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EXPLOSIVE REACTIONS OF LIQUID MIXTURES OF CHLORINE TRIFLUORIDE WITH HYDROCARBONS AND HALOCARBONS

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SUMMARY

Combinations of liquid ClF_3 with several hydrocarbons and halocarbons have been caused to explode by sudden mixing at various temperatures from 25^0 downward. The mixtures occasionally detonate.

By fast recording of pressure, flame ionization, and carbon deposition it is found that mixtures derived from all of the fuels tested except perfluorohexane initiate in less than 1 ms at all temperatures down to -70^0. An ionic mechanism is proposed. Analysis of the explosion gases indicates that all chemical bonds including C-H are labilized owing to the extremely high temperature. Calorimetric measurements agree with calculated heats of explosion.

INTRODUCTION

The explosive reaction of chlorine trifluoride with hydrocarbons has a number of potential applications in which it is desired to release a large amount of energy in a small volume

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simply by mixing components which are stable separately. It has attracted interest as a hypergolic rocket propellant system. [1,2,3] It has also been used to ignite an explosion in which a projectile carries the fuel and air is the oxidizer [4]. On the basis of simp thermochemical calculations it appears that the energy release per unit mass of mixture will prove to exceed that of PETN or RDX and that the temperature may rise above 5000 K. A search of the literature has brought to light only one study of the chemistry of this reaction, and it deals solely with gaseous mixtures of methane and propane with chlorine trifluoride [5]. Information on the behavior of liquid mixtures with a variety of fuels is therefore needed. In the present study we report the results of rapid injection of a pure hydrocarbon or halogenated hydrocarbon into a thick walled, closed container containing chlorine trifluoride. During and following the explosion the following observations have been made: (1) the effect of temperature on the duration of the induction period (2) measurement of pressure by a fast-acting dynamic transducer (3) flame conductivity and carbon deposition (4) heat of explosion by direct calorimetry and (5) identification and quantitative analysis of reaction products.

RESULTS AND DISCUSSION

Description of Explosions

Details of the apparatus and procedures are given in the experimental section, but it may be helpful to describe the phenomena briefly before presenting the results. The reactor is a thick-walled stainless steel vessel of 8 mL capacity in which liquid ClF_3 (usually 3 mmoles) and a hydrocarbon or halogenated hydrocarbon (usually 12 mmoles of $-CH_2-$ or $-CH=$) are suddenly mixed by rupture of a diaphragm which causes the fuel to be sprayed downward a distance of 0.5 cm onto the ClF_3 at the bottom of the vessel. The explosion gives an audible click which appears to be simultaneous with rupture of the diaphragm. The design is intended to limit the peak pressure to about 100 bars (assuming no detonation) and contain the product gases at about 10 bars for sampling and analysis. The apparatus has provisions for temperature control, calorimetry, and monitoring of pressure, flame conductivity, and carbon deposition during the explosion.

Explosion Products Containing Halogen

The more interesting and technically important type of mixture contains excess fuel. A few stoichiometric mixtures were studied, and as expected the products were HF, HCl, CF_4, Cl_2, C, and small amounts of $CClF_3$ and traces of CCl_2F_2. Approximately half of the chlorine took the form of Cl_2, and all of the fluorine could be accounted for as HF and CF_4. In most experiments the fuel was present in approximately five-fold excess. Table I shows the distribution of halogen-containing products derived from several hydrocarbons and halogenated hydrocarbons. The numbers shown are the atomic percentages of each halogen in each species of product based on the quantity of ClF_3 used. Typically, about 90% could be accounted for in these forms. A few of the carbonaceous residues were analyzed by fusion with metallic sodium, and additional small quantities of halogen were found. Extraction of the residues and analysis by GC/MS failed to account for any additional halogen. It will be noted that the totals may

TABLE I

Distribution of Halogen in Products (atom %)

	F			Cl		
	HF	CF_4	$CClF_3$	$CClF_3$	HCl	Cl_2
Heptane	50	18	5	5	29	29
Cyclohexane	42	44	2	2	16	74
"	48	39	5	5	15	78
" [a]	77	17	3	3	63	6
Decalin	80	16	4	4	26	54
Toluene	74	22	2	2	2	45
"	79	13	4	4	46	4
"	44	25	10	10	3	72
"	49	46	5	5	78	20
Dichloro-	38	37	5	5	46	209
methane	70	14	4	4	14	130
Perfluoro-	0	215	8	8	0	62
hexane	0	224	8	8	0	73

[a] Detonation

exceed 100% when a halogenated hydrocarbon is used. The excess is obviously derived from the fuel in these cases.

Because the H-F bond energy is 20 Kcal/mole greater than that of C-F and because the first stage of the reaction surely would involve hydrogen abstraction rather than C-C bond scission, it was thought that use of a fuel-rich mixture would give chiefly HF and HCl rather than halocarbon. The data of Table 1 show however that 17-51% of the fluorine is found in halocarbons. Perhaps this results from a limitation by transport since the fuel is not necessarily present in excess in the region of mixing and reaction of the two phases. On the scale of our experiments the reaction time is usually 1-4 ms which indicates a transport-limited reaction rate. On rare occasions, however, the mixture detonated as evidenced by plastic deformation of the reactor and its internal parts. An example is the third entry for cyclohexane in Table 1. Here it can be seen that the ratio of CF_4 to HF is unusually low, probably because the two liquids had nearly formed a homogeneous solution before the transition to explosion.

Dichloromethane was included in the series of fuels in order to test for scrambling of halogens among the products. If the two C-Cl bonds remained intact, the chief halocarbon product would be CCl_2F_2. It was found, however, that CF_4 predominates and that CCl_2F_2 was present only in trace amount as with non-chlorinated fuels. The result can be ascribed to a radical substitution reaction: $RCl + F \longrightarrow RF + Cl$.

Perfluorohexane also gives an explosive reaction although it initiates more slowly with delays up to 15 ms. This may be due to the different character of the reaction which requires substitution on carbon rather than abstraction of hydrogen, or it may be caused by the very low miscibility of perfluorohexane with other nonpolar liquids. Since every carbon atom already has at least two fluorine atoms, the yield of CF_4 exceeds 200% based on ClF_3. It is noteworthy that the reaction of PTFE tape with ClF_3 under the same conditions is extremely slow.

Several precautions were taken to ensure that significant amounts of halogen were not present in gases other than those shown in Table 1. Likely candidates would be halogenated alkenes such as C_2F_4 and monohalomethanes. Any of these would have been detected at low levels in the FTIR spectra of the explosion gases. Analysis by GC/MS at -20^0 also failed to show any additional components. Baddiel and Cullis [5] reported CH_3Cl

and CH_3F as explosion products of gaseous mixtures of ClF_3 and CH_4, but we have been unable to reproduce their results. In some of their experiments (which ones were not specified) the reactor was packed with copper gauze which may have preserved certain intermediates by rapid quenching. The fact that our material balance is usually about 10% low is ascribed to losses in transfer and the presence of halogen in the carbonaceous residue.

Pyrolysis Products

The excess of fuel is carbonized and significant amounts of methane are almost always present. The chief products of pyrolysis of alkanes at temperatures up to 1000°, namely ethylene and acetylene, are found only in trace quantities or not at all. Toluene gives much methane and a just detectable trace of benzene. This indicates scission of toluene to phenyl and methyl which is reported to begin competing with scission to benzyl and H at 1500^{o} and above [6]. The absence of acetylene in explosion gases from alkanes and toluene and benzene is probably due to decomposition on cooling because its formation from toluene is kinetically favored at lower temperatures (80 mole % yield at 1800^{o}) [7] and thermodynamically favored over the observed products, methane and graphite, at temperatures above 2000^{o}. When a gaseous mixture of propane and ClF_3 was formed and exploded by heating in a vessel filled with stainless steel fractionating column packing we did observe acetylene bands in the FTIR spectrum. On the other hand, the explosion of liquid cyclohexane and liquid ClF_3 in a packed reactor gave only the usual trace quantity. Ethylene is almost never observed even when the fuel is cyclohexane. Hydrogen has been found by combustion analysis, but it is necessary to substract the weight of water formed by the known methane content and the result is not very accurate. In a typical experiment using cyclohexane with a basis of one mole the yield of methane was 0.15 mole and the yield of hydrogen was also 0.15 mole. Even benzene gave 0.09 moles of methane on the same basis.

All of the observations, the formation of methane, graphite and hydrogen from all fuels except perfluorohexane, the absence of ethylene, the low yield of acetylene, and the scrambling of halogens from CH_2Cl_2, indicate that pyrolysis occurs at an extremely high temperature. At the peak the principal pyrolysis product is probably acetylene which decomposes on cooling to give graphite, hydrogen, and methane.

Measurement of Time of Initiation at Various Temperatures

The time of initiation can be determined from the oscilloscope record of the pressure transducer since it clearly indicates a drop when the diaphragm ruptures and a rise when the explosion begins as illustrated in Fig. 1. With the exception

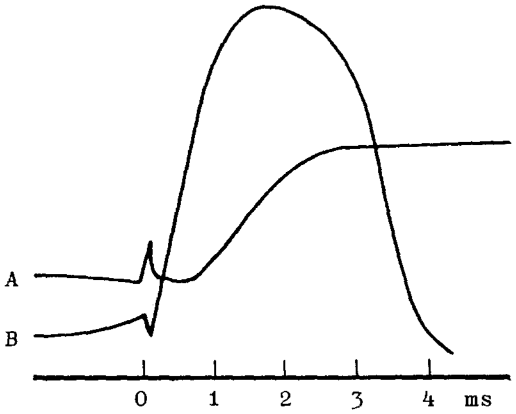
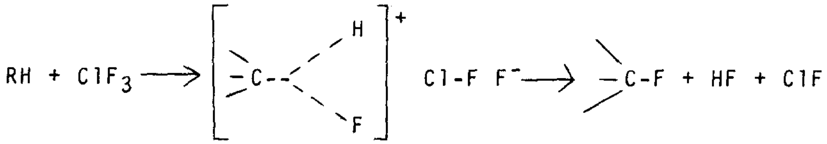


Fig. 1. Oscilloscope Traces.
A, Electrode voltage; B Pressure signal.

of perfluorohexane all fuels reacted in less than 1 ms even at temperatures just above the melting point of ClF_3 which is -76°. In one experiment at -70° heptane initiated at 50 μs. This is approximately equal to the time of flight of the fuel to the ClF_3 layer as calculated from the estimated velocity of 100 m/s and confirmed by an experiment in which the fuel was replaced by an electrolyte solution which was sprayed onto an electrode 0.5 cm below. Attempts to measure an 'activation energy' for the initiating process were vitiated by these results. It is questionable whether a reaction having a half life less than 1 ms at -70° should even be regarded as an activated process since the barrier could scarcely be as high as 10 kcal/mole for any reasonable assumed value of the activation entropy.

Reaction Mechanism

In view of the nearly instantaneous reaction between ClF_3 and hydrocarbons at -70° it is an astonishing fact that gaseous mixtures of ClF_3 with methane and propane at partial pressures near 1 bar each do not react at room temperature over a period of many hours. Baddiel and Cullis [5] observed the low reactivity of gaseous mixtures, and we have confirmed it. An enormous difference in reaction rate between liquid and gaseous states implies a mechanism which is ionic rather than homolytic. The behavior of CF_3OF as reagent for replacement H by F on alkanes has been explained by an ionic electrophilic mechanism [7]. We therefore propose that ClF_3 reacts with RH to give RF, HF, and ClF by way of a front-sided transition state as follows:



Flame Ionization and Carbon Deposition

A simple copper electrode insulated by PTFE was installed in the reactor and connected to a 6 V battery. Current from the electrode to the body of the reactor was monitored by the oscilloscope. A representative record is shown in Fig. 1. Initiation of the explosion was accompanied by a simultaneous conduction peak which we ascribe to flame ionization. Its duration was usually about 100 microseconds. In the next few milliseconds the electrode was short-circuited by deposition of carbon on the insulator. It is possible that this deposition is governed by the rate of decomposition of acetylene on cooling although there is undoubtedly some unknown lag between formation of carbon and its deposition.

Peak Pressure and Temperature

The peak pressures indicated by the quartz piezoelectric transducer were often surprisingly high. In order to reassure ourselves that the results were not spurious, a miniature crusher gage was also installed, and satisfactory agreement was obtained. Pressures as high as 30 MPa (300 bars) were generated by explosion of 3 mmoles of ClF_3 with excess fuel in a volume of 8 mL. When hydrocarbon is used it is difficult to calculate the number of moles of gas during explosion because of the complex equilibria among CH_4, C_2H_2, H_2, C, etc., but it is more feasible in the case of perfluorohexane. The reaction of 1.63 mmoles with 3 mmoles of ClF_3 is calculated to give 7.2 mmoles of CX_4 and 1.2 mmoles of C_2X_4. A total of 7.9 mmoles of gas was measured after cooling. The measured peak pressure was 27 MPa which gives a temperature of 3160 K by the ideal gas law for 8.4 mmoles of gas. The calculated and measured enthalpy changes agree well at 157 kcal/mole of ClF_3. Heat capacities of the gases are essentially classical at about 24 cal/mole-deg, and the calculated temperature is 2800 K. We conclude that the explosions are essentially adiabatic during the time in which measurements are taken.

Thermochemistry

The enthalpy change can readily be calculated for the following reactions in which reactants are liquids and products are gases except for graphite:

$-CH_2CH_2- + ClF_3 \longrightarrow 3\ HF + HCl + 2\ C\ (g)$, -162 kcal (1)

$-CH_2CH_2- + 3\ ClF_3 \longrightarrow 3\ HF + HCl + 2\ CClF_3$, -420 kcal (2)

$C_6F_{14} + 2.5\ ClF_3 \longrightarrow 2.5\ CClF_3 + 3.5\ CF_4$, -372 kcal (3)

Reaction (1) gives 1751 cal/g of ClF_3 and reactions (2) and (3) give 1362 and 1610 cal/g, respectively. By use of the classical limiting heat capacities, at constant volume, the temperatures are found to be not less than 4050 K for (1), 5500 K for (2) and 2600 K for (3). In this calculation it is assumed that the internal energy is constant because the gas expands into a vacuum. Explosions with excess cyclohexane correspond approximately to reaction (1), and calorimetric measurements give an average value of 1730 +/- 80 cal/g.

Detonations

On two of the many occasions when cyclohexane was used as fuel and the reactor was cooled, the explosion was a high-order detonation. The first one burst a prototype reactor with thinner walls and caused minor personal injury. The reactor was tested to 60 MPa before each experiment, and we had estimated its bursting strength at 200 MPa. The highest pressure recorded by the transducer in any other experiment was 30 MPa. Several subsequent detonations in a thick-walled reactor resulted in visible plastic deformation of the reactor and internal parts. In a deliberate attempt to provoke detonation we used dichloromethane as fuel on the assumption that it would be less reactive to electrophiles or radicals because of the inductive effect. This fuel gave detonations in two out of five trials.

Numerical Simulation of Detonation and Product Composition

A BKW computer program developed by C.L. Mader [8] was applied to a liquid equimolar mixture of ClF_3 and cyclopentane. The density was calculated on the assumption of a negligible volume change of mixing which is usually valid within 1% for nonpolar liquids. The calculated parameters are shown in Table II, together with those of other explosives.

TABLE II

Detonation Parameters

	ClF_3-C_5H_{10}	TFENA[a]	RDX	TNT
CJ Pressure (kbar)	181	160	148	107
Detonation velocity (ms^{-1})	7165	6500	6690	5690

[a] Trifluoroethylnitramine

It can be seen that a ClF_3-fuel mixture is potentially very powerful although in practice the explosion is usually not a high-order detonation.

The program was modified to calculate the equilibrium product composition at an expansion ratio of 30 with a temperature of 4000^{o}. These conditions correspond approximately to the explosion peak in our reactor. The results indicate that ClF_3 should be converted almost quantitatively to HCl and HF as we predicted earlier on the basis of bond energies alone. In fact, however, we observe a substantial amount of Cl_2. The excess fuel should be pyrolyzed to 3 moles of carbon, 1 mole of acetylene, .01 moles of methane, and 2 moles of hydrogen. In the cooled gases we observe almost no acetylene and roughly equal amounts of hydrogen and methane. This can be ascribed to decomposition of acetylene on cooling.

EXPERIMENTAL

Reactor

A cross-sectional view of the stainless steel reactor is shown in Fig.2. The interior free volume is 8 mL. After being cleaned and assembled, it is charged with 3 mmoles of ClF_3 from a gas reservoir by surrounding the reactor with a cooling bath at -15^{o}. A pressure transducer on the reservoir is used to meter the ClF_3. For experiments involving reduced temperature the reactor is fitted with a cup for cooling with liquid nitrogen and a thermocouple is attached. The assembly is then placed in a tubular steel shield. For calorimetry the reactor is placed in a large Dewar flask containing 800 mL of water. Once the reactor is shielded, the inner chamber is loaded with fuel by insertion of a metal capillary tube through the central hole of the top plug. The tube fitting which leads to the pressure transducer and nitrogen reservoir is then connected. After the system has reached constant temperature a small volume

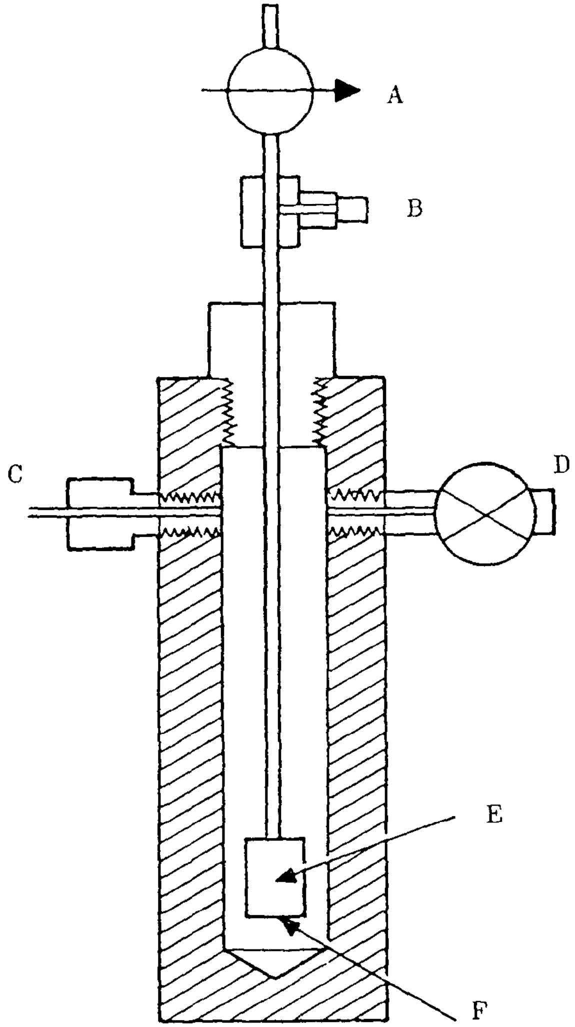


Fig. 2. Reactor.

A Inlet for fuel and N_2;
B Pressure transducer;
C Electrode;
D ClF_3 inlet and product outlet;
E Fuel chamber;
F Brass diaphragm (.0007").

of nitrogen at 30 bars pressure is admitted to the fuel chamber by suddenly opening the top valve. The pressure pulse of the entering gas triggers the oscilloscope which is adjusted for several ms of pre-trigger measurement and ruptures the thin brass diaphragm on the bottom of the fuel chamber. This causes sudden mixing and explosion of the fuel and ClF_3.

Oscilloscope

A Nicolet Model 3091 oscilloscope was used to monitor both the pressure transducer and the voltage drop across a one thousand ohm resistor connected in series with a 6 V battery and the electrode shown in Fig. 2. The trace has 4000 data points and a time base of 20 μs was commonly used.

Pressure Transducer

Dynamic pressure was measured with a PCB Piezotronics Model 105B-2 transducer having a range of 5000PSI and a 2 μs rise time. Since this device is known to be susceptible to shock and heating effects, we also constructed a miniature crusher gage of conventional type in which a #6 lead shot pellet was crushed by a piston, and the deformation was measured. Both gages were calibrated hydrostatically and agreement within the 15% variability of the crusher gage was obtained when explosions were monitored. For these tests the gage was installed in place of the electrode.

Analysis of Explosion Gases

A 100-mL heavy duty glass syringe equipped with a 1/8" Swagelok fitting and containing 15 mL of distilled water was attached to the side valve of the reactor, and the gases were allowed to bubble through the water and expand the syringe. A smaller syringe filled with water was connected to the top valve and used to fill the reactor with water and displace the remaining gas into the large syringe. The water portions were combined for analysis by titration. Dissolved Cl_2 was determined by adding NaI to an aliquot and titrating with standard $Na_2S_2O_3$. Total acidity was measured by titration of an aliquot with standard NaOH to a permanent endpoint allowing for hydrolysis of fluosilicic acid. A third aliquot was warmed to expel chlorine and analyzed for chloride by potentiometric titration with standard $AgNO_3$. The quantity of HF was found by subtracting the chloride content from total acidity. Gaseous Cl_2 in the large syringe was removed by washing with NaI solution and measured by titration with $Na_2S_2O_3$.

The volume of residual gas (CF_4, $CClF_3$, CH_4, H_2, and N_2) was measured, and a 27 mL sample was drawn through a drying tube into an evacuated IR gas cell. The quantities of the first three gases were calculated from the optical densities at 2560 and 2190 cm^{-1} (CF_4), 797 cm^{-1} ($CClF_3$) and 3086 cm^{-1} (a rotational band of CH_4). The halocarbons gave good Beers' law plots, but the plot for CH_4 was curved. The quantity of N_2 was measured by dummy experiments in which no fuel or ClF_3 was used. In a few cases the gas was analyzed for H_2 in a combustion train adapted for injection of a gaseous sample. The weight of water formed by CH_4 was subtracted from the total in order to obtain the amount of H_2. Summation to 100% was satisfactory in view of the indirectness and uncertainty of the measurement of each component.

Analysis of Carbonaceous Residues

In a few cases the black deposit in the reactor was collected by filtration and analyzed by fusion with sodium metal at 600° followed by precipitation of fluoride as PbFCl. Up to 3% of the total fluorine content was found in these residues, but about 7% is missing from the summation of HF, CF_4, $CClF_3$, and residue. There are some losses in transfer which are difficult to estimate.

Gaseous Reaction of Methane and Propane with ClF_3

A 9-mL stainless steel vessel was carefully cleaned and filled with ClF_3 at 640 torr and room temperature. An equimolar quantity of methane was then pumped in with a syringe. Explosions would usually not occur until the temperature was raised to about 120°. A sample allowed to stand at room temperature for three days was transferred to the IR gas cell where it showed the absorption bands of methane, ClF_3 (1028 cm^{-1}) and no others. Propane occasionally exploded during injection at room temperature, but with cooling and return to room temperature there was no explosion until the temperature was raised to 40-50°. The explosion products were typical of liquid-phase explosions as descibed in Table 1.

ACKNOWLEDGEMENT

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