585. *The Polarographic Reduction of Xanthone and Methoxyxanthones.*

By W. E. WHITMAN and L. A. WILES.

Xanthone and its monomethyl ethers are polarographically reducible in a one-electron reversible process.

THE markedly basic character of polycyclic ketones in which the carbonyl group is situated in the *peri*-position to methoxyl has been the subject of a number of investigations. For methoxyanthraquinones in strongly acid solution Wiles [1] showed that when both carbonyl groups have *o*-methoxy-groups (OMe at 1, 4, 5, or 8) no polarographic reduction wave was obtained, but when one (or both) of the carbonyl groups had no methoxyl so placed the compound was reducible irreversibly.

The Reduction of Methoxyxanthones.—The present work was undertaken to determine whether all other polycyclic *o*-methoxy-ketones are reducible in solutions of low pH. The result for 1-methoxyxanthone ($E_{\frac{1}{2}} = -0{\cdot}77$ v) shows that this is not so. This difference between xanthones and anthraquinones led to an investigation of the reduction mechanism and the effect of differently situated methoxy-groups on the half-wave potentials of xanthones.

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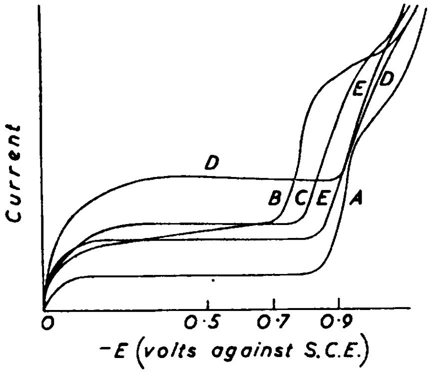
[1] Wiles, *J.*, 1952, 1358.

The polarography of xanthone at pH 1·0—12·7 has been examined.[2] A single reduction wave was observed but the mechanism was not closely investigated. Flavone and its monosubstituted derivatives give two reduction waves in acid solution, while flavanones show only one wave. It has been postulated [3] that these are one-electron reactions, but the question of the reversibility or otherwise of the reactions was not settled.

The following Table and the Figure give the results for xanthone and its monomethyl ethers.

	Compound	Half-wave potential	Wave height × sensitivity^{-1} *
A	Xanthone	−0·91	470
B	1-Methoxyxanthone	−0·77	450
C	2-Methoxyxanthone	−0·88	480
D	3-Methoxyxanthone	−0·97	320
E	4-Methoxyxanthone	−0·92	420

* 1 Unit of wave height = 4·45 × 10^{-6} A. Galvanometer sensitivity = 1/20.

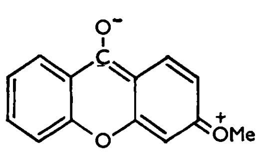


Polarograms for xanthone and its monomethyl ethers.

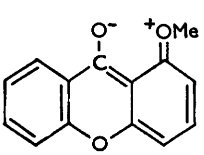
Discussion of Results.—Methoxyl groups *ortho* and *para* to the carbonyl group markedly influence the ease of reduction. 3-Methoxyxanthone is the most difficult to reduce, and this is understandable from the mesomeric character of the methoxy-group. The resonance contribution of (I) diminishes the positive charge on the carbon of the carbonyl group, and the addition of an electron at the electron-deficient carbon atom will be more difficult. A similar effect has been reported in the polarography of benzophenones in which the half-wave potential is made more negative by substitution of methoxyl in the *para*-positions.[4]

For 1-methoxyxanthone the *ortho*-quinonoid structure (II) is possible and if this contributes appreciably the compound should also be reducible with difficulty. The reverse is, however, the case. The inductive action of the methoxyl group is oppositely directed to its mesomeric influence and its greatest effect on the carbonyl group will be from the α-positions. It is, however, quite unlikely that the inductive effect will dominate the mesomeric effect. We have obtained evidence for structure (I) and the lack of importance of structure (II) from the observation that there is no decrease in the infrared stretching frequency of the carbonyl group in 1-methoxyxanthone compared with the value for xanthone, but in 3-methoxyxanthone there is an appreciable diminution.[5] It is

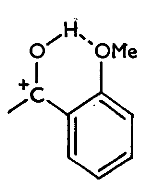
(I)



(II)



(III)



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[2] Day and Biggers, *J. Amer. Chem. Soc.*, 1953, **75**, 738.
[3] Geissman and Friess, *ibid.*, 1949, **71**, 3893.
[4] Brockman and Pearson, *ibid.*, 1952, **74**, 4128.
[5] Wiles and Thomas, unpublished observations.

suggested that the ready reduction of 1-methoxyxanthone must be attributed to the enhanced basic strength of this compound. Protonation of the carbonyl group in the acid medium confers a positive charge on the carbon atom, $>\overset{+}{\mathrm{C}}{=}\mathrm{OH}$, and hence will increase its attraction for electrons in the reduction process. A similar effect is to be noticed in those α-methoxyanthraquinones which are reducible.[1] In this earlier work it was supposed that the enhanced basic strength of ketones which have a *peri*-methoxyl group was due to hydrogen-bond formation as in (III). However, infrared spectroscopic measurements [6] show the carbonyl stretching frequency in salts of methoxyanthraquinones to be little changed from that of the parent methoxyanthraquinones, and it is unlikely that such bonding exists. Moreover, the earlier assumption that the polarographic reduction of 1-methoxyanthraquinone is at the carbonyl group in the 10-position must now be considered doubtful.

2- and 4-Methoxyxanthone, in which the methoxyl groups are not conjugated with the carbonyl group, have $E_{\frac{1}{2}}$ values which do not markedly differ from that of xanthone.

Mechanism of the Reduction.—The constancy of the product, wave-height × sensitivity^{-1}, for most of the xanthones is an indication that the reduction process is the same for each compound. The low value for 3-methoxyxanthone is due to the masking effect of the hydrogen discharge which, in the stock solution used, begins at about —0·95 v.

The following evidence shows clearly that, in strong acid, the reduction of xanthone and its monomethyl ethers is a one-electron, reversible process.

(i) Heyrovsky and Ilkovic [7] found that for reversible oxidation–reduction reactions a graph of the applied voltage (E) against $\log_{10}i/(i_d - i)$ (at any point on the polarographic wave i is the current produced by the applied voltage, and i_d is the diffusion current) gives, at 25°, a straight line of slope $0{\cdot}059/n$, where n is the number of electrons involved in the reaction. Gilbert and Rideal [8] have criticised the use of this relation for the determination of n, but as a test of reversibility it stands.

Polarograms obtained by manual operation of the instrument were recorded for 1- and 4-methoxyxanthone, and the plots of the above quantities gave, in both cases, straight lines of slope 0·060, indicating a one-electron reversible reduction.

(ii) The value of n can be determined from coulometry. Gilbert and Rideal's method [8] uses only 0·3 ml. of 10^{-3}M-solution, and the data are obtained in 3 hr. with use of a simple apparatus. The rate of decrease of concentration of a substance being reduced at a mercury cathode is proportional to the diffusion current measured in arbitrary units of wave-height, h, and it is inversely proportional to n, whence $\mathrm{d}c/\mathrm{d}t = k_2h/nv\boldsymbol{F}$, where k_2 is the diffusion current (A) corresponding to a wave-height of one unit, and where v is the volume of the solution (in l.). It follows that $\mathrm{d}(\log h)/\mathrm{d}t = -k_2/2{\cdot}30n\boldsymbol{F}vk_1$, where $k_1 =$ concentration required to give a wave-height of one unit = concentration/initial wave-height.

The method was applied to a $0{\cdot}95 \times 10^{-3}$M-solution of 1-methoxyxanthone, in which $v = 3{\cdot}0 \times 10^{-4}$ l.; $k_2 = 8{\cdot}9 \times 10^{-8}$ A/unit. The measured values for h and t are given below. The initial and final values of h were found from photographic polarograms. The other two were read as the current difference between voltages of —0·7 and —0·9 v. From this, n = 1·1 electrons per molecule.

h	20·0	16·5	14·5	13·0
$\log_{10} h$	1·3010	1·2175	1·1614	1·1139
t (sec.)	0	3000	5400	7200

(iii) Ilkovic's equation $i_d = 607nD^{\frac{1}{2}}Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ was also applied to 1-methoxyxanthone, the following data being used: $i_d = k_2h = 1{\cdot}78 \times 10^{-6}$ A; $D = 3{\cdot}27 \times 10^{-6}$ cm.^{2} sec.$^{-1}$; $C = 0{\cdot}951$ millimole l.$^{-1}$; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}71$. The diffusion coefficient (D) was estimated as follows. Sen [9] measured the maximum radius of the anthraquinone molecule as 3·74 Å,

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[6] Wiles and Thomas, to be published.

[7] Heyrovsky and Ilkovic, *Coll. Czech. Chem. Comm.*, 1935, **7**, 198.

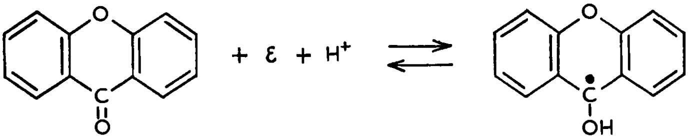
[8] Gilbert and Rideal, *Trans. Faraday Soc.*, 1951, **47**, 396.

[9] Sen, *Indian J. Phys.*, 1948, **22**, 347.

and the molecule of a methoxyxanthone will be roughly of the same size. It is approximately a flat disc for which Holmes [10] has derived the equation $D = \boldsymbol{RT}/12\eta r\boldsymbol{N}$, where η = viscosity of the solution = 0·0247 g. cm.$^{-1}$ sec.$^{-1}$. The value of D for 1-methoxyxanthone agrees reasonably with the value of $4·0 \times 10^{-6}$ cm.^{2} sec.$^{-1}$ for alizarin.[11]. From the above n = 1·0 electron per molecule.

(iv) In reversible reductions $E_{\frac{1}{2}}$ may vary linearly with pH, although this is not an entirely reliable criterion of reversibility. A study of 3-methoxyxanthone in buffered solutions of "apparent" pH 1·24, 4·80, and 8·00 gave $E_{\frac{1}{2}}$ values of —0·77, —1·22, and —1·42 v, and a plot of these values is linear.

The reversible reduction of the methoxyxanthones is in contrast to the irreversible process for methoxyanthraquinones. Geissman and Friess [3] suggest that the single-wave reduction of a flavone produces a free radical, and a similar reaction could occur with xanthones, the radical finally undergoing dimerisation :



The xanthenyl group is known to exercise a stabilising effect on free radicals.[12]

EXPERIMENTAL

A Cambridge Instrument Company polarograph giving photographic recordings of the current-voltage curves was used, and the technique employed did not differ materially from that used by Wiles.[1] The viscosities required for the Ilkovic equation were measured by an Ostwald viscometer.

1-Hydroxyxanthone was prepared by Michael's method,[13] and was methylated by using the process adopted for hydroxyanthraquinones.[1] 2-Hydroxyxanthone [14] had m. p. 235° (lit. 229—231°, 231°, 237°, 240°). 3-Hydroxyxanthone [14] gave the methyl ether, m. p. 129° (lit., 125—126°, 129°). 4-Hydroxyxanthone [14] gave the methyl ether, m. p. 176° (lit., 165°, 173°).

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[10] Holmes, " A Review of the Literature on Diffusion in Solution and the Estimation of the Particle Size from Diffusion Measurements." Manchester : British Cotton Industries Research Association, 1945.

[11] Furman and Stone, *J. Amer. Chem. Soc.*, 1948, **70**, 3055.

[12] Conant and Evans, *ibid.*, 1929, **51**, 1925.

[13] Michael, *Amer. Chem. J.*, 1883, **5**, 91.

[14] Kostanecki and Rutishauser, *Ber.*, 1892, **25**, 1648.

[15] Ullmann and Zlokasoff, *Ber.*, 1905, **38**, 2119.