# Boiling Points and Boiling Point Numbers of Organoboron Compounds

HERBERT H. ANDERSON
Chemistry Department, Drexel Institute of Technology, Philadelphia, Pa.

**Application of the Kinney equation to normal boiling points of boron containing compounds, furnishes the new boiling point numbers for boron and for a hydrogen atom attached to boron. New boiling point numbers of 37 configurations of alkyl groups, alkoxy groups or halogens have been obtained, and the calculated and observed boiling points of 5 boron hydrides and 51 organoboron compounds show an average error of 2.3°.**

APPLICATION of the Kinney equation (*2, 17, 20*)

$$\text{B.p. in } ^\circ\text{C.} = 230.14\ (\text{total boiling point number})^{1/3} - 543 \qquad (1)$$

to the normal boiling points of $B_2H_6$, $B_4H_{10}$, $B_5H_9$, $B_5H_{11}$ and $B_{10}H_{14}$ furnishes the new boiling point number (b.p.n.) 3.40 for boron and the new b.p.n. 0.104 for a hydrogen atom attached to boron.

Calculations following standard procedures furnish values of b.p.n. for the various configurations of alkyl groups, alkoxy groups or halogens; this involves a least squares fit to a standard linear regression model with the use of an IBM 1620 computer. Programming for the computer requires preliminary adjustment through substraction of the portion of the total b.p.n. due to boron and due to any hydrogen attached to boron. It is necessary to assume simultaneous variation of the individual b.p.n. for the alkyl groups, alkoxy groups and halogen atoms in the compounds. The computer then obtains the best fit between the 19 configurations and the 38 adjusted total b.p.n. for the compounds. This procedure does not include 3 compounds of the $R_2R'B$ type or 7 compounds with the vinyl group attached to boron. Although some compounds of the type are available, this method of calculation does not fit compounds such as $B_2Cl_4$ or $(CH_3O)_4B_2$. Extrapolated normal boiling points of 82.2° (*13*) and 108° (*9*) for $B_6H_{10}$ are in poor agreement both with each other and with the calculated b.p. of 96.4°; thus this boron hydride does not appear in Table II.

A previous method for $(C_2H_5O)_4Si$ and related compounds (*36*) uses the b.p.n. of 1.1 per oxygen atom, 0.7 per hydrogen atom, 0.8 per carbon atom and 4.2 per silicon atom; this method appears inapplicable to organoboron compounds.

Table I lists 37 configurations of alkyl group, alkoxy group or halogen. B.p.n. for alkyl, alkoxy or halogen not requiring use of the computer are available in 13 unsubstituted compounds with the following normal boiling points in °C: $(CH_3)_3B$, −21.8 (*19*), $(C_2H_3)_3B$, 85.7 (*14*), $(C_2H_5)_3B$, 95.0 (*26*), $(n\text{—}C_3H_7)_3B$, 159.6 (*26*), $(iso\text{—}C_3H_7)_3B$, 150 (*3*), $(n\text{—}C_4H_9)_3B$, 210 (*6*), $(iso\text{—}C_4H_9)_3B$, 189 (*16*), $(CH_3O)_3B$, 68.7 (*35*), $(C_2H_5O)_3B$, 117.4 (*35*), $BF_3$, −99, $BCl_3$, 12.5, $BBr_3$, 91.2 and $BI_3$, 209.5 (*1*).

In Table II there is information on 56 boron compounds, including total b.p.n. calculated and found, normal boiling points calculated and found, the errors in calculation of boiling point (calcd. b.p. − observed b.p.), and the references. Only the compound $n\text{—}C_4H_9(C_2H_5O)BCl$ presents complications in configurations. This compound apparently contains one $n\text{—}C_4H_9$ group of the RB= type; the best further assignment is of one $C_2H_5O$ group of the $(RO)_2B\text{—}$ type and of one chlorine atom of the $-BX_2$ type, for a calculated total b.p.n. of 25.94. The alternate assignment of the ROB= and the =BCl types furnishes a total b.p.n. of 27.05—too high—and a calculated b.p. of 147.9°—too high.

## DISCUSSION OF RESULTS

Calculated boiling points of 56 compounds in Table II involve an average error of 2.3°, with the greatest average error, 4.0°, in the 13 methylboron compounds. There is difficulty in obtaining accurate boiling points for the organoboron compounds, since 19 of the compounds in Table II have boiling points obtained by extrapolation to 760 mm. pressure. Errors of more than 5.7° in calculations of normal b.p. occur only with 4 compounds: $(CH_3)_2BH\text{-}BH_2CH_3$, at −8.3°, $CH_3BF_2$, at −11.2°, $CH_3BCl_2$, at 7.5°, and $(C_2H_3)_2BF$, at 7.3°.

In the boron hydrides the numerical contribution of the individual boron atom, b.p.n. 3.40, is relatively dominant over that of the b.p.n. of the hydrogen atom, b.p.n. 0.104. Only in the germanium hydrides—b.p.n. (*2*) of Ge, 7.413 and b.p.n. of H, 0.085—does the numerical contribution of the hydrogen have less relative importance. In the hydrocarbons (*17*) —b.p.n of C, 0.8, and b.p.n. of H, 1.0—hydrogen reaches its greatest relative importance. In the

Table I. Boiling Point Numbers of Atoms and Groups
[B, 3.40; H (to B), 0.104]

Configurations of Alkyl Groups

| Group | $R_3B^a$ | $R_2B\text{—}$ | $RB=$ |
|---|---|---|---|
| $CH_3$ | 2.74 | 2.90 | 3.11 |
| $C_2H_5$ | 5.97 | 5.91 | 5.85 |
| $n\text{—}C_3H_7$ | 8.35 | 8.47 | 8.25 |
| $iso\text{—}C_3H_7$ | 7.97 | . . . | 7.69 |
| $n\text{—}C_4H_9$ | 10.54 | 10.95 | 10.93 |
| $iso\text{—}C_4H_9$ | 9.56 | $10.09^b$ | $10.08^b$ |
| $CH_2{=}CH$ | 5.66 | $5.45^a$ | $5.23^a$ |

Configurations of Alkoxy Groups

| Group | $(RO)_3B^a$ | $(RO)_2B\text{—}$ | $ROB=$ |
|---|---|---|---|
| $CH_3O$ | 5.13 | 5.65 | 5.95 |
| $C_2H_5O$ | 6.74 | 7.60 | $8.22^b$ |

Configurations of Halogen

| Halogen | $BX_3^a$ | $\text{—}BX_2$ | $=BX$ |
|---|---|---|---|
| F | 1.26 | 0.99 | 1.22 |
| Cl | 3.55 | 4.01 | 4.50 |
| Br | 5.84 | 5.97 | 6.36 |
| I | 10.52 | . . . | 9.74 |

[a] Values obtained without any use of the computer.
[b] Three configurations of alkyl or alkoxy occur only once each in these compounds and do not require direct use of the computer.

Table II. Calculations of Boiling Point

| Compound | Total B.p.n. | | B.p., ° C. | | | Ref. |
|---|---|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found | Error, ° C. | |
| $B_2H_6$ | 7.42 | 7.50 | −93.9 | −92.5 | −1.4 | *(32)* |
| $B_4H_{10}$ | 14.64 | 14.48 | 20.0 | 18 | 2.0 | *(32)* |
| $B_5H_9$ | 17.94 | 17.99 | 59.4 | 60.0 | −0.6 | *(30)* |
| $B_5H_{11}$ | 18.14 | 18.26 | 61.7 | 63 | −1.3 | *(10)* |
| $B_{10}H_{14}$ | 35.46 | 35.45 | 213.1 | 213[a] | 0.1 | *(33)* |
| $(CH_3)_2BHBH(CH_3)_2$ | 18.61 | 18.77 | 66.9 | 68.6 | −1.7 | *(29)* |
| $(CH_3)_2BHBH_3$ | 13.02 | 12.95 | −1.6 | −2.6 | 1.0 | *(29)* |
| $(CH_3)_2BHBH_2CH_3$ | 16.02 | 16.72 | 37.2 | 45.5 | −8.3 | *(29)* |
| $(CH_3)_2BF$ | 10.42 | 10.30 | −40.4 | −42.2 | 1.8 | *(8)* |
| $(CH_3)_2BCl$ | 13.70 | 13.49 | 7.7 | 4.9[a] | 2.8 | *(12, 18)* |
| $(CH_3)_2BBr$ | 15.56 | 15.54 | 31.6 | 31.3[a] | 0.3 | *(12, 18)* |
| $(CH_3)_2BI$ | 18.94 | 18.79 | 70.5 | 68.8[a] | 1.7 | *(12, 18)* |
| $(CH_3)_2BOCH_3$ | 15.15 | 14.72 | 26.5 | 21[a] | 5.5 | *(11)* |
| $CH_3BH_2BH_2CH_3$ | 13.44 | 13.49 | 4.2 | 4.9[a] | −0.7 | *(27)* |
| $CH_3BF_2$ | 8.49 | 9.11 | −73.5 | −62.3 | −11.2 | *(8)* |
| $CH_3BCl_2$ | 14.53 | 13.96 | 18.6 | 11.1[a] | 7.5 | *(18)* |
| $CH_3BBr_2$ | 18.45 | 17.99 | 65.1 | 60[a] | 5.1 | *(18)* |
| $CH_3B(OCH_3)_2$ | 17.81 | 17.41 | 58.0 | 53.5 | 4.5 | *(34)* |
| $(C_2H_5)_2BHBH_3$ | 18.94 | 18.63 | 70.5 | 67.1[a] | 3.4 | *(28)* |
| $(C_2H_5)_2BF$ | 16.44 | 16.56 | 42.2 | 43.6[a] | −1.4 | *(4)* |
| $(C_2H_5)_2BCl$ | 19.72 | 19.69 | 78.8 | 78.5[a] | 0.3 | *(12, 18)* |
| $(C_2H_5)_2BBr$ | 21.58 | 21.91 | 97.7 | 101 | −3.3 | *(12, 18)* |
| $C_2H_5BF_2$ | 11.23 | 11.38 | −27.6 | −25.4[a] | −2.2 | *(4)* |
| $C_2H_5BCl_2$ | 17.27 | 17.16 | 51.9 | 50.6 | 1.3 | *(21)* |
| $C_2H_5BBr_2$ | 21.19 | 21.16 | 93.9 | 93.6 | 0.3 | *(25)* |
| $C_2H_5B(OC_2H_5)_2$ | 24.45 | 24.45 | 125.0 | 125 | 0.0 | *(19)* |
| $(n\text{—}C_3H_7)_2BCl$ | 24.84 | 24.67 | 128.5 | 127 | 1.5 | *(12)* |
| $(n\text{—}C_3H_7)_2BBr$ | 26.70 | 26.72 | 144.9 | 145 | −0.1 | *(12)* |
| $(n\text{—}C_3H_7)_2BI$ | 30.08 | 30.24 | 172.8 | 174 | −1.2 | *(12)* |
| $n\text{—}C_3H_7BF_2$ | 13.63 | 13.21 | 6.8 | 1.1 | 5.7 | *(7)* |
| $n\text{—}C_3H_7BCl_2$ | 19.67 | 19.73 | 78.3 | 78.9 | −0.6 | *(22)* |
| $n\text{—}C_3H_7BBr_2$ | 23.59 | 23.96 | 117.1 | 120.5 | −3.4 | *(25)* |
| $\mathit{iso}\text{—}C_3H_7BCl_2$ | 19.11 | 19.03 | 72.3 | 71.4 | 0.9 | *(21)* |
| $\mathit{iso}\text{—}C_3H_7BBr_2$ | 23.03 | 23.11 | 111.8 | 112.5 | −0.7 | *(25)* |
| $(n\text{—}C_4H_9)_2BCl$ | 29.80 | 30.11 | 170.5 | 173 | −2.5 | *(6)* |
| $(n\text{—}C_4H_9)_2BBr$ | 31.66 | 31.33 | 185.1 | 182.5[a] | 2.6 | *(31)* |
| $n\text{—}C_4H_9BF_2$ | 16.31 | 15.99 | 40.6 | 36.8 | 3.8 | *(23)* |
| $n\text{—}C_4H_9BCl_2$ | 22.35 | 22.62 | 105.3 | 107.9 | −2.6 | *(6)* |
| $n\text{—}C_4H_9(C_2H_5O)BCl$ | 25.94 | 26.02 | 138.3 | 139 | −0.7 | *(22)* |
| $(\mathit{iso}\text{—}C_4H_9)_2BCl$ | 28.08 | 28.08 | 156.5 | 156.5 | 0.0[b] | *(24)* |
| $\mathit{iso}\text{—}C_4H_9BCl_2$ | 21.50 | 21.50 | 97.0 | 97.0 | 0.0[b] | *(22)* |
| $(CH_3O)_2BH$ | 14.80 | 15.10 | 22.0 | 25.9 | −3.9 | *(10)* |
| $(CH_3O)_2BCl$ | 19.20 | 19.33 | 73.3 | 74.7 | −1.4 | *(35)* |
| $CH_3OBCl_2$ | 17.37 | 17.81 | 53.0 | 58 | −5.0 | *(35)* |
| $(C_2H_5O)_2BCl$ | 23.10 | 23.08 | 112.5 | 112.3 | 0.2 | *(35)* |
| $C_2H_5OBCl_2$ | 19.64 | 19.64 | 77.9 | 77.9 | 0.0[b] | *(35)* |
| $(CH_3)_2BC_2H_5$ | 14.95 | 14.80 | 24.0 | 22 | 2.0 | *(5)* |
| $CH_3B(C_2H_5)_2$ | 18.08 | 17.81 | 61.0 | 58 | 3.0 | *(5)* |
| $(CH_3)_2B\text{—}n\text{—}C_3H_7$ | 17.23 | 17.19 | 51.4 | 51 | 0.4 | *(5)* |
| $C_2H_3BF_2$ | 10.61 | 10.50 | −37.3 | −39.1[a] | 1.8 | *(14)* |
| $C_2H_3BCl_2$ | 16.65 | 16.67 | 44.7 | 46.0 | −1.3 | *(14)* |
| $(C_2H_3)_2BF$ | 15.52 | 14.94 | 31.1 | 23.8[a] | 7.3 | *(7)* |
| $(C_2H_3)_2BCl$ | 18.80 | 19.00 | 69.0 | 71.1[a] | −2.1 | *(7)* |
| $(C_2H_3)_2BCH_3$ | 17.46 | 17.25 | 54.0 | 51.7[a] | 2.3 | *(14)* |
| $C_2H_3B(CH_3)_2$ | 14.54 | 14.41 | 18.7 | 17.1[a] | 1.6 | *(14)* |
| $(CH_3)(C_2H_3)BCl$ | 16.25 | 16.20 | 39.9 | 39.3[a] | 0.6 | *(14)* |

[a] Extrapolated normal boiling point. [b] Three configurations of alkyl or alkoxy occur only once each in these compounds and do not require direct use of the computer.

silanes the silicon at b.p.n. 4.20 is dominant over the hydrogen at 0.6 for the b.p.n. *(20)*.

The absence of molecular association in liquid organoboron compounds is necessary or the Kinney equation (Equation 1) will not be valid. Neither dimeric $CH_3OBF_2$, b.p. 85.2°, *(15)* nor partially associated $(CH_3O)_2BF$, b.p. 52.7°, appear in Table II.

An earlier publication gives a sample calculation of b.p. *(2)* and the method of assignment of configuration of alkyl groups. This paper also shows the attempted use of equations other than the Kinney equation (Equation 1).

## LITERATURE CITED

(1) Andersen, H.C., Belz, L.H., *J. Am. Chem. Soc.* **75**, 4823 (1953).
(2) Anderson, H.H., J. CHEM. ENG. DATA **7**, 565 (1962).
(3) Ashikari, N., *Bull. Chem. Soc. Japan* **31**, 229 (1958).
(4) Bartocha, B., Graham, W.A.G., Stone, F.G.A., *J. Inorg. Nuclear Chem.* **6**, 129 (1958).
(5) Birchall, J.M., Haszeldine, R.N., Marsh, J.F., *Chem. Ind. (London)* **1961**, 1080.
(6) Booth, R.D., Kraus, C.A., *J. Am. Chem. Soc.* **74**, 1415 (1952).
(7) Brinckman, F.E., Stone, F.G.A., *Ibid.* **82**, 6218 (1960).

(8) Burg, A,B., *Ibid.* **62**, 2228 (1940).
(9) Burg, A.B., Kratzer, R., *Inorg. Chem.* **1**, 729 (1962).
(10) Burg, A.B., Schlesinger, H.I., *J. Am. Chem. Soc.* **55**, 4009, 4020 (1933).
(11) Burg, A.B., Wagner, R.I., *Ibid.* **75**, 3872 (1953).
(12) Dollimore, D., Long, L.H., *J. Chem. Soc. (London)* **1953**, 3906.
(13) Gibbins, S.G., Shapiro, I., *J. Chem. Phys.* **30**, 1483 (1959).
(14) Good, C.D., Ritter, D.M., J. CHEM. ENG. DATA **7**, 416 (1962).
(15) Goubeau, J., Lücke, K.E., *Ann. Chem.* **575**, 39 (1952).
(16) Hennion, G.F., McCusker, P.A., Ashby, E.C., Rutkowski, A.J., *J. Am. Chem. Soc.* **79**, 5190 (1957).
(17) Kinney, C.R., *Ibid.* **60**, 3022 (1938); *J. Org. Chem.* **6**, 220, 224 (1941); **7**, 111 (1942); **14**, 71 (1949).
(18) Klemm, W., ed., "FIAT Reviews of German science," Vol. **I**, pp. 235-237, Office of Military government for Germany, Wiesbaden, Germany, 1948.
(19) Lappert, M.F., *Chem. Revs.* **56**, 959 (1956).
(20) Lewis, R.N., Newkirk, A.E., *J. Am. Chem. Soc.* **69**, 701 (1947).
(21) Lynds, L., Stern, D.R., *Ibid.* **81**, 5006 (1959).
(22) McCusker, P.A., Ashby, E.C., Makowski, H.S., *Ibid.* **79**, 5182 (1957).
(23) McCusker, P.A., Glunz, L.J., *Ibid.* **77**, 4253 (1955).
(24) McCusker, P.A., Hennion, G.F., Ashby, E.C., *Ibid.* **79**, 5192 (1957).
(25) Mikhaĭlov, B.M., Kozminskaya, T.K., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1959**, 1866; **1960**, 2247.
(26) Rosenblum, L., *J. Org. Chem.* **25**, 1652 (1960).
(27) Schlesinger, H.I., Floodin, N.W., Burg, A.B., *J. Am. Chem. Soc.* **61**, 1078 (1939).
(28) Schlesinger, H.I., Horvitz, L., Burg, A.B., *Ibid.* **58**, 407 (1936).
(29) Schlesinger, H.I., Walker, A.O., *Ibid.* **57**, 621 (1935).
(30) Shapiro, I., Ditter, J.F., *J. Chem. Phys.* **26**, 801 (1957).
(31) Skinner, H.A., Tees, T.F.S., *J. Chem. Soc. (London)* **1953**, 3378.
(32) Stock, A., Kusz, E., *Ber.* **56 B**, 801 (1923).
(33) Stock, A., Pohland, E., *Ibid.* **62 B**, 90 (1929).
(34) Wiberg, E., Krüerke, U., *Z. Naturforsch.* **8 B**, 608 (1953).
(35) Wiberg, E., Sütterlin, W., *Z. anorg. u. allgem. Chem.* **202**, 1 (1931).
(36) Wright, J.R., J. CHEM. ENG. DATA **5**, 206 (1960).

RECEIVED for review August 9, 1962. Accepted July 1, 1963.

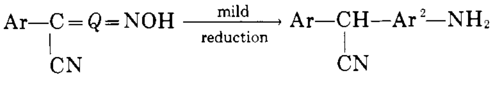
# Condensation of Aromatic Nitro Compounds with Arylacetonitriles

## V. Some Reactions of Arylcyanomethylenequinone Oximes

RALPH B. DAVIS and JOSEPH D. BENIGNI
Department of Chemistry, University of Notre Dame, Notre Dame, Ind.

**Mild chemical and catalytic reduction convert the arylcyanomethylenequinone oximes to *p*-aminoarylarylacetonitriles. The amino-nitrile compounds are readily hydrolyzed to the corresponding amino-acids. More vigorous catalytic reduction converts the arylcyanomethylenequinone oximes to *p*-aminoarylarylethylamines. There is described the preparation and characterization of many new amino-compounds which would be difficult to prepare by other methods.**

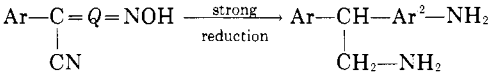
THIS REPORT concerns a continuation of the systematic investigation of the chemical behavior of six representative arylcyanomethylenequinone oximes (*4*), which are more properly named, 4-oxo-$\alpha$-aryl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oximes. The arylcyanomethylenequinone oximes are reduced to the corresponding *p*-aminoarylarylacetonitriles in good yield using zinc and acetic acid in methanol and some water, or hydrogen and Raney nickel in methanol. The mild reduction of the arylcyanomethylenequinone oximes, which apparently involves an initial 1,6-addition of hydrogen to the *p*-quinoid system, similar to the reduction of fuchsone (*3*), can be represented by the following general equation in which $Q$ signifies a *p*-quinoid structure and $Ar^2$ signifies a *p*-bivalent aromatic radical having the same chemical formula and arrangement of substituents as $Q$.



$$\mathrm{Ar{-}\underset{\underset{CN}{|}}{C}{=}}Q\mathrm{{=}NOH} \xrightarrow[\text{reduction}]{\text{mild}} \mathrm{Ar{-}\underset{\underset{CN}{|}}{C}H{-}Ar^2{-}NH_2}$$

As part of the proof of structure of the *p*-aminoarylarylacetonitriles, *p*-aminophenylphenylacetonitrile and *p*-aminophenyl-*p*-chlorophenylacetonitrile were independently synthesized by the mild reduction of the corresponding nitro compounds. In addition, the infrared spectra of the mild reduction products possessed characteristic amino group absorption peaks in the 2.8 to 3.0$\mu$ region (*2*) and characteristic non-conjugated nitrile group absorption peaks in the 4.47$\mu$ region (*5*). The *p*-aminoarylarylacetonitriles were converted to their hydrochloride salts and also to the corresponding amino-acids (*1*) by conventional procedures.

More vigorous reducing conditions using hydrogen and Raney nickel in methanol, converts the arylcyanomethylenequinone oximes to the corresponding *p*-aminoarylarylethylamines.



$$\mathrm{Ar{-}\underset{\underset{CN}{|}}{C}{=}}Q\mathrm{{=}NOH} \xrightarrow[\text{reduction}]{\text{strong}} \mathrm{Ar{-}\underset{\underset{CH_2{-}NH_2}{|}}{C}H{-}Ar^2{-}NH_2}$$

As suggested by other workers (*6, 7*), ammonia may be used in these reactions in order to keep secondary amine formation to a minimum. However, the ammonia must be introduced only after the initial stages of reduction have taken place, otherwise the expected diamines are not produced in good yield.