CCCCXLVII.—*The Reaction at the Quinhydrone Electrode in Methyl Alcohol.*

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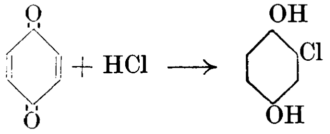
THE establishment of an oxidation–reduction equilibrium between quinone and quinol permits the use of the molecular compound of the two, *viz.*, quinhydrone, as a substitute for the hydrogen electrode. The equation for the potential of the quinhydrone electrode takes the form

$$\pi = \pi_0 + \frac{RT}{2F}\ln\frac{Q}{HQ} + \frac{RT}{F}\ln a_{H^\cdot} \quad . \quad . \quad . \quad (1)$$

where $a_{H^\cdot}$ is the activity of the hydrogen ions in the solution, Q and HQ are the concentrations of quinone and quinol respectively, R and T have their usual significance, and F is the Faraday constant.

Although the quinhydrone electrode gives steady potentials in acid solutions in water, it has been observed that in alcoholic solutions the potential falls off rapidly from its initial value. Buckley and Hartley (*Phil. Mag.*, 1929, **8**, 320) found that various types of electrode gave irregular results in methyl-alcoholic solutions of hydrogen chloride. Ebert (*Z. Elektrochem.*, 1925, **31**, 113) interpreted the fall in potential as being due to reaction between quinone and hydrogen chloride, which is known to take place in other organic solvents. By measurements of the *E.M.F.*, the conductivity, and the extinction coefficients of the reacting mixture, he sought to elucidate the kinetics of the reaction. The first product of interaction was said to be chloroquinol. This then reacted further with



. . . . . (2)

quinone to give chloroquinone and quinol, equilibrium being established according to the scheme

$$C_6H_3Cl(OH)_2 + C_6H_4O_2 \rightleftharpoons C_6H_4(OH)_2 + C_6H_3ClO_2 \qquad (3)$$

As far as the first reaction is concerned, the rate should be proportional to the concentration of quinone and to that of hydrogen chloride. The establishment of the second equilibrium makes the equation more complicated, so the disentanglement of the kinetics is a matter of some difficulty. To obtain the velocity coefficient of the first reaction, Ebert was forced to assume that the equilibrium constant of the second has the same value in methyl alcohol as in aqueous solution, in which it was determined by the oxidation–reduction potential measurements of LaMer and Baker. He was thus able to calculate the change in potential at any time in terms of a function of q, the ratio of the concentration of quinone to that of quinol. Owing to algebraic errors in his treatment, however, it would appear that his published velocity coefficients are incorrect.

Although Ebert measured the fall of *E.M.F.* at a series of hydrogen chloride concentrations, he omitted to examine the effect of varying the concentration of quinhydrone while keeping that of hydrogen chloride constant. Such measurements show that the order of reaction with respect to quinhydrone concentration is incompatible with the simple mechanism stated above.

EXPERIMENTAL.

The rate of reaction at 25° was followed by measurements of the *E.M.F.* of cells of the type Ag,AgCl|HCl in MeOH|Quinhydrone, Pt.

The potentiometer system, the form of the Durosil glass cells, and the preparation of silver–silver chloride reference electrodes that exert potentials constant and reproducible to 0·1 millivolt have already been described (*Phil. Mag.*, in the press). Methyl alcohol was prepared by the method of Hartley and Raikes (J., 1925, **127**, 524) and contained less than 0·01% of water and 0·02% of aldehyde. Hydrogen chloride solutions were prepared by absorption of the pure dry gas in methyl alcohol and titrated by weight against standard baryta. They were then diluted to the required concentration by weight addition of pure solvent.

Quinhydrone was made from quinol by the method of Biilmann (*Ann. Chim.*, 1921, **16**, 320) and dried by long standing over calcium chloride in a desiccator. Since the substance dissolves rapidly in alcohol, measurements could be started within 15 minutes of making up the solution. For this purpose the silver chloride half-cell, the junction vessel, and the junction limb of the quinhydrone half-cell were previously filled with the hydrogen chloride solution. When the body of the quinhydrone half-cell had been filled with the solution, communication with the junction limb could be established by the turning of a tap. To prevent diffusion of the quinhydrone, which would alter its concentration in the solution and might affect the potential of the reference electrodes, this tap was kept closed except while measurements were being made.

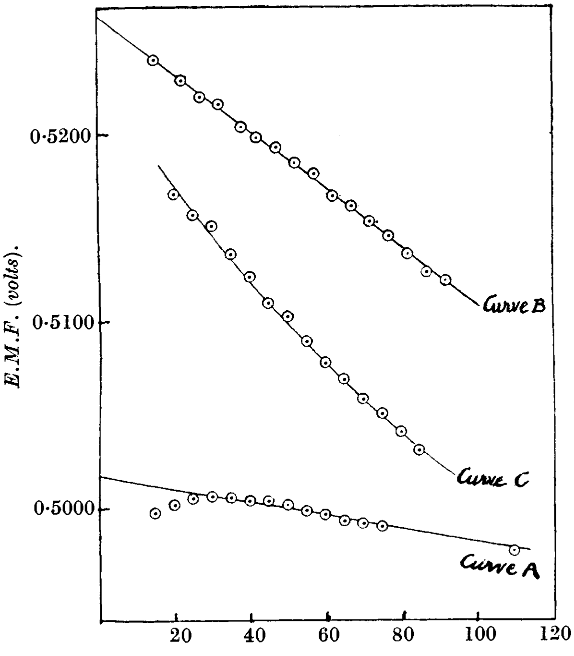
Three types of platinum electrode were tested : (1) spirals of thin platinum wire as used by Ebert, (2) more massive grids of bright platinum, and (3) the same grids coated electrolytically with platinum black. The rate of fall of potential with the first two types of electrode was approximately the same, but with the third was considerably greater, whilst the readings tended to be erratic. The independence of the *E.M.F.* of surface area in the first two experiments suggests that the reaction does not primarily occur at the electrode surface, but from the third it can be inferred that at a surface of high catalytic activity further disturbance can occur. The first type of electrode was adopted throughout, in order that the results might be comparable both among themselves and with those of Ebert. The platinum was cleaned and the glass seals tested for cracks according to the method of Morgan, Lammert, and Campbell (*J. Amer. Chem. Soc.*, 1931, **53**, 454, 597).

Results.—The mechanism of the reaction was investigated by the method of initial rates. In the earlier experiments a rise in *E.M.F.* was observed at the beginning of the reaction. This was traced to the time required for the silver–silver chloride electrodes to attain equilibrium, and was remedied by allowing the cells to stand in the thermostat for about an hour before the addition of the quinhydrone solution. Nevertheless, some time must elapse before the quinhydrone solution and the platinum electrode come to temperature equilibrium, so no great significance can be attached to the first few readings. This is the more unfortunate because the *E.M.F.* is not strictly a linear function of the time, as the curves in Fig. 1 show. Extrapolation of the *E.M.F.* to zero time cannot therefore be accurately carried out, but approximate values may be obtained by drawing straight lines through the linear portions of the curves. When the *E.M.F.* is falling rapidly, it is a difficult matter to determine its value accurately at short intervals of time. Since the measurements plotted in Fig. 1 lie on smooth curves, however, it is unlikely that they are seriously in error from this cause.

The dependence of the rate of fall of *E.M.F.* on the concentration of hydrogen chloride was determined by measurements in $0{\cdot}025M$- and $0{\cdot}0485M$-solutions. In both these experiments the concentration of quinhydrone was $0{\cdot}0037M$. From the slopes of the curves (A and B in the figure), it may be deduced that $d\pi/dt = -k[\mathrm{HCl}]^{2{\cdot}2}$, or, within the limits of accuracy of these experiments, that the rate of fall of *E.M.F.* is proportional to the square of the hydrogen chloride concentration.

Further experiments with the same hydrogen chloride solutions, but with a quinhydrone concentration of 0·00185M, showed more rapid rates of reaction. The slopes in 0·025M-hydrogen chloride solution approximate closely to an inverse proportionality between rate of fall of $E.M.F.$ and concentration of quinhydrone. In the 0·0485M-hydrogen chloride solutions, the ratio of the slopes is only 1·7 instead of 2·0, but, as may be seen from curve C in the figure, this is due to the greater divergence from linearity when the reaction is more rapid. (Curves B and C should extrapolate to the same value for the $E.M.F.$ at zero time.)

FIG. 1.



Concentrations of hydrogen chloride :—in A, 0·025M ; *in* B *and* C, 0·0485M.
Concentrations of quinhydrone :—in A *and* B, 0·0037M ; *in* C, 0·00185M.

Discussion.

Since the potential of the quinhydrone electrode becomes less positive, the ratio of the concentration of quinone to that of quinol decreases during the reaction; but since the rate of fall of potential is inversely proportional to the quinhydrone concentration, the rate of the primary reaction must be independent of it. The following mechanism is a possible method of accounting for these facts.

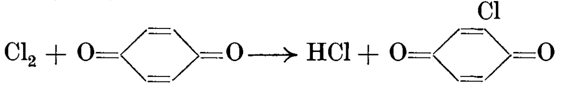
It is assumed that the primary reaction is the slow oxidation of hydrogen chloride by oxygen in solution :

$$2HCl + \tfrac{1}{2}O_2 \longrightarrow Cl_2 + H_2O \quad . \quad . \quad . \quad . \quad (4)$$

This is strictly analogous to the reactions shown by Güntelberg (*Z. physikal. Chem.*, 1926, **123**, 202) and by Randall and Young (*J. Amer. Chem. Soc.*, 1928, **50**, 989) to be responsible for the unsteady potentials of the silver–silver chloride and mercury–calomel electrodes :

$$2Ag + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2AgCl + H_2O,$$
$$2Hg + 2HCl + \tfrac{1}{2}O_2 \longrightarrow Hg_2Cl_2 + H_2O.$$

The chlorine formed reacts in this case with quinone to form chloroquinone and hydrogen chloride :



(5)

This reaction is said to take place in chloroform solution (Meyer u. Jacobsen, "Lehrbuch," Vol. II, i, 444). Finally, equilibrium is established as in (3) :

$$QCl + HQ \rightleftharpoons HQCl + Q$$

where QCl is the symbol adopted for chloroquinone, Q that for quinone, HQCl that for chloroquinol and HQ that for quinol.

If it is assumed that reaction (4) is slow as compared with (5), every molecule of chlorine reacts as soon as formed, and the independence of the reaction rate of the quinhydrone concentration is assured. Further, since of every two molecules of hydrogen chloride removed in (4) one is restored in (5), the rate of change of its concentration is given by the equation

$$d[HCl]/dt = -\, k_1[O_2]^{\frac{1}{2}}\, [HCl]^2$$

The solubility of oxygen in methyl alcohol is large, and its concentration is therefore sensibly constant throughout the reaction, so that this equation may be rewritten in the form

$$d[HCl]/dt = -\, k_2[HCl]^2 . \quad . \quad . \quad . \quad . \quad (6)$$

where k_2 is the velocity coefficient of reaction (4) multiplied by the function of the oxygen concentration. It also follows from (3) and (5) that

$$d[HCl]/dt = d[HQ]/dt + d[Q]/dt \quad . \quad . \quad . \quad (7)$$

while the expression for the equilibrium constant in (3) is :

$$[Q][HQCl]/[HQ][QCl] = K_3$$

Hence

$$[Q]\cdot\frac{d[HQCl]}{dt} + [HQCl)\,.\frac{d[Q]}{dt} = K_3\left([QCl\,.\frac{d[HQ]}{dt} + [HQ]\,.\frac{d[QCl]}{dt}\right) \quad (8)$$

From (3) $d[\mathrm{HQCl}]/dt = -d[\mathrm{HQ}]/dt$
while from (3) and (5) $d[\mathrm{QCl}]/dt = -d[\mathrm{Q}]dt$

Substituting these values in (8),

$$([\mathrm{HQCl}] + K_3[\mathrm{HQ}])\frac{d[\mathrm{Q}]}{dt} = ([\mathrm{Q}] + K_3[\mathrm{QCl}])\frac{d[\mathrm{HQ}]}{dt}$$

$$\therefore \quad \frac{d[\mathrm{HQ}]}{dt} = \frac{[\mathrm{HQCl}] + K_3[\mathrm{HQ}]}{[\mathrm{Q}] + K_3[\mathrm{QCl}]} \cdot \frac{d[\mathrm{Q}]}{dt}$$

or, on substituting for K_3,

$$\frac{d[\mathrm{HQ}]}{dt} = \frac{[\mathrm{HQCl}]}{[\mathrm{Q}]} \cdot \frac{[\mathrm{QCl}] + [\mathrm{Q}]}{[\mathrm{HQ}] + [\mathrm{HQCl}]} \cdot \frac{[\mathrm{HQ}]}{[\mathrm{QCl}]} \cdot \frac{d[\mathrm{Q}]}{dt}$$

But, since [QCl] and [HQCl] are small in comparison with [Q] and [HQ],

$$d[\mathrm{HQ}]/dt = [\mathrm{HQCl}]/[\mathrm{QCl}] \,.\, d[\mathrm{Q}]/dt = K_3[\mathrm{HQ}]/[\mathrm{Q}] \,.\, d[\mathrm{Q}]/dt \qquad (9)$$

Substituting this value in (7), it is found that

$$\{1 + K_3[\mathrm{HQ}]/[\mathrm{Q}]\} \,.\, d[\mathrm{Q}]/dt = d[\mathrm{HCl}]/dt$$

Since quinhydrone is being used, in the early stages of the reaction [Q] can be equated to [HQ]; hence

$$(1 + K_3) \,.\, d[\mathrm{Q}]/dt = d[\mathrm{HCl}]/dt \quad . \quad . \quad . \quad (10)$$

Now differentiation of (1) gives

$$\frac{d\pi}{dt} = \frac{RT}{2F}\left[\frac{1}{[\mathrm{Q}]} \cdot \frac{d[\mathrm{Q}]}{dt} - \frac{1}{[\mathrm{HQ}]} \cdot \frac{d[\mathrm{HQ}]}{dt}\right] + \frac{RT}{F} \frac{1}{[\mathrm{HCl}]} \cdot \frac{d[\mathrm{HCl}]}{dt}$$

whence, from (9),

$$\frac{d\pi}{dt} = \frac{RT}{2F}\left[\frac{1}{[\mathrm{Q}]} - \frac{K_3}{[\mathrm{Q}]}\right]\frac{d[\mathrm{Q}]}{dt} + \frac{RT}{F} \frac{1}{[\mathrm{HCl}]} \cdot \frac{d[\mathrm{HCl}]}{dt}$$

from (10),

$$\frac{d\pi}{dt} = \frac{RT}{2F} \cdot \frac{1 - K_3}{1 + K_3} \cdot \frac{1}{[\mathrm{Q}]} \cdot \frac{d[\mathrm{HCl}]}{dt} + \frac{RT}{F} \cdot \frac{1}{[\mathrm{HCl}]} \cdot \frac{d[\mathrm{HCl}]}{dt}$$

and from (6)

$$\frac{d\pi}{dt} = -\frac{RT}{2F} \cdot k_2 \cdot \frac{1 - K_3}{1 + K_3} \cdot \frac{[\mathrm{HCl}]^2}{[\mathrm{Q}]} - \frac{RT}{F} k_2 \cdot [\mathrm{HCl}] \quad . \quad . \quad (11)$$

This equation provides for the fall in potential that is observed, as long as K_3 is less than unity; the value found by LaMer and Baker in aqueous solution was 0·6. If the concentration of hydrogen chloride is large compared to that of quinone, the second term on the right-hand side of the equation will be negligible in comparison with the first, and the expression for the rate of change of potential becomes

$$\frac{d\pi}{dt} = -\frac{RT}{2F} \cdot k_2 \cdot \frac{1 - K_3}{1 + K_3} \cdot \frac{[\mathrm{HCl}]^2}{[\mathrm{Q}]} \quad . \quad . \quad . \quad (12)$$

This condition is satisfied in the present measurements. The extent to which quinhydrone is dissociated into quinone and quinol is unknown, so that it is impossible, by substitution of the quinone concentration in equation (11) or (12), to evaluate the velocity coefficient, k_2, or the equilibrium constant, K_3. It is obvious, however, that this mechanism is sufficient to account for the observed rate of fall of potential, *i.e.*, a rate proportional to the square of the hydrogen chloride concentration and inversely proportional to that of quinhydrone.

Experiments made in solutions of hydrogen perchlorate show that a similar reaction occurs with the formation, presumably, of a quinone perchlorate. This compound does not appear to have been isolated, probably owing to the oxidising action of hydrogen perchlorate in concentrated solution.

If this theory of the reaction between quinhydrone and hydrogen chloride is correct, the fully chlorinated compound should maintain stable oxidation–reduction potentials in alcoholic solutions. Measurements are now in progress with octachloroquinhydrone, which, it is hoped, will prove an effective substitute for the hydrogen electrode.

Summary.

The reaction between quinhydrone and hydrogen chloride has been investigated in solutions of methyl alcohol by means of measurements of electromotive force. A mechanism has been suggested to account for the observed rate of reaction.

In conclusion, I should like to express my indebtedness to Sir Harold Hartley for his valuable advice and kind supervision of the course of this work.

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[*Received, November 5th,* 1931.]