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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 CH_2-groups.

Specific oxidants are peroxo mono sulfuric acid,[3)] Mn^{+++}, and SeO_2.[4)] Anodic oxidation at conventional anodes displays a behaviour in analogy to this. At PbO_2 anodes, cyclohexanone and acetylacetone[5)] as well as 1,3-cyclohexanedione[6)] 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% H_2SO_4 (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/PbO_2, 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 cm^2.[7,8)] A divided plate and frame cell, A = 100 cm^2, 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 H_2SO_4. 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. H_2SO_4 (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 acccording 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 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

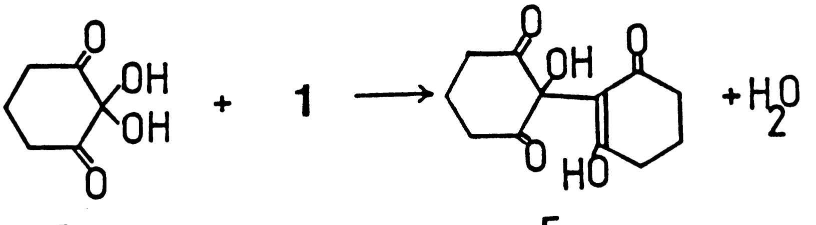
Entry	Type of cell	Electrolyte	c(**1**)/M	j/mA cm^{-2}	Cyclohexanetrione **2**		Glutaric acid **3**	
					MY/%	CE/%	MY/%	CE/%
1	quasi divid.	0.05 M H_2SO_4	0.05	30	64	32	4	4
2	plate & frame	0.05 M H_2SO_4	0.5	30	37	12	10	3
3	quasi divid.	1 M H_2SO_4	0.05	10	72	52	7	10
4	plate & frame	1 M H_2SO_4	0.05	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 prepd. **2**: C, 43.64; H, 2.90; N, 22.73%.

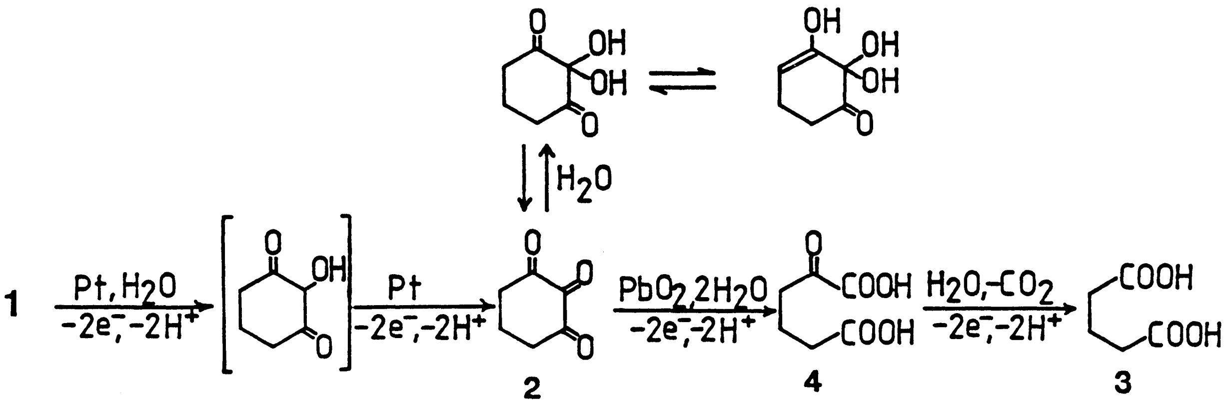
As the kinetic curves (a plot of mole numbers vs. time) in the case of platinum point out, **2** accumulates early, whereas the formation of **3**, as the final oxidation product is rather retarded at the initial stage. A third product exhibits typical intermediate behaviour. The maximum is at 16 F/mol.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



2 **5**

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 acid⁽⁶⁾ as well:



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