A direct precipitation of more than a trace of the sulfide metals with hydrogen sulfide from a 0.3 N acid solution usually resulted in loss of gallium due to its being carried down with the sulfide precipitate, except with the small amount of germanium which was present. In this case, a quantitative separation was obtained by precipitating this element with hydrogen sulfide from 6 to 8 N hydrochloric acid. Results obtained are shown in Table VI.

General Procedure.—Obtain the substance in a hydrochloric acid solution and filter off any silver, lead and mercurous mercury which may have precipitated as chloride. Follow this by the procedure given under "The determination of Gallium in the presence of Lead, Copper, Tin, Antimony, Germanium and Platinum." Next separate iron, indium and aluminum, and determine gallium according to the procedure given under "The determination of Gallium in the presence of Iron and Aluminum." This will remove all interfering elements except vanadium and molybdenum, for which no satisfactory separation was found. As much as 100 mg. of lead, copper, antimony, tin, zinc, indium and doubtless that much platinum and germanium may be present, but more than 10 mg. of aluminum and one milligram of iron cause difficulty.

Summary

1. A method for the colorimetric determination of gallium has been developed, based upon the formation of a pink to amethyst colored lake with quinalizarin. The optimum condition is a solution which is normal in ammonium acetate, 0.5 N in ammonium chloride, of pH 5.0 and containing 0.5 g. of sodium fluoride per liter. Under these conditions 0.02 mg. of gallium per liter can be distinguished. The best concentrations for comparison, using 50-ml. Nessler tubes, lie between 0.02 and 0.2 mg. of gallium per liter.

2. Methods have been developed for separating minute amounts of gallium from 100 mg. of those metals which interfere by giving colored lakes under the same conditions, namely, lead, copper, tin, antimony, indium, platinum and germanium, except that not more than 10 mg. of aluminum, nor 1 mg. of iron should be present, while vanadium and molybdenum must be absent.

ANN ARBOR, MICH. RECEIVED SEPTEMBER 24, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 569]

The Hydration of Unsaturated Compounds. IV. The Rate of Hydration of Isobutene in the Presence of Silver Ion. The Nature of the Isobutene–Silver Complex[1]

BY W. F. EBERZ, H. J. WELGE, DON M. YOST AND H. J. LUCAS

It has been shown that certain soluble metallic salts, such as those of copper, nickel, manganese, etc., have little or no effect upon the rate with which dilute nitric acid catalyzes the hydration of isobutene,[2] whereas in the presence of mercuric nitrate only the isobutene which is not combined with the mercury undergoes hydration. A similar study of the hydration of isobutene in the presence of silver ion is of interest, not only from the theoretical but also from the practical point of view, since silver salts are often added to acids in order to aid the absorption of olefins.

In order to interpret the experimental data obtained from the hydration of isobutene in the presence of silver ion, it is necessary to know the nature of the silver–isobutene complex and the value of the hydration constant of isobutene in the absence of silver ion. The latter is already known.[2]

Nature of the Silver–Isobutene Complex.—This was determined by measuring the distribution ratio of isobutene between, first, carbon tetrachloride and aqueous potassium nitrate, and, second, between carbon tetrachloride and aqueous silver nitrate. In these measurements the ionic strength was maintained constant at 1 N by adjusting the concentration of potassium nitrate. In addition to these data, the distribution ratios of isobutene between carbon tetrachloride and pure water, and between carbon tetrachloride and 2 N potassium nitrate were also determined. The experimental results are shown in Tables I and II. All concentrations are expressed in moles per liter of solution.

In developing the expressions for the formation of the complex between butene and silver ion,

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[1] For the previous publication in this series, see Lucas and Liu, THIS JOURNAL, **56**, 2138 (1934).

[2] Lucas and Eberz, *ibid.*, **56**, 460 (1934).

TABLE I

DISTRIBUTION RATIO, $(B)_c/(B)$, OF ISOBUTENE BETWEEN CCl_4 AND H_2O AT 25°

Molal concn. of C_4H_8 in CCl_4 $(B)_c$	H_2O (B)	K_D
1.234	0.002055	602
0.989	.001623	609
.782	.001268	616
.4845	.000802	604
.428	.000702	609
.378	.000632	598
.3378	.0005565	606
		Mean 606
CCl_4 and 1 N KNO_3 at 25°		
1.0775	0.001287	838
0.667	.000812	822
		Mean 830
CCl_4 and 2 N KNO_3 at 25°		
0.910	0.000850	1070
.666	.000611	1090
		Mean 1080

TABLE II

DISTRIBUTION OF ISOBUTENE BETWEEN CCl_4 AND $AgNO_3$ + KNO_3 AQ. AT 1μ, AND THE EQUILIBRIUM CONSTANT, K_C, FOR THE ISOBUTENE–SILVER COMPLEX

$AgNO_3$	Molal concn. of C_4H_8 in		
(Agt) m	CCl_4 $(B)_c$	H_2O (Bt)	K_C
1.000	0.1460	0.01096	62.0
0.978	.06898	.005176	63.0
.965	.06938	.005176	63.5
.7477	.1492	.00845	62.2
.4948	.15415	.00560	59.6
.2484	.1555	.00294	59.8
			Mean 61.7

and for the hydration rate in silver nitrate solution, the following notation is used:

(Bt) = Total isobutene concentration, moles per liter, at time t
(B) = Free isobutene concentration, moles per liter, at time t
(BAg) = Complexed isobutene concentration, moles per liter, at time t
$(Ag)^+$ = Free silver concentration, moles per liter, at time t
(Agt) = Total silver concentration, moles per liter, at any time
$(B)_c$ = Butene concentration, moles per liter, in carbon tetrachloride
K_D = Distribution constant of isobutene between carbon tetrachloride and 1 N potassium nitrate = 830
K_C = Equilibrium constant for the formation of the isobutene–silver complex
$-S$ = The observed specific rate of disappearance of isobutene
k' = The reaction rate constant for the hydration of free butene under the conditions of the run under consideration
k'' = Same, of the complexed butene
k'_e = The expected rate constant for free butene, under the same conditions

$$K_D = (B)_c/(B) \quad (1)$$
$$K_C = (BAg)/(B)(Ag^+) \quad (2)$$

Equation (2) is true if the complex is made up of one mole of isobutene and one of silver ion.

Combining (1) and (2)

$$K_C = K_D(BAg)/(B)_c(Ag^+) \quad (3)$$

and, by the proper substitutions, it is possible to obtain K_C in terms of quantities which can be determined experimentally, that is

$$K_C = K_D[(Bt) - (B)_c/K_D]/(B)_c[(Agt) - (Bt) + (B)_c/K_D] \quad (4)$$

The values of K_C calculated by the use of equation (4), are shown in Table II. There seems to be a slight trend in these values, for they are smallest at the lowest silver concentrations. But since K_C is quite sensitive to variations in (Bt), especially when the latter has a small value, the trend is probably less significant than it appears to be. The fact that K_C is fairly constant over a fourfold change in the silver ion concentration shows that the correct ratio of butene to silver in the complex is 1:1. This ratio raises the question of the nature of the bond or bonds between the silver ion and the isobutene molecule, for generally the coördination number of silver is two. In order to gain a better understanding of compounds of this type, complexes of silver ion with other olefins, and complexes of isobutene with other metallic ions are being investigated.

Hydration in the Presence of Silver Ion.—The amount of isobutene hydrated in unit time at a given total butene concentration is very much decreased on the addition of silver nitrate, but the amount which actually hydrates exceeds that expected from the calculated free butene concentration. Because this relationship holds in the five experiments where the silver nitrate concentration is substantial (0.24 to 0.74 N), it was thought at first that possibly the complexed, as well as the free, butene hydrates. On this assumption reaction rate constants were calculated for the hydration of the complex. These were found not to be constant, but to vary substantially inversely as the concentration of silver ion. This led to the conclusion that only the free butene hydrates.

The following relations between observed and derived quantities were used. The expressions developed are rigorous, as no simplifying assumptions were made in deriving them. The concentration of silver ion, which can also be obtained from a second, somewhat complicated, expression, results more simply by using the concentration of free butene. For that reason, the derivation of the expression for the butene concentration (equation 12) is given.

Expressions for (B) and (Ag^+), the Concentrations of Free Butene and of Silver Ion.—

$$(Agt) = (Ag^+) + (BAg) \qquad (5)$$

$$(Bt) = (B) + (BAg) \qquad (6)$$

Combining (5) and (6)

$$(Ag^+) = (Agt) - (Bt) + (B) \qquad (7)$$

From (2), (6) and (7)

$$K_C = \frac{(Bt) - (B)}{(B)[(Agt) - (Bt) + (B)]} \qquad (8)$$

$$K_C(B)(Agt) - K_C(B)(Bt) + K_C(B)^2 = (Bt) - (B) \qquad (9)$$

$$K_C(B)^2 - (B)[K_C(Bt) - K_C(Agt) + 1] - (Bt) = 0 \qquad (10)$$

Let

$$K_C(Bt) - K_C(Agt) + 1 = U \qquad (11)$$

then

$$(B) = \frac{U \pm \sqrt{U^2 + 4K_C(Bt)}}{2K_C} \qquad (12)$$

Derivation of the Rate Expression.—Assuming that only the free butene hydrates, the rate of disappearance is given by equation (13)

$$-\,d(Bt)/dt = k'(B) \qquad (13)$$

Combining (2) and (6)

$$(B) = (Bt)/1 + K_C(Ag^+) \qquad (14)$$

Combining (13) and (14)

$$-\frac{d(Bt)}{dt} = \frac{k'(Bt)}{1 + K_C(Ag^+)} \qquad (15)$$

$$-S = -\frac{d\ln(Bt)}{dt} = \frac{k'}{1 + K_C(Ag^+)} \qquad (16)$$

That is, the slope of the plot of ln (B*t*) against *t*, which is the observed specific rate of disappearance of isobutene in silver nitrate solution, is related to *k'*, the rate constant of hydration of free isobutene; equations 16, 12 and 7 permit the calculation of *k'*.

In case the complexed butene also is assumed to hydrate, the rate expression is

$$-\,d(Bt)/dt = k_c'(B) + k''(BAg) \qquad (17)$$

and it may be shown that

$$k'' = -\frac{S\{1 + K_C[(Agt) - (Bt) + (B)]\} - k_c'}{K_C[(Agt) - (Bt) + (B)]} \qquad (18)$$

Materials and Analytical Methods.—The isobutene was prepared in the manner previously described;[2] the carbon tetrachloride was purified with dichromate and sulfuric acid,[3] and the other chemicals used were of C. P. grade. Silver ion was precipitated by the addition of potassium bromide before adding the standard bromate solution. The precipitate of silver bromide did not interfere with the analytical procedure previously described.[2]

Distribution Measurements.—In a 2-liter flask provided with a mechanical stirrer was placed about 150 ml. of carbon tetrachloride; isobutene was passed through until a sufficient amount was dissolved. In those measurements involving aqueous solutions not containing silver nitrate, the flask was nearly filled with the aqueous phase and the two phase system, immersed in a thermostat at 25.00 ± 0.03°, was agitated for one and one-half hours. After standing for two hours the drops of carbon tetrachloride clinging to the surface were shaken down and samples of each phase were removed under pressure, using a pipet with three-way stopcock, as previously described.[2] The sample of the aqueous phase measured 100 ml., and of the carbon tetrachloride phase, either 3.149 ml. or 10.40 ml. When the aqueous phase contained silver nitrate, a smaller flask containing a smaller volume of the aqueous phase was used, and a smaller sample of this was taken for analysis.

Reaction Rate Measurements.—The solutions were prepared by nearly saturating an aqueous solution of silver nitrate and potassium nitrate with isobutene, and then adding the desired amount of standardized nitric acid to yield the final solution of known concentration of silver nitrate, nitric acid and potassium nitrate. The ionic strength was kept at 1 *N*. The rate measurements were carried out at 25° in the apparatus and according to the procedure previously described. The experimental data and calculated constants are shown in Table III. Two sets of data and constants are given for each run, *viz.*, a set of initial values and a set of subsequent values. These last are either the final ones for the run, or else, in case the final slope is not the best one, intermediate values. In all cases there is a marked decrease in butene concentration between the initial and later values.

The Rate Constants.—In Table III, in the eighth column under $-S$, are given the values of the observed rate constants. These were obtained by multiplying by 2.303 the slopes of the curves of runs 1 to 5 inclusive in Fig. 1; these are the plots of $\log_{10}(Bt) + 2$ against the time in hours. In the ninth column under *k'*, are the

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(3) Griffin, "Technical Methods of Analyses," McGraw-Hill Book Co., Inc., New York, 1921, p. 77.

Table III

Results of the Hydration Experiments, and the Hydration Constants

Expt.	HNO_3 m	KNO_3 m	$AgNO_3$ m (Agt)	C_4H_8 m (Bt)	(B) m calcd.	(Ag^+) m calcd.	$-S$ hrs.$^{-1}$	k' hrs.$^{-1}$	k_e' hrs.$^{-1}$	k'' hrs.$^{-1}$
1	0.2427	0.50	0.2431	0.04259	0.00314	0.2036	0.0472	0.634	0.5005	0.0111
1	.2427	.50	.2431	.01302	.00085	.2301	.0425	.649	.5005	.0104
2	.2428	.375	.3639	.06162	.00310	.3054	.0335	.664	.4994	.00877
2	.2428	.375	.3639	.02943	.00135	.3359	.03065	.667	.4994	.00803
3	.2427	.25	.490	.08503	.00325	.408	.02435	.637	.4996	.00549
3	.2427	.25	.490	.03500	.00120	.456	.02215	.646	.4996	.00519
4	.2433	.125	.6157	.1268	.00404	.4929	.02045	.655	.5011	.00465
4	.2433	.125	.6157	.0320	.00086	.5846	.01845	.685	.5011	.00507
5	.2417	.00	.7346	.1551	.00419	.5836	.01733	.641	.4954	.00406
5	.2417	.00	.7346	.0504	.00116	.6854	.01480	.641	.4954	.00344
6	.100	.0125	.0125	.00933	.00596	.0091	.0853	.133	.140	
6	.100	.0125	.0125	.00544	.00332	.0104	.0853	.139	.140	

values of the reaction rate constant calculated by means of equation (16), and in the tenth column, under k_e', the values of the reaction rate constant which would be expected from the known rate of hydration of isobutene[2] in the absence of silver ion, at the same acidity and ionic strength. It is assumed, in calculating k_e', that silver ion and potassium ion are equivalent in regard to ionic strength.

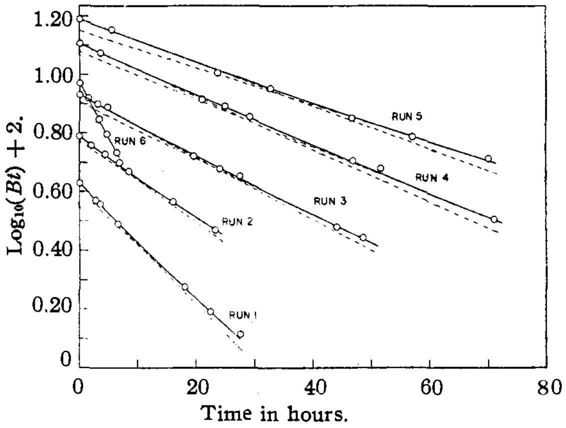

Fig. 1.

The fair constancy of k' at constant acidity and practically constant ionic strength (expts. 1 to 5), over a five-fold change in (B) and a three-fold change in (Ag^+), shows that the rate is first order with respect to uncomplexed butene. Because of the errors involved in taking slopes, the variations in k' are not significant. However, the average value of k', in experiments 1 to 5, is 0.652, whereas 0.499 is the average value of k_e'. Inspection of equation (16) shows that when (Ag^+) becomes zero, k' should be the rate constant in the absence of silver nitrate.

Equation (16) accounts for the observation that $-S$ is substantially inversely proportional to the silver concentration when (Agt) exceeds (Bt) by a factor of five or more. Also, in any given experiment, $-S$ gradually decreases because (Ag^+) is slowly increasing as the butene undergoes hydration.

The discrepancy between k' and k_e' (expts. 1 to 5) is not due to the hydration of the butene complex since the values of k'', eleventh column, Table III are not constant, but bear an inverse relationship to the concentration of silver ion. In calculating k'' by the use of equation (18), the value of k_e' shown in Table III were used. The discrepancy might be due to an error in K_C. In order for k' to agree with k_e', K_C would have to be smaller by about 25%. This is possible, for there is a slight trend in the values of K_C (Table II). They decrease slightly with a decrease in the ratio of (Agt) to (Bt). Since this ratio lies between 85 and 188 in the distribution experiments, and between 4.7 and 19 in the rate experiments 1 to 5, the trend in the values of K_C, if there is a trend, would tend to decrease the values of k'. This might account for the discrepancy between k' and k_e' when (Agt)/(Bt) is large, especially since, in experiment 6, where this ratio lies between 1.2 and 2.3, there is good agreement between k' and k_e'.

Summary

Isobutene and silver ion in aqueous solution form a complex ion for which the formula $C_4H_8Ag^+$ and the equilibrium constant $(C_4H_8Ag^+)/(C_4H_8)(Ag^+) = 61.7$, were determined by distribution measurements.

In 0.25 N nitric acid containing silver nitrate the amount of isobutene which hydrates in unit time, at a given concentration of total butene,

is much less than in the absence of silver nitrate, but is greater than corresponds to the amount of free butene. However, satisfactory rate constants were found when it was assumed that only the free butene present in the silver nitrate solution hydrates. The average value of the constants is greater than the known constant in the absence of silver ion. It is concluded that complexed butene does not hydrate.

PASADENA, CALIF. RECEIVED SEPTEMBER 30, 1936

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Analysis of Gamma-Fructoside Mixtures by Means of Invertase. V. Methylated and Acetylated Derivatives of Crystalline α-Methyl- and α-Benzylfructofuranoside[1]

BY C. B. PURVES AND C. S. HUDSON

The products obtained by the action of chemical reagents on fructose are in most instances complex mixtures not easily separable into their constituents by crystallization or by other methods. This circumstance adds greatly to the experimental difficulty of studying the chemistry of the ketose and in consequence also adds to the value of the few crystalline derivatives which have been prepared from it. The very readily hydrolyzed or gamma-methylfructoside isolated two years ago[2b] was a pure crystalline individual[3] and therefore provided a welcome new starting material for such studies, some of which are recorded in this article.

When the highly dextrorotatory tetramethyl derivative of the glycoside was hydrolyzed with aqueous acid, the less dextrorotatory liquid product was found to be tetramethyl fructofuranose.[4] These facts proved that the "crystalline gamma-methylfructoside" or the "glycoside c" of earlier articles[2b,5a,5b] was in reality α-methylfructofuranoside. The methylation of this substance was not easy. Silver oxide and methyl iodide with anhydrous dioxane as an initial solvent yielded fully methylated products with low and variable specific rotations in water (112, 118°) even after the removal of the methylated methyl esters which they contained (up to 17.6%). Dipotassium and tetrapotassium derivatives reacted very slowly and incompletely with methyl iodide even in the absence of liquid ammonia.[6] The satisfactory methylations, carried out with the help of thallous ethylate by a special method adapted from the work of Menzies,[7] gave tetramethyl α-methylfructofuranoside as a mobile liquid free from esters and with a specific rotation of 129.4° in water. An interesting liquid dimethylfructose, whose optical rotation passed through a minimum near 10° and whose methoxyl groups perhaps occupied the 3,4 positions, was prepared from the corresponding dimethyl α-methylfuranoside. The latter was an intermediate product in the thallous ethylate methylations.

A brief search for derivatives of the glycoside which might be of use in its separation from mixtures resulted in the discovery of tetraacetyl α-methylfructofuranoside in the form of crystals melting at 48–48.5° and having a specific dextrorotation of 88.1° in chloroform. The first crystals were obtained after long delay by acetylating the carefully purified glycoside with Liebermann's reagents but were subsequently prepared from sucrose. The fructofuranoside failed to form a sparingly soluble derivative with barium hydroxide or methylate and yielded no crystalline addition compound with alcoholic potassium acetate.[8] When equimolecular amounts of α-methylfructofuranoside and of hydrogen chloride were mixed in concentrated anhydrous dioxane solution, however, a white, gelatinous carbohydrate–hydrogen chloride addition compound immediately separated and at once began to decompose to a dark, copper reducing tar. Although this ill-defined and highly unstable complex was of a type new to sugar chemistry, such compounds have been inferred to exist as transitory inter-

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Purves and Hudson, (a) THIS JOURNAL, **56**, 702 (1934); (b) **56**, 708 (1934).

(3) Melting at 80.5–81° and not at 69° as previously stated.

(4) Haworth, Hirst and Nicolson, *J. Chem. Soc.*, 1513 (1927).

(5) Purves, THIS JOURNAL, (a) **56**, 1969 (1934); (b) **56**, 1973 (1934).

(6) Muskat, *ibid.*, **56**, 2449 (1934).

(7) Fear and Menzies, *J. Chem. Soc.*, 937 (1926).

(8) *Cf.* Watters, Hockett and Hudson, THIS JOURNAL, **56**, 2199 (1934).