Acid Catalyzed Disproportionation of Anthrahydroquinone to Anthraquinone and Anthrone

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The reversible organic redox couple anthraquinone/anthrahydroquinone is of considerable interest for an application in metal free rechargeable batteries, mainly in acid electrolytes, e.g. in aqueous sulfuric acid. But the anthrahydroquinone undergoes an acid catalyzed disproportionation reaction to yield anthraquinone and anthrone. The dependency of this irreversible second order side reaction on the type of the acid, the acid concentration and the solvent was investigated by kinetic measurements in homogeneous solutions.

1 INTRODUCTION

Quinones are well known to form reversible organic redox couples. The kinetics of the benzoquinone/benzohydroquinone redox system was studied in detail four decades ago¹⁾. For a possible metal free secondary battery application chloroanil was proposed as the positive (redox potential, vs. SHE, $U_{H,0} = 0.67$ V, electrochemical equivalent, $m_e = 0.22$ Ah g⁻¹) and anthrahydroquinone as the negative ($U_{H,0} = 0.15$ V, $m_e = 0.26$ Ah g⁻¹) using sulphuric acid as electrolyte. This type of a "quinone battery"²⁾, however, exhibited a voltage of only 0.5 V. More recently, the negative anthraquinone system was combined with the very positive graphite intercalation compounds of the graphite salt type in acids of medium concentrations to yield threefold cell voltages of 1.5 V^{3,4)}. In this connection, an irreversible side reaction, the acid catalyzed disproportionation of the anthrahydroquinone **1** to anthraquinone **2** and anthrone **3** according to equation (1) became interesting. Besides a qualitative observation⁵⁾ and an electrode kinetic study in 85 wt %

H_2SO_4 ⁶⁾, no kinetic data were available in acid electrolytes of medium concentrations. It is the aim of this paper to fill this gap.

2 EXPERIMENTAL

Galvanostatic cycling of an anthraquinone/carbon black single electrode was performed in a cylindric polyethylene cell with a 44 cm² horizontal Acheson graphite electrode at the bottom of the cell. A mixture of 1.326 g **2** with 30 wt % carbon black c.b. (Corax L) was spread evenly on this current collector. A microporous separator was pressed onto this layer. The counter electrode was Pt. Cycling was performed at $j = 3$ mA/cm² between the potential limits +0.58....-0.31 V vs. SHE.

For the evaluation of the disproportionation kinetics two different systems were investigated. Because of the low water solubility of **1**, $2 \cdot 10^{-5}$ M (= mol dm⁻³), the following organic solvents were applied: 80 vol% CH₃CN, acetic

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acid, HOAc, and acetic anhydride, Ac_2O , with 1, 3 and 5 M H_2SO_4 . For the pure aqueous systems with three different acids, H_2SO_4 (1 M, 3 M and 5 M), H_2F_2 (2 M and 20 M), and HBF_4 (2 M and 4 M), the water soluble (10^{-2} M) anthrahydroquinone-2-sulphonic acid 4 was employed. The two anthrahydroquinones were prepared by reduction of the anthraquinones (each 0.1 mol), introduced as a finely dispersed solid into 200 ml of an aqueous solution, containing 0.1 mol sodiumdithionite and 0.4 mol NaOH^{71} . The sodium salt of AQH₂ 1, $\text{C}_{14}\text{H}_8\text{O}_2\text{Na}_2$, was formed from AQ 2. All procedures were performed under an argon atmosphere to rule out a parallel autoxidation. In the case of 4 an aqueous solution of the sodium salt of anthraquinone-2-sulphonic acid $\text{C}_{14}\text{H}_7\text{SO}_5\text{Na}$ was used instead of the free acid. It was reduced to the anthrahydroquinone sodium salt $\text{C}_{14}\text{H}_7\text{SO}_5\text{Na}_3$. Rapid conversion to 4 was accomplished by adding to the large excess of acid media.

For the kinetic studies of reaction (1) in acid, the standard starting concentration of 1 and 4 was 6 mM. The overall volume at the beginning was 200 ml. In the course of the kinetic measurements the concentration of non-converted 1 and 4, respectively, was determined by redox titration with 0.0125 M FeCl_3 solution. A 10 ml probe of the reaction solution was diluted with 40 ml 1:1 vol/vol acetone/water mixture in the case of 1 and 40 ml water in the case of 4. The titration solution had to be changed to 0.1 M $\text{Ce}(\text{SO}_4)_2$ solution in the case of H_2F_2 .

3 RESULTS

Figure 1 shows the active material utilization μ in the course of the galvanostatic cycling experiments with 0.5, 2, 6 and 8 M HBF_4 . μ refers to the theoretical value for 2 F/mol AQ, which is 860 C. At the beginning, μ is in the range of 50–60 %. But it decreases significantly

Fig.1 μ for galvanostatic cycling of AQ (30% c.b.) in HBF_4 . 1: 0.5 M; 2: 2 M; 3: 6 M; 4: 8 M

in the course of the initial 42 cycles at the higher acid concentrations. $\mu = 50\%$ corresponds to a discharge time of 3257 seconds.

The kinetic measurements in acid solutions of the anthrahydroquinones 1 and 4 led to the following results: The reaction order for 1 was determined after the half-life method to be $\nu = 1.8$ in the average with respect to the substrate 1. Consequently, the kinetic results were plotted in Figures 2 and 3 (see next page) according to a second order law. Clearly, straight lines are found in all cases. Figure 2 displays the kinetic curves in 1–5 M H_2SO_4 in 80 vol% CH_3CN . 1 is relatively stable in 2 M H_2SO_4 , but it decomposes rapidly in 3 M and even more in 5 M H_2SO_4 (80 vol% CH_3CN). In 1 M H_2SO_4 in this solvent, virtual stability is achieved. Second order rate constants are derived from this, and they are compiled in Table 1. Very high rates were found in acetic acid (No 14, 3 M H_2SO_4) and even more in acetic anhydride (No 15, 1 M H_2SO_4).

The solvent effect as well as the substituent effect was studied in the course of further measurements, which are compiled in Fig. 3. It can be seen, that the decomposition is appreciable slower for 4, and it varies only slightly with the H_2SO_4 -concentration. A comparison of curves 3 and 5 for 4 at the same H_2SO_4 -concentration (3 M) shows, that the rates are much faster in 80 vol% CH_3CN . Table 1 includes also a previous result in 85% H_2SO_4 (entry No 13⁸¹) and with other acids.

Fig. 2 Kinetic curves of the disproportionation of **1** (6 mM) in 80 vol% CH_3CN with various H_2SO_4 concentrations: 1: 1 M; 2: 2 M; 3: 3 M; 4: 5M

4 DISCUSSION

A dramatic effect of the acid concentrations c_A on k_2 is shown in Table 1, entries 1–4, in the case of the unsubstituted AQH_2 **1**, k_2 rises exponentially with c_A . However this holds only for 80 vol% CH_3CN , where this is attributed to the presence of the very strong acid $(\text{CH}_3\text{CNH})^+$ in the equilibrium. Acetic acid (entry 14) exhibits also a pronounced amplification of the acidity of the dissolved acids as usual. The strong effect of acetanhydride (entry 15) may be rationalized through the presence of an acetyl cation CH_3CO^+ .

There is also a substituent effect operative, as demonstrated with the anthrahydroquinone-2-sulphonic acid **4**. The rate constants k_2 are lower by a factor 10 with respect to **1** in 80 vol% CH_3CN , cf. entry 5. This may be a consequence of the electron withdrawing substituent, which retards the initial protonation step in the mechanism⁶⁾. The standard redox potential was 0.19 V vs. SHE, which is more positive than that of AQ (0.15 V vs. SHE).

Entries 6–8 in Table 1 demonstrate, that in water, the acidity effect is much lower in 1–5 M H_2SO_4 and in the other aqueous acids, cf. entries No 6–12. This is interesting for the application in batteries with aqueous acids. Even in 15.4 M H_2SO_4 , this effect is maintained (entry No 13). k_2 is relatively low, it would be 13 orders of magnitude higher, if the exponential rise of k_2 in 1–5 M H_2SO_4 in 80 vol% CH_3CN would be continued up to 15.4 M H_2SO_4 .

In batteries, electrodes of the second kind, represented by a mixture of AQ and carbon black, will be employed, cf.⁸⁾ As the solubility of AQ and AQH_2 is very low, $c_s = 2 \cdot 10^{-5}$ M in the diluted acids according to our analytical determination, the rate of the second order reaction (1) is appreciably lower according to $-dc/dt = k_2 c^2$. As $c_0 = 6$ mM, but $c_s \approx 0.01$ mM, it is a factor $(1/600)^2 = 1/360\,000$ with respect to the initial rate. Unfortunately, we do not know k_2 for acids of medium concentra-

Fig. 3 Kinetic curves of the disproportionation of **1** and **4** (6 mM) for various H_2SO_4 concentrations (M). 80 vol% CH_3CN : 1: **1** (1 M), 5: **4** (3 M), 6: **1** (3 M), 7: **1** (5 M); water: 2: **4** (1 M), 3: **4** (3 M), 4: **4** (5 M)

Table 1 Rate constants for the 2nd order reaction (1) measured at 20 °C

No	Educt	Solvent	Acid	c_A / M	$k_2 / dm^3 mol^{-1} h^{-1}$
1	<u>1</u>	80 vol% CH ₃ CN	H ₂ SO ₄	1	0.2
2	<u>1</u>	80 vol% CH ₃ CN	H ₂ SO ₄	2	4.4
3	<u>1</u>	80 vol% CH ₃ CN	H ₂ SO ₄	3	126
4	<u>1</u>	80 vol% CH ₃ CN	H ₂ SO ₄	5	1575
5	<u>4</u>	80 vol% CH ₃ CN	H ₂ SO ₄	3	12
6	<u>4</u>	H ₂ O	H ₂ SO ₄	1	3.0
7	<u>4</u>	H ₂ O	H ₂ SO ₄	3	4.0
8	<u>4</u>	H ₂ O	H ₂ SO ₄	5	6.5
9	<u>4</u>	H ₂ O	HB F ₄	2	2.0
10	<u>4</u>	H ₂ O	HB F ₄	4	2.7
11	<u>4</u>	H ₂ O	H ₂ F ₂	2	7.0
12	<u>4</u>	H ₂ O	H ₂ F ₂	20	9.0
13	<u>1</u>	H ₂ O	H ₂ SO ₄	15	$3.0 \cdot 10^4$ ⁶⁾
14	<u>1</u>	HOAc	H ₂ SO ₄	3	1035
15	<u>1</u>	Ac ₂ O	H ₂ SO ₄	1	$5.0 \cdot 10^6$

tions. But for 85% H₂SO₄, $k_2 = 3 \cdot 10^4$ was established formerly by three independent electrochemical methods⁶⁾. If we assume a small acid concentration effect in aqueous acids, cf. entries 6–13 in Table 1, the relevant values for the cycling experiment (Figure 1) should be not very much below this value. The μ drops linearly in the later stages of the cycling experiment, with a rate of about 1% per cycle as it is to be expected from $c_s = \text{constant}$. The "residence time" of the AQH₂ can be estimated to be about 1 hour per cycle. According to Vetter's theory⁹⁾, an electrode of the second kind in batteries, e.g. Pb/PbSO₄, works through the transport of free, dissolved species, e.g. Pb⁺⁺, within the pores of the electrode. The transport length is rather constricted. The following expression can be easily derived:

$$k_2 = \Delta m / (\Delta t c_s^2 M V) \quad (2)$$

where V = electrolyte volume and M = mole mass of AQH₂. With $\Delta m / \Delta t = 0.013$ g/h, $c_s = 2 \cdot 10^{-5}$ M, see above, and $V = 0.2$ l, $k_2 \approx 10^6$ l

mol⁻¹ h⁻¹ is obtained, which is even somewhat higher as the evaluation given above. In conclusion, substituted anthraquinones must be developed with a lower k_2 ⁴⁾.

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REFERENCES

- 1) K. J. Vetter, *Z. Elektrochem.*, **56**, 797 (1952).
- 2) H. Alt, H. Binder, A. Köhling and G. Sandstede, *J. Electrochem. Soc.*, **118**, 1950 (1971).
- 3) F. Beck, T. Boinowitz, H. Krohn, U. Tormin and E. Ther, *Mol. Cryst., Liq. Cryst.*, **245**, 177 (1994).
- 4) German Pat. Appl. 43 33 040 (30.9.1993), I. Barsukov.
- 5) M. A. Matthews, *J. Chem. Soc. (London)*, **1926**, 237.
- 6) F. Beck and G. Heydecke, *Ber. Bunsenges. Phys. Chem.*, **91**, 37 (1987).
- 7) D. R. Dimmel and D. Shepard, *J. Org. Chem.*, **47**, 26 (1982).
- 8) V. V. Matveev, N. V. Korneev, V. Z. Barsukov and N. B. Ilyuk, *J. Power Sourc.*, (1994), in press.
- 9) K. J. Vetter, *Chem.-Ing.-Tech.* **45**, 213 (1973).