[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Reaction Heats of Organic Fluorine Compounds. I. Apparatus and the Heat of Chlorination of Tetrafluoroethylene[1]

BY J. R. LACHER, J. J. MCKINLEY, C. M. SNOW, L. MICHEL, G. NELSON AND J. D. PARK

Since the pioneering work of Swarts[2] very few thermochemical data on organic fluorine compounds have been obtained. Wartenberg and Schütte,[3] using elemental fluorine, measured the heat of formation of carbon tetrafluoride. However, since higher fluorides of carbon were probably formed in the reaction, the actual value for the heat may be greater than that reported. In the case of organic chlorine and bromine compounds the situation is not much better. Kistiakowsky and co-workers[4] have measured the heat of chlorination of ethylene and the heats of bromination of several simple olefins. The heats of combustion of some chloro derivatives of benzene have been measured recently by Hubbard, Knowlton and Huffman,[5] and by L. Smith.[5a]

Thermochemical data are necessary for the thermodynamic and statistical calculations of equilibrium constants. They give valuable information concerning the nature of a chemical bond and are useful in the design of process equipment. Accordingly a long range program is being undertaken to measure directly the heats of vapor phase reactions of organic halogen compounds. The calorimeter constructed for this purpose possesses the flow characteristics of the one described by Kistiakowsky and co-workers[6] but it operates at constant temperature in a manner similar to those described by Kraus,[7] Tong and Kenyon[8] and Coon and Daniels.[9]

The operation of the calorimeter is simple in principle and is essentially one of substitution. The gaseous reactants are led into a catalyst chamber where the reaction takes place, and the products pass through a heat exchanger out to a collecting system. A volatile liquid surrounding the heat exchanger absorbs the heat of reaction. At the same time nitrogen is bubbled through this liquid thereby removing heat by vaporization at such a rate as to maintain the temperature constant. When equilibrium has been established on the catalyst, the flow of reactants is stopped and direct electrical heating substituted for that due to the reaction, the nitrogen flow remaining constant. The electrical energy required is then equal to that produced by the reaction. From the rate of energy input and the rate of formation of product, the heat of reaction can be calculated.

Apparatus.—The essential parts of the calorimeter are shown in Fig. 1. The reaction chamber was machined from a cylinder of monel metal 1″ × 10″. The chamber is charged with catalyst through a cap at the bottom which is soldered in place. The reactants are led into the catalyst chamber through two concentric tubes and mix at the top of the catalyst bed. The products are taken from the bottom and led through a heat exchanger made of six feet of $^1/_4$″ copper tubing and thence to the collecting system. This chamber and accessories were suspended from a circular brass plate so that they could be immersed in a 960-ml. wide-mouth dewar flask. This dewar contained chlorobenzene and the heat of reaction was transferred to it. In order to remove heat from the system, dry nitrogen was bubbled through the chlorobenzene and was dispersed by means of a size B fritted glass distributor. The metal-to-glass joint was below the liquid level in the dewar. The waste nitrogen and chlorobenzene were led out through a $^1/_2$″ thin-walled brass tube. The upper part served as a condenser to return most of the chlorobenzene.

A bare nichrome heater, made of number 32 wire and having a resistance of 42 ohms, was fastened to the glass distributor tube. The potential and current leads were led out through the nitrogen line. The heating current was supplied by four lead storage batteries in series. During a run the batteries were charged at a slightly lower rate than the power requirement.[10] In this way very constant currents were obtained. The electrical energy input was obtained by measuring the e. m. f. across a standard resistance in series with the heater and also the potential drop across the heater. A Rubicon type B potentiometer and high sensitivity galvanometer were used for these measurements. In case of the potential drop across the heater, a voltage divider was necessary.

A 12-junction copper–constantan thermel was used to measure the temperature differential between the chlorobenzene and the oil-bath in which the whole assembly was immersed. One end of the thermel was located in a well made of telescopic iron tubing and extending about midway into the

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[1] Presented before the Division of Inorganic and Physical Chemistry, 114th meeting of the American Chemical Society, Portland, Oregon, Sept. 13–17, 1948.

[2] F. Swarts, *J. chim. phys.*, **17**, 3 (1919); W. Swietoslawski and J. Bobinska, *ibid.*, **24**, 545 (1927).

[3] H. Wartenberg and R. Schütte, *Z. anorg. Chem.*, **211**, 222 (1933).

[4] J. B. Conn, G. B. Kistiakowsky and E. Smith, THIS JOURNAL, **60**, 2764 (1938).

[5] W. N. Hubbard, J. W. Knowlton and H. M. Huffman, to be published.

[5a] L. Smith, "The Svedberg" (Mem. Vol.), 352 (1944).

[6] G. B. Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935).

[7] C. A. Kraus and J. A. Riddenhoff, *ibid.*, **56**, 79 (1934).

[8] L. K. J. Tong and W. O. Kenyon, *ibid.*, **67**, 1278 (1945).

[9] E. D. Coon and F. Daniels, *J. Phys. Chem.*, **37**, 1 (1933).

[10] We wish to thank Dr. D. M. Stull, of the Dow Chemical Co., Midland, Michigan for suggesting this to us.

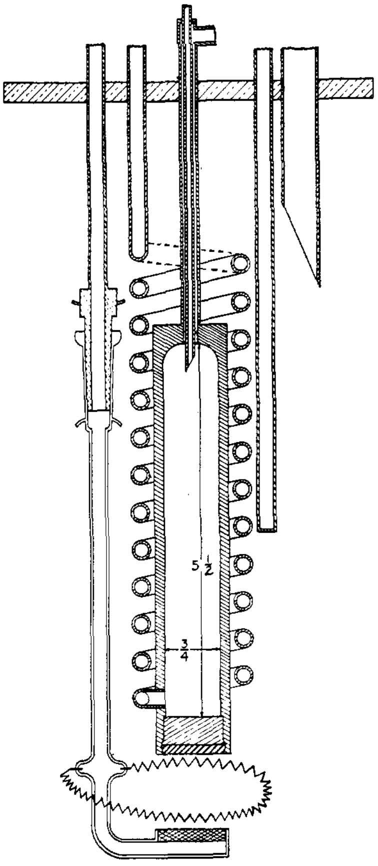

Fig. 1.

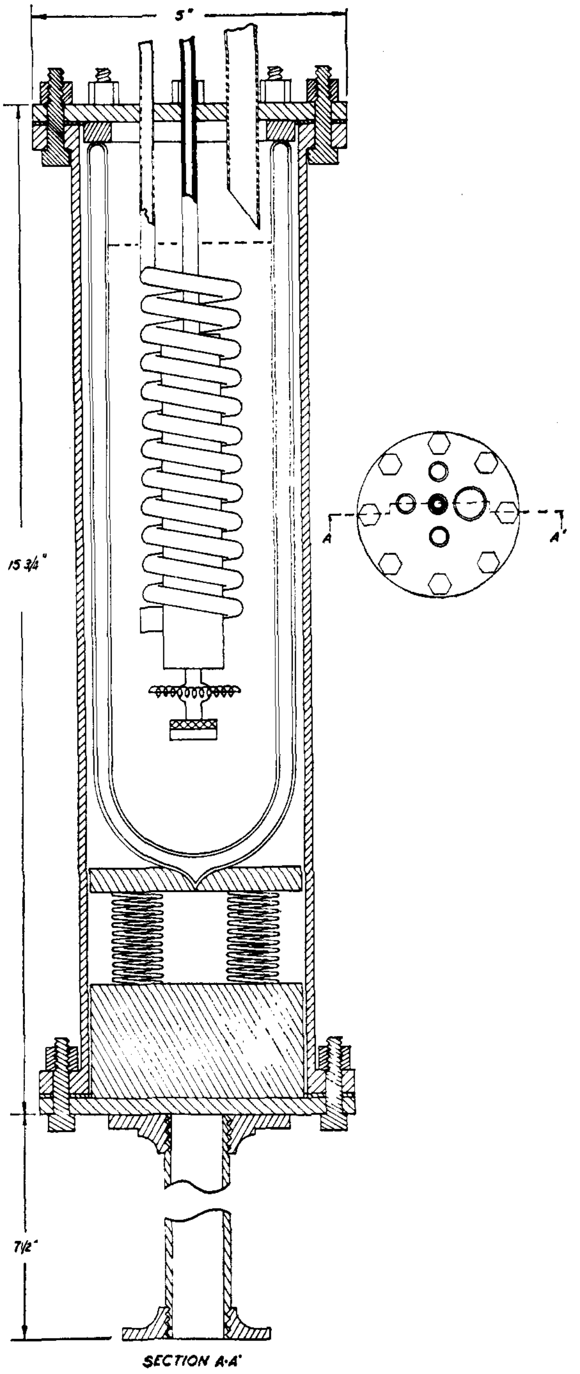

Fig. 2.

chlorobenzene (shown in Fig. 1). The other end was located in the surrounding oil-bath. By means of a suitable switching arrangement, the e. m. f. of the thermel could be read on a potentiometer or placed directly on the high sensitivity galvanometer or on a Rubicon photoelectric galvanometer depending on the sensitivity required. When the reacting system had reached a steady state during a run, the e. m. f. of the thermel would fluctuate about zero.

The 960 ml. wide-mouth dewar containing the chlorobenzene was tightly contained in a brass cylinder as shown diagrammatically in Fig. 2. The dewar rested on a platform supported by three stiff metal springs. The bottom plate of the brass cylinder was fitted with a $^3/_4''$ pipe flange and a pipe extension in order that the assembly could be supported from the bottom of the thermostat. The top plate held the catalyst chamber and auxiliary equipment. It was tightly bolted on using sheet gaskets. The gases entering the calorimeter were brought to temperature by passing them through heat exchangers made of $^1/_4''$ copper tubing immersed in the oil thermostat.

The thermostat consisted of a cubical iron tank containing 110 gallons of lubricating oil. It was thoroughly insulated with "Sil-o-cell" brick and is designed for operation up to 200°. Continuous heating was supplied by nichrome elements evenly spaced in the top, bottom and sides of the thermostat. Intermediate heating was obtained by four nichrome immersion heaters. These surround the propeller shafts located in each of the four corner "wells" in the tank. The temperature was controlled by a d. c. bridge-photoelectric cell system. The temperature sensing element was a thermister (type D 169,604), developed by the Bell Telephone

Laboratories and formed one arm of the bridge. When the heating current was on, a reversible "Telechron" increased the voltage of the "Variac" controlling the heaters. On the other hand, when this current was off, this voltage was slowly decreased. The system sought a condition where the current was on half the time. A 25-ohm platinum resistance thermometer and Mueller bridge were used to measure temperatures. No gradients could be measured in the bath while operating at 80° and temperature fluctuations were less than 0.001° over a period of several hours.

The flow rate of the nitrogen used to cool the chlorobenzene was carefully controlled. Nitrogen from a commercial cylinder was supplied to a Moore[11] "Nullmatic" pressure regulator at a pressure of six pounds by means of a standard reducing valve. It then passed to an adjustable head overflow tower, buffer tank and through an ordinary capillary flow meter. Several manometers were included in the line for observation of back pressures. It was necessary only to maintain a constant nitrogen flow once the catalyst had reached a steady state and while the electrical energy balance was being made. A differential of more than 100 mm. across the flow meter could be held constant to 0.2 mm. during the course of a run.

Experimental

Hydrogenation of Cyclohexene.—The cyclohexene was prepared from commercial cyclohexanol after the methods of Kistiakowsky, *et al.*,[12] and Coleman and Johnstone.[13] The crude cyclohexene obtained was distilled twice in a vacuum-jacketed column packed with glass helices, having a total condensation head and a variable magnetic take-off. The middle fraction consisting of 60% of the crude material was used. The refractive index, $n^{20}\text{D}$ 1.4466, of this product was in close agreement with that of Kistiakowsky.[11] The catalyst used for hydrogenation was platinum black on asbestos found satisfactory by Kistiakowsky[11] and prepared by the method of Shiels.[14]

The hydrogen, from a commercial cylinder, was led through heated copper and a "Drierite" and "Ascarite" tower. It then passed through a Moore pressure regulator, Moore constant flow regulator, precatalyst chamber and to a valve system whereby it could be sent either directly to the calorimeter or to a gas-saturating device containing cyclohexene. In this cyclohexene bubbler, the hydrogen becomes partially saturated. The temperature was so controlled that hydrogen was in excess when the mixture was led to the calorimeter. The amount of cyclohexane formed was determined by condensing it from the excess hydrogen and weighing the product. In order to test the effectiveness of the collecting system used, the hydrogen stream was saturated with cyclohexane in auxiliary experiments. The amount of cyclohexane recovered was compared with that removed by the hydrogen from a weighed sample. The results, shown in Table I, indicate that the per cent. loss decreases with increasing size of the sample. We were not able to recover quantitatively all of the cyclohexane, due apparently to a small initial loss by entrainment which was stopped when the glass wool in the trap became matted with crystals of cyclohexane.

Table I

Recovery of Cyclohexane from a Hydrogen Stream

Grams of cyclohexane Lost from saturator	Grams of cyclohexane Condensed in collector	Loss, %
2.998	2.930	2.3
3.352	3.290	1.8
5.144	5.134	0.2
6.334	6.296	0.6

In making a calorimetric run, hydrogen was first passed through the calorimeter and collecting system to flush out air. An arbitrary flow of nitrogen through the chlorobenzene was chosen and sufficient electrical energy supplied to establish isothermal conditions. The amount of energy required was independent of the flow rate of hydrogen through the system. After a balance was obtained, the electrical heating was discontinued and the hydrogen was sent to the cyclohexene bubbler. The rate of reaction on the catalyst was adjusted to again give isothermal conditions. After collecting a sample, the flow of reactants was stopped and the electrical energy required for the same nitrogen flow was again measured. The final results obtained are shown in Table II. The second column gives the time during which the product was collected. The weight was increased steadily from 2.8 g. in sample 1 to 6.6 g. in sample 5. The amount of cyclohexane formed in moles per minute was obtained from the weight of the sample collected and the time. Owing to the fact that complete conversion of the cyclohexene did not occur on the catalyst, a correction was applied. The amount of cyclohexene present in the product was determined by measurement of refractive index. The catalyst slowly lost activity during these runs and the conversion which was initially 99% fell to 93%. The heat of hydrogenation in calories per mole was obtained by dividing the heat input in calories per minute by the rate of formation of cyclohexane in moles per minute. The per cent. deviations in the values so obtained from that found by Kistiakowsky[12] are shown in the last column. It is apparent that, if a sufficiently large sample is collected, the results agree to within a per cent. Since this is the accuracy desired, it was not thought worthwhile to .improve the collecting system further.

Table II

Hydrogenation of Cyclohexene at 78°

Run	Sampling time, min.	Cyclohexane formed[a] moles/min. × 10^{+4}	Energy input cal./min.	$-\Delta H_{351°}$, cal./mole	% Deviation from 28,592
1	59.0	5.713	16.829	29,457	+3.0
2	60.0	9.384	28.179	30,029	+5.0
3	63.0	9.635	28.141	29,207	+2.1
4	60.04	10.267	29.728	28,955	+1.3
5	72.0	10.130	29.247	28,872	+0.97

[a] Corrected for unreacted cyclohexene.

Heat of Formation of Hydrogen Chloride.—Commercial hydrogen was purified by passing it over calcium chloride, hot copper gauze, and phosphorus pentoxide before entering the "Nullmatic" pressure regulating valve. This resulted in water-free hydrogen at the exit of the valve. The gas then went through a flow meter, a pre-catalyst chamber (palladium-on-carbon) and directly to the calorimeter. It was found, on treating this hydrogen with chlorine, that considerable amounts of water were discharged from the calorimeter indicating that either the hydrogen or chlorine contained oxygen which reacted in the palladium–carbon catalyst chamber. When two pre-catalyst chambers were installed in the hydrogen line and followed by three phosphorus pentoxide-drying tubes, very little, if any, water was formed in the main catalyst chamber.

Earlier work in this Laboratory showed that commercial

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(11) Manufactured by Moore Products Co., Philadelphia, Pa.

(12) G. B. Kistiakowsky, *et al.*, This Journal, **58**, 137 (1936).

(13) Coleman and Johnstone, "Organic Synthesis," Coll. Vol. I, p. 183.

(14) D. O. Shiels, *J. Phys. Chem.*, **33**, 1167 (1929).

chlorine must be purified by a low temperature distillation before it could be used in calorimetric studies. Chlorine[15] from Matheson gave satisfactory results without further purification and was used in all experiments reported here. The cylinder was maintained at 0° to minimize pressure fluctuations. The chlorine was dried over phosphorus pentoxide and run through a suitable series of needle valves, constant pressure overflow tower to a capillary glass tube flow-meter. Several manometers were in the line to indicate back pressures. From the flow-meter, the chlorine could be sent either directly to the calorimeter or to a potassium hydroxide absorption tower.

The catalyst was prepared on "Columbia" activated carbon sized to pass a no. 6 and be retained on no. 20 screens. A suspension of $PdCl_2 \cdot 2H_2O$ in carbon tetrachloride was poured over the carbon (10% by weight of the chloride based on carbon was used). The solvent was removed by heating at 120° and hydrogen was used to reduce palladium chloride to palladium at the same temperature. The catalyst was then heated to 200° *in vacuo* for three hours. Upon cooling, nitrogen was admitted and the catalyst transferred to the calorimeter.

In making a run the flow rates of hydrogen and chlorine were arbitrarily chosen with hydrogen being in excess. The heat of reaction was removed by adjusting the nitrogen flow. One and one-half to two hours were required for an isothermal balance. After the balance had been obtained, the exit flow was sent through a collecting tower of 6 *N* potassium iodide to determine the amount of unreacted chlorine. The flow of chlorine was then directed from the calorimeter to a waste line and the hydrogen flow continued through the catalyst chamber for ten to fifteen minutes, electrical energy being substituted for that produced by the reaction. The hydrogen flow was then shut off and the nitrogen flow balanced with electrical energy. The chlorine was then sent through a collecting tower of 3 *N* potassium hydroxide for a definite time to determine the input of chlorine to the calorimeter. The same chlorine flow was used throughout. The amount of chlorine in the sample was determined, after reduction with hydrogen peroxide, by adding an excess of silver nitrate and back-titrating with potassium thiocyanate in the usual way. The analytical procedure was shown to average 0.2% low by analyzing weighed samples of chlorine dissolved in potassium hydroxide.

The results obtained are shown in Table III. Only those runs are included which were carried out after the installation of two pre-catalyst chambers and phosphorus pentoxide drying towers in the hydrogen line. Rossini[16] burned hydrogen and chlorine at constant pressure in a flame calorimeter and obtained heats of formation of HCl(g) to be 22,063 and 22,060 calories per mole at 25 and 18°, respectively. From heat capacity data, the heat of reaction is estimated to be −22,120 calories at 90°. The per cent. deviation of the values listed in Table III from this are given in the last column. The agreement is better than one per cent.

TABLE III

HEAT OF FORMATION OF HYDROGEN CHLORIDE AT 90°

H_2 flow, moles/min. $\times 10^{+4}$	Cl_2 flow, moles/min. $\times 10^{+4}$	% Cl_2 reacted	Energy rate, cal./min.	$-\Delta H$, cal./mole of HCl	% Deviation from −22,120
6.514	3.333	98.92	14.5574	22,077	−0.2
6.481	3.8477	98.42	16.7869	22,164	+ .2
6.481	3.770	97.99	16.4164	22,246	+ .6

Chlorination of Tetrafluoroethylene.—Matheson chlorine was used in all experiments. The tetrafluoroethylene,[17] taken from a cylinder, was passed through a purification train consisting of concentrated sulfuric acid, 10% sodium hydroxide, water, and a calcium chloride drying tower followed by phosphorus pentoxide. An ordinary capillary glass flow meter indicated the flow and the gas was then sent directly to the calorimeter.

The catalyst used was 10% by weight of ferric chloride on "Columbia" activated carbon. The carbon was sized to go through no. 6 and retained on no. 20 screens. It was then activated by heating under vacuum at 250°, cooled and mixed with iron powder obtained by reduction. After charging it in the calorimeter, the iron was converted to the chloride by passing chlorine through the chamber for several hours. When no further reaction took place, as indicated by the heat generated, the conversion was assumed to be complete. Antimony chloride catalyst, prepared in the same way, will quantitatively chlorinate the tetrafluorethylene at room temperature.

In making a run, the olefin was used in excess and the amount of reaction was taken as being equal to the amount of chlorine consumed. If the catalyst was active and if the reactants were sufficiently pure, neither chlorine nor hydrogen chloride could be detected in the product gases with fresh starch-potassium iodide and moist litmus paper. Since the carbon catalyst adsorbs considerable amounts of the gases in reaching a steady state, the flows of both reactants were carefully controlled. In starting a run, the flow of olefin and chlorine were arbitrarily set and the ni-

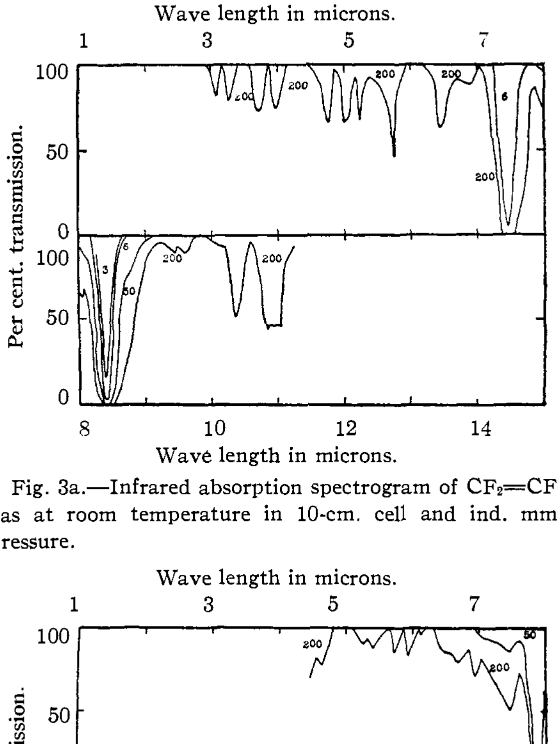

Fig. 3a.—Infrared absorption spectrogram of $CF_2{=\!=}CF_2$ gas at room temperature in 10-cm. cell and ind. mm. pressure.

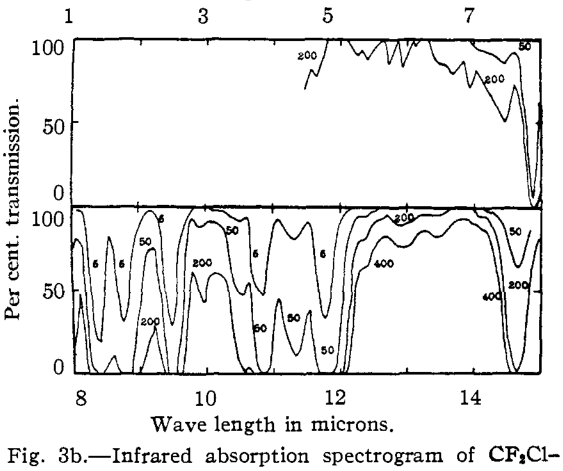

Fig. 3b.—Infrared absorption spectrogram of CF_2Cl–CF_2Cl gas at room temperature in 10-cm. cell at ind. mm. pressure.

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[15] Matheson Co., Inc., Purity 99.5%.

[16] F. D. Rossini, *Bur. Stand. J. Research*, **8**, 119 (1932).

[17] The tetrafluoroethylene was furnished us through the kindness of the Jackson Laboratory, du Pont Co., Wilmington, Del.

trogen flow adjusted to give isothermal conditions at a steady state. This meant that the energy balance was obtained only at the end of the run. While this energy balance was being taken, the chlorine was directed to the potassium hydroxide tower and a sample collected at the same flow rate as used in the reaction. The amount of chlorine in the sample was determined as described previously.

The products resulting while the calorimeter was at a steady state were condensed in a trap at −80°. Infrared absorption spectra[18] were taken on the first, middle and last fraction of the sample. By comparing the curves so obtained with those given by the pure olefin and dichloride, it was shown that no appreciable amounts of disproportionation or degradation reactions took place on the catalyst. The curves for the pure materials are given in Figs. 3a and 3b.

The data obtained on the chlorination of tetrafluoroethylene are summarized in Table IV. The results are quite reproducible and show that the heat of chlorination of this olefin is considerably greater than that of ethylene which is 43,600 calories.[3]

Table IV

Heat of Chlorination of Tetrafluoroethylene at 90°

Run no.	Olefin flow, moles/min. × 10^{+4}	Chlorine flow, moles/min. × 10^4	Energy rate, cal./min.	$-\Delta H$, cal./mole
29	7.60	5.101	29.22	57,283
30[a]	8.25	5.77	33.04	57,262
31	9.04	6.071	34.86	57,420
32	6.93	6.109	35.02	57,325

[a] The chlorine flow was read off the flow meter in this case rather than being determined by direct analysis.

Acknowledgment.—This work was made possible by a grant from the Research Corporation of New York. A special grant from the Regents of the University of Colorado made possible the purchasing of the infrared spectrometer. We wish to thank Mr. C. Walden and K. Lea for assistance in operating the calorimeter and infrared spectrometer. Mr. D. K. Vail assisted in the preparation of some of the compounds used and Mrs. C. M. Snow carried out the analysis for chlorine. Mr. E. Holderby constructed the calorimeter proper and most of the accessories in the shops of the University of Colorado.

Summary

An isothermal constant-flow calorimeter is described which is suitable for measuring heats of vapor phase reactions at temperatures up to 90°. By measuring the heat of hydrogenation of cyclohexene and the heat of formation of hydrogen chloride and comparing the results obtained with data existing in the literature, the calorimeter was shown to give heats of reactions to an accuracy of one per cent. The vapor phase heat of chlorination of tetrafluoroethylene was measured to be $\Delta H = -57,322 \pm 200$ calories per mole at 90°.

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[18] The instrument is a model 12B manufactured by the Perkin-Elmer Corporation of Glennbrook, Conn.

[Contribution from the University of Colorado]

Reaction Heats of Organic Fluorine Compounds. II. The Vapor Phase Heats of Chlorination of Some Simple Fluoroölefins[1,2]

By J. R. Lacher, J. J. McKinley, C. Walden, K. Lea and J. D. Park

In the first paper of this series[2] an isothermal constant flow calorimeter was described. The performance of the equipment was determined by measuring the heat of hydrogenation of cyclohexene and the heat of formation of gaseous hydrogen chloride. New data on the vapor phase chlorination of tetrafluoroethylene were also presented. The present paper deals with the vapor phase heats of chlorination of trifluorochloroethylene, 1,1-dichloro-2,2-difluoroethylene, perfluoropropene and perfluorocyclobutene.

Preparation of Compounds.—The trifluorochloroethylene[3] was purified by a low temperature distillation in a vacuum-jacketed column packed with glass helices using a magnetic take-off head and a reflux ratio greater than 5 to 1. The still head was cooled by circulating a carbon tetrachloride–chloroform–Dry Ice mixture from a reservoir at such a rate as to maintain about a 20° differential between the still head and the boiling point of the olefin. A forecut was discarded and the center fraction having a boiling point variation of less than 0.1° was collected and stored in a steel cylinder for subsequent use. The infrared absorption spectrum is shown in Fig. 1a. Using auxiliary equipment, a sample of the chlorine adduct of trifluorochloroethylene was prepared. A flow system identical with that used in the calorimeter was employed and the chlorination was carried out in the presence of ferric chloride–impregnated carbon catalyst previously described. After distillation, the product, 1,1,2-trifluoro-1,2,2-trichloroethane, gave an absorption spectrum as shown in Fig. 1b. The isomer of this compound,[3] 1,1,1-trifluoro-2,2,2-trichloroethane, gives an absorption spectrum as shown in Fig. 1c. By studying the spectrum of the product formed in an actual calorimetric run, it was concluded that little or no disproportionation occurred on the catalyst. However, if the olefin was not pure, the absorption spectrum of the calorimeter product was not a combination of those shown in Figs. 1a and 1b. Instead, anomalous absorption peaks appeared at 6.50 and 11.77 μ, hydrochloric acid was in the effluent gases and the heat of reaction was low. The trouble was overcome by scrubbing the olefin in the purification train described in Paper I of this series.[2] The 1,1-dichloro-2,2-difluoroethylene and perfluoropropene[3] were passed through the purification train and then sent directly to the calorimeter. The infrared absorption spectra of 1,1-dichloro-2,2-difluoroethylene and its chlorine adduct, 1,1,1,2-tetrachloro-2,2-

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[1] Presented before the Division of Inorganic and Physical Chemistry, 114th Meeting of the American Chemical Society, Portland, Oregon, September 13-17, 1948.

[2] J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson and J. D. Park, This Journal, **71**, 1330 (1949).

[3] A generous sample was supplied us through the couretsy of the Jackson Laboratory, du Pont Co., Wilmington, Delaware.