hydrogenation are nearly identical[6]; also in both reactions the bromines go into secondary positions and the hydrogen in primary ones.[7] Since the hydrobromination reactions of the three isomeric butenes yield the same product, the thermal data may be used to calculate the heat of their isomerization reactions. The results are given in Table II. The heats of these reactions may also be calculated from Kistiakowsky's hydrogenation data[6] and the information is also included in the table. Our data were obtained at about 373°K. and Kistiakowsky's at 355°K. The agreement is excellent.

TABLE II

HEATS OF ISOMERIZATION

Reaction	$-\Delta H$, cal. Present	$-\Delta H$, cal. Kistiakowsky
Butene-1 → *trans*-butene-2	2804	2720
Butene-1 → *cis*-butene-2	1800	1771
cis-Butene-2 → *trans*-butene-2	1004	949

The reaction of bromine with a saturated hydrocarbon may be regarded as one of dehydrogenation followed by the addition of hydrogen bromide. The heat of substitution of a secondary hydrogen in propane may be calculated as

$$CH_3{-}CH_2{-}CH_3 \longrightarrow CH_3{-}CH{=}CH_2 + H_2 \qquad \Delta H = 30{,}115 \text{ cal./mole}$$

$$CH_3{-}CH{=}CH_2 + HBr \longrightarrow CH_3{-}CHBr{-}CH_3 \qquad \Delta H = -20{,}182 \text{ cal./mole}$$

$$Br_2(g) + H_2 \longrightarrow 2HBr \qquad \Delta H = -24{,}900 \text{ cal./mole}$$ [8]

adding

$$CH_3{-}CH_2{-}CH_3 + Br_2(g) \longrightarrow CH_3{-}CHBr{-}CH_3 + HBr \qquad \Delta H = -14{,}967$$

In case of butane it may be dehydrogenated to give butene-1, *cis-* or *trans*-butene-2. The addition of hydrogen bromide gives 2-bromobutane in any case. The average for the three possible processes gives

$$CH_3{-}CH_2{-}CH_2{-}CH_3 + Br_2(g) \longrightarrow CH_3{-}CH_2{-}CHBr{-}CH_3 + HBr \qquad \Delta H = -14{,}765 \text{ cal./mole}$$

The heats of substitution of a secondary hydrogen in propane and butane by bromine are thus nearly the same.

BOULDER, COLORADO

---

(6) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **57**, 876 (1935).

(7) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *ibid.*, **60**, 2764 (1938).

(8) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[CONTRIBUTION OF THE UNIVERSITY OF COLORADO]

The Vapor Phase Heat of Chlorination of Diborane[1]

BY J. R. LACHER, R. E. SCRUBY[2] AND J. D. PARK

RECEIVED APRIL 21, 1952

Using an isothermal constant flow calorimeter, the heat of the gaseous reaction, $B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6HCl$, has been measured. The results at 25° give $-\Delta H = 343$ kcal. per mole of B_2H_6. The accuracy is estimated to be 1%. It is shown that existing data on the heats of formation of diborane and boron trichloride are not consistent.

A study of the heat of reaction of diborane with chlorine was undertaken originally because of the lack of reliable data on its heat of formation. Previous estimates on this quantity were based on the heat of hydrolysis of diborane with water[3] and a knowledge of the heat of formation of B_2O_3. Direct measurements of the heat of formation of B_2O_3 have given widely diverging values. Some recent ones are: 349,[3] 335,[4] 339.8[5] and 281[6] kcal. per mole. Using this information one calculates that the heat of formation of diborane lies somewhere between −26 and +42 kcal. While the present work was being initiated, Prosen and coworkers[7] measured the heat of formation of diborane by its direct decomposition into the elements. The value obtained was −7.5 kcal. per mole.

If one measures the heat of the reaction

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

one can calculate the heat of formation of diborane if those of boron trichloride and hydrogen chloride are known. The heat of formation of hydrogen chloride has been measured by Rossini[8] and we have been able to check his results in this Laboratory.[9] Some uncertainty exists in the heat of formation of boron trichloride. Roth[5] favors a value of 104 kcal., while the Bureau of Standards[10] indicates a value of 94.5 kcal. However, the results of the present investigation provide a valuable check on the consistency of the heats of formation of diborane and boron trichloride; in fact, they indicate some lack of consistency.

Experimental Details

The calorimeter and its method of operation have been described previously.[9] A new monel metal reaction chamber, which differs only slightly from the previous design, was used in this work. The volume of the catalyst chamber has been increased twofold. The reactants enter through concentric tubes which reach nearly to the bottom of the cham-

---

(1) This research was supported in part by the Office of Naval Research, United States Navy, Contract N6-onr-231, Task Order VI.

(2) Gerard Swope Fellow, General Electric Educational Fund.

(3) W. A. Roth and E. Börger, *Ber.*, **70B**, 48, 971 (1937).

(4) B. J. Todd and R. R. Miller, THIS JOURNAL, **68**, 530 (1946).

(5) W. A. Roth, *Z. Naturforsch.*, **1**, 574 (1946).

(6) W. Eggersgluess, A. G. Monroe and W. G. Parker, *Trans. Faraday Soc.*, **45**, 661 (1949).

(7) E. J. Prosen, W. H. Johnson and F. A. Yenchius, Nat. Bur. Stand. (U.S.A.), Technical Report on Project NA-onr-8-47, dated 9/30/48.

(8) F. D. Rossini, *J. Research Natl. Bur. Stand.*, **9**, 679 (1932).

(9) J. R. Lacher, J. D. Park, *et al.*, THIS JOURNAL, **71**, 1330 (1949).

(10) Private communication.

ber. The exit line has been extended within the reaction chamber nearly to the top where the product gases enter it through small perforations. The reaction thus takes place mainly in the lower part of the chamber.

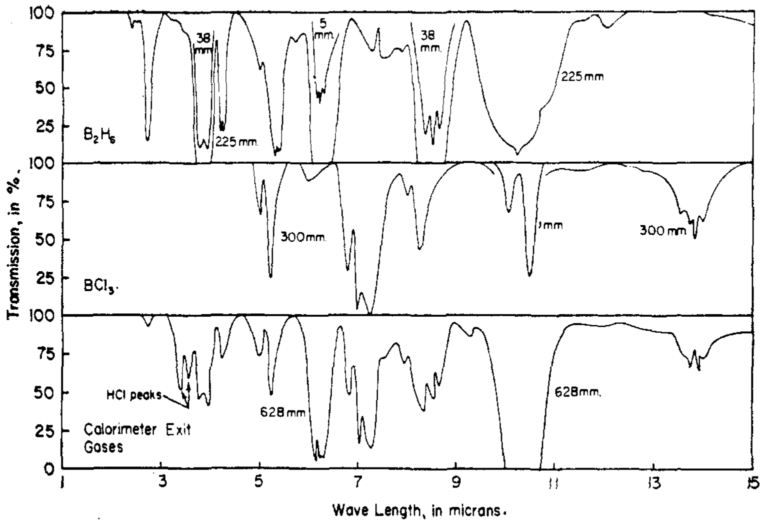

Fig. 1.—Infrared absorption spectra, 10 cm. cell, and indicated pressure in mm.

Diborane was prepared by the reaction of lithium aluminum hydride in ether solution with boron trichloride etherate.[11] Lithium aluminum hydride was obtained from Metal Hydrides, Incorporated. The ether solution was prepared by refluxing 10 g. of the hydride in about 130 g. of anhydrous ether for six hours. The infrared spectrum of boron trichloride (obtained from the Matheson Company) showed the presence of phosgene, hydrogen chloride and other unidentified impurities. Distillation in an efficient fractionating column removed practically all of the impurities except the phosgene. Since the latter is easily removed during the preparation and purification of the diborane, further purification was not attempted. The boron chloride etherate was prepared by bubbling the distilled boron trichloride into anhydrous ethyl ether.

Diborane was generated and purified in the all-glass apparatus. Special stopcocks with mercury seals were used. For the preparation of about 500 ml. of gaseous diborane 17.5 g. of the hydride solution and 11 g. of the boron chloride etherate were used. The entire system was evacuated for several hours and then dry nitrogen added until the pressure was about 300 mm. The hydride solution was added through a dropping funnel and frozen into the reaction flask with liquid nitrogen. Boron chloride etherate was then slowly added to the reaction flask through the dropping funnel and frozen on top of the hydride solution. Dry ice was placed in a cold finger condenser. A Dry Ice–carbon tetrachloride–chloroform freezing mixture was used to cool the first trap and liquid nitrogen the next two traps. The reactants were allowed to heat very slowly to room temperature. As soon as the materials in the reaction flask became melted, the reaction between them commenced. The cold finger condenser returned the ether to the reaction flask. A small amount of ether was trapped in the first trap and diborane was trapped in the following two. When the reactants reached room temperature they were stirred slowly with a magnetic stirrer for about one hour. The reaction flask and first trap were then isolated from the rest of the system and the diborane was purified in the second, third and fourth traps. The nitrogen was pumped off and the diborane was purified by simple trap-to-trap distillation first through a Dry Ice trap and then through a trap cooled by melting carbon disulfide. Any residue was transferred to the removable trap. It was also necessary to pump off non-condensable gases during the purification. This procedure was continued until the vapor pressure of diborane was 225 mm. when trapped at the melting point of carbon disulfide.[12] It was observed that after prolonged standing at room temperature, the diborane always contained a small amount of residual gases. For this reason it was always purified immediately before use. The criteria for its purity were (1) absence of non-condensable gases, (2) vapor pressure at the melting point of carbon disulfide and (3) infrared absorption spectra. The latter is given in Fig. 1. It agrees in all respects with those previously given in the literature.[13,14] The diborane flow system consisted of two mercury displacement pumps in parallel. The gas was caused to flow into the calorimeter by a motor which raised a mercury reservoir at a given rate. Due to the different amounts of mercury present at various heights, the rate was not constant but increased about 5% as the reservoir was raised. Since the diborane was used in excess over the chlorine, this introduced no error.

Previous work[9] has shown that chlorine from the Matheson Company may be used without purification. The arrangement used to produce a constant flow of chlorine was as previously described. A precise measurement of its rate was made by diverting it to a collection tower for a definite period of time. 75 ml. of 3 *N* KI was used as the absorbing liquid. The iodine liberated was titrated with a standard thiosulfate solution using a starch indicator. In runs 5 and 6 of Table I, the chlorine was absorbed in 5 *N* KOH solution. The mixture was made weakly alkaline and reduced with hydrogen peroxide to give chlorides. The latter were precipitated in acid solution with silver nitrate and the resulting silver chloride weighed. The two methods gave similar results.

TABLE I

HEATS OF CHLORINATION REACTIONS

A, $^1/_2Cl_2 + ^1/_2H_2 \rightarrow HCl$; $-\Delta H_{av} = 22{,}130$ cal.

Run	Temp., °C.	H_2 flow, moles/min. $\times 10^{+4}$	Cl_2 flow, moles/min. $\times 10^4$	Heat input, cal./min.	$-\Delta H$, cal./mole HCl
1	95.3	10.9	2.09	9.5068	22,300
2	79.8	11.3	1.566	6.9817	22,290
3	85.3	11.9	4.921	21.494	21,840
4	85.3	11.9	4.960	21.900	22,080

B, $6Cl_2 + B_2H_6 \rightarrow 2BCl_3 + 6HCl$; $-\Delta H_{av} = 342.4$ kcal.

Run	Temp., °C.	B_2H_6 flow, moles/min. $\times 10^4$	Cl_2 flow, moles/min. $\times 10^4$	Heat input, cal./min.	$-\Delta H$, kcal./mole B_2H_6
1	85.2	0.67	3.745	21.317	341.5
2	95.1	.67	3.711	21.340	345.0
3	66.0	.67	3.686	20.721	337.4
4	77.3	1.34	6.503	36.979	341.5
5	77.6	1.34	6.098	35.137	345.7
6	77.6	1.34	5.774	33.032	343.3

Palladium-on-asbestos was used as a catalyst for the reaction of chlorine both with diborane and hydrogen. An initial pilot plant run on the reaction of diborane and chlorine was carried out using only glass beads in the reaction chamber. The reaction took place, as an infrared analysis showed, but popping noises were heard in the chamber. With the palladium catalyst, the reaction took place very smoothly. The catalyst was prepared by placing washed and ignited asbestos fibers in a 2% solution of $PdCl_2 \cdot 2H_2O$ in CCl_4. The solution was slowly evaporated to dryness and the asbestos transferred to the catalyst chamber. After heating to 200°, the chamber was evacuated for 15 minutes, and then hydrogen was passed through until the reduction was complete.

Experimental Results and Discussion

In order to check the operation of the calorimeter and the analytical techniques used, four runs were made on the reaction between hydrogen and chlo-

---

[11] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

[12] H. I. Schlesinger, G. W. Schaeffer and G. D. Barbaras, United States A.E.C., MDDC-1338, 1944.

[13] F. Stitt, *J. Chem. Phys.*, **9**, 780 (1941).

[14] W. C. Price, *ibid.*, **16**, 894 (1948).

rine. The results are given in Table IA. The average value of −22,130 calories agrees very well with that of −22,120 calories given by Rossini[8] when corrected to the same temperature.

Six runs were made on the reaction of diborane with chlorine, and the results are given in Table IB. The average value for the heat of reaction from these runs is −342.4 kcal. per mole of diborane with a maximum deviation from the average value of 1.5%. When corrected to 25° by heat capacity data this becomes −343.0 kcal.

Figure 1 is offered as proof that the products of the reaction are boron trichloride and hydrogen chloride. It gives the infrared spectra of diborane, boron trichloride and the calorimeter exit gases. From the intensities of absorption of the various peaks, it is found that boron trichloride is present in the exit gases to the extent of about 150 mm. and diborane about 15 mm. The peaks at 3.4 and 3.6 μ are due to hydrogen chloride and indicate a partial pressure of about 450 mm. Since no extraneous peaks are present, it is doubtful if any side reactions have taken place. The absence of chlorine in the exit gases was shown by ultraviolet absorption spectra.

If one takes the heats of formation of diborane,[7] boron trichloride,[10] and hydrogen chloride to be −7.5, +94.5 and +22.06, respectively, the heat of reaction may be calculated to be −328.9 kcal. This is lower than the observed value by 4% and is considerably greater than our experimental error which is estimated to be about 1%. If one takes the heat of formation of diborane to be −7.5, one may calculate that the heat of formation of boron trichloride is 102 kcal. This is fairly close to the value of 104 recommended by Roth.[5] On the other hand, if we take the heat of formation of boron trichloride to be 94.5 kcal., then one may calculate the heat of formation of diborane to be −22 kcal. This is in fairly good agreement with the values recommended by Roth[5] and Eggersgluess.[6] The existing data on the heats of formation of these compounds are not consistent.

BOULDER, COLORADO

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Sulfur and Selenium Compounds

BY MAX T. ROGERS AND K. J. GROSS

RECEIVED APRIL 9, 1952

The electric moments and molecular refractions of nitrogen tetrasulfide, phosphorus sesquisulfide, cyanogen sulfide cyanogen triselenide and perchloromethyl mercaptan have been measured in solution in non-polar solvents at 25°. Some conclusions concerning the structures of these molecules are drawn from the data.

The structure of nitrogen tetrasulfide, N_4S_4, has been the subject of extensive research[1–4] but is still uncertain. Several of the proposed structures would have zero dipole moment but the compound has been reported[4] to have a dipole moment of 0.72 *D* in benzene solution. Since small dipole moments are occasionally reported for non-polar compounds as a result of solvent effects, or of errors, it appeared worthwhile to redetermine the dipole moment and molecular refraction of N_4S_4 in both benzene and carbon bisulfide solution. A reasonable structure for phosphorus sesquisulfide, P_4S_3, has been proposed by Hassel and Petterson[5] on the basis of an electron diffraction investigation; we have measured the electric moment of P_4S_3 and find that it is consistent with their results. No physical measurements have been reported previously on cyanogen sulfide, $S(CN)_2$, or cyanogen triselenide, $Se_3(CN)_2$; we have measured the dipole moments to obtain some information concerning their structures.

An estimated value 0.45 *D* for the S–Cl bond moment is obtained from the ∠ Cl–S–Cl = 102° found by electron diffraction[6] and the dipole moment calculated by Smith[7] from an early measurement of the molar polarization.[8] Some doubt has been thrown on this value by the large electric moment reported for sulfur monochloride S_2Cl_2, by Smyth, *et al.*,[9] so we have obtained an independent estimate of the S–Cl bond moment by measuring the electric moment of perchloromethyl mercaptan, Cl_3–C–S–Cl.

Experimental Part

Materials. Benzene.—C.P. thiophene-free benzene was purified by drying over sodium and distilling before use, d^{25}_4 0.87344, n^{25}_D 1.4979.

Carbon Tetrachloride.—This was prepared according to the recommendations of Fieser[10] by treatment of C.P. carbon tetrachloride with concd. potassium hydroxide solution and alcohol, water, concd. sulfuric acid, water and anhydrous calcium chloride, in turn, d^{25}_4 1.58427, n^{25}_D 1.4573.

Carbon Bisulfide.—C.P. carbon bisulfide was shaken with mercury, mercuric chloride solution, potassium permanganate solution, washed, dried and distilled, as outlined by Fieser,[10] d^{25}_4 1.25566, n^{25}_D 1.6239.

Cyanogen Triselenide.—This was prepared by passing chlorine over potassium selenocyanate solution until the reaction was complete.[11] The yellow precipitate was refluxed in chloroform with charcoal and the hot solution filtered. Yellow plates, m.p. 133–134°, crystallized out and were recrystallized from benzene giving orange needles, m.p. 133–134°. The two crystal forms were investigated separately but gave the same molar polarization.

---

(1) C. S. Lu and J. Donohue, THIS JOURNAL, **66**, 818 (1944).

(2) O. Hassel and H. Viervoll, *Tids. Kjemi Bergvesen Met.*, **3**, 7 (1943).

(3) M. H. M. Arnold, J. A. C. Hugill and J. M. Hutson, *J. Chem. Soc.*, 1645 (1936).

(4) N. L. Phalnikar and B. V. Bhide, *Current Sci.*, **8**, 473 (1939).

(5) O. Hassel and A. Petterson, *Tids. Kjemi Bergvesen Met.*, **1**, 57 (1941).

(6) D. P. Stevenson and J. Y. Beach, THIS JOURNAL, **60**, 2872 (1938).

(7) J. W. Smith, *Proc. Roy. Soc.* (*London*), **A138**, 154 (1932).

(8) T. M. Lowry and G. Jessop, *J. Chem. Soc.*, 782 (1930).

(9) C. P. Smyth, G. L. Lewis, A. J. Grossman and F. B. Jennings III THIS JOURNAL, **62**, 1219 (1940).

(10) L. F. Fieser, "Experiments in Organic Chemistry," Second Edition, D. C. Heath and Co., New York, N. Y., 1941.

(11) A. Verneuil, *Ann. chim. phys.*, [6] **9**, 326 (1886).