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# Coördination of Silver Ion with Unsaturated Compounds. VIII. Alkynes[1]

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Quasi thermodynamic equilibrium constants, $K_\alpha$, of the reactions of aqueous silver nitrate with a number of alkynes have been determined by solubility measurements at ionic strength $\mu = 1$ and in the absence of oxygen. Whereas $\Delta H$ calculated with $K_1$ has the respective unrealistic values of 0.0 and +6.8 kcal. for 3-hexyne and 2,2,5,5-tetramethyl-3-hexyne, the respective $\Delta H$ values are $-4.5$ and $-5.0$ kcal. when calculation is made with $K_\alpha$. In 3-hexyne and its $\alpha$-methyl homologs the value of $K_\alpha$ is reduced to about one third for each substitution of an $\alpha$-hydrogen atom by a methyl group.

The ability of 3-hexyne to complex with silver nitrate, as determined by a distribution method,[3] is approximately that of an alkene, for it is somewhat greater than that of a *trans*-hexene and somewhat less than that of a *cis*-hexene. The solubility method of Andrews and Keefer[4] is much more rapid than the distribution method and was adopted for the investigation of other alkynes. However, we interpret our results in a different way.

So far, only hydrocarbons have given satisfactory results. $\alpha$-Halogenated alkynes are reactive with silver ion, $\alpha$-hydroxy alkynes are oxidized and $\alpha$-carbonyl alkynes are not stable under the conditions employed, presumably due to reactivity with water.

**The Method.**—The alkynes were distilled and stored under 99.9% nitrogen.[5] Some, as for example 1-butyne, were stored in sealed ampoules.

An ampoule of alkyne is placed in an equilibration flask, capacity 250 ml., provided with sufficient outlets to allow transferal of solutions under nitrogen. The flask is evacuated to less than 1 mm. of mercury, nitrogen is admitted to atmospheric pressure, and the operation is repeated. The ampoule is broken by swirling or shaking. Sufficient oxygen-free 1 $M$ silver nitrate and/or 1 $M$ potassium nitrate are separately forced into the flask to give 100 to 200 ml. of solution, ionic strength $\mu = 1$, having approximately the desired concentration of silver nitrate. Sufficient alkyne is taken to leave about 0.5 ml. undissolved. The flask is covered with aluminum foil to exclude light.

Saturation at 25° is assured by: (1) cooling the flask contents under a slight nitrogen pressure for about five minutes in an ice-water bath; (2) swirling the contents; (3) replacing the flask in the 25° bath, and (4) after 0.5 hour swirling for one minute seven times at five-minute intervals. Since the solubility of the alkyne is greater at the lower temperature the aqueous phase is supersaturated initially after reaching 25° and then is saturated in contact with the organic phase. After standing one hour at 25° two samples of the aqueous phase are taken for the determination of silver and alkyne, respectively. Silver is determined by addition of an excess of standard potassium chloride and back titration with standard silver nitrate, chromate being the indicator.[6]

The sample for alkyne analysis is run into an appropriate volume of especially purified[3] carbon tetrachloride[7] and 5 $M$ potassium cyanide[8] at about 10° in a grease-free mixing cylinder. After this has been shaken mechanically for 0.5 hour the phases are separated and the organic phase is dried with magnesium sulfate. From measurement of the intensity of the C–H band at about 3.4 $\mu$ the concentration of alkyne in the carbon tetrachloride phase is determined. The concentration of alkyne in the aqueous phase at $\mu = 1$ is calculated.

**Data.**—These at 25° are given in Tables I to VI, respectively, for 3-hexyne, I; 2-methyl-3-

Table I

Solubility of 3-Hexyne, I, at $\mu = 1$ in Aqueous Silver Nitrate

| $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^4$ | $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^4$ |
|---|---|---|---|
| At 25° | | At 35° | |
| 0.000 | 68 | 0.000 | 64 |
| .108 | 199 | .074 | 129 |
| .128 | 233 | .190 | 244 |
| .272 | 405 | .307 | 361 |
| .318 | 478 | .360 | 408 |
| .338 | 496 | .548 | 619 |
| .531 | 756 | .730 | 822 |
| .761 | 1102 | .752 | 843 |
| 1.000 | 1475 | 1.000 | 1135 |

Table II

Solubility of 2-Methyl-3-hexyne, II, at 25.0° and $\mu = 1$ in Aqueous Silver Nitrate

| $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^5$ | $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^5$ |
|---|---|---|---|
| 0.000 | 180 | 0.675 | 3090 |
| .096 | 553 | .675 | 3120 |
| .175 | 895 | 1.000 | 4800 |
| .358 | 1670 | | |

Table III

Solubility of 2,2-Dimethyl-3-hexyne, III, at 25.0° and $\mu = 1$ in Aqueous Silver Nitrate

| $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^5$ | $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^5$ |
|---|---|---|---|
| 0.000 | 72 | 0.579 | 900 |
| .165 | 284 | .707 | 1110 |
| .360 | 564 | .927 | 1470 |

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[1] This investigation has been made possible by support extended the California Institute of Technology by the Office of Naval Research under Contract Nonr-270(00).

[2] To whom requests for reprints should be sent.

[3] W. S. Dorsey and H. J. Lucas, This Journal, **78**, 1665 (1956).

[4] L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1939).

[5] Linde Air Products Company.

[6] E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1950, p. 87.

[7] The correct volume to give a final optical density of 0.2 to 0.5 in the Perkin–Elmer double-beam IR spectrophotometer.

[8] This completely liberates the alkyne from the silver–alkyne complex.

TABLE IV

SOLUBILITY OF 2,2,5-TRIMETHYL-3-HEXYNE, IV, AT 25.0° AND $\mu = 1$ IN AQUEOUS SILVER NITRATE

| $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^6$ | $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^6$ |
|---|---|---|---|
| 0.000 | 241 | 0.380 | 2340 |
| .127 | 885 | 0.641 | 3860 |
| .284 | 1746 | 1.000 | 6120 |

hexyne, II; 2,2-dimethyl-3-hexyne, III; 2,2,5-trimethyl-3-hexyne, IV; 2,2,5,5-tetramethyl-3-hexyne, V; and 2-heptyne, VI. The data at 35° are given in Tables I and V, respectively, for I and V.

When the solubility of any alkyne is plotted against silver ion concentration the plot has an upward curvature. This indicates a greater solubility than would be given by a 1-to-1 complex of alkyne with silver ion, eq. 1, and is believed to be the result of a 1-to-2 complex,[9] eq. 2. The equilibrium constants for the formation of these two complexes are given by eq. 3 and 4, respectively. Here (Un) is the concentration of the uncomplexed alkyne, Un, $(Un{\cdot}Ag^+)$ is the concentration

$$\mathrm{Un} + \mathrm{Ag}^+ \rightleftarrows \mathrm{Un{\cdot}Ag}^+ \qquad (1)$$

$$\mathrm{Un{\cdot}Ag}^+ + \mathrm{Ag}^+ \rightleftarrows \mathrm{Un{\cdot}2Ag}^+ \qquad (2)$$

$$K_1 = \frac{(\mathrm{Un{\cdot}Ag}^+)}{(\mathrm{Un})(\mathrm{Ag}^+)} \qquad (3)$$

$$K_2 = \frac{(\mathrm{Un{\cdot}2Ag}^+)}{(\mathrm{Un{\cdot}Ag}^+)(\mathrm{Ag}^+)} \qquad (4)$$

of the 1-to-1 complex, $Un{\cdot}Ag,^+$ and $(Un{\cdot}2Ag^+)$ is the concentration of the 1-to-2 complex, $Un{\cdot}2Ag^+$.

**Calculation of Argentation Constants.**—Rigorous values can be obtained for $K_1$ and $K_2$, assuming only that there are no other complexes present except the 1-to-1 and 1-to-2 complexes. Equations 5 and 6 are the respective expressions for the concentrations of total alkyne, $Un_t$, and of total silver, $Ag_t$, in terms of the concentrations of uncomplexed and complexed materials.

$$(\mathrm{Un_t}) = (\mathrm{Un}) + (\mathrm{Un{\cdot}Ag}^+) + (\mathrm{Un{\cdot}2Ag}^+) \qquad (5)$$

$$(\mathrm{Ag_t}) = (\mathrm{Ag}^+) + (\mathrm{Un{\cdot}Ag}^+) + 2(\mathrm{Un{\cdot}2Ag}^+) \qquad (6)$$

Equation 7 expresses $(Un_t)$ in terms of $(Ag_t^+)$, $K_1$, $K_2$ and (Un), the solubility of the alkyne in 1 $M$ potassium nitrate.

$$(\mathrm{Un_t}) = (\mathrm{Un}) + (\mathrm{Ag_t}^+)/2 - \frac{[K_1(\mathrm{Un}) - 1]\{K_1(\mathrm{Un}) + 1 - \sqrt{[K_1(\mathrm{Un}) + 1]^2 + 8K_1K_2(\mathrm{Un})(\mathrm{Ag_t}^+)\}}}{8K_1K_2(\mathrm{Un})} \qquad (7)$$

Differentiation of eq. 7 gives eq. 8, which reduces to eq. 9 at $(Ag_t^+) = 0$.

$$\frac{d(\mathrm{Un_t})}{d(\mathrm{Ag_t}^+)} = {}^1/_2 + \frac{K_1(\mathrm{Un}) - 1}{2\{[K_1(\mathrm{Un}) + 1]^2 + 8K_1K_2(\mathrm{Un})(\mathrm{Ag_t}^+)\}^{1/2}} \qquad (8)$$

$$\left[\frac{d(\mathrm{Un_t})}{d(\mathrm{Ag_t}^+)}\right]_{(\mathrm{Ag_t}^+)\,=\,0} = \frac{K_1(\mathrm{Un})}{1 + K_1(\mathrm{Un})} \qquad (9)$$

The experimental data for each alkyne were fitted to a curve of the form of eq. 10 where $a$, the ordinate intercept, can be identified with (Un).

$$(\mathrm{Un_t}) = a + b(\mathrm{Ag_t}^+) + c(\mathrm{Ag_t}^+)^2 \qquad (10)$$

TABLE V

SOLUBILITY OF 2,2,5,5-TETRAMETHYL-3-HEXYNE, V, AT $\mu = 1$ IN AQUEOUS SILVER NITRATE

| $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^6$ | $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^6$ |
|---|---|---|---|
| At 25° | | At 35° | |
| 0.000 | 147 | 0.000 | 77 |
| .217 | 568 | .055 | 148 |
| .368 | 914 | .163 | 332 |
| .395 | 955 | .293 | 537 |
| .446 | 1082 | .436 | 778 |
| .483 | 1217 | .521 | 895 |
| .651 | 1637 | .707 | 1293 |
| .733 | 1798 | 1.000 | 1838 |
| .793 | 1970 | | |
| 1.000 | 2533 | | |

TABLE VI

SOLUBILITY OF 2-HEPTYNE, VI, AT 25.0° AND $\mu = 1$ IN AQUEOUS SILVER NITRATE

| $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^6$ | $(Ag_t^+)$, $M$ | $(Un_t)$, $M \times 10^6$ |
|---|---|---|---|
| 0.000 | 170 | 0.528 | 1345 |
| .146 | 474 | .585 | 1501 |
| .290 | 795 | .786 | 2028 |
| .290 | 807 | 1.000 | 2674 |
| .441 | 1115 | | |

Similarly $b$ and $c$ can be identified with the coefficients of the $(Ag_t^+)$ and $(Ag_t^+)^2$ terms in the expanded form of eq. 7, where terms containing $(Ag_t^+)^3$ and higher orders are dropped. If this identification is made, values of $b$ and $c$ are those shown by eq. 11 and 12. The slope of eq. 7 at $(Ag_t^+) = 0$ is $b$, as eq. 9 indicates.

$$b = \frac{K_1(\mathrm{Un})}{K_1(\mathrm{Un}) + 1} = \frac{K_1a}{K_1a + 1} \qquad (11)$$

$$c = \frac{[K_1(\mathrm{Un}) - 1]}{[K_1(\mathrm{Un}) + 1]^3}\,K_1K_2(\mathrm{Un}) \qquad (12)$$

Best values of $a$, $b$ and $c$ are determined by the method of least squares from the solubility data. The coefficients of eq. 10 for the various alkynes are shown in Table VII. $K_1$ was calculated with eq. 11, using the values of $a$ and $b$ from their least squares determination. By direct substitution into eq. 7, $K_2$ was calculated from (Un), $K_1$ and simultaneous values of $(Un_t)$ and $(Ag_t^+)$, as empirically determined from eq. 10. This method of calculating $K_1$ and $K_2$ involves no simplifying assumptions once the model is assumed. $K_1$ and $K_2$ are not thermodynamic equilibrium constants.

TABLE VII

LEAST SQUARES EQUATIONS (EQ. 10)

| Alkyne | Temp., °C. | $a$ | $b$ | $c$ |
|---|---|---|---|---|
| I | 25 | 0.00758 | 0.1157 | 0.0250 |
| I | 35 | .00599 | .0940 | .0136 |
| II | 25 | .00188 | .03856 | .00747 |
| III | 25 | .00068 | .01302 | .00230 |
| IV | 25 | .000226 | .005255 | .000641 |
| V | 25 | .000149 | .001900 | .000484 |
| V | 35 | .000078 | .001454 | .000316 |
| VI | 25 | .00170 | .0200 | .00470 |

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[9] However, the solubilities of cyclohexene and carbon tetrachloride in 1 $M$ potassium nitrate are each about 6% less than in 1 $M$ silver nitrate (N. Koenig, Ph.D. Thesis, California Institute of Technology, 1950). The salting out effect of potassium ion on alkynes may likewise be greater than that of silver ion. This may account for about half of the increased solubility ascribed to silver ion. Thus the values of $K_2$ calculated may be too large.

At zero silver concentration the activity coefficients of $Ag^+$ and $Ag \cdot Un^+$ can be considered to be essentially unity. In such a case the ratio of the two is unity, eq. 13

$$\gamma_{Un \cdot Ag^+}/\gamma_{Ag^+} = 1 \qquad (13)$$

In its saturated aqueous solution at $\mu = 1$ the activity of Un is equal to the activity of the hydrocarbon in equilibrium with the solution. If the activity of the pure hydrocarbon at 25° is taken as unity,[10] then the activity of Un in the aqueous solution is approximately equal to unity, eq. 14. However the activity is not exactly unity because the

$$(Un)\ \gamma_{Un} \cong 1 \qquad (14)$$

hydrocarbon phase is not pure Un owing to the presence of some dissolved water.

The product of eq. 3, eq. 13 and $1/\gamma_{Un}$ gives eq. 15. Here $K_1/\gamma_{Un}$ is a true thermodynamic equilibrium constant, and $K_\alpha$ is an approximation to a

$$\frac{K_1}{\gamma_{Un}} = \frac{(Un \cdot Ag^+)}{(Un)(Ag^+)} \cdot \frac{\gamma_{Un \cdot Ag^+}}{\gamma_{Un}\gamma_{Ag^+}} = K_\alpha = K_1(Un) \qquad (15)$$

thermodynamic equilibrium constant. Its validity is restricted by eq. 13 and 14. Multiplication of the experimentally determined $K_1$ by (Un) gives the value of $K_\alpha$. $K_\alpha$ is a better constant than $K_1$ for comparing different alkynes because it is the equilibrium constant of the reaction of the liquid hydrocarbon with aqueous silver ion to form the aqueous complex ion.

**Results.**—In Table VIII are data on the solubilities of the alkynes in 1 *M* potassium nitrate, (Un), and the values of the equilibrium constants, $K_1$, $K_2$ and $K_\alpha$. The $K_1$ value, 17.3, and the $K_2$ value, 0.36, of 3-hexyne agree well with the respective values, 19.1 and 0.22, obtained by the distribution method.[3] The $K_\alpha$ value of $13.1 \times 10^{-2}$ is sixteen times the $K_0$ value of $0.82 \times 10^{-2}$ obtained by the distribution method.[3] Here $K_0 = K_1/K_D$, where $K_D$ is the distribution constant of Un between aqueous potassium nitrate, 1 *M*, and carbon tetrachloride.[11]

TABLE VIII

DATA ON ALKYNES; SOLUBILITIES IN 1 *M* POTASSIUM NITRATE AND VALUES OF $K_1$, $K_2$ AND $K_\alpha$

| | Temp., °C. | (Un),[a] $M \times 10^4$ | $K_1$ | $K_2$ | $K_\alpha \times 10^3$ |
|---|---|---|---|---|---|
| 3-Hexyne | 25.0 | 75.8 | 17.3[b] | 0.36[b] | 131[b] |
| 3-Hexyne | 35.0 | 59.9 | 17.3 | .21 | 103 |
| 2-Methyl-3-hexyne | 25.0 | 18.8 | 20.5 | .28 | 38.6 |
| 2,2-Dimethyl-3-hexyne | 25.0 | 6.8 | 19.1 | .30 | 13.0 |
| 2,2,5-Trimethyl-3-hexyne | 25.0 | 2.26 | 23.4 | .34 | 5.29 |
| 2,2,5,5-Tetramethyl-3-hexyne | 25.0 | 1.49 | 12.8 | .53 | 1.91 |
| 2,2,5,5-Tetramethyl-3-hexyne | 35.0 | 0.78 | 18.6 | .33 | 1.45 |
| 2-Heptyne | 25.0 | 17.0 | 11.9 | .26 | 20.4 |

[a] Solubility in 1 *M* $KNO_3$. [b] By the distribution method,[3] $K_1 = 19.1$, $K_2 = 0.22$, and $K_0 = 8.2 \times 10^{-3}$.

In order to be able to compare $K_\alpha$ and $K_0$ they must be calculated with mole fractions instead of with concentrations and activity coefficients.[12] Since $K_\alpha$ and $K_0$ are constants for the reaction of silver ion with the alkyne in the organic phase the recalculation is made with mole fraction of alkyne in the organic phase. The value of $K_\alpha$ (solubility method) remains unchanged at $13.1 \times 10^{-2}$ because mole fraction of approximate unity replaces activity of approximate unity (eq. 14) of liquid 3-hexyne. The value of $K_0$ (distribution method) becomes $8.6 \times 10^{-2}$ because the molarity of Un in 0.2 *M* carbon tetrachloride, namely 0.2, is replaced by mole fraction, namely 0.019, and this increases the value of $K_0$ by a factor[13] of 10.5.

The discrepancy of about 50% between $K_0$ and $K_\alpha$ based on mole fractions is narrowed to about 40% by the factor 17.3/19.1 = 0.91, the ratio of $K_1$, solubility method, to $K_1$, distribution method. On going from more concentrated to more dilute systems of Un there is an increase in the ratio $\gamma_{Un_w}/\gamma_{Un_o}$ (w = water, o = organic). The rise in $K_D$ with a drop in the concentration of $(Un)_o$, as plotted in Fig. 2, ref. 3, shows that the activity ratio does so change. Therefore, a part of the drop of $K_\alpha$ to $K_0$ is due to a drop in this ratio, for concentration in the $K_\alpha$ measurement is the higher of the two. Since the two corresponding values of $K_1$ are also influenced by the activity ratio, it can be assumed that $K_\alpha$ and $K_0$ are affected similarly, that is, by the factor 0.91, above.

If $K_\alpha$ is kept constant at $13.1 \times 10^{-2}$, $K_0$ becomes $9.5 \times 10^{-2}$. An agreement within 40% is satisfactory in view of the influence of unknown factors, such as the limitations of eq. 13 and 14 and the different salting out effects of silver and potassium ions.

There is little difference in the values of $K_1$ and $K_2$ among the different alkynes (Table VIII), the former varying without any definite trend from 11.9 to 23.4, the latter, from 0.21 to 0.53. However, $K_\alpha$ becomes smaller every time a methyl group replaces an α-hydrogen atom. The factor is roughly $^1/_3$; four methyl substitutions into 3-hexyne cause a drop from $131 \times 10^{-3}$ to $2 \times 10^{-3}$. A similar influence of methyl substitution on argentation constants has been noted with alkenes.[11]

Calculation of $\Delta H$ for the argentation reactions of 3-hexyne and 2,2,5,5-tetramethyl-3-hexyne from the $K_1$ values at 25 and 35° gives the unrealistic values of 0.0 kcal. and 6.8 kcal., respectively, whereas from $K_\alpha$ the realistic values of −4.5 and −5.0 kcal., respectively, are obtained. These last $\Delta H$ values are comparable to those of alkenes[11] and indicate that $K_\alpha$ is a more satisfactory constant than $K_1$. $K_\alpha$ probably is close to a thermodynamic equilibrium constant and is here designated a quasi equilibrium constant. Reported values of

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(10) In this treatment, the activity coefficient of a pure liquid is taken as unity. It is assumed that positive Raoult's Law deviations occur in aqueous solutions and that the activity coefficient of the liquid in aqueous solution increases with dilution; J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 29 and Fig. 8, p. 32.

(11) S. Winstein and H. J. Lucas, This Journal, **60**, 836 (1938).

(12) The importance of mole fractions was pointed out to one of us by Professor Edwin Lassettre, of Ohio State University.

(13) This is because in the expression for $K_0$, as given in eq. 7 by F. R. Hepner, K. Trueblood and H. J. Lucas, This Journal, **74**, 1333 (1952), $(Un)_o$ is included in the denominator owing to its appearing in the denominator of eq. 5, the expression for $K_D$, from which $K_0$ is derived.

TABLE IX

ALKYNES STUDIED

| | Lit. | B.p., °C., cor. | Pres., mm. | $n^{25}_D$ | $d^{25}_4$ | $MR_D$ Calcd.$^a$ | $MR_D$ Calcd.$^b$ | $MR_D$ Obsd. | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Chlorine, % Calcd. | Chlorine, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3-Hexyne | | 80.9–81.0 | 748 | 1.4090 | 0.7185 | 27.90 | 28.25 | 28.26 | | | | | | |
| | 18 | 81.43 | 760 | 1.4112$^c$ | .7226$^c$ | | | 28.24$^d$ | | | | | | |
| 2-Methyl-3-hexyne | | 93.0–93.3 | 746 | 1.4089 | .7173 | 32.52 | 33.05 | 33.15 | | | | | | |
| | 18 | 95.2 | 760 | 1.4120$^c$ | .7249$^c$ | | | 33.01$^d$ | | | | | | |
| 2,2-Dimethyl-3-hexyne | | 100.2–101.0 | 746 | 1.4085 | .7188 | 37.14 | 37.86 | 37.86 | 87.19 | 87.31 | 12.81 | 12.91 | | |
| | | 56.6–57.5 | 155 | | | | | | | | | | | |
| 2,2,5-Trimethyl-3-hexyne | | 110.0–110.2$^e$ | 747 | 1.4084$^f$ | .7124$^f$ | 41.76 | 42.66 | 43.05 | 87.02 | 86.92 | 12.98 | 13.10 | | |
| 2,2,5,5-Tetramethyl-3-hexyne | | 110.9–111.5 | 746 | 1.4036 | .7074 | 46.38 | 47.47 | 47.74 | | | | | | |
| | 29 | 111.1 | 730 | 1.4026 | .7080 | | | 47.64 | | | | | | |
| 2-Heptyne | | 110.0–110.6 | 747 | 1.4194 | .7440 | 32.52 | 32.69 | 32.67 | | | | | | |
| | 34b | 110.5–111 | | 1.4192 | | | | | | | | | | |
| INTERMEDIATE COMPOUNDS | | | | | | | | | | | | | | |
| 2-Methyl-3-hexyne-2-ol | | 53.4–54.3 | 15 | 1.4389 | .8547 | 34.05 | 34.58 | 34.51 | 74.95 | 74.86 | 10.78 | 10.89 | | |
| 2-Chloro-2-methyl-3-hexyne | | 78.5 | 100 | 1.4479$^g$ | .9054 | 37.39 | 37.92 | 38.61 | | | | | 27.15 | 26.66 |
| 2,5-Dimethyl-3-hexyne-2-ol | | 60.0–60.2 | 15 | 1.4338 | .8357 | 38.67 | 39.38 | 39.39 | 76.14 | 76.14 | 11.18 | 11.24 | | |
| 2-Chloro-2,5-dimethyl-3-hexyne | | 81.5 | 100 | 1.4400 | .8778 | 42.01 | 42.73 | 43.43 | | | | | 24.51 | 24.74 |
| 2,5,5-Trimethyl-3-hexyne-2-ol | | 85.0$^h$ | 60 | 1.4282 | .8167 | 43.29 | 44.19 | 44.19 | | | | | | |
| | 29 | 85$^i$ | 60 | 1.4222$^j$ | .8064$^j$ | | | 44.20$^d$ | | | | | | |
| 2-Chloro-2,5,5-trimethyl-3-hexyne | | 80.5–81.1 | 100 | | .8558 | | | | | | | | | |
| | 29 | 81–81.5 | 100 | 1.4343$^c$ | .8585$^c$ | 46.63 | 47.53 | 48.11$^d$ | | | | | | |

$^a$ Ref. 16. $^b$ Ref. 17. $^c$ At 20°. $^d$ Calculation by H, C and L. $^e$ Thrice distilled. $^f$ Twice distilled. $^g$ Refractive index increases on standing. $^h$ F.p. 31.5–30.0°. $^i$ F.p., 32.0–31.8°. $^j$ At 38°.

$K_1$ calculated from solubility measurements[4,14,15] might prove to be of greater interest if recalculated to $K_\alpha$.

**Alkynes.**—Constants of alkynes investigated and of intermediate compounds in some of the syntheses are shown in Table IX. Molar refractions have been calculated with two sets of atomic refractions, *i.e.*, standard values[16] and values suggested by Hennion and Banigan[17] for alkynes. Values of $MR_D$ observed for alkynes agree well with those calculated by the method of H. and B. except that the value of 2,2,5-trimethyl-3-hexyne is high. Constants of 3-hexyne and 2-methyl-3-hexyne at 20° are those of Pomerantz, *et al.*[18]

Values of $MR_D$ observed for the three acetylenic alcohols agree quite well with $MR_D$ calculated by the method of H. and B., using the standard atomic polarization of O in OH, namely, 1.525. This would seem to indicate that no correction is needed for the proximity of the triple bond. However, $MR_D$ of chloro compounds in all cases is high. The refractive index of 2-chloro-2-methyl-3-hexyne was found to increase on standing. Such a change could account for the high values of $MR_D$. The change may be the result of isomerization[19] or polymerization. A part of the enhancement of $MR_D$ may be due to the influence of the triple bond on Cl, similar[17] to that on C.

## Preparation of Alkynes[20,21]

**3-Hexyne.**—Most of this was obtained from Farchan Research Laboratories. It was shaken five times with aqueous ferrous sulfate. The development of heat was an indication that peroxides were being removed.

**2-Methyl-3-hexyne.**—This was synthesized from isoamyl alcohol by the method of Gredy[22] through the steps: isoamylene,[23] isoamylene dibromide,[24] bromoisopentene,[22,25] 3-methyl-1-butyne[22,26] and 2-methyl-3-hexyne.[27]

**2,2-Dimethyl-3-hexyne.**—This was prepared from acetylene through the steps: 1-butyne,[28,29] 1-butynylmagnesium bromide, 2-methyl-3-hexyne-2-ol[30] (69%), 2-chloro-2-methyl-3-hexyne[19] (88%), and 2,2-dimethyl-3-hexyne (25%; over-all, 12–14%).

**2,2,5-Trimethyl-3-hexyne.**—3-Methyl-1-butyne by the procedure of Hennion and Banigan[29] was converted through

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(14) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **72**, 3113, 5034 (1950).

(15) R. E. Kofahl and H. J. Lucas, *ibid.*, **76**, 3931 (1954).

(16) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio, 1956, p. 1391.

(17) G. F. Hennion and T. F. Banigan, Jr., THIS JOURNAL, **68**, 1381 (1946).

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(20) The authors acknowledge their indebtedness to Mr. T. H. Applewhite for assistance.

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(22) B. Gredy, *Bull. soc. chim.*, **2**, 1951 (1933); A. Lewinsohn, *Perfumery Essent. Oil Rec.*, **14**, 291 (1923).

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(24) By the method of "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 171. The dibromide, b.p. 62.5–65.0° (15 mm.), was obtained in 86% yield.

(25) With potassium hydroxide in ethylene glycol at bath temperatures up to 230°, yield, essentially quantitative.

(26) L. S. Dedusenko, *Trudy Khim. Inst. Azerbaidzhan. Filiala Akad. Nauk*, **4**, No. 1, 15 (1940); *Khim. Referat. Zhur.*, **4**, No. 9, 53 (1941); *cf. C. A.*, **38**, 1466 (1944). Yield, last step 60%; over-all, 45%.

(27) By ethylation of the ethylmagnesium salt; S. D. Thorn, G. F. Hennion and J. A. Nieuwland, THIS JOURNAL, **58**, 796 (1936); yield: crude, 20%; pure, 13.5%.

(28) T. H. Vaughn, G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1937). Most of the ammonia was removed by countercurrent flow of water in a scrubbing tower of Raschig rings, and the remainder by bubbling through 25% sulfuric acid. Dissolved acetylene was removed by refluxing from a condenser cooled to −20°. Crude yields were 79 to 94%.

(29) Subsequent steps are analogous to those employed by G. F. Hennion and T. F. Banigan, Jr., for converting *t*-butylacetylene to di-*t*-butylacetylene; THIS JOURNAL, **68**, 1202 (1946).

(30) 3,5-Dinitrobenzoate, m.p. 97.7–98.4°. *Anal.* Calcd. for $C_{14}H_{14}O_6N_2$: N, 9.11. Found: N, 9.67.

the steps, 2-methyl-1-butynylmagnesium bromide, 2,5-dimethyl-3-hexyne-2-ol (86%) and 2-chloro-2,5-dimethyl-3-hexyne[19] (80%) to 2,2,5-trimethyl-3-hexyne (54%; over-all, 20%).

**2,2,5,5-Tetramethyl-3-hexyne.**—This was prepared from pinacol through the steps, pinacolone,[31] 2,2-dichloro-3,3-dimethylbutane, 3,3-dimethyl-1-butyne[32,33] (from pinacol, 26%), 3,3-dimethyl-1-butynylmagnesium bromide, 2,5,5-trimethyl-3-hexyne-2-ol (83%), 2-chloro-2,5,5-trimethyl-3-hexyne[19] (89%), and 2,2,5,5-tetramethyl-3-hexyne (35%; from 3,3-dimethyl-1-butyne, 35%).

**2-Heptyne.**—This was prepared by methylation of 1-hexyne.[28,34]

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[31] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 462.

[32] P. Ivitzky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

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

# The Separation of Hydrogen and Deuterium by the Reaction of Iron with Steam

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The separation of hydrogen and deuterium during the reaction of steam and iron was measured over the range of 118 to 340°. Separation factors from 1.4 to 3.2 were observed. The data were found to be correlated by the equation $\log \alpha = 273.1/T - 0.2039$ where $\alpha$ is the isotope separation factor and $T$ is the absolute temperature. Isotope separation factors obtained with cadmium agreed within experimental error with those obtained with iron. The separation of hydrogen and deuterium occurring during the reduction of magnetic iron oxide was measured and found to approach the equilibrium value. This is believed to have been caused by isotope exchange catalyzed by the freshly reduced iron.

The separation of hydrogen isotopes as a result of the reaction of steam and metals has been observed by previous workers. Horiuti and Polanyi[1] observed that when iron reacted with an excess of steam at 500° the hydrogen which was produced contained a lower concentration of deuterium than the steam. A separation factor of 1.6 can be calculated from their data. Bleakney and Gould[2] investigated the same reaction at 510° and obtained data from which a separation factor of 1.3 can be calculated. Henderson[3] measured the separation factor for this reaction using freshly reduced iron over the range 200 to 400°. He obtained values from 1.60 to 1.42 which were in fair agreement with the values of the equilibrium separation factor and concluded that the separation was caused by isotope exchange between the steam and the hydrogen.

Horiuti and Szabo[4] measured the separation of these isotopes in the reaction of water vapor and sodium and found a separation factor of 2.2. Henderson and Bernstein[5] measured this separation in the reaction of steam and zinc over the range of 295 to 415°. The separation factor was found to be 1.6 at 400° and had a temperature gradient of −0.0011 per degree.

Eyring and Cagle[6] have calculated the separation of hydrogen and deuterium in the electrolytic process by means of the absolute rate theory assuming that the breaking of the hydrogen–deuterium bond is the rate-controlling step. They obtained the equation

$$\alpha = \frac{\sinh (h\nu_{\mathrm{OH}}/2kT)}{\sinh (h\nu_{\mathrm{OD}}/2kT)} \qquad (1)$$

For ordinary temperatures this may be simplified to

$$\alpha = e^{708/T} \qquad (2)$$

According to Fricke, Walter and Loher[7] steam reacts with iron to produce hydrogen and magnetic iron oxide, $Fe_3O_4$, at temperatures below 540–560°. At higher temperatures ferrous oxide is formed. All of the work reported in this paper fell in the lower temperature range.

## Experimental

The steam-iron and steam-cadmium reactions were carried out in the apparatus shown in Fig. 1. The water flowed from the buret down into the reaction tube. It was volatilized in a heated trap at the top of the tube. From here it passed in the form of steam down through the heated bed of the powdered metal and down through a condenser and water collection flask. After this it passed through a glass wool packed cold trap which was immersed in a mixture of Dry Ice and acetone. This removed the last of the unreacted water from the hydrogen. The hydrogen then entered a tube containing copper oxide at a temperature in excess of 300° where it was oxidized quantitatively to water. This water was collected in a second cold trap.

The reaction tube was constructed of standard $^3/_4$-inch copper tubing and standard brass flare fittings. All joints other than the flare joints were silver soldered. The condenser and the tube from the buret to the reaction tube were also made of copper. The rest of the system with the exception of the Bourdon gages was made of Pyrex glass. All glass parts were connected with ground glass joints lubricated with Apiezon M stopcock grease.

The reaction tube was heated in a furnace which consisted of a Pyrex tube wound with nichrome wire and insulated with glass wool held in place by asbestos tape. The temperature was controlled by means of a variable transformer. The temperature was measured by means of a potentiometer and a copper–constantan thermocouple located in a copper thermocouple well which projected up inside the reaction tube into the bed of powdered metal.

The iron powder was Merck Iron by Hydrogen. It had a surface area of 1.63 square meters per gram as determined by nitrogen adsorption using the B.E.T. method. The iron had 90.4% of the reducing capacity of pure iron as determined by the amount of hydrogen evolved in the reaction of a known weight of iron with hydrochloric acid.

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