either Cu, Co, Fe, Zn, Cd, Ni, Mn or Mg or trivalent cations of Fe, Cr or Al were combined with either neutral or acid nicotine sulfate to produce hydrated double sulfates. Methods of preparation and properties are described.

PHILADELPHIA 18, PA. RECEIVED OCTOBER 15, 1948

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

Reaction Rates by Distillation. I. The Etherification of Phenylcarbinols and the Transetherification of their Ethers[1]

BY ERNEST F. PRATT AND J. DANIEL DRAPER[2]

The results of studies directed toward the determination of the relative ease of formation of the ten possible ethers from butyl alcohol, benzyl alcohol, benzhydrol and triphenylcarbinol are reported here.

These etherifications were carried out and followed by observing the rate at which the by-product water collected when a benzene solution of equivalent amounts of two of the alcohols and a small amount of *p*-toluenesulfonic acid was refluxed in an apparatus equipped with an automatic water separator. Several transetherifications were studied by the same general method.

Five out of the ten ethers formed smoothly.[3] The results for these together with results for the *n*-heptyl and *n*-decyl ethers of triphenylcarbinol are given in Table I. It is evident that the rate of etherification of triphenylcarbinol is independent of the chain length of the second alcohol (expts. 1, 2 and 3); that the rate more than doubles when the catalyst concentration is doubled[4] (expts. 1 and 4); and that triphenylcarbinol is etherified much more easily than is benzhydrol (expts. 4, 6, 5 and 7).

TABLE I

ETHERIFICATION OF TRIPHENYLCARBINOL AND BENZHYDROL

Expt.	Reactants		Cat. concn. moles/l.	$t_{1/2}$, minutes	Yield,[a] %	Reaction rate constants, minutes^{-1} × 10^{-3}						
						30%[d]	40%	50%	60%	70%	80%	Av.
1	$(C_6H_5)_3COH$	$CH_3(CH_2)_3OH$	0.0005	25.6	93	31.2	31.6	32.1	32.1	32.3	32.6	32.0
2	$(C_6H_5)_3COH$	$CH_3(CH_2)_6OH$	.0005	23.8	91	32.3	32.4	33.8	35.2	36.2	36.4	34.4
3	$(C_6H_5)_3COH$	$CH_3(CH_2)_9OH$	.0005	25.3	91	32.8	33.2	34.2	33.1	34.6	35.5	33.9
4	$(C_6H_5)_3COH$	$CH_3(CH_2)_3OH$	.00025	59.4	..[c]	11.2	11.4	11.8	12.1	12.2	12.1	11.8
5	$(C_6H_5)_3COH$	$C_6H_5CH_2OH$	.00025	18.4	90	44.1	43.5	43.8	43.3	42.5	42.3	43.2
6	$(C_6H_5)_2CHOH$	$CH_3(CH_2)_3OH$	.0020	303.0	93	2.45	2.43	2.52	2.53	2.53	2.46	2.49
7	$(C_6H_5)_2CHOH$	$C_6H_5CH_2OH$	.0020	76.1	96	10.1	10.0	10.1	10.4	10.8	11.0	10.4
8	$(C_6H_5)_2CHOH$	$(C_6H_5)_2CHOH$[b]	.0020	35.8	95	25.2	23.6	26.0	26.7	26.5	25.4	25.6

[a] Yield of once distilled or once recrystallized product. The yield of water was almost invariably 98 to 100%. [b] 0.125 mole of benzhydrol used instead of 0.125 mole of each of two alcohols as per the standard procedure. [c] Product not isolated. [d] Values in this column calculated from data taken when reaction 20 and 30% complete; values in 40% column calculated from data at 20 and 40% complete, etc.

It appears that the decreased rates obtained with butyl alcohol as compared to benzyl alcohol (expts. 4, 5, 6, and 7) are not due to any fundamental differences in reactivity of these two alchols. To test this point an experiment like expt. 6, except that an equivalent amount of benzyl alcohol was also present, was carried out. Benzhydryl butyl ether and benzhydryl benzyl ether were obtained in yields of 43 and 41%, respectively. This result might be expected if the carbonium ion mechanism applies.[5] It appears probable that the decreased rates with butyl alcohol are due to the fact that in benzene solution butyl alcohol is more basic than benzyl alcohol so that the butyl alcohol coördinates with and thereby "deactivates" the catalyst to the greater extent.[6,7] The same effect appeared in the transetherification of dibenzhydryl ether (Table II).

The absence of dibenzhydryl ether in the products of expts. 6 and 7 although this ether forms very readily (expt. 8) may, perhaps, best be ascribed to the fact that there is less steric hindrance when butyl or benzyl alcohol reacts in place of benzhydrol. The relatively high rate in expt. 8 in spite of the steric hindrance suggests

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[1] From a portion of a thesis presented by J. D. D. in partial fulfillment of the requirements for the Ph.D. degree, Sept. 1947.

[2] Present address: Phillips Petroleum Co., Bartlesville, Oklahoma.

[3] Related etherification studies have been made by Norris and Rigby, THIS JOURNAL, **54**, 2088 (1932), by Senderens, *Compt. rend.*, **188**, 1073 (1929), and earlier papers, and by Ward, *J. Chem. Soc.*, 2291 (1927).

[4] A referee has pointed out that this is inconsistent with the carbonium ion mechanism (ref. 5) unless a very large salt effect exists. This point is being further investigated.

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 300.

[6] In these benzene solutions the coördination may involve formation of a hydrogen bond with a molecule of un-ionized *p*-toluenesulfonic acid rather than reaction with a proton.

[7] A modification of the procedure used here is being applied in an investigation of the relative basicity of alcohols, ethers and other extremely weak bases.

that benzhydrol is less basic than either butyl or benzyl alcohol so that the activity of the catalyst is greater. Since satisfactory rate constants were obtained in expts. 6 and 7 it is improbable that dibenzhydryl ether formed and then transetherified the benzyl or butyl alcohol.

TABLE II

TRANSETHERIFICATIONS

Ether	Alcohol	Cat. concn., moles/l.	Time for 90% reaction,[e] hours	Yield,[a] %
$(C_6H_5)_2CHOHC(C_6H_5)_2$	$CH_3(CH_2)_3OH$	0.004	15.0	88
$(C_6H_5)_2CHOHC(C_6H_5)_2$	$C_6H_5CH_2OH$	.004	2.1	85
$(C_6H_5)_2CHOHC(C_6H_5)_2$	$(C_6H_5)_3COH$	.004	..	..[b]
$(C_6H_5)_3COCH(C_6H_5)_2$	$CH_3(CH_2)_3OH$	.0005	0.7	91[c]
$C_6H_5CH_2OCH_2C_6H_5$	$CH_3(CH_2)_3OH$	.256	16.8	48[d]

[a] Yield of water 98 to 100% unless otherwise noted. [b] No water was evolved even when the catalyst concentration was doubled. [c] A 90% yield of benzhydryl butyl ether and a 92% yield of triphenylmethyl butyl ether were isolated. [d] A 29% yield of diphenylmethane was also isolated. [e] Time for 90% reaction given since it was more accurately determinable than the time for complete reaction.

When triphenylcarbinol and benzhydrol were allowed to react at three different catalyst concentrations the rate curves of Fig. 1 were obtained. It is reasonable to suppose, and evidence given in the Experimental indicates, that the reactions stopped before the theoretical volume of water was evolved because all of the benzhydrol was converted to either diphenylmethyl triphenylmethyl ether or to dibenzhydryl ether. This requires that some triphenylcarbinol be left unreacted which is consistent with results from the attempted self-etherification and transetherification of this carbinol described below.

The decrease in yield of water with increase in catalyst concentration shown in Fig. 1 appears to be due to the occurrence of the following reaction to increasing extents.

$$(C_6H_5)_3COCH(C_6H_5)_2 + (C_6H_5)_2CHOH \longrightarrow (C_6H_5)_3COH + (C_6H_5)_2CHOCH(C_6H_5)_2$$

Transetherification studies (Table II) showed that the reverse of this reaction would not occur under these conditions. The forward reaction was carried out at the catalyst concentration used for Curve III (Fig. 1). Of course self-etherification of the benzhydrol also occurred, but its extent was measured by the amount of water evolved. Triphenylcarbinol and dibenzhydryl ether were isolated from the reaction mixture in 80 to 85% of the calculated yields.[8]

Attempts to self-etherify triphenylcarbinol,[9] benzyl alcohol or butyl alcohol gave unsatisfactory results. Considerable alkylation of the solvent occurred in the experiment with benzyl alcohol as well as in an attempted etherification of benzyl alcohol with butyl alcohol.[10]

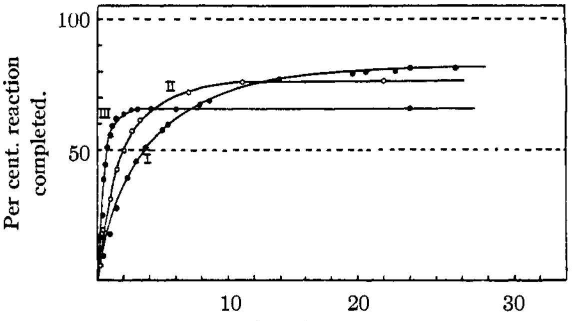

Fig. 1.—Etherification of triphenylcarbinol and benzhydrol at various catalyst concentrations: I, 0.00025 molar; II, 0.0005 molar; III, 0.0020 molar.

The results of several transetherification reactions are summarized in Table II.[11] In these reactions the rate of water formation increased during about the first half of the process and then gradually decreased. This suggests that, with dibenzhydryl ether for example, the following reaction occurred first and that the water was produced in the subsequent etherification of another molecule of ROH by the benzhydrol.

$$(C_6H_5)_2CHOHC(C_6H_5)_2 + ROH \rightleftarrows (C_6H_5)_2CHOR + (C_6H_5)_2CHOH$$

The rate constants of Table I were calculated on the assumption that the reactions are first order with respect to one of the alcohols. They are given at this time primarily to show that the reactions follow the same general course so that valid comparisons of reactivities can be made. Further studies on the scope of this method of etherification and the mechanism of the process are in progress. Other reactions in which water is a by-product are also being investigated by this distillation method.

Acknowledgment.—It is a pleasure to acknowledge generous financial support by the Research Corporation which greatly aided the progress of this work.

Experimental[12,13]

Purification of Materials.—The physical constants of the alcohols, purified by the usual methods, were as follows: *n*-butyl alcohol, $n^{20}D$ 1.3980; *n*-heptyl alcohol, $n^{25}D$ 1.4185, d^{25}_4 0.8190; *n*-decyl alcohol, $n^{20}D$ 1.4352; benzyl alcohol, $n^{20}D$ 1.5402; benzhydrol, m. p. 67–67.5°; triphenylcarbinol, m. p. 161–162°. The benzene was dried and purified by distillation discarding the first and last 15%; $n^{25}D$ 1.4982. Eastman Kodak Co. white label *p*-toluenesulfonic acid monohydrate was used without further purifi-

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[8] A comparison of the half-reaction time of about four hours for Curve I with the half-reaction times for expts. 4 and 5 (Table I) indicates that steric hindrance greatly decreased the rate of formation of diphenylmethyl triphenylmethyl ether.

[9] The preparation of bis-triphenylmethyl ether is described by Gomberg, THIS JOURNAL, **35**, 200 (1913).

[10] Alkylations by this general procedure will be the subject of the second paper of this series.

[11] In the transetherifications carried out heretofore a large excess of the reacting alcohol was ordinarily required. See Helferich, Speidel and Toeldte, *Ber.*, **56**, 766 (1923), and Nef, *Ann.*, **298**, 255 (1897).

[12] Microanalyses by Dr. Eleanor Werble. Values given are averages of duplicates.

[13] All melting points are corrected.

cation since it melted at 103–104° and had a neutral equivalent of 191 (calcd. 190).

Standard Procedure.—The procedure given below was followed in all cases unless otherwise noted.

A one-liter, one-neck flask containing a thermometer well was fitted with an automatic water separator[14] calibrated in 0.1-ml. divisions to a total volume of 5 ml. The separator held a reflux condenser to the top of which was attached a calcium chloride tube. All connections were ground-glass.

Five hundred ml. of a benzene solution containing 0.125 mole of each of the two alcohols was brought to reflux. A 1-ml. beaker containing the catalyst was then dropped in. If more than 0.001 mole of catalyst was required the water of crystallization was removed by refluxing 450 ml. of a benzene solution of the catalyst in the reaction apparatus after which 50 ml. of a warm benzene solution of the two alcohols was added.

The reaction mixture was heated by means of a "Glas-Col" hemispherical mantle rated at 380 watts for 110 volts; the applied voltage was, however, set at 70 by means of a "Variac." Repeat runs on expt. 1 (Table I) at 60 and 75 volts gave essentially identical rate curves although this increase of 15 volts more than doubled the reflux rate. Voltages above 75 flood the condenser. Catalyst concentrations were adjusted so that none of the reactions proceeded at a rate significantly above that of expt. 1. The proper concentration of catalyst was determined in a preliminary run in which the concentration was increased according to the following progression: 0.000125 molar, 2(0.000125) molar, 4(0.000125 molar), etc. A determination of the catalyst concentration both by titration and by the glass electrode at intervals during the course of a run like expt. 1 showed that there was no significant variation.

Within a given experiment the temperature did not vary more than ±0.2° over the 20 to 80% portion of the reaction. Among all the experiments the temperature was 82.5 ± 1° and for most of the experiments the temperature was 82.5 ± 0.5°.

A considerable number of check runs were made. It was found that for the 20 to 80% portion of the rate curves the per cent. reaction at a given time could be readily reproduced to within 3%.

After the evolution of water had stopped the reaction mixture was washed with sodium bicarbonate solution and with water. The benzene was removed under reduced pressure and the product was isolated by crystallization or distillation.

When the etherification of triphenylcarbinol with ethanol was attempted appreciable amounts of the ethanol appeared in the aqueous layer. No significant errors arose from this source when butyl alcohol or less volatile and less water soluble alcohols were used.

The reaction rate constants (Table I) were calculated from data read from a careful plot of the rate curves. This appeared to be the most accurate procedure and it facilitated tabulation of results. Data used in the calculations were limited to those taken over the 20 to 80% portion of the reaction since unavoidable fluctuations appeared at the beginning and end of the process.

The transetherifications (Table II) were carried out according to the standard procedure for etherifications except that 0.0625 mole of the ether replaced the 0.125 mole of one of the alcohols.

Reactions of Tables I and II.—Physical constants and analytical results for the products of the reactions of Tables I and II were as follows: Triphenylmethyl butyl ether, b. p. 138–140° (0.1 mm.), $n^{25}D$ 1.5840. *Anal.* Calcd. for $C_{23}H_{24}O$: C, 87.30; H, 7.64. Found: C, 87.48; H, 7.92. Triphenylmethyl heptyl ether, b. p. 152–156° (0.1 mm.), $n^{25}D$ 1.5665. *Anal.* Calcd. for $C_{26}H_{30}O$: C, 87.10; H, 8.43. Found: C, 87.33; H, 8.72. Triphenylmethyl decyl ether, b. p. 174–177° (0.08 mm.), $n^{20}D$ 1.5538. *Anal.* Calcd. for $C_{29}H_{36}O$: C, 86.94; H, 9.06. Found: C, 87.11; H, 9.40. Triphenylmethyl benzyl ether, recrystallized from diethyl ether, m. p. 105.5–106° (lit. m. p. 103–104°[15] and 106–107°[16]). Benzhydryl butyl ether, b. p. 116–117° (0.5 mm.), $n^{25}D$ 1.5480. *Anal.* Calcd. for $C_{17}H_{20}O$: C, 84.96; H, 8.38. Found: C, 85.15; H, 8.22. Benzhydryl benzyl ether, recrystallized from ethanol, m. p. 50–50.2°. *Anal.* Calcd. for $C_{20}H_{18}O$; C, 87.55; H, 6.61. Found: C, 87.52; H, 6.58. Dibenzhydryl ether, recrystallized from benzene, m. p. 107–107.5° (lit. m. p. 107.5–108°[17]).

Reaction of Triphenylcarbinol and Benzhydrol.—The results of experiments at three concentrations of catalyst are given in Fig. 1. On the assumption that the reaction stops when all the benzhydrol has been converted to triphenylmethyl diphenylmethyl ether or to dibenzhydryl ether it may be calculated from the total amount of water evolved that as the catalyst concentration was increased the yield of the unsymmetrical ether fell from 63 to 54 to 33% while the yield of the symmetrical ether rose from 37 to 46 to 67%.

After the volume of water from the reaction at the lowest catalyst concentration (0.00025 molar) had become constant the catalyst concentration was increased to 0.032 molar, but no further reaction occurred. Triphenylmethyl diphenylmethyl ether was isolated from the reaction mixture in 55% yield. Three recrystallizations from acetone gave a product which melted at 152–153°.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 90.19; H, 6.27.

When the volume of water from the reaction at the intermediate catalyst concentration (0.0005 molar) had become constant (1.73 ml., 77%) 0.375 mole of *n*-butyl alcohol was added. Upon continued refluxing for twenty-three hours the volume of water became constant at 2.73 ml. The theoretical volume for the etherification of the unreacted triphenylcarbinol is 2.76 ml. No further reaction occurred when the catalyst concentration was raised to 0.001 molar, but when this concentration was doubled the volume of water rose to 4.43 ml. over a period of about one hundred hours. The theoretical volume for the transetherification of both the dibenzhydryl ether and the diphenylmethyl triphenylmethyl ether is 4.50 ml. Apparently the excess of butyl alcohol "deactivated" the catalyst so that a higher concentration was required here than for the standard transetherification of diphenylmethyl triphenylmethyl ether (Table II). A 93% yield (25.2 g.) of benzhydryl butyl ether and a 92% yield (34.6 g.) of triphenylmethyl butyl ether were isolated from the reaction mixture.

The same two ethers were obtained in essentially the same yields when the reaction mixture from the experiment at the highest catalyst concentration (0.002 molar) was allowed to react with excess butyl alcohol at a catalyst concentration of 0.004 molar.

In order to investigate the cause of the decrease in yield of water with increasing catalyst concentration (Fig. 1) the following experiment was carried out. Triphenylmethyl diphenylmethyl ether and benzhydrol were allowed to react at a catalyst concentration of 0.002 molar according to the standard procedure for transetherification. After three hours the evolution of water stopped at 0.71 ml. On the basis of the reactions considered in the discussion it may be calculated that 0.0854 mole of dibenzhydryl ether, 0.046 mole of triphenylcarbinol, and 0.0165 mole of triphenylmethyl diphenylmethyl ether were present. The reaction mixture was washed with sodium bicarbonate solution and with water and the benzene was evaporated. Concentration of a carbon tetrachloride solution of the residue gave 85% (10.25 g.) of the calculated amount of triphenylcarbinol. It melted at 158–160° alone and when mixed with authentic triphenylcarbinol; mixed with triphenylmethyl diphenylmethyl ether (m. p. 152–153°) it melted at 120–135°. When the carbon tetrachloride was evaporated from the mother liquors and a solution of the residue in absolute ethanol was concentrated 80% (24.0 g.) of the calculated amount of dibenzhydryl ether was

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[14] Ace Glass Inc., cat. no. 7735.

[15] Norris and Young, THIS JOURNAL, **52**, 753 (1930).

[16] Stadnikoff, *Ber.*, **57**, 1 (1924).

[17] Adams and Weeks, THIS JOURNAL, **38**, 2518 (1916).

obtained. It melted at 105–107° alone and when mixed with authentic dibenzhydryl ether.

Attempted Self-Etherification of Triphenylcarbinol, Butyl Alcohol and Benzyl Alcohol.—In the triphenylcarbinol experiment a total of only 0.125 mole of the alcohol was used. Little, if any, reaction occurred until the catalyst concentration was increased to 0.064 molar. Twice the theoretical volume of water for etherification (*i. e.*, 100% of theory for alkylation) was then evolved over a period of eighteen hours. A 32% yield (9.75 g.) of triphenylmethane, instead of the expected tetraphenylmethane, was isolated. After four recrystallizations from benzene the product melted at 93–93.5° alone and when mixed with authentic triphenylmethane.[18] A mixture of solids which have not been characterized was isolated from the mother liquors.

No water was evolved when attempts were made to etherify *n*-butyl alcohol with itself.

One-fourth mole of benzyl alcohol and 0.128 molar catalyst was used in an attempt to form dibenzyl ether. A 99% yield of water, calculated for alkylation, was evolved in thirteen hours. A 66% yield of diphenylmethane (f. p. 25–25.2°) and a 17% yield of *m*-dibenzylbenzene (m. p. 58–58.5°) were isolated by distillation (lit. m. p. 58–59° for meta-, 78° for ortho- and 86° for para-dibenzylbenzene).

Alkylation of the solvent also occurred in an attempted etherification of benzyl alcohol with butyl alcohol. A 96% yield of water (calculated for etherification) was evolved in eighty hours at a catalyst concentration of 0.128 molar. Fractionation of the product gave a 40% yield of benzyl butyl ether and a 33% yield of diphenylmethane. The ether boiled at 113–113.5° (22 mm.), n^{25}_{D} 1.4892.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.50; H, 9.82. Found: C, 80.84; H, 10.01.

Summary

A study of the relative ease of formation of a number of ethers of triphenylcarbinol, benzhydrol, benzyl alcohol and butyl alcohol has been made. Certain transetherifications were also investigated. Both the etherifications and transetherifications were carried out and followed by a method which involved removal of the byproduct water by azeotropic distillation.

COLLEGE PARK, MD. RECEIVED[19] APRIL 4, 1949

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(18) The ease of reduction of triphenylcarbinol to triphenylmethane has been emphasized by Kauffman and Gromach, *Ber.*, **38**, 2706 (1905). The decomposition of ethers of triphenylcarbinol to triphenylmethane has been studied by Norris and Young, THIS JOURNAL, **52**, 753 (1930).

(19) Original manuscript received August 4, 1948.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE]

Oxidation–Reduction Potentials of Thiol–Disulfide Systems. III. Substituted Thioureas and Compounds Containing Two Thioureido Groups

BY PAUL W. PREISLER

Organic compounds having -SH or -SS- constituent groups are frequently used for activation or inactivation of enzymatic processes. To increase the available selection of such reagents and to assist in a more systematic approach to the study of the mechanisms of the reactions involved, a number of thiol and dithiol compounds have been prepared and the equilibrium oxidation–reduction potentials with their corresponding disulfides have been measured.

Series of methyl and of ethyl substituted thioureas and various other thioureas were investigated. The thioureas were selected because the thiourea(RSH)–formamidine disulfide (RSSR) system had been shown to give stable reproducible potentials[1] which follow the theoretical mathematical equations applicable to systems of the type: 2 reductant = oxidant + 2 H.

A series of compounds containing two thiourea type (thioureido)-SH groups was also prepared. Oxidation of these groups might result in either a disulfide of the R-SS-R type in a chain series or in a disulfide with the -SS- in a ring structure or in a combination of both. The reversible oxidation of dithiobiuret (2-SH groups) to 3,5-diimino-1,2,4-dithiazolidine (-SS- in ring) gives stable potentials[2] following the mathematical equations of the systems of the type: reductant = oxidant + 2H. The potentials of the several members of this series which were determined indicate that the predominant oxidation is to form the ring structure.

Experimental

The oxidation–reduction potential apparatus and procedure generally used for such measurements were employed. The potentials of platinum wire electrodes immersed in the test solution were measured against a saturated potassium chloride calomel half-cell connected by a saturated potassium chloride–4% agar bridge. A Leeds and Northrup Type K potentiometer and a No. 2420-C galvanometer were used. Liquid junction potentials were considered negligible. The electrode, vessel and calomel cell were kept in a water-bath at 30° and the test solution was deoxygenated and stirred with cylinder nitrogen gas previously purified by passing over hot copper. The recorded potentials have been converted into E_h values (normal hydrogen electrode taken as zero). The potentials of the two electrodes usually were within 0.001 volt and, after the first two minutes allowed for mixing and reaction, remained constant for several minutes except in a few systems where rapid decomposition of the oxidant obviously was taking place. In such cases the titration was performed more rapidly by measuring only the principal points: $^{1}/_{4}$, $^{1}/_{2}$ and $^{3}/_{4}$ oxidized (or reduced). Values in parentheses in the table are uncertain because of such decompositions.

The potentials of the systems were measured with mixtures prepared by titration of the reductants with 0.005 *N* thallic sulfate in *N* sulfuric acid or 0.1 *N* sulfuric acid containing 0.45 *M* potassium sulfate. From three to ten mixtures were made for each system at both acidities, always including those for 25, 50 and 75% total equivalents oxidized. The experimentally obtained values corresponded to the calculated to within 0.001 volt.

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(1) P. W. Preisler and L. Berger, THIS JOURNAL, **69**, 322 (1947).

(2) P. W. Preisler and M. M. Bateman, *ibid.*, **69**, 2632 (1947).