When an alkyl or aryl oxalyl chloride was substituted for oxalyl chloride, equimolar quantities of the reactants were used.

ACKNOWLEDGMENT

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Thermochemistry of Phosphorus Trifluoride

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The heat of reaction between CaF_2 and PCl_3 was obtained at 356.6° C. by a novel technique using a fluidized bed as the reactor. The observed value corrected to 25° C. (298.16° K.) gave $\Delta H = -2.361$ kcal./mole PCl_3. Reaction was substantially complete and in good agreement with the conversion calculated from the observed enthalpy change and the known entropy change. The enthalpy of formation for PF_3 was calculated to be −226.03 kcal./mole at 298.16° K.

NO THERMOCHEMICAL STUDIES have been made on PF_3 since 1885 when Berthelot (*1*) obtained a limited supply from the discoverer, Henri Moissan, which he submitted to calorimetric measurement by absorption in KOH. Only three determinations were made giving 109.7, 107.1, and 106.2 kcal./mole PF_3 absorbed, which Berthelot did not regard as very concordant. The reaction was complex and he was unable to establish its course with the analytical methods then available.

Another reaction has now been found which is suitable for thermochemical studies, namely, the metathesis of calcium fluoride with phosphorus trichloride:

$$PCl_3(g) + \tfrac{3}{2}CaF_2(s) \rightarrow PF_3(g) + \tfrac{3}{2}CaCl_2(s)$$

The reactants are readily available, and there are no significant by-products, but special techniques must be employed for the measurements. A temperature of 350° C. is needed to get rates rapid enough to follow by simple thermometric equipment. Since one reactant is solid while the other is gaseous, a flow calorimeter using a fluidized bed is also required. To obtain a gas stream adequate for fluidization, the PF_3 must be carried in with an additional volume of inert gas such as nitrogen. A bath of boiling mercury surrounding the apparatus maintains the reaction temperature.

PRINCIPLE OF THE CALORIMETRIC MEASUREMENT

The bed of solid is first brought up to the reaction temperature and then the gaseous reactant is introduced preheated to the same temperature. As the reaction proceeds, the gas continues to enter at constant temperature while the solid bed and outlet gas rise in temperature from the heat evolved. Some heat is carried away in the gas while the remainder appears as sensible heat in the solid. When the solid and gas are completely fluidized the two temperatures must be equal, and the heat balance then gives the following differential equation between reaction temperature and amount of PCl_3 converted:

$$q\,dm = C_s dT + C_g(T - T_0)dm \qquad (1)$$

q = heat evolved per unit of PCl_3
dm = differential amount of PCl_3 reacted
dT = temperature rise in the solid
C_s = heat capacity of the solid, including calorimeter walls and thermometer
C_g = heat capacity of the carrier gas and PCl_3
T = temperature of the bed
T_0 = inlet temperature of the gas stream

The first term on the right in Equation 1 represents the sensible heat stored in the solid; the second is the heat carried away by an infinitesimal amount of reactant gas which suffers a finite temperature rise ($T - T_0$).

Integration of Equation 1 gives:

$$m = \frac{-C_s}{C_g} \ln\left[q - C_g(T - T_0)\right] + I \qquad (2)$$

The initial conditions ($m = 0$, $T = T_0$) determine the integration constant ($I = C_s/C_g \ln q$) and the final equation after rearrangement is:

$$q = C_g(T - T_0)\,(1 - e^{-mC_g/C_s})^{-1} \qquad (3)$$

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While Equation 3 relates the unknown heat of reaction to experimentally determined quantities, it is still necessary to operate in such a way that the observations reflect the assumptions made in its derivation. The most important precaution is to feed the reactant so slowly that calorimeter walls, thermometer, and fluidized bed, may equilibrate with the gas stream. With a fast rate, the temperature rise is highly erratic but usually on the high side. A rate with a temperature rise of 1-2° C. in 30-60 minutes gives the optimum reproducibility for the particular apparatus used.

A second reason for limiting the feed rate is to get maximum conversion of 99% or better on the PCl_3 so that corrections for incomplete reaction may be minimized.

It is also convenient to maintain a constant feed rate so that the time-temperature curve may be directly related to the quantity of PCl_3 admitted.

Finally, to make the apparatus compact, the preheater for the inlet gas, should enclose the reaction zone, and to minimize heat losses, an evacuated annular space is provided around the reactor itself.

APPARATUS AND PROCEDURE

A sketch of the reaction train is shown in Figure 1. Nitrogen was admitted from the laboratory supply and maintained at constant pressure by allowing a small amount to bubble up through a side arm immersed in a cylinder of water to a depth of about 35 cm. It could pass either directly to the reactor in boiling mercury or through a PCl_3 saturator at a constant temperature by opening and closing of the by-pass connections. After leaving the reactor, the PF_3 of the product gas was absorbed by KOH in a bubbling bottle and the nitrogen collected in a constant level bottle which measured the volume by the water spilled over into a graduate. The flow rate was controlled by adjusting the setting of a screw cock on the outlet hose.

Reactor. The essential part of the reactor (Figure 2) was a 25-mm. fritted disk filter (coarse) enclosed in a vacuum jacket (32 mm.) which in turn was sealed into a 50-mm. outer jacket immersed in the bath. Inlet and outlet tubes were sealed into this outer jacket as well as tubes for inserting thermometers into the fluidized bed and the entering gas. No etching was observed in the borosilicate glass from the PF_3 in the reaction zone. The thermometer glass was less resistant and showed slight etching but none in the outer jacket where it was exposed only to PCl_3. Apparently the readings were unaffected but the stems became abnormally brittle and broke at a very slight jar.

Tapping Device. At gas rates of 10-40 cc./min. the bed was visibly fluidized but channeling was occasionally noted. To avoid this, a No. 10 rubber stopper was mounted eccentrically on the shaft of a slow speed motor to give the reactor one tap per second.

PCl_3 Saturator. The PCl_3 saturator was a graduated cylinder (10cc.) provided with a sealed in tube dipping into the liquid and placed in a constant temperature bath. Weighings were made before and after a run and combined with the measured volume of exit nitrogen to give the N_2/PCl_3 ratio.

Absorber. The absorber was a 250-cc. Erlenmeyer filter flask containing 100 cc. of 5% aqueous potassium hydroxide. The gas inlet line was expanded to 25 mm. after passing through the rubber stopper and dipped just below the surface of the absorbent to provide maximum time of contact between the gas and the solution.

Thermometers. The thermometers were graduated to 0.5° C. over the range 245-420° C. (W. H. Kessler Etched Stem JL-8) and could be read to 0.2° C. In a single run with a rise of 2° C. the error was thus approximately 10% and at least 10 check runs were needed to insure reasonable confidence limits.

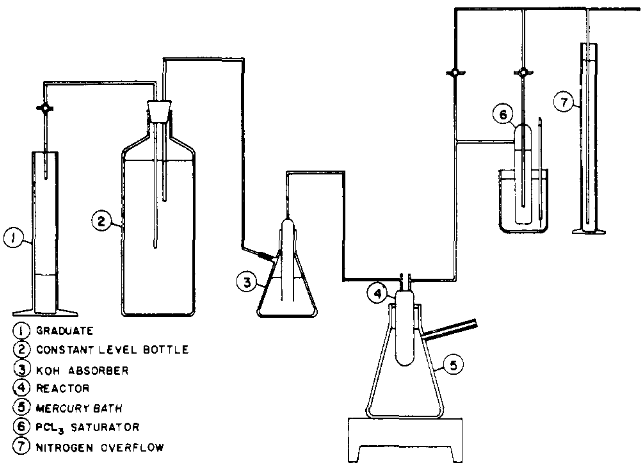

Figure 1. Reaction train

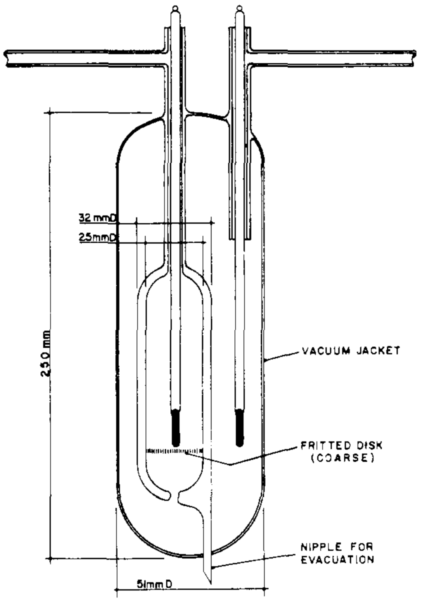

Figure 2. Reactor tube

MATERIALS

PCl_3. Malinckrodt Analytical Reagent. The vapor pressure agreed with that given in the Landolt-Bornstein Tables (1912).

CaF_2. Baker and Adamson Standard Purity. The material was a precipitated powder. Before use it was dried out for several days at 105° C., but still retained traces of moisture which were driven off in preliminary heating to 356° C. by the stream of nitrogen going through the bed. The material was said to be free of $CaSO_4$, but as will be mentioned later, traces of H_2S were always observed in the reaction products.

ANALYSES

In choosing the analytical methods to supplement the calorimetric study, the two objectives were first, to determine the amount of reactant converted in the main reaction, and, second to make sure that no extraneous reactions occurred either from by-products or significant impurities in the starting materials. The second objective required confirmation of results by various independent procedures.

Chloride Analysis. Calcium chloride was leached from the reaction residue by boiling with 100 cc. of water for 30 min. after which the slurry of undissolved CaF_2 was transferred to a fritted glass filter (150 cc. capacity). Liquid trickled through by gravity, and the initial filtrate was returned until the matte was thick enough to hold back the fine dispersion (presumably CaF_2). Four washes with 80 cc. hot water followed to displace the mother liquor.

Filtrate and washings were made up to 500 cc. and titrated with $0.10NAgNo_3$ added in small portions to the hot liquid with intermediate filtration until no more precipitate formed. Precision was about 2%. The more rapid titration with thiocyanate using $Fe(NO_3)_3$ indicator proved unreliable since there was interference from the small amount of dissolved CaF_2.

The $CaCl_2$ analysis was taken as a measure of the amount of PCl_3 converted and used for the thermochemical calculations.

Gain in Weight of Reaction Residue. A rapid but not very precise analysis was merely to find the gain in weight of the residue as the chlorine displaced the fluorine.

Weight of Product Leached out by Water. The loss in weight of the solid residue after water leaching would be a measure of the amount of $CaCl_2$ formed. This again was a rapid analytical method but not very precise and only useful in exploratory studies.

PCl_3 Carried into the Reactor. The amount of PCl_3 carried into the reactor was obtained from the difference in weight of the saturator before and after a run. The method proved more accurate than had been anticipated, and the amount added was essentially equivalent to the $CaCl_2$ formed by the chloride analysis, showing that the conversion was substantially complete with no significant side reactions.

Amount of PF_3 Formed. The KOH absorber following the reactor was intended to hydrolyze the PF_3 to KF and K_3PO_3. The fluoride should precipitate as CaF_2 for gravimetric determination. However, the precipitation was incomplete, and the clear filtrate threw out further precipitates on boiling. Berthelot's study involved the same hydrolysis and his titrations appeared somewhat ambiguous. The work reported here confirmed that the hydrolysis is a complex process but the matter was not further pursued.

Unconverted PCl_3. Unconverted PCl_3 would also be hydrolyzed in the KOH absorber, and the amounts were determined by titration with $AgNO_3$ after acidification with HNO_3. In most cases, only traces were found but occasionally the amounts were 2–3% of those estimated from the chloride analysis of the residue. The substantial absence of PCl_3 in the product gas indicated that the reaction was nearly complete at the contact times provided in the runs.

H_2S Formation. A distinct odor of H_2S was always noted in the acidified KOH solution. The origin seems to be traces of $CaSO_4$ in the precipitated CaF_2. However, there was never enough sulfide ion to give more than a faint brownish black turbidity when $AgNO_3$ was added to test for chloride.

HEAT CAPACITIES

The total heat capacity of reactants and apparatus was obtained as the summation of the products of specific heats and masses. The mass of the glass in the reactor walls and thermometer was estimated by noting the depth of the fluidized bed to which they were exposed and then calculating the volume which was multiplied by the density. Values for a typical run in cal./° C. were: glass 6.0; CaF_2 8.2; PCl_3 0.29; N_2 0.70. These values were based on a PCl_3 dosage equivalent to 1% of the CaF_2 which gave a total rise of about 2° C. With these ratios of solid and gaseous heat capacities most of the heat was retained in the solid. A larger dosage of PCl_3 would have converted more CaF_2; given a greater temperature rise; and raised the gaseous heat capacity for a fixed weight of solid. The greater temperature increment would have given a more precise measurement, but it would also have resulted in higher parasitic heat losses, since the time could not have been shortened without risking failure of the glass to follow the bed temperature.

TIME-TEMPERATURE RELATIONS

The temperature rise was noticeable almost immediately after the introduction of PCl_3. It was rather rapid for about 15–20 minutes after which it steadied to a slow rise during the remainder of the run for a total elapsed time of 50–100 minutes. The anomalous initial rise was probably due to the lag in the heat transfer to the glass walls. With too high flow rates a quite large initial rise was observed which was followed by a slight drop before the final steady rise was established.

RESULTS

Two series of runs were made which allowed some estimate of the correction to be made for heat losses. The first series of eleven was made in the laboratories of the Plastics Dept. of E. I. Du Pont de Nemours and Co., and gave a mean value of 2270 ± 310 cal. evolved per mole of PCL_3 (95% confidence level). The mean temperature rise was 2.4° C.

The second series of seven at the University of Massachusetts (*3*) gave a value of 1570 ± 336 cal., but the mean temperature rise was 4.8° C.

The same reactor was used in both series with minor modifications in the reaction train. The products were examined by chromatographic analysis in the second series and confirmed the findings of the other series that the PCl_3 was substantially all converted to PF_3.

Since the heat losses from the reaction zone to the mercury bath will be proportional to the temperature difference the two results were extrapolated linearly to a rise of 0° C. when there could be no heat losses. The final value thus obtained was 2970 ± 300 cal. per mole of PCl_3 reacted at 356.6° C. (629.8° K.)

From the tables of Kelley (*2*) the increase in heat contents of the components between 298.16° K. and 629.8° K. are: PCl_3, 6.113; 3/2 CaF_2, 8.910; PF_3, 5.299; 3/2 $CaCl_2$, 9.115 kcal. Using these values to correct to 298.16° K., we get $\Delta H_{298.16} = -2970 + 609 = -2361$ cal./mole PCl_3.

DISCUSSION

The entropies of all the components are known (*4*) at 298.16° K. and may be corrected to 629.8° K. by Kelley's (*2*) tables to give an entropy change of 4.36 cal./mole/° C. Combining this value with the observed enthalpy change at the same temperature, the equilibrium constant at 629.8° K. is calculated by the relation:

$$-RT \ln (PF_3)/(PCl_3) = 2970 - T(4.36)$$

which corresponds to a constant of 99 and a conversion of 99% of the PCl_3.

As noted in a previous section, the unconverted PCl_3 was no more than 2–3% in occasional runs though only traces in most cases. These findings are consistent with the calculated conversions. Exact agreement could not be expected because the measurements could not be run under conditions that would insure equilibrium. The calculated conversion will also reflect any errors in the entropy values.

HEAT OF FORMATION OF PF_3

Using the tabulated molal values for ΔH_f of the other three components at 298.16° K. and the ΔH of the reaction as −2.361 kcal., ΔH_f for PF_3 is −226.03 kcal./mole at 298.16° K.

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Tetrasubstituted Ureas as Thermally Stable Fluids

Blocking of β-Elimination by Fluorine Substitution

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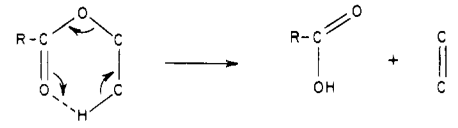
Six tetrasubstituted ureas were synthesized and evaluated for thermal and oxidative stability. This work was based on the premise that unsymmetrical tetrasubstituted ureas containing only aromatic and fluorinated alkyl substituents could not decompose by the β-elimination mechanism and would have low enough melting points to be useful as high-temperature fluids. These compounds were found to have good oxidative and thermal stability, but relatively high volatility and limited liquid range.

AWARENESS of the high bond energies of such bonds as B—O, Al—O, and Sn—O has led in recent years to numerous attempts to prepare high temperature inorganic-organic polymers which would be stable to 1000° F.

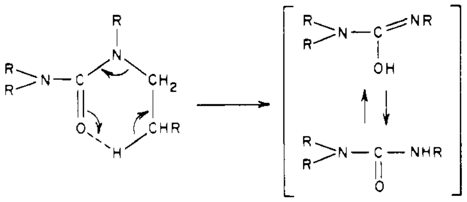
One fundamental difficulty in the study of these inorganic-organic systems is that part of the bond dissociation energy of many of these bonds is a function of electronegativity difference— in other words there is a large ionic contribution. The consequences are hydrolytic and oxidative susceptibility, and the ability to change partners.

For the immediate future, it is suggested that practical results will be obtained by utilizing current concepts to improve more familiar systems. The carbon-carbon bond requires 80-90 kcal. to effect homolytic cleavage. This represents a decomposition rate of about 1% per hour at 700° C. Most organic compounds decompose at temperatures far below those expected from consideration of bond dissociation energies since, whenever possible, a molecule will decompose by processes requiring less energy than that of simple homolytic cleavage. A well-documented example is the cleavage of esters, a process which takes place so smoothly at moderate temperatures that the reaction is used as a convenient route to olefins. It is generally assumed that a quasi six-membered ring is involved (*3*).



This mechanism amounts to concerted cleavage of a beta C—H bond and the ester-C—O bond assisted by simultaneous attack of a carbonyl group. Blocking this mechanism by use of phenyl esters or by substitution of alkyl groups or fluorine on the β-carbon atom increases thermal stability.

Aliphatic ureas probably decompose thermally through a similar mechanism, the initial stage of which is shown.



This mechanism is not permitted to tetra-aryl ureas which, in consequence, show enhanced stability (*1*). Their utility as thermally stable fluids, however, is limited by their high melting points. The work reported here was