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ONE-ELECTRON REDUCTION OF PYRYLIUM SALTS

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Abstract—The polarographic reduction of 2,4,6-trimethylpyrylium salts is a one-electron process, as shown by the slope of the wave and by microcoulometry. The half-wave potential is pH-independent. The reduction product is a dimer, which may be obtained more conveniently by chemical reduction with zinc dust.

IN a previous paper,[1] the half-wave potentials for the electro-reduction of several alkyl- and phenyl-substituted pyrylium salts was reported. The present paper describes further results obtained with 2,4,6-trimethylpyrylium salts, concerning the number of electrons involved in the reduction process, the influence of pH, and the nature of the reduction product.

Determination of the number of electrons involved

By measuring the slope of the diffusion current of 2,4,6-trimethylpyrylium perchlorate (in 10^{-3} M aqueous solution with acetate buffer at pH = 2·32), as indicated in Fig. 1, an intercept of 96 mV is obtained, hence the number n of electrons involved in the reduction process is:[2]

$$n = 100{\cdot}7/96 = 1{\cdot}04$$

A similar value is obtained from the difference $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (cf. Fig. 1), the result being in this case:

$$n = 0{\cdot}0564/(0{\cdot}923 - 0{\cdot}873) = 1{\cdot}12$$

While the previous method requires the reversibility of the electroreduction process, the microcoulometric method at constant potential does not involve this assumption. A volume v = 0·4 ml of aqueous solution of 2,4,6-trimethylpyrylium perchlorate ($C_0 = 10^{-3}$ M) was used with a dropping mercury electrode in an equipment constructed after Stromberg.[3] The decrease of the limiting current gave an almost linear plot of log (i_0/i) versus time, with a mean slope K = 12,400 sec (Fig. 2). The initial limiting current was $i_0 = 7{\cdot}4\ \mu$A. These values give:

$$n = Ki_0/222\ C_0V = 1{\cdot}03$$

These two methods indicate therefore that one electron takes part in the reduction. Recently, Feldman and Winstein[4] found that 2,4,6-trimethylpyrylium perchlorate has $E_{\frac{1}{2}} = -0{\cdot}85$ V vs. S.C.E. in 0·05 M acetate buffer in agreement with our results reported previously;[1] with the assumption that diffusion coefficients of the 2,4,6-trimethylpyrylium and tropylium cations are identical, the comparison of the diffusion currents of these cations also indicated that the reduction of 2,4,6-trimethylpyrylium is a one-electron process.[4] Thus the electroreduction differs fundamentally from

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[1] E. Gîrd and A. T. Balaban, *J. Electroanal. Chem.* **4**, 48 (1962).
[2] M. V. Stackelberg, *Polarographische Arbeitsmethoden* p. 282. W. de Gruyter Verlag, Berlin (1950).
[3] A. Stromberg and T. M. Markacheva, *Zhurn. Fiz. Khim.* **28**, 671 (1954).
[4] M. Feldman and S. Winstein, *Tetrahedron Letters* 853 (1962).

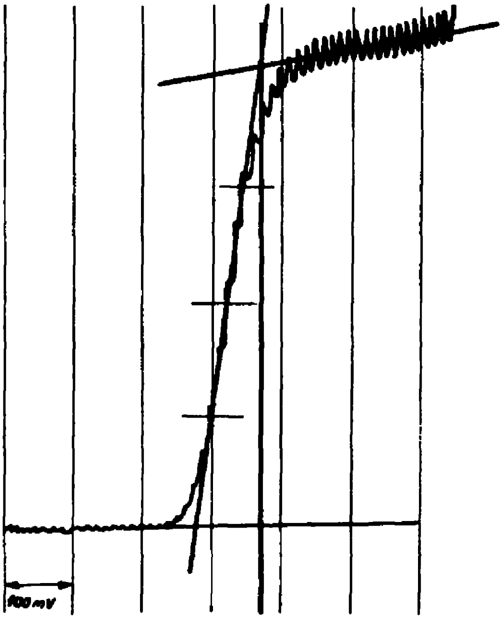

FIG. 1. Polarogram of 2,4,6-trimethylpyrylium perchlorate (10^{-3} M in acetate buffer at pH 2·32).

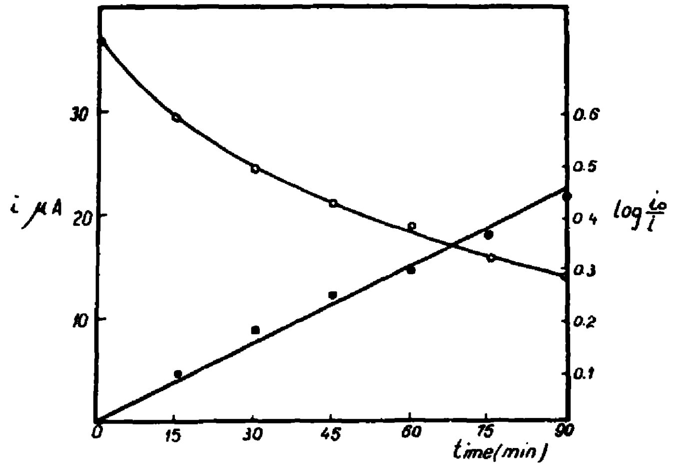

FIG. 2. Variation with time of diffusion current in the microcoulometric determination (○ ○) and of log (i_0/i) (● ●) (10^{-3} M, in acetate buffer at pH 2·32, volume of the solution 0·4 ml).

the chemical reduction of pyrylium salts by sodium borohydride which is a two-electron process.[5]

Effect of pH variation

Up to pH values of ca. 5, acetate buffers do not react with 2,4,6-trimethylpyrylium salts. Polarograms of aqueous solutions of 2,4,6-trimethylpyrylium perchlorate ($8 . 10^{-4}$ M) in sodium acetate–hydrochloric acid buffers (containing $4 . 10^{-4}$% methylene blue as maximum suppressor) showed no variation of the half-wave potential (Fig. 3) in the pH range 0·65 to 4·19: $E_{\frac{1}{2}} = 855 \pm 2$mV vs. S.C.E. Identical values were obtained with the chloroferrate[6] and iodide[7] of the same cation. Hence no proton is involved in the electroreduction process which is to be depicted simply as:

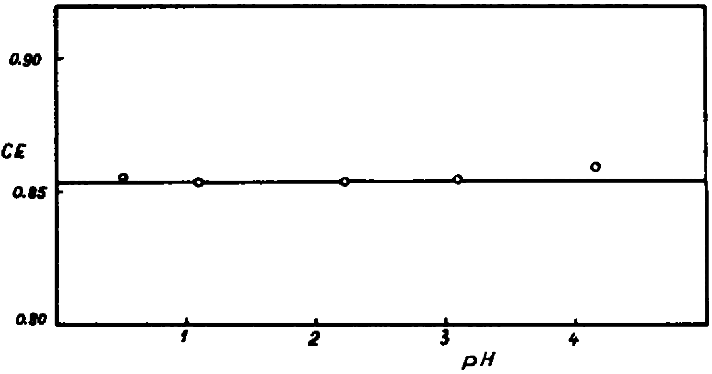

FIG. 3. Independence of half-wave potential of 2,4,6-trimethylpyrylium perchlorate on pH value ($8 . 10^{-4}$ M in sodium acetate—hydrochloric acid buffers).

$$C_8H_{11}O^{\oplus} + e^{\ominus} \rightarrow C_8H_{11}O\cdot \rightarrow \tfrac{1}{2}C_{16}H_{22}O_2$$

Thus pyrylium salts parallel tropylium salts in their behaviour.[8]

Nature of this reduction product

By treating an aqueous solution (the same result is obtained in ethanol) of 2,4,6-trimethylpyrylium tetrachloroferrate $C_8H_{11}O^{\oplus}$ $FeCl_4^{\ominus}$ (the perchlorate is so slightly soluble and the iodide is not available in large amounts; both yield, however, the same product as the chloroferrate) with zinc dust in the presence of ether at room temperature, a rapid reaction takes place. By evaporation of the ethereal layer, a white readily crystallizable compound m.p. 119·5–120° is obtained. Elementary analysis and molecular weight determination agree with the formula $C_{16}H_{22}O_2$ of a dimer obtained by one-electron reduction. The identity of this compound with the electroreduction product was shown by extracting with carbon tetrachloride the aqueous solution of the perchlorate (acidified with hydrochloric acid) which had been electrolyzed for 2–3 hours with a platinum anode and a mercury cathode pool separated

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[5] A. T. Balaban, G. Mihai and C. D. Nenitzescu, *Tetrahedron* **18**, 257 (1962).

[6] A. T. Balaban and C. D. Nenitzescu, *J. Chem. Soc.* 3553 (1961).

[7] A. T. Balaban, *C. R. Acad. Sci. Paris*, **256**, 4041 (1963).

[8] P. Zuman and J. Chodkovsky, *Coll. Czech. Chem. Comm.* **27**, 759 (1962) and other references therein.

by a Gooch–4 diaphragm. The carbon tetrachloride extract had, after drying over calcium chloride, an IR spectrum identical with that of the $C_{16}H_{22}O_2$ dimer. IR and NMR spectra of this compound are identical with those of 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-4H-pyran obtained from 2,4,6-trimethylpyrylium salts and sodium salts of cyclooctatetraene, benzophenone or anthracene.[9] However, in the present reduction with zinc the yield is quantitative, while in the reduction with organic anions the optimum yield was 50%. The actual value of the enol enter IR stretching band is 1714 cm^{-1} instead of 1705 cm^{-1} as reported.[9] The hexamethylbipyran presents in cyclohexane no absorption maximum above 215 $m\mu$. Although it may be sublimed in high vacuum, it dehydrates exothermally on distillation under reduced pressure above 165°. The distillation product affords a crystalline compound with m.p. 134° presenting strong bands at 1650 and 1670 cm^{-1} and UV maxima at 241 and 312 $m\mu$ ($\lg \epsilon$ 3·95 and 4·25) in cyclohexane. From the reaction mixture obtained by acid treatment of the dimer, a crystalline isomerized product, m.p. 139°, isolated by distillation, presenting a strong band at 1665 cm^{-1} and maximum in cyclohexane at 223 $m\mu$ ($\lg \epsilon$ 3·96). The structure of these products is under investigation.

Similar reduction with zinc of 2,4,6-triphenylpyrylium perchlorate affords a product with m.p. 110°, presenting bands at 1667 and 1690 cm^{-1} (substitution of methyl groups by phenyl is expected to lower the enol ether absorption frequency[9]) and one maximum at 248 $m\mu$. This compound, presumably hexaphenylbypyran, could not be obtained by reduction with organic anions;[9] its solution in toluene decolorizes diphenylpicrylhydrazyl on heating.

The reversibility of the reductive dimerization was shown by treating the hexamethylbipyran in aqueous dioxane with chromium trioxide and perchloric acid; the mixture becomes hot and on cooling deposits 2,4,6-trimethylpyrylium perchlorate in 30–50% yield. Electroöxidation of the same hexamethylbipyran in $KClO_4$-containing acetonitrile on a rotating platinum anode with a silver nitrate reference electrode 10^{-2}M shows a di-electronic wave with $E_{\frac{1}{2}} = +0{\cdot}88$ V; by adding ether to the electroöxidized acetonitrile solution, a precipitate containing trimethylpyrylium perchlorate (identified by IR spectrum) was obtained. A full account on the dissociation and oxidation of bipyrans will be published later.

The exclusive linking of the two pyran radicals in γ-position is in marked contrast to reactions of pyrylium salts with nucleophiles where α-addition predominates. This is probably due to the enhanced stability of the symmetric 2,4,6-trimethyl-4H-pyran-4-yl resonance structure.

EXPERIMENTAL

Polarographic determinations. A Heyrovsky-polarograph LP-55 and an H-cell with external saturated calomel electrode were used. All potentials are therefore given in V vs. S. C. E. Characteristics of the capillary are given in the previous note.[1] The microcoulometric cell was identical with that described by Stromberg[8] and the capillary had $t_1 = 0{\cdot}7$ sec, $m = 10{\cdot}62$ $mg.sec^{-1}$ at $h = 15$ cm. The pH measurements were performed by means of an Orion pH-meter with glass electrode. Sodium acetate–HCl buffers were used throughout, since phosphate buffers apparently react with 2,4,6-trimethylpyrylium salts. Purified N_2 was used for deaeration.

Pyrylium salts were prepared as described previously:[6] the perchlorate from t-butanol, acetic anhydride and 70%-perchloric acid, and the tetrachloroferrate from the perchlorate, by dissolving it in cold conc. HCl and adding a solution of $FeCl_3$ in HCl.

Reduction with zinc. A solution prepared by dissolving 32 g (0·1 mole) 2,4,6-trimethylpyrylium

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[9] K. Conrow and P. C. Radlick, *J. Org. Chem.* **26**, 2260 (1961).

tetrachloroferrate in 100 ml cold water was treated, with external cooling to 0°, with 100 ml ether and 6·5 g (2 equiv.) Zn dust added with efficient stirring in portions during 20 min. After filtration, the ethereal layer was dried (K_2CO_3) and evaporated (red. press.). The crystalline residue (12 g, 100% yield) was recrystallized from methanol or ethanol; m.p. of the colourless product 119·5–120° (Found: C, 78·15; H, 9·21. $C_{16}H_{22}O_2$ requires: C, 78·02; H, 9·02%). Mol wt found (micro-Rast) 256; required by $C_{16}H_{22}O_2$: 246. IR spectrum (in CCl_4 and CS_2): 807 vs, 877 m, 905 ms, 977 m, 1057 m, 1085 m, 1160 vs, 1232 m, 1294 vs, 1365 m, 1380 s, 1437 m, 1452 ms, 1670 m, 1714 vs, 2845 w, 2863 m, 2877 ms, 2921 s, 2945 ms, 2963 s, 2990 ms, 3050 m.

This dimer yields a 2,4-DNP and was oxidized by NaOBr but the respective derivatives could not be isolated in a pure state as they are decomposed by acids. Hydroxylamine and semicarbazide, as well as sodium in alcohol or $LiAlH_4$ do not react. The catalytic hydrogenation (Pd–$CaCO_3$) resulted in the absorption of one mole H_2.

By heating 25 g of this compound in a Claisen flask, as soon as the melt reached 160–165° an exothermal reaction set in with formation of water. Distillation afforded ca. 12 g product, b.p. 150–165°/4 Torr, which slowly deposited crystals, m.p. 133–134° after recrystallization from dil. methanol. (Found: C, 83·42; H, 9·12. $C_{16}H_{20}O$ requires: C, 84·16; H, 8·83%). The IR spectrum has remarkably few bands: 870 mw, 955 mw, 1038 w, 1216 s, 1320 m, 1330 ms, 1358 ms, 1381 ms, 1395 s, 1458 m, 1490 mw, 1570 s, 1585 s, 1650 s, 1670 s, 2870 m, 2925 ms, 2935 ms, 2970 s, 3010 mw.

By introducing 25 g dimer gradually into a hot mixture of 100 ml ethanol and 3 ml conc. HCl, an exothermal reaction takes place. After refluxing 1 hr, the solution was diluted with 300 ml water and extracted with ether. The ethereal layer was washed (Na_2CO_3 aq), dried ($MgSO_4$) and evaporated. Fractionation of the residue yielded a yellowish liquid, b.p. 135–145°/2 Torr which slowly crystallized, m.p. 139° (from dil. methanol). (Found: C, 77·63; H, 9·53. $C_{16}H_{22}O_2$ requires: C, 78·02; H, 9·02; $C_{16}H_{24}O_2$ requires: C, 77·37; H, 9·74%). IR spectrum: 597 m, 803 m, 871 s, 898 ms, 948 s, 1082 m, 1110 m, 1126 ms, 1153 s, 1182 ms, 1237 ms, 1251 s, 1280 s, 1320 ms, 1365 ms, 1384 vs, 1440 s, 1450 s, 1665 vs, 2870 ms, 2910 s, 2932 s, 2993 s, 2970 vs, 3035 w.

Reduction of 2,4,6-triphenylpyrylium perchlorate with Zn in ethanol also afforded a dimer, m.p. 110° (from ethanol). (Found: C, 89·30; H, 5·49. $C_{46}H_{34}O_2$ requires: C, 89·29; H, 5·54%). The product has in cyclohexane a band at 248 mμ (lg ε 4·41), and presents the following IR bands: 700 vs, 912 w, 970 mw, 1030 m, 1035 sh, 1077 mw, 1184 m, 1218 ms, 1241 mw, 1283 mw, 1356 mw, 1453 ms, 1502 ms, 1585 mw, 1606 ms, 1667 m, 1690 ms, 3030 m, 3060 ms, 3085 mw.

Acknowledgement—NMR spectra were kindly taken in CCl_4 10% solution with a 40 Mc Perkin-Elmer spectrometer by Dr. G. R. Bedford and Prof. A. R. Katritzky to whom our thanks are given.