[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# The Chemistry of Vitamin E. XXIX.[1] Studies of the Behavior of Compounds Related to Vitamin E at the Dropping Mercury Electrode

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A polarographic study has been made of compounds related to Vitamin E. It is known that hydroxychromans and hydroxycoumarans can be oxidized to corresponding paraquinones. This oxidation is irreversible and the paraquinones upon reduction yield hydroquinones, the latter reaction being reversible. In our work it was found that hydroxychromans and hydroxycoumarans under the proper conditions yield anodic waves. It was the purpose of this investigation to study the characteristics of these waves more in detail and to find the relation between the polarographically found half wave oxidation potentials of these compounds and the true oxidation potentials of the corresponding quinone–hydroquinone systems. The latter also can be determined with the dropping mercury electrode as has been shown by Müller and Baumberger[2] although it should be added that the potentials obtained at the zero current potential should be corrected for the residual current.[3]

## Experimental

The manual apparatus similar to that described by Kolthoff and Lingane[4] was used with the exception of the cell which was similar to that described by Lingane and Laitinen[5] but without a sintered glass disk. A 0.1 *N* potassium nitrate agar plug was used to make connection with a large external saturated calomel electrode.

The experiments were carried out in a water thermostat regulated to 25 ± 0.01°. In order to minimize vibrations, the bath was stirred by passing a current of air through the liquid.

The capillary used had the following characteristics. At a pressure of 62.7 cm. of mercury the drop time in 0.1 *N* potassium chloride solution was 3.68 sec., $m$ = 1.50 mg. sec.$^{-1}$ and $m^{2/3}e^{1/6}$ = 1.630. For 0.001 *M* thallous chloride in 0.1 *M* potassium chloride, a diffusion current of 4.56 microamperes was obtained, while the calculated value was 4.41.[4]

The buffers used in the experiments had the following compositions.

I. A mixture which was 0.1 *M* in anilinium perchlorate and 0.1 *M* in aniline in 50% methanol by volume; *p*H 3.56; resistance, 1050 ohms. Drop time of the capillary in this buffer was 3.7 sec.

II. A mixture which was 0.1 *M* in acetic acid and 0.1 *M* in sodium acetate in 50% methanol by volume; *p*H 5.40; resistance, 3260 ohms; drop time, 4.02 sec.

III. A mixture which was 0.0452 *M* in sodium acetate and 0.0095 *M* in acetic acid in 50% methanol by volume; *p*H 6.06; resistance, 1920 ohms; drop time, 4.04 sec.

IV. A mixture which was 0.02 *M* in monopotassium phosphate and 0.03 *M* in disodium phosphate in 50% methanol by volume; *p*H 7.97; resistance, 2650 ohms; drop time, 3.94 sec.

The *p*H of the buffers was measured by means of a hydrogen electrode in a cell similar to that used during the electrolysis.

The resistance of the buffers was determined by means of a conventional Wheatstone bridge apparatus under identically the same conditions as were used in measuring the current voltage curves. All half wave potentials given in this paper are corrected for *iR* and are referred to the saturated calomel electrode at 25°.

The drop time in each case was measured with an open circuit.

The residual current was measured for each buffer and was subtracted from the measured current. As an example the residual current of buffer II is given in Fig. 1. Air was removed by bubbling purified nitrogen through the solution for at least an hour. A trace of methyl red was always added to suppress maxima.

Compounds related to Vitamin E were prepared by methods given in the references. The various methyl quinones, already on hand, were purified by sublimation at atmospheric pressure. The corresponding hydroquinones were prepared by reducing the purified quinones with sodium hydrosulfite.

## Experimental Results

Substituted 6-hydroxychromans and 5-hydroxycoumarans yield anodic waves at the dropping electrode. These waves were determined in buffer I (aniline–anilinium perchlorate, *p*H 3.56). The current–voltage curves of the oxidation products, the para quinones, were determined in all four buffers mentioned in the previous section. To show that the polarographic method yielded reliable results, half wave potentials were determined for various methyl quinones and they were compared, after correcting for *iR*, with the standard potentials reported in the literature.

In Fig. 2 are given typical waves, uncorrected for residual current and *iR*, which were obtained with substituted 5,7,8-trimethyl-6-hydroxychromans. Figure 3 shows the same waves after correction for the residual current. Current–

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[1] Paper XXVIII, *J. Org. Chem.*, **6**, in press (1941).

[2] Müller and Baumberger, *Trans. Electrochem. Soc.*, **71**, 169, 181 (1937).

[3] Kolthoff and Orlemann, THIS JOURNAL, **63**, 664 (1941).

[4] Kolthoff and Lingane, *Chem. Rev.*, **24**, 1 (1939).

[5] Lingane and Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 504 (1939).

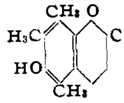
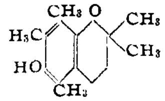
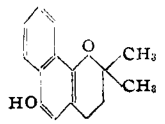
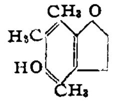
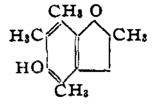
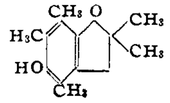
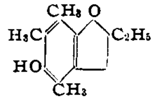
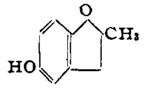
voltage curves obtained with 2,2,5-trimethyl-7,8-benzo-6-hydroxychroman were corrected only for the residual current. Figure 4 shows typical waves, corrected for the residual current, which were obtained with substituted 4,6,7-trimethyl-5-hydroxycoumarans.

Table I gives the values of the diffusion currents $i_d$ (corrected for $i_r$) and the half wave potentials $\pi_{1/2}$ against the saturated calomel electrode (corrected for $iR$).

TABLE I

ANODIC WAVES OF 6-HYDROXYCHROMANS AND 5-HYDROXYCOUMARANS IN BUFFER I

($p$H 3.6) at 25°

| Compound | Ref. | Concn. Molar | $i_d \times 10^6$ | $(i_d/C) \times 10^3$ | $\pi^1/_2$ (S. C. E.) |
|---|---|---|---|---|---|
|  | 6 | 0.000626 | 2.34 | 3.74 | +0.227 |
| | | .000939 | 3.49 | 3.72 | + .232 |
| | | .001252 | 4.64 | 3.70 | + .230 |
| | | | | Av. | + .230 |
|  | 7 | .0005 | 1.79 | 3.58 | + .232 |
| | | .0010 | 3.55 | 3.55 | + .234 |
| | | .0015 | 5.25 | 3.50 | + .231 |
| | | | | Av. | + .232 |
|  | 8 | .000438 | 1.88 | 4.29 | + .112 |
| | | .000900 | 3.94 | 4.38 | + .115 |
| | | .001350 | 6.07 | 4.50 | + .115 |
| | | | | Av. | + .114 |
|  | 8 | .000635 | 2.30 | 3.62 | + .218 |
| | | .000952 | 3.39 | 3.56 | + .218 |
| | | .001629 | 5.91 | 3.63 | + .215 |
| | | | | Av. | + .217 |
|  | 9 | .005 | 1.28 | 2.56 | + .219 |
| | | .0010 | 2.59 | 2.59 | + .219 |
| | | .0015 | 3.75 | 2.50 | + .221 |
| | | .000906[a] | 3.23[a] | 3.57[a] | + .218 |
| | | | | Av. | + .219 |
|  | 8 | .00052 | 1.93 | 3.71 | + .217 |
| | | .00102 | 3.79 | 3.70 | + .218 |
| | | .00141 | 5.14 | 3.65 | + .221 |
| | | | | Av. | + .219 |
|  | 10 | .00024 | 0.87 | 3.63 | + .214 |
| | | .00051 | 1.85 | 3.63 | + .214 |
| | | .000752 | 2.75 | 3.66 | + .213 |
| | | | | Av. | + .214 |
|  | 11 | The anodic wave occurs at too positive potentials to be measured with the dropping mercury electrode. | | | |

[a] A purified product was used.

From the results obtained it can be seen that the half wave potentials of 6-hydroxychromans differ from those of corresponding 5-hydroxycoumarans by approximately ten millivolts. This difference is significant and it offers a method of distinguishing between $p$-hydroxychromans and -coumarans. It has not been possible to distinguish between these two classes of compounds by means of differences in their ultraviolet absorption data.[12]

The diffusion current of the various compounds is proportional to the concentration in the range studied (between 0.0005–0.001 $M$) as can be seen from the fair constancy of the values of $i_d/C$.

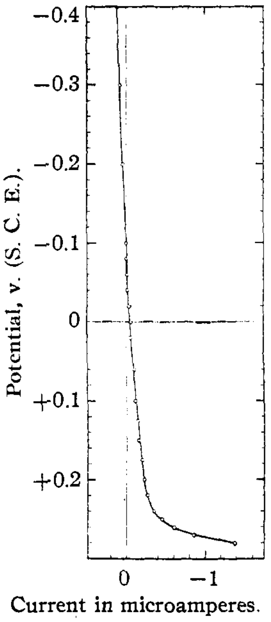


Fig. 1.—Residual current in buffer II.

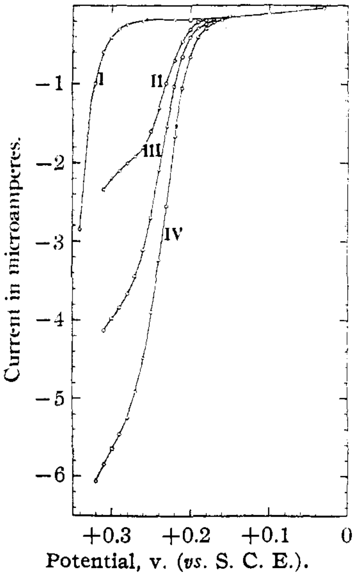


Fig. 2.—Substituted 5,7,8-trimethyl-6-hydroxychroman waves in buffer I, $p$H 3.56: I, buffer; II, buffer with 0.0005 $M$ chroman; III, buffer with 0.001 $M$ chroman; IV, buffer with 0.0015 $M$ chroman.

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(6) Prepared according to John and Gunther, *Ber.*, **72**, 1652 (1939).

(7) Smith, Ungnade, Hoehn and Wawzonek, *J. Org. Chem.*, **4**, 311 (1939).

(8) Smith, Wawzonek and Miller, *ibid.*, **6**, in press (1941).

(9) Smith, Ungnade, Hoehn and Wawzonek, *ibid.*, **4**, 305 (1939).

(10) Karrer, Escher and Rentschler, *Helv. Chim. Acta*, **22**, 1287 (1939).

(11) Smith, Hoehn and Whitney, THIS JOURNAL, **62**, 1863 (1940).

(12) See however, John, Dietzel and Emte, *Z. physiol. Chem.*, **257**, 173 (1939), who found noticeable differences in the absorption spectra of the corresponding allophanates.

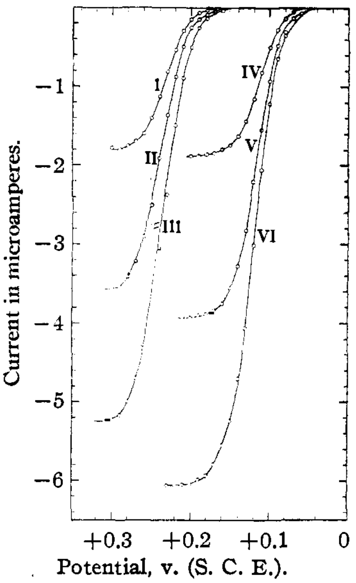

Fig. 3.—Waves (corr. for $i_r$) obtained for a substituted 5,7,8-trimethyl-6-hydroxychroman and for 2,2,5-trimethyl-7,8-benzo-6-hydroxychroman in buffer I: I, 0.0005 *M* chroman; II, 0.001 *M* chroman; III, 0.0015 *M* chroman; IV, 0.00044 *M* benzochroman; V, 0.0009 *M* benzochroman; VI, 0.00135 *M* benzochroman.

The effect of impurities upon the diffusion current can be seen from the values obtained for 2,4,6,7-tetramethyl-5-hydroxycoumaran. The first three values given were obtained with a sample melting at 126–127° while the fourth was obtained with a specimen melting at 130.5–131°. All other compounds used were either analytical samples or had melting points corresponding to those reported in the literature.

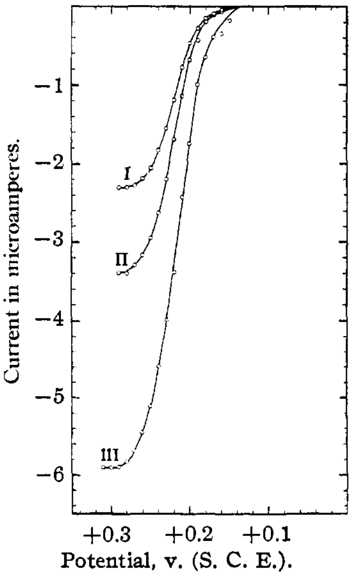

Fig. 4.—Waves (cor. for $i_r$) obtained for substituted 4,6,7-trimethyl-5-hydroxycoumarans in buffer I: I, 0.000635 *M* coumaran; II, 0.000952 *M* coumaran; III, 0.00163 *M* coumaran.

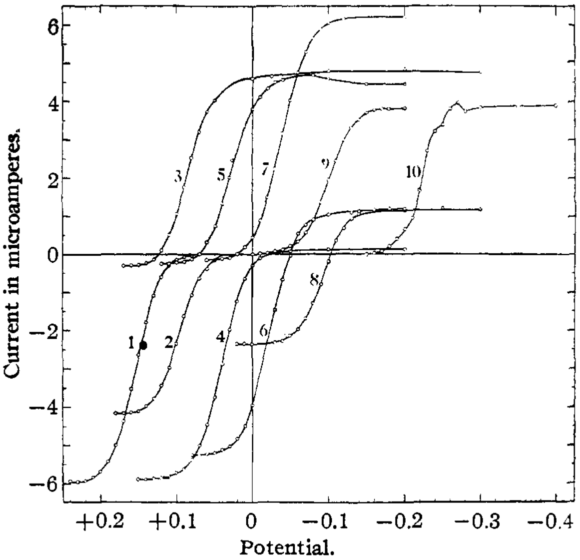

Fig. 5.—Current–voltage curves for various quinone–hydroquinone systems in buffer II: 1, hydroquinone; 2, toluhydroquinone; 3, toluquinone; 4, *p*-xylohydroquinone; 5, *p*-xyloquinone; 6, pseudocumohydroquinone; 7, pseudocumoquinone; 8, durohydroquinone; 9, duroquinone; 10, 2,3-dimethyl-1,4-naphthoquinone.

From Table I it is seen that the half wave potentials of the various compounds studied were found to be independent of the concentration. Hence these half wave potentials are characteristic for the particular compounds.

Attempts were made to determine the current–voltage curves of various chromans and coumarans in buffer solutions II and III in order to find the effect of *p*H upon the half wave potentials. No conclusive results could be obtained since the curves were too close to the anodic solution curves of mercury in the buffer solutions alone.

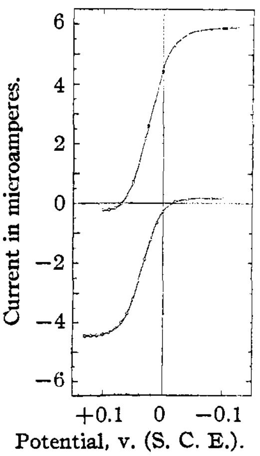

Fig. 6.—Waves for *m*-xylohydroquinone and *m*-xyloquinone in buffer II (cor. for $i_r$).

The results obtained with various quinones and hydroquinones are given in Table II.

TABLE II

CATHODIC AND ANODIC WAVES OF VARIOUS QUINONES AND HYDROQUINONES IN DIFFERENT BUFFER SOLUTIONS IN 50% METHANOL

| Compound | Concentration molar | $i_d \times 10^6$ | $(i_d/C) \times 10^3$ | $\pi^{1}/_{2}$ (S. C. E.) |
|---|---|---|---|---|
| Buffer II. *p*H 5.40 | | | | |
| Hydroquinone | 0.001372 | 5.95 | 4.33 | +0.146 |
| Benzoquinone | .000936 | 5.37 | 5.74 | |
| Toluhydroquinone | .00103 | 4.16 | 4.04 | + .089 |
| Toluquinone | .00095 | 5.08 | 5.34 | + .090 |
| *p*-Xylohydroquinone | .00143 | 6.02 | 4.21 | + .032 |
| *p*-Xyloquinone | .000970 | 4.71 | 4.85 | + .036 |
| *m*-Xylohydroquinone | .001094 | 4.62 | 4.24 | + .027 |
| *m*-Xyloquinone | .00119 | 6.11 | 5.13 | + .031 |
| Pseudocumohydroquinone | .00148 | 6.48 | 4.38 | − .030 |
| Pseudocumoquinone | .00133 | 6.38 | 4.80 | − .027 |
| Durohydroquinone | .000844 | 4.0 | 4.74 | − .094 |
| Duroquinone | .000881 | 3.84 | 4.36 | − .093 |
| 2,3,5-Trimethyl-6-[3'-hydroxy-3'-methylbutyl]-hydroquinone[13] | .000679 | 2.27 | 3.35 | − .093 |
| 2,3,5-Trimethyl-6-[3'-hydroxy-3'-methylbutyl]benzoquinone[13] | .00105 | 3.67 | 3.49 | − .090 |
| 2,3,5-Trimethyl-6-[3'-hydroxybutyl]-hydroquinone[13] | .00111 | 3.78 | 3.41 | − .093 |
| 2,3,5-Trimethyl-6-[3'-hydroxybutyl]-benzoquinone[13] | .000946 | 3.55 | 3.75 | − .092 |
| 2,3,5-Trimethyl-6-[2'-hydroxypropyl]-hydroquinone[13] | .000738 | 2.85 | 3.86 | − .084 |
| | .000538 | 2.10 | 3.90 | − .083 |
| 2,3,5-Trimethyl-6-[2'-hydroxypropyl]-benzoquinone[13] | .000577 | 2.35 | 4.07 | − .080 |
| 2,3,5-Trimethyl-6-[2'-hydroxybutyl]-hydroquinone[13] | .00101 | 3.84 | 3.80 | − .084 |
| | .00152 | 5.34 | 3.51 | − .082 |
| 2,3-Dimethyl-1,4-napthoquinone | .000874 | 3.89 | 4.46 | − .216 |
| Buffer III. (*p*H 6.06) | | | | |
| Hydroquinone | 0.0006 | 2.65 | 4.42 | +0.11 |
| | .0012 | 5.40 | 4.50 | + .112 |
| 2,3,5-Trimethyl-6-[2'-hydroxypropyl]-hydroquinone[13] | .000307 | 1.42 | 4.63 | − .124 |
| Buffer IV. (*p*H 7.97) | | | | |
| Hydroquinone | 0.001362 | 5.93 | 4.36 | −0.007 |
| 2,3,5-Trimethyl-6-[2'-hydroxypropyl]-hydroquinone[13] | .000567 | 2.03 | 3.58 | − .240 |
| 2,3,5-Trimethyl-6-[2'-hydroxypropyl]-benzoquinone[13] | .000539 | 2.24 | 4.16 | − .240 |
| Buffer I. (*p*H 3.56) | | | | |
| 2,3,5-Trimethyl-6-[3'-hydroxy-3'-methylbutyl]-benzoquinone[13] | 0.000853 | 3.09 | 3.62 | − 0.047 |

No half wave is reported for benzoquinone due to difficulty in completely eliminating maxima in the medium of 50% methanol.

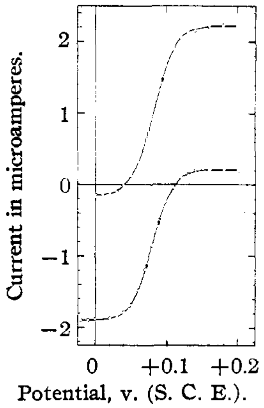

Fig. 7.—Waves for a $\beta$-hydroxyalkylpseudocumohydroquinone – $\beta$-hydroxyalkylpseudocumoquinone system.

From the values in Table II it can be seen that $i_d/C$ becomes smaller as the quinone or hydroquinone becomes more highly substituted. It is very peculiar that in all cases $i_d/C$ for a quinone is greater than that of the corresponding hydroquinone. A similar relation was found for benzoquinone and hydroquinone in water by Kolthoff and Orlemann.[3] Quite generally, it seems that the diffusion coefficient of a quinone in a polar solvent is distinctly greater than that of the corresponding hydroquinone.

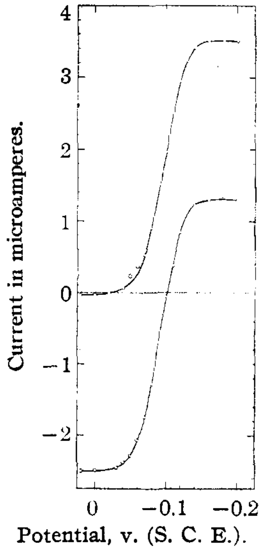

Fig. 8.—Waves for a $\gamma$-hydroxyalkylpseudocumohydroquinone–$\gamma$-hydroxyalkylpseudocumoquinone system.

In Fig. 5 and Fig. 6 are given the curves, corrected for the residual current but not for *iR*, which were obtained for the various methyl quinones in buffer II. Typical curves, corrected for residual current but not for *iR*, obtained for $\beta$-hydroxyalkylpseudocumohydroquinones and -pseudocumoquinones, and for $\gamma$-hydroxyalkylpseudocumohydroquinones and -pseudocumoquinones are given in Fig. 7 and Fig. 8, respectively. In the reversible oxidation of a hydroquinone to quinone or the reduction of quinone to hydroquinone the oxidation potential increases 0.0591 volt per unit decrease of *p*H at 25°. Since the half wave potential (after correction for *iR*)

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[13] Smith, Ruoff and Wawzonek, *J. Org. Chem.*, **6**, in press (1941).

corresponds to the classical oxidation potential the former also should shift 0.0591 volt per unit decrease of *p*H. The effect of *p*H is shown in Table III, and it is seen that the calculated change of the half wave potential is in satisfactory agreement with the experimental one.

Table III

Change of $\pi_{1/2}$ with *p*H for Hydroquinones–Quinones

| *p*H | 5.40 | | 6.06 | | 7.97 |
|---|---|---|---|---|---|
| $\pi_{1/2}{}^{a}$ | +0.146 | | +0.112 | | −0.007 |
| $\Delta\pi_{1/2}/\Delta p\mathrm{H}^{a}$ | | 0.0515 | | 0.0623 | |
| $\pi_{1/2}{}^{b}$ | −0.082 | | −0.124 | | −0.240 |
| $\Delta\pi_{1/2}/\Delta p\mathrm{H}^{b}$ | | 0.0636 | | 0.0606 | |

[a] Benzohydroquinone; [b] 2,3,5-Trimethyl-6-[2′-hydroxypropyl]-hydroquinone.

An analysis of the waves also shows that the reduction of the hydroquinones and the oxidation of the quinones is reversible at the dropping electrode. It can easily be shown that in these cases the plot of the potential against $\log i/i_d - i$ should yield a straight line with a slope of 0.0296. As an example line II in Fig. 9 gives the line obtained in the oxidation of 2,3,5-trimethyl-6-[2′-hydroxypropyl]-hydroquinone. The slope of 0.031 is in good agreement with the theoretical value which was calculated on the basis of a reversible two-electron transfer.

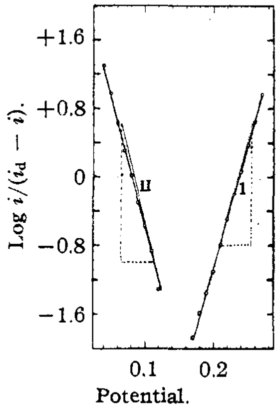


Fig. 9.—Analyses of waves: I, 0.001 *M* 2,2,5,7,8-pentamethyl-6-hydroxychroman; II, 0.000538 *M* 2,3,5-trimethyl-6-[2′-hydroxypropyl]-hydroquinone in buffer II.

The high value of the half wave potential obtained for 2,3,5-trimethyl-6-[3′-hydroxy-3′-methylbutyl]-benzoquinone in buffer I is probably due to some interaction with the buffer. The diffusion current of this compound in buffer I was of the same magnitude as that of its corresponding chroman.

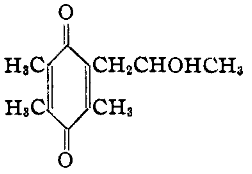
In Table IV is listed a comparison of normal oxidation potentials of various quinones as calculated from the half wave potentials with the normal oxidation potentials of the same compounds determined in the classical way by Conant and Fieser.[14] The latter authors determined the potentials in 50% ethanol, and found the same values when 95% ethanol was used as a solvent. Conant and Fieser determined the potentials in hydrochloric acid solutions and referred the values to the normal hydrogen electrode. Our values were determined in a buffer solution with a *p*H of 5.4. In order to find the standard normal potential against the normal hydrogen electrode the potentials were calculated for a *p*H of zero, using 0.246 v. as the standard potential of the saturated calomel electrode. It is seen that our values are in excellent agreement with those of Conant and Fieser.

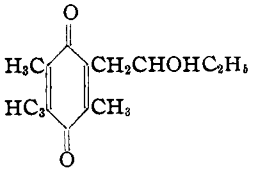
Table IV

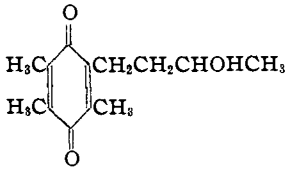
Comparison of Normal Oxidation Potentials of Quinones Calculated from Half Wave Potentials with Values of Conant and Fieser

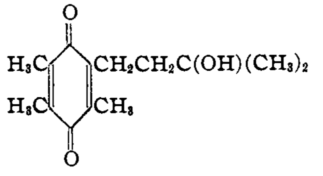
| Compound | $E_0$ calculated from polarographic data | $E_0$ (Conant and Fieser) |
|---|---|---|
| Quinone | 0.711 | 0.711 |
| Toluquinone | .654 | .656 |
| *p*-Xyloquinone | .599 | .597 |
| Duroquinone | .471 | .466 |
| 2,3-Dimethyl-1,4-naphthoquinone | .349 | .340 |

The effect of the position of a hydroxyl group in a side chain upon the oxidation potential (*vs.* S. C. E.) of a quinone, as illustrated by the following examples, is in approximate agreement with the observation of Ball[15] for the oxidation


−0.082


−0.083


−0.092


−0.092

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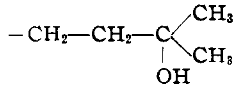
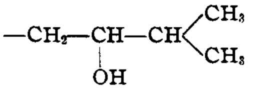
[14] Conant and Fieser, This Journal, **45**, 2194 (1923); Fieser and Conant, *ibid.*, **57**, 491 (1935).

[15] Ball, *J. Biol. Chem.*, **114**, 649 (1936).

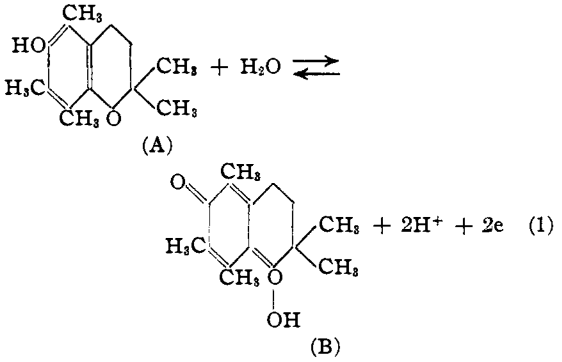
potentials of related hydroxynaphthoquinones; thus

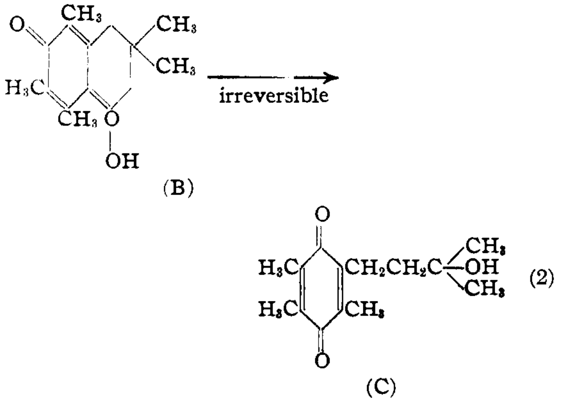

$E_0 = 0.3000$ v.


$E_0 = 0.3055$ v.

## Discussion

From Table I it is seen that the half wave potentials of *p*-hydroxychromans are 10 millivolts more positive than those of the corresponding *p*-hydroxycoumarans. This means that $\gamma$-hydroxyalkylquinones are formed more difficultly from these chromans than $\beta$-hydroxyalkyl quinones are formed from the coumarans. The net oxidation of the chromans and the coumarans to the corresponding quinones is irreversible. From an analysis of the waves of the chromans and the coumarans it is evident that the electrochemical oxidation involves a reversible reaction and that the oxidation product formed is unstable and is irreversibly transformed to the corresponding quinone. The mechanism of the reaction is postulated as





The net reaction is represented by the equation

$$A + H_2O \longrightarrow C + 2H^+ + 2e$$

On the other hand, the potential $\pi$ of the electrode is determined by reaction (1) and is given by the expression

$$\pi = \text{Const.} + \frac{RT}{2F}\ln\frac{[B_0]}{[A_0]} + \frac{RT}{F}\ln\,[H^+]_0 \quad (3)$$

The subscript zero denotes the concentration at the electrode, concentrations being written instead of activities. Since all the experiments were carried out in well buffered solutions $[H^+]_0$ may be taken equal to the hydrogen ion concentration in the bulk of the solution.

When the current has become equal to the diffusion current $i_d$, the relation holds

$$i_d = k[A] \quad (4)$$

in which [A] is the concentration of the chroman in the bulk of the solution. Since

$$i = k\{[A] - [A_0]\} \quad (5)$$

it follows from (4) and (5) that

$$[A_0] = \frac{i_d - i}{k} \quad (6)$$

The concentration of B at the surface of the electrode $[B_0]$ is unknown as B is being transformed to C, the latter being the end-product. The rate at which C is formed is proportional to the concentration of B. Hence, we can write

$$[B_0] = a[C_0] \quad (7)$$

$[C_0]$ in turn is proportional to the current $i$, and we find

$$i = k'[C_0] = \frac{k'}{a}\,[B_0] \quad (8)$$

or

$$[B_0] = ia/k' \quad (9)$$

Since A and C have about the same molecular size $k$ (eq. 6) may be taken equal to $k'$ (eq. 9). Introducing expressions (6) and (9) into (3) we find in a well buffered solution

$$\begin{aligned}\pi &= \text{Const.} + \frac{RT}{2F}\ln\frac{i}{(i_d - i)}\frac{ka}{k'} + \frac{RT}{F}\ln\,[H^+] \\ &= \text{Const.} + \frac{RT}{2F}\ln\frac{i}{(i_d - i)}\,a + \frac{RT}{F}\ln\,[H^+] \quad (10)\end{aligned}$$

when the $p$H is kept constant we can write at 25°

$$\pi = \text{Const.}' + 0.0296\log\frac{i}{(i_d - i)} \quad (11)$$

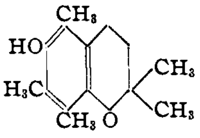
and the half wave potential $\pi_{1/2}$ is

$$\pi_{1/2} = \text{Const.}' \quad (12)$$

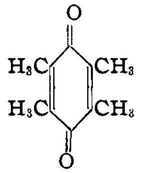
According to the proposed mechanism the half wave potential is not only determined by the standard potential of reaction (1) but also by the rate constant of the rearrangement of the hydroxide B to the quinone C (reaction 2). The latter reaction is analogous to the rearrangement of pyridinium hydroxides to α-hydroxydihydropyridines. According to equation (12) the half wave potential at constant *p*H and temperature should be constant and independent of the concentration. This was actually found. When log $[i/(i_d - i)]$ is plotted against the potential $\pi$ a straight line should be obtained according to equation (11) with a slope of 0.0296. Such a plot of the analysis of the anodic wave of 2,2,5,7,8-pentamethyl-6-hydroxychroman is given by line II in Fig. 9. A straight line with a slope of 0.0326 was found in good agreement with the theory.

The rate constant *a* of reaction B to C (equation 2) cannot be derived from the experimental data.

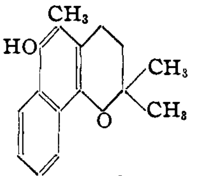
It is of interest to note that the difference in half wave potential of two hydroxychromans was found equal to the difference in oxidation potential of the corresponding quinones, as is shown by the following case



$\pi_{1/2} = +0.232$

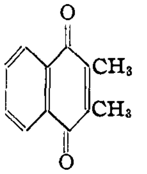


$\pi_{1/2} = -0.093$



$\pi_{1/2} = +0.114$

$\Delta = 0.12$



$\pi_{1/2} = -0.216$

$\Delta = 0.12$

The fact that coumarans were found to be more easily oxidized at the dropping electrode than the corresponding chromans indicates a greater stability of six-membered rings with a double bond than that of five-membered rings with a double bond.[16] Further work on the mechanism of the oxidation and also on the oxidation of Vitamin E is in progress.

## Summary

1. Current–voltage curves at the dropping electrode of 6-hydroxychromans and 5-hydroxycoumarans have been determined in 50% methanol in well buffered solutions. The half wave potentials of the various compounds were found to be unaffected by the concentration. The difference in half wave potentials of chromans and corresponding coumarans was found to be 10 millivolts, the coumarans being more easily oxidized than the chromans. A reaction mechanism of the electrode reactions has been proposed which accounts for the experimental facts.

2. Current–voltage curves and half wave potentials have been determined for a great number of hydroquinones and quinones. The half wave potentials were found to correspond to the standard oxidation potentials of the various systems.

3. Compounds related to Vitamin E can be determined polarographically.

[16] Brockway and Taylor, *Ann. Reports of the Progress of Chemistry*, The Chem. Soc., London, **34**, 219 (1937).

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[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY, THE UNIVERSITY OF MARYLAND]

# A Spectrophotometric Study of the Characteristics of Some Halogen Substituted Sulfonphthalein Indicators

BY MALCOLM M. HARING AND HUGH A. HELLER[1]

The advantages of the sulfonphthaleins as indicators have encouraged numerous efforts to synthesize substituted forms. Among others, Harden and Drake[2] reported the preparation of eleven members of a series having four halogen atoms in the sulfobenzoic acid part of the molecule. They also determined approximately the useful ranges.

Since precision hydrogen ion colorimetry requires a knowledge of the indicator constant, the present study has been undertaken to determine *pK* for each of seven of these indicators which were available. At the same time the useful ranges were redetermined and general suitability studied, but no investigation of salt and protein errors was made. The indicators studied were

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[1] Part of a thesis submitted by H. A. Heller to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. For seven additional spectrum photographs, order ADI Document 1494, American Documentation Institute, 2101 Constitution Ave., Washington, D. C., remitting 27¢ for microfilm or $0.90 for photoprint copies.

[2] W. C. Harden and N. L. Drake, THIS JOURNAL, **51**, 562 (1929).