the simpler derivatives. An investigation of the higher membered oxides such as trimethylene oxide and tetrahydrofuran was not undertaken, since the lesser reactivity of these compounds made it seem doubtful that an appreciable reaction would take place.

Summary

Ethylene oxides react with aldehydes and ketones in the presence of metallic chlorides to form cyclic acetals, in yields varying from 25 to 35%

By this method six new acetals and ketals were prepared, some of which would be difficult or impossible to make by the use of a glycol.

NEW YORK, N. Y.

RECEIVED MAY 11, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of Oxidation-Reduction Potentials in Glacial Acetic Acid Solutions

BY J. B. CONANT AND B. F. CHOW

It was shown eight years ago[1] that the ion of a halochromic salt and a free radical such as triphenylmethyl form a mobile oxidation-reduction system whose potential can be measured in a non-aqueous medium. The lack of adequate information about the properties of acids and bases in such non-aqueous media prevented a detailed quantitative study of the problem at that time. A study of glacial acetic acid solutions was undertaken therefore, and has now reached a point where it is possible to return to the study of oxidation-reduction potentials in this and similar non-aqueous media. In this paper we shall present the results of the study of certain dyes and quinones of the type which has been studied extensively in water; in a later paper we shall consider the rather unique system composed of a free radical and a halochromic salt.

The measurements were all made using glacial acetic acid as the solvent. The hydrogen-ion activity was kept constant in each experiment by means of suitable "buffers," which in most instances consisted of an organic base partially neutralized with sulfuric acid. The ionic strength was constant at 0.2 in all the buffers, and where necessary a neutral salt was added to bring the value of the ionic strength to 0.2. The exact composition of the buffers is given in Table I together with the $(P\text{H})^{\text{HAc}}$ values determined by means of a chloranil electrode as previously described in papers from this Laboratory.

The Acidity Scale in Acetic Acid

A few words are necessary in regard to the significance of the $(P\text{H})^{\text{HAc}}$ values. Since the first work from this Laboratory on glacial acetic acid,

---

[1] Conant, Small and Taylor, THIS JOURNAL, **47**, 1959 (1925).

TABLE I

COMPOSITION OF BUFFERED GLACIAL ACETIC ACID SOLUTIONS

The glacial acetic acid employed melted at 16.5°. Solution 10 was not very stable. In two weeks time its $P\mathrm{H}$ changed from -0.95 to $+0.02$. Only the freshly made solutions were used in the experiments. Unless otherwise noted the neutral salt added was trimethylammonium *p*-toluene sulfonate.

Soln.	Concn. of base in moles per liter	Neutralized with H_2SO_4, %	Moles of neutral salts per liter	$(P\mathrm{H})^{\mathrm{HAc}}$	
1	1.0 Pyridine	0	0.200	+4.24	
2	0.1 Pyridine	0	.200	+3.64	+3.52
3	.05 Acetoxime	0	.200	+2.47	+2.29
4	.05 Antipyrine	50	.175	+1.66	
5	.05 Urea	0	.200	+1.86	+1.61
6	.05 Acetoxime	50	.175	+1.00	
7	.05 Urea	15	.1925[a]	+0.34	
8	.30 Acetoxime	65	.005	+ .25	
9	.25 Acetoxime	80	.000	− .15	
10	.05 Acetamide	70	.163	− .98	
11	.1 Benzamide	9	.110	−2.10	

[a] Indicates that the neutral salt was triethylammonium perchlorate. A partially neutralized urea buffer of $(P\mathrm{H})^{\mathrm{HAc}}$ value -0.63 with somewhat less ionic strength was also used in some experiments.

it has become evident that it is impossible to relate the fugacities of an individual ion from two solvents. It has further become evident[2] from a series of experimental results in acetic acid solutions of varying ionic strength that the relation of the base strength of two bases in acetic acid and in water depends on (a) the charge of the base, and (b) the ionic strength of the acetic acid. For practical purposes a very dilute solution of a base in acetic acid is of no value, but a solution containing enough neutral salt so that $\mu = 0.2$ is conveniently prepared. Slight changes in ionic strength at this point have little effect, although a change of the neutral salt may cause shifts in the apparent $(pK)^{\mathrm{HAc}}$ value of as much as 0.5 of a unit (see Fig. 3, Conant and Werner, THIS JOURNAL, **52,** 4442 (1930)).

Hammett and Deyrup[3] have greatly clarified the subject of non-aqueous solutions by defining an acidity function of such solutions by the equation

$$H_0 = -\log a_{\mathrm{H}^+}(f_{\mathrm{B}}/f_{\mathrm{BH}^+})$$

The acidity function will depend on the charge on the base and they propose the symbol H_0 for bases like urea, H_- for bases like the acetate ion, etc. To the extent that the ratio $f_{\mathrm{B}}/f_{\mathrm{BH}^+}$ in a given solution is the same for all bases, this definition is exact and has real meaning. The pK'_{B} value of a base defined in terms of this scale of acidity function is independent of the solvent to the extent that the assumption just mentioned is exact. We may now redefine our $(P\mathrm{H})^{\mathrm{HAc}}$ scale in terms of Hammett and Deyrup's

---

(2) Guggenheim, *J. Phys. Chem.*, **33,** 842 (1929).

(3) Hammett and Deyrup, THIS JOURNAL, **54,** 2721 (1932).

acidity function referred to a base of the zero charge type (H_0) and defining our solvent as glacial acetic acid with neutral salt added to give $\mu = 0.2$.

The best comparison now available of the relative strengths of two bases in water and an acetic acid solution of high ionic strength is given in Fig. 4, of the paper by Conant and Werner. From the data there given the apparent pK values of urea and acetoxime are $+1.1$ and $+0.3$, the corresponding values in water are about $+1.75$ and $+0.1$; the uncertainties in the acetic acid values are at least ± 0.2 and the values in aqueous solution of such very weak bases may be in error to a considerable extent. The zero point of the $(P\text{H})^{\text{HAc}}$ scale was originally chosen in part because the value of $(pK)^{\text{HAc}}$ for urea titrated in a 0.2 M solution ($\mu = 0.2$ at the mid-point) closely coincided with the pK value in water. It is evident that if urea is used for the comparison, $(P\text{H})^{\text{HAc}} = H_0$ within the limits of experimental error; if acetoxime is used for the comparison, the old $(P\text{H})^{\text{HAc}}$ scale should be corrected by about 0.6 of a unit. The discrepancy between these two bases of the same charge type may in part reflect experimental uncertainties but may also represent the limit of accuracy of the assumption that $f_{\text{B}}/f_{\text{BH}^+}$ for the two bases is the same. At all events, it seems best to continue the use of the old $(P\text{H})^{\text{HAc}}$ scale for acetic acid solutions where $\mu = 0.2$, as any correction of it to make it coincide more closely with the H_0 scale is perhaps impossible.

It should be borne in mind that at low values of μ, the $(P\text{H})^{\text{HAc}}$ scale must be corrected to make it correspond even approximately with the H_0 scale. For example, at $\mu = 0.025$ (the half-neutralized base contributing the salt), Hall[4] found a fairly consistent spread of about 2 units between $(pK)^{\text{HAc}}$ (defined on the old $(P\text{H})^{\text{HAc}}$ scale) and $pK^{(\text{H}_2\text{O})}$ for a variety of bases of the zero type. Therefore at $\mu = 0.025$, $H_0 \cong (P\text{H})^{\text{HAc}} + 2$. The irregularities may be certainly as much as 0.5 of a unit, however. The impossibility of making any of these definitions exact must be emphasized; the assumption of the constant ratio of the activity coefficients is certainly inexact and in solutions of high ionic strength experiment has shown that the nature of the neutral salt may affect the apparent pK values by several tenths of a unit.

The Measurement of Oxidation-Reduction Potentials

We shall define our oxidation-reduction potentials (E_{h}) in glacial acetic acid solutions with reference to a hypothetical hydrogen electrode (1 atm.) functioning in a buffered solution of ionic strength 0.2 and $(P\text{H})^{\text{HAc}} = 0$. Actually the oxidation-reduction half-cell was measured against a saturated aqueous calomel electrode through a lithium chloride bridge. Since the same arrangement was used in measuring the $(P\text{H})^{\text{HAc}}$ values of the buffer with the chloranil electrode, the aqueous electrode and the salt bridge cancel in the final calculations. By the definition of our original

---

(4) Hall, THIS JOURNAL, **52**, 5115 (Fig. 2) (1930).

$(P_H)^{HAc}$ scale, the saturated chloranil electrode at $(P_H)^{HAc} = 0$ was given the value of +0.566 referred to aqueous calomel through the lithium chloride bridge.[1a] The value of the saturated chloranil electrode against the hydrogen electrode is independent of the solvent and has the value +0.664. From this it follows that the potential of a hypothetical hydrogen electrode in acetic acid $(P_H)^{HAc} = 0$, against aqueous calomel is $0.566 - 0.664 = -0.098$ volt (European convention in regard to sign). The value of E_h of the oxidation-reduction potential is thus 98 millivolts greater than the observed potentials measured against the aqueous calomel electrode.

The apparatus used was very similar to that employed in the measurement of $(P_H)^{HAc}$ values (see Fig. 6, Ref. 1). The stirrer was omitted and an inlet tube for oxygen-free nitrogen dipped well beneath the liquid. The air-tight rubber stopper carried two bright platinum electrodes, a buret tip and an exit tube. A slow stream of nitrogen supplied sufficient agitation. The temperature was 25 ± 2°. Two methods of varying the ratio of oxidant and reductant were employed. One was the well-known method of mixtures, the other was by titration of the oxidant with chromous acetate. The reductant in most cases was prepared by reducing the oxidant with hydrogen and platinized asbestos; the solution was kept in a reservoir connected to a buret in an atmosphere of oxygen-free nitrogen. Five cc. of buffer solution was placed in the cell in each experiment and 0.25 to 1.00 cc. of a 0.0060 *M* solution of the oxidant or reductant added; the total concentration of oxidant and reductant at the midpoint was therefore about 0.0017 molar.

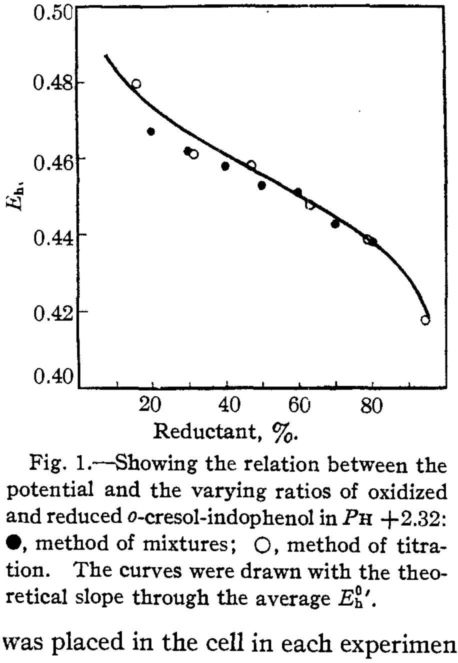


Fig. 1.—Showing the relation between the potential and the varying ratios of oxidized and reduced *o*-cresol-indophenol in P_H +2.32: ●, method of mixtures; ○, method of titration. The curves were drawn with the theoretical slope through the average $E_h^{0\prime}$.

The accuracy of the results is, of course, much less than that obtained using aqueous solutions. Figures 1 and 2 illustrate typical results. In Fig. 1 are plotted results obtained by the method of mixtures and by titration (using $Cr(Ac)_2$); the usual sigmoid curve was drawn to correspond to the equation

$$E_h = E_h^0 + \frac{RT}{2F} \ln \frac{[\text{Oxid.}]}{[\text{Red.}]}$$

The value of E_h^0 obtained by considering the titration results alone was 0.455 and that obtained from the method of mixtures 0.453. In Fig. 2 a logarithmic plot presents the results obtained with indothymol in four different buffers by the method of mixtures. The straight lines are drawn with a slope corresponding to the equation given above. The value of E_h^0 calculated from all the points in an experiment usually deviated not more than ±2 millivolts from the average value. In the case of benzoquinone at $(PH)^{HAc} = +3.52$, both the titration method and the method of mixtures gave a value of E_h^0 identical within half a millivolt.

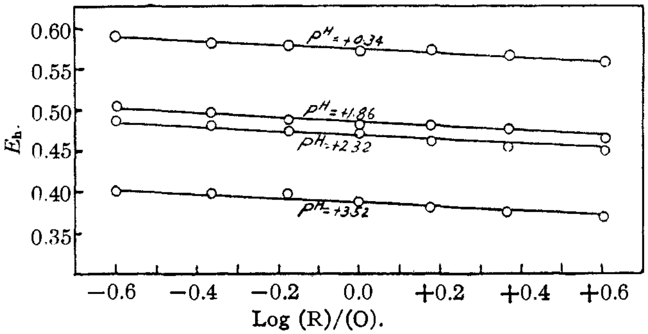


Fig. 2.—Potentials of indothymol in different P_H. Lines are drawn with the theoretical slope.

The values of E_h^0 are plotted against $(P_H)^{HAc}$ for five compounds in Fig. 3. The values for chloranil and benzoquinone were obtained simply

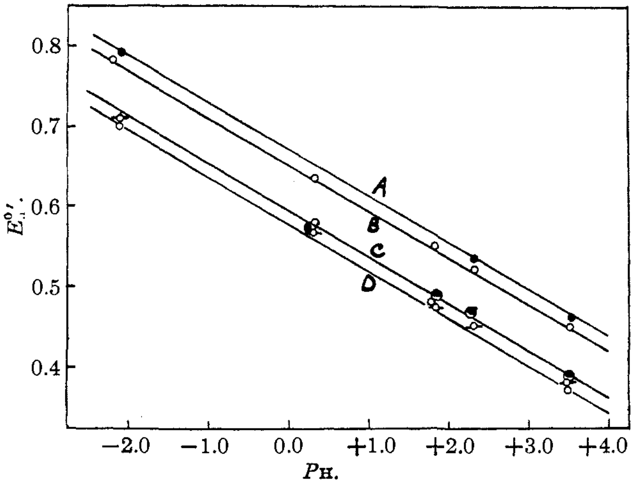
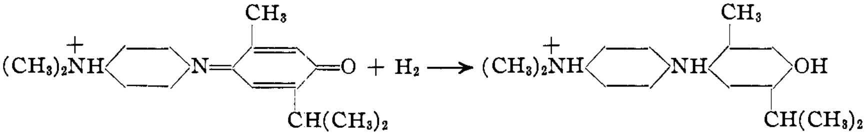


Fig. 3.—Showing the relationship between P_H and $E_h^{0\prime}$. The lines were drawn with the theoretical slope: A, chloranil; B, benzoquinone; C (●), indothymol; D, -○- indo-*o*-cresol; ⊙ *o*-cresol-indophenol.

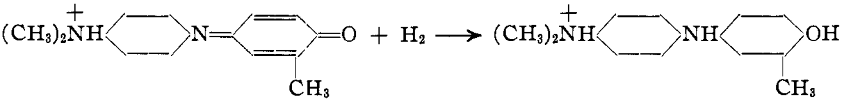
by using an equimolecular mixture of the reductant and oxidant in each buffer (except $(P_H)^{HAc} = 3.52$ where the titration method was also employed with benzoquinone). The values for the three dyes are the average of a number of points obtained by the method of mixtures or in a few cases by titration with chromous acetate as explained above. To save space we are omitting the several hundred individual determinations of E_h from which the average values of E^0_h were calculated for each buffer. The slope of the lines in Fig. 3 corresponds to $\Delta E^0_h/\Delta(P\text{H}) = -0.060$. A close agreement of the experimental points to this line is, of course, to be expected in the case of quinone and tetrachloroquinone (chloranil) since the dissociation of the phenolic groups lies far beyond the most alkaline end of this range of $(P\text{H})^{\text{HAc}}$ values (much more alkaline than can be reached in glacial acetic acid, in fact). The value of E^0_h at $(P\text{H})^{\text{HAc}} = 0$ corresponds to the free energy of the reduction of the quinone by hydrogen; we shall designate it as E_0'. The values from Fig. 3 are 0.675 for chloranil and 0.650 for benzoquinone. These values differ from those in alcoholic solution which are 0.703 and 0.711, respectively, as might be expected. The fact that chloranil in acetic acid is a stronger oxidizing agent than benzoquinone is of interest as the free energies referred to the gaseous state are in the same order with even a greater difference between the two compounds.[5]

The equations for the reduction of the three dyestuffs in the range of acidity we are here concerned with, are as follows

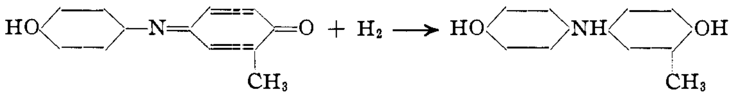
(1) Indothymol: $E_0' = 0.600$



(2) Indo-*o*-cresol: $E_0' = 0.575$



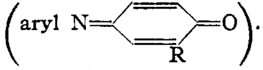
(3) *o*-Cresol-indophenol: $E_0' = 0.575$



The free energy of each of the reactions written above is equal to $-2FE_0'$ where E_0' is the value of E^0_h at $(P\text{H})^{\text{HAc}} = 0$. The values of E_0' given above were obtained by graphical interpolation of the lines of Fig. 3. Any differences between E_0' for (2) and (3) are within our experimental error, which is probably as much as ±7 millivolts because of the difficulties attending the preparation and measurement of $(P\text{H})^{\text{HAc}}$ of the buffer solutions. The small difference between even (1) and (3) is not surprising

---

[5] THIS JOURNAL, **49**, 293 (1927).

since in all three cases the group undergoing reduction is very nearly the same . The linear relationship between $(P_{\rm H})^{\rm HAc}$ values and $E^0_{\rm h}$ is surprising since it might be expected that the diphenylamine grouping of the reductant would unite with a proton at about $(P_{\rm H})^{\rm HAc} = 0$. (The value of $pK_{\rm B}$ for diphenylamine is about 0.) This should result in a bend of the curve as many examples studied in aqueous solution have shown. Evidently the hydroxyl group in the para position has made the base still weaker than diphenylamine.

In all the experiments recorded in this paper, the ionic strength of the glacial acetic acid solutions has been kept constant at $\mu = 0.2$. In such a solvent $(P_{\rm H})^{\rm HAc} = H_0$ as explained early in this paper. H_0, therefore, might replace $(P_{\rm H})^{\rm HAc}$ in the plot in Fig. 3 without change It is interesting to note that if the oxidation–reduction potential of one of the substances is determined in a buffer solution of different ionic strength, the result will also fall on the straight line of Fig. 3, but the position of the point will then depend on whether $(P_{\rm H})^{\rm HAc}$ (as defined in all our work) or H_0 is plotted horizontally.

Summary

It has been shown that the oxidation–reduction potential of quinones and certain dyes may be measured in glacial acetic acid by the method of mixtures or by titration of the oxidant with chromous acetate. The results obtained in a series of buffers with constant ionic strength lie on a straight line with the theoretical slope when $E^0_{\rm h}$ is plotted against $(P_{\rm H})^{\rm HAc}$. The relation of the $(P_{\rm H})^{\rm HAc}$ scale to Hammett and Deyrup's acidity function is discussed briefly.

CAMBRIDGE, MASSACHUSETTS

RECEIVED MAY 12, 1933
PUBLISHED SEPTEMBER 5, 1933