TABLE VII

2-Methylpentane

T, °K.	298.16	318.2	333.5
S^0, liq.	69.45	72.52	74.82
Vaporization, $\Delta H_{vap.}$ T	23.95	21.58	19.92
Compression, $R \ln (P/760)$	−2.54	−1.02	0.00
Gas imperfection	0.11	0.16	0.22
S^0, gas	90.97	93.24	94.96
	±0.20	±0.20	±0.20

2,3-Dimethylbutane

T, °K.	298.16	313.13	331.15
S^0, liq.	66.33	68.57	71.22
Vaporization, $\Delta H_{vap.}/T$	23.34	21.62	19.69
Compression, $R \ln (P/760)$	−2.34	−1.20	0.00
Gas imperfection	0.10	0.13	0.18
S^0, gas	87.43	89.12	91.09
	±0.20	±0.20	±0.20

3-Methylpentane

T, °K.	298.16	323.8	336.5
Vaporization, $\Delta H_{vap.}/T$	24.27	21.28	19.95
Compression, $R \ln (P/760)$	−2.76	−0.83	0.00
Gas imperfection	0.07	0.13	0.18
ΔS°_{v}, liquid to ideal gas at 1 atm.	21.58	20.58	20.12
	±0.05	±0.05	±0.05

Summary

The vapor heat capacities of 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane have been measured over the temperature range 325 to 471°K. Values of the heat capacity of the ideal gases are given by the following empirical equations.

2-Methylpentane:
$$C^{\circ}_p = 1.55 + 0.11963T - 3.478 \times 10^{-5}T^2$$
3-Methylpentane:
$$C^{\circ}_p = 1.40 + 0.11776T - 3.291 \times 10^{-5}T^2$$
2,3-Dimethylbutane:
$$C^{\circ}_p = -2.65 + 0.13692T - 5.433 \times 10^{-5}T^2$$

Heats of vaporization for the three compounds were measured at three temperatures ranging from about 25° to the normal boiling point. For interpolation the following equations may be used:

2-Methylpentane:
$$\Delta H_{vap.} = 9173 - 0.2673T - 0.02196T^2$$
3-Methylpentane: $\Delta H_{vap.} = 9688 - 3.366T - 0.01629T^2$
2,3-Dimethylbutane:
$$\Delta H_{vap.} = 8461 - 2.233T - 0.02438T^2$$

Entropies of 2-methylpentane and 2,3-dimethylbutane in the ideal gas state are given at the normal boiling points, at 298.16°K. and at an intermediate temperature.

Second virial coefficients derived from the thermal data are shown to be consistent with literature data on vapor densities.

BARTLESVILLE, OKLA. RECEIVED MAY 16, 1949

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Solubility of Cuprous Chloride and Silver Bromate in Aqueous Solutions of Unsaturated Alcohols[1a]

BY R. M. KEEFER, L. J. ANDREWS AND R. E. KEPNER

Extensive information concerning the reactions of allyl alcohol and certain unsaturated acids to form water-soluble complexes with cuprous ion and cuprous chloride has been accumulated.[1b,c,d,e,f]

By solubility measurements of the type used in previous investigations data have now been obtained concerning the tendency for certain allylic alcohols to form cuprous complexes. The equilibrium constants for these metalation reactions are reported here and are compared with those obtained for the unsaturated acids. Measurements of the solubility of silver bromate in aqueous solutions of certain of these alcohols and of a few other compounds of interest are also reported, the results of which may be explained satisfactorily on the assumption that a 1:1 complex between silver ion and the unsaturate is formed.[2] Thus data are available for a comparison of the relative tendencies for cuprous and silver ions to coördinate with a carbon–carbon double bond.

The Solubility Measurements.—The method of determining the solubility of cuprous chloride in aqueous solutions of unsaturated compounds has been described previously.[1d,e,f] All solutions were prepared and saturated with cuprous chloride or silver bromate at 25.0°. For the cuprous chloride series the chloride-ion concentration was varied by addition of hydrochloric acid and the ionic strength maintained at 0.100 by addition of perchloric acid prior to addition of solid cuprous chloride. In the silver bromate experiments potassium nitrate was added to the aqueous solutions of the unsaturated compounds to adjust the ionic strength to 0.10 prior to addition of solid silver bromate. Aliquots of the solutions saturated with silver bromate were analyzed for total silver ion by adding a measured excess of 0.0500 M

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(1) (a) Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. V.

(1) (b) Kepner and Andrews, *J. Org. Chem.*, **13**, 208 (1948); (c) Andrews and Keefer, THIS JOURNAL, **70**, 3261 (1948); (d) Keefer and Andrews, *ibid.*, **71**, 1723 (1949); (e) Andrews and Keefer, *ibid.*, **71**, 2379 (1949); (f) Keefer, Andrews and Kepner, *ibid.*, **71**, 2381 (1949).

(2) *Cf.* Winstein and Lucas, *ibid.*, **60**, 836 (1938).

sodium chloride solution and back titrating the excess chloride ion using 0.0250 *M* silver nitrate with dichlorofluorescein as an indicator. High concentrations of alcohol interfere with the action of the indicator. In the case of 4-methyl-4-penten-2-ol, γ,γ-dimethylallyl alcohol, 3-methyl-3-buten-2-ol and 2-methyl-2-buten-1-ol the low solubility of the alcohols in water did not allow a wide variation in alcohol concentrations. With vinylacetic acid (μ = 1.0 using perchloric acid) and phenol (μ = 0.10 using potassium nitrate) the saturated solutions were analyzed for total silver ion by adding excess sodium bromide and weighing the silver bromide formed. The solubility product of silver bromate was determined in 1.00 *N* perchloric acid and in 0.100 *N* potassium nitrate. High concentrations of β-chloroallyl alcohol were needed in aqueous solution to dissolve measureable amounts of cuprous chloride. The equilibrium constants for this compound were found to vary somewhat with alcohol concentration of the medium. The results reported for this compound are thus significant only as regards the relative magnitude of the equilibrium constants as compared to those for the other alcohols studied.

Cuprous Chloride and Silver Bromate.—Cuprous chloride was prepared as described previously.[1b] Silver bromate was prepared according to the directions of Neuman.[3] The product was dried for two hours at 110°, powdered and analyzed for silver content.[4] Found: Ag, 45.90. Calcd.: Ag, 45.75.

The Unsaturated Alcohols.—The crotyl alcohol (b. p. 121.0–121.2°) was prepared from crotonaldehyde.[5] Methylvinylcarbinol (b. p. 97.3°) was prepared by hydrolysis of a butenyl chloride mixture.[6] Ethylvinylcarbinol (b. p. 113.8–114.0°) was prepared from ethylmagnesium bromide and acrolein.[7] Samples of β-methallyl alcohol (b. p. 142°), β-chloroallyl alcohol (b. p. 134.0°) and 4-methyl-4-penten-2-ol (b. p. 130.3°), furnished through the courtesy of the Shell Chemical Corporation, were dried and fractionated before use. Small samples of 3-methyl-3-buten-2-ol (b. p. 115–117°), 2-methyl-2-buten-1-ol (b. p. 138.0°), α,α-dimethylallyl alcohol (b. p. 96.0–96.5°) and γ,γ-dimethylallyl alcohol (b. p. 142–143°), kindly furnished by Professor W. G. Young and Mr. J. Rule of the University of California at Los Angeles, were dried and fractionated. J. T. Baker C. P. phenol was distilled and a fraction of b. p. 177–178° (uncor.) was collected. The preparation of the sample of vinylacetic acid has been described previously.[1e]

Results

The solubility of cuprous chloride in aqueous solutions of unsaturated alcohols is given in Table I. As in the studies of unsaturated acids[1e,f] the following equations may be shown to account for the formation of water soluble cuprous species in the experiments reported in this communication.

$$\mathrm{CuCl} = \mathrm{Cu^+} + \mathrm{Cl^-} \quad \mathrm{S.\ P.} = 1.85 \times 10^{-7} \qquad (1)$$

$$\mathrm{Cu^+} + 2\mathrm{Cl^-} = \mathrm{CuCl_2^-}$$

$$K_2 = (\mathrm{CuCl_2^-})/(\mathrm{Cu^+})(\mathrm{Cl^-})^2 = 3.51 \times 10^5 \qquad (2)$$

$$\mathrm{Cu^+} + \mathrm{Un} = \mathrm{Un{\cdot}Cu^+}$$

$$K_3 = (\mathrm{Un{\cdot}Cu^+})/(\mathrm{Un})(\mathrm{Cu^+}) \qquad (3)$$

$$\mathrm{Cu^+} + \mathrm{Cl^-} + \mathrm{Un} = \mathrm{Un{\cdot}CuCl}$$

$$K_4 = (\mathrm{Un{\cdot}CuCl})/(\mathrm{Un})(\mathrm{Cu^+})(\mathrm{Cl^-}) \qquad (4)$$

The unsaturated compound has been designated as Un and the water soluble complexes formed as Un·Cu$^+$ and Un·CuCl. The detailed procedure for evaluating K_3 and K_4 is the same as that used in previous work. The values of K_3 and K_4 are given in Table III. Table I gives the calculated

TABLE I

THE SOLUBILITY OF CUPROUS CHLORIDE IN AQUEOUS SOLUTIONS OF UNSATURATED ALCOHOLS AT 25.0° (μ = 0.10)

(Un$_i$) mole/liter	(Cu^+_T) mole/liter × 10^3					
	(Cl^-_i) = 0		(Cl^-_i) = 0.100 *M*		(Cl^-_i) = 0.010 *M*	
	meas.	calcd.	meas.	calcd.	meas.	calcd.
Ethylvinylcarbinol						
0.0929	35.6	37.8	30.5	30.4	34.2	34.9
.0464	21.7	21.8	18.4	18.6	19.6	19.6
.0232	12.8	12.8	12.3	12.3	..	..
.0116	8.1	7.4	..	..	..	..
Methylvinylcarbinol						
.0728	30.6	30.8	25.8	26.2	..	..
.0546	24.6	24.5	21.1	21.2	..	..
.0364	18.0	17.9	16.0	16.2	16.2	15.8
.0182	10.3	10.4	..	..	..	..
α,α-Dimethylallyl alcohol						
.0910	31.1	31.7	25.3	25.5	..	..
.0682	25.2	25.2	20.5	20.6	22.5	22.7
.0455	18.5	18.5	15.8	15.9	16.5	16.2
.0228	10.9	11.0	..	..	..	..
4-Methyl-4-penten-2-ol						
.0336	12.8	12.6	11.6	12.0	10.3	10.4
.0168	7.6	7.6	9.0	9.0	6.1	5.9
.0884	4.3	4.6	..	..	..	..
γ,γ-Dimethylallyl alcohol						
.0328	10.7	10.5	10.2	10.4	7.9	7.9
.0164	..	..	8.1	8.2	5.5	5.4
3-Methyl-3-buten-2-ol						
.0504	9.1	9.3	10.0	10.1	6.8	7.1
.0378	7.7	7.6	9.0	9.1	5.5	5.4
2-Methyl-2-buten-1-ol						
.0189	4.9	5.0	8.0	8.1	3.5	3.5
β-Chloroallyl alcohol						
.500	8.2	8.0	9.5	9.5	5.8	5.6
β-Methallyl alcohol						
			(Cl^-_i) = 0.101 *M*		(Cl^-_i) = 0.0101 *M*	
0.0708	17.8	17.9	15.8	16.0	15.0	15.1
.0472	13.2	13.4	12.1	12.7	10.8	10.7
.0236	8.1	8.0	9.6	9.4	..	..
Crotyl alcohol						
			(Cl^-_i) = 0.102 *M*		(Cl^-_i) = 0.0102 *M*	
0.142	26.8	27.6	22.0	21.4	23.7	24.5
.106	..	..	17.4	17.6	18.7	19.3
.0708	..	..	13.9	13.8	..	..
.0688	16.6	16.3	..	..	..	..
.0342	10.2	10.0	..	..	..	..

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(3) Neuman, THIS JOURNAL, **56**, 28 (1934).

(4) Ricci and Aleshnick, *ibid.*, **66**, 980 (1944).

(5) Young, Hartung and Crossley, *ibid.*, **58**, 100 (1936).

(6) Young and Andrews, *ibid.*, **66**, 421 (1944).

(7) (a) Delaby, *Compt. rend.*, **175**, 967 (1922); (b) Prévost, *Ann. Chim.*, [10] **113**, 147 (1928).

solubilities of cuprous chloride in solutions of the unsaturated compounds (Cu^+_T calcd.) using the values of K_3 and K_4 given.[1e,f] The agreement between experimental (Cu^+_T measd.) and calculated values is as good as may be expected considering the experimental errors.

The solubility of silver bromate in aqueous solutions of unsaturated compounds (Ag^+_T) is reported in Table II. These results may be explained on the assumption that equations (5) and (6) account for the formation of all water-soluble forms of silver ion.[8]

$$AgBrO_3 = Ag^+ + BrO_3^- \qquad S.\ P. = 1.00 \times 10^{-4} \quad (5)$$

$$Ag^+ + Un = Un{\cdot}Ag^+$$

$$K_6 = (Un{\cdot}Ag^+)/(Un)(Ag^+) \quad (6)$$

TABLE II

THE SOLUBILITY OF SILVER BROMATE IN AQUEOUS SOLUTIONS OF UNSATURATED COMPOUNDS AT 25.0° (μ = 0.10)

(Un_i) mole/liter	(Ag^+_T) mole/liter × 10^2	K_6	(Un_i) mole/liter	(Ag^+_T) mole/liter × 10^2	K_6
Allyl alcohol			Methallyl alcohol		
0.585	2.98	14.0	0.470	2.42	10.8
.293	2.20	14.0	2.35	1.84	10.8
.146	1.69	13.8	.118	1.48	10.8
.0732	1.38	13.6	.059	1.27	11.2
Crotyl alcohol			Methylvinylcarbinol		
.702	1.87	3.6	.255	2.12	14.7
.527	1.73	3.9	.204	1.93	14.3
.351	1.54	4.0	.102	1.53	14.5
.176	1.30	4.0	.051	1.28	13.9
.0878	1.16	4.1	.025	1.14	12.9
Ethylvinylcarbinol			2-Methyl-2-buten-1-ol		
.472	2.68	13.8	.100	1.21	4.8
.236	2.04	14.2	.050	1.12	4.9
.0944	1.52	15.3	.020	1.05	5.5
.0472	1.28	15.2			
Vinylacetic acid[a,b]			Phenol[a]		
.467	2.90	16.2	.448	1.28	1.54
.234	2.15	16.1	.224	1.14	1.48
.117	1.67	16.1	.112	1.07	1.59
.0585	1.37	15.8	0	0.989	...
0	1.01	..			

[a] Analysis by silver bromide precipitation method. [b] μ adjusted to 1 using perchloric acid.

The concentrations of substances needed to calculate K_6 were readily obtained by use of equation (5) and equations (7) and (8) in which (Ag^+_T) represents the total molar concentration of free and complexed silver ion in solution at equilibrium, and (Un_i) is the initial molar concentration of the unsaturate in aqueous solution before the addition of silver bromate. The values of K_6 calculated are given in Table II and some of these are summarized in Table III to permit comparison with the K_3 values obtained for the formation of the corresponding cuprous complexes.

TABLE III

EQUILIBRIUM CONSTANTS FOR FORMATION OF THE COPPER AND SILVER COMPLEXES OF THE UNSATURATED ALCOHOLS AT 25° (μ = 0.1)

Unsaturate	Ag^+ complex $K_6 \times 10^{-3}$	Cu^+ complexes $K_3 \times 10^{-3}$	$K_4 \times 10^{-5}$
Allyl alcohol	0.014	52[a]	22[a]
Ethylvinylcarbinol	.014	39	15
Methylvinylcarbinol	.014	33	17
α,α-Dimethylallyl alcohol	....	25	12
4-Methyl-4-penten-2-ol	....	16	9.7
γ,γ-Dimethylallyl alcohol	.002	11	7.0
Crotyl alcohol	.0039	10	5.4
β-Methallyl alcohol	.011	9.2	7.6
3-Methyl-3-buten-2-ol	....	4.0	4.2
2-Methyl-2-buten-1-ol	.005	3.5	5.9
β-Chloroallyl alcohol	0	0.22	0.35

[a] Calculated from data of Ref. 1d.

$$(Ag^+_T) = (BrO_3^-) = (Ag^+) + (Un{\cdot}Ag^+) \quad (7)$$

$$(Un) = (Un_i) - (Un{\cdot}Ag^+) \quad (8)$$

Structures of the type previously proposed for silver or cuprous complexes of compounds containing carbon–carbon double bonds[1,2] seem appropriate to describe the complexes formed by the unsaturated alcohols investigated in the present study. In general the K_3 and K_4 values for cuprous complex formation of the α,β-unsaturated alcohols are somewhat higher than those observed for the α,β-unsaturated acids investigated previously. Since a carboxyl group conjugated with a carbon–carbon double bond should markedly decrease the electron density at the double bond through both resonance and inductive effects, this observation seems reasonable. As in the case of the unsaturated acids, replacement of hydrogen atoms by methyl substituents at the double bond in the unsaturated alcohols reduces the magnitude of K_3 and K_4. As previously noted this may result from steric effects of the methyl substituents. It is interesting to note that α-alkyl-substituted allyl alcohols (*cf.* crotyl alcohol and methylvinylcarbinol) also show lower K_3 and K_4 values than does allyl alcohol. Molecular models show that such alkyl substituents might inhibit the tendency for cation complexing at the double bond because of steric effects. In the case of β-chloroallyl alcohol low values of K_3 and K_4 were found as compared to those for allyl alcohol, as might be expected in view of the inductive effect of a chlorine substituent.

The values of K_3/K_4, representing the equilibrium constant for the ionization of $Un{\cdot}CuCl$ to produce $Un{\cdot}Cu^+$ and chloride ion, vary from 2.4 × 10^{-2} for allyl alcohol to 0.6 × 10^{-2} for 2-methyl-2-buten-1-ol and β-chloroallyl alcohol. These

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(8) The value for the solubility product of silver bromate is based on measurements of the solubility of silver bromate in 0.1 *N* potassium nitrate solution by titration procedures and is in good agreement with the results of Dalton, Pomeroy and Weymouth, THIS JOURNAL, **46**, 60 (1924). In the experiments with phenol using a gravimetric method of analysis for silver a solubility product of 0.978 × 10^{-4} was obtained for silver bromate in 0.1 *N* potassium nitrate solution. For the runs using vinylacetic acid the silver bromate solubility product was determined for 1 *N* perchloric acid solution by the gravimetric method as 1.029 × 10^{-4}.

values are of the same order of magnitude as were obtained for the corresponding equilibrium constants determined in the studies of the unsaturated acids.[1f] It is interesting to note that the earlier observation[1e] that the magnitude of K_3/K_4 is much less affected by changes in structure of the unsaturate than are the K_3 and K_4 values is upheld in the present investigation.

The equilibrium constants for the silver complexes of phenol, crotyl alcohol and allyl alcohol reported in Table II agree favorably with those obtained by somewhat different procedures by Winstein and Lucas[2] (2.19, 5.17 and 12, respectively) for solutions of ionic strength equal to 1. The change in ionic strength should have little effect on the equilibrium constants so that the values may be compared directly. Structures of the type previously proposed for silver ion and aromatic compounds would seem appropriate for the silver ion-phenol complex.[2,9] In general the values of K_6 follow the same trends as do the values of K_3. However, the effect of varying substituents at the double bond does not produce as marked an effect on K_6 as on K_3. It is interesting to note that the cuprous complexes are much more stable than the silver complexes as may be seen by comparing the values of K_3 and K_6 given in Table III. As in the case of the cuprous complexes, silver ion complexes vinylacetic acid to about the same extent as it does allyl alcohol. Even with saturated solutions of maleic and fumaric acid no indication of complex formation with silver ion could be obtained. This again would be in agreement with the results obtained with cuprous ion which indicated that the maleic and fumaric acid complexes were much less stable than the vinylacetic acid complex.

Summary

By measurement of the solubility of cuprous chloride or silver bromate in aqueous solutions of unsaturated alcohols, equilibrium constants for the reactions to form the complexes Un·Cu$^+$, Un·CuCl and Un·Ag$^+$ at 25° have been determined. The cuprous ion complexes are considerably more stable than the corresponding silver ion complexes. α,β-Unsaturated alcohols show a somewhat greater tendency for this type of complex formation than do α,β-unsaturated acids. When hydrogen atoms at the double bond are replaced by methyl groups, the tendency for the unsaturated alcohols to undergo cuprous complex formation is reduced.

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[9] Keefer and Andrews, THIS JOURNAL, **71**, 3644 (1949).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Exchange Reaction between Antimony(III) and Antimony(V) in Hydrochloric Acid Solutions

BY NORMAN A. BONNER

This paper deals with a preliminary study of the exchange reaction between antimony(III) and antimony(V) in hydrochloric acid solutions. The kinetics of the exchange have been studied in 6 *f* hydrochloric acid, and in addition, the rates of exchange have been measured in 3 *f* and 12 *f* hydrochloric acid. In 6 *f* acid, half-times in the neighborhood of sixty hours were observed and the rate was found to depend critically on the hydrochloric acid concentration.

Experimental

Tracers.—The 60-day Sb^{124} tracer was obtained from the Atomic Energy Commission in the form of 200 mg. of metallic antimony which had been irradiated in the Clinton Pile. The metal was boiled with a small amount of aqua regia, the resulting oxide dissolved in concentrated hydrochloric acid, and the solution boiled to remove chlorine and nitrogen oxides. Stock +3 tracer solutions were made by diluting aliquots of the above solution to about 3 *f* hydrochloric acid and passing hydrogen sulfide into the boiling solution until the antimony sulfide turned black. The sulfide was filtered off, washed, dissolved in 6 *f* hydrochloric acid, boiled to remove hydrogen sulfide and diluted to a known volume with 6 *f* hydrochloric acid.

The +5 tracer solutions were prepared in the same manner except that after the sulfide precipitate had been dissolved and the hydrogen sulfide removed, the 6 *f* hydrochloric acid solution was diluted with an equal volume of distilled water and chlorine gas bubbled through the hot solution for several hours. The solution was then boiled to remove chlorine and bring the hydrochloric acid concentration to 6 *f*. The final, known volume was obtained by dilution with 6 *f* hydrochloric acid.

As a check on the radiochemical purity of the tracer, a sample was sealed in a test-tube and the γ-radiation counted at intervals in a standard geometry with the same brass-wall Geiger–Mueller counter. The counter itself was checked against a similar 5.3-year Co^{60} standard and found to give the same corrected counting rate, within the statistical counting error, at all times.

The antimony sample decayed with a 60 ± 1-day half-life over a period of five half-lives in satisfactory agreement with the previously determined value.[1] The antimony had been received from Oak Ridge more than a month before these particular experiments were started and the standard was prepared so the activity of the 2.8-day Sb^{122} (and any short-lived impurities) had decreased to an immeasurably small value.

Reagents.—Analytical reagents were used.

The +3 and +5 antimony carriers were made up in the same manner as the corresponding tracers, but the starting material was an accurately weighed sample of antimony trioxide instead of antimony metal. The trioxide was analyzed by triiodide titration and found to be 99.9% pure.

The carrier, tracer and hydrochloric acid solutions were all analyzed gravimetrically for total chloride by the pre-

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[1] Seaborg and Perlman, *Rev. Modern Phys.*, **20**, 585 (1948), list the half-life as sixty days.