obtained. Analysis of the product was achieved by gravimetric determination of the iodoform produced by treatment with iodine and potassium hydroxide.

Hydration of one-third mole (32 g.) of 2-heptyne in 80% methanol at 65° gave 26 g. of distilled ketones, b. p. 70–70.5° (50 mm.), $n^{25}D$ 1.4067, d^{25} 0.8128. Six analyses showed a 2-heptanone content of 47 ± 2%. A similar experiment with 70% acetic acid yielded 24 g. of ketones, $n^{25}D$ 1.4067, d^{25} 0.8123, containing 48% 2-heptanone.

It is well known that terminal acetylenes, $R-C\equiv CH$, produce methyl ketones, $R-CO-CH_3$, *exclusively*. Hence the formation of the two possible products (from both 2-pentyne[5] and 2-heptyne) *in substantially equal amounts* is noteworthy. This implies that the direction of electromeric polarization of the triple bond in alkyl- and dialkylacetylenes is not seriously affected by hyperconjugation or other factors ascribable to simple alkyl groups.

Experimental

Preparation of 2-Heptyne.—Acetylene was converted to the acetylide with 69 g. of sodium in 2.5 l. of liquid ammonia and the solution treated, in turn, with 3 moles of butyl bromide, 3 moles of sodamide[7] and an excess (200 ml.) of liquid methyl bromide. The product was recovered in the usual way[8]; yield 140 g. (48%), b. p. 110.5–111°, $n^{25}D$ 1.4192 (lit.[9] b. p. 111.8°, $n^{20}D$ 1.4237).

Hydrations.—2-Heptyne (0.33 mole) was converted to the heptanones in 100 ml. of 80% methanol at 65° and in 50 ml. of 70% acetic acid at 105°, as previously described.[6] The catalyst in each case consisted of 1 g. of mercuric oxide and 1 ml. of concentrated sulfuric acid.

Analytical Method.—Carefully purified 2-heptanone and 3-heptanone, separately and together, were weighed into a 100-ml. volumetric flask so that the total sample was about 2 g. and diluted to the mark with reagent grade methanol. After thorough mixing, 2.0 ml. of the solution was transferred to a 125 ml. glass-stoppered erlenmeyer flask. Ten ml. of methanol, 10 ml. of 2 *N* potassium hydroxide and 5 ml. of 2 *N* iodine solution were then admitted, the mixture shaken for thirty seconds, and an additional 2 ml. of potassium hydroxide added. Ten ml. of 1 *N* sodium thiosulfate was then added, the iodoform extracted with 10 ml. of ether and the ether extract in turn washed with 10 ml. of water. The ethereal solution was evaporated to dryness on a 10-cm. weighed watch glass. The iodoform was carefully washed with 5 ml. of distilled water, the washings removed with a fine capillary pipet. The iodoform, now in the form of clean yellow crystals, was air-dried and weighed. Blank determinations were run and corrections made in the usual way. Typical results are given in Table I. While the yields of iodoform did not correspond to the theoretical amounts, a plot of yield *vs.* composition (columns 1 and 4) yielded a straight line. This empirical relationship was employed for the analytical work, following the procedure described.

TABLE I

YIELDS OF IODOFORM FROM MIXTURES OF 2- AND 3-HEPTANONES

2-Heptanone content, %	Sample, mg.[a]	Iodoform, mg.[b]	Ratio, iodof./sample
0	42.5	10.3	0.24
20.6	43.1	26.2	0.61
37.6	42.9	42.9	1.00
41.6	73.1	83.2	1.14
48.2	43.5	52.5	1.21
50.9	42.1	53.7	1.28
60.8	44.9	67.3	1.50
77.3	46.5	83.9	1.80
87.0	41.0	81.7	1.99
100.0	41.9	93.2	2.22

[a] Two ml. of methanol solution containing about 2 g. per 100 ml. [b] Average of two or three determinations.

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[9] Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Co., New York, N. Y., 1939, Vol. I, p. 369.

Thermal Properties of the Compound BPO_4

BY F. A. HUMMEL AND T. A. KUPINSKI

The purpose of this note is to report some data on the thermal stability and expansion of the compound boron phosphate. The binary compound is unusual since it is far more refractory than either B_2O_3 or P_2O_5, it is related to the high cristobalite form of silica crystallographically, and it shows reluctance to form a glass although its components comprise two of the most common glass-forming oxides known to ceramists.

G. E. R. Schulze[1] reported the X-ray structure analysis and some of the optical properties of boron phosphate. He apparently was the first to recognize the structure as a distorted high cristobalite type, and observed the crystal in the form of tetragonal bipyramids with indices 1.595 and 1.601. Both P^{+5} and B^{+3} were shown tetrahedrally coördinated with oxygen and the density calculated from X-ray data was 2.802.

The boron phosphate was obtained from the Victor Chemical Works and contained 31.0% B_2O_3, 64.4% P_2O_5, and 3.0% ignition loss; the ignited product was then 32.5% B_2O_3 and 67.5% P_2O_5. An X-ray pattern of the material as received showed it to be the compound boron phosphate.

Batches of 0.2–0.5 g. of the material were heated in platinum envelopes by the conventional quench technique to determine thermal stability. The quenching procedure, which has been described in detail elsewhere,[2] consists of enclosing small charges of material to be studied in a thin platinum envelope, inserting these charges in the hot zone of a platinum-wound furnace, holding for a desired length of time at a particular temperature to attain equilibrium in the charge, and then quickly dropping the envelope and charge into a quenching medium such as carbon tetrachloride or mercury in order to freeze in the high temperature equilibrium state. The accuracy of temperature measurement during the experiments was ±4°.

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[1] G. E. R. Schulze, *Z. physik. Chem.*, **B24**, 215 (1934).

[2] G. W. Morey, *J. Soc. Glass Technol.*, **20** [80], 245 (1936); *Cer. Abs.*, **17** [1], 39 (1938).

Phase identification was done principally by means of X-ray patterns taken on a Norelco recording spectrometer using CuKα radiation (λ = 1.537 kX.). The following data of Schulze[1] were used as a standard:

d/n	Rel. int.	Indices
3.63	130	(101)
2.25	90	(112)
1.86	48	(211)
1.45	52	(114) or (213)

The quench results are most easily summarized in the form of tables. Table I gives the heat treatments and phase analyses of quenched samples of boron phosphate, while Table II gives the X-ray patterns of these same samples.

TABLE I

RESULTS OF QUENCH DATA ON BPO_4

Heat treatment Temp., °C.	Time, hr.	Phases present
Recd. from Victor	...	BPO_4
1005	7.5	BPO_4
1250	1	PBO_4
1355	1	BPO_4
1403	1	BPO_4
1452	5 min.	Sample partly vaporized, remainder BPO_4
1462	1	Sample completely vaporized

TABLE II

X-RAY DATA ON BPO_4

BPO_4 (as recd.)		BPO_4 (1005°, 1250°, 1355°, 1403°)		BPO_4 (1452°)	
d/n	Rel. int.	d/n	Rel. int.	d/n	Rel. int.
3.63	1.00	3.61	1.00	3.61	1.00
3.08	0.04	3.05	0.19	..	..
2.87	.03	2.88	.08	..	..
2.24	.32	2.25	.54	2.24	0.42
1.86	.08	1.86	.36	1.85	.18
1.81	.03	1.81	.25	1.81	.12
1.46	.06	1.45	.45	1.45	.18
1.31	.02	1.31	.20	..	..
1.19	.02	1.21	.08	..	..

From the quench data obtained, it is likely that BPO_4 vaporizes as such and does not decompose into the constituent oxides, B_2O_3 and P_2O_5, although there is no direct proof that this is the case. Phosphorus pentoxide has a very high vapor pressure at the temperatures used in the experiment,[3] and while anhydrous B_2O_3 does not vaporize as freely as P_2O_5 at these temperatures, in the presence of water vapor the hydrated forms vaporize readily.[4]

Using microscopic and X-ray methods on the partly vaporized sample quenched from 1452°, no free P_2O_5, B_2O_3 or H_3BO_3 was detected, indicating that the compound probably does not decompose into the component oxides. Further work would be necessary to conclusively prove this point.

Thermal expansion data were obtained on four-inch samples of sintered boron phosphate using a fused silica type dilatometer with dial gage reading to 0.0001″. The compound was sintered at 1130° for 1.5 hr. and at 1260° for 1 hr., and gave practically identical reversible thermal expansion curves after each heat treatment. The calculated coefficient of expansion in the range 25–1000° was 90×10^{-7} cm./cm./°C.

Conclusions.—Boron phosphate begins to vaporize in the neighborhood of 1450°, and will disappear completely at 1462° if held for one hour at this temperature. The coefficient of thermal expansion of BPO_4 sintered at 1260° is 90×10^{-7} cm./cm./°C. in the range 25–1000°.

Acknowledgment.—The authors are grateful to Mr. Howard Adler, Chief Chemist of the Victor Chemical Works, for supplying data on the compound BPO_4 and for the sample of BPO_4 used in the experimental work.

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Chemical Effects of the Cu^{63} (γ,n) Cu^{62} Reaction with Copper Salicylaldehyde-*o*-phenylenediimine

BY O. G. HOLMES AND K. J. MCCALLUM

Duffield and Calvin[1] have shown that when copper salicylaldehyde-*o*-phenylenediimine is bombarded with thermal neutrons, the Szilard–Chalmers effect permits a concentration of Cu^{64} with an inorganic carrier. In their work, the chelate complex was bombarded both in the solid state and in pyridine solution, and the resulting distributions of Cu^{64} between the complex and inorganic carrier were reported.

We have done similar experiments with the Cu^{63} (γ,n)Cu^{62} reaction on the same complex. The material was irradiated with γ-rays of 18 ± 0.5 Mev. peak energy in the betatron[2] at the University of Saskatchewan. The maximum recoil energy imparted to the Cu^{62} nucleus is approximately 0.1 Mev., since a threshold γ-ray energy of 11 Mev. has been reported for this reaction.[3]

Irradiation of the chelate complex was carried out with the material in the solid form and also in solution in pyridine. Carrier copper was separated from the complex,[1] precipitated as CuS, and the activities of the CuS precipitate and the residual complex were determined using a Geiger counter and scale-of-64.

The percentage of the total activity remaining with the chelate complex, or the retention, as found from duplicate experiments, is reported in Table I for irradiations under different conditions. The values for the retentions are corrected for self-absorption[4,5] and for decay of the 10.5-

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