[CONTRIBUTION OF THE UNIVERSITY OF COLORADO]

Vapor Phase Heats of Hydrobromination of the Isomeric Butenes[1]

BY J. R. LACHER, T. J. BILLINGS, D. E. CAMPION, K. R. LEA AND J. D. PARK

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The vapor phase heats of hydrobromination of butene-1, *cis*-butene-2, and *trans*-butene-2 have been measured at about 100°. The product of the reactions is 2-bromobutane. The data permit the calculation of heats of isomerization of the various butenes. Sufficient data are now available to permit the calculation of the heats of the reactions of bromine with propane and butane to give isopropyl bromide and 2-bromobutane.

In a previous paper[2] the vapor phase heats of hydrobromination of propylene and cyclopropane were reported. The present paper reports the heats of hydrobromination of butene-1, *cis*- and *trans*-butene-2.

Experimental

Research grade butene-1 and *cis*-butene-2 were obtained from the Phillips Petroleum Company. Since the impurity (1% maximum) was stated to be butane (which will not react in the calorimeter), they were used without purification. *trans*-Butene-2 was obtained by distillation of a 50% mixture of butene-2 in a 100-plate "Hypercal" Podbielniak column. The purity of the product obtained was checked by comparing its infrared spectra to that reported by the Shell Oil Company.[3] The agreement was excellent. The spectra of the three starting olefins are in agreement with the work of others.[4] Research-grade hydrogen bromide from the Matheson Company was used without further purification. "Columbia" activated carbon was used as a catalyst. After screening to size, it was heated *in vacuo* at 200–250° for 3 to 4 hours. On cooling it was transferred to the calorimeter catalyst chamber and again evacuated for one hour at about 100°. Finally it was saturated with hydrogen bromide and was ready for use.

The procedure used in making the runs was similar to that previously described.[2] An excess of the olefin was used so that if the reaction went to completion, no hydrogen bromide appeared in the exit gases. This was the case for *cis*- and *trans*-butene-2; however, butene-1 consumed 97 to 98% of the hydrogen bromide. In order to determine the amount of hydrogen bromide in the exit gases, they were sent to a tower containing cold water for a definite period of time. Generally 45 minutes elapsed between the start of a collection and the completion of the analysis. Since the bromide hydrolyzed slowly in cold water, aliquot samples were also analyzed 2, 4 and 24 hours after collection. The results were then extrapolated to zero time. Hydrogen bromide analyses were carried out using the method previously described.

An analysis of the calorimeter products was carried out by determining their infrared spectra. Both *cis*- and *trans*-butene-2 yielded 2-bromobutane exclusively. Butene-1 gave a hydrogen bromide adduct which was principally 2-bromobutane; however, the spectra showed traces of *n*-bromobutane. Known mixtures of 2-bromo- and *n*-bromobutane were then made up and analyzed. From these data it was inferred that about 0.2% of normal bromobutane was present in the reaction product.

It has been reported that some bromohexanes are formed when hydrogen bromide adds to propylene.[5] In the present case one might expect bromoöctanes. In order to check this a fairly large quantity (150 ml.) of the product obtained by treating butene-1 and hydrogen bromide in the calorimeter was collected and carefully distilled in a 100-plate Hypercal Podbielniak column. The infrared spectra of the various fractions were examined. No evidence for octanes or *t*-butyl bromide was obtained. However, *n*-bromobutane was found in the pot residue in an amount corresponding to approximately 0.5% of the original sample. Nothing else could be found. The hydrobromination of isobutene, on the other hand, runs quite differently. When this reaction was carried out in the calorimeter, the catalyst chamber filled up with a high boiling liquid. This could have been a bromoöctane.

Experimental Results and Discussion

The experimental results obtained in the hydrobromination of the three isomeric butanes are summarized in Table I. In case of butene-1, the product contains 0.2–0.5% *n*-bromobutane. If one assumes that the heat of isomerization of *n*-bromobutane to 2-bromobutane is the same as normal to isopropyl bromide,[2] then 5–15 calories should be added to the observed heat. This will be neglected. The heat of hydrobromination of butene-1 is practically identical to the value of −20,182 cal./mole previously reported for propylene.[2] This is to be expected since their heats of

TABLE I

VAPOR PHASE HEATS OF HYDROBROMINATION

Run no.	HBr flow, moles/min. × 10⁴	Olefin flow, moles/min. × 10⁴	Heat input, cal./min.	$-\Delta H$, cal./mole	Per cent. utilization of HBr
Butene-1 at 94°					
1	2.265	5.2	4.6013	20,315	97.5
2	1.946	5.5	3.9026	20,052	98.4
4	2.106	4.0	4.2542	20,200	96.9
5	2.267	4.4	4.5366	20,010	98.4
Average: $-\Delta H_{367}$ = 20,144 ± 180 cal./mole; product: 2-bromobutane containing 0.2–0.5% *n*-bromobutane					
cis-Butene-2 at 100°					
10	4.361	17.0	7.9378	18,203	
11	4.712	22.0	8.7261	18,518	
12	5.390	22.5	9.8126	18,203	
13	4.709	21	8.6093	18,282	
14	4.107	15.5	7.6031	18,512	
Average: $-\Delta H_{373}$ = 18,344 ± 157 cal./mole; product: 2-bromobutane					
trans-Butene-2 at 110°					
1	2.793	5.5	4.8790	17,469	
2	2.951	6.1	5.1611	17,488	
3	2.839	5.7	4.9108	17,293	
4	3.234	6.1	5.5744	17,234	
6	3.193	5.6	5.4994	17,218	
Average: $-\Delta H_{383}$ = 17,340 ± 135 cal./mole; product: 2-bromobutane					

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[1] This research was supported, in part, by the Office of Naval Research, Contract N6-onr-231, Task Order VI, United States Navy, and by grants-in-aid from the Research Corp. of New York.

[2] J. R. Lacher and J. D. Park, *et al.*, THIS JOURNAL, **72**, 331 (1950).

[3] R. B. Barnes, R. C. Gore, U. Liddel and Van Zant Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1946, pp. 19–20.

[4] A.P.I. Research Project 44, National Bureau of Standards, Serial nos. 19 and 444.

[5] O. Maass and C. H. Wright, THIS JOURNAL, **46**, 2664 (1924).

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

	$-\Delta H$, cal.	
Reaction	Present	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

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

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

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

adding

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

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

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

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

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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-

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(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.