzed. The following reaction scheme includes the overoxidation to glutaric acid⁶⁾ as well:



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