Kurze Mitteilungen

The acid dissociation constants of mellitic acid *

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Abstract

The acid dissociation constants of mellitic acid were evaluated at 25 °C from potentiometric titrations in aqueous solutions of the constant Na^+ molarity 3 M consisting preponderantly of $NaClO_4$. The obtained values are summarized in the table.
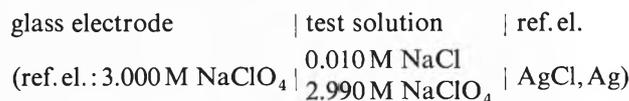
Current work on the protolytic behaviour and the ligand properties of fulvic acids lead us to test the chosen experimental method using mellitic acid (H_6B, benzenehexacarbonic acid) as a model substance. The obvious difficulties encountered in studies with polyprotic acids of medium strength are:

a) the control of the activity coefficients of the resulting anionic species,

b) the elimination of the liquid junction potential in solutions of high acidity.

It was thus decided to perform a series of potentiometric titrations in solutions of the constant Na^+ molarity 3 M.
Solutions S 1 ($[H_6B]_{tot} = A$ M, $[H^+] = H$ M, $[Na^+] = 3.000$ M, $[ClO_4^-] = 3.000 + H)$ M) were titrated at 25 ± 0.5 °C with solutions S 2 ($[OH^-] = B$ M, $[Na^+] = 3.000$ M, $[ClO_4^-] = (3.000 - B)$ M). The determination of K_{a_1} required high values for both A (0,85) and H (0.20) whereas low values for A (0.03) were necessary for the upper range of the titration curve to prevent

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the precipitation of Na_6B. After each addition of S 2, the prevailing equilibrium concentration h of hydrogen ions was mesured using the cell

glass electrode	| test solution	| ref.el.
(ref.el.: 3.000 M $NaClO_4$ |	0.010 M NaCl 2.990 M $NaClO_4$	| AgCl,Ag)

The e.m.f. was found to follow the equation

$E = E^0 + 59.157 \log [H^+] - 3.69 [H^+]$.

The average number Z of dissociated protons is obtained from the charge condition

$$Z = \frac{\Sigma (6\text{-}n) [H_n B^{(6\text{-}n)-}]}{A} = ([Na^+] + [H^+] - [ClO_4^-] - \frac{K_w}{[H^+]})/A$$

($K_w = 10^{-14.22}$, 3 M $NaClO_4$, 25 °C [1]).

Z and the stepwise acidity constants are related by the equation

$$Z = (1 - Z) K_{a_1} h^{-1} + (2 - Z) K_{a_1} K_{a_2} h^{-2} + \ldots$$
$$+ (6 - Z) K_{a_1} K_{a_2} \ldots K_{a_6} h^{-6}.$$

On the basis of 53 data pairs (Z, h) the acidity constants were computed using a general non linear least square program [2].
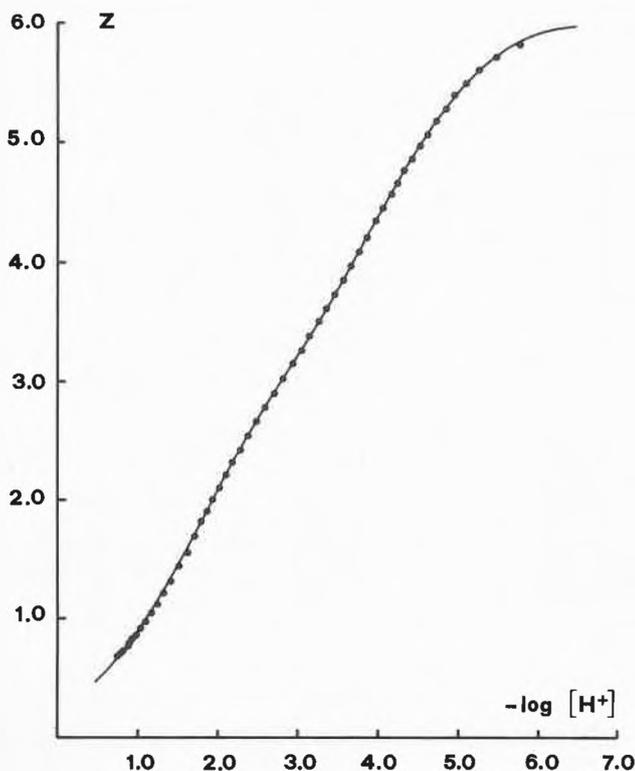The results are presented in table 1. The observed and calculated titration curves are shown in the figure 1.

Figure 1: Titration of mellitic acid: Z as a function of log [H⁺]. The full drawn curve was calculated with the constants given in the table 1.

The results of the present work indicates that mellitic acid is considerably stronger than concluded by *Maxwell* and *Partington* [3]. The large difference between

Table 1: Acid dissociation constants of mellitic acid

Present work $(I = 3\,M,\ T = 25\,°C)$	*Maxwell* and *Partington* [3] $(I = 0.03\,M,\ I = 25\,°C)$
$\log K_1 = -0.636 \pm 0.02\,*$	$\log K_1 = -1.40$
$\log K_2 = -1.66 \pm 0.03$	$\log K_2 = -2.19$
$\log K_3 = -2.25 \pm 0.03$	$\log K_3 = -3.31$
$\log K_4 = -3.32 \pm 0.03$	$\log K_4 = -4.78$
$\log K_5 = -4.07 \pm 0.03$	$\log K_5 = -5.89$
$\log K_6 = -5.03 \pm 0.03$	$\log K_6 = -6.96$

* 95% confidence limit

our results and the previous work may partially be attributed to the fact that solutions of high ionic strength favour the formation of charged species. The satisfactory precision of the obtained values seems to confirm the suitability of the chosen experimental approach.

Experimental:

Mellitic acid *(Fluka,* purity $\geqslant 99\%$) was recrystallized three times from HNO_3 (65%).

Literature

1 G. *Biedermann* and L. G. *Sillén:* Arkiv Kemi 5 (1952) 425.
2 R. E. *Mesmer* and Ch. F. *Baes:* The Hydrolysis of Cations, John Wiley & Sons, New York 1976.
3 W. R. *Maxwell* and J. R. *Partington:* Trans. Faraday Soc. *31* (1935) 922; *33* (1937) 670.

Heterogeneous and Homogeneous Quenching of $(^3CT)\,Ru(Bipy)_3^{2+}$ as Observed in a Photogalvanic Cell *

Preliminary communication

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Abstract

$(^3CT)\,Ru(bipy)_3^{2+}$ generated by light irradiation, is quenched heterogeneously by a gold electrode, yielding $Ru(bipy)_3^+$ which can be reoxidized at the counter-electrode to $Ru(bipy)_3^{2+}$. The current-yield is decreased by O_2 which acts as an energy transfer quencher, but it is strongly increased by Fe^{3+} which quenches $(^3CT)\,Ru(bipy)_3^{2+}$ by an electron transfer mechanism.

In the present communication we report on a photogalvanic effect which is due to a direct electron transfer

process between an excited state transition metal complex and the metal electrode. The complex used is tris-(2,2'-bipyridine) ruthenium (II) which has as its lowest excited state a charge transfer triplet state $(^3CT)\,Ru(bipy)_3^{2+}$ emitting at 610 nm with an emission lifetime of ca. 650 ns. [1] The cell used for the experiments is shown in fig. 1.

Light from an argon-ion laser or from a tungsten lamp is shone perpendicularly onto the surface of a bright gold foil electrode (1.4 cm × 4 cm) which is placed in a flat part of the apparatus (shown in side view in fig. 1). The wall to wall distance is approximately 0.5 mm and the thickness of the gold foil is 0.2 mm giving an average flow rate of the solution of ca. 50 cm/s between the
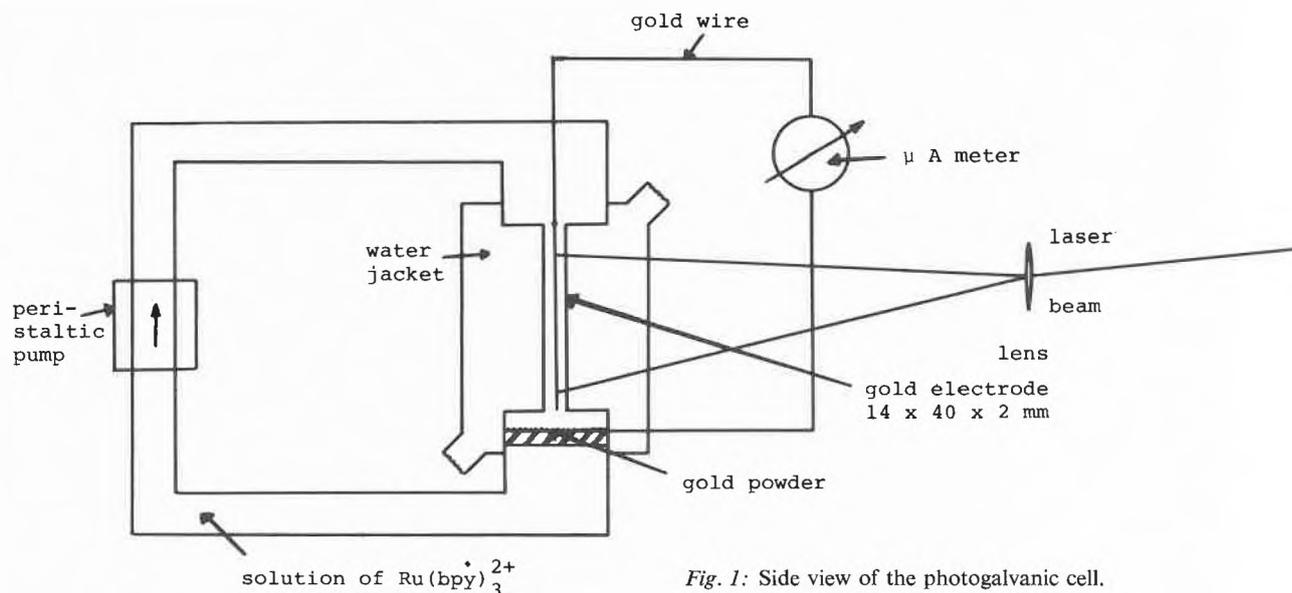
Fig. 1: Side view of the photogalvanic cell.

electrode and the wall. The solution containing 10^{-3} M Ru(bipy)$_3^{2+}$ in acid solution (e.g., HCl 0.5 M) is circulated by a peristaltic pump from the illuminated electrode downwards through a porous electrode made up of gold-powder with 0.01 mm particle size. The cell compartment temperature is maintained at 21 °C using a water jacket. The d.c. resistance between the two electrodes is ca. 7000 Ω. The laser beam is defocussed to an area of about 1 cm² on the surface of the electrode.
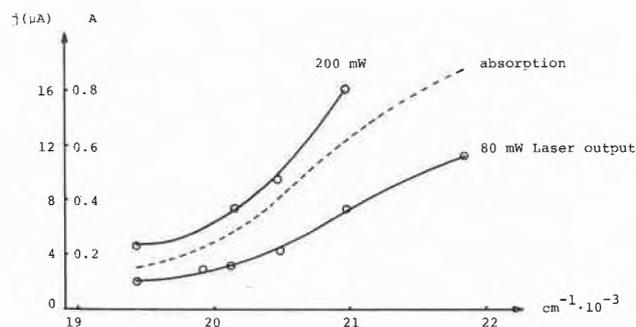
Fig. 2: Plot of photocurrent vs. wavenumber. The light absorption (----) for Ru(dipy)$_3^{2+}$ is also given.

Illumination of the electrode results in an electrical current if the cell is short-circuited with a galvanometer between the two electrodes. A plot of current vs. wavelength of incident radiation is shown in fig. 2 for successive lines of the argon-ion laser at different power levels. Together with these curves, the absorption spectrum of Ru(bipy)$_3^{2+}$ is also given in fig. 2. This suggests proportionality $j(\tilde{\nu}) = c \cdot p \cdot \varepsilon(\tilde{\nu})$ where c is a proportionality constant, $\tilde{\nu}$ the wave number of incident radiation, p its power, and $\varepsilon(\tilde{\nu})$ the molar absorption coefficient. Using 36 values for $j(\tilde{\nu})$, a coefficient of correlation for the proportionality relationship of $r = 0.94$ is obtained. The general scheme in which the

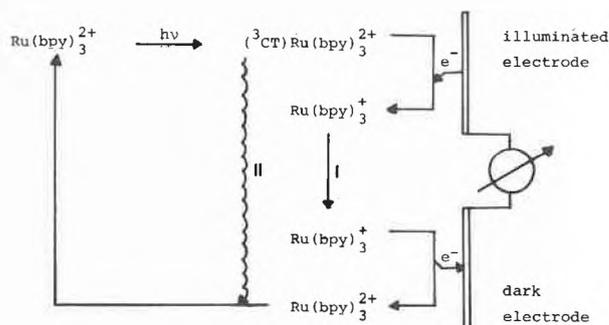observed phenomena can be interpreted is the following (fig. 3):

Fig. 3: General reaction schema.

The process yielding the electrical current through the cell is the *heterogeneous quenching* reaction

$$(^3CT)\,Ru(bipy)_3^{2+} + eQ \rightarrow Ru(bipy)_3^{+} + Q$$

where the solid electrode (eQ) acts as a charge transfer quencher (donor). A deactivation by oxidative quenching

$$(^3CT)\,Ru(bipy)_3^{2+} + Q \rightarrow (^3CT)\,Ru(bipy)_3^{3+} + eQ$$

can be excluded on grounds of the polarity of the cell. One can estimate that, in the present system, process II, which deactivates the excited complex through a radiative or a thermal process, is about 10^5 times more probable than the electrode process I, and the current-yield is therefore very low. Nevertheless, the electrode process can be easily detected.

The current of the cell depends on the concentration of dissolved molecular oxygen. If the solution is flushed with N₂, the current-yield is higher than in air-saturated solutions. An increase in osygen pressure to 1 atm decreases the current to $\sim 50\%$ of the value

obtained under the same experimental conditions except that the cell is purged with pure N_2. This change of the current is reversible. Molecular O_2 is known to act as an energy transfer quencher towards (^3CT) $Ru(bipy)_3^{2+}$ forming $(^1\Delta)O_2$ [2]. This homogeneous quenching reaction therefore competes with the heterogeneous quenching at the electrode surface, reducing thereby the current-yield of the cell. Contrary to molecular oxygen, Fe^{3+} acts as a very efficient charge-transfer-quencher [3], according to (1).

$$(^3CT)Ru(bipy)_3^{2+} + Fe^{3+} \rightarrow Ru(bipy)_3^{3-} \; Fe^{2+} \qquad (1)$$
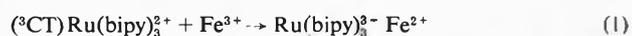
The electrode process is [4] $Ru(bipy)_3^{3+} + e \rightarrow Ru(bipy)_3^{2+}$ and the Fe^{2+} is reoxidized at the counter electrode to Fe^{3+}. The polarity of the cell is not changed but the current yield is strongly increased by adding Fe^{3+}, since the charge transfer process is now a homogeneous one. Competing with the electrode process which now takes place with a ground state species is reaction (2).

$$Fe^{2+} + Ru(bipy)_3^{3+} \rightarrow Fe^{3+} + Ru(bipy)_3^{2+} \qquad (2)$$
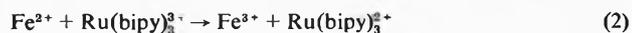
This is a relatively slow process [3] and therefore not very effective in decreasing the concentration of $Ru(dipy)_3^{3+}$. Addition of Fe^{2+} to the solution decreases the current because it increases the rate of reaction (2).

Experiments with other Ru-complexes are promising in that they indicate the possibility of increasing further the quantum yield of the process.

Information about mechanisms of the electrode processes, including electrode kinetics, can be obtained when a chopped beam is used. With this technique, the sensitivity can be strongly increased using a phase sensitive amplifier. Preliminary experiments with this apparatus corroborate all the conclusions drawn from the d.c. measurements and have given already a wealth of kinetic information. The sensitivity of the cell has reached the stage, where the effect of illuminating the electrode with the light of *one* ordinary candle can be detected.

Literature

1   *R. Bensasson, C. Salet* and *V. Balzani:* J. Amer. Chem. Soc., *98* (1976) 3722.
2   *J. N. Demas, D. Diemente* and *E. W. Harris:* J. Amer. Chem. Soc., *95* (1973) 6864.
3   *C.-T. Lin, W. Böttcher, M. Chan, C. Creutz* and *N. Sutin:* J. Amer. Chem. Soc., *98* (1976) 6536.
4   *C.-T. Lin* and *N. Sutin:* J. Phys. Chem., *80* (1976) 97.