[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTROCHEMICAL RELATION OF FREE RADICALS TO HALOCHROMIC SALTS[1]

BY J. B. CONANT, L. F. SMALL AND B. S. TAYLOR

RECEIVED JANUARY 30, 1925 PUBLISHED JULY 3, 1925

The intense color of solutions of triphenylcarbinol and its derivatives in acetic acid or alcohol containing a mineral acid is generally considered to be due to the formation of the so-called halochromic salts. Many such colored salts have been obtained in the solid state and their analyses correspond to the formula $(Ar_3C)X$, although they often contain in addition a molecule of HX (where $X = SO_4H, ClO_4, NO_3$, etc.).[2] While a number of different views have been expressed in regard to the structure of these salts most investigators now agree that in solution they are very largely present as the ions $(Ar_3C)^+X^-$, and that their formation is expressed by the reversible equation

$$Ar_3COH + HX \rightleftharpoons (Ar_3C)^+ + X^- + H_2O \qquad (1)$$

Among the many pieces of evidence in support of this equation, the determination of the apparent molecular weight of triphenylcarbinol in concentrated sulfuric acid is particularly convincing.[3] The reversibility of the process is evident from the fact that on diluting the halochromic solutions with water, the color vanishes and the carbinol is recovered unchanged. It has long been recognized that the formal relationship of these halochromic salts to free radicals of the type Ar_3C— is that of an inorganic salt to a metal. It is the purpose of this paper to show that certain electrochemical implications of this analogy can be demonstrated experimentally. We have found that, just as a metal in contact with a solution of its salts has a characteristic electromotive force, so a mixture of a free radical and the corresponding halochromic salt has a definite potential. If a reducing agent with an oxidation-reduction potential lower than a certain value is added to a solution of a metallic salt, the metal precipitates; in exactly the same manner free radicals may be prepared by the action of suitable reducing agents on solutions of halochromic salts. In a preliminary paper from this Laboratory[4] it was shown that certain oxonium and pyridinium salts were reduced by vanadous chloride and that hexaphenylethane could be obtained in small amounts by the action of the same reagent on solutions of triphenylcarbinol in concentrated acids. We have now developed a satisfactory method of preparing hexaphenylethane and similar substances directly from the corresponding carbinols.

---

[1] Presented before the Organic Division of the American Chemical Society in Washington, D. C., April, 1924.

[2] Schmidlin, "Das Triphenylmethyl," **1914**, p. 107.

[3] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); *Ber.*, **55**, 953 (1922).

[4] Conant and Sloan, THIS JOURNAL, **45**, 2466 (1923).

The application of this method to the preparation of certain hitherto inaccessible ethanes (dissociated and undissociated) will be the subject of other papers.

I. Electromotive Force Measurements

Two methods of measuring the potential of free radicals may be employed; one the method of mixtures, and the other the titration method. The problem is very similar to the determination of the oxidation-reduction potential of quinones and related substances, and both methods have been carefully studied in the last few years in connection with this problem.[5] The investigation of the potentials of free radicals is complicated by a number of factors which do not affect the study of quinones, and the data presented in this paper are consequently much less accurate than the electromotive force measurements of these other reversible organic systems. Indeed, in this paper we shall only attempt to establish the fact that significant potentials can be measured and that they determine the behavior of halochromic salts towards reducing agents. If certain experimental complications mentioned below can be mastered, it may be possible at some later time to determine accurately the potentials of various free radicals, but our present data are only certain within some 10 to 20 millivolts.

The extreme reactivity of the free radicals is the cause of the chief experimental obstacles; in acid solution free radicals more or less rapidly undergo two changes; one, an irreversible polymerization, and the other, a simultaneous reduction and oxidation to the triarylmethane and the triarylcarbinol. Consequently, cells containing both the free radicals and the halochromic salt (by necessity in the presence of acids) maintain a constant composition only for a short time. The stability of the different free radicals towards acids varies greatly, triphenylmethyl being one of the most stable and the methoxy compounds being among the least. Most of our experiments have been performed with triphenylmethyl.

The theoretical interpretation of the potential measurements is complicated by the hydrolysis of the halochromic salt, according to Equation 1 above, and by the association of the free radical to the hexa-aryl ethane (Equation 2); at present it cannot be determined whether or not the quinoidization of the free radical demonstrated by Gomberg is also a complication.

$$2Ar_3C \rightleftharpoons Ar_3C{-}CAr_3 \qquad (2)$$

Method of Mixtures

Our most satisfactory results have been obtained by measuring the

---

[5] Granger and Nelson, This Journal, **43**, 1401 (1921). W. M. Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920); *Public Health Reports*, **38**, 443, 666 933, 1669 (1923). Biilmann, *Ann. chim.*, **16**, 321 (1921); **19**, 137 (1923). La Mer and Baker, This Journal, **44**, 1954 (1922). Conant, Kahn, Fieser and Lutz, *ibid.*, **44**, 1382 (1922). Conant and Fieser, *ibid.*, **44**, 2480 (1922); **45**, 2194 (1923).

potential of triphenylmethyl (hexaphenylethane) by the method of mixtures. To this end we have measured the e.m.f. of the following cell consisting of a saturated solution of tetrachloroquinone (chloranil) and tetrachlorohydroquinone on one side and varying proportions of triphenylmethyl and triphenylmethyl sulfate on the other:

$$\begin{array}{clc|clc}
\overset{+}{\mathrm{Pt}} & C_6Cl_4O_2 & \text{Solvent} & \text{Solvent} & (C_6H_5)_3C & \overset{-}{\mathrm{Pt}} \\
 & C_6Cl_4(OH)_2 & \overset{+}{H_2SO_4} & \overset{+}{H_2SO_4} & [(C_6H_5)_3C]SO_4H & \\
 & \text{Saturated} & & & &
\end{array}$$

The e.m.f. of this cell corresponds to the free energy of the reaction,

$$C_6Cl_4O_2(S) + 2Ar_3C + 2H^+ \rightleftharpoons C_6Cl_4(OH)_2(S) + 2Ar_3C^+ \qquad (3)$$

We may therefore write the following equations using activities throughout and letting $\Delta F^\circ = -2F\mathbf{E}^\circ$ be the free energy of the reaction referred to the solid as the standard state for the quinone and the hydroquinone, a ratio of the activities of triphenylmethyl and the halochromic ion as unity and the activity of the hydrogen ion referred to a basis to be discussed later.

$$-2\mathbf{E}F = \Delta F = \Delta F^\circ + RT\,ln\,\frac{[Ar_3C^+]^2}{[Ar_3C]^2\,[H^+]^2}$$

or,

$$\mathbf{E} = \mathbf{E}^\circ - \frac{RT}{F}\,ln\,\frac{[Ar_3C^+]}{[Ar_3C]} + \frac{RT}{F}\,ln\,[H^+] \qquad (4)$$

If we denote the total concentration of ethane dissociated and undissociated by $[\mathrm{Eth}]_T$ and the degree of dissociation by α, then $[Ar_3C] = 2\alpha[\mathrm{Eth}]_T$. Substituting this in Equation 4 and assuming the activity and concentration to coincide in the dilute solutions (0.01 *M*) employed, we have, at 25°, Equation 5. With a fixed solvent and acid concentration and a fixed concentration of ethane, $[H^+]$ and α may be considered constant and we may write Equation 6.

$$\mathbf{E} = \mathbf{E}^\circ - 0.059\log\frac{[Ar_3C^+]}{2[\mathrm{Eth}]_T} + 0.059\log[H^+] + 0.059\log\alpha \qquad (5)$$

$$\mathbf{E} = \mathbf{E}_1{}^\circ - 0.059\log\frac{[Ar_3C^+]}{2[\mathrm{Eth}]_T} \qquad (6)$$

The solvent actually employed in our experiments was a mixture of glacial acetic acid (100 cc.), bromobenzene (26 cc.) and 98% sulfuric acid (15 cc.). In such a solvent triphenyl carbinol readily dissolves, forming the colored halochromic sulfate, and we are safe in assuming that in this strong anhydrous acid solution the formation of the halochromic salt is complete. We therefore introduced into one-half of our cell weighed amounts of hexaphenylethane and triphenylcarbinol and calculated the ratio of total free radical (associated and free) to halochromic salt from the weights of the materials thus added. The cell, which was of the H type, consisted of two parts connected by a stopcock: one side had a capacity of about 15 cc. and contained the solvent saturated with tetrachloroquinone and tetrachlorohydroquinone; the other side, which held about

40–50 cc. of liquid, was closed by a rubber stopper carrying two electrodes of platinum foil, gas inlet and outlet tubes and a tube for introducing the solvent. A small plug of cotton wool placed in the side tube of the smaller container near the stopcock prevented too rapid diffusion. The electrode in the chloranil half-cell was a coil of bright platinum wire.

In making a determination, the larger arm of the cell was cleaned and dried and then shut off from the smaller arm by turning the stopcock. The weighed amounts of hexaphenylethane and triphenylcarbinol were rapidly introduced, the stopper was sealed in place with a little collodion and the half-cell alternately exhausted and filled with pure dry nitrogen four or five times. A slow stream of nitrogen was then passed through the cell and the solvent added through a suitable tube. A saturated solution of the chloroquinone and chlorohydroquinone was placed in the other limb of the cell, the stopcock turned to connect the two arms and the e.m.f. of the cell determined. Throughout all the experiments it was found that the potentials of the two electrodes agreed within 1 or 2 millivolts. The contents of the cell were adequately stirred by the nitrogen stream and solution was complete in 2 to 5 minutes. Since the internal resistance of the cell was very high, a very sensitive galvanometer was employed in connection with the usual type of potentiometer which was accurate to 0.5 millivolt. The temperature in the experiments was 23° ± 1°.

The hexaphenylethane was recrystallized from acetone in an atmosphere of carbon dioxide, filtered and dried without exposure to air; its oxygen capacity, determined in the usual manner,[6] corresponded to a purity of 95–100% with different samples prepared at different times.

Because of the decomposition of the hexaphenylethane in the presence of the strong acid, the e.m.f. of the cell diminished rapidly in each experiment. The rate of change in most cases was fairly uniform and between 1 and 2 millivolts per minute. In Table I the highest observed e.m.f. is recorded as well as the rate of change during the first ten minutes, and from these figures was calculated an extrapolated value for the e.m.f. before any decomposition had occurred. Considering all the experimental difficulties, it is questionable whether these extrapolated values are much more significant than the maximum potentials which were reached in from 3 to 7 minutes. The first column of the table records the ratio of total carbinol to total free radical, $[\mathrm{Ar_3C}] = 2[\mathrm{Eth}]_T$, as actually weighed into the cell, the next the value of the term $\log \frac{[\mathrm{Ar_3C^+}]}{2[\mathrm{Eth}]_T}$ (assuming that $[\mathrm{Ar_3COH}]_{Total} = [\mathrm{Ar_3C^+}]$). The last two columns give the value of $\mathbf{E}_1°$ (Equation 6) calculated from the maximum e.m.f. and also from the extrapolated potentials. The values for $\mathbf{E}_1°$ in all the experiments are strictly comparable, since the chloranil cell was saturated and the same solvent

---

[6] Gomberg, THIS JOURNAL, 39, 1652 (1917).

employed each time, although actually a new solution was introduced after Experiment 3. The data are plotted in Fig. 1.

An inspection of Table I shows that while **E**$_1°$ varies somewhat the results are in as good agreement with the electrochemical equation as can be expected, and in general conform to the logarithmic equation as shown in Fig. 1. Each value of **E**$_1°$ corresponds essentially to a new cell and one can state therefore with assurance that *mixtures of triphenylmethyl and triphenylmethyl sulfate give reproducible potentials* in accord with the usual

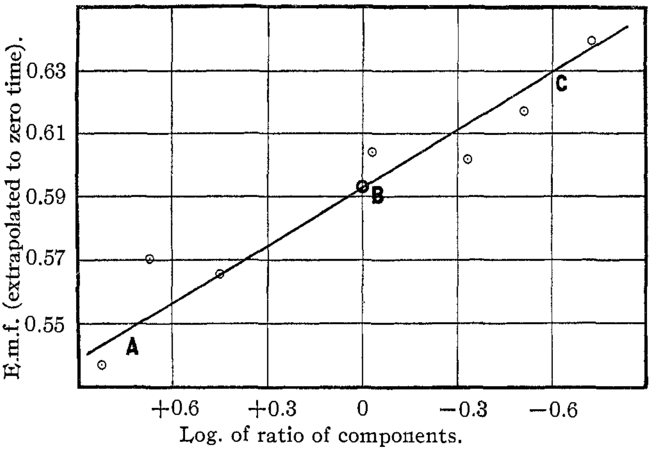


Fig. 1.—The potential of triphenylmethyl-triphenylmethyl sulfate. The e.m.f. of the cell at zero time is plotted vertically; $\log \frac{[Ar_3C^+]}{2[Eth]_T}$ horizontally. The experimental points are indicated by circles; the line ABC is the curve of the electrochemical equation drawn through the point B which is the average value of **E**$_1°$.

TABLE I

E.M.F. OF CHLORANIL-TRIPHENYLMETHYL CELL WITH ACETIC ACID AT 23° ± 1°

Exp. No.	Ratio (moles) $(C_6H_5)_3COH$ to $(C_6H_5)_3C$	$\text{Log} \frac{[Ar_3C^+]}{2[Eth]_T}$	$0.059 \log \frac{[Ar_3C^+]}{2[Eth]_T}$	Max. e.m.f. volts	Time when max. e.m.f. reached (min.)	Rate of change of e.m.f. Mv. per min.	E.m.f. at zero time (extrapot.)	**E**$_1°$ from max. e.m.f.	**E**$_1°$ from extra. e.m.f.
1	0.934	—0.030	—0.002	0.595	7	1.3	0.604	0.593	0.602
2	4.67	+0.669	+0.033	0.554	7	1.0	0.571	0.587	0.604
3	0.187	—0.728	—0.043	0.615	8	3.0	0.639	0.572	0.596
4	0.307	—0.513	—0.030	0.614	3	1.0	0.617	0.584	0.587
5	2.80	+0.447	+0.027	0.562	3	1.4	0.566	0.589	0.593
6	6.55	+0.816	+0.048	0.534	4	0.75	0.537	0.582	0.585
7	0.468	—0.330	—0.020	0.593	7	1.3	0.602	0.573	0.582
							Average	0.583	0.593

The molar concentration of triphenylmethyl in each experiment was 0.006 *M;* the weight of triphenylcarbinol employed was such as to give the ratio of molalities listed above.

electrochemical equation. It should be mentioned, in addition, that when air is blown through such a cell for a few minutes, the e.m.f. falls to an ill-defined level some 0.2 to 0.3 volt below the previous value, corresponding to the complete change of free radical to peroxide.

Titration Method

If a solution of triphenylcarbinol in an acidic medium is treated with increments of an aqueous solution of vanadous salt, a rapid and quantitative reduction to triphenylmethyl occurs. If this process is carried out in a suitable cell equipped with inert electrodes, the usual type of titration curve can be obtained (Fig. 2). The mid-point of this curve corresponds to an equimolecular mixture of halochromic salt (assuming all the carbinol to be present as such) and free radical, and corresponds to the normal potential as measured by the method of mixtures. As solvents we have employed acetic acid and acetone containing varying amounts of mineral acids and water. The amount of carbinol employed (about 0.0004 mole in 80 cc. of solvent) was such that a homogeneous solution was present throughout the titration. To avoid as much as possible the decomposition of the free radical, the titrations were performed rapidly, the increments of reducing agent being determined by counting the number of drops from the buret tip, and in every case were completed in 3 to 5 minutes. The equilibrium at the electrodes seems to be attained very rapidly, since two elec-

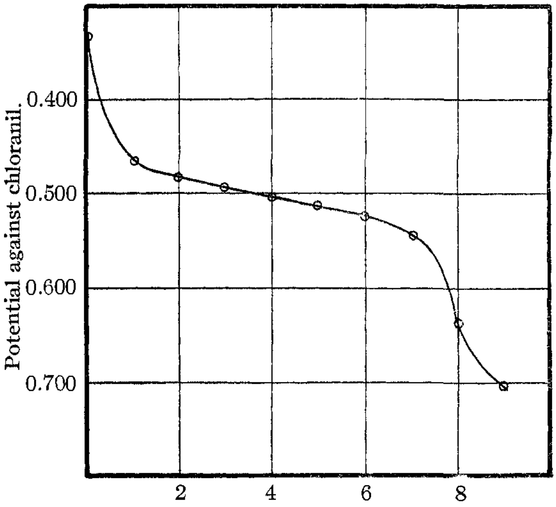


Fig. 2.—Titration of triphenylcarbinol in acetic-sulfuric acid (Sol. A) with vanadous sulfate; potentials against chloranil electrode (A_1) plotted vertically, increments of reducing agent horizontally.

trodes always gave the same value within a few millivolts; in contrast to the behavior of many quinones, there seems to be no difficulty on this score. The apparatus employed was similar to that previously used in the titration of quinones in this and other laboratories[7] and consists of a titration cell of about 150cc. capacity, and a half-cell of known potential connected by a suitable bridge. The contents of the titration cell were, of course, stirred mechanically, and freed from oxygen by a current of pure nitrogen.

The half-cell used in these experiments consisted of a platinum electrode immersed in 5–10 cc. of a mixture of acetic acid and sulfuric acid saturated with tetrachloroquinone (chloranil) and tetrachlorohydroquinone. A glass siphon tube tightly plugged at both ends with filter paper and filled with the same acetic acid mixture connected the half-cell with the titration vessel. The potential of this half-cell and the liquid junctions involved appear to be reproducible within 5 or 10 millivolts, if a new cell is made up every day. The acetic acid mixture employed was that designated as A_1 in Table II and we shall therefore refer to this half-cell as chloranil A_1 electrode. A number of titrations at 23° of triphenylcarbinol in an acetic acid-sulfuric acid mixture (Solution A, Table II) using such a half-cell as the other electrode gave a mean value for the e.m.f. at the mid-point of 0.505 ± 0.005. By direct comparison, chloranil electrode A_1 was found to be 0.095 less positive than a chloranil half-cell, such as that employed in measuring the potential by the method of mixtures. The mean value of $\mathbf{E}_1^\circ$ (Table I) referred to the chloranil cell A_1 is thus 0.493; the difference between the titration method and the method of mixtures is thus within the limits of our experimental errors. The results are comparable since the dilution was not very different in the two sets of experiments and the value of α (Equation 5) should thus be nearly the same in both instances.

The Evaluation of Single Electrode Potentials and the Effect of the Hydrolysis of the Halochromic Salt.—It is necessary to attempt to evaluate single electrode potentials of the free radicals in order to apply the electrochemical point of view to the action of reducing agents on carbinols in solutions of varying acidity. Because of the difficulty of measuring or calculating liquid-junction potentials, it is not possible to make this treatment of the subject rigorous at this time. The following development of approximate equations seems justified, however, as a first attempt at a quantitative statement of the various factors involved in the behavior of mixtures of free radicals and carbinols under different conditions. At some later time when the electrochemistry of non-aqueous solutions has developed further, it should be possible to substitute a more exact treatment.

[7] Ref. 1.

The single electrode potential[8] at 25° of a saturated chloranil half-cell referred to the normal hydrogen electrode is

$$\Pi_s = 0.664 + 0.059 \log [H^+] \qquad (7)$$

The value 0.664 has been determined in this Laboratory.[9] Neglecting liquid junction potentials, measurements of the following cells enable us to evaluate single electrode potentials of the free radicals referred to the normal (aqueous) hydrogen electrode and also the activity of the hydrogen ion $[H^+]$ in the non-aqueous solutions employed.

$^+$Chloranil Electrode A_1	Chloranil Electrode in 0.2 *N* HCl	(A)
Chloranil Electrode A_1	Chloranil Electrode in non-aqueous sol. $[H^+] = ?$	(B)

The e.m.f. of cell A was found to be 0.075 at 23°, and taking the activity of the hydrogen ion in 0.2 *N* HCl as 0.16, the potential of chloranil electrode A_1 referred to the normal hydrogen electrode is therefore +0.693, and the value of —log $[H^+]$ of Solution A_1 is —0.5 or $[H^+] = 10^{0.5}$.

In Table II are listed the non-aqueous solutions we have employed, together with the value of —log $[H^+]$ calculated from the e.m.f. of a suitable cell of Type B, liquid-junction potentials being ignored. It should be noted that these values of —log $[H^+]$ are negative in solutions more acidic than normal acid and positive in less acid solutions; in aqueous solutions they are, of course, essentially the Sörensen values. By the use of solutions with varying activity of acid, it has been possible to measure

TABLE II

Sol.	Composition	Obs. e.m.f. of chloranil half-cell against half-cell A_1	Calcd. e.m.f. of chloranil half-cell against normal hydrogen electrode	—log $[H^+]$
A	200 cc. glac. acetic acid, 20 cc. H_2SO_4	+0.095	+0.123	—2.1
A_1	100 cc. sol. A, 16 cc. H_2O	.000	+ .028	—0.5
A_2	100 cc. sol. A, 3.3 cc. H_2O	+ .074	+ .102	—1.7
A_3	100 cc. sol. A, 20 cc. H_2O	— .005	+ .023	—0.4
B	200 cc. acetone, 10 cc. H_2O, 40 cc. H_2SO_4	+ .065	+ .093	—1.6
B_1	200 cc. acetone, 10 cc. H_2O, 20 cc. H_2SO_4	+ .020	+ .048	—0.8
B_2	200 cc. acetone, 10 cc. H_2O, 5 cc. H_2SO_4	— .040	— .012	+0.2
B_3	200 cc. acetone, 10 cc. H_2O, 25 cc. acetic acid	— .090	— .062	+1.0
B_4	200 cc. acetone, 3 g. anthranilic acid, 1 g. LiCl, 2 cc. H_2O	— .130	— .102	+1.7

---

[8] The European convention in regard to sign of *single electrodes* has been used throughout this paper.

[9] Conant and Fieser, THIS JOURNAL, **45,** 2194 (1923).

TABLE III

SINGLE ELECTRODE POTENTIALS OF FREE RADICALS IN SOLUTIONS OF VARYING ACIDITY AT 23° ± 1°

Sol.	—log [H⁺]	Π_1 (Referred to normal hydrogen electrode) $(C_6H_5)_3C—$ volts	 $C_6H_5\overset{\vert}{C}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$ volts	 $C_6H_5\overset{\vert}{C}\left\langle\begin{matrix}C_6H_3—OCH_3\\C_6H_3—OCH_3\end{matrix}\right\rangle O$ volts
A	—2.1*	+0.188	+0.055(?)	
A_2	—1.7	+ .193		
B	—1.6	+ .160	+ .045	
B_1	—0.8	+ .100	+ .060	
A_1	—0.5	+ .093	+ .050(?)	
A_3	—0.4	+ .060(s)		
B_2	+0.2	†	+ .055	—0.200(?)
B_3	+1.0		+ .005	— .200
B_4	+1.7		— .070(s)	— .190

The results marked (?) are somewhat uncertain, as the difference between Π_1 and the VCl_2 was too small for a sharp end-point.

* Due to the addition of a small amount of water in the titrating solution (VCl_2), the actual value is probably somewhat lower.

(s) Indicates that the reaction with VCl_2 is slower than in solutions of higher acidity, a few minutes being required for equilibrium to be reached.

† Indicates that the reaction is too slow to enable the titration method to be employed.

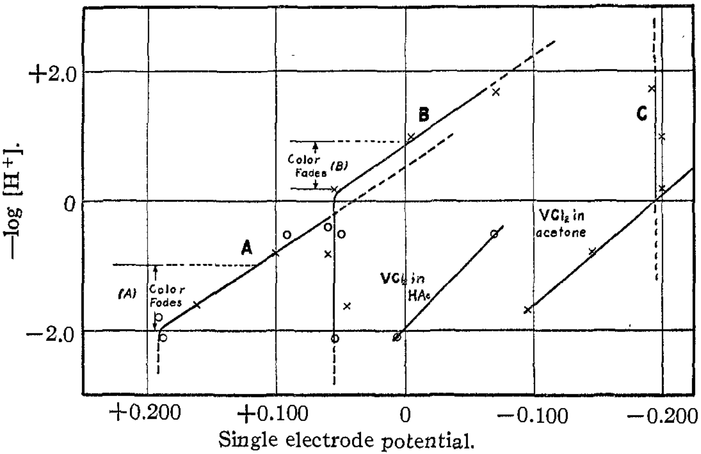


Fig. 3.—Single electrode potentials of certain free radicals in solutions of varying acidity. *A* = triphenylmethyl-triphenylcarbinol system; *B* = phenylxanthyl-phenylxanthenol system; *C* = phenyldimethoxyxanthyl-phenyldimethoxyxanthenol system. Crosses indicate determinations in acetone solutions; circles determinations in acetic acid solutions. The range of acidity is indicated in which the halochromic color fades with decreasing acidity for triphenylcarbinol (*A*) and phenylxanthenol (*B*); in solutions less acidic than this range a solution of the carbinol is colorless.

the single electrode potential of free radicals over a wide range of $[H^+]$; these solutions were essentially "buffer solutions," since the stoichiometric amount of acid present was always large as compared to the organic material. The results are listed in Table III and plotted graphically in Fig. 3, the value of —log $[H^+]$ being plotted vertically and the single electrode potentials horizontally. In every case these potentials were actually measured against a chloranil cell A_1 and the results calculated to the normal hydrogen electrode basis.

The equation for the single electrode potential of a free radical (referred to the normal hydrogen electrode ignoring liquid junctions) is given by Equation 8 which is obtained by subtracting Equation 5 from Equation 7. If we assume that α is constant under the conditions of the experiments

$$\Pi = \Pi_0 + 0.059 \log \frac{[Ar_3C^+]}{2[Eth]_T} - 0.059 \log \alpha \qquad (8)$$

(which is probably true if the same dilution and temperature are used throughout) the first and last terms can be combined as Π_1, giving Equation 9. It is this potential, Π_1, which we have referred to above as the

$$\Pi = \Pi_1 + 0.059 \log \frac{[Ar_3C^+]}{2[Eth]_T} \qquad (9)$$

single electrode potential of the free radical and plotted in Fig. 3. The term Π_1 is analogous to the single electrode potentials of the metals; the latter, however, are necessarily the potentials of a solution saturated with the metal rather than one in which the last term of Equation 9 is zero.

In the experiments considered up to this point we have assumed that practically all the carbinol was present as the halochromic salt; this is true in mixtures of concentrated sulfuric and acetic acids, such as represented by Solution A, Table II, as evidenced by the intense color. On adding water to such solutions the color lightens and finally disappears; similarly, in acetone solutions containing considerable sulfuric acid (Sol. B), triphenylcarbinol gives a faintly colored solution, while with less acid the solution is colorless. The hydrolysis of a halochromic salt may be expressed by Equation 10.

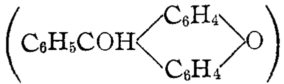
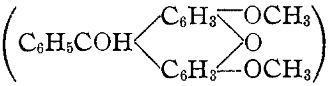
$$\frac{[Ar_3COH]\,[H^+]}{[Ar_3C^+]\,[H_2O]} = K \qquad (10)$$

If we assume that total carbinol = $[Ar_3COH]_T = [Ar_3COH] + [Ar_3C^+]$, it follows that $[Ar_3C^+] = \dfrac{[Ar_3COH]_T}{\left(1 + K\dfrac{[H_2O]}{[H^+]}\right)}$, and substituting in Equation 9, we have,

$$\Pi = \Pi_1 + 0.059 \log \frac{[Ar_3COH]_T}{2[Eth]_T} - 0.059 \log \left(1 + K\frac{[H_2O]}{[H^+]}\right) \qquad (11)$$

It is evident that when $K[H_2O] < [H^+]$ the last term is negligible and we have Equation 9; this is true when practically no hydrolysis of the halochromic salt occurs, since $\frac{[Ar_3COH]}{[Ar_3C^+]} = \frac{K[H_2O]}{[H^+]}$. When $[H^+] < K[H_2O]$ the equation takes the form

$$\Pi = \Pi_1 + 0.059 \log \frac{[Ar_3COH]_T}{2[Eth]_T} + 0.059 \log [H^+] - 0.059 \log K\,[H_2O] \qquad (12)$$

In other words, when the hydrolysis of the halochromic salt is negligible, the potential is independent of the value of $[H^+]$, when hydrolysis is complete, the potential is a straight line function of $[H^+]$. The experimental results plotted in Fig. 3 are in excellent agreement with these equations. The bend in the single electrode potential curves occurs at just that range of acidity where experiments show that the halochromic color fades; the difference between the "basicity" of the three carbinols—triphenylcarbinol, phenylxanthenol  $\left(C_6H_5COH\begin{matrix}C_6H_4\\C_6H_4\end{matrix}O\right)$ and phenyldimethoxyxanthenol  $\left(C_6H_5COH\begin{matrix}C_6H_3-OCH_3\\O\\C_6H_3-OCH_3\end{matrix}\right)$ is reflected in the very different points at which the effect of the last term of Equation 11 becomes appreciable. In the case of the most "basic" carbinol, the hydrolysis is not evident in the experimental range investigated (this substance is still halochromic in an aqueous buffer of $[H^+] = 10^{-4}$). In plotting Fig. 3, and in this discussion, we have assumed that the activity of the water is the same in all the different solvents; this assumption is not correct, but probably introduces only a slight error except in the cases of the acetic acid solutions. Some of the divergence of the points from the curve may be due to this effect, which we hope at some later time to elucidate in connection with the general problem of the activity of acids in non-aqueous solvents and the hydrolysis of salts of very weak bases and pseudo bases.

It is of interest in connection with the general problem of reversible and irreversible oxidation-reduction systems to note that it was not possible to obtain reproducible or significant potentials with ethanes which do not dissociate into free radicals. Thus, no potentials could be evaluated by the method of mixtures with tetraphenylethane or bixanthyl and the corresponding halochromic salts. The halochromic salts are rapidly reduced to the ethanes by vanadous salts, but the potentials observed when the titration method is employed are indefinite and not reproducible. It is also true that whereas the ethanes which dissociate are instantly oxidized to the halochromic salt by ferric chloride or chloranil in suitable solvents, tetraphenylethane or bixanthyl do not behave in this manner. *The reduction of carbinols to ethanes which dissociate is therefore a strictly reversible process; the reduction of carbinols to undissociated ethanes is an irreversible transformation.*[10]

---

[10] Compare Conant and Lutz, This Journal, **45,** 1047 (1923); **46,** 1295 (1924). Conant and Cutter, *J. Phys. Chem.*, **28,** 1096 (1924).

Too few facts are now available to draw any conclusions in regard to the relation between the structure of a free radical and its single electrode potential. A few preliminary experiments with α-naphthyldiphenylmethyl, *p,p*-ditolylphenylmethyl and *p,p*-dichlorodiphenyl-phenylmethyl indicate that the single electrode potentials of these substances are not very different (20–40 millivolts) from that of triphenylmethyl. On the other hand, the values of Π_1 for phenylxanthyl and phenyldimethoxyxanthyl are very different from each other and from that of triphenylmethyl. It should be noted, however, that the potentials of triphenylmethyl, phenylxanthyl and probably phenyldimethoxyxanthyl are in the reverse order in solutions in which hydrolysis is complete and lie nearer together. Thus, in comparing the potentials, it makes a great difference whether one is dealing with the e.m.f. corresponding to the free-energy change of reaction A or B.

$$Ar_3COH + H_2 \rightleftharpoons Ar_3C— + H_2O \quad (A)$$
$$2Ar_3C^+ + H_2 \rightleftharpoons Ar_3C— + 2H^+ \quad (B)$$

The value of α (the degree of dissociation of the ethane) is included in our term Π_1, but variations from compound to compound in this respect alone would probably affect the potential by not more than 60 millivolts (a change from $\alpha = 0.09$ to $\alpha = 0.9$).

II. The Preparation of Dissociated and Undissociated Ethanes

The data summarized in Table III and Fig. 3 are the basis for a very rapid and convenient method of preparing ethanes directly from the corresponding carbinols. The carbinol is dissolved in a suitable solvent containing a certain amount of acid, a concentrated aqueous solution of vanadous salt introduced and, after the reduction is complete, water is added and the precipitate filtered and washed with water. As solvents, acetone or glacial acetic acid may be employed or, if the carbinol is sufficiently basic, it may be dissolved in aqueous acid or the halochromic salt prepared and dissolved in water. If acetone is employed the ethane often crystallizes from the reaction mixture and may be filtered off without the addition of water.

The rapidity of the reduction appears to be a function of the activity of the hydrogen ion, other things being equal. The action of the reducing agent is practically instantaneous if the acidity is such that an appreciable halochromic color is visible; the process is also very rapid in solutions slightly less acidic than those necessary to give halochromism. At considerably lower values of $[H^+]$, however, the reduction proceeds so slowly that it is not feasible to carry out an electrometric titration (for example, solution of $(C_6H_5)_3COH$ in B_2, Table III) and on a preparative scale the process may require many minutes, hours or even days. With the dissociated ethanes, the best results are obtained if the reduction is relatively fast, since otherwise by-products are formed by the action of the acid on the free radical.

If it be assumed that the reducing agent acts only on the ionized halochromic salt $(Ar_3C)^+ + V^{++} \longrightarrow Ar_3C + V^{+++}$, the effect of the acidity on the rate of reduction is readily explained. In colorless solutions in which hydrolysis is practically complete, the concentration of the halochromic ion must be very minute and, of course, is a function of the activity of the hydrogen ion (Equation 10). If the speed of the reaction between the halochromic salt and reducing agent is governed by the usual bimolecular equation,

$$\frac{dx}{dt} = k_1[Ar_3C^+]\ [V^{++}] \qquad (13)$$

it is evident, since $[Ar_3C^+] = \dfrac{[Ar_3COH]_T\ [H^+]}{K[H_2O]}$ when hydrolysis is practically complete, that

$$\frac{dx}{dt} = k_1[Ar_3COH]_T\ [V^{++}]\ \frac{[H^+]}{K[H_2O]} \qquad (14)$$

At a constant concentration of carbinol and reducing agent, the rate is a function of $[H^+]$ if $[H_2O]$ is also constant. It should further be noted that although the order of magnitude of k_1 be such that the reaction is very fast when no hydrolysis occurs, the effect of multiplying this constant by $\dfrac{[H^+]}{K[H_2O]}$ when $K[H_2O]$ is much greater than $[H^+]$, makes the apparent constant much smaller; indeed, the reaction may proceed at such a rate as to be immeasurable if the value of $[H^+]$ is sufficiently low. *In general, the less basic the carbinol, the more acidic the solution required for its reduction.* This has been found to be the case, both in the titrations mentioned above and the preparative experiments given below; this correlation seems to show that our interpretation of the process is correct.

Titanous chloride can be used in place of vanadous chloride for the preparation of certain ethanes. Its potential lies just below that of triphenylmethyl in acetic acid and acetone solutions; it is, however, a much less general reagent than vanadous chloride or sulfate. It must be borne in mind that whether or not a given reagent will precipitate an ethane from a solution of the carbinol or halochromic salt depends not only on the factors represented by Fig. 3 and the corresponding equations, but also on the solubility of the ethane in the medium employed. It often happens, therefore, that titanous chloride may be used for preparing ethanes whose "normal" potentials are below that of titanous chloride itself.

The Preparation of Hexaphenylethane (Triphenylmethyl).—The best procedure for preparing this substance directly from the carbinol is illustrated by the following typical experiment. One g. (0.0038 mole) of triphenylcarbinol was dissolved in 20 cc. of acetone in a small flask which had been swept out with carbon dioxide. Four cc. of normal vanadous chloride (made by reducing V_2O_5 with zinc and hydrochloric acid) was added and then slowly 2 cc. of concd. hydrochloric acid. The ethane began to crystallize from the solution in a few minutes and a further increment of 2 cc. of acid was then added, followed by 4 cc. more of VCl_2. After four or five minutes, a final addition of 2 cc. of hydrochloric acid was made and then after a few moments 50 cc. of boiled water (cooled to room temperature) was added. The precipitate was filtered off rapidly, washed with boiled water and dried in nitrogen. The yield was 0.92 g. of hexaphenylethane, having an oxygen absorbing power in bromobenzene of 86% of that calculated.[11] In a parallel experiment the entire moist precipitate was transferred to the usual apparatus for determining oxygen absorbing capacity. The amount of oxygen absorbed corresponded to 100% of that calculated from the carbinol employed. Hexaphenylethane can also be prepared by reduction in acetic acid solution, the yields of active material being 60 to 80%. To obtain material 100% pure, the crude product must be recrystallized from acetone in a special apparatus.

The Preparation of Di-α-Naphthyltetraphenylethane in Acetic Acid Solution.—To illustrate the use of glacial acetic acid as a solvent the following typical experiment with α-naphthyldiphenylcarbinol may be mentioned; the reaction can be carried out in acetone solution, also, but the yield is only about 60% of active material and in general the process is less satisfactory than with triphenylcarbinol. Half a gram (0.0016 mole) of α-naphthyldiphenylcarbinol was dissolved in 25 cc. of glacial acetic acid and 3 cc. of concd. sulfuric acid. The mixture was cooled in an ice-bath and 4 cc. of 0.6 *M* vanadous sulfate solution added during half a minute, the flask being shaken to insure complete mixing of the solutions. The contents were then poured into 100–200 cc. of cold boiled water and the resulting yellow precipitate was filtered off and washed rapidly with water. The oxygen capacity of the precipitate corresponded to 85% of the theoretical amount of free radical calculated from the carbinol employed. The well-known peroxide can be obtained by dissolving the crude free radical in ether and shaking with air. A great number of experiments showed that the amounts of acetic acid and sulfuric acid given above are the most satisfactory. We are indebted to Mr. W. J. Fried for this work.

9-Phenyl-3,6-dimethoxyxanthyl.—This free radical. like many others[12] containing the methoxy group, was so unstable that it could not be prepared in a pure state or kept for any length of time. The titrations listed in Table III and the oxygen absorbing power of the freshly prepared material prove that a free radical is formed by the action of vanadous chloride on an aqueous solution of 9-phenyl-3,6-dimethoxy-xanthylium chloride. The carbinol is so basic, in this instance, that the chloride can be dissolved in water without appreciable hydrolysis. In a typical experiment 0.33 g. of the yellow chloride-hydrochloride,[13] m. p., 137–140°, was dissolved in boiled water and slightly more than the calculated amount of vanadous chloride added. A precipitate was formed immediately which was rapidly filtered off, washed with water and introduced into the usual apparatus for determining oxygen absorbing capacity. The amount of oxygen absorbed was 40% of the calculated. In other experiments, the reduction was carried out in an inert atmosphere in a special apparatus so that the precipitate could be rapidly dissolved in a layer of bromobenzene which was then run into a small bulb which was sealed off and the oxygen absorbing power determined. A number of such experiments showed an oxygen capacity of 44–45% of the theoretical, if the bromobenzene solution of the free radical stood not more than two minutes. If the solution was allowed to stand 15–25 minutes, the oxygen capacity was lowered about half, and one hour's standing reduced it to zero. The free radical gives a very dark red color in bromobenzene, which becomes a light brown on shaking with air. A number of experiments with the chloride of 9-phenyl(11-carboxylic acid methyl ester)-3,6-dimeth-

---

[11] Gomberg, This Journal, **39**, 1652 (1917).

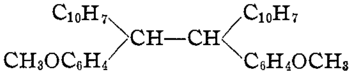
[12] Gomberg and Buchler, *ibid.*, **45**, 207 (1923).

[13] Kehrmann, *Ber.*, **42**, 873 (1909).

oxyxanthylium chloride yielded similar results, a free radical being formed which gave an almost black solution, the color of which was destroyed by shaking with air. Oxygen absorptions of 51–54% of the theoretical were obtained if the manipulations were carried out rapidly.

Dianisyl-di-α-naphthylethane and Dixanthyl.—Undissociated ethanes may be prepared by the same general procedure, glacial acetic acid or acetone being used as the solvents. Since these compounds do not spontaneously undergo changes in the presence of mineral acid, there is no necessity for the process being carried out rapidly and, of course, the products are not sensitive to oxygen. It seems very probable that the first step in this reaction is exactly analogous to that in the formation of dissociated ethanes, but the free radical first formed immediately and irreversibly polymerizes to the undissociated ethane.

Tetraphenylethane.—Diphenyl carbinol is so weakly basic that it is necessary to operate in the presence of considerable acid and even then the reduction requires many hours. Diphenylcarbinol (0.82 g. = 0.005 mole) was dissolved in 15 cc. of acetone, 3 cc. of concd. hydrochloric acid and 5 cc. of *N* vanadous chloride solution added. The solution was allowed to stand for two days in an atmosphere of carbon dioxide, an additional 5 cc. of Vanadous chloride being added after the first day. In the course of 10 hours large crystals of tetraphenylethane began to separate. The solution was finally filtered, yielding 0.51 g. of tetraphenylethane; m. p., 200–203° uncorr.; a small amount of material was also obtained after adding water to the filtrate.

Di-α-naphthyl-dianisylethane,  $(C_{10}H_7)(CH_3OC_6H_4)CH{-}CH(C_{10}H_7)(C_6H_4OCH_3)$.—Anisyl-α-naphthylcarbinol is much more basic than diphenylcarbinol and is correspondingly more rapidly reduced in only slightly acidic solutions. The ethane may be readily prepared by reduction in an acetic acid solution of hydrochloric acid or in acetone containing a little mineral acid.

Reduction in Acetic Acid.—In a typical experiment 4.16 g. of α-naphthylanisylcarbinol,[14] m. p. 88°, was dissolved in 400 cc. of glacial acetic acid and 50 cc. of fuming hydrochloric acid added, giving a pale lavender solution. To this 50 cc. of 0.6 *M* vanadous sulfate solution was added, which immediately resulted in the formation of a white precipitate. The mixture was poured into ice water and the precipitate filtered off, washed and dried. There was thus formed 3.56 g. of a colorless material which was somewhat difficult to purify by recrystallization because of the presence of a certain amount of non-crystalline material. The best procedure was as follows: the crude material was suspended in petroleum ether (200 cc.), which was heated to boiling and 15 to 20 cc. of benzene added; on stirring, the somewhat sticky solid changed to crystalline flakes which were filtered off, dried and recrystallized twice from acetone. The yield of pure product was 2.3 g. or 58% of the theoretical. The compound crystallizes with one molecule of acetone which it loses on heating. If slowly heated in a melting-point tube, it melts at 226°; if very rapidly heated to 180° (by immersion in a melting-point bath), it melts at this temperature, solidifies again and finally melts at 226°.

Anal. Material dried in a vacuum lost 9.8% of its weight on heating to constant weight at the melting point. Calcd. for one molecule of acetone: 10.5%. A combustion of the acetone-free compound gave: C, 87.0; H, 6.1. Calcd. for $C_{36}H_{28}O_2$: C, 87.4; H, 6.5.

Reduction in Acetone.—A solution of 1.3 g. (0.005 mole) of the carbinol in 15 cc. of acetone was treated with 5 cc. of *N* vanadous chloride and 1 cc. of concd. hydrochloric

---

[14] *J. Russ. Phys.-Chem.*, **41,** 1687; *Chem. centr.*, **110,** I, 1145.

acid; reduction was apparent in a few seconds, a white crystalline precipitate forming in the course of a minute. After two or three minutes 5 cc. more of vanadous chloride and 2 cc. more of hydrochloric acid were added and after ten minutes 50 cc. of boiled water was added. The precipitate was filtered off, washed and dried. It weighed 1.2 g.; recrystallized as described above, it yielded 0.7 g. of pure product.

Dixanthyl.—Half a gram of xanthydrol was dissolved in 15 cc. of acetone; 3 cc. of *N* vanadous chloride and a few drops of hydrochloric acid were added. Reduction was rapid and after a few minutes a further addition of 3 cc. of vanadous chloride and 1 cc. of hydrochloric acid was made and then the mixture was diluted with boiled water, the crystalline precipitate filtered off and dried. There was thus obtained 0.38 g. of dixanthyl; m. p., 204–205°.

We wish to express our indebtedness to the Wolcott Gibbs Fund of the National Academy for a grant in aid of this investigation.

Summary

1. Mixtures of triphenylmethyl (hexaphenylethane) and triphenylmethyl sulfate in glacial acetic acid give reproducible potentials which accord with the usual electrochemical equations.

2. The single electrode potentials of triphenylmethyl, phenylxanthyl and phenyldimethoxyxanthyl have been measured by a titration method, in acetic acid and acetone solutions of varying acidity.

3. A method has been developed of estimating the activity of the hydrogen ion in non-aqueous solvents by means of oxidation-reduction cells involving tetrachloroquinone (chloranil).

4. The changes of the single electrode potentials of the free radicals with changes in hydrogen-ion activity of the solutions are in accord with an electrochemical equation which has been derived.

5. A new convenient method of preparing dissociated and undissociated ethanes directly from the carbinols is described.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DERMATOLOGICAL RESEARCH LABORATORIES]

MERCURY DERIVATIVES OF AZO DYES

BY A. PROSKOURIAKOFF AND GEORGE W. RAIZISS

RECEIVED MARCH 2, 1925 PUBLISHED JULY 3, 1925

Dimroth, who of early workers contributed most to the subject of organic mercury compounds, suggested the use of mercuric acetate for the mercuration of organic compounds. He demonstrated that mercuric acetate reacts readily with aromatic amines and phenols, one or more acetoxy-mercury groups entering the *ortho* or *para* position with respect to the amino or hydroxyl groups. He further found that mercury does not enter in the *meta* position to the amino or hydroxyl groups. Raiziss and Proskouriakoff[1] also showed that mercury takes a position either

---

[1] Raiziss and Proskouriakoff, THIS JOURNAL, **44**, 787 (1922).