in accordance with observations on density and on the specific heat of the sorbed water. Data for other liquids are adduced for comparison.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# Action of Radon on Some Unsaturated Hydrocarbons. III. Vinylacetylene and Butadiene

BY G. B. HEISIG

The polymerization of acetylene by radon involves an abnormally large number of molecules reacting per ion pair formed, compared to the number of molecules of other unsaturated hydrocarbons condensing per ion pair formed ($-M/N$). An examination shows that the ratio of hydrogen and methane formed to the decrease of pressure of the hydrocarbon, $\Delta(H_2 + CH_4)/-\Delta HC$, is lowest for acetylene. Ethylene, on the other hand, has a relatively low value of the $-M/N$ and a comparatively high value for the $\Delta(H_2 + CH_4)/-\Delta HC$. The effect of alpha particles on a molecule containing both a double and a triple bond is, therefore, of interest. Both vinylacetylene ($H_2C{=}CHC{\equiv}CH$) and butadiene ($H_2C{=}CH{-}CH{=}CH_2$) are known to polymerize readily when heated,[1] and since therefore they might be expected to act readily under the influence of alpha particles, they were selected for this work.

The procedure and methods of calculation are similar to those used in a previous paper.[2]

The results of this investigation are summarized in Table I.

TABLE I

| | P drop of HC, mm. | % of P drop used in calcn. | $\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta HC}$ | $-M/N$ | Product |
|---|---|---|---|---|---|
| Vinylacetylene | 302.8 | 100.00 | 2.4 | 10.8 | White solid—yellow to orange |
| Butadiene I | 507.0 | 79.9 | 3.5 | 9.1 | Lt. colored, liquid becoming more viscous |
| Butadiene II | 413.4 | 88.6 | 3.1 | 8.9 | |

Nieuwland, Calcott, Downing and Carter[3] state that under pressure with or without the usual polymerization catalysts, vinylacetylene is readily polymerized by heat to form viscous drying oils and finally hard resinous solids. In the present work, however, no liquid apparently was formed. The first product noted in the polymerization by alpha particles was a

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(1) Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197–4202 (1931); Lebedev and Skrawonskaja, *Chem. Centr.*, I, 1440 (1912); *J. Russ. Phys.-Chem Soc.*, **43**, 1124–31 (1911); Lebedev. *Chem. Abstracts*, **9**, 799 (1915); *J. Russ. Phys.-Chem. Soc.*, **45**, 1373–88 (1913).

(2) Heisig, THIS JOURNAL, **53**, 3245–3263 (1931).

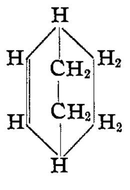
(3) Ref. 1, p. 4200.

white solid. As the action progressed the white product became cream colored and finally orange. The product could not be distinguished from cuprene by its appearance. Vinylacetylene is a polymer formed by the addition of a molecule of acetylene to a second molecule of acetylene, *i. e.*, the first step in the building up of cuprene has been carried out. Since the $-M/N$ of vinylacetylene is 10.8, the number of carbon atoms condensed per alpha particle is approximately the same as the number condensed per alpha particle in the case of acetylene, which has a $-M/N$ value of 18. In the first paper a method of predicting the $-M/N$ was given. The calculated value of $-M/N$ for vinylacetylene is given by the expression $(4.8 + 18.0)/2 = 11.4$. The experimental value of 10.8 agrees very well with the predicted value. The heat of formation from $H_2$ and diamond calculated from Fajan's atomic linkages is 727.6 kg.-cal. The $-M/N$ value obtained is that which would be expected from the heat of formation.[4]

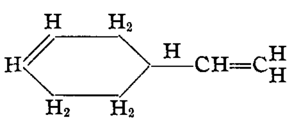
The evolution of hydrogen and methane is very low—only a little greater than that of acetylene. The values for the $-M/N$ and $\Delta(H_2 + CH_4 \times 100)/-\Delta HC$ of vinylacetylene lie on the general curve obtained by plotting $-M/N$ against $\Delta(H_2 + CH_4) \times 100/-\Delta HC$.

The thermal polymerization of butadiene has been studied recently by Vaughan[5] and found to be bimolecular between 326–436°. He obtains a break in the curve obtained by plotting $k$ (in mm.$^{-1}$ min.$^{-1}$) against fraction of butadiene converted when the pressure falls to approximately 60%. This, together with the fact that in several experiments the pressure dropped to one-half of the initial pressure, led him to state that a dimer was formed. He supports the evidence with determinations of the density, refractive index, and a molecular refractive index which he compares with a value calculated by assuming that the formula of the dimer is A.

A



B



Vaughan apparently overlooked the work of Lebedev and Skrawonskaja[1] in which butadiene was heated at 150° for ten days. Sufficient product was obtained to enable it to be distilled in a vapor of carbon dioxide. About 86% of dimer was obtained and 14% of polymers. The constitution of the carefully purified dimer was proved by hydrogenation, oxidation, ozonidation and found to be B. The boiling point was found to be 65–66° 100 mm., 129.5–130.5° 760 mm., the density $^{20}_{4}$ 0.8320 and refractive

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(4) Heisig, *J. Phys. Chem.*, **36**, 1000–1005 (1932).

(5) Vaughan, THIS JOURNAL, **54**, 3863–3876 (1932).

index 1.46529. Vaughan finds the density at 25° to be 0.867 and 0.848, and the refractive index using sodium light to be 1.469, 1.461 and 1.460. Hoffman and Tank, cited by Vaughan,[6] state that their work shows that the polymerization product has the formula given by Lebedev, but no experimental details are given.

The first product formed in the polymerization by alpha particles is a light colored mobile liquid, but this undergoes further polymerization to give a viscous product which later on becomes wax-like and light yellowish-brown in color. The evolution of hydrogen was only slightly greater than that obtained with vinylacetylene. The compound thus does not resemble other ethylene derivatives, but is more nearly like acetylene.

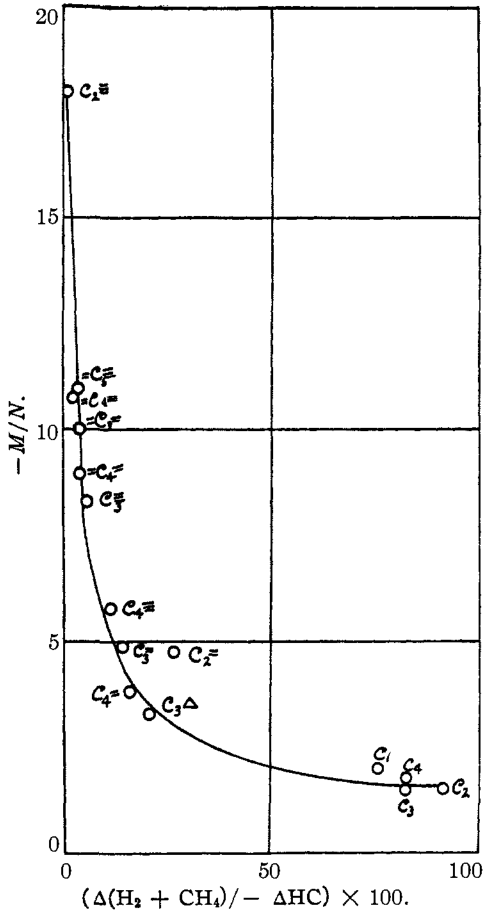

Fig. 1. $=C_4\equiv$ designates $H_2C{=}CHC{\equiv}CH$; $C_2\equiv$, $HC{\equiv}CH$; etc.

There seems to be an indication of a break in the constancy of the velocity constant when the pressure of hydrocarbon drops to 60–70% of the original pressure. This can hardly be due to the accumulation of dimer in the vapor phase since its vapor pressure must be low, for according to Lebedev and Skrawonskaja[1] the boiling point is 129.5–130.5°. Further, at −78.20° the vapor pressure of liquefied gas remaining in the reaction bulb was only slightly greater than that of pure butadiene. The predicted $-M/N$ for butadiene is $(4.8 + 4.8)/2 = 4.8$, which is far from the experimental value. This is the first case in which no semblance of an agreement was obtained between predicted and calculated values.

The heat of formation of butadiene from hydrogen and diamond calculated by the means of Fajan's atomic linkages, the heat of dissociation of hydrogen, and that of the sublimation of diamond, is −23.5, which

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[6] Hoffman and Tank, *Z. angew. Chem.*, **25**, 1465 (1912).

would lead one to expect a $-M/N$ value of about 12.0 instead of that actually observed.[4]

The $\Delta(H_2 + CH_4) \times 100/-\Delta HC$ and $-M/N$ fit very nicely into the general curve of these values, as can be seen from Fig. 1. Dimethylacetylene and butadiene are isomeric; however, the polymerization of butadiene more nearly resembles that of acetylene than does dimethylacetylene.

The vapor pressure and boiling point of butadiene have been determined by Vaughan.[5]

An equation was given to permit the calculation of the $\log_{10} P_{\text{mm.}}$ However, a comparison of his experimental and calculated pressures shows differences varying from +5.5 mm. at −38.5° and an observed pressure of 156.9 mm. to −39 mm. at +0.5° and an observed pressure of 862.6 mm. The calculated and experimental values are the same at −81.9° and −79.1°. The vapor pressure of a portion of the very carefully purified sample of butadiene was determined by the writer at a number of temperatures and the data were fitted to an equation

$$\log_{10} P_{\text{mm.}} = 1251.8/T + 7.543$$

The pressures at temperatures used by Vaughan calculated by this equation show smaller differences from his experimental values than when his equation was used except at pressures above 760 mm. The boiling point calculated by means of this expression is −4.6. The values of the boiling point given in the literature vary from +1 to −5°.

## Experimental

**Purification of Vinylacetylene.**—Vinylacetylene[7] was distilled from a 40% solution in xylene through a Davis column.[8]

With the exception of the first few cc. the sample distilled at +6°. The head of the column was kept at +3° to ensure a constant drip back into the distilling flask. This sample was then further purified by low temperature distillations until the vapor pressure was constant at 0°. The vapor pressure at the melting point of ice was the same irrespective of the temperature at which the sample was distilled, thus proving the absence of constant boiling mixtures. In all distillations only the middle fraction was kept. At 0° the vapor pressure was 619 mm. corr. to 0°. Nieuwland, Calcott, Downing and Carter[9] report the vapor pressure as 621 mm. at 0° The temperature of the mercury column is not given.

**Action with Radon.**—A snow white solid deposited on the lower fifth of the container within an hour after mixing with radon. The solid deposited gradually became cream colored and after a day and a half the solid next to the walls became orange. The appearance of the deposit was the same as that obtained in the polymerization of acetylene by radon.

In view of small amounts of hydrogen and methane no gas analysis was made. The data are given in Table II.

**Preparation of Butadiene.**—Butadiene was prepared by the action of zinc on 1,2,3,4-tetrabromobutane. The tetrabromobutane was obtained by warming the liquid which

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[7] Furnished through the courtesy of Dr. H. W. Elley of the Manufacturing Division of E. I. du Pont de Nemours and Co.

[8] Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61–64 (1929).

[9] Ref. 1, p. 4200.

TABLE II

POLYMERIZATION OF VINYLACETYLENE BY ALPHA RAYS FROM RADON

$x\mathrm{C_4H_4}$ gas $\longrightarrow (\mathrm{C_4H_4})_x$ solid. Temp., 25°; $is = 2.74$; $i = 1.21$; $s = 2.25$. Reaction sphere: vol., 29.548 cc.; radius, 1.918 cm.; $E$, 0.0303 curie

| Time Days | Time Hours | Radon, % | Pressure Total | Pressure $C_4H_4$ | Pressure $H_2 + CH_4$ | $\frac{\Delta(H_2 + CH_4)}{-\Delta HC} \times 100$ | Velocity constant $(k\mu/\lambda)'$ | $\frac{-M_{C_4H_4}}{N_{C_4H_4^+}}$ |
|---|---|---|---|---|---|---|---|---|
| | 0 | | 365.1 | 365.1 | 0.0 | 0.0 | | |
| | 1.0 | 99.253 | 360.4 | 360.4 | .0 | .0 | 57.0 | 8.8 |
| | 4.0 | 97.045 | 345.7 | 345.7 | .0 | .0 | 62.3 | 9.5 |
| | 7.05 | 94.920 | 332.8 | 332.8 | .0 | .0 | 59.0 | 9.1 |
| | 10.53 | 93.141 | 319.5 | 319.5 | .0 | .0 | 75.6 | 11.7 |
| | 12.87 | 90.798 | 309.0 | 309.0 | .0 | .0 | 70.6 | 11.0 |
| | 16.00 | 88.692 | 296.8 | 295.5 | 1.3 | 9.6 | 82.9 | 12.9 |
| 1 | 0.05 | 83.496 | 269.3 | 268.3 | 1.0 | −1.1 | 61.4 | 9.7 |
| 1 | 4.1 | 80.997 | 254.4 | 253.4 | 1.0 | 0.0 | 75.4 | 11.8 |
| 1 | 7.52 | 78.947 | 244.8 | 243.5 | 1.3 | 3.3 | 64.1 | 10.1 |
| 1 | 11.17 | 76.815 | 234.9 | 233.7 | 1.2 | 1.0 | 63.5 | 10.1 |
| 1 | 15.05 | 74.610 | 225.4 | 223.0 | 2.4 | 11.2 | 70.3 | 11.1 |
| 2 | 1.47 | 69.003 | 200.2 | 197.8 | 2.4 | 0.0 | 70.6 | 11.4 |
| 2 | 6.2 | 66.599 | 192.5 | 189.8 | 2.7 | 3.8 | 56.6 | 9.0 |
| 2 | 10.12 | 64.668 | 185.3 | 182.6 | 2.7 | 0.0 | 66.1 | 10.6 |
| 2 | 14.3 | 62.673 | 178.0 | 175.0 | 3.0 | 4.0 | 70.5 | 11.2 |
| 3 | 2.33 | 57.261 | 160.3 | 156.9 | 3.4 | 3.3 | 66.6 | 10.6 |
| 3 | 7.2 | 55.215 | 153.7 | 150.3 | 3.4 | 0.0 | 69.1 | 11.0 |
| 3 | 13.5 | 52.666 | 146.0 | 142.6 | 3.4 | 0.0 | 68.3 | 10.9 |
| 4 | 2.0 | 47.953 | 133.2 | 128.5 | 3.7 | 2.1 | 72.9 | 11.6 |
| 4 | 11.0 | 44.824 | 125.3 | 120.6 | 4.7 | 1.3 | 66.8 | 10.6 |
| 5 | 2.42 | 39.930 | 113.8 | 108.8 | 5.0 | 2.5 | 69.6 | 11.0 |
| 5 | 11.43 | 37.314 | 107.6 | 102.2 | 5.4 | 6.1 | 78.7 | 12.5 |
| 6 | 11.5 | 31.152 | 96.0 | 89.9 | 6.1 | 5.7 | 68.7 | 10.9 |
| 7 | 5.97 | 27.127 | 88.9 | 83.2 | 5.7 | −6.0 | 63.6 | 10.0 |
| 8 | 4.65 | 22.883 | 81.6 | 74.9 | 6.7 | 12.1 | 81.7 | 12.8 |
| 9 | 13.15 | 17.913 | 74.3 | 67.9 | 6.4 | −4.3 | 65.2 | 10.2 |
| 11 | 11.4 | 12.564 | 67.1 | 60.0 | 7.1 | 8.9 | 76.3 | 11.7 |
| 13 | 8.5 | 9.036 | 62.3 | 55.6 | 6.7 | −9.1 | 71.3 | 11.0 |
| | | | | | | Weighted average 2.4% | | 10.8 |

condenses in tanks used for the storage of Pintsch gas.[10] The gas which passed through a 6-foot Peters column and a Liebig condenser was led into a flask containing bromine. When nearly all the bromine had reacted, the flask was removed from the cool water in which it had been immersed to prevent overheating of the reaction mixture. When all the bromine had reacted, the mixture of bromides was cooled to 0° and the colorless precipitate of somewhat impure 1,2,3,4-tetrabromobutane was washed with petroleum ether and then crystallized from alcohol. The melting point of the crude tetrabromo derivative was 113–114° and that of the pure product was 116–116.5°.

**Removal of Bromine from 1,2,3,4-Tetrabromobutane.**—The tetrabromobutane (100 g.) was put in a large Soxhlet extraction apparatus, the siphon of which had been reduced to one-quarter of the usual height. The flask was equipped with an electric stirrer, and contained 300 cc. of alcohol and 200 g. of zinc dust. The effluent gas was

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(10) The method used was essentially that given by Birch [*Ind. Eng. Chem.*, **20**, 474 (1928)] for the preparation of butadiene from "Railway hydrocarbon." The yields were essentially the same as those reported by Birch.

bubbled through three wash bottles containing water, passed through calcium chloride, and then condensed using an alcohol–carbon dioxide bath.

**Purification of Butadiene.**—The butadiene was first fractionated using a Davis column. The first fraction (8 cc.) boiled from −6 to −5.5°. The second fraction (18 cc.) boiled from −5.5 to −5° and the third (28 cc.) boiled −5.0 to −4.5°. A residue of 3 cc. remained in the flask. On redistilling the second and third fractions the first 5 cc. was rejected. The remainder boiled at −5.0 to −4.7°. The barometric pressure was about 745 mm.

A portion of the sample was distilled between liquid air traps until the vapor pressure was constant at −7°. The molecular weight of a sample determined by the method of Maass and Russell[11] gave 55.84 under ideal conditions. Run I was made on a portion of this sample. In an effort to confirm its purity, 15 g. was reconverted to the tetrabromide by bubbling the hydrocarbon into 90 g. of bromine maintained at 0°. The tetrabromide was purified by crystallizing several times from alcohol. A yield of 62% of product melting between 116.5–117° was obtained. The tetrabromide was then converted to butadiene as before. The product was further carefully purified by washing in three bubbling towers, drying with calcium chloride and phosphorus pentoxide, and distilling six times between liquid air traps. At −24° the vapor pressure of the middle fraction after the last distillation was the same as that of the accumulated low and

TABLE III

POLYMERIZATION OF BUTADIENE BY ALPHA RAYS FROM RADON

$H_2C{=}CH{-}CH{=}CH_2 \longrightarrow$ liq. Temp., 25°; $s = 2.42$; $i = 1.28$; $is = 3.09$; $E = 0.02757$. Reaction sphere: vol., 30.785 cc.; diameter, 3.888 cm.

| Time | | | Pressure | | | | | |
|---|---|---|---|---|---|---|---|---|
| Days | Hours | Radon, % | Total | $C_4H_6$ | $H_2 + CH_2$ | $\frac{\Delta(H_2 + CH_4)}{-\Delta C_4H_6} \times 100$ | $(k\mu/\lambda)'$ | $\frac{-M_{C_4H_6}}{N_{C_4H_6^+}}$ |
| | | 100.000 | 707.2 | 720.6 | 0.0 | | | |
| | 2.98 | 97.760 | 692.5 | 692.5 | .0 | | 64.5 | 9.2 |
| | 5.47 | 95.981 | 670.5 | 670.2 | .3 | 1.4 | 66.7 | 8.9 |
| | 8.00 | 94.176 | 647.1 | 646.3 | .8 | 2.1 | 73.1 | 9.8 |
| | 12.00 | 91.393 | 615.1 | 612.1 | 3.0 | 6.4 | 70.8 | 9.4 |
| | 22.67 | 84.365 | 539.8 | 533.8 | 5.0 | 2.6 | 70.6 | 9.3 |
| 1 | 3.00 | 81.669 | 513.5 | 507.0 | 5.9 | 3.4 | 69.4 | 8.9 |
| 1 | 6.50 | 79.553 | 493.7 | 487.2 | 6.5 | 3.0 | 68.3 | 9.1 |
| 1 | 11.53 | 76.608 | 467.8 | 460.4 | 7.4 | 3.4 | 69.8 | 9.3 |
| 1 | 22.75 | 70.425 | 419.3 | 409.9 | 9.4 | 4.0 | 68.1 | 9.2 |
| 2 | 5.03 | 67.187 | 396.3 | 386.3 | 10.3 | 3.8 | 66.5 | 9.1 |
| 2 | 8.30 | 65.558 | 385.5 | 374.7 | 10.8 | 4.7 | 67.7 | 9.4 |
| 2 | 1.30 | 63.288 | 371.2 | 360.1 | 11.1 | 2.1 | 63.7 | 8.9 |
| 3 | 0.95 | 57.865 | 339.9 | 326.8 | 13.1 | 6.0 | 64.8 | 9.1 |
| 3 | 4.73 | 56.248 | 331.2 | 317.8 | 13.4 | 3.3 | 62.5 | 8.9 |
| 3 | 10.82 | 53.736 | 317.9 | 304.1 | 13.8 | 2.9 | 63.8 | 9.2 |
| 3 | 23.33 | 48.917 | 296.4 | 280.6 | 15.8 | 8.5 | 60.5 | 8.8 |
| 4 | 12.0 | 44.486 | 278.5 | 263.0 | 15.5 | −1.7 | 53.0 | 7.7 |
| 4 | 23.4 | 40.842 | 264.2 | 247.7 | 16.5 | 6.5 | 59.8 | 8.8 |
| 5 | 8.2 | 38.232 | 254.8 | 238.0 | 16.8 | 3.0 | 55.4 | 8.9 |
| 6 | 22.9 | 28.603 | 225.4 | 206.5 | 18.9 | 9.8 | 53.5 | 7.9 |
| 9 | 1.0 | 19.644 | 200.7 | 180.5 | 20.2 | 5.0 | 53.5 | 8.0 |
| | | | | | | Weighted average 3.5 | | 9.1 |

Percentage of pressure drop used in calculations 79.9

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[11] Maass and Russell, THIS JOURNAL, **40**, 1847–1852 (1918).

high boiling portions. The vapor pressure of the middle fraction was the same as that of the butadiene before being converted to the tetrabromide. Run II was made using a portion of this sample.

**Action with Radon.**—A fog was formed within a few minutes after mixing the hydrocarbon with the radon. Within an hour small droplets formed on the side of the container and a small pool of a light transparent liquid settled on the bottom of the sphere. The viscosity increased as the exposure to radon progressed, but no solid was obtained. The partial pressure of the hydrogen and methane formed was obtained by measuring the pressure at the temperature of liquid oxygen. The data are given in Tables III and IV.

TABLE IV

POLYMERIZATION OF BUTADIENE BY ALPHA RAYS FROM RADON

$H_2C{=}CH{-}CH{=}CH_2 \longrightarrow$ liq. Temp., 25°; $s = 2.42$; $i = 1.28$; $is = 3.09$; $E_0 =$ 0.03542 curie. Reaction sphere: vol., 32.655 cc.; diameter, 3.966 cm.

| Time | | Radon, % | Pressure | | | $\frac{\Delta(H_2 + CH_4)}{-\Delta C_4H_6} \times 100$ | $(k\mu/\lambda)'$ | $\frac{-M_{C_4H_6}}{N_{C_4H_6^+}}$ |
|---|---|---|---|---|---|---|---|---|
| Days | Hours | | Total | $C_4H_6$ | $H_2 + CH_4$ | | | |
| | 0.0 | 100.00 | 702.5 | 702.5 | 0.0 | 0.0 | | |
| | 5.2 | 96.175 | 642.8 | 642.8 | 0.0 | 0.0 | 65.6 | 9.1 |
| | 8.18 | 94.049 | 612.2 | 611.2 | 1.0 | 3.2 | 67.0 | 9.2 |
| | 11.33 | 91.852 | 582.1 | 580.4 | 1.7 | 2.3 | 66.6 | 9.1 |
| | 20.22 | 85.930 | 509.5 | 505.2 | 4.3 | 3.5 | 66.1 | 9.1 |
| | 23.18 | 84.043 | 488.4 | 482.4 | 6.0 | 7.5 | 69.2 | 9.5 |
| 1 | 2.88 | 81.743 | 464.2 | 457.5 | 6.7 | 2.7 | 65.0 | 9.0 |
| 1 | 6.20 | 79.733 | 444.1 | 437.8 | 6.3 | −2.0 | 61.8 | 8.6 |
| 1 | 10.25 | 77.347 | 420.7 | 413.0 | 7.7 | 5.4 | 68.9 | 9.7 |
| 1 | 20.35 | 71.704 | 374.5 | 364.1 | 10.4 | 5.4 | 63.1 | 9.0 |
| 2 | 0.20 | 69.664 | 360.0 | 348.6 | 11.4 | 6.4 | 60.2 | 8.8 |
| 2 | 4.83 | 67.288 | 343.4 | 331.4 | 12.0 | 3.5 | 59.9 | 8.8 |
| 2 | 10.28 | 64.591 | 325.7 | 313.3 | 12.4 | 2.2 | 58.8 | 8.6 |
| 2 | 20.35 | 59.894 | 298.8 | 284.7 | 14.1 | 6.0 | 57.6 | 8.6 |
| 3 | 0.57 | 58.029 | 289.1 | 274.4 | 14.7 | 5.8 | 55.8 | 8.4 |
| 3 | 5.33 | 55.993 | 279.3 | 264.3 | 15.0 | 3.0 | 52.0 | 7.9 |
| 3 | 10.88 | 53.711 | 268.5 | 252.3 | 16.2 | 10.0 | 57.5 | 7.8 |
| 3 | 20.4 | 50.010 | 252.4 | 234.7 | 17.7 | 8.7 | 55.2 | 9.2 |
| 4 | 1.28 | 48.213 | 245.4 | 227.2 | 18.2 | 6.7 | 51.0 | 7.9 |
| 4 | 6.18 | 46.471 | 238.3 | 219.4 | 18.9 | 9.0 | 56.7 | 8.9 |
| | | | | | Weighted average | 3.1 | | 8.9 |

Percentage of pressure drop used in calculations, 88.6

**Vapor Pressure of Butadiene.**—The vapor pressure of butadiene was determined by measuring the height of the column of mercury sustained in a closed manometer. The sample was immersed in a low temperature thermostat to be described by the writer elsewhere and maintained at the various temperatures until equilibrium had been established. The variation in the temperature was not more than ±0.01°. At least four different readings of the pressure were made using an accurate cathetometer. The heights of the columns of mercury are reduced to 0°. The temperatures were measured by means of an accurate mercury thermometer and below the freezing point of mercury by means of a platinum resistance thermometer previously described.[12] The extreme deviation in a series of pressure measurements at any temperature was 0.5 mm. The data are given in Table V.

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[12] Livingston and Heisig, THIS JOURNAL, **52**, 2409–2410 (1930).

TABLE V

VAPOR PRESSURE OF BUTADIENE

| $T_c$ | $T_{abs.}$ | $P_{exp.}$ | $P_{calcd.}$ | Diff. in mm. |
|---|---|---|---|---|
| −75.5 | 197.6 | 14.6 | 16.1 | −1.5 |
| 63.4 | 209.7 | 35.4 | 37.4 | −2.0 |
| 51.6 | 221.5 | 77.1 | 77.8 | −0.7 |
| 39.4 | 233.7 | 153.4 | 153.7 | −0.3 |
| 38.6 | 234.5 | 161.7 | 160.5 | +1.2 |
| 32.7 | 240.4 | 219.0 | 216.6 | +2.4 |
| 26.1 | 247.0 | 301.4 | 298.3 | +3.1 |
| 19.9 | 253.1 | 400.5 | 397.8 | +2.7 |
| 15.5 | 257.6 | 484.2 | 482.6 | +1.6 |
| 10.4 | 262.7 | 599.9 | 599.1 | +0.8 |
| 5.6 | 267.5 | 729.7 | 731.0 | −1.3 |
| − 1.5 | 271.6 | 854.0 | 859.1 | −4.9 |

## Summary

The number of molecules of vinylacetylene and butadiene condensing per alpha particle from radon is found to be 10.8 and 9, respectively. The $(\Delta(H_2 + CH_4))/-\Delta HC$ for these hydrocarbons is very low—practically the same as acetylene.

The predicted value of the $-M/N$ value for vinylacetylene agrees with the experimental value but there is no correspondence in the case of butadiene.

The vapor pressure of butadiene has been determined at a number of temperatures and the data have been fitted to a linear equation.

The boiling point is found to be −4.6°.

MINNEAPOLIS, MINNESOTA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

# The Solubility of Silver Oxide in Water, in Alkali and in Alkaline Salt Solutions. The Amphoteric Character of Silver Hydroxide

BY HERRICK L. JOHNSTON, FRANTISEK CUTA[1] AND ALFRED B. GARRETT

This investigation had its inception in the effort to throw possible light on the uncertain behavior of the silver–silver oxide electrode in contact with alkali. Buehrer,[2] in an extensive investigation of cells which contained this electrode, found that the cells did not possess satisfactory reproducibility. Among the causes which may have contributed to this, Buehrer suggested the extremely low solubility of the oxide in contact with alkali. Some support was given to this suggestion by the fact that, with barium hydroxide as electrolyte, the measurements were somewhat more

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(2) Buehrer, Ph.D. Thesis, The University of California, 1921.