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HEAT OF REACTION OF CHLORINE TRIFLUORIDE WITH WATER

G. D. Oliver and J. W. Grisard

Work Supervised by
W. Davis, Jr.
Laboratory Division
F. W. Hurd, Superintendent

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Since nontechnical and nonessential prefatory material has been deleted, the first page of the report is page 4.

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ABSTRACT

A measurement of the heat liberated when chlorine trifluoride reacts with water has been made in a simple Dewar calorimeter. The chlorine trifluoride vapor was bubbled into approximately 20 moles of water; the weight of material used, heat equivalent of the calorimeter, and the temperature rise of the water and calorimeter were determined. From these data an average value for the heat of reaction was calculated to be 81.0 ± 0.4 kcal/mole. Analysis of the reaction solution and evolved gas showed the following to be present: hydrogen fluoride, hydrogen chloride, chlorine, oxygen, and probably oxygen-chlorine compounds.

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HEAT OF REACTION OF CHLORINE TRIFLUORIDE WITH WATER

SINCE all products of this reaction are not known, the heat of reaction cannot be calculated by a combination of known reactions; therefore, by following a simple procedure a practical value for the heat of reaction was measured. Preliminary experiments showed that the heat of reaction could be determined by passing a small stream of vapor into a volume of water and measuring the resulting temperature rise. For the reason stated above, the usual corrections for heats of dilution and solution were not made on the measured value.

EXPERIMENTAL

Materials. The samples of chlorine trifluoride were taken from the batch of previously described material (1) which had a purity of 99.96 mole per cent, when first prepared. The sample for the reactions of series C was frozen with dry ice before use each day and the volatile material was pumped off. Air-saturated distilled water was used in all experiments.

Apparatus. A platinum resistance thermometer certified by the National Bureau of Standards, an electric heater, and a chimney stirrer were assembled inside a silvered glass Dewar, of 400 ml. capacity, which was clamped to a supporting cover plate of Fluorothene plastic. The resistance thermometer was mounted through a hole in the cover plate at a point midway between the wall of the Dewar and stirrer chimney.

The heater was made of B. & S. No. 34 constantan wire and coiled around the thin copper chimney. Thin-walled monel tubing of 1/8 inch diameter was soldered to the chimney and extended through the cover plate to serve as a hanger for the chimney and as a protector for copper leadwires of the heater.

A section of rubber tubing placed in the cover plate and lubricated with Fluorothene grease was used as a gas-tight bearing for the 1/8 inch monel tubing stirrer shaft. The stirrer was chain driven at 360 rpm. by a constant speed motor. A strong downward circulation of water was obtained by adjusting the stirrer vanes midway in the chimney.

A heavy coating of Fluorothene wax was applied to the metal and glass surfaces inside the Dewar to prevent their reaction with the acid products. The wax was also used to obtain gas-tight seals at the cover plate.

Chlorine trifluoride vapor was delivered through 1/8 inch Fluorothene tubing to a point just below the stirrer vanes so that the vapor-liquid contact time would be as large as practicable. Similar tubes inserted through the cover plate were used to empty the reaction calorimeter and fill it with water, and to vent the reaction gases, which were collected over water in an inverted graduate. The assembled calorimeter was suspended in a constant temperature bath maintained at 25.00°C.

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The Fluorothene part of the chlorine trifluoride delivery tube was connected to a nickel tube which was coiled in the bath and extended outside to a pipette and a 1/4 inch flare fitting on the storage cylinder. Compressed nitrogen admitted through the pipette was used to purge the delivery tube. The 100 ml. storage cylinder and small bellows-type valve were made of nickel and had a tare weight of 93.7 grams.

Resistance measurements on the thermometer and necessary potential measurements for energy calculations were made on the White potentiometer set-up described by Oliver, Grisard, and Anderson (2).

Procedure. The storage cylinder containing chlorine trifluoride was weighed on an analytical balance and attached to the delivery line, which was flushed and kept dry with a slow continuous stream of dried nitrogen. Approximately 20 moles of distilled water was placed in the reaction Dewar and the stirrer was started.

Heat equivalents of the water and calorimeter were determined before and after each reaction by supplying a definite amount of electrical energy through the heater and measuring the temperature rise of the water. A description of procedure for precisely measuring this electrical energy has been reported (2). Rates of change of temperature caused by stirring and heat exchange with the bath were observed for a period of time before and after each run, and the temperature rise during each run was corrected accordingly. Immediately following initial heat equivalent measurements, the flow of nitrogen was stopped and chlorine trifluoride vapor was slowly bubbled into the rapidly stirred water. The rate of temperature rise was controlled at 0.5 to 0.7 degrees Centigrade per minute. After a desired temperature rise had been obtained, chlorine trifluoride was swept from the delivery line into the water with a pipette of dry nitrogen. The volume of vented reaction gases was measured and nitrogen was adjusted to flow very slowly during measurement of the final temperature and heat equivalent. The chlorine trifluoride cylinder was removed and weighed to determine the amount of material used. After removing the resulting acid solution, the calorimeter was washed twice with water before making another run.

RESULTS AND DISCUSSION

A heat of reaction value for each experiment was calculated by means of equation 1.

$$\Delta H = Q \times \frac{M.W.}{g.} \times \Delta T \quad (1)$$

where,

ΔH = molar heat of reaction

M.W. = molecular weight, 92.457

g. = weight material used

ΔT = temperature rise of the calorimeter

Q = average heat equivalent of water-filled calorimeter.

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Experimental data used for the calculations are included in table I with the heat of reaction value for each experiment. The amount of water for the various runs varied from 300 to 350 ml. and was measured to $\pm 1\%$. Heat equivalents, Q , were determined on the water and calorimeter under as nearly identical conditions of the reactions as were feasible. Several heat of reaction experiments were made with approximate temperature rises of 0.5, 1.0, 2.0, and 3.0°C. as reported in table I. Experiments having higher ΔT values were considered unreliable since large heat corrections were necessary. Any variation of the heat of reaction with amount of material used, or with acidity of the resulting acid solution is probably due to impurities. This fact is further emphasized when the ΔH values of series C alone are considered, since for this series the sample was frozen with dry ice and volatile materials pumped off. The presence of volatile impurities such as chlorine monofluoride and fluorine might explain the variation in ΔH values. Also, the rate of flow of chlorine trifluoride gas into the water varied the amount of heat liberated, especially if a rapid rate was used. Usually, a degree rise in temperature occurred in about 2 minutes and consumed approximately 0.4 g. of gas.

The 95% confidence intervals of the means of B and C series, respectively, are 81.2 ± 0.5 and 81.0 ± 0.4 kcal./mole. Even though these means are not significantly different at a high probability level, the precision of measurement was apparently improved by removal of volatile materials from the chlorine trifluoride. This improvement is significant at the 90% probability level, and because of the apparent difference in precision the data have not been combined to give an overall average and confidence interval.

No correction has been made for secondary heat effects (heat of solution and/or heat of dilution) associated with the products of the reaction; therefore 81.0 ± 4 kcal./mole cannot be considered a true heat of reaction value. However, considering the concentration of acid in the resulting reaction solution, these corrections should range from 1 to 2%. At the present time identification of all the products formed has not been made, but there are definite indications of the presence of hydrogen fluoride, hydrogen chloride, oxygen, and chlorine.

Some of the resulting acid solutions of the reaction were analyzed for normality, total chlorides, fluorides, and free chlorine. These data are summarized in table I under Acid Solution Analysis and opposite the respective heat of reaction data. By chemical analysis, there were found 3-1/2 of 4 possible acid equivalents, and the theoretical amount of fluoride ion which could account for 3 of the acid equivalents. The chloride ion concentration varied from 25 to 55% of the theoretical amount, assuming that all the chlorine in solution existed as chloride ion. Both the chloride ion and free chlorine concentrations varied considerably; however, part of this inconsistency may be due to variation in time between reaction and solution analysis. A postulation may be made that part of the chlorine was used in formation of free chlorine and part in the formation of chlorides and oxychlorides, which could account for the remaining one-half acid

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TABLE I
HEAT OF REACTION SUMMARY

Series	Reaction Data			Normality	Acid Solution Analysis		
	ΔH , kcal./mole	Wt. of Sample, g.	ΔT , °C.		Total Cl^- , mg./ml.	Total F^- , mg./ml.	Free Cl_2 , mg./ml.
B	80.65	0.2352	0.505				
B	81.39	0.1930	0.419				
B	80.77	0.2174	0.488				
B	80.76	0.2319	0.525	0.025	0.12	0.41	0.028
C	80.95	0.2796	0.684	0.034			
C	81.17	0.3126	0.768	0.038	0.12	0.53	0.036
B	80.78	0.4040	0.920	0.045			
B	80.60	0.4358	0.992	0.046	0.19	0.71	0.031
B	80.19	0.4455	1.037	0.049			
C	81.32	0.5409	1.326				
B	81.44	0.8448	1.958	0.093			
B	81.07	0.8720	2.006	0.094			
B	82.02	0.9046	2.087	0.097	0.29	1.54	0.156
C	81.84	0.8805	2.142	0.099			
C	80.32	0.9125	2.188	0.108			
B	80.95	1.3019	2.957				
B	82.76	1.2691	2.959	0.138	0.40	2.19	0.05
C	81.21	1.2345	3.021				
B	82.91	1.2861	3.026	0.142			
C	80.76	1.2699	3.092				
C	80.56	1.2200	3.192	0.157	0.67		0.30

C series average, 81.0 kcal./mole

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equivalent. The gaseous products collected over water varied in quantity by a factor of two, which was probably due to solution in the water, and variation in the amount of gas formed. An analysis of this gas showed the major portion to be oxygen, plus a small amount of chlorine.

CONCLUSIONS

The best value for the heat generated when gaseous chlorine trifluoride reacts with an excess of water is 81.0 ± 0.4 kcal./mole.

There are definite indications of the presence of hydrogen fluoride, hydrogen chloride, oxygen, and chlorine in the reaction products.

Three and a half of the possible four acid equivalents were found in the resulting acid solution of the reaction.

The theoretical amount of the fluoride ion was found in solution, whereas the chloride or chlorine content varied considerably.

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NOTEBOOK REFERENCES

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Experimental work was completed July, 1950.

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