

crystallized four or more times from petroleum ether) and 4.5 ml. of 95% sulfuric acid in 14 ml. of water was cooled to 0° with the formation of a thick paste of the precipitated sulfate. Ethyl nitrite was bubbled with stirring into this paste until the precipitate almost completely dissolved. The temperature was maintained between 0 and 5°. This solution was filtered through a sintered glass funnel, and then was mixed with 150 ml. of cold acetone. The white crystalline solid which precipitated was filtered into a sintered glass funnel, washed five or six times with acetone, and then was dried by drawing air, desiccated with sulfuric acid, through the crystalline salt. The diazonium salt was very white and of high purity. It may be preserved for long periods of time in the dark at a freezing temperature.

Anal. HSO₄, 44.7; calcd. 44.9; C₇H₇N₂ (by precipitation with β -naphthol and purifying and weighing the product), 55.2, calcd. 55.1.

Description of the Apparatus. (a) **The Mixing of the Diazonium Salt with Water.**—After the apparatus had been set up, 850 ml. of doubly distilled water was placed in the reaction flask (F, Fig. 1). While the water came to temperature in the bath (constant within $\pm 0.01^\circ$) the entire system was flushed out with nitrogen. Next 1.9460 g. (0.009 M) of the crystalline diazonium salt was placed in tube A. Tubes A and E were then filled with nitrogen. To start the run stopcocks C and D were opened and plunger E was raised. The water drawn into Tube A dissolved the diazonium salt, and this solution was immediately forced back into the reaction flask. After several rinsings stopcocks C and D were closed. The pressure inside the reaction flask was equalized to atmospheric pressure by opening the outlet at O. The time at which the diazonium salt first dissolved was taken as the starting time.

(b) **The Stirrer.**—The efficiency of the apparatus de-

(7) Ordinary stopcock greases were generally unsatisfactory at 40 or 50°, and silicone grease was unsatisfactory at any temperature. A very satisfactory stopcock preparation was made by emulsifying finely powdered graphite with a rubber base stopcock grease.

pended upon the efficiency of the "aeration" stirrer. The speed of rotation was 1750 r.p.m. In order to avoid vibration the stirrer was kept carefully balanced and centered. Paraffin sealed the lucite bearings at M against mercury leakage, and the mercury seal made the bearing gas tight.

Since an overly rapid rotation of the solution reduced the efficiency of the aeration process by reducing the speed of flow of the liquid past the stirrer outlets, the baffle at J was introduced to slow the rate of flow of the liquid.

The heat resulting from stirring has caused a temperature rise as much as 0.2°. Therefore, it was necessary to install a temperature control unit inside the reaction flask. The diagram of the system is shown in Fig. 2. The flow of cooling water through tube L was controlled by the magnetic mercury valve at D₁. In operation this unit allowed a temperature variation of less than $\pm 0.01^\circ$.

(c) **The Measurement of Gas Volume.**—While the stirrer was in operation stopcock R was kept open, and the three-way stopcock U was turned so that the ammonium sulfate solution, which was replaced by the nitrogen bubbling into buret T, dripped into flask W. Since the outlets at W and R were stationary and approximately equal in height, a pressure equal to atmospheric was maintained within the reaction flask. When it was desired to read the volume of gas in the buret, the stirrer was stopped, the pressure in the reaction flask was exactly equalized to atmospheric pressure by tapping the tube at R and observing the manometer at Q. Stopcock R was then closed and stopcock U reversed. The nitrogen within the buret was adjusted to atmospheric with the aid of the leveling bulb V. After the reading had been taken this procedure was reversed, and the collection of nitrogen continued again. The observed volumes were corrected to standard conditions with the aid of the readings of the temperature of the buret jacket, the reading of atmospheric pressure, and the value for the vapor pressure of the ammonium sulfate solution. If there was a change of atmospheric pressure during a run, a small correction was made for the change in volume of the gas within the reaction flask.

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Coördination of Silver Ion with Unsaturated Compounds. IV. The Butenes¹

BY F. R. HEPNER, K. N. TRUEBLOOD AND H. J. LUCAS

The coördination of aqueous silver ion with the four isomeric butenes has been studied by a distribution method. The constants K_f for the formation of 1:1 complexes are: 1-butene, 119.4; *cis*-2-butene, 62.3; *trans*-2-butene, 24.6; 2-methylpropene, 71.5. This variation is provisionally interpreted in terms of steric effects involving the hydrated silver ion. Approximate values for the constants for the formation of the comparatively unimportant disilver complexes are estimated.

Within recent years there has been a growing interest in three-membered cyclic positive ions because of their importance as intermediate species in organic reactions. Such ions may be formed in a variety of ways, such as coördination of a metallic ion with an olefinic compound,² coördination of a metallic ion with an acetylenic compound,³ or participation of a neighboring atom or group during various reactions.⁴ The transient formation of

(1) Some preliminary results were presented at the 25th meeting of the Pacific Division, A.A.A.S., Pasadena, California, June 20, 1941.

(2) (a) W. F. Eberz, H. J. Weige, D. M. Yost and H. J. Lucas, *THIS JOURNAL*, **59**, 45 (1937); (b) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938); (c) H. J. Lucas, F. Hepner and S. Winstein, *ibid.*, **61**, 3102 (1939); (d) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943); (e) H. J. Lucas, F. W. Billmeyer, Jr., and D. Pressman, *ibid.*, **65**, 230 (1943); (f) R. M. Keefer and L. J. Andrews, *ibid.*, **71**, 1723 (1949); R. M. Keefer, L. J. Andrews and R. E. Kepner, *ibid.*, **71**, 2381, 3906 (1949).

(3) See for example R. N. Keller, *Chem. Rev.*, **28**, 239 (1941); A. Hel'man, S. Bukhovets and E. Meilakh, *Compt. rend. acad. sci. U.R.S.S.* **46**, 105 (1945); W. S. Dorsey, Ph.D. Thesis, California Institute of Technology, 1950.

(4) For a general review see S. Winstein, *Bull. soc. chim.*, [5] **18**, C. 55 (1951).

cyclic ions in the addition of halogens to olefinic compounds explains the well-known phenomenon of *trans* addition.^{4,5}

These three-membered cyclic positive ions may be formulated as resonance hybrids of a number of simple structures^{2b,4}; alternatively, it is sometimes useful to consider them as π -complexes formed by the interaction of the coördinating ion with the π -orbitals of the unsaturated compound.⁶ The latter view is especially attractive in extending the picture to coördination with aromatic compounds.⁷⁻¹⁰

The present study of the complexes formed by

(5) I. Roberts and G. E. Kimball, *THIS JOURNAL*, **59**, 947 (1937).

(6) M. J. S. Dewar, *Nature*, **156**, 784 (1945); *J. Chem. Soc.*, 406, 777 (1946); A. D. Walsh, *Nature*, **159**, 165, 712 (1947); A. E. A. Werner, *ibid.*, **160**, 644 (1947); M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949.

(7) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **71**, 3644 (1949); **72**, 3113, 5034 (1950).

(8) H. C. Brown and J. Brady, *ibid.*, **71**, 3573 (1949).

(9) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(10) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); F. Fairbrother, *J. Chem. Soc.*, 1051 (1948).

aqueous silver ion with the four isomeric butenes was made to obtain information on the effect of stereoisomerism and position isomerism on the stability of silver-olefin complexes. This communication forms a part of a series of studies on the complexes of silver ion with the lower olefins, completed and summarized elsewhere.¹¹

The method employed was essentially that used in the earlier studies.^{2b-e} The distribution ratio of the olefin between carbon tetrachloride and aqueous potassium nitrate was determined and was then combined with data on the distribution of the olefin between carbon tetrachloride and aqueous silver nitrate to give the argentation constants. The equilibrium constants of the pure hydrocarbons which were evaluated K_W , K_D , K_1 , K_2 and K_{01} , equations 1 to 5, are the respective equilibrium constants (here formulated with concentrations rather than activities) for the reactions shown by equations 1a to 5a. Here (B), (Bt) and (Agt) refer to the concentrations in an aqueous phase of unit ionic strength of the uncomplexed olefin, the total olefin, and the total dissolved silver, respectively; subscripts attached to the concentration terms refer to concentrations in carbon tetrachloride, (c), and in pure water, (W), while the absence of any subscript implies that the phase involved is an aqueous solution of unit ionic strength. K_E (or K_0) is the equilibrium constant evaluated directly from the experimental data; K_1 (or K_{01}) and K_2 are calculated from it.¹² Since K_D is defined only for conditions under which the ionic strength is unity, we will use the symbol K_D^* for the corresponding term when the aqueous solution has a lower ionic strength.

$$K_W = (B)_o / (B)_W \quad (1)$$

$$K_D = (B)_o / (B) \quad (2)$$

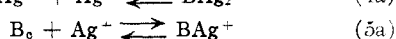
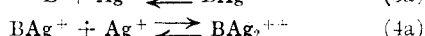
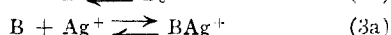
$$K_1 = (B\text{Ag}^+) / (B)(\text{Ag}^+) \quad (3)$$

$$K_2 = (B\text{Ag}_2^{++}) / (B\text{Ag}^+)(\text{Ag}^+) \quad (4)$$

$$K_{01} = (B\text{Ag}^+) / (B)_c(\text{Ag}^+) \quad (5)$$

$$K_E = K_D \{ (\text{Bt}) - (B)_o / K_D \} / (B)_c \{ (\text{Agt}) - (\text{Bt}) + (B)_o / K_D \} \quad (6)$$

$$K_0 = K_E / K_D \quad (7)$$



We shall employ the common convention of representing the concentration of A by (A), the activity of A by [A] and the activity coefficient of A by γ_A ; thus [A] = $\gamma_A(A)$. Although the "constants" defined by equations (1) to (5) have been those customarily evaluated in this work, they are of course not true thermodynamic equilibrium constants inasmuch as they are formulated with concentrations rather than activities. An effort will be made here to indicate wherein these concentration-evaluated "constants" are reliable and wherein they differ significantly from the

(11) (a) K. N. Trueblood and H. J. Lucas, THIS JOURNAL, 74, 1338 (1952); (b) K. N. Trueblood, to be published.

(12) The distinction between K_0 and K_{01} as here defined has not previously been made but it is necessary for those olefins which tend to form a disilver complex.

corresponding true equilibrium constants, that is, to estimate the importance of activity effects. We shall later employ primed symbols (e.g., K'_{01}) to designate the true equilibrium constants, in order to distinguish them from the terms defined by (1) to (5).

Experimental

Materials.—All inorganic chemicals were of C.P. or reagent grade¹³ except potassium iodide, which was U.S.P. Standard solutions were made up by weight. The bromide-bromate solution¹⁴ was 0.06 M in potassium bromide and 0.01 M in potassium bromate and was thus 0.06 N in bromine. This solution, which contained a 20% excess of bromide ion, was found to give faster analysis than one containing the theoretical quantity. Standard sodium thiosulfate was about 0.02 N. It was checked frequently against the standard bromide-bromate.

Carbon tetrachloride was purified with chlorine as described previously.^{2b} *cis*-2-Butene and *trans*-2-butene were prepared from the respective dibromides¹⁵ by the action of metallic zinc in the presence of alcohol. The hydrocarbons were passed through water to remove alcohol and condensed without drying in nitrogen-filled ampoules at Dry Ice temperature. The ampoules were kept sealed at all times except for brief intervals when they were opened for sampling.

1-Butene, prepared from allyl bromide and methylmagnesium iodide^{16,17} was purified by distillation at 490–510 mm. pressure in a Poddelniak column at a temperature of about -15° . It was redistilled at -5° (747 mm.); m.p., -130° ; d_4^{20} 0.668.

2-Methylpropene was prepared by heating *t*-butyl alcohol with oxalic acid.¹⁸ After having been scrubbed with water it was condensed in an ampoule at Dry Ice temperature and was then allowed to distil at room temperature into a second nitrogen-filled ampoule.

Distributions.—For each of the four butenes, distributions were made against water, 1 N potassium nitrate, and 0.25 N, 0.5 N and 1 N silver nitrate; in addition, with 2-methylpropene, distributions were made against 0.5 N potassium nitrate, and also against mixtures of silver nitrate and potassium nitrate of total ionic strength unity with the concentration of silver ion equal to 0.1 N, 0.25 N and 0.5 N.

The distributions with 2-methylpropene were carried out in a 0.5-liter three-necked flask fitted with a mercury-sealed stirrer and a two-holed rubber stopper,^{20,19} one hole of which carried a three-way stopcock while the other served for insertion of the sampling pipet. The stopcock was used to introduce nitrogen for sweeping out the flask and for forcing out the sample. For most of the distributions with 1-butene, *cis*-2-butene and *trans*-2-butene a 200-ml. flask was preferred.

The distributions were carried out as follows. The flask, containing the aqueous phase, was first swept out with nitrogen; then either a solution of the olefin in carbon tetrachloride was added or the olefin and carbon tetrachloride

(13) Some of the potassium nitrate gave a cloudiness when used in conjunction with silver nitrate. It was recrystallized until no precipitate was obtained.

(14) H. S. Davis, G. S. Crandall and W. E. Higbee, Jr., *Ind. Eng. Chem., Anal. Ed.*, 3, 108 (1931).

(15) We are indebted to C. W. Gould, Jr., for supplying *cis*-2-butene and to H. S. Sargent for *trans*-2,3-epoxybutane. *cis*-2-Butene was prepared from *meso*-2,3-butanediol, m. p. 33.90–34.15° (99.5%) through the steps: *meso*-2,3-butanediol, *meso*-2,3-diacetoxybutane, DL-2,3-dibromobutane, and *cis*-2-butene, according to the procedure described by C. E. Wilson and H. J. Lucas, THIS JOURNAL, 58, 2396 (1936). *trans*-2-Butene was prepared through the steps: *trans*-2,3-epoxybutane, *meso*-2,3-dibromobutane, *trans*-2-butene (Wilson and Lucas, see above).

(16) H. J. Lucas and D. Pressman, "Principles and Practice in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 203.

(17) We are indebted to K. Howard for the preparation of this hydrocarbon.

(18) C. D. Hurd and L. U. Spence, THIS JOURNAL, 51, 3561 (1929).

(19) Rubber was not a detriment with the butenes in the time needed for the distributions, even though it must be avoided with pentenes and higher alkenes.²¹ For a diagram of the apparatus see Fig. 1 in the paper by H. J. Lucas, F. R. Hepner and S. Weinstein, *ibid.*, 61, 3102 (1939).

were added separately, and nitrogen was again passed through for several minutes. The flask was immersed in a thermostat at $25.00 \pm 0.03^\circ$, and the contents were stirred for about 1 hour and were then allowed to stand for another hour, a time sufficient for a satisfactory settling of the organic phase. The appropriate sample of each phase was removed by forcing it, by means of nitrogen pressure, into a special pipet²⁰ calibrated to contain and fitted with a three-way stopcock to facilitate rinsing of the sample into the bromination flask.

Analysis.—The bromination of the alkene was accomplished with acidified standard aqueous bromate-bromide, according to the general procedure of Davis, Crandall and Higbee,¹⁴ but following the modifications previously described,^{21,22} in particular the use of the special pipet and of an evacuated flask fitted with a stopcock in the stopper and covered with a black cloth. The excess bromine was determined at the end of the shaking time by addition of potassium iodide and titration of the liberated iodine with standard thiosulfate.

When the aqueous sample contained silver ion, an additional amount of potassium bromide, more than that equivalent to the silver ion present, was added just ahead of the sample; in addition, the amount of potassium iodide added later was more than sufficient to methathesize all of the silver bromide formed. In general, duplicate analyses of each phase were made, and these usually agreed within 1 or 2%.

Results

The experimental values of K_W and K_D for each of the butenes are listed in Table I; in addition, an experimental value of $K_{D, 0.5 N}$ (the distribution constant between carbon tetrachloride and 0.5 *N* potassium nitrate) for 2-methylpropene is presented. The fact that $K_{D, 0.5 N}$ for 2-methylpropene differs only about 1% from the value of 696 which would be predicted by linear interpolation between K_W and K_D indicates that a linear interpolation procedure for obtaining K_D^* for various ionic strengths between 0 and 1 would be satisfactory to this extent, at least when the only electrolyte present is potassium nitrate; on the other hand the fact that the experimental value is less than that obtained by linear interpolation suggests that the Setschenow equation²² could be applied. The data were found to fit this equation remarkably well²³; consequently it was used

TABLE I

DISTRIBUTION CONSTANTS FOR THE BUTENES BETWEEN CCl_4 AND NON-COMPLEXING AQUEOUS MEDIA

Compound	K_W	K_D	$K_{D, 0.5 N}^*$	$K_{D, 0.25 N}^*$
1-Butene	683 ± 8	898 ± 17	(784) ^a	(731) ^a
<i>cis</i> -2-Butene	665 ± 9	890 ± 10	(770) ^a	(715) ^a
<i>trans</i> -2-Butene	757 ± 13	1019 ± 3	(878) ^a	(815) ^a
2-Methylpropene	586 ± 8	806 ± 5	688 ± 2	(635) ^a

^a Calculated with the Setschenow equation.²³

(20) W. F. Eberz and H. J. Lucas, *THIS JOURNAL*, **56**, 1232 (1934).

(21) H. J. Lucas and W. F. Eberz, *ibid.*, **56**, 460 (1934).

(22) See for example H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950, p. 397.

(23) The Setschenow equation is $\log \gamma = kc$, where γ is the activity coefficient of a non-electrolyte in a salt solution of concentration c relative to its solution in pure water as the standard state, and k is a proportionality constant. If we make the entirely reasonable assumption that Henry's law is obeyed throughout the range of concentrations employed here in both the aqueous and organic phases, then the Setschenow equation implies that the solubility of an olefin in salt solutions will vary exponentially with the salt concentration, or, for 1:1 electrolytes, with ionic strength. For a solution of ionic strength μ , we may express the activity coefficient of the olefin relative to its solution in pure water, as $\gamma_\mu = (B)_W / (B)_\mu = \{ (B)_0 / (B)_\mu \} (B)_W / (B)_0 = K_D^* \mu / K_W$. Applying the Setschenow equation to the data for 2-methylpropene, we have $(\log \gamma_{0.5 N}) - (\log \gamma_{0.25 N}) = 0.5k = (\log \gamma_{1.0 N}) - (\log \gamma_{0.5 N})$, and thus $\gamma_{0.5 N}^2 = \gamma_{0.25 N} \gamma_{1.0 N} = \gamma_{1.0 N}$. Since $\gamma_{0.5 N} = K_{D, 0.5 N}^* / K_W$ and $\gamma_{1.0 N} = K_D / K_W$, we can calculate immediately $(K_{D, 0.5 N}^*)^2 = K_D K_W$. This leads to the value 687 for $K_{D, 0.5 N}^*$ in excellent agreement with the experimental value, 688.

for the interpolation of all of the values enclosed in parentheses in Table I.

For each of the four butenes, measurements were made of the distribution between carbon tetrachloride and aqueous silver nitrate of varying concentration, with no added potassium nitrate. The results are presented in Table II.

TABLE II

$K_0 \times 10^4$ FOR THE BUTENES AT VARYING CONCENTRATIONS OF SILVER NITRATE^{a, b}

Olefin	1.000	(Agt), <i>N</i> 0.500	0.250	0.100	0.000 ^c
1-Butene	1568 ± 15 (3)	1480 ± 4 (3)	1384 ± 21 (3)	1359 (1)	1330
<i>cis</i> -2-Butene	808 ± 14 (12)	759 ± 7 (7)	730 ± 7 (5)	700
<i>trans</i> -2-Butene	286 ± 2 (5)	265 ± 3 (3)	252 ± 3 (4)	241
2-Methylpropene	759 ± 7 (9)	822 ± 6 (4)	852 ± 6 (4)	874 ± 3 (4)	886

^a No other electrolyte was present; thus $\mu = (\text{Agt})$.
^b The number in parentheses beneath each value is the number of determinations upon which that value is based.
^c By graphical extrapolation.

In considering the data of Table II it is essential that we examine carefully the reasons for the variation of the measured constant with variation in silver ion concentration. Recalling that we will represent by primed symbols the true thermodynamic equilibrium constants corresponding to each of the "constants" we have defined in terms of concentrations in equations (1) to (5), we have

$$K'_{01} = K_{01} \gamma_{B_{Ag}^+} / \gamma_{B_0} \gamma_{Ag^+} = K_{01} \gamma_{B_{Ag}^+} / \gamma_{Ag^+} \quad (8)$$

since γ_{B_0} may be taken to be unity inasmuch as Henry's law is undoubtedly obeyed and the composition of the organic phase never changes appreciably. Now K_{01} is equal to K_0 only if the sole complex formed is the 1:1 complex; this is strictly the case only in the limit as (Ag^+) approaches zero.²⁴ When there is no electrolyte other than silver nitrate present, the term $\gamma_{B_{Ag}^+} / \gamma_{Ag^+}$ should approach unity as the concentration of silver nitrate approaches zero. Hence it is reasonable to assume that the value of K_0 extrapolated to $(\text{Agt}) = 0$ (the final column of Table II) represents the value of K'_{01} for each of the butenes, and thus is a true thermodynamic equilibrium constant.

If we multiply each of these values of K'_{01} by the corresponding K_D we get K'_1 , the thermodynamic equilibrium constant for the formation of the monosilver complex in aqueous solution (from a solution of the olefin at unit ionic strength). The values of K'_1 are:

1-butene	119.4
<i>cis</i> -2-butene	62.3
<i>trans</i> -2-butene	24.6
2-methylpropene	71.5

For comparison with most of the other olefins, for which studies at varying silver ion concentration are not usually available, it is desirable that we also have K_B at unit silver ion concentration. By multiplying each of the values of K_0 at $(\text{Agt}) = 1.000$ (Table II) by the corresponding K_D , we get for K_B under these conditions:

1-butene	140.9
<i>cis</i> -2-butene	72.0
<i>trans</i> -2-butene	29.2
2-methylpropene	61.2

For a particular olefin the relative values of K_1 measured under different conditions, for example, different silver ion concentrations, will be precisely the same as the relative values of K_{01} under the same conditions, since these "constants" are always related by the same factor, K_D for that particular olefin. On the other hand, for comparison among different olefins, the relative values of K_1 are very different from the relative values of K_{01} because K_D varies from one olefin to another; as discussed in a later paper,^{11b}

(24) We have found no evidence in this or previous studies of complexes of the type B_2Ag^+ for the simple olefins and shall assume that they are not present in any significant concentration.

comparison of the values of K_1 gives information about the specific effects of silver ion in the coordination with the olefins and is more meaningful for our present purposes. Consequently it is the values of K_1 or, in this case, K'_1 , which we wish to compare, although actually among the butenes the variation in K_D is relatively small and a comparison of K_{01} would be practically acceptable although theoretically unjustified.

Relative Argentation of the Different Butenes.

—The values of K'_1 listed above show an appreciable variation which appears on first inspection to demonstrate the importance of steric factors in the stability of these complexes. Thus, 1-butene, in which there is but one alkyl substituent at the double bond, forms the strongest complex by a factor of nearly two. Furthermore, *cis*-2-butene forms a significantly more stable complex than does the *trans* compound, just as was observed for the 2-pentenes.^{2d} The magnitude of the difference here is somewhat surprising in view of the fact that these complexes are presumably formed by silver ion with the π -electrons of the double bond so that the most favorable position of the silver ion in the complex would seem to be directly over the double bond, out of the plane of the two doubly-bonded atoms and the four atoms bonded directly to them. Perhaps, however, van der Waals interaction with the methyl groups on one side in the *cis* compound, makes the most stable position of the silver ion (the one in which it can achieve the maximum overlap with the π -orbital) slightly displaced from the position directly over the double bond, but still symmetrically located with respect to this bond. Such van der Waals effects would also be operative in the *trans* compound; however here only a non-symmetrical²⁵ shift of the silver ion, or a displacement of it further from the plane defined by the doubly-bonded atoms and their immediate neighbors, would result, with, presumably, a significantly lower stability of the complex so formed. The stability of the complexes with 2-methylpropene and *cis*-2-butene are approximately the same; sterically this seems reasonable in view of the comparable accessibility of the double bond in these two compounds.

This interpretation of the variation of the argentation constants as a manifestation of steric hindrance to the approach of the silver ion to the π -orbital receives some support from the recent report that the primary species of silver ion in water is a tetraaquo ion.²⁶ Bjerrum²⁷ also has suggested that there may be tetraaquo silver ions, with two of the water molecules held firmly and two held more loosely. It is especially significant that Andrews and Keefer⁷ find that the argentation constants of methyl-substituted benzenes in aqueous solution increase with the first methyl substituent (toluene > benzene), remain substantially constant with the second such substitution (xylenes ~ toluene) and then drop markedly (mesitylene < benzene). Since Rundle and Goring²⁸

(25) With respect to the doubly-bonded carbon atoms.

(26) H. B. Jonassen and P. C. Yates, Paper 25 at a Symposium on Equilibrium and Rate Behavior of Complex Ions, University of Chicago, February 21-23, 1951.

(27) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 107.

(28) R. B. Rundle and J. H. Goring, THIS JOURNAL, **72**, 5337 (1950).

have found that (in the crystalline state at least) the silver ion appears to lie far from the axis of the aromatic ring and thus to coordinate essentially with one of the "double bonds" of the ring, this coordination might be significantly hindered if it involved a highly hydrated silver ion and a symmetrically tri- (or higher) substituted ring.

It is noteworthy in this regard that when the basic strengths of these methyl-substituted benzenes are measured in non-aqueous media with such agents as hydrogen chloride,⁸ iodine,¹⁰ bromine,^{29a} iodine monochloride^{29b} and hydrogen fluoride-boron trifluoride⁹ there is a progressive increase as the number of methyl substituents increases in all observed cases (in some cases through the trimethyl compounds). It seems likely to us that if the silver coordination could be measured in a non-aqueous medium this same parallel would exist; indeed, the qualitative results reported by Jura, Grotz and Hildebrand³⁰ concerning the interaction of silver ion and other metal ions in silica gel with aromatic hydrocarbons support this contention.

It must be pointed out however, that the assumption, implicit throughout the preceding discussion, that all of the variation in the argentation constants here considered is caused by a difference in the enthalpy of interaction, is by no means necessarily valid. At least a portion of the rather small observed differences in free energy (of the order of one-half kcal.) may be caused by variations in the entropy of argentation; accurate measurements of ΔH° , and thus of ΔS° , for the different argentation reactions have not yet been made. However, certain approximations are possible on the basis of the available data; these will be considered in a later paper.^{11b}

Formation of Disilver Complexes.—We showed above that we consider the values of K_0 extrapolated to $(\text{Agt}) = 0$ and $\mu = 0$ (Table II) to represent the true thermodynamic equilibrium constants K'_{01} . The values of K_0 listed in Table II at finite silver ion concentrations differ from the extrapolated values chiefly for two reasons: first, the relative amount of disilver complex formed increases as (Agt) increases, and this effect is ignored in evaluating K_0 ; and second, the term $\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+}$ may vary as the ionic strength is varied. These effects might be approximately isolated if data were available concerning the variation of K_0 at constant ionic strength with varying silver ion concentration; then the second effect should be small, and, to a first approximation at least, all of the variation of K_0 with (Agt) could be attributed to the formation of the disilver complex.

In the present work, such data are available only for 2-methylpropene (Table III). It can readily be shown⁷ that if (BAg_2^{++}) is negligible relative to (Ag^+) (as it is in all of the present work), then $K_E = K_1 + K_1K_2(\text{Ag}^+)$, or, dividing by K_D , $K_0 = K_{01} + K_{01}K_2(\text{Ag}^+)$. Thus a plot of K_0 (or K_E) against (Ag^+) should be linear, and the first and sec-

(29) (a) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950); (b) *ibid.*, **72**, 5170 (1950).

(30) G. Jura, L. Grotz and J. H. Hildebrand, Abstracts of the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

ond argentation constants should be directly calculable from the intercept and the slope. A plot of the data in Table III is indeed reasonably linear and gives the values $K_{01} = 0.0672$ (at $\mu = 1$), $K_1 = 54.1$, and $K_2 = 0.13$. This value for K_2 is approximately the same as those of 0.15 and 0.11 for ethylene and propene^{11a}; for mononuclear aromatic hydrocarbons and certain of their derivatives,⁷ values of K_2 generally are in the range 0.1 to 0.3.³¹

TABLE III

 $K_0 \times 10^4$ FOR 2-METHYLPROPENE AT UNIT IONIC STRENGTH^a

(Ag ⁺), <i>N</i>	$K_0 \times 10^4$	No. of detns.
1.000	759 ± 7	8
0.500	722 ± 13	7
.250	690 ± 6	7
.100	684 ± 7	7
.000	672 ^b	

^a Silver nitrate plus potassium nitrate. ^b By graphical extrapolation.

From a comparison of the concentration-evaluated expressions for K_{01} for 2-methylpropene at $\mu = 1$ and $\mu = 0$, we can estimate that, since

$$(K_{01})_{\mu=1}(\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+})_{\mu=1} = K'_1 = (K_{01})_{\mu=0}(\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+})_{\mu=0},$$

then

$$(\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+})_{\mu=1} = 0.0886/0.0672 = 1.32$$

(31) The assumption that silver ion and potassium ion are equivalent in their effect on $\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+}$ is of course not necessarily valid. N. Koenig (Ph.D. Thesis, California Institute of Technology, 1950) has found that the solubilities of cyclohexane and carbon tetrachloride in 1 *N* potassium nitrate are each about 6% less than in 1 *N* silver nitrate, indicating that for such non-electrolytes at least the potassium salt is a slightly, but perhaps significantly, more effective salting-out agent. Thus it seems possible that the activity coefficient of the silver-olefin complex may also increase slightly as potassium ion replaces silver ion. Since γ_{Ag^+} presumably remains approximately constant, this would mean an increase in $\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+}$ under these conditions, and consequently a decrease in K_E (or K_0) as evaluated from the concentrations. Although we do not believe that this would be a large effect, a fraction of the observed decrease of K_E (or K_0) as potassium ion replaces silver ion at unit ionic strength may be due to this variation rather than to the postulated formation of BAg_2^{++} . However, for the aromatic compounds, and especially for the polynuclear hydrocarbons and iodo compounds, the effects are so large that there can be little doubt that there is significant formation of the disilver complexes.

Since γ_{\pm} for 1.0 *N* silver nitrate³² is 0.429 at 25° and presumably will vary very little in mixtures with potassium nitrate at $\mu = 1$ (at 25° γ_{\pm} for 1.0 *N* potassium nitrate³² is 0.443), we can estimate that at unit ionic strength $\gamma_{\text{BAg}^+} = (1.32)(0.43) = 0.57$ (for the 2-methylpropene-silver ion complex). It seems reasonable³³ that γ_{BAg^+} is significantly larger than γ_{Ag^+} since the complex ion is undoubtedly appreciably larger than even the hydrated silver ion.

Since no data at constant ionic strength are available for the other butenes, values of K_2 can only be approximated for them. It is to be noted in Table II that the trend in K_0 with decreasing concentration of silver ion is very similar for these three compounds, a decrease of about 15%, while for 2-methylpropene the effect is just the opposite, an increase of 15% in K_0 . If the two effects discussed above are in reality the only important ones operating here, then this difference must be due to a pronounced difference in disilver complex formation, or to a markedly different variation of $\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+}$, or perhaps of course to both. If we assume that $\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+} = 1.32$ at $\mu = 1$ for all of the butenes as it does for 2-methylpropene, we can then attribute the remaining difference between K_0 at $\mu = 1$ and K_0 at $\mu = 0$ to the formation of a disilver complex. The approximate values of K_2 so obtained are: 1-butene, 0.56; *cis*-2-butene, 0.53; *trans*-2-butene, 0.56. On the other hand, if we assume that for these other butenes the ratio of activity coefficients is essentially constant at unity as potassium ion replaces silver ion, we get for K_2 : 1-butene, 0.18; *cis*-2-butene, 0.15; *trans*-2-butene, 0.19. These values seem more reasonable when compared with those for the other olefins. However, the reason for the marked difference in the activity coefficient of the 2-methylpropene-silver ion as compared with the other butene-silver ions is then unclear. Further experimental data are needed to resolve this point.

(32) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(33) Reference 22, Chapter 3, Sections 4 and 5.