[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Vapor Phase Heats of Hydrobromination of Cyclopropane and Propylene

BY J. R. LACHER,* C. H. WALDEN,[1] K. R. LEA AND J. D. PARK

Two previous papers by Lacher, Park, *et al.*,[2,3] described an isothermal constant-flow calorimeter and presented results on the heats of chlorination of some simple fluoro-olefins. The calorimeter used in the present study is essentially the same as the one previously described.[2] However, a few improvements and modifications were made to adapt the calorimeter for hydrobromination reactions.

Experimental

Since hydrogen bromide reacts with copper and brass, the valves, tubing, and the calorimeter itself were constructed of "Monel" metal. The fritted-glass nitrogen distributor was replaced by an all-metal one. The leads from the nichrome heater were taken out directly through the circular brass plate on the top of the calorimeter through "Teflon"-insulated binding posts. The "Teflon" and ceramic-covered copper wire was found to be very useful in fabricating electrical connections for the heater.[4] Because of its lower vapor pressure, bromobenzene was substituted for chlorobenzene as the volatile liquid surrounding the reaction chamber.

Anesthetic-grade cyclopropane, kindly furnished by the Mallinckrodt Chemical Works, was used without further purification. Research-grade propylene, containing less than 1% propane as an impurity, was obtained from the Phillips Petroleum Company and was used without further purification. Infrared absorption spectra of these materials are shown in Figs. 1 and 2 and are in agreement with work of others.[5] Research-grade hydrogen bromide was obtained from the Matheson Company with a purity of 99.7%. Analysis showed that it contained less than 0.1% free bromine. The catalyst employed in both of these reactions was "Columbia" carbon sized to pass no. 6 and be retained on no. 20 standard screens. It was activated by heating *in vacuo* at 250° for four hours.

The procedure used in making these determinations was similar to that described for the chlorination reactions.[2,3] The exit gases from the calorimeter were sent through a collecting tower and absorbed in distilled water in order to determine the amount of unreacted hydrogen bromide leaving the calorimeter. It was necessary to titrate the samples immediately after their collection to prevent extensive hydrolysis of the propyl bromides. In the case of the hydrobromination of cyclopropane, the reaction was 99.6% complete; and for propylene, it was 99.9%. The flow of hydrogen bromide fed into the calorimeter was directed to a collecting tower of 3 *N* potassium hydroxide for a measured length of time to determine the hydrogen bromide flow rate. The amount of hydrogen bromide in the sample, so collected, was determined by adding an excess of silver nitrate and back titrating with standard potassium thiocyanate in the usual manner.

To prove that no side reactions were taking place, infrared absorption spectra were obtained from both the high and low boiling fractions of the sample of product collected at the exit of the calorimeter. By comparing these with the spectra of the compounds involved, it was found that no appreciable amount of undesirable side reactions had taken place. It was noted, however, that the product from the hydrobromination of cyclopropane contained a trace of isopropyl bromide in addition to the expected *n*-propyl bromide while the product from the hydrobromination of propylene contained a small amount of the *n*-propyl bromide in addition to the expected isopropyl bromide. Infrared absorption spectra were obtained, at low pressures, for gaseous samples of the calorimeter products and by comparing these spectra with those given by mixtures of the two isomers of known and practically identical composition it was possible to determine the per cent. of each isomer present in the calorimeter sample. Samples of the pure isomers were obtained from the Dow Chemical Company, and their infrared spectra are shown in Figs. 3 and 4. The product of the hydrobromination of cyclopropane contained 99.7% of the *n*-propyl bromide and 0.3% of the isopropyl bromide while the product from the

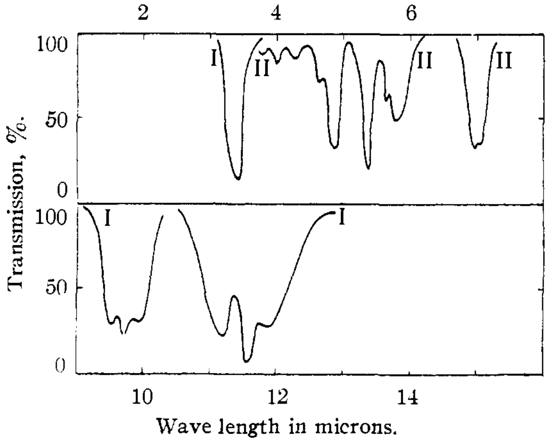

Fig. 1.—Infrared absorption spectrogram of cyclopropane at room temperature in a 10-cm. gas cell at ind. pressure, I, 100 mm.; and II, 630 mm.

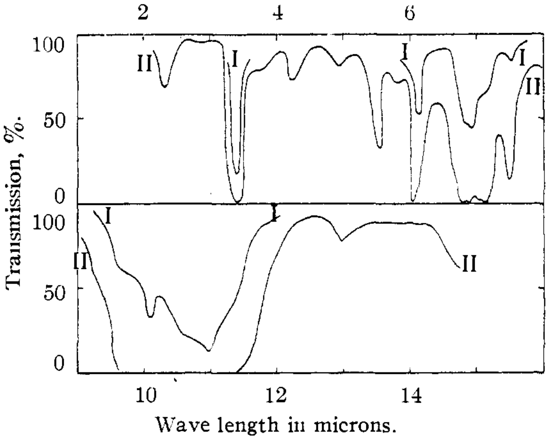

Fig. 2.—Infrared absorption spectrogram of propylene at room temperature in a 10-cm. gas cell at ind. pressure, I, 70 mm.; and II, 410 mm.

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* Harvard University Ph.D. 1936.

(1) American Cyanamid Fellow 1948-1949.

(2) J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson and J. D. Park, THIS JOURNAL, **71**, 1330 (1949).

(3) J. R. Lacher, J. J. McKinley, C. Walden, K. Lea and J. D. Park, *ibid.*, **71**, 1334 (1949).

(4) We wish to thank the Sprague Electric Company of North Adams, Mass. for a sample of this wire. It bears a trade name of "Ceroc."

(5) A. P. I. Research Project 44, National Bureau of Standards, Serial Nos. 19 and 445.

hydrobromination of propylene consisted of 98.5% isopropyl bromide and 1.5% of *n*-propyl bromide.

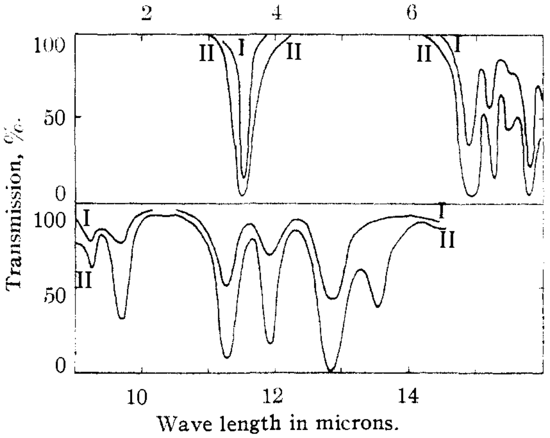


Fig. 3.—Infrared absorption spectrogram of *n*-propyl bromide at room temperature, I, in a 10-cm. gas cell at 123 mm. and II, in a 0.1-mm. liquid cell.

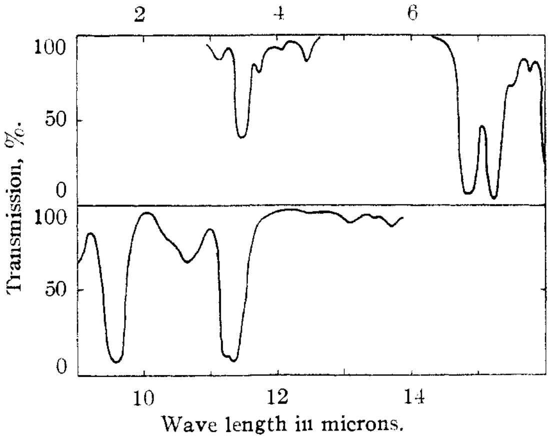


Fig. 4.—Infrared absorption spectrogram of isopropyl bromide at room temperature in a 10-cm. gas cell at 190 mm. pressure.

Experimental Results and Discussion.—The experimental results obtained in the hydrobromination of cyclopropane and propylene are summarized in Table I. Since cyclopropane yields 99.7% *n*-propyl bromide and propylene yields 98.5% of isopropyl bromide, a correction is necessary in order to arrive at the heats of reaction for the pure isomers. The heat of isomerization of the normal to isopropyl bromide is needed for the calculation but has not been directly measured. Brouwer and Wibaut[6] have found that an equilibrium mixture of the two isomers at 250° contains 70% of the isopropyl bromide while at 275° it is 67%. An approximate value of the heat of isomerization may then be obtained from these data and the following statistical equation

$$K = e^{-\Delta H/RT}\,\sigma_n/\sigma_i = N_i/N_n$$

Table I

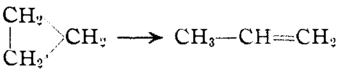
Vapor Phase Heats of Hydrobromination at 94°

Run	Olefin flow, moles/min. × 10⁴	HBr flow moles/min. × 10⁴	Energy input, cal./min.	$-\Delta H_{367°K.}$, cal./mole
		Cyclopropane		
1	3.3	2.4231	5.5048	22,718
2	6.3	2.4620	5.5575	22,573
3	3.1	2.1260	4.8331	22,733
5	3.5	2.6093	5.9004	22,613
6	3.8	2.3420	5.3519	22,851
Average	$\Delta H_{367°K.}$ = −22,697 ± 155 cal./mole			
Product:	99.7% *n*-propyl bromide, 0.3% isopropyl bromide			
		Propylene		
5	4.3	2.2060	4.4891	20,349
6	4.5	2.1240	4.3086	20,285
7	4.7	2.2919	4.5966	20,055
8	3.7	2.5200	5.0154	19,902
9	5.1	2.5750	5.1910	20,159
10	4.5	2.2300	4.4831	20,103
Average	$\Delta H_{367°K.}$ = −20,140 ± 240 cal./mole			
Product:	98.5% isopropyl bromide, 1.5% *n*-propyl bromide			

This equation assumes that the entropy change in reaction may be expressed by the symmetry number ratio, σ_n/σ_i. The heats of isomerization so obtained are −2,022 and −1,967 cal./mole at 250 and 275°, respectively; the average value is −1,995 cal./mole. The heat of hydrobromination of cyclopropane to give pure *n*-propyl bromide becomes −22,691 cal./mole and that of propylene to give isopropyl bromide is −20,170 cal./mole.

Using Pauling's table of covalent bond energies,[7] the heat of reaction of propylene and hydrogen bromide is calculated to be −12,600 cal./mole. A somewhat better value of −18,720 cal./mole is obtained from Kistiakowsky's rule for obtaining the heats of hydrohalogenation.[8]

Sufficient data are now available to permit one to calculate the heat of isomerization of cyclopropane to propylene



$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!CH_2 \longrightarrow CH_3{-}CH{=}CH_2$$

$$\Delta H = -4516 \text{ cal./mole}$$

Since the heat of formation of propylene is known to be 4,879 cal./mole,[9] the heat of formation of cyclopropane is 9,392 cal./mole. This latter is to be compared with a value of 12,310 cal./mole given by the combustion data of Thompson[10] and 19,900 cal./mole from that of Berthelot.[11]

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[6] L. G. Brouwer and J. P. Wibaut, *Rec. trav. chim.*, **53**, 1001 (1934).

[7] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 53.

[8] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, This Journal, **60**, 2764 (1938).

[9] E. J. Prosen and F. D. Rossini, *Bur. Stand. J. Research*, **36**, 296 (1946).

[10] J. Thompson, "Thermochemistry," Longmans, Green and Co., London, 1908, p. 189.

[11] M. Berthelot and C. Matignon, *Ann. chim. phys.*, [6] **30**, 547 (1893).

Summary

The vapor phase heats of hydrobromination of cyclopropane and propylene have been measured at 94°. A numerical value for the heat of formation of cyclopropane has been calculated by applying these data, the known heat of formation of propylene, and an estimate of the heat of isomerization of n-propyl bromide to isopropyl bromide.

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Magnetic Susceptibilities of the Halogen Derivatives of Methane[1]

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Introduction.—In conjunction with the calorimetric work being carried on in this Laboratory, a systematic research is being carried out on the magnetic susceptibilities of the simpler organic halogen compounds. In addition to shedding further light on the magnetic properties of these compounds, it is hoped that as the work progresses a correlation between the change of susceptibility and the heat of a reaction will become apparent. It is the intention of this paper to present the experimental data for six mixed halogenomethanes and to summarize and present a correlation of the magnetic susceptibilities of the seventy halogenated derivatives of methane.

Experimental.—Magnetic susceptibilities of the following compounds have been measured: $CClBrH_2$, $CHBrCl_2$, $CHClBr_2$, $CBrCl_3$, CBr_2Cl_2 and $CClF_3$. The five chlorobromomethanes were distilled in an efficient column packed with glass helices in order to remove any trace of paramagnetic impurities. Freezing points and an estimation of purity of the compounds were obtained from the time–temperature freezing curves using an apparatus similar to that of the National Bureau of Standards.[2] The curves were analyzed according to their procedure. Refractive indices at 20 and 25° were also measured.

The magnetic susceptibilities of the chlorobromomethanes were measured by means of the Quincke method.[3] A field strength maximum of about 20,000 oersteds was used. This produced a depression in liquid level in the Quincke tube of about one millimeter. Carefully purified benzene ($\chi = 0.702$)[4] was used as standard for these measurements. The susceptibility of $CClF_3$ was measured by means of a modification of the Quincke method using a high pressure container.[5] Unfortunately at room temperature the liquid is only a few degrees below its critical temperature. Considerable difficulty was encountered in observing the meniscus. For this reason the value of susceptibility obtained for this compound is subject to considerable uncertainty. The experimental results are given in Table I. With these results and values of susceptibility from other sources, experimental data are now available for fourteen of the fifteen possible chlorobromo derivatives of methane, for all but five of the fluoro-chloro derivatives and for all the iodo derivatives.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF SOME HALOGENATED METHANES

Compound	χ_M expt.	$n^{20}D$	$n^{25}D$	t_{f0}, °C.	Purity, mole %
C_6H_6[a]		1.5007	1.4975	5.5	99.65
$CClBrH_2$	55.0 ± 0.6	1.4842	1.4811	−90	97.9
$CHBrCl_2$	66.3 ± 0.3	1.4979	1.4951	−57.1	97.9
$CHClBr_2$	75.1 ± 0.4	1.5478	1.5449	−30.0	98.4
$CBrCl_3$	73.1 ± 0.7	1.5063	1.5034	− 5.6	98.9
CBr_2Cl_2	81.1 ± 0.4		1.5499	22.7	98.9
$CClF_3$	45.3 ± 1.5				

[a] Used as standard ($\chi = 0.702$).

Correlation of Data.—With the aid of these data various correlations have been examined in an effort to determine what factors must be considered to reproduce the experimental results in a satisfactory manner. The first correlation considered is one of atomic increments only. Values of the increments for this correlation were calculated from the experimental data by the method of least squares in order to give the best possible fit to the data. However, the average deviation was then considerably larger than the maximum probable error of the experimental values. Other methods of correlation are those of Pascal,[6] Gray and Cruickshank[7] and Anantakrishnan.[8] Although these correlations contain terms in addition to atomic increments, they may be reduced for all practical purposes to an atomic

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* Harvard University Ph.D. 1936.

[1] This work was supported by Contract N6onr-231, Task Order VI, with the Office of Naval Research, United States Navy. Presented before the Symposium on Fluorine Chemistry, 116th Meeting of the American Chemical Society, Atlantic City, N. J., September 18-23, 1949.

[2] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, R. P. 1676 (1945).

[3] G. Quincke, *Ann. Physik*, **24**, 347 (1885); **34**, 401 (1888).

[4] The factor -1×10^{-6} is to be understood with all values of magnetic susceptibility and increments of susceptibility given in this paper.

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[7] F. W. Gray and J. H. Cruickshank, *Trans. Faraday Soc.*, **31** 1491 (1935).

[8] S. V. Anantakrishnan, *Proc. Ind. Acad. Sci.*, **21A**, 114 (1945).