

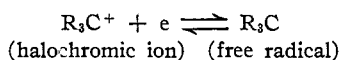
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Potential of Free Radicals of the Triphenylmethyl Type in Glacial Acetic Acid Solutions

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

In a preceding paper¹ it was shown that the oxidation-reduction potentials of quinones and certain dyes could be measured in a series of glacial acetic acid buffer solutions by the usual procedure. In this paper we shall consider the application of these methods to the problem of the potential between a free carbon radical and a halochromic salt—a problem stated and partially solved in an earlier paper from this Laboratory.² The buffer solutions employed were the same as those used in the preceding paper and their $(P_H)^{HAc}$ values were measured with the chloranil electrode as previously described.

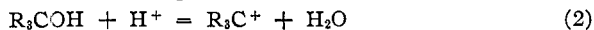
The electrode reaction involved in all the cases studied may be written in the general form



At constant hydrogen-ion activity the potential will depend on the relative amounts of the halochromic ion and free radical according to the usual electrochemical equation (1).

$$E_h = E_0 + \frac{RT}{F} \ln \frac{[R_3C^+]}{[R_3C]}$$

As usual, the potential is referred to a hypothetical hydrogen electrode operating in a buffer solution in glacial acetic acid of $(P_H)^{HAc} = 0$. The relation of this scale to Hammett and Deyrup's acidity function has been discussed in the preceding paper.¹ The relation between the concentration of free radical and the total reductant expressed as moles of ethane (associated form) is as follows $[R_3C] = 2\alpha[\text{Ethane}]_T$. At a given dilution and temperature we may consider that α , the degree of dissociation of the ethane, is essentially constant and therefore substitute in equation 1 the term $2\alpha(\text{Ethane})_T$ for the term $[R_3C]$. The halochromic salt is formed from the carbinol by the action of a proton



The equilibrium constant for this reaction may be expressed by equation 3

$$K = \frac{[R_3COH][H^+]}{[R_3C^+][H_2O]} \quad (3)$$

The concentration of total carbinol $[\text{Carb.}]_T$ is equal to $[R_3COH] + [R_3C^+]$ therefore substituting for $[R_3COH]$ in equation 3, the terms $[\text{Carb.}]_T - [R_3C^+]$ we obtain equation 3a

$$[R_3C^+] = \frac{[\text{Carb.}]_T [H^+]}{[H^+] + K[H_2O]} \quad (3a)$$

(1) THIS JOURNAL, **55**, 3745 (1933).

(2) Conant, Small and Taylor. *ibid.*, **47**, 1959 (1925).

Now making the appropriate substitutions in equation 1, we therefore arrive at the general equation 4

$$E_h = E_0 - \frac{RT}{F} \ln \alpha + \frac{RT}{F} \ln \frac{[\text{Carb.}]_T}{2[\text{Ethane}]_T} - \frac{RT}{F} \ln \frac{[\text{H}^+] + K[\text{H}_2\text{O}]}{[\text{H}^+]} \quad (4)$$

At constant volume we may consider that α is constant and set E'_0 equal to $E_0 - RT \ln \alpha/F$. At constant hydrogen-ion activity and constant water content the potential of a solution in which $(\text{Carb.})_T = 2(\text{Ethane})_T$ may be called E''_0 . It will be noted if the concentration of the reductant is expressed in terms of the dissociated compound that this would be an equimolecular mixture of oxidant and reductant. Inspection of the last term of equation 4 which contains the hydrogen-ion activity makes it evident that when the value of $K[\text{H}_2\text{O}]$ is much greater than (H^+) the value of E''_0 will be a linear function of the hydrogen-ion activity and $E''_0 = E'_0 - (RT/F) \ln K(\text{H}_2\text{O})$. At the point where $K[\text{H}_2\text{O}]$ is less than (H^+) the potential will be independent of the hydrogen-ion activity and $E''_0 = E'_0$. There should thus be a sharp bend in the $E''_0 : (P_H)^{\text{HAc}}$ curve at a point corresponding to the change of the oxidant from being almost exclusively in the carbinol form to being almost exclusively in the halochromic ion form. Such breaks do occur as will be shown below.

The apparatus employed in measuring the oxidation-reduction potentials of the free radicals was identical with that used in the study of quinones and certain dyes. The potential was actually measured in every instance against a saturated aqueous calomel electrode and these readings were converted to the hydrogen electrode scale by adding 98 mv., which we have calculated in the previous paper to be the potential of the hypothetical hydrogen electrode against saturated calomel at $(P_H)^{\text{HAc}} = 0$. It is, of course, necessary that all the measurements be carried out in the complete absence of oxygen, as the free radicals react very rapidly with this gas. Three different methods were employed of varying the ratio of oxidant and reductant. In the method of mixtures a solution of the free radical in dry bromobenzene was placed in an atmosphere of oxygen-free nitrogen. Varying quantities of such a solution were then added to the glacial acetic acid buffer which contained a solution of the halochromic ion. The latter was usually formed by dissolving the corresponding carbinol directly in the buffer solution. Varying quantities of the reductant (the free radical) were added and the potential measured. Bright platinum electrodes were used in all of the work. Two titration methods were also employed. In one of these the halochromic salt solution was titrated with a chromous acetate. The other procedure depended on the fact that the indophenols in glacial acetic acid are much more powerful oxidizing agents than the halochromic salts. As a result it is possible to titrate the free radical with a solution of the oxidized form of indophenol dye. A very satisfactory end-point can be determined electrometrically, since there is a change of potential of some 200 mv. at the end-point. The end-point could also be estimated visually by the color change and these results always agreed satisfactorily with the electrometric end-point. In each experiment 5 cc. of buffer solution was employed; the concentration of carbinol and total reductant at the midpoint was usually about 0.001 molar.

To save space the three methods are illustrated by the three diagrams shown in Figs. 1, 2 and 3, illustrating, respectively, the method of mixtures (with a logarithmic plot of the ratio of oxidant to reductant), the titration of triphenylcarbinol with chro-

mous acetate, and the titration of diphenyldixanthyl with indothymol. In each case the values plotted are E_0'' .

The agreement between the method of mixtures and the titration methods was within the experimental error (10 millivolts). For example, with the triphenylmethyl system at $(P_H)^{HA_0} = -0.98$, the method of mixtures yielded a value for E_0'' of 0.277 while the chromous acetate titration gave 0.277; with phenylxanthyl at $(P_H)^{HA_0} = +0.24$, E_0'' by mixtures was 0.098, by titration with indothymol $+0.084$. In the more acid solutions the potentials were not stable for any long period as there is, of course, a decomposition of the free radicals by the action of the acids present. The temperature was kept at $25 \pm 1^\circ$ by means of a jacket around the electrochemical cell through which water at a constant temperature was allowed to flow. In one experiment with the triphenylmethyl system at $(P_H)^{HA_0} = -0.98$ it was found that an increase in temperature of 10° changed the potential less than 2 mv. It is therefore clear that the temperature coefficient of such a system is so small that the control of temperature is not a significant factor.

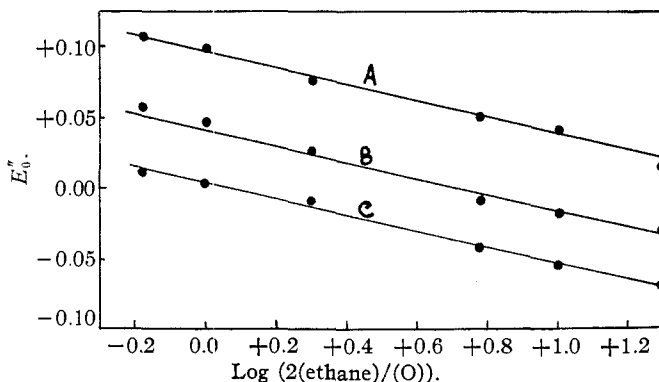


Fig. 1.—Potentials of diphenyldixanthyl by the method of mixtures: A at $P_H +1.00$, B at $P_H +2.47$, C at $P_H +3.68$. Lines were drawn with the theoretical slope.

In Fig. 4 are plotted all the final results with the three free radical systems which have been studied, namely, triphenylmethyl, phenylxanthyl and benzylxanthyl. The values plotted are those of E_0'' vs. $(P_H)^{HA_0}$; the ionic strength of all the buffers was 0.2. The various symbols show whether the results were obtained by the method of titration or the method of mixtures. It will be seen that the agreement between the two methods is all that could be expected considering the difficulties of handling the free radicals and non-aqueous solutions.

The concentration of water in our solutions we estimate to be about 0.006 molar, due primarily to the water formed in the neutralization of the added carbinol. This is essentially the water concentration in previous work of Conant and Werner³ on the basic strength of the carbinols and therefore their values of (pK) are directly comparable with those in this paper. We have measured the value of pK' of benzylxanthyl by

(3) Conant and Werner, *THIS JOURNAL*, **52**, 4436 (1930).

titration at $\mu = 0.2$ following the previous method and found a value of $+0.70$. The values of $pK' = -\log K(\text{H}_2\text{O})$ for the three carbinols studied are therefore $(\text{C}_6\text{H}_5)_3\text{COH}$, -1.47 , $\text{C}_6\text{H}_5\text{COH}(\text{C}_6\text{H}_4)_2\text{O}$, $+1.91$, $\text{C}_6\text{H}_5\text{CH}_2\text{COH}(\text{C}_6\text{H}_4)_2\text{O}$, $+0.70$. The inflection of the E_0'' vs. $(P_{\text{H}})^{\text{HAc}}$ curve of Fig. 4 should occur at the corresponding values of $(P_{\text{H}})^{\text{HAc}}$. The points are indicated by the arrows. It is evident that in the case of the benzylxanthrydrol system, the inflection occurs at exactly the right point; in the case of the phenylxanthrydrol system there is a discrepancy of about 0.25 of a P_{H} unit, which is about the experimental uncertainty. Unfortunately we were unable to obtain satisfactory potentials with the triphenylmethyl system in solutions sufficiently acid to give a fair test of the relation between theory and experiment in this instance. It may be that the E_0'' vs. $(P_{\text{H}})^{\text{HAc}}$ curve becomes flat between $(P_{\text{H}})^{\text{HAc}} = 0$ and -1 , but we believe that it is more probable that the point at -1 is in error and the curve takes the course shown in Fig. 4.

The horizontal portions of the curves in Fig. 4 correspond to the value of E_0' ; corrected for the value of α these give values of E_0 which is a measure of ΔF for the reduction of the halochromic ion to the free radical. The value of ΔF for the reduction of the carbinol to the free radical and water (in acetic acid at $0.006 M$ in water) can be calculated from this value and the term $-RT \ln K[\text{H}_2\text{O}]$. (These values correspond to the intercept of the diagonal lines with the $(P_{\text{H}})^{\text{HAc}} = 0$ axis when the correction for α is duly applied.) In Table I we have summarized the values of ΔF expressed in volt electrons and for comparison the values of ΔF of dissociation of the ethane (the associated free radical). The data necessary for estimating α are indicated in the footnote of the table. The change of volume during an experiment would affect α in the case of triphenylmethyl and benzylxanthryl but we have calculated that the maximum change is not

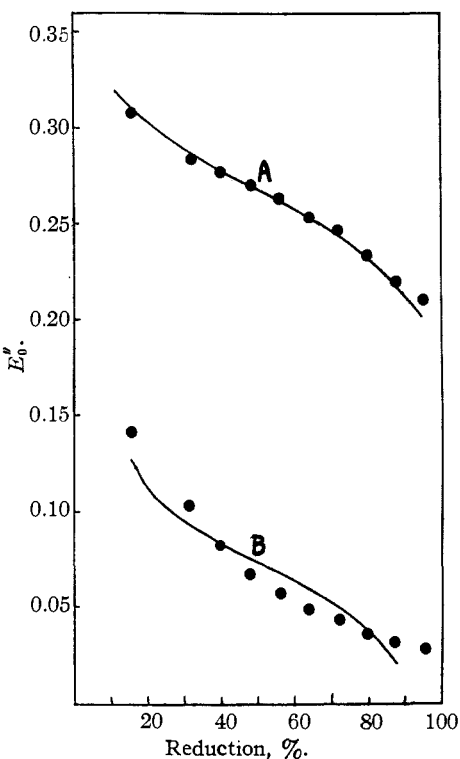


Fig. 2.—Reduction of triphenylcarbinol with chromous acetate. Theoretical curves were drawn through average E_0'' : A at $P_{\text{H}} = 0.97$, B at $P_{\text{H}} = +3.64$.

more than 14 mv. over the whole range; the values used in calculating the data in Table I correspond to the midpoint. Probably some of the discrepancies illustrated by the data in Figs. 1-3 are due to the change of α during the experiment but it did not seem worth while to carry out the calculations to make the necessary corrections.

TABLE I
FREE ENERGY OF REDUCTION OF HALOCHROMIC CARBINOLS TO FREE RADICALS

Carbinol	E_0'	Estimated α at dilution of expt.	ΔF of reduction of halochromic ion, E_0	ΔF of reduction of carbinol, E_0	ΔF of dissociation of ethane
$(C_6H_5)_3COH$	+0.315	0.38	+0.290	+0.225	-0.26
$(C_6H_5COH)(C_6H_5)_2O$	+0.095	.92	+ .095	+ .175	- .16
$C_6H_5CH_2COH(C_6H_5)_2O$	+ .150	5×10^{-3}	- .062	- .017	- .50

The value of α for hexaphenylethane was taken from Ziegler's data;⁴ the value for phenylxanthyl and benzylxanthyl from calculations appearing

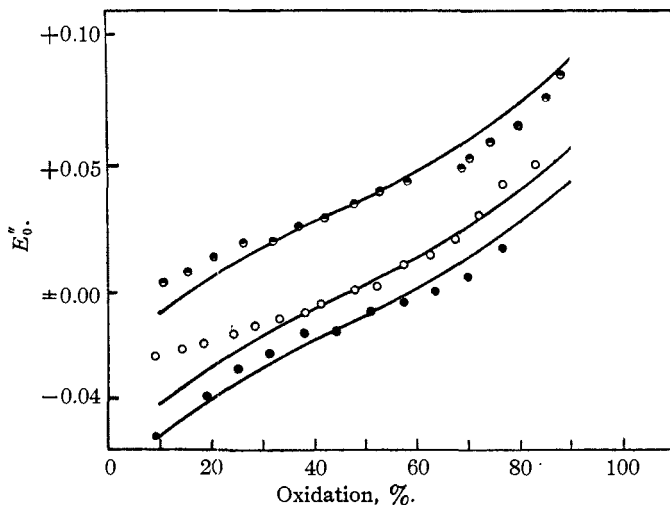
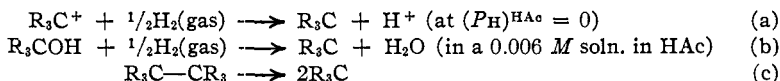


Fig. 3.—Oxidation of diphenyldixanthyl with indoethylol. Theoretical curves were drawn through the average E_0' . A at $P_H + 2.47$, B at $P_H + 3.68$, C at $P_H + 4.24$.

in another paper from this Laboratory. In this paper the value of ΔF of dissociation of these compounds is also estimated. The values of ΔF in columns 3, 4 and 5 correspond, respectively, to the processes



An inspection of the results shows that the free energies of reactions (a) and (c) are influenced to a greater degree by changes in structure than are the

(4) Ziegler, *Ann.*, **473**, 163 (1929).

values for reaction (b). In even this latter case, however, there is a difference of 0.242 volt (the corresponding extreme difference for reaction (a) is 0.350 volt). The orders of the three compounds for reactions (a) and (b) are the same but clearly bear no relation to the free energy of dissociation (reaction c). At first sight it is surprising that there should be greater differences in the free energy of reduction of the ion than the carbinol in a

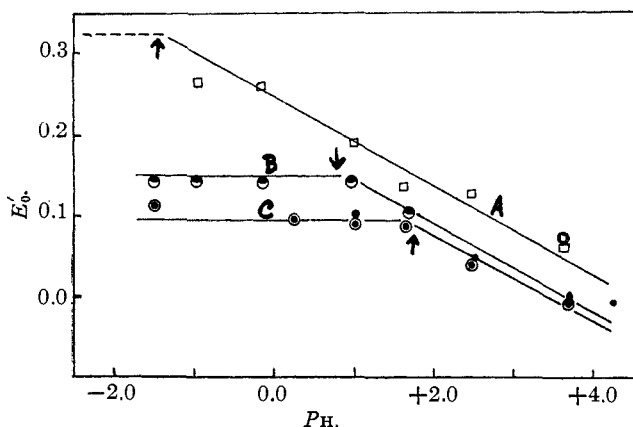
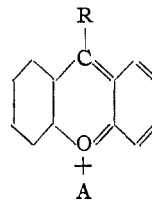


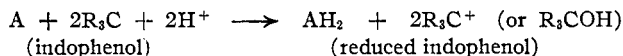
Fig. 4.—Change of E'_h with the change of P_H . A for triphenylmethyl, B for benzylxanthyl, C for phenylxanthyl. Curves were drawn with the theoretical slope. Points in circles were obtained by titration.

series of compounds, particularly in view of the work of Bent,⁵ which has shown that the affinity of free radicals for an electron is relatively little influenced by changes in structure. It seems probable that the explanation is due to the fact that in the case of the xanthyl ions, the halochromic ion is in part in the oxonium form (A). This ion cannot be reduced to a free radical only as a result of an electronic rearrangement. The relatively extreme basicity of the xanthyl compounds is, of course, merely another reflection of this same tendency. The few results obtained in our preliminary paper with the free radical from the very basic $C_6H_5COH-(C_6H_3OCH_3)_2O$ indicate that the value for ΔF of reduction of the ion would here be even much more divergent from the value for the reduction of the carbinol. This compound is too basic to measure in glacial acetic acid. It would be a matter of considerable interest to measure the potentials of the free radicals from this compound and other very basic carbinols such as trianisylcarbinol in a series of non-aqueous buffers in such a solvent as butyl carbitol, and it is hoped that this may be soon accomplished. Such results would provide a drastic test of the hypothesis offered above.

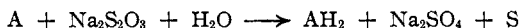


(5) Bent, *THIS JOURNAL*, **52**, 1498 (1930); **53**, 1786 (1931)

In conclusion we may point out an interesting consequence of the low oxidation-reduction potential of the free radical and the relatively high oxidation-reduction potential of the indophenol dyes. The free radical is oxidized by the dye to the corresponding halochromic ion (or, at the proper acidities, to the corresponding carbinol). As a result it is possible to titrate a free radical with indothymol. An excess of the dye is employed in a solution of acetic acid and bromobenzene. The excess of dye is then titrated with an aqueous solution of sodium thiosulfate. It was proved conclusively that these dyestuffs are quantitatively reduced by sodium thiosulfate according to the equation



The titration of the dye with sodium thiosulfate was shown to correspond to the reaction



A typical experiment was as follows: 2 cc. of a 0.006 *M* indothymol solution in acetic acid (glacial) was placed in a 50-cc. flask containing 1 cc. of bromobenzene. A weighed sample of free radical was introduced into the flask in a carbon dioxide atmosphere. After a few moments' agitation, 3 cc. of water was added and the excess of dye with thiosulfate; 2.329 mg. of diphenyldixanthyl required 0.834 cc. of 0.00926 *N* $Na_2S_2O_3$ for the back titration as compared with 1.318 cc. required by 2 cc. of the dye without addition of the free radical. Purity of diphenyldixanthyl 99%; by oxygen absorption in bromobenzene the purity was 98%.

The purity of the triphenylmethyl (hexaphenylethane) and the other free radicals used in this work were checked by oxygen absorption measurements in bromobenzene or by titration with indothymol. Since these free radicals have been prepared repeatedly in many laboratories, we will not take the space to detail their preparation in this paper. In all cases the purity was at least 98% as determined by one of the two methods.

Summary

The oxidation-reduction potentials of three free radicals and their halochromic salts have been measured in glacial acetic acid solutions. The changes of potential with changes in acidity of the buffer solutions are in accord with the theory developed in a preliminary paper.

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