[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Heat of Formation of Perchloryl Fluoride[1]

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The standard heat of formation of gaseous perchloryl fluoride was determined from the heat of hydrogenation in a bomb calorimeter to be −5.12 ± 0.68 kcal./mole.

Introduction

Perchloryl fluoride (ClO_3F) is a relatively new compound, having recently been discovered by Engelbrecht and Atzwanger.[2] The preparation and many of the properties of ClO_3F have been described in detail,[3] and many more physical and chemical properties have now been determined by the Technical Division of the Pennsylvania Salt Manufacturing Company. No previous measurements of its heat of formation have been carried out. The reaction used in this investigation was

$$ClO_3F(g) + 4H_2(g) = HF(aq., 0.6M) + HCl(aq., 0.6M) + 3H_2O(l) \quad (1)$$

Experimental

Apparatus and Method.—The isothermal calorimeter and the method of measuring the temperature rise for this experiment have been described previously.[4] The essential components were the calorimeter jacket, kept at 24.80 ± 0.002°, the calorimeter cup of 5-l. capacity, the double valve Parr illium bomb having a volume of 360 ml., and the platinum resistance thermometer in conjunction with the Mueller bridge, both of which were calibrated.

The calorimeter was calibrated with benzoic acid (National Bureau of Standards sample 39g) having an isothermal heat of combustion at 25° of 26.4338 abs. kj. per gram mass under certificate conditions. In the calibration experiments 2-g. samples were used in order to achieve about the same temperature rise as attained in ClO_3F-experiments. Twelve combustions of benzoic acid yielded a value of 4695.00 cal./deg. for the energy equivalent of the calorimeter at 25°. The average deviation from the mean for these experiments was 0.066% and the maximum deviation was 0.14%.

Uncertainties and Precision.—The uncertainties in the reported values of the heats of formation were calculated by taking the square root of the sum of the squares of the precision error, the accuracy error and the calibration error. The precision error reflects the reproducibility of the experiments and is given by the formula $2\sqrt{\Sigma\Delta^2/n(n-1)}$, where Δ denotes the deviation from the mean, and n the number of trials. The accuracy error is arrived at by estimating the effect of various factors on the reaction, such as the purity of the reactants used.

The Purity of Perchloryl Fluoride.—The perchloryl fluoride was provided for this research by the Pennsylvania Salt Manufacturing Co. It was somewhat difficult to determine the purity of the samples; oxygen especially is difficult to detect since it is similar to perchloryl fluoride in its reactivity, and since the mass spectrum of pure perchloryl fluoride apparently has a small mass 32 peak. The mass spectrum of perchloryl fluoride sample II was: ClO_3F^+, 45; ClO_3^+, 100; ClO_2^+, 50; $FClO^+$, 3.9; ClF^+, 1.7; ClO^+, 36; Cl^+, 28; F^+, 0.69; O^+, 8.7; O_2^+, 2.5. These peak heights are in fair agreement with those obtained by the Bureau of Standards,[5] where a 99.9% pure sample was investigated. The NBS peak for mass 32 was 2.6. Thus the samples used in this investigation were probably quite oxygen free, since the peak at mass 32 probably can be attributed to O_2 fragments formed during the electron bombardment of ClO_3F.

In sample II, nitrogen was present to the extent of about 12% on the basis of mass spectrographic analysis. However, no ammonia or nitric acid was produced in the hydrogenation experiments, since the analysis based on acid titration was not consistently on one side of that based on chloride precipitation.

In sample II there was 3–4% CO_2. To find out whether this had any effect on the heat of hydrogenation, $^1/_2$ atm. of CO_2 (about 16%) was added to the charge of ClO_3F and H_2 in trial 5. The heat of reaction for this run did not differ significantly from the average.

Sample III contained 3.5% of nitrogen and no carbon dioxide at all.

The Hydrogenation of Perchloryl Fluoride.—The following procedure was followed in charging the bomb. First, 50 ml. of distilled water was added to the bomb by pipet. It was then closed air tight and flushed 8 times with pure hydrogen by filling the bomb to a pressure of 5 atm. and then releasing it. The filling connection leading to the ClO_3F tank was then screwed to the bomb, but was not tightened. The valve on the perchloryl fluoride tank was now opened and any air which may have been in the filling connection was swept out. The connection was then tightened and perchloryl fluoride was admitted to a pressure of 2–3 atm. Finally, the hydrogen tank was connected again, the filling connection swept clear of air as before, and hydrogen was added until the total pressure was 25 atm.

In the calorimeter this charge was ignited by electrically heating a thin platinum wire, 1 cm. long and fastened to the two electrodes. Its resistance was about 0.4 ohm. A current of approx. 10 amp. was passed through this wire at 4.5 volts for $^1/_2$ to 1 sec., producing from 5 to 10 cal. This was generally sufficient to cause ignition.

The reaction produced a loud explosion which could be heard through the calorimeter jacket. However, the platinum resistance thermometer and the position of the bomb in the calorimeter cup were not affected by this explosion. When the bomb was opened after the completion of the run, it was seen that the walls of the bomb and the bomb head were completely wet and washed clean. This seems to indicate that during the explosion the water in the bomb is thrown upward and wets the entire interior of the bomb. This has two beneficial results: first, in the reaction 3 moles of water is produced, a large part of which condenses on the walls of the bomb. If the HF and HCl formed then dissolved mainly in this thin film of water, this would produce a very concentrated solution of the acids on the bomb walls, with a heat of formation which is lower than that of the solution proper. It is quite difficult to make corrections for this difference in concentration. This was avoided since the bulk water dissolved HF and HCl and washed the interior of the bomb, leaving a film of solution of a concentration essentially the same as that of the bulk solution.

Secondly, it was noted during combustion experiments with methylene fluoride that if a film of highly concentrated HF solution is formed on the walls of the bomb, the illium metal and especially the stainless steel valves will corrode to some extent, giving a solution of chromium and nickel ions. Due to dilution with the bulk water extensive corrosion of the bomb was avoided in this experiment. However, some corrosion did take place since the solution of the aqueous acids, when titrated with 0.1 *N* standard NaOH, turned to a faint green shortly before the phenolphthalein endpoint, indicating the precipitation of heavy metal hydroxides. At worst this amounted to $^1/_2$% of the total hydrogen ion content. If one assumes that this reaction proceeds at uniform speed, its effect is almost, but not entirely, cancelled by the slightly slower drop of the temperature in the after period. In one experiment the corrosion was artifi-

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[1] Presented before the Division of Industrial and Engineering Chemistry, Fluorine Chemistry Symposium, at the 130th ACS Meeting, Atlantic City, New Jersey, on Sept. 20, 1956.

[2] A. Engelbrecht and H. Atzwanger, *Monatsh.*, **83**, 1087 (1952).

[3] (a) A. Engelbrecht and H. Atzwanger, *J. Inorg. Nuc. Chem.*, **2**, 348 (1956); (b) G. Barth-Wehrenalp, *ibid.*, **2**, 266 (1956).

[4] C. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.*, **60**, 1318 (1956).

[5] The National Bureau of Standards, private communication.

cially increased to 4% of the total hydrogen ion content by adding a stainless steel nut to the water initially. The result for this run did not differ appreciably from the average.

To determine the amount of the ClO_3F which underwent reaction, the bomb was opened after the run and carefully rinsed out to ensure quantitative recovery of the solution. The acids were diluted to 1000 ml., 100-ml. aliquots of which were titrated with standard 0.1 *N* NaOH, which in turn was standardized against Bureau of Standards benzoic acid sample 39g. To a 400-ml. sample of the solution silver nitrate was added and the chloride content was determined gravimetrically. The two analyses generally agreed within 0.3%, and within 0.6% at worst.

Results and Calculations

The data refer to a standard temperature of 25°. The atomic weights used were reported by THIS JOURNAL in 1953. The energy unit is the calorie defined as equal to 4.1840 abs. joules. Heats of formation for HF(aq), HCl(aq) and H_2O were taken from National Bureau of Standards Circular 500.

TABLE I

THE HEAT OF HYDROGENATION OF ClO_3F

Trial	1/2 moles H^+	Moles Cl^-	$-q$, cal.	Weighted $-\Delta E_B$, kcal./mole	$-\Delta H_c{}^0$ kcal./mole	$-\Delta H_f{}^0$ (right side eq. 1)	$-\Delta H_f{}^0$ ClO_3F at 298° K.
			Sample II				
1	0.03538	0.03567	11058	312.02	314.88	320.113	5.23
2	.02768[a]	.02738	8528	311.43	314.29	320.113	5.90
3	.02850	.02856	8923	312.92	315.78	320.183	4.40
4	.02904	.02919[a]	9049	311.63	314.49	320.177	5.69
5[b]	.03085	.03077	9633	312.43	315.29	320.161	4.87
6	.02865	.02836[a]	8956	312.60	315.46	320.181	4.72
7	.02934	.02920	9128	311.47	314.33	320.175	5.85
8	.03272	.03252	10223	312.89	315.75	320.143	4.39
9	.02920	.02908	9138	313.24	316.10	320.176	4.08
10	.03893	.03888	12133	311.76	314.62	320.079	5.46
11	.04025	.04005	12576	312.84	315.70	320.066	4.37
				Av. for sample II is 5.00 kcal./mole			
			Sample III				
1	0.04754	0.04779	14859	311.72	314.58	320.003	5.42
2	.03310	.03324	10339	311.70	314.56	320.137	5.58
3	.03385[a]	.03418	10646	311.33	314.19	320.128	5.94
4	.03358	.03355	10482	312.31	315.17	320.133	4.96
				Av. for sample III is −5.47 kcal./mole			

[a] Analysis was discarded. [b] 1/2 atm. of CO_2 added.

In Table I are the results of studies on two different ClO_3F samples. Preliminary studies on another sample of lower purity have been reported.[1] The second and third column in the table give the analysis of the runs based on acid titration and silver chloride precipitation, respectively. It turns out that the values for the heat of reaction per mole based on acid analysis are somewhat more consistent than those based on chloride analysis, although the respective averages are nearly the same. The analysis was therefore weighted 3 to 1 in favor of the acid values. The fourth column gives *q*, the total number of calories produced in the reaction minus the ignition energy. In the fifth column, weighted $-\Delta E_B$ is the heat of reaction per mole under the conditions of the bomb process. This value was then reduced to ΔH^0_c (column 6), the corrected decrease in enthalpy with each of the reactants and products in its thermodynamic standard state, by making the non-ideality and ΔnRT corrections. The corrections for H_2 were obtained using the relation $(\partial E/\partial P)_T = 1.0$ cal./atm./mole at 22.5 atm., and $(\partial E/\partial P)_T = 0.705$ cal./atm./mole at 12.5 atm. These relations were derived from the variation of the differential coefficient $(\partial Z/\partial T)_P$ divided by *P* with pressure, and the variation of the compressibility coefficient with pressure at constant temperature.[6] Perchloryl fluoride was assumed to behave in a manner similar to carbon dioxide, and was corrected to unit fugacity by using the relation $(\partial E/\partial P)_T = -13.0$ cal./mole/atm. This was estimated from the critical constants of ClO_3F, and by assuming that its pressure–volume product changes with pressure according to $(\partial(PV)/\partial P)_T = -5.2$ cal./atm./mole. The total non-ideality correction was 0.10 kcal./mole, to be added to ΔE_B. The ΔnRT correction was −2.96 kcal. Because of the low solubility of hydrogen gas and the relatively low pressure of perchloryl fluoride in these experiments, the heats of solution of these gases in the aqueous phase was neglected.

To obtain the standard heat of formation of ClO_3F (column 8), one subtracts the standard enthalpy of the reaction (column 6) from the sum of the standard heats of formation of the products (column 7). The values in column 7 vary somewhat since the solutions of HF and HCl were produced in different concentrations from run to run. Since the data on the heat of formation of solutions containing both HF and HCl were not available, the assumption was made that the heat of formation of each aqueous acid was that corresponding to the total acid concentration, and not the actual concentration.

This assumption was shown to be a reasonable one in the following experiment. In a simple Dewar flask calorimeter 25 ml. of 4 *N* HCl was mixed with 250 ml. of 0.4 *N* HF, and the heat of mixing was observed with a Beckmann thermometer. The calorimeter was previously calibrated by observing the heat of mixing between 25 ml. of 4 *N* HCl and 250 ml. of water. From the calculated heat of dilution the heat capacity of the calorimeter was calculated. The reproducibility of the experiments was within 3.5% at worst. The actual heat of mixing observed when 1 mole of 4 *N* HCl is diluted to 0.4 *N* HCl with 0.4 *N* HF was −755 cal./mole. The calculated heat of mixing, using the above assumption, would be −790 cal./mole. If it had been assumed that the heat of formation of one acid was independent of the other, the calculated heat of mixing would have been −919 cal./mole, or a 22% deviation from the observed heat of mixing. This indicates that the heat of formation of the mixture of acids was actually 0.035 kcal./mole more endothermic than assumed. On the other hand, the difference (4.5%) is not significantly different from the reproducibility of the calorimeter. The acids were actually formed in concentrations somewhat higher than 0.4 *N* (0.6 *N* on the average), but if an error of 0.10 kcal./mole, or three times the observed deviation from the assumption at 0.4 *N*, is attached to the estimates at higher concentrations, it is probably well within reason.

Column 8 then gives the standard heat of for-

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[6] The NBS–NACA Tables of Thermal Properties of Gases, Table 7.20, Washington, D. C., 1949.

mation of gaseous perchloryl fluoride at 25°. The precision error was 0.40 kcal., the calibration error was taken as 0.20 kcal., and the accuracy error was estimated as 0.50 kcal. The final value for the standard heat of formation of ClO_3F is then -5.12 ± 0.68 kcal./mole.

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Thermodynamic Data from Electron-impact Measurements on Acetylene and Substituted Acetylenes*

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Earlier measurements of electron-impact data for propyne and 2-butyne have been extended to other substituted acetylenes: 1-butyne, diacetylene, 1-Br-1-propyne, 1-Cl-1-propyne and phenoxyacetylene. From these the heat of formation of C_2H was determined to be 112 kcal./mole. Bond energies for the carbon–hydrogen and carbon–carbon bonds in acetylene and for certain bonds in the substituted acetylenes can then be evaluated.

Studies of the various dissociation processes for acetylenic compounds by electron-impact techniques furnish a possible source of information on the energies involved in the formation of various free radicals which may be of significance in the thermal decomposition reactions of these compounds. For this reason the appearance potentials for a number of ions from a series of substituted acetylenes have been determined. Experimental data on propyne and 2-butyne have been presented earlier.[1] The determinations of appearance potentials have now been extended to 1-butyne and diacetylene. Since phenoxyacetylene and 1-chloropropyne and 1-bromopropyne all gave evidence of unusual reactivity in decomposition flames of acetylene,[2] they were also included in these determinations.

Experimental

Materials.—The propyne and the butynes were supplied by the Farchan Laboratories of Cleveland. The argon and krypton used as standards were obtained from General Electric Laboratories.

The halopropynes and diacetylene were supplied by Dr. Lewis F. Hatch and his co-workers at the University of Texas. The 1-bromo-1-propyne was prepared by the action of hypobromite on propyne.[3] One sample of 1-chloro-1-propyne was prepared here by dehydrobromination of 1-bromo-1-chloro-1-propene. A second sample was made available through the kindness of Dr. L. C. Leitch.[4] The identity and purity of the halogen-substituted propynes were confirmed by infrared analysis. The phenoxyacetylene was prepared by dehydrobromination of 1-bromo-2-phenoxyethene.[5]

The diacetylene was prepared by dehydrochlorination of 1,4-dichloro-2-butyne.

Preliminary mass scans of each compound were made and compared with mass spectra from the literature.[6] These tests showed no impurities which would interfere with the appearance potential measurements.

Appearance Potentials.—The experimental method for appearance potentials has been described previously.[1] They were measured by the method of vanishing ion currents using a Westinghouse Type LV Mass Spectrometer.

Excess Kinetic Energies.—In these measurements two approaches were used, both of which are based on the fact that the ion-collecting and focussing properties of a sector-type mass spectrometer depend upon the amount of kinetic energy with which an ion is formed. The first of these was originally suggested by Hagstrum and Tate[7] and simply involves comparing the ion accelerating voltage needed to focus the ion under investigation with that calculated from the mass spectrometer focussing equation, mv = constant. As a reference voltage for the calculation, the observed voltage for some ion known to be formed with no kinetic energy is used.

In determining the product of mass and focussing voltage for several thermal ions such as Kr^+, A^+ and Ne^+, it was found that this product is not constant for this instrument. However it was found that over small ranges the change in the mv product per mass unit is constant, and this value for $\Delta mv/\Delta m$ was evaluated by determining the focussing conditions for several ions in the appropriate mass range which are known to be formed with zero kinetic energy.

The second method is that of Berry[8] who has shown that because of discrimination at the collector slit against passage of ions formed with initial kinetic energy, the observed ion current for a particular ion should remain constant as the ion accelerating voltage is decreased to a certain critical value (varying the magnetic field to keep the ion in focus) and should then decrease linearly.

In measuring discrimination effects it was only necessary to measure the observed ion current for a particular ion as a function of the ion accelerating voltage and compare this with similar data for an ion known to involve no appreciable excess kinetic energy. The chief difficulty with this measurement lies in the rather limited range of the ion accelerating voltages available with this particular instrument.

Results

Appearance Potentials.—The experimental results are summarized in Table I. For purposes of comparison and reference the data on acetylene, propyne and 2-butyne which were reported earlier[1] are included here.

The value found here by direct electron impact for the ionization potential of diacetylene is appreciably lower than the figure of 10.9 v. calculated

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