[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 399]

The Hydration of Unsaturated Compounds. II. The Equilibrium between *i*-Butene and *t*-Butanol and the Free Energy of Hydration of *i*-Butene[1]

BY W. FERDINAND EBERZ AND HOWARD J. LUCAS

Parks and Huffman[2] deplore the fact that the free energies of unsaturated hydrocarbons are in an unsatisfactory state, especially since these hydrocarbons are becoming increasingly important from an industrial standpoint. The accurate determination of the free energy change of hydration of such a hydrocarbon is of value, even though it does not in itself give the free energy of the hydrocarbon.

The attainment of satisfactory conditions for measuring the hydration equilibria of olefins has, in general, not been realized. Marek and Flege,[3] in their study of the hydration of 1-butene at elevated temperatures, found that polymerization was an interfering factor.

During an investigation of the rate of hydration of isobutene in a solution containing nitric acid and silver nitrate,[4] it was noted that the reaction is reversible, although only to a small extent. It is the purpose of this paper to describe the measurement of the equilibrium constant of the reaction between isobutene, water and tertiary butanol and the calculation of thermodynamic constants of the reaction.

Francis[5] has measured the gas phase hydration of isobutene and from his results Parks and Huffman have calculated the following

$$(CH_3)_2C{=}CH_2(g) + H_2O(l) = (CH_3)_3COH(l); \qquad \Delta F^\circ_{298} = -1890 \text{ cal.}$$

The maximum error is one or two thousand calories. The data (preliminary) of Francis indicate that the third law calculation of the free energy of this change is, as Parks and Huffman have pointed out, considerably in error. Our value for ΔF°_{298} is -1330 ± 20 cal., with which the value of Francis is in substantial agreement. The method employed, *i. e.*, the hydration at 25° in aqueous solution, has advantages over the gas phase equilibrium in that the butene, although present in very small amounts, can be determined accurately and extrapolation is avoided.

Experimental

The equilibrium was established at 25 or at 35° in a one-liter glass-stoppered bottle of known capacity containing the alcohol, water, nitric acid at either 0.2 or 0.1 *N*, and sufficient potassium nitrate to give an ionic strength of 0.2 *N*. Because of the necessity of making several minor corrections, it is desirable to describe the procedure employed in considerable detail.

Materials.—Eastman tertiary butyl alcohol, m. p. 22°, was purified by repeated crystallizations until the melting point was 25.10°, when approximately 95% was solid. Since roughly 1% of water lowers the melting point by 5°, the depression of 0.43° indicated a purity of 99.8–99.9% on the assumption that the impurity was water. This product was regarded as sufficiently pure to determine the concentration of the alcohol by weighing it.

Procedure.—About 500 ml. of water was placed in the one-liter bottle, the desired amount of alcohol was weighed in, and the contents thoroughly mixed. Since the alcohol is contaminated by a very small amount of unsaturated material, the mixture was completely purified from this by two extractions with carbon tetrachloride in the following way. Twenty ml. of the solvent was added, the bottle was filled to the stopper with water, except for a quite small bubble, and then rotated end over end at 70 r. p. m. for one hour. The carbon tetrachloride was removed, another 20 ml. added, and the extraction repeated. The carbon tetrachloride was removed quantitatively through a capillary tube drawn down to a fine point and attached to an evacuated iodine flask through a stopcock. Since the moderate agitation did not produce an emulsion, the carbon tetrachloride fortunately could be collected at the bottom of the bottle and removed completely. Its removal must be complete, otherwise a serious error would arise later in the analysis of the butene contained in the equilibrium mixture. During this operation a small amount of the aqueous phase was also drawn over. This was measured.

The solution was brought to the desired acidity by adding the calculated amount of standardized nitric acid from a buret. Sufficient water was then added to fill the bottle, leaving only a minute air space when the glass stopper was inserted tightly. The bottle was rotated for fifteen minutes, then immersed up to the neck in water at 25.00 ± 0.02° and left for a period varying from two to eight days.

At the desired time the bottle was removed from the thermostat and the equilibrium was "frozen" by adding a 5% excess of anhydrous sodium tetraborate after having quickly pipetted out a suitable quantity of the solution (usually 35 ml.) and having added 20 ml. of purified carbon tetrachloride. The bottle was then filled as before and placed on the rotating machine for one hour. If these operations, which could be performed in sixty seconds or less, were not performed quickly the equilibrium

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(1) For the previous publication in this series see Lucas and Eberz, THIS JOURNAL, **56**, 460 (1934).

(2) Parks and Huffman, "Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932.

(3) Marek and Flege, *Ind. Eng. Chem.*, **24**, 1428 (1932).

(4) By H. Welge, in this Laboratory.

(5) Ref. 2, p. 124; private communication to P. and H.

would shift, due to extraction of butene before the acid was neutralized. Sodium borate was ideal for the latter purpose because no gas was evolved and the heat effect was small; thus no butene was lost and the bottle did not break. When sodium hydroxide was used, carbon dioxide was evolved and several bottles broke. At the acidities of 0.1 and 0.2 *N* the boric acid which separated out gave no trouble.

The carbon tetrachloride layer was drawn off into the evacuated iodine flask containing 10.00 ml. of 0.05 *N* potassium bromate–potassium bromide. Extraction of the equilibrium mixture was repeated with three 10-ml. portions of the purified carbon tetrachloride with the bottle completely filled but rotating for one-half hour instead of one hour. The extent to which the butene was removed by the individual extractions was found to agree well with an assumed distribution ratio of 300, rather than with a more probable value of 550,[6] as shown in Table I, which gives the volumes of standard sodium thiosulfate solution used by the different carbon tetrachloride extractions.

TABLE I

BUTENE REMOVED BY SUCCESSIVE EXTRACTIONS

CCl_4 extract	0.02 *N* $Na_2S_2O_3$, ml. Calcd.	Found
First, 20 ml.	3.01	3.00
Second, 10 ml.	0.38	0.38
Third, 10 ml.	.09	.10
Fourth, 10 ml.	.03	.03

Thus four extractions were found to be sufficient for the quantitative removal.

The titration of the combined carbon tetrachloride extracts in the evacuated iodine flask was made in the usual way,[1] except that the bromination time was five minutes, instead of ten. From this result the concentration of butene in the equilibrium mixture could be calculated. The concentration of alcohol remaining was known.

Before the equilibrium constant could be calculated it was necessary to correct for (a) the loss of alcohol during the first extraction with carbon tetrachloride through extraction by this solvent; (b) the loss of alcohol during this extraction through the removal of some of the aqueous phase; (c) the loss of both alcohol and butene through removal of a part of the equilibrium mixture before "freezing" the equilibrium; (d) the effect of alcohol, dissolved out by the carbon tetrachloride during the analytical extraction, upon the bromine titration. Of these, (a), which can be calculated from the known distribution[7] of tertiary butanol between water and carbon tetrachloride, was usually about 0.65%; (b) and (c) were obtained from the measured volumes. The effect of (d) was noted by adding 10 ml. of tertiary butyl alcohol to the usual amount of standard bromate–bromide solution in the absence of carbon tetrachloride and noting the amount of bromine consumed after the alcohol and the liberated bromine stood for different periods of time. It is to be noted from the data in Table II that there is an impurity in the alcohol which reacts in five minutes with an amount of bromine equivalent to 0.17 ml. of 0.02 *N* thiosulfate and that thereafter bromine disappears at a slow uniform rate equivalent to 0.04 ml. every five minutes.

TABLE II

BROMINE USED BY TERTIARY BUTYL ALCOHOL

Time, minutes	5	10	60
0.02 *N* $Na_2S_2O_3$, ml.	0.17	0.21	0.63

Since the quantity of alcohol in this test is approximately seven-fold that present during an actual titration, it is evident that the small amount of alcohol present can have no appreciable effect upon a butene analysis.

Before the free energy values could be calculated from the equilibrium data it was necessary to determine the vapor pressure of tertiary butyl alcohol from the equilibrium mixtures, 0.20 *M* in potassium nitrate instead of nitric acid, and to determine also the solubility of isobutene in these same mixtures. Instead of directly determining the vapor pressure of the alcohol, the ratio of the partial pressure of alcohol to that of water was determined and the partial pressure of the alcohol was calculated from that of the water on the assumption that the latter was proportional to its mole fraction, which was either 0.992 or 0.987. The ratio of the partial pressures was calculated from the composition of the condensate obtained by cooling, with a bath of solid carbon dioxide and isopropyl ether, the air which had been passed through the equilibrium mixture.

A comparatively simple modification of Dobson's apparatus[8] for vapor pressure determinations consisted of three spiral wash-bottles in series containing the equilibrium mixture and completely immersed in the thermostat at 25°, a heating coil on the exit tube leading from the last wash-bottle to the collecting tube and a Dewar flask containing "dry ice" and isopropyl ether to cool the latter. A plug of cotton was placed in the exit tube to catch any spray. This plug was never observed to have accumulated any liquid at the end of any run. The efficiency of the apparatus for saturating the air stream was demonstrated by noting that the change in density of the third bottle (see Table III) was negligible after a volume of air had been passed through which carried over 6 ml. of liquid aqueous alcohol, an amount about twice that usually obtained.

TABLE III

EFFICIENCY OF SATURATORS

	Density	Change in density
Original solution	1.00706	.....
Third bottle	1.00712	0.00006
Second bottle	1.00740	.00034
First bottle	1.00890	.00184

Even if saturation were slightly incomplete, no error would arise in determining the partial pressure of butanol in the equilibrium mixtures, since this was calculated from the mole fractions of the distillate. The composition of

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[6] The distribution ratio of isobutene between carbon tetrachloride and water at 25°, to be reported in more detail later, is 606.

[7] This constant is 6.15 ± 0.2, when the concentration of the alcohol in the aqueous phase is 9%, as determined by H. Welge in this Laboratory.

[8] Dobson, *J. Chem. Soc.*, **127**, 2866 (1925).

the distillate was obtained by density measurements.[9] The vapor pressure results are shown in Table IV.

TABLE IV

VAPOR PRESSURE OF TERTIARY BUTANOL FROM AQUEOUS SOLUTIONS, 0.200 *M* IN KNO_3

Temperature, °C.	25	25	35
Molality of alcohol	0.25	0.50	0.25
Vapor pressure of alcohol, mm.	2.39	4.80	5.27

The solubility of isobutene in the equilibrium mixture (0.2 *M* in potassium nitrate) was determined by passing gaseous isobutene, at one atmosphere pressure, first through two spiral wash-bottles containing the equilibrium mixture in order to saturate the gas with water and with the butanol, then into a 500-ml. conical flask containing 400 ml. of the equilibrium mixture and finally into a cold trap for recovery of the butene. The wash bottles and flask were immersed in a thermostat, the latter not completely, since the neck by which it was clamped was exposed. The flask was closed by a stopper carrying the inlet and outlet tubes and a third short glass tube to which a short piece of rubber closed by a clamp was attached. The inlet tube did not dip beneath the surface of the liquid. Saturation of the liquid was obtained by closing off first the inlet and then the outlet tubes and shaking vigorously for a short time.

A sample was pipetted out by inserting the special pipet (see Fig. 1) of 10 ml. capacity through the third tube but not below the surface, closing the exit tube, increasing the flow of butene until the pipet was filled with it, then dipping the lower end below the surface. The liquid was forced into the pipet and up into arm A. Then the stopcock was closed, the tip of the pipet was attached to the evacuated iodine flask, the funnel B was filled with water, and the stopcock opened to admit air through B, thus washing the contents into the titration flask. The pipet was rinsed out with water into the latter and the butene determined in the usual way. By the above procedure none of the volatile butene was lost. The procedure was repeated until successive determinations of the butene content checked.

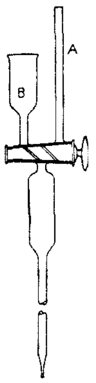

Fig. 1.

The solubilities of butene in the equilibrium mixtures, corrected to 760 mm. of butene, are shown in Table V.

TABLE V

SOLUBILITY OF ISOBUTENE IN AQUEOUS TERTIARY BUTYL ALCOHOL

$P_{C_4H_8}$ = 760 mm.		KNO_3 = 0.200 *M*	
Temperature, °C.	25	25	35
Tertiary butanol, *M*	0.25	0.50	0.25
Isobutene, *M*	.00543	.00566	.00454

Discussion

In Table VI are shown the final, corrected molalities, the partial pressures of the alcohol, the calculated partial pressures of the hydrocarbon, the mole fractions of water, the calculated equilibrium constants, $K_c = (C_4H_9OH)/(C_4H_8)N_{H_2O}$, $K = R_{C_4H_9OH}/P_{C_4H_8}N_{H_2O}$ and the free energy changes. In the expressions for K_c and K, molality is represented by brackets, mole fraction by N, and partial pressure in atmospheres by P. $R_{C_4H_9OH}$ signifies the ratio of the partial pressure of the alcohol to the vapor pressure of the pure liquid at the same temperature. The latter was taken as 42 mm. at 25° and as 76.3 mm. at 35°.[10]

The conditions of the experiments were varied. The trebling of the time in runs 5 and 6 as compared with runs 1, 2, 3 and 4 (these were practically identical) produced no substantial change in the constant, a result which indicated that polymerization was a negligible factor. The similarity of results when the acid is halved, as in runs 7 and 8, indicated that complex formation also is negligible.[11] A doubling of the alcohol concentration and an increase in the time (runs 9 and 10) did not change the constant, nor did a doubling of the alcohol and a decrease in the time (runs 11 and 12). At 25° the constant is smaller, showing that the equilibrium in equation 1 is shifted toward the left (runs 13, 14 and 15).

$$C_4H_8 + H_2O + H_3O^+ = C_4H_9OH + H_3O^+ \qquad (1)$$

In treating the kinetics of this reaction at some definite ionic strength, in this case 0.2 *N*, activities can be neglected. Therefore the rate of disappearance of isobutene is given by equation 2

$$-\mathrm{d}_{C_4H_8}/\mathrm{d}t = k_{01}(C_4H_8)(N_{H_2O})(H_3O)^+ \qquad (2)$$

and its rate of formation by equation 3, on the assumption that the rate is first order with respect to the alcohol:

$$\mathrm{d}_{C_4H_8}/\mathrm{d}t = k_{02}(C_4H_9OH)(H_3O^+) \qquad (3)$$

Here k_{01} and k_{02} are the specific reaction rates of the disappearance and the formation of isobutene, respectively. Since the measured rate of disappearance (Ref. 1) is $k_1 = k_{01}\ (H_3O^+)$ and a measurable rate of formation would similarly be $k_2 = k_{02}\ (H_3O^+)$, these measurable rates at equilibrium are related to each other as shown in equation 4.

$$\frac{k_1}{k_2} = \frac{(C_4H_9OH)}{(C_4H_8)N_{H_2O}} = K_c \qquad (4)$$

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[9] "International Critical Tables," McGraw-Hill Book Co., New York, 1926, Vol. 3, p. 112.

[10] Parks and Barton, THIS JOURNAL, **50**, 25 (1928).

[11] In this case the ionic strength was kept at 0.2 *N* by the addition of potassium nitrate. It has been shown (Ref. 1) that nitric acid and potassium nitrate have an equal salt effect on the hydration reaction, and hence are probably of equal effect on the equilibrium.

TABLE VI

EXPERIMENTAL DATA, EQUILIBRIUM CONSTANTS AND FREE ENERGY OF THE REACTION $i\text{-}C_4H_8 + H_2O = t\text{-}C_4H_9OH$ AT 25°

			Molality		Mole fract.	Partial Press.		Equilibrium consts.		
No.	HNO_3 *N*	Time, hrs.	$C_4H_{10}O$ *M*	C_4H_8 $M \times 10^5$	H_2O N_{H_2O}	$P_{C_4H_{10}O}$ mm.	$P_{C_4H_8}$ mm.	$K_c \times 10^{-3}$	*K*	$-\Delta F$ cal.
1	0.200	24	0.2465	3.273	0.992	2.357	4.581	7.59	9.385	1326
2	.200	24	.2496	3.393	.992	2.386	4.749	7.42	9.165	1312
3	.200	24	.2457	3.390	.992	2.349	4.745	7.31	9.027	1303
4	.200	25	.2432	3.186	.992	2.325	4.459	7.69	9.562	1334
5	.200	70	.2462	3.314	.992	2.354	4.638	7.49	9.260	1318
6	.200	71	.2508	3.473	.992	2.398	4.861	7.28	8.997	1301
7	.100[a]	70	.2449	3.313	.992	2.341	4.637	7.45	9.212	1315
8	.100[a]	68	.2394	3.259	.992	2.289	4.561	7.41	9.165	1312
							Mean	7.46	9.222	1315
9	.200	92	.4861	6.616	.987	4.667	8.884	7.44	9.642	1342
10	.200	93	.4755	6.455	.987	4.565	8.667	7.46	9.658	1343
11	.200	22	.4773	6.408	.987	4.582	8.604	7.55	9.773	1350
12	.200	23	.4762	6.395	.987	4.572	8.587	7.54	9.756	1349
							Mean	7.50	9.707	1346
					At 35°					
13	.200	40	.2425	6.190	.992	5.112	10.362	3.949	4.706	948
14	.200	44	.2376	6.021	.992	5.009	10.079	3.978	4.737	952
15	.200	45	.2470	6.408	.992	5.207	10.727	3.885	4.630	938
							Mean	3.937	4.691	946

[a] Contained KNO_3, 0.100 *N*.

Calculation of $\Delta F°$.—The standard free energy change, $-\Delta F°$, for the reaction shown in equation 5

$$C_4H_8(1\text{ atm.}) + H_2O(l) = C_4H_9OH(l) \qquad (5)$$

is given by equation 6, in which *R* was taken as 1.9869

$$-\Delta F° = RT \ln K \qquad (6)$$

It is to be observed that, whereas the average equilibrium constant K_c of the runs at 25° is 7.46×10^3 when the alcohol concentration is 0.25 *M* and 7.50×10^3 when it is 0.5 *M*, the agreement in the corresponding free energy values, *viz.*, $-\Delta F°_{298} =$ 1315 cal. and 1346 cal., is not quite as satisfactory. This is due to the fact that although isobutene is somewhat more soluble in the solution which is 0.5 *M* in alcohol, the amount of isobutene at equilibrium in this solution is practically twice as great, instead of somewhat more than twice as great as in the solution 0.25 *M* in tertiary butyl alcohol. This effect, however, is not very large and leads to a deviation of only about 25 cal. We shall take the mean of the two values, namely, $\Delta F°_{298} = -1330 \pm 20$ cal.

Calculation of ΔH.—On combining the average free energy values of the first twelve runs at 25° and the average of the last three at 35° by means of equation 7, and assuming that ΔH is constant over this small interval

$$\Delta H = \frac{d(\Delta F/T)}{d(1/T)} = \frac{-(946/308.1) + (1330/298.1)}{(1/308.1) - (1/298.1)} = -12{,}775 \text{ cal.} \qquad (7)$$

It is possible to calculate the ΔH value also by combining the observed entropy of tertiary butyl alcohol and the estimated entropy of isobutene as given by Parks and Huffman[12] with the new ΔF value, as follows

$$\begin{array}{lllll} & C_4H_8(1\text{ atm.}) + & H_2O(l) & = C_4H_9OH(l) & \\ S_{298.1} & 67.3 & 16.9^{13} & 45.3 & \Delta S = -38.9 \text{ E. U.} \end{array}$$

$$\Delta H = \Delta F + T\Delta S = -1330 - 298.1 \times 38.9 = -12{,}900 \text{ cal.} \qquad (8)$$

The satisfactory agreement of these two values, in spite of the fact that the temperature interval is not very large, confirms the entropy approximation.

The Dehydration of Tertiary Butyl Alcohol.—From the equilibrium constant K_c and the previously determined rate of hydration of isobutene, it is possible to calculate the dehydration of the alcohol at an ionic strength of 0.2 *N*, on the assumption that the rate is first order with respect to the alcohol. From equation 4 it is evident that the rate of dehydration of tertiary butyl alcohol, k_2 is

$$k_2 = k_1/K_c \qquad (9)$$

Since the equilibrium is not shifted by a change in the acidity, it is evident that the dehydration rate must be first order with respect to the acidity. This is illustrated in Table VII, in which are shown the calculated values of k_2. The values

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(12) Reference 2, pp. 108 and 81, respectively.

(13) Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

of k_1 have been interpolated from data previously given (Ref. 1).

TABLE VII

RATE OF DEHYDRATION OF TERTIARY BUTYL ALCOHOL k_2, AT 0.2 *N*

Run No.	*T.* °C.	HNO_3 *M*	KNO_3 *M*	k_1 hrs.$^{-1}$	K_c $\times 10^{-3}$	k_2 hrs.$^{-1}$ $\times 10^6$
2	25	0.200	. . .	0.286	7.42	3.85
8	25	.100	0.100	.143	7.41	1.93
10	25	.200	. . .	.286	7.46	3.835
13	35	.200	. . .	1.022	3.949	25.88

The temperature coefficient and the heat of activation are shown in Table VIII in which, for comparison, are given also similar data for the hydration reaction. The temperature coefficient of the dehydration rate has the exceedingly high value of 6.73.

TABLE VIII

TEMPERATURE COEFFICIENT AND HEAT OF ACTIVATION

	Temp. coeff., k_{35}/k_{25}	Heat of activation kg. cal./mole
Dehydration of $(CH_3)_3COH$	6.73	34.82
Hydration of $(CH_3)_2C{=}CH_2$	3.57	23.26
ΔH in aqueous solution		11.56

Summary

The equilibrium between isobutene, water and tertiary butyl alcohol has been measured in dilute aqueous solution in the presence of 0.1 and 0.2 *N* nitric acid, starting from the alcohol side. The equilibrium constant at an ionic strength of 0.2 *N* has a value of 7.48×10^3 at 25° and 3.94×10^3 at 35°.

The free energy change has been calculated and found to be:

$$C_4H_8(g) + H_2O(l) = C_4H_9OH(l)$$
$$\Delta F^\circ_{298\cdot 1} = -1330 \text{ cal}; \quad \Delta F_{308\cdot 1} = -946 \text{ cal.}$$

When ΔH is calculated by two different methods, *viz.*, from the change in ΔF with temperature and from the relation $\Delta H = \Delta F + T\Delta S$, two values are obtained, *viz.*, −12,800 cal. and −12,900 cal., respectively.

On the assumption that the reverse reaction of dehydration of tertiary butyl alcohol is first order with respect to the alcohol, the dehydration rate was calculated by combining the equilibrium constant with the known rate of hydration of isobutene. It was found that (a) the dehydration rate at an ionic strength of 0.2 *N* is proportional to the acid concentration, (b) the temperature coefficient of this reaction for the ten-degree interval between 25 and 35° is 6.73, an unusually high value, and (c) the heat of activation is 34.82 kg. cal. per mole.

PASADENA, CALIF. RECEIVED FEBRUARY 15, 1934

[CONTRIBUTION FROM THE GENERAL MOTORS RESEARCH LABORATORIES]

The Decomposition of Tetraethyllead in Ethylene and Hydrogen in Benzene Solution

BY PAUL L. CRAMER

A study of the thermal decomposition of tetraethyllead in various types of hydrocarbons has been made in this Laboratory during the past two years. This work was started with the idea of investigating the possible alkylation of olefins by means of free radicals and the work was later extended to include a study of the possible reactions of free radicals with paraffin and aromatic hydrocarbons. These reactions were carried out in the liquid phase at relatively low temperatures and high pressures. For this study, this method offered several advantages over vapor phase methods; namely, large amounts of reactants could be used without the danger of excessive reaction temperatures, the complete decomposition of tetraethyllead could be effected at reasonably low temperatures, and the reactions would be very much less affected by variations in temperature and pressure as well as by other factors which are known to influence vapor phase reactions.

This first paper presents the results obtained from the thermal decomposition of tetraethyllead in benzene solution and in benzene solution in the presence of varying amounts of ethylene and hydrogen. No previous work has been reported concerning the decomposition of tetraethyllead in solution in the presence of ethylene. Taylor and Jones[1] have investigated the decomposition of tetraethyllead in the presence of ethylene and hydrogen by vapor phase methods. The thermal

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[1] Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).