$n^{25}D$ 1.4003, d^{25}_4 0.8389. The product obtained also had a mixed boiling point with di-isobutyl formal (Favre,[11] b. p. 164.5°) of 164–166°.

The general procedure developed for the preparation of the bromoethers was similar to method D. Equimolar quantities of bromomethanol and an alcohol were intimately mixed and reduced pressure was applied to the flask containing the mixture. At the first indication of the formation of water, the use of reduced pressure was discontinued and the reaction was allowed to proceed of its own accord.

E. By the Reaction between a Formal, Paraformaldehyde and Hydrogen Bromide.—Into a 250-ml. round-bottom flask, cooled by running tap water and containing 50.6 g. (0.5 mole) of di-isobutyl formal, was placed 15 g. of paraformaldehyde. Hydrogen bromide was bubbled through the mixture until two layers separated, and thereafter for five minutes. The product of the reaction was isolated as in procedure A and yielded 76.8 g. (91.5%) of bromomethyl isobutyl ether, b. p. 40–42° at 23 mm., $n^{25}D$ 1.4401, d^{25}_4 1.2350.

Anal. Calcd. for $C_5H_{11}BrO$: Br, 47.83; *MR*, 34.698. Found: Br, 47.91; *MR*, 35.887.

The Identification of the Alkyl Portions of the Bromomethyl Alkyl Ethers.—A 10-g. sample of the purified bromoether was hydrolyzed by refluxing with 20 ml. of a 10% solution of sodium hydroxide for thirty minutes. The alcohol obtained was isolated and the 3,5-dinitrobenzoate prepared. The ester obtained was compared with that obtained from the known alcohol by melting point and mixed melting point determinations.

Acknowledgment.—The authors wish to express gratitude to the Research Corporation for a Frederick Gardner Cottrell grant which helped to support this investigation.

Summary

The bromomethyl ethers of seven branched-chain alcohols in the C_3 to C_1 range have been prepared. The physical constants determined include the boiling point, density, refractive index and the heat of vaporization. Evidence suggests the possibility that these bromomethyl alkyl ethers are formed in the Henry synthesis by way of a hemiformal as an intermediate.

TUSKEGEE INSTITUTE
ALABAMA

RECEIVED JULY 12, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

The Two-Step Reduction–Oxidation of Thiaxanthone-5-dioxide and Thiaxanthenol-5-dioxide[1]

BY HANS HEYMANN

In connection with another investigation the synthesis of the acetate of thiaxanthenol-5-dioxide was required. The interesting color phenomena exhibited by this ester, by the related alcohol and by the corresponding ketone prompted the study reported here. Carl Graebe[1a] had noted that thiaxanthone-5-dioxide gives blue solutions when heated with zinc and alkali or on heating with alcoholic potassium hydroxide; he observed that the color disappeared on continued heating with zinc and base. Ullmann and Glenck[2] found that the compound can be vatted with alkaline dithionite to give colored solutions. Recently Amstutz and his collaborators have again noted color phenomena akin to those seen by the earlier workers, and have voiced the suggestion that the colors appearing during the reduction of thiaxanthone-5-dioxides are due to semiquinone intermediates.[3] The same thought had occurred to us and we wish to present substantiation of the hypothesis in the present paper.[4]

A. Preparative Part

The synthetic reactions are summarized in the accompanying flow sheet. The ketone I was obtained according to well-known procedures.[1,2] Reduction to thiaxanthenol-5-dioxide was achieved smoothly by means of zinc dust in 80% acetic acid, conditions under which substituted sulfone-ketones like I may be reduced to the corresponding thiaxanthene-5-dioxides.[3] The alcohol II melts sharply when heated relatively rapidly (*ca.* 0.5° per minute), but the behavior of a sample that is permitted to resolidify after melting indicates that a change accompanies protracted heating: the alcohol is transformed into the ether V, much as benzhydrol upon distillation goes to benzhydryl ether.

The carbinol II may be acetylated smoothly with acetic anhydride in pyridine to yield the acetate IV, and the same compound is conveniently prepared by reductive acetylation of I in the presence of little triethylamine. Larger amounts of base lead to the formation of small quantities of a yellow by-product of unknown nature. The acetate IV was also obtained by displacement with silver acetate of the bromine atom in 10-bromothiaxanthene-5-dioxide (VI), which was the sole product of the action of bromine in carbon tetrachloride on III. The correlation described confirms the assignment of the bromine atom to position 10.

The conditions of hydrolysis or displacement of

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[1] A preliminary report of this work was presented to a meeting of the Oregon Academy of Science on Jan. 17, 1948, in Salem, Oregon.

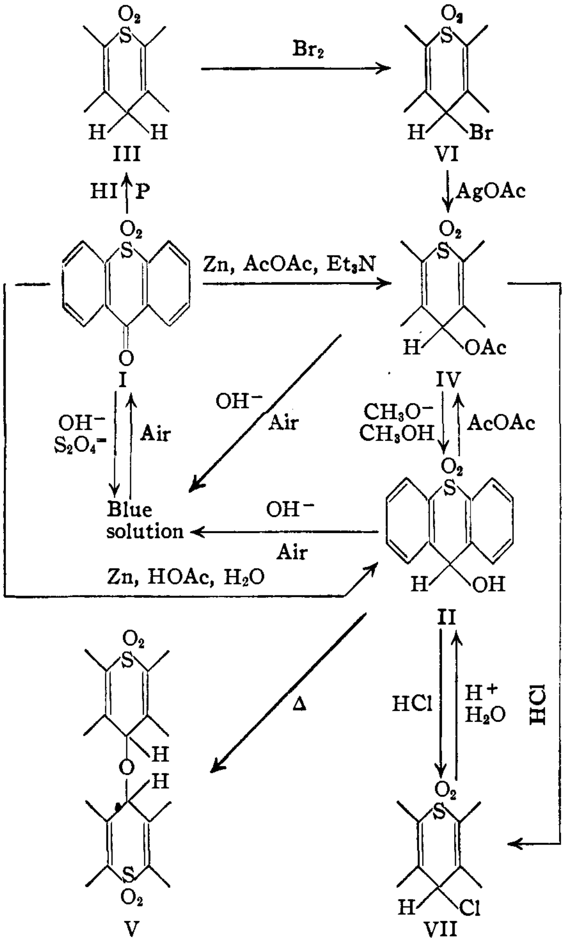
[1a] Graebe and Schulthess, *Ann.*, **263**, 11 (1891).

[2] Ullmann and Glenck, *Ber.*, **49**, 2509 (1916).

[3] Amstutz, Fehnel and Hunsberger, THIS JOURNAL, **70**, 133 (1948).

[4] Our work had been in progress for over a year when Dr. Amstutz's publication appeared. In his friendly reply to our inquiry Dr. Amstutz informed us that he does not intend to investigate, at the present time, the oxidation–reduction properties of the thiaxanthone dioxides.

FLOW SHEET



the acetate group in IV were investigated briefly because (see below) IV and the alcohol II appeared to be indistinguishable as far as their oxidation behavior in alkaline medium is concerned. When a warm solution of IV in acetic acid was treated with concentrated hydrochloric acid the insoluble 10-chlorothiaxanthene-5-dioxide (VII) crystallized instantaneously; when the mixture was boiled for two hours, during which much hydrogen chloride escaped, the alcohol II was formed in a not clean-cut reaction. Thus the bond from position 10 to the oxygen atom must be rather tenuous, as one would expect, and it is natural that the alcohol II yields the chloride as easily as does the acetate when subjected to the same conditions. The formation of the alcohol II from the chloride presumably involves a slow solvolysis, as encountered in the benzhydryl halide series. Sulfuric acid in aqueous acetic acid or in aqueous alcohol hydrolyzes IV rapidly but the reaction is not smooth, the yield is poor, and the product is generally contaminated with the ether V; presumably the insolubility of VII and the greater apparent affinity of the chlorine atom for position 10 prevent side reactions from occurring with hydrogen chloride.

Next the acetate IV was exposed to prolonged action of sodium benzoate in alcoholic solution in order to learn whether a weakly nucleophilic agent would attack at position 10, although the observations cited argue against this possibility and, indeed, only the unchanged acetate (63%) was isolated after boiling for forty-eight hours. However, sodium methoxide in practically oxygen-free absolute methanol and under rigid exclusion of oxygen from the air rapidly produced II in 87% yield. Had position 10 been attacked by the base the methyl ether of II should have been the product. Thus one may conclude that under basic and acidic conditions IV is rapidly hydrolyzed to II.

B. Study of the Reduction-Oxidation Equilibrium

The alcohol II and the acetate IV both develop an intense blue color when their solutions in alcohol are treated with alkali. In the case of the acetate hydrolysis no doubt precedes color formation. The blue tint is decolorized on shaking with air, returns after a short time, may be discharged again, etc., until finally the solution remains colorless and contains the ketone I. In an experiment of this sort, using aqueous pyridine as the solvent, the ketone was isolated in 93% yield; the mother liquor had a pale orange color owing to the occurrence of a non-identified and apparently negligible side-reaction. Color formation is virtually suppressed by thorough expulsion of oxygen from both the solution of the alcohol II and from the alcoholic alkali before mixing. When, however, oxygen-free alcoholic potash is added to an oxygen-free solution of equimolar amounts of I and II the intense blue color appears immediately. The blue species described here is no doubt identical with the coloration seen by Graebe.[1] Since alcoholic potash alone is capable of producing the color from I upon heating, and since this must involve a reducing action exerted by ethoxide ion, we tried to isolate acetaldehyde from such a blue solution, but without success. Probably the small amounts of aldehyde present are rapidly aldolized in the strongly basic medium. However, even in neutral solutions and at room temperature I oxidizes alcohol at a measurable rate: an alcoholic solution of I had acquired a strong odor of acetaldehyde after having stood for about a month; the aldehyde was flushed from the solution by nitrogen and identified by means of a solid derivative.

By scanning the adsorption spectrum of the blue material as it exists in aqueous pyridine solutions of varying alkalinity (0.025, 0.14, 0.9 *M* in hydroxide ion) we found absorption bands at 370 and 570 mμ, separated by an absorption minimum at 475 mμ. The spectral curves have approximately the same shape; for the least alkaline sample the ratio $D_{570}:D_{475}$ is somewhat smaller than for the more alkaline solutions (D refers to log I_0/I). However, in view of the rather crude experimental technique employed the difference of the ratios described may not be significant.

The color intensity of the oxidation–reduction system increases markedly with rising *p*H, at constant concentration. This intensification was demonstrated objectively by colorimetry with the aid of a suitably modified Thunberg tube in which equimolar amounts of I and II were brought together with aqueous alkaline pyridine in the absence of oxygen. The relative optical density of a system containing, before contact with alkali, 8.4×10^{-3} mole/l. of each I and II varied as 1:2.5:8.0 as the hydroxide concentration changed from 0.027 to 0.14 to 0.91 *M*.

There is evidence that besides the blue species a red entity exists in the oxidation–reduction system. Samples at low alkalinity appear purplish rather than blue, particularly in aqueous dioxane solution, and the smaller ratio $D_{570}:D_{475}$ mentioned above conceivably indicates an increased absorption at 475 mμ. Furthermore, when samples of the blue system are subjected, in an inert atmosphere, to controlled oxidation by means of ferricyanide solution or simply by means of air-saturated buffer, the color changes from blue to purple to pure pink before it is discharged completely. Spectroscopic examination of the red body was not very satisfactory because of the low concentration and high air-sensitivity of the compound; none the less, an absorption maximum between 470 and 480 mμ was recognized.

In sealed-glass vessels the blue solutions appear to be unchanged over long periods of time, but on heating at 110° for two days the color is discharged and in the resulting solution sulfite and xanthone (10–15%) were found, besides a small amount of unchanged I. The course of this interesting cleavage is not known at present.

Rapid neutralization with acid of the blue solution led to a mixture from which pure I and pure II were isolated, but there was no evidence of the presence of any other compound, in contradistinction to Bachmann's findings regarding the colored solutions of metal ketyls in aprotic solvents[5] from which high yields of the corresponding pinacols were obtained by acid decomposition.

The observations related so far strongly indicate that the colored body is an intermediate between I and II differing in oxidation level from these substances by one additional or one lacking electron, respectively, that the relative amount of the intermediate increases with rising *p*H, and that the intermediate comprises a blue and a red species. The intermediate may be considered to be a new type of semiquinone, derived from a simple ketone, to be added to the list of well-known one-step intermediates in two-electron oxidation–reduction reactions. However, more definite and more conclusive information was desirable, and we considered that an apparently mobile system like that of I and II might be susceptible to electrochemical investigation.

The fundamental studies of Michaelis[6] and of Elema[7] have shown how to interpret potentiometric titration curves obtainable from mobile, reversible oxidation–reduction systems with particular reference to the detection of one-electron steps in multi-electron reactions. We found that the system under discussion did, indeed, give rise to stable potentials on oxidative titration with ferricyanide in a medium containing 30% by volume of pyridine or dioxane; inclusion of such a large proportion of organic solvent was required by the low solubility of I. The potentials are established with practicable rapidity only at alkali concentrations greater than about 0.01 *M*. Tables I and II summarize the results obtained by potentiometric titrations; the symbols used are those introduced by Michaelis.[6] E_m is the mean normal potential, referred to the normal hydrogen electrode, for the over-all reaction $\mathrm{I} \leftrightarrows \mathrm{II}$; E_{i25} and E_{i75} are the index potentials, *i. e.*, the numerical differences between E_m and the e. m. f. of the galvanic chain at 25 and 75% completion of the oxidation. The index potential serves as a convenient measure of the degree to which the theoretical mid-point slope $RT/2F$ of a titration curve for a two-electron change is modified by the participation of two one-electron reactions. Knowledge of E_i permits computing the amount of semiquinone in equilibrium with the reduced and the oxidized forms, and therewith E_1 and E_2, the normal potentials of the first and the second one-electron steps.

Table I shows the results obtained in a series of oxidative titrations in pyridine-containing media covering a *p*H-range from the most alkaline phosphate buffer capable of existence through various concentrations of sodium hydroxide to about 1 *N* tetramethylammonium hydroxide. The last-named base was employed because pyridine is not miscible with sodium hydroxide more concentrated than about 0.4 *M*. E_i is seen to increase with rising alkalinity indicating that the two-step change becomes more and more prevalent at higher basicity.

Species intermediate in oxidation level between alcohols and ketones must have an odd electron and they may also bear an ionic charge, *i. e.*, they are neutral or ion-radicals and such radicals may exist in equilibrium with their dimers. If they do, the shape of the titration curve should depend on the total concentration of the oxidation-reduction system.[6] As experiments 6 and 7, 10 and 11, and 15 and 16 in Table I show, dimerization does not appear to take place to a degree detectable within the limits of the experimental accuracy.

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(5) Bachmann, THIS JOURNAL, **55**, 1179 (1933).

(6) For a recent review see Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, 39 (1940).

(7) Elema, *J. Biol. Chem.*, **100**, 149 (1933).

In the experiments referred to by Table I the ionic strength underwent a more than ten-fold change; the alkaline agent employed was not the same for all runs, and the reproducibility of the measurements was not satisfactory. Therefore, another series of titrations was carried out, so designed as to employ the same alkaline agent throughout, and by incorporation in the medium of suitable amounts of potassium chloride the ionic strength was held constant at 1.4 for all runs. Furthermore, the temperature and the alkalinity were controlled more carefully. Dioxane was substituted for pyridine as the organic solvent, because dioxane permitted the use of higher concentrations of alkali hydroxide. Runs 1a to 6a, and 1b to 6b in Table II, represent two independent series of determinations, carried out with separate sets of reagents, and the results are seen to be reasonably well reproducible. Runs 7a are duplicate determinations of the a-series, and runs 8a and 9a, agreeing with one another, again show the absence of measurable dimerization of the semiquinone. Runs 2c to 5c were carried out in the absence of potassium chloride, thus involving a variation of the ionic strength from 0.03 to 0.3. It is of interest to note that with increasing alkalinity the hydrogen ion activity as well as E_m diverge more and more from the values observed in series a and b, but that the values for E_i are very nearly alike for solutions of the same molarity of alkali hydroxide, irrespective of the ionic strength. In another case[8] E_i varied appreciably with the ionic strength of the medium.

The dependence of E_m upon alkalinity is a consequence of the fact that I and II differ by two protons in addition to their disparate state of oxidation. Clark and Cohen have formulated the relation[9] between bends in an E_m *versus* pH curve and the pKa values of the protolytic dissociations pertaining to the species involved in the oxidation–reduction equilibrium. It is of great interest to construct a potential-pH diagram for the three potentials E_1, E_2 and E_m of the system under discussion. The quantity referred to as pH in this article was calculated in the usual way from the e. m. f. of a cell consisting of the saturated calomel electrode and of the system hydrogen, colloidal palladium, platinum immersed in the fully reduced oxidation–reduction system, as recommended by Michaelis. The question of the significance of pH values of this nature is involved; all of the values are considerably higher than those to be expected from purely aqueous solutions of equal molarity. However, it seems not inconceivable to us that pH values calculated from potentials measured in such solvents as we have used might, up to a certain point, constitute a self-consistent pH scale which has a consistent relation to the normal potentials of a oxidation–reduction system involving protolytic equilibria. In the hope of detecting the presence of such dissociations and of gaining qualitative information about the nature of the colored intermediate we have plotted the experimental results in Fig. 1.

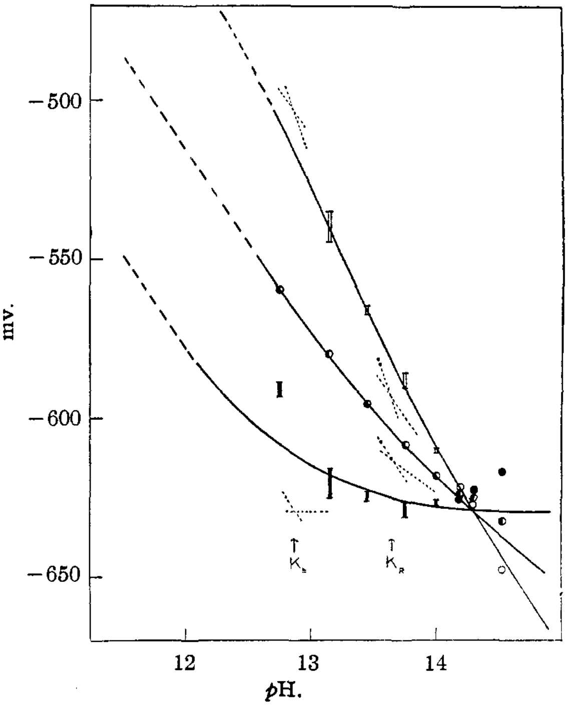

Fig. 1.—The three normal potentials of the oxidation–reduction system from oxidative titrations in aqueous dioxane. The lines drawn are theoretical curves: ○, E_1; ◐, E_m; ●, E_2.

Figure 1 contains the more reliable data, those obtained in the experiments with aqueous dioxane as the solvent. On this graph we have drawn an E_m-curve that begins with a slope of 59 mv. per pH unit at the low-alkalinity end of the plot and and gradually bends over to a slope of 29 mv. as one passes to higher values of pH. Continuations of the straight-line portions of the curve intersect at a point labelled K_R. The curve drawn is a *theoretical* curve of the type characteristic of oxidation–reduction systems, in which the reduced form differs from the oxidized form by two protons and two electrons; a bend like the one drawn occurs when pH approaches and passes through pK_a of the first dissociable proton.[10] However, inspection of the experimental points shows that the steepest slope realized by measurement is only 55 mv. Since in well-studied cases of the dependence of oxidation–reduction potentials upon pH the non-linear portion of the curves extends over one to two pH units, a range comparable to that covered by all of the measurements in Table II, we consider it plausible that owing to the im-

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(8) Michaelis and Fetcher, THIS JOURNAL, 59, 2460 (1937).

(9) W. M. Clark and Cohen, U. S. Pub. Health Repts., 38, 933 (1923).

(10) In view of the unknown relation between the normal pH scale and our "pH" values the usual interpretation that the pH at the intersection equals pK_a is, of course, inadmissible.

mobility of the equilibrium at low alkalinities our measurements could not be extended to reach the region where the slope becomes equal to the theoretical value of 59 mv. Even at the lowest *p*H used, we feel, the over-all reaction is to be represented by both of the following equilibria,[11] with the second equilibrium becoming more and more prevalent as the alkalinity increases. Since RH_2 (II) dissolves readily to give a colorless solution in 30% aqueous dioxane containing

$$RH_2 \rightleftarrows T + 2H^+ + 2e^-$$
$$RH^- \rightleftarrows T + H^+ + 2e^-$$

potassium hydroxide in 1.4 *M* concentration, when air is excluded and the system is kept in the reduced state by means of dithionite, whereas in the absence of potassium hydroxide the solubility of II in the same solvent is small, we do not doubt the reality of the acidic function of RH_2 implied in the E_m curve.

At the flatter end of the E_m curve the experimental points seem to deviate from the theoretical curve in a minor way. However, as the alkali concentration is increased with concomitant reduction of the potassium chloride concentration, the potential at the liquid junction $KCl_{satd.}$ KOH, KCl no doubt changes by greater and greater increments, and introduces a larger and larger error into the potential measurements. We hope to show presently that the values of E_m and *p*H may be trusted up to a *p*H of 14 to 14.2 (0.2 to 0.3 *M* potassium hydroxide); there is reason to think that beyond that point the seemingly fair agreement of the data with the theoretical curve is spurious.

The *index potentials* should be reliable regardless of any error caused by the liquid junction potential, because they are relative values that depend only on the shape of the titration curves and not on the absolute values of the mid-point potentials. Consequently the values of the semiquinone formation constant $k = (S)^2/(R)\times(T)$ are significant, and so are the values for $E_2 - E_1$ computable from k. Unfortunately most of our values for $E_2 - E_1$ had to be calculated in that region where small variations of E_1 cause a large uncertainty in the value of this potential difference; nonetheless we feel that to the left of *p*H 14 the data for E_2 and E_1 conform at least qualitatively to the theoretical curves which we have drawn for these two potentials in Fig. 1. From this agreement we draw the conclusion that the values for E_m and *p*H may also be fairly reliable within the same region.

The slope of the E_2-curve changes from 59 mv. to zero at a region labelled K_S, which corresponds to a transition from the first to the second of the following equilibria. In the region of

$$SH \leftrightarrows T + H^+ + e^-$$
$$S^- \leftrightarrows T + e^-$$

zero slope the semiquinone differs from the ketone I merely by one additional electron. Because of the proximity of K_S and K_R as drawn in Fig. 1 the bends in the theoretical E_1-curve are not clearly visible; we have tried to indicate changes from slope 59 to 118 and back to 59, corresponding to the equilibria

$$RH_2 \leftrightarrows SH + H^+ + e^-$$
$$RH_2 \leftrightarrows S^- + 2H^+ + e^-$$
$$RH \leftrightarrows S^- + H^+ e^-$$

The theoretical E_2-curve continues beyond *p*H 14 with a slope of zero, and the other two curves are drawn accordingly. The experimental values of E_2 and E_1, calculated by adding $\pm(E_2-E_1)/2$ to the measured value of E_m diverge markedly from the lines; indeed, E_2 seems to rise again. We have considered the possibility that this might indicate a second acidic dissociation of the semiquinone, involving a species SOH^{--}. This idea is not acceptable on electrochemical grounds and on the basis of other considerations; *e. g.*, it is inconceivable that S^-, a negative ion, should act as a Lewis acid to accept a hydroxyl ion when T (I), which does not bear any charge, shows no signs whatever of such a dissociation. Furthermore, in the light of the great stability of the S-form relative to *R* and *T* in the region under discussion (k for runs 8a and 9a equals 3.2–3.5) existence of the semiquinone as SOH^{--} is excluded because any structural expression of such an entity implies that it would be of very high energy. Thus we believe that the theoretical system of curves approximates the true situation; the experimental points deviate because beyond *p*H 14.2 both E_m and *p*H are falsified by increasingly larger errors. For instance, in runs 8a and 9a $E_2 - E_1$ equals 31 mv.; the curves drawn differ by this amount at "*p*H" 14.80, where the E_m-curve has a value of −647 mv. This is taken to mean that the potential measurements upon which *p*H and E_m are based must have been in error by +15 to +16 mv.[12]

The data of Table I give rise to a plot of similar pattern (not included in this article). Although the experimental points show considerable scatter, which is to be expected in view of the variable conditions in this series of experiments, we believe that the plot corroborates the conclusions we have drawn from Fig. 1.

We do not intend to attach quantitative significance to the values of K_R and K_S which, in any

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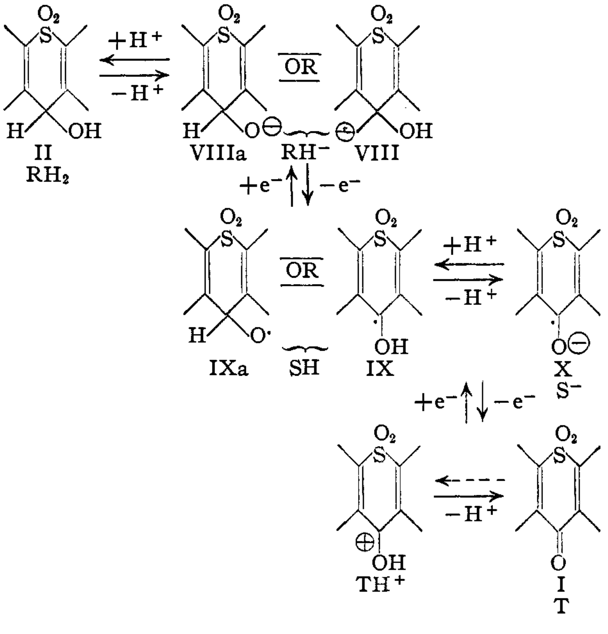
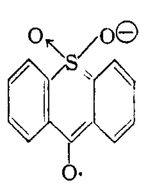
[11] It is convenient, in slight modification of existing usage,[8,9] to use the letters T, S and R for general reference to the oxidized, semiquinone and reduced forms in an oxidation–reduction equilibrium, and to indicate charges and dissociable protons by means of the usual symbols and by the letter H, respectively, attached to these letters in discussions of protolytic equilibria. Thus a reduced form with two dissociable protons can give rise to the species RH_2, RH^- and R^{--}.

[12] We are indebted to Dr. L. Michaelis for the suggestion that the possibility of measuring index potentials in highly alkaline media may be used to extend the *p*H scale toward the alkaline side similarly to its extension to strongly acid media by Michaelis and Granick, THIS JOURNAL, **64**, 1861 (1942).

case, would be hard to interpret, nor do we believe that the relative positions of these bends on the graph should be taken as precise. We do feel, however, that the data and the interpretation attempted make probable in a qualitative way the actual existence of the several protolytic and oxidation–reduction equilibria discussed. The colorimetric measurements agree with the view that S^- is the blue entity, the relative amount of which increases rapidly as one approaches the region where most of the reduction–oxidation system exists, at half-oxidation, as the semiquinone form. The purplish appearance of the solution at lower alkalinity is quite possibly due to SH, the conjugate acid of the semiquinone, which may perhaps be identified with the red species described before. If one ascribes greater tinctorial power to S^- than to SH, which appears to be a reasonable assumption (*cf.* formulas IX and X), the preponderance of the blue color even at low alkalinity becomes understandable, although in this region SH must be present in concentrations comparable to, or greater than, those of S^-. A region where the solution was of a pure pink at the midpoint of the titration was not realized experimentally, and the appearance of the pink color only at the extreme ends of the oxidation process is puzzling. Since no reversion of the pink to purple was visible within thirty minutes, we do not believe that sluggish establishment of the equilibrium near the end-point is the cause; on the other hand, the ratio $(S^-)/(SH)$ should be independent of the total concentration of the S-form for any given *p*H. At this time we cannot offer an adequate explanation for the phenomenon.

We have formulated the species involved in the equilibria considered in this discussion in the accompanying set of structures, which are so arranged that horizontal displacements correspond to protolytic equilibria, vertical ones to oxidation–reduction changes. The species TH^+ is included for the sake of clarity; there is no reason to believe that it is present and therefore the appropriate equilibrium arrow is shown as a broken line. Both VIII and VIIIa must be considered as expressions for RH^- and the present work does not furnish conclusive evidence in favor of either one. The known mobility of the hydrogen atom in benzohydryl ethyl ether[13] as well as such phenomena as the ready isomerization oxanthrone–anthrahydroquinone might be cited as precedent supporting the carbanion structure VIII. Such an ion would be expected to be stabilized by resonance to a considerable degree, but it might also be expected to show some color, which was not observed in the alkaline solution of RH_2. The intrinsic greater mobility of a proton bound to oxygen argues in favor of structure VIIIa, but when one considers the formulations IXa and IX for SH, which results from RH^- by loss of one electron, formula IX alone seems capable of accounting for the small but definite stability of this free radical. Since the formation of IX is best understood if VIII is assumed to be its precursor, we consider the carbanion formula VIII preferable to the alkoxide structure VIIIa. The stable form of the semiquinone, S^-, is formulated as the ion-radical structure X. Species S^- should be represented by two structures showing the usual resonance of a metal ketyl grouping; furthermore, both the charge and the lone electron must be thought of as distributed over the lateral rings so that for X one has to consider at least 13 additional structures (excluding Kekule resonance) of comparable energy. In most of the known cases of stable semiquinones one can write limiting structures in which the charge and the lone electron are distributed to both of two atoms other than carbon, such as nitrogen or oxygen, so that a state of more or less equivalent resonance exists. We should like to raise the question whether in a formulation of S^- structures involving distribution of the charge and of the lone electron to the sulfone oxygens ought to be considered, *e. g.*, structures like XI.





XI

This consideration touches upon the problem whether sulfur is capable of expanding its valence shell with utilization of a 4s or 3d orbital without a great increase in the energy of the system. Although this problem has recently been discussed in

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[13] Wooster and Dean, THIS JOURNAL, 57, 113 (1937).

TABLE I

OXIDATIVE TITRATIONS OF II IN AQUEOUS PYRIDINE AT 24–28°

The buffers were made by mixing 15 cc. of pyridine with 35 cc. of an alkali solution of the composition listed and adding potassium chloride to a total concentration of 0.07 M

Expt.	Molarity × 10^3	Alkali solution	pH	E_i 25%, mv.	E_i 75%[a] mv.	E_m, mv.
1	3.3	33.2 cc. of 0.03 M disodium phosphate and 1.8 cc. of 1 M NaOH[b]	11.85 ± 0.15	14.8 (?)[c]		−520.7
2	0.67	0.02 M NaOH	12.47 ± 0.11	17.6		−549.5
3	Same	Same	12.43 ± 0.10	17.2		−551.2
4	0.67	0.036 Me_4NOH	12.87 ± 0.03	15.5 (?)	16.7	−564.3
5	1.7	Same	12.88 ± 0.09	16.9	16.3	−566.8
6	3.3	0.1 M NaOH	13.08 ± 0.06	17.4		−588.9
7	0.67	Same	13.08 ± 0.06	17.4		−588.9
8	0.67	0.2 M NaOH	13.44 ± 0.04	18.3	18.2	−597.0
9	3.3	0.5 M NaOH	13.80 ± 0.1	20.6		−609.8
10	0.33	0.6 M NaOH	13.82 ± 0.04	20.9	20.5	−610.4
11	3.3	Same	13.86 ± 0.04	19.3	20.3	−611.8
12	1.7	0.51 M Me_4NOH	13.86 ± 0.03	23.9	24.0	−611.9 (?)
13	1.7	0.8 M Me_4NOH	14.09 ± 0.02	29.1	29.4	−616.1
14	1.7	1 M Me_4NOH	14.35 ± 0.05	36.5	36.0	−621.0
15	0.33	1.3 M Me_4NOH[b]	14.38 ± 0.05	44.8	41.7	−623.4
16	3.3	Same[b]	14.38 ± 0.05	43.3	41.5	−625.3
17	1.7	1.3 M Me_4NOH	14.35 ± 0.05	46.3	43.0	−628.9
18	Same	Same	14.35 ± 0.04	45.8	44.9	−629.4

[a] When only one value for E_i is listed this was obtained from the straight line of a plot of the e. m. f. *versus* the logarithm of the ratio % oxidized/(100 − % oxidized). The important section of such plots deviated only negligibly from linearity. [b] No potassium chloride was added in these runs. [c] Owing to the slowness of the equilibrium this run required six hours for completion and $E_{i\,\text{left}}$ differed by three to four mv. from $E_{i\,\text{right}}$. The value listed pertains to the left-hand side; it is not considered reliable.

TABLE II

OXIDATIVE TITRATIONS OF II IN AQUEOUS DIOXANE AT 24.5 ± 0.5°

In all experiments except no. 9a the concentration of II was 10^{-3} M; in run 9a it was 3×10^{-3} M. The buffer consisted of 16 cc. of dioxane and 35 cc. of an alkali solution of the composition listed.

	Composition of alkali solution					
Expt.	KOH M	KCl M	pH	E_i 25%, mv.	E_i 75%, mv.	E_m, mv.
1a	0.02	1.98	12.75 ± 0.07	16.1	16.5	−560.6
1b	Same	Same	12.72 ± 0.08	16.2	16.0	−559.0
2a	0.041	1.96	13.15 ± 0.04	15.9	15.8	−579.2
2b	Same	Same	13.12 ± 0.03	15.6	15.4	−580.6
2c	Same	...	13.16 ± 0.04	15.6	15.7	−580.0
3a	0.08	1.92	13.45 ± 0.03	16.6	16.3	−594.2
3b	Same	Same	13.40 ± 0.02	16.3	16.5	−596.4
(3bb)	Same	Same	13.37 ± 0.01	16.0	16.3	−592.5[a]
3c	Same	...	13.41 ± 0.01	16.4	16.3	−592.3
4a	0.16	1.84	13.76 ± 0.03	17.4	17.8	−608.2
4b	Same	Same	13.73 ± 0.02	17.0	17.2	−608.5
4c	Same	...	13.68 ±	17.4	17.9	−602.9
5a	0.33	1.67	13.98 ± 0.03	19.3	19.3	−618.2
5b	Same	Same	14.00 ± 0.01	19.5	19.6	−618.7
5c	Same	...	13.90 ±	19.2	19.1	−609.9
6a	0.49	1.51	14.19 ± 0.03	20.8	21.2	−624.2
6b	Same	Same	14.17 ± 0.01	20.9	20.9	−623.8
6c	Same	...	14.06 ± 0.01	20.8	21.0	−614.8
7a	0.65	1.35	14.30 ± 0.03	21.8	22.4	−625.1
			14.27 ± 0.03	21.9	22.4	−625.3
8a	1.31	0.69	14.52 ± 0.02	27.1	27.3	−632.2
9a	1.31	0.69	14.53 ± 0.01	26.8	27.2	−633.1

[a] Run 3bb was carried out by retitrating the sample used in run 3b after the reduction for the final measurement of pH. The same amount of ferricyanide was consumed; possibly the slight change in the medium is responsible for the rise of 3 mv. of E_m.

several places[14] the question remains open. The remarkable stability of the ion-radical X may have some bearing on this point.

Finally we should like to consider the slow step in the oxidation–reduction equilibrium manifest during air oxidations and visible during titrations in the lower pH region. Here each addition of a portion of oxidizing agent discharges the blue color immediately; the tint returns after a short period of time and reaches a maximum density. Simultaneously the e. m. f. becomes constant with time. Apparently the conversion of S to T is fast and the regeneration of S is slow. The process most likely to be time-consuming is the dissociation of RH_2 to RH^-, because a number of carbon–hydrogen dissociations on record are known to be slow, and it is reasonable to assume that RH^- rather than RH_2 is the species that is being oxidized by ferricyanide or by T to give SH and then S^-. The observation that at low pH the potentials are established very slowly agrees with this interpretation.

Experimental[15]

A. Preparative Part

Thiaxanthenol-5-dioxide (II). (a) By Reduction of I.—A solution of 8.9 g. of I in 150 cc. of glacial acetic acid and 30 cc. of water was boiled for five minutes with 10 g. of zinc dust, filtered, and diluted with much water when

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[14] (a) Bordwell and Albisetti, THIS JOURNAL, **70**, 1558 (1948); (b) Doering and Levy, Acidity of a Bicyclic Trisulfone, presented at the 112th meeting of the American Chemical Society, New York, N. Y., September, 1947; (c) Woodward and Eastman, THIS JOURNAL, **68**, 2229 (1946). There earlier references may be found.

[15] All melting points are corrected.

7.48 g. of a hydrate of II separated. Recrystallization from 400 cc. of benzene yielded 6.6 g. (73.5%) of large prisms of II, m. p. 184.2–186.2°, and another 0.5 g. (6%) was obtained from the mother liquors. The pure alcohol melts at 186–187.5°; the melting point is somewhat uncertain because on slow melting the alcohol partly changes to the ether V.

(b) **By Alkaline Hydrolysis of IV in Methyl Alcohol.**—Into a glass-stoppered flask equipped with gas-inlet and outlet tubes fitted with stopcocks was placed a small test-tube containing 1 g. of IV, 50 cc. of absolute methanol (commercial) and 1.15 g. of sodium. Contact between the contents of the test tube and the solvent was avoided. After the metal had dissolved oxygen-free nitrogen was passed through the liquid for twenty-five minutes; then the system was closed and the acetate was caused to fall into the methoxide solution. The solid dissolved and a very faint lavender color developed. After the mixture had stood at room temperature for one hour 10 cc. of 6 *N* hydrochloric acid was added quickly, followed by 200 cc. of water. The excess acid was neutralized with bicarbonate and 800 mg. (87.3%) of II was collected, m. p. 186.5–187°.

(c) **By Acid Hydrolysis of IV.**—This reaction proceeds rapidly in hot solutions, but the product is contaminated with the chloride VII when hydrochloric in acetic acid is used, and with the ether V in the case of sulfuric acid.

Anal. Calcd. for $C_{13}H_{10}O_3S$: C, 63.40; H, 4.09. Found: C, 63.29, 63.55; H, 4.11, 4.23.

10-Bromothiaxanthene-5-dioxide (VI).—To a solution of 10.4 g. of III in 1 l. of carbon tetrachloride was added 7.6 g. of bromine dissolved in the same solvent, and the mixture was boiled for one and three-quarters of an hour. The bromide began to crystallize during this period; it was obtained in the form of a tan powder. The yield was 12.25 g. (87.6%). The material may be recrystallized from hot dioxane; it darkens at 260° but does not melt.

Anal. Calcd. for $C_{13}H_9O_2SBr$: C, 50.50; H, 2.93; Br, 25.85. Found: C, 50.85; H, 3.19; Br, 25.83, 26.83.

10-Chlorothiaxanthene-5-dioxide (VII).—To the solution of 0.4 g. of IV in 7.5 cc. of hot glacial acetic acid was added 2.5 cc. of concentrated hydrochloric acid. After a few seconds VII began to separate; heating was continued for one and one-half minutes, then the mixture was cooled and filtered. Water precipitated a small additional amount of VII from the filtrate. The yield was 0.35 g. (95%); recrystallization from benzene yielded shiny prisms that melt with discoloration at 253–258°. The compound gives a strong Beilstein test.

The alcohol II is converted to the same substance when treated as described.

Anal. Calcd. for $C_{13}H_9O_2SCl$: C, 58.98; H, 3.43. Found: C, 59.49, 58.95; H, 3.67, 3.51.

10-Acetoxythiaxanthene-5-dioxide (IV).—(a) **By reductive acetylation.**—To a mixture of 0.5 g. of I and 0.5 g. of zinc dust was added 5 cc. of acetic anhydride and one drop of triethylamine. The mixture became warm during five minutes and then cooled off again. It was heated for five minutes on the steam-bath, filtered, and decomposed with water at 100°. The product separated as a colorless solid weighing 0.52 g. (88%), m. p. 154–156°. Recrystallization from benzene or from alcohol yields the pure acetate, m. p. 155.6–157°. The substance may appear in the form of needles or leaflets, and of hexagonal plates; occasionally a sample resolidifies after melting as described and remelts at 158–158.5° or 159–160°. The use of larger amounts of base during the acetylation leads to contamination of the product by a small quantity of an unidentified yellow substance.

(b) **From the Bromide VI.**—A mixture of 12.25 g. of VI, 7 g. of silver acetate, and 100 cc. of glacial acetic acid was stirred on the steam-bath for one-quarter of an hour. After filtration water was added and the whitish product was collected. Recrystallization from alcohol afforded 8.4 g. (73.5%) of pure IV, m. p. 154.8–156.8°.

Acetylation of II in the usual manner with pyridine and acetic anhydride gave IV in 99% yield.

Anal. Calcd. for $C_{15}H_{12}O_4S$: C, 62.48; H, 4.19. Found: C, 62.46, 62.53; H, 4.33, 4.45.

Ether of Thiaxanthenol-5-dioxide (V).—The alcohol II (0.2 g.) was heated in an oil-bath at 197 ± 5° for one-half hour when the melt solidified to a compound melting at 262–272° with discoloration. The solid was recrystallized from glacial acetic acid (15 cc.) which deposited 0.14 g. (72%) of a colorless crystal powder having the composition of V and melting at 280–283° with darkening.

Anal. Calcd. for $C_{26}H_{18}O_5S_2$: C, 65.80; H, 3.82. Found: C, 65.95, 65.66; H, 4.00, 3.93.

Solubility of II in Alkali.—To 20 mg. of II contained in a small ampoule was added 1 cc. of a mixture of 1.5 cc. of dioxane, 3.5 cc. of potassium hydroxide and 66 mg. of sodium dithionite. The vessel was sealed, and the blue color that had developed disappeared soon. The solid dissolved within a few minutes of agitation at room temperature. When the vessel was opened the blue color reappeared rapidly.

When 20 mg. of II was treated similarly with 1 cc. of 30% aqueous dioxane, partial solution occurred only on heating, and most of the material crystallized again on cooling to room temperature.

B. Study of the Oxidation Reduction Equilibrium

Alkaline Cleavage of the Oxidation Reduction System.—A mixture of 100 mg. of each ketone I and alcohol II, 5 cc. of pyridine and 10 cc. of 0.6 *N* sodium hydroxide was sealed into a pyrex glass ampoule, without any special precautions to keep out oxygen from the air. The deep blue liquid was heated at 110° for two days at the end of which the color had faded to a very pale yellow. The originally homogeneous solution had separated into two phases, one of which had a volume of about 2 cc. and appeared to be a concentrated alkaline solution of sodium silicate. On dilution with water a white solid separated, which was collected, dried, and extracted with benzene. A residue of silica was left undissolved; the filtrate contained 22 mg. of a white compound melting at 174–176°, which after recrystallization melted at 175.4–176° and did not depress the melting point of authentic xanthone.

The alkaline pyridine–water filtrate was freed of pyridine under reduced pressure and a small amount of solid separated, identified as I by its color reaction with zinc and alcoholic potash. On acidification of the filtrate a strong odor of sulfur dioxide was observed, but no other identifiable fission products were isolated.

Acid Decomposition of the Blue Solution.—To 40 cc. of ethanol in an erlenmeyer flask equipped with a ground-glass stopper was added 1.9 g. of sodium, while the flask was cooled with ice. After dissolution of the metal 0.5 g. each of I and II was added rapidly and the flask was stoppered. After agitation with slight warming for fifteen minutes most of the material had dissolved and the liquid was a dark inky blue. The material was poured rapidly into 6 cc. of acetic acid and the flask was rinsed with a few additional cc. of the same acid. By filtration of the solution, dissolution of the precipitated sodium acetate with water, collection of the organic material precipitated by more water, and finally removal of the organic solvents under reduced pressure and recrystallization from ethanol of the deposited organic material, four crops of I totalling 242 mg., m. p. 187.2–188.6°, were obtained.

The ethanolic mother liquor was diluted with water and the precipitated solid was collected and dried. Owing to mechanical loss the weight of this fraction is not known precisely but estimated at 200 to 250 mg. On recrystallization from benzene 50 mg. of II was obtained, m. p. 186–187° alone or when mixed with authentic II.

Although only a fraction of the total material was accounted for, the conclusion is justified that no significant amounts of the pinacol could have been present because this substance should have appeared among the least soluble, high-melting fractions, yet no trace of such a compound was detected at any point during the separation.

Air Oxidation of II.—To a solution of 500 mg. of II in 4 cc. of pyridine and 3 cc. of water was added 7 cc. of 1 *N* tetramethylammonium hydroxide. An inky blue coloration resulted at once and white crystals were being deposited. The solution was agitated for seven minutes when the blue color had disappeared permanently. The pale orange liquid was filtered from the solid which weighed 460 mg. (93%), m. p. 186–187.8°.

Colorimetry.—A Thunberg tube was equipped with gas inlet tubes fitted with stopcocks and extending to the bottom of the main compartment and of the side-arm. Into the side-arm was placed 0.5 cc. of a solution containing 8.4×10^{-3} mole/l. of each I and II in pyridine; the main compartment contained 4.5 cc. of a pyridine-buffer mixture. Hydrogen was passed through for ten minutes, admitted through an all-glass train; then the vessel was closed, inserted into a Klett colorimeter (red filter, no. 66) and the galvanometer was zeroed. The liquids were mixed, the tube was replaced in the same position and the optical density was read as usual. The results are as follows:

Alkali *M*	Optical density
0.027	0.106
.11	.265
.91	.850

Spectrophotometry.—Flat-bottomed ampoules drawn from a piece of 16-mm. pyrex tubing were filled with pyridine-alkali mixtures as used in runs 4, 8 and 17 in Table I and pure nitrogen was bubbled through the liquid for ten minutes. The ampoule was closed with a rubber cap and a small amount of a strong solution (about 0.01 *M*) of II in pyridine was added by means of a syringe and hypodermic needle. The oxygen contained in the pyridine solution as well as oxygen remaining in the buffer mixture caused the immediate appearance of the blue color of the semiquinone. When the intensity appeared suitable the ampoule was sealed; some heat decomposition near the neck of the ampoule could not be avoided. After several attempts samples suitable for spectrophotometry were obtained; the degree of oxidation or the concentration of the oxidation–reduction system are, of course, not known. The ampoules were placed into the cell holder of a Beckman spectrophotometer and the place for the blank solvent was occupied by an ampoule filled with pyridine-alkali. In spite of the optically most unsatisfactory shape of the ampoules the optical densities appeared to be reproducible within about ±1% of their numerical values on successive measurements when the cell holder was shifted from and restored to its rest position in the instrument. The results are listed.

Alkali *M*	λmax. (mμ)	*D* max.	λmin. (mμ)	*D* min.	λmax. (mμ)	*D* max.	$\frac{D_{570}}{D_{475}}$
0.027	370	1.76	475	0.258	570	0.79	2.54
.14	370	2.9	475	.431	570	1.46	3.39
.91	370	2.9	475	.509	570	1.29	3.06

The columns labelled *D* refer to the optical density registered; the densities at 370 mμ are so high that their quantitative significance is very small.

The red form in aqueous dioxane was studied in the presence of 0.11 mole/liter potassium hydroxide in a square Corex glass cell equipped with a ground-in glass-stopper, into which the liquid was forced by nitrogen pressure from a titration cell where it had been obtained by careful oxidation of a blue solution with air-saturated buffer. No change in color was visible after such a pink solution had stood in the titration cell under nitrogen for one-half hour. Because of the low concentration and the sensitivity of the system, some air oxidation could not be avoided during the transfer, and the optical density of the solution finally secured in the cell was very low: at the absorption maximum at 470 and 480 mμ the sample had an optical density of only 0.051. The red form could also be seen during the potentiometric titrations, although, as shown by a separate experiment, the palladium colloid tends to obscure the color.

Existence of the red form could be demonstrated not only at the *p*H mentioned but also at lower and higher alkalinity. On the basis of visual inspection the red form seems to make a greater contribution to the total color at low alkalinity, but apart from the somewhat debatable spectroscopic data there is no objective evidence for this subjective estimation of color.

Potentiometry.—The procedure was based on Michaelis' recommendations.[16] The nitrogen was purified by passage through Fieser solution followed by lead acetate solution and a 25-cm. section of copper filings heated to 450°. The gas was conducted to the titration cell through all-glass connections made flexible by means of a ball-and-socket joint, and proved to be inert toward moist white phosphorus. The cell was equipped with two electrodes of shiny platinum (*ca.* 1 sq. cm.), gas outlet, buret, etc., and an externally operated electromagnetic stirrer was found to be a convenient means of agitation. A sleeve-type saturated calomel half-cell was used to complete the galvanic chain. Potentials were measured with a type K-2 potentiometer and a Leeds and Northrup box-type galvanometer having a sensitivity of 1.7×10^{-8} amp. per mm.

The pyridine used as a solvent was purchased from the Barrett Company, New York ("Barrett refined") and purified by distillation through a Widmer column. The dioxane was purified by the customary treatment with hydrochloric acid and then sodium metal.

Stock solutions of II appeared to be stable for a week or two when pyridine was the solvent. After this length of time they were generally discarded because of the appearance of a faint yellow tinge. No discoloration was noticeable with dioxane solutions, but some change did take place within a month of standing. As a rule, only fresh solutions were used.

The composition of the reaction media is listed in Tables I and II. At the beginning of a run the added II was partly or wholly oxidized to I by the oxygen contained in the solvents. Colloidal palladium was added and hydrogen was passed in until the blue color had been discharged and the potential of the chain had become constant and equal to within 0.1 mv. for the two electrodes; the *p*H was computed from the e. m. f. thus observed. Some difficulty was experienced in the most alkaline media because of premature coagulation and deactivation of the colloid. The e. m. f. would reach a maximum value, keep this value for a few minutes, and then, while hydrogen was still being admitted, the potential would begin to drift away from its steady position. An additional amount of palladium would generally restore the e. m. f. close to its previous steady value, and there is no reason to doubt that this potential does correspond to equilibrium conditions. At the highest alkalinities it was sometimes found difficult to expel the hydrogen from the system prior to the beginning of the oxidative titration, presumably owing to retention of the gas by the coagulated palladium. If in such cases a reasonable rise of the potential could not be achieved within about one-half hour after the addition of the first few per cent. of oxidizing agent the run was discarded. Three kinds of palladium colloid were investigated; a commercial product ("Baker Colloid 46"), a colloid stabilized with gum arabic[17] and one containing sodium protalbinate.[18] The last-named preparation, obtained according to Paal's original recommendation by reduction of palladous chloride with hydrazine, proved to be the most satisfactory for our purposes. The sodium protalbinate had been made from a sample of commercial egg albumin.

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(16) See Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1946, p. 1085 ff.

(17) Wohl and Mylo, *Ber.*, **45**, 340 (1912).

(18) Paal and Amberger, *ibid.*, **37**, 134 (1904).

The oxidizing agent was potassium ferricyanide, used in aqueous buffer solutions for the pyridine runs; the concentrations were chosen so that from 3 to 5 cc. of oxidizing solution was added to the 50-cc. volume containing the oxidation-reduction system in the titration cell. In the dioxane runs the ferricyanide was dissolved freshly for each experiment in the same solvent mixture that was used as buffer in the titration cell; the volumes added were between 3 and 4 cc. for 50 cc. of buffer containing the oxidation-reduction system.

In most runs the potentials were established about as rapidly as the potentiometer could be adjusted, and the potentials registered by the two electrodes agreed with one another within ±0.1 mv. or better, except in the regions of 0 to 5% and 95 to 100% completion. The potentials were stable with time and in general showed no noticeable drift. At the lower alkalinities potentials were established more and more sluggishly and, particularly toward the end-point, long periods of waiting became necessary. In such cases it was advantageous to use the return of the blue color as a guide rather than to wait for the potential to fall to a constant value.

Finally the *p*H was measured again after addition of more palladium colloid, and the tables give the average of the initial and final *p*H value together with the deviation of these figures from the average. In all cases the higher *p*H is the initial one.

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Summary

1. Thiaxanthenol-5-dioxide and several of its derivatives have been prepared and characterized.

2. The existence of a mobile, two-step oxidation-reduction equilibrium between thiaxanthenol-5-dioxide and thiaxanthone-5-dioxide in alkaline solution has been established. By optical, chemical and electrochemical means it was shown that the colored entity in this equilibrium is a semiquinone.

3. The structure of the semiquinone is discussed with particular reference to potential *vs.* *p*H diagrams.

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The Relative Reactivities of Chloromethyltrimethylsilane and Chloromethylpentamethyldisiloxane

BY GEORGE F. ROEDEL

When chloromethyl siloxanes are treated with alkaline reagents, Si–C cleavage of the $-SiCH_2Cl$ group occurs to form methyl chloride.[1] It has been claimed that the cleavage is accompanied by a competitive hydrolysis of the C–Cl bond.[1] On the other hand no Si–C cleavage of the $-SiCH_2Cl$ group was reported when chloromethyltrimethylsilane was treated with basic reagents.[2] Since methyl chloride, the cleavage product, reacts with the alkaline reagents used in the previous work cited, it was not clearly established that hydrolysis of the C–Cl bond in chloromethyl siloxanes occurs to any significant degree nor that Si–C cleavage is absent with chloromethyltrimethylsilane. In an effort to establish these points and to further elaborate the effect of silicon-bonded oxygen on the behavior of the functional group attached to the silicon, the reactivities of $(CH_3)_3SiCH_2Cl$ (I) and $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$ (II) have been compared in this paper.

The activating effect of oxygen bound to silicon has previously been shown by Sommer, Bailey, Strong and Whitmore.[3] They found markedly greater reactivity of the C–Cl bond in α-chloroethyldiethylsilanol as compared with α-chloroethylmethyldiethylsilane toward such reagents as sodium ethoxide in ethanol and potassium acetate in glacial acetic acid.

Whitmore and Sommer[2] found that chloromethyltrimethylsilane (I) with sodium iodide in dry acetone gave a good yield of the corresponding iodide. In this study chloromethylpentamethyldisiloxane (II) was found to behave similarly with this reagent to also give the iodide in good yield.

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + NaI \longrightarrow \underset{\text{III}}{(CH_3)_3SiOSi(CH_3)_2CH_2I} + NaCl$$

Neither α-chloroethyldiethylsilanol,[3] nor I, nor II reacts with aqueous or ethanolic silver nitrate. Iodomethyltrimethylsilane is also unreactive with silver nitrate reagents,[2] but iodomethylpentamethyldisiloxane (III) reacts readily with ethanolic silver nitrate to precipitate silver iodide.

Both chloro-(II) and iodomethylpentamethyldisiloxane (III) readily form Grignard reagents in a similar manner to chloro-(I) and iodomethyltrimethylsilane.[2]

The Si–C bond of the chloromethylsilyl group, $-SiCH_2Cl$, is not split by sulfuric acid at room temperature. This was shown by adding small amounts of I and II to methyl siloxane systems of known functionality and equilibrating with sulfuric acid.[4] The viscosities of the oils obtained

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(1) Krieble and Elliott, THIS JOURNAL, **68**, 2291 (1946).

(2) Whitmore and Sommer, *ibid.*, **68**, 481 (1946).

(3) Sommer, Bailey, Strong and Whitmore, *ibid.*, **68**, 1881 (1946).

(4) Roedel, *Anal. Chem.*, **20**, 705 (1948).