The results are summarized in Table II.

The present value of -20,430 for the heat of hydrobromination of propylene agrees well with the value of -20,140 previously reported.² The value of -25,790 cal./mole for the heat of hydrobromi-

nation of cyclopropane is 3100 cal. more exothermic than the value previously obtained. We believe that the earlier experiments were in error due possibly to not achieving complete equilibrium on the

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catalyst.

REACTION HEATS OF ORGANIC HALOGEN COMPOUNDS. IX. THE CATALYTIC HYDROGENATION OF VINYL AND PER-FLUOROVINYL BROMIDE¹

By J. R. Lacher, A. Kianpour P. Montgomery, H. Knedler and J. D. Park

Department of Chemistry, University of Colorado, Boulder, Colorado Received April 5, 1957

The present paper of this series² deals with the catalytic hydrogenation of vinyl bromide and perfluorovinyl bromide. In the case of vinyl bromide, the reaction was quantitative, and calorimetric measurements could be carried out. In the case of the perfluoro compound, the activity of the catalyst varied. Initially the catalyst was sufficiently active to replace the bromine and saturate the double bond. With increasing use, it would continue to replace the bromine, but it would become less effective in saturating the double bond. Accurate calorimetric data could not be obtained.

Experimental Details.—Vinyl bromide was purchased from the Matheson Company, and perfluorovinyl bromide was prepared according to the method described by Haszeldine.³ The compounds were purified in a high temperature Podbielniak distillation column. Since it was necessary for them to be completely free of air, the distillation was carried out in an atmosphere of nitrogen, which was removed by the following procedure. (The cylinder containing the compound was cooled to -78° in a Dry Iceisopropyl alcohol bath, evacuated for 15 minutes, and then allowed to warm up to room temperature. It was placed on a shaker for 15 minutes, then cooled down to -78° again.) This procedure was repeated until a purity of >99% was obtained. Purity was determined by means of a double beam infrared spectrometer with sodium chloride prism and by chromatographic gas phase analysis.

touche beam initiated spectrometer with solutin enformed prism and by chromatographic gas phase analysis. The catalyst used consisted of 2.5% by weight of palladium-on-carbon. The carbon was sized to pass a 6- and be retained on a 14-mesh screen. In order to remove sulfur from the carbon, it was first washed with 10% hydrochloric acid and then heated in a stream of hydrogen at 400° for five days. The purified carbon was cooled to room temperature and poured directly into a dilute palladium chloride solution. Reduction took place immediately, and the metal produced a silvery coating on the carbon. The catalyst was dried *in vacuo*; when drying was complete, the vacuum was broken with hydrogen, which was passed over the catalyst for 24 hours at 250°.

In making a run, vinyl bromide and hydrogen in excess were sent to the catalyst chamber at a constant rate. An examination of the product gases by infrared and vapor phase chromatographic equipment showed that the following reaction was taking place quantitatively.

$CH_2 = CHBr + 2H_2 \longrightarrow CH_3 - CH_3 + HBr$

In order to determine the amount of reaction which took place in a given time, the product gases were sent to an absorption tower. The hydrobromic acid formed was titrated with 0.05 N potassium hydroxide. The experimental data obtained are given in Table I.

| | TABLE 1 | |
|--|------------------------------|--------------------------|
| HEAT OF HYDRO | GENATION OF VINYL | BROMIDE, 128° |
| HBr flow, moles/min. × 10 ⁴ | Energy rate, cal./min. | $- \Delta H,$ kcal./mole |
| 2.115 | 10.344 | 48.86 |
| 1.628 | 7.823 | 48.02 |
| 1.950 | 9.638 | 49.43 |
| 1.475 | 7.158 | 48.53 |
| 1.635 | 7.812 | 47.78 |
| 1.6125 | 7.790 | 48.31 |
| 1.598 | 7.631 | 47.70 |
| | -•∆ <i>H</i> | av. = 48.38 |

Twice the stand. dev. from the mean $\pm 0.94\%$

When perfluorovinyl bromide was used, the reaction appeared to give CF_2H-CFH_2 quantitatively, and the heat liberated was about 56,000 cal. per mole. On succeeding runs, the heat liberated per mole fell off, and an examination of the product gases showed the presence of a considerable amount of CF_2 -CFH. In one of the latter experiments, this olefin was produced in 95% yield, and the heat liberated was 26,000 cal./mole. The catalyst activity was not reproducible; thus, reliable thermochemical measurements could not be made.

In the reaction between hydrogen and vinyl bromide, sufficient heat capacity data are available to permit a calculation of the temperature variation of ΔH . The heat capacities for H₂, C₂H₈ and HBr have been tabulated by the Bureau of Standards.⁴ R. E. Richards⁶ has calculated the heat capacity of CH₂==CBrH. With this information, the reaction at 25° was calculated to be less exothermic by 772 cal. The correct ΔH is entered in Table II. The heats of formation of gaseous HBr and C₂H₆ are given as -8,660 and -20,266 cal. per mole, respectively.⁴ Using this information, we calculated the heat of formation of vinyl bromide. The result is included as the second entry in Table II. We have found no literature value for the heat of formation of vinyl bromide.

TABLE II

HEATS OF REACTION AT 25°

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| Reaction | cal./mole |
|---|-----------|
| $C_2H_3Br + 2H_2 \rightarrow C_2H_6 + HBr$ | 47,610 |
| $2C(gr) + 3/2H_2 + 1/2Br_2(l) \rightarrow C_2H_8Br$ | -18,680 |
| $CH_2 = CHBr + H_2 \rightarrow CH_2 = CH_2 + HBr$ | 14.880 |

However, if we assume that the heat of addition of hydrogen to vinyl bromide is the same as it is to vinyl chloride,⁶

(4) "Selected Values of Properties of Hydrocarbons," A.P.I. Research Project 44, National Bureau of Standards.

(5) R. E. Richards, J. Chem. Soc., 1931 (1948).

(6) J. R. Lacher, A. Kianpour, F. Oetting and J. D. Park, Trans. Faraday Soc., 52 (1956).

⁽¹⁾ This research is being supported by United States Air Force Research and Development Command, Contract Number AF 18(600)-1151.

⁽²⁾ For the previous paper see J. R. Lacher, A. Kianpour and J. D. Park, THIS JOURNAL, 60, 1454 (1956).

⁽³⁾ R. N. Haszeldine, J. Chem. Soc., 4259 (1952).

$$CH_2 = CHBr + H_2 \longrightarrow CH_8 - CH_2Br$$
$$\Delta H = -34,570 \text{ cal./mole}$$

The value of -15.9 kcal./mole compares with the value of -13.0 given in reference 4. Linnett⁷ and co-workers have studied the equilibrium between ethylene, hydrogen bromide and ethyl bromide. From their data, they calculated the heat of formation of ethyl bromide to be -15.3 kcal. at 25°. The addition of hydrogen to vinyl bromide is apparently stepwise and involves, first, substitution of the bromine and then saturation of the double bond in ethylene. Since the heat of hydrogenation of ethylene is known,⁸ the heat involved in substituting the bromine may be calculated. The results are given in Table II. The value of -15.370 cal./mole is about 3000 cal. less exothermic than the corresponding reaction of vinyl chloride.⁵

(7) M. R. Lane, J. W. Linnett and H. G. Oswin, Proc. Roy. Soc. (London), **A216**, 361 (1953).

(8) G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, J. Am. Chem. Soc., **57**, 65 (1935).

POLAROGRAPHY OF THE FERRICYANIDE ION IN THE ABSENCE OF INERT ELECTROLYTE

By P. Kivalo

Finland Institute of Technology, Department of Chemistry, Helsinki, Finland

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The polarographic reduction of ferricyanide produces a well-defined diffusion current which is directly proportional to the concentration in various supporting electrolytes, e.g., 0.1 M KCl or NaClO₄.¹ The reduction starts at a positive potential referred to S.C.E. and is accompanied with



Fig. 1.—Polarograms of 1, 5 and 8 mM concentrations of ferricyanide obtained without supporting electrolyte and using a Leeds & Northrup Electrochemograph recording polarograph. The corresponding cell resistances are 8500, 2700 and 2000 ohms; $t^{1/em^{2/3}} = 1.84$.



Fig. 2.—Polarograms of 1 mM ferricyanide solutions obtained with a Radiometer Model PO3k recording polarograph at various concentrations of the supporting electrolyte; $t^{1/em^{2/3}} = 2.28$: Curve 1, 0 M NaClO₄; Curve 2, 0.005 M; Curve 3, 0.04 M; Curve 4, 0.05 M.

(1) J. J. Lingane and I. M. Kolthoff, J. Am. Chem. Soc., 61, 825 (1939).

a pronounced maximum which, however, is easily suppressed.

Frumkin and Florianovich² have recently reported to have found a "dip" in the diffusion plateau of the ferricyanide ion. The current is said to drop between -0.4 and -0.8 v. vs. S.C.E. for concentrations below 0.01 N and in the absence of inert electrolyte. The authors were able to observe only the fall in the current without a subsequent rise in it.

Since the polarographic reduction of ferricyanide is of particular interest from the point of view of a proposed reduction mechanism of certain other anions³ that produce minima in their diffusion plateaus (which, however, also show a subsequent rise in the current to the original diffusion value), its reinvestigation was deemed desirable.

In Fig. 1 polarograms of 1, 5 and 8 mM solutions of ferricyanide obtained in the absence of supporting electrolyte are shown. It is clearly seen that a very pronounced maximum starts the waves and that the maximum drops off between -0.5 and -0.6 v. vs S.C.E. Furthermore, the limiting currents are practically constant. The diffusion control of the current was tested using 1 mM concentration at -1.0 v. varying the height of the mercury column

| em. | 40 | 50 | 60 | 70 | 80 |
|----------------|----|------|----------|------|------|
| $\sqrt{h/h_0}$ | 1 | 1.12 | $1 \ 23$ | 1.32 | 1.41 |
| i/i_0 | 1 | 1.11 | 1.21 | 1.29 | 1.36 |

It may be mentioned that the maximum was present even at as low a concentration as 0.2 mmole per liter.

In the absence of inert electrolyte, the limiting current is lower than the "true" diffusion current owing to the migration current which in this case decreases the latter.⁴ Addition of supporting electrolyte should increase the limiting current. The results of these experiments are presented in Fig. 2. The concentration of the ferricyanide was 1 mmole per liter. Upon increasing the NaClO₄ concentration from 0 to 0.05 M the plateau current rose to a value which then remained practically constant and independent of further addition of the supporting electrolyte. At the same time it is seen that the maximum is suppressed and disappears above 0.05 M concentration of NaClO₄. An increase in the ferricyanide concentration again develops the maximum.

The diffusion current constant calculated from polarogram 4 in Fig. 2 gives a value of 1.84 in good agreement with the value reported by Meites.⁵ The relation i_{1}^{0}/i_{d} was here found to be 0.7 which agrees with the calculated value based on i_{1}^{0}/i_{d} = $1/1 + T_{-}^{0}$ where T_{-}^{0} is the anion transference number, assumed to be equal to 0.5.⁶

Based on the above findings the present author

(2) A. N. Frumkin and G. M. Florianovich, Doklady Akad. Nauk, S.S.S.R., 80, 907 (1951).

(3) P. Kivalo and H. A. Laitinen, J. Am. Chem. Soc., 77, 5205 (1955).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 122.

(5) L. Meites, J. Am. Chem. Soc., 73, 1581 (1951).
(6) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., New York, N. Y., 1952, p. 166.