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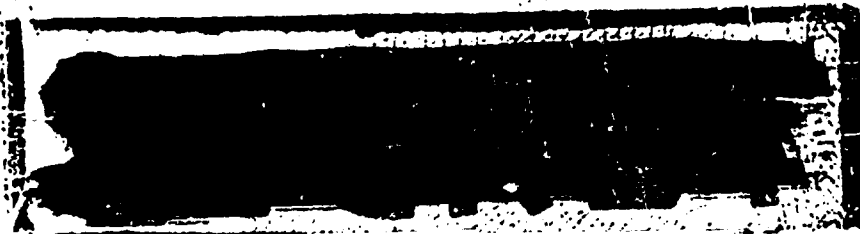
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ROYAL AIRCRAFT ESTABLISHMENT
BARNBOROUGH, HANTS

TECHNICAL NOTE No: CHEM.1194

**EXPERIMENTS ON THE
IGNITION OF HYDROCARBON FUELS
BY HALOGEN FLUORIDES**

by

G. KINNER and R. STRAKER

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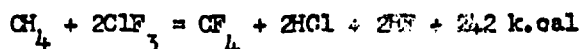
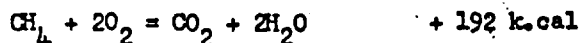
1. Introduction

The halogen fluorides are amongst the most chemically reactive substances known. Their use as incendiary compounds has therefore been proposed as a means of attacking the fuel tanks of aircraft in flight.

It is, of course, recognised that the chemical nature of the contents of an attacking high-speed projectile is only one factor contributing towards its overall destructive effect. For example, there is evidence that ignition of the contents of fuel tanks may also arise from conversion of the kinetic energy of the projectile on impact. Such conversion may become manifest as heat release, due to viscous heating of the fuel, or may cause ignition on account of adiabatic compression of air pockets. Break-up of the fuel into droplets or spray on passage of the projectile will also provide a condition for more ready ignition. The extent to which such factors are important in practice will only be resolved by a suitable combination of laboratory study and practical firing trials. The Armament Design Establishment is concerned with the latter aspect. Chemistry Department RAE has agreed to help in the laboratory study and the present note describes the results of preliminary tests to assess the reactivity of the halogen fluorides towards hydrocarbons.

In particular, chlorine trifluoride is one of the compounds proposed for assessment and by way of general indication of its chemical reactivity, it may be mentioned that it reacts explosively with water and incandescently with such materials as cork, rubber and paper; even a dilute solution in carbon tetrachloride explodes violently on warming and immediate explosive reaction is obtained in the cold with such fire extinguishants as dichlorobromomethane. However, chlorine trifluoride is an exothermic compound and may be safely handled in suitably designed equipment, constructed in metal and which has been carefully freed from all traces of grease and dirt.

A further illustration of the potential value of the halogen fluorides as incendiary compounds is afforded by comparison of the values for the theoretical heat of reaction between, say, methane and oxygen on the one hand and methane and gaseous chlorine trifluoride on the other:-



(the thermal values quoted refer to standard gas state at 1 atmosphere pressure and 25°C).

Chlorine trifluoride (m.pt. -76°C; b.pt. 12°C) is a gas at normal temperatures and alternative special compounds, which may be easier to handle in practice, are also being studied.

Compound AC is a white solid, fuming strongly in moist air, and is understood to consist of a complex compound formed by reaction of equimolecular proportions of chlorine trifluoride and arsenic pentafluoride. Compound AC2 is a colourless, mobile, clear liquid, obtained by dissolving AC in excess chlorine trifluoride, the molecular proportions of chlorine trifluoride to arsenic pentafluoride being in the ratio 2:1. It is observed that AC volatilises fairly rapidly when placed in a current of air at ordinary temperature and that AC2 rapidly sets to a

white solid when exposed to atmosphere, presumably because of loss of gaseous chlorine trifluoride. These features are undesirable, in that they represent lack of persistence and stability in the two compounds, respectively. However, the suppliers, I.C.I. Ltd., have more recently made available samples of further alternative materials, as follows:-

<u>Designation</u>	<u>Composition</u>	<u>Boiling Pt.</u>
BC1	15.8% BrF ₃ 84.2% ClF ₃	25°C (calc.)
BC2	22.3% BrF ₃ 77.7% ClF ₃	30°C "
BC3	32.1% BrF ₃ 67.9% ClF ₃	39°C "
-	Bromine pentafluoride	40°C

These four materials are mobile liquids at room temperature.

2 Experimental

2.1 Reactions with gaseous hydrocarbons

Preliminary experiments made with impinging jets of methane and gaseous chlorine trifluoride showed that ignition was not spontaneous. Explosive ignition could, however, readily be obtained by momentarily placing a hard-glass rod in the gas stream. The resulting flame was intense and visually estimated to have a temperature of about 2800°C. An inner pale greenish-coloured zone was also apparent in which C₂ bands were prominent. These bands are similarly observed in the combustion of hydrocarbons in air or oxygen.

Using a burner comprised of three concentric copper tubes, methane was metered through the innermost tube, chlorine trifluoride through the intermediate one and a nitrogen shroud through the outermost tube. (Here, too, spontaneous ignition only occurred if the burner tip were contaminated from earlier products of combustion.) On lighting the gas stream an intensely white flame was obtained which was accompanied by the copious formation of large flocculent soot particles and the rapid build-up of a carbon cone on the methane jet. Dilution of the chlorine trifluoride, by promoting with nitrogen, caused a marked reduction in flame temperature. At a diluent/reactant volumetric ratio of 3:1 the flame was luminous throughout. At greater dilution a non-luminous zone first appeared at the root of the flame and the entire flame became non-luminous at a ratio of 10:1. The introduction of more nitrogen then revealed only a thin, barely visible reaction zone in the region corresponding to initial contact of the chlorine trifluoride and methane just above the burner tip. This effect persisted and was still evident at a dilution ratio of 16:1.

In a second series of experiments, air/propane mixtures of known composition were prepared in a cylindrical copper vessel of about 1 litre capacity. Compound AC was introduced on a deflagrating spoon but, over the whole range of mixture strengths, from the weak limit of inflammability up to undiluted propane, no ignition of the gases was obtained. Similar results were found with gaseous chlorine trifluoride admitted from a gas pipette. However, with liquified chlorine trifluoride explosive reaction occurred in the approximate range 2.5 to 11.5 per cent propane by volume and, at higher propane concentrations, local reaction occurred as each drop of chlorine trifluoride entered the gas space. Compound BC2 gave results similar to those obtained with liquified chlorine trifluoride but bromine pentafluoride failed to cause ignition at any propane concentration.

In further tests, where premixed air/propane mixtures were passed over AC contained in a copper boat in a hard glass tube, carbon and tar formation occurred downstream when the propane concentration reached approximately 5 per cent by volume. At slightly higher concentrations (ca. 7 per cent by volume) the surface of the AC began to glow with a pale green light, but this reaction remained purely local.

2.2 Reactions with liquid spray

A 'one-shot' spray of fine droplet size was obtained by forceful ejection of liquid hydrocarbon from a suitable nozzle connected to a hand-operated diesel fuel pump. The spray was directed horizontally at 0.5 - 1.0g. of AC placed on a copper plate inclined at an angle of 30° to the horizontal. Immediate ignition of the spray was obtained with n-hexane and n-heptane, but in the case of n-nonane only that part of the spray deflected by the plate was ignited and the liquid remaining on the metal surface did not burn. With kerosine only local flashes of flame occurred at the surface of the AC. Replacement of the metal sheet by a copper gauze resulted in non-ignition of the spray even with n-heptane. In contrast to these results, sprays of isododecane and kerosine were immediately ignited on being directed at a stream of chlorine trifluoride gas issuing slowly from a copper tube.

Compound BC2 gave immediate ignition of hexane and kerosine when sprays of these liquids were directed at falling droplets of the incendiary material. Violent explosive ignition was also found by directing sprays of n-hexane, n-heptane, kerosine, iso-dodecane, aviation gasoline (100/130 Grade) and wide-out gasoline at falling droplets of bromine pentafluoride.

The tests with AC on copper sheet were repeated at reduced atmospheric pressure, in order to simulate altitude effect, but no ignition could be obtained with kerosine (down to pressures corresponding to an altitude of 70,000 ft.) and a spray of n-hexane failed to take fire at pressures below 350 mm. Hg (20,000 ft. altitude, approximately).

2.3 Reactions with liquid hydrocarbons

In a preliminary test to examine the reactivity of chlorine trifluoride towards liquid hydrocarbons, the gas was directed vertically downwards from a jet placed close to the surface of a sample of white spirit. Immediate ignition of the liquid occurred, but predilution of the gas with nitrogen caused ignition delay until, when the volumetric ratio of diluent to reactant was 3:1, no ignition occurred even after several minutes exposure.

In a second test, Compound AC was placed on a sheet of copper inclined to the horizontal and liquid hydrocarbon was allowed to flow down the metal and make contact with the AC. Immediate ignition was obtained with n-hexane, n-pentane, ethanol, acetone and benzene, but n-nonane, isododecane and kerosine caused only local flashes of flame to occur at the surface of the incendiary compound.

Further tests with liquid hydrocarbons were made by allowing the incendiary compound to drip slowly into 1-2 ml. of the fuel contained in a hard glass (6" x 1") tube. In the case of Compound AC, a small quantity of the solid material was dropped into the liquid hydrocarbon. A simplified summary of observations made under these conditions is given in Tables I and II, together with the results of similar tests made at low temperature and of tests made where the glass tube was pre-filled with a carbon dioxide atmosphere.

TABLE I

Observed reactions between incendiary compounds
and liquid hydrocarbons at room temperature

Test fuel	Compound AC	Compound AC2	Compound BC2	Bromine penta-fluoride
N-hexane	F	F	X	h
N-heptane	f	X		h F
Iso-octane				h X
N-nonane	f	X		X
Iso-dodecane	f	X		h X
Kerosine (Avtur)	f	X	X	h X
Aviation Gasoline (100/130)	f			h X
Wide-Cut Gasoline (Avtag)	F			h
Liq. Paraffin		X	X	X
Benzene	f			h X
Acetone	X		F	

- X denotes explosion
- F inflammation of bulk liquid without explosion
- f local flashes of flame at AC surface only
- h hissing as individual drops enter
- h X hissing, followed later by explosive ignition
- h F hissing, followed later by inflammation

TABLE II

Observed reactions between liquid chlorine trifluoride
and liquid hydrocarbons

Test fuel	At room temperature		At -40°C	At -65°C
	In normal atmosphere	In CO ₂ atmosphere		
Propane				X
N-hexane	X	X	X	X
N-heptane	X	X	X	X
Iso-octane	X	X	X	X
N-nonane	X	X		
Iso-dodecane	X	X	X	X
Kerosine (Avtur)	X	X	X	
Aviation Gasoline (100/130)				
Wide-Cut Gasoline (Avtag)	X	X		
Liq. Paraffin	X	X		
Benzene	X	X		
Acetone	X	X		

X denotes explosion

3 Discussion

3.1 Gas phase reactions

Very high flame temperatures were observed in gas phase reactions with chlorine trifluoride. Contributory factors are the high heat of formation of hydrogen fluoride and carbon tetrafluoride, the probable simple nature of the reaction products and the relatively low degree of dissociation, at a given temperature, of a fluorine compound compared with that of the corresponding oxygen compound. However, beyond the fact that there is a pronounced tendency towards the formation of free carbon, the detailed nature of the reaction products remains for further study.

Compound AC, gaseous chlorine trifluoride and bromine pentafluoride were non-effective in causing ignition of gaseous hydrocarbons but Compound BC2 and liquid chlorine trifluoride readily ignited propane/air mixtures of composition extending over the whole range from the weak to the rich limit of inflammability. The intensity of gas phase reactions with chlorine trifluoride is greatly reduced by dilution with inert atmosphere and it is probable that Compound AC behaves initially as diluted chlorine trifluoride. The heat of reaction is then frequently insufficient to promote renewal of the active constituent from within the bulk of the complex. It is hoped to elucidate this further by making suitable tests with finely divided AC, such as would be obtained in practice by scattering after strike of a high speed projectile. It has also been noted that the surface of Compound AC frequently becomes coated with tar-like reaction products which, no doubt, also tend to reduce its effectiveness.

3.2 Reactions in condensed systems

A study of the behaviour of these compounds towards liquid hydrocarbon sprays of fine droplet size is not yet complete. Compound AC itself is disappointing as an incendiary agent under these conditions, failing, even with n-hexane, to cause ignition at atmospheric pressures below 350 mm.Hg. Later it is hoped to establish whether the alternative materials are more effective under simulated high altitude conditions.

Compound AC has also been found inferior in causing ignition of bulk liquid hydrocarbons. Where localised flashes of flame were seen to occur, these were rapidly quenched by the cooling effect of the liquid.

Compound AC2 probably behaves largely as a source of undiluted chlorine trifluoride vapour and its physical state permits continued release of the active constituent. Although not detailed in Table I, it was noted that the violence of the explosive reactions with Compound AC2 and liquid hydrocarbons decreased with decrease in molecular weight of the latter. The same effect was obtained with bromine pentafluoride which failed to ignite n-hexane even after admission of numerous drops of the material. In such cases the heat of reaction is most likely dissipated in causing formation of hydrocarbon vapour, which, as has already been noted, it not readily ignited except by liquid chlorine trifluoride and Compound BC2.

Liquid chlorine trifluoride generally caused very violent explosive ignition of all the hydrocarbons tested and the violence was in no way reduced by carrying out the reactions at temperatures as low as -65°C. Neither was any decrease in violence observed when the hydrocarbon was

outgassed and blanketed with an atmosphere of carbon dioxide. However, in an attempt to distinguish any differences in behaviour towards the more volatile hydrocarbons, as opposed to a material such as kerosine, a photographic record was made of reactions at room temperature. The record was made on 16 mm. film at a camera speed of 2000 frames per second and selected prints from the film are included in this report.

Fig.1 illustrates the progress and speed of reaction obtained with n-hexane contained in a 6" x 1" glass tube. The entering drop of chlorine trifluoride first falls through the liquid hexane and initial reaction is observed to be relatively slow. The reaction zone or "hot spot" round the drop increases progressively in size over a period of time of about 35 milli-seconds (Fig.1, a to d). The reaction then accelerates violently, leading to a sudden explosion (Fig.1e) within an ensuing time interval of less than 0.5 milli-seconds. The light emitted by the reaction is of a relatively low intensity. The first stage of the reaction probably causes generation and mass transfer of vapour away from the hot spot and this is suggested by Fig.1d, where the apparent volume of the hexane has appreciably increased. The reaction then appears to pass over to a low order detonation but the speed of the camera used was too low to enable an estimate to be made of the rate of progress of the flame front.

A repeat test made with n-hexane contained in a glass tube of 1 in. diameter and length 1½ in. led to almost identical results. In a third test, however, and again using a 6" x 1" tube, the first drop of chlorine trifluoride failed to cause an explosion and merely heated the hexane, giving a vapour-rich atmosphere in the tube. In this case the ensuing drop of chlorine trifluoride was expended in reacting with the hexane vapour. Fig.2a shows the commencement of this intense but local reaction and 40 milli-seconds later (Fig.2b) reaction has spread as the drop continues to fall and leaves a wake of soot particles in its path.

In the case of kerosine, a material of low vapour pressure at ordinary temperatures, the nature of the reaction is somewhat different. The chlorine trifluoride droplet was observed to react immediately it reached the surface of the hydrocarbon and Figs.3a and b illustrate the instants before and after explosion respectively, the time interval between these records being 0.5 milli-seconds. Fig.3c is a record taken 2.5 milli-second later to show the growth of flame and soot cloud. It is also interesting to observe the undisturbed liquid (Fig.3b) close to the walls of the tube immediately after explosion. A repeat test confirmed that this type of reaction was typical with kerosine and that the light emitted by the reaction was more intense than with hexane. It will be noted that the glass tube was not shattered during the kerosine explosion and this is thought to be due to the cushioning effect of liquid remote from the point of initiation. It could also be explained by the fact that little in the way of first stage reaction occurs, i.e. where vapour formation is preponderant, that the reaction is therefore overall more rapid than with hexane and that unreacted chlorine trifluoride is ejected from the mouth of the tube.

4 Practical significance of the tests

The preliminary laboratory tests described illustrate satisfactorily the marked chemical reactivity of selected halogen fluorides towards hydrocarbon fuels. In particular, liquid chlorine trifluoride and Compound BC2 have been found most effective in causing explosive ignition of hydrocarbon vapour and of a variety of hydrocarbon fuels both in spray and bulk liquid form. Such results suggest that practical trials with these two materials would be worthwhile. On the other hand less promising results have been observed with Compound AC; these results also suggest that its effectiveness would be still further reduced under conditions of flight at high altitude.

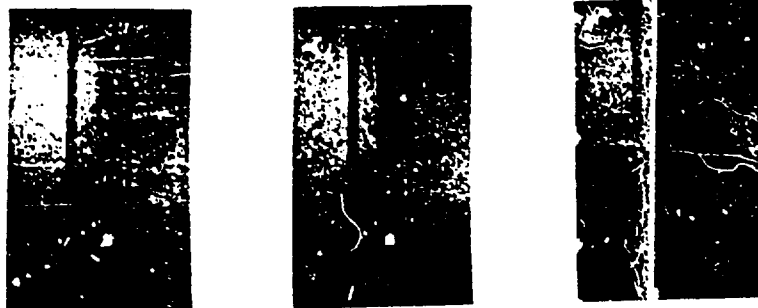
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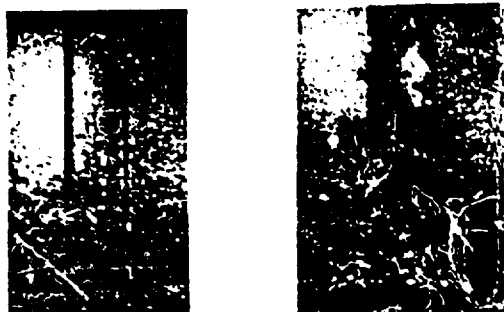
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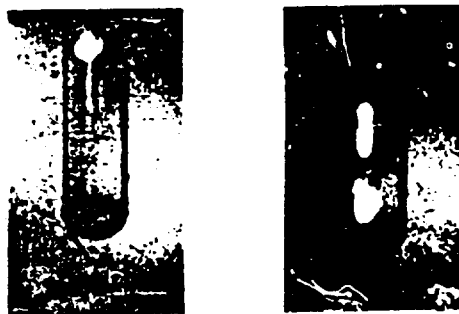
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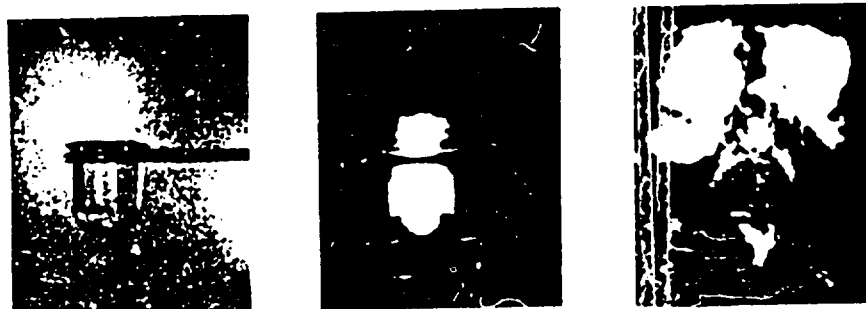
FIG.1. REACTION OF LIQUID ClF_3
WITH n - HEXANE



a

b

FIG.2. REACTION OF LIQUID ClF_3 WITH
n - HEXANE VAPOUR



a

b

c

FIG.3. REACTION OF LIQUID ClF_3 WITH KEROSENE

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