1073. *The Gaseous Reaction of Chlorine Trifluoride with Methane.*

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Minimum ignition temperatures, measured at pressures from 80 to 600 mm., show that a 3 : 2 mixture of methane and chlorine trifluoride is the most prone to explosion. A characteristic property, which persists even in packed vessels or in the presence of an excess of inert diluent, is the very sudden transition from negligibly slow to explosively rapid reaction. The kinetic features of the slow reaction cannot therefore be determined and analytical studies are confined to the products of the explosive reaction.

Under all conditions, hydrogen fluoride is much the most abundant gaseous product and methyl chloride is the predominant organic product. After explosion of pure reactant mixtures, considerable amounts of acetylene, ethylene, and ethane are formed, together with smaller quantities of some fully halogenated methanes. In the presence of an excess of nitrogen, the production of C_2 hydrocarbons is largely suppressed and certain partly halogenated methanes become important organic products.

It is concluded that the reaction occurs by a free-radical chain mechanism. The analytical results suggest that the chlorine trifluoride acts primarily by " stripping off " of hydrogen from the hydrocarbon by the combined fluorine. The probable mode of formation of the principal organic products is also discussed.

For some time after the discovery of the halogen fluorides,[1] their reactions with organic compounds were little studied. In earlier attempts to use these compounds as halogenating agents, attention was paid chiefly to bromine trifluoride [2,3] and iodine pentafluoride,[3,4] but in recent years, there have been several investigations concerned with the use of the more highly reactive chlorine trifluoride for this pupose.[5] In many cases, the principal object of such work has been the preparation of polyhalogen (and, if possible, perhalogen) compounds for use as chemically inert lubricants, and most of these studies have yielded little fundamental information regarding the reactions taking place. Musgrave and his co-workers, in an attempt to obtain some insight into the mechanism of halogenation by chlorine trifluoride, made more detailed investigations of its reaction with benzene and some of its derivatives [6] and with trichloroacetic acid and the corresponding acid chloride.[7]

These researches and indeed almost all previous work on the reactions of chlorine trifluoride with organic compounds have been carried out in the liquid phase, the halogen fluoride, often diluted with nitrogen, being bubbled into the liquid organic compound or its solution in a suitable solvent. Apart from some unpublished work,[8] on the halogenation of benzene in the vapour phase, which evidently exhibits some marked differences from the corresponding liquid-phase reaction, little or no information appears to be available regarding the gaseous interaction of chlorine trifluoride with organic compounds. For several years, some work has been in progress in these laboratories on the reactions of this interhalogen compound with gaseous paraffin hydrocarbons and the present paper describes some results obtained with the chlorine trifluoride–methane system.

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[1] Ruff *et al.*, *Z. angew. Chem.*, 1928, **41**, 1289 *et seq.*; *Z. anorg. Chem.*, 1928, **176**, 258 *et seq.*

[2] Nutting and Petrie, U.S.P. 1,961,622; McBee, Lindgren, and Ligett, *Ind. Eng. Chem.*, 1947, **39**, 378; U.S.P. 2,432,977, 2,471,831.

[3] Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2188.

[4] Ruff and Keim, *Z. anorg. Chem.*, 1931, **201**, 245; Simons, Bond, and McArthur, *J. Amer. Chem. Soc.*, 1940, **62**, 3477; Simons and Brice, U.S.P. 2,614,131; Haszeldine and Kidd, *J.*, 1953, 3219.

[5] Leech and Burnett, B.P. 633,678; Pennsylvania Salt Manufacturing Co., B.P. 665,253; Burnett, B.P. 676,374; Mantell, Passino, and Teeters, U.S.P. 2,684,987.

[6] Ellis and Musgrave, *J.*, 1950, 3608; 1953, 1063.

[7] Cuthbertson, Holmes, Musgrave, and Tanner, *J. Appl. Chem.*, 1958, **8**, 390.

[8] *E.g.*, Banks, Musgrave, and Sowler, unpublished results quoted in " Advances in Fluorine Chemistry," Vol. I, Butterworths Scientific Publ., London, 1960, p. 23.

EXPERIMENTAL

Materials.—Chlorine trifluoride, obtained from a commercial cylinder, was passed first through two U-tubes containing sodium fluoride in order to remove hydrogen fluoride [9] and then through a series of traps in which the liquid was fractionally distilled. Methane of 99·8% purity was dried over magnesium perchlorate and was passed through traps at −196° to remove any other condensable impurities. Commercial "oxygen-free" nitrogen was used without further purification.

Apparatus and Procedure.—The apparatus consisted essentially of a cylindrical copper reaction vessel, 14·8 cm. long and 6·6 cm. in diameter, which was placed in a water thermostat and was attached to lines for separate admision of the reactants and for withdrawal and analysis of the products. All parts of the system which came into contact with chlorine trifluoride were made of copper, which was freshly reduced before use, and the purification and storage lines for methane and nitrogen were constructed of Pyrex glass. Pressures were measured on Budenberg anti-chlorine metal Bourdon gauges which were not attacked chemically by chlorine trifluoride or by the reaction products.

The normal experimental procedure was to admit a known pressure of chlorine trifluoride to the reaction vessel and then to connect this momentarily to another vessel of known volume filled to a predetermined higher pressure either with pure methane or with a methane–nitrogen mixture. In this way, the required amount of the hydrocarbon could be rapidly added to the halogen fluoride.

Four different methods were used to analyse the reaction mixtures since no one method on its own gave sufficiently detailed information.

(a) *Volumetric analysis.* An aliquot part of an aqueous solution of the products was titrated with sodium hydroxide to determine total hydrogen halides. Another part was treated with an excess of silver nitrate and the remaining silver ions were back-titrated with ammonium thiocyanate; this gave the amount of hydrogen chloride present and hydrogen fluoride was then determined by difference.

(b) *Gas–liquid chromatography.* None of the stationary phases investigated separated completely all the volatile species present unless the excess of hydrogen fluoride and unchanged methane, which tended to overload the column, were first removed. The reaction mixture was therefore condensed in liquid oxygen and any methane was pumped off. Hydrogen fluoride was then absorbed over solid potassium hydroxide, and the remaining products were analysed by gas-chromatography. In some early work, the instrument used had a 12-ft. dinonyl phthalate column and a carbon monoxide flame detector. In later work, the apparatus had a 24-ft. squalane column and was fitted with a katharometer detector.

(c) *Infrared spectroscopy.* The products were introduced into a gas cell with rock-salt windows and analyses were carried out on a double-beam infrared spectrometer, fitted with a rock-salt prism which transmitted in the region 4000—650 cm.$^{-1}$.

(d) *Nuclear magnetic resonance spectroscopy.* Reaction mixtures were condensed in thick-walled glass tubes, 12 cm. long and 0·3 cm. in diameter, filled to one-quarter of their depth with carbon tetrachloride. The amount introduced was such that at room temperature the total pressure developed was 25—30 atm. The sample tubes were introduced into the metal probe of the spectrometer which contained the radiofrequency source. The probe was placed between the poles of an electromagnet in a position such that the magnetic field over the sample was effectively homogeneous. The radiation used had a frequency of either 40 or 56 mc./sec. and under these conditions hydrogen and fluorine (^{19}F) resonances occur at field strengths of about 9346 and 9950 gauss, respectively, so that there was no overlapping of the two spectra. For hydrogen, the maximum range of shifts corresponded to *ca.* 0·3 gauss while for fluorine the range was *ca.* 6 gauss. The various species present were identified from the characteristic resonance line positions which had previously been determined by calibration with pure components. A semiquantitative indication of the concentrations of the products was given by the corrected relative intensities of the resonance lines. However, although the relative amounts of hydrogen- and fluorine-containing constituents may be obtained by comparisons within each separate group of compounds, the results for the two classes cannot be compared with one another. This is due to the fact that the two regions of the resonance spectrum concerned had to be investigated under different conditions of power and sweep rate.

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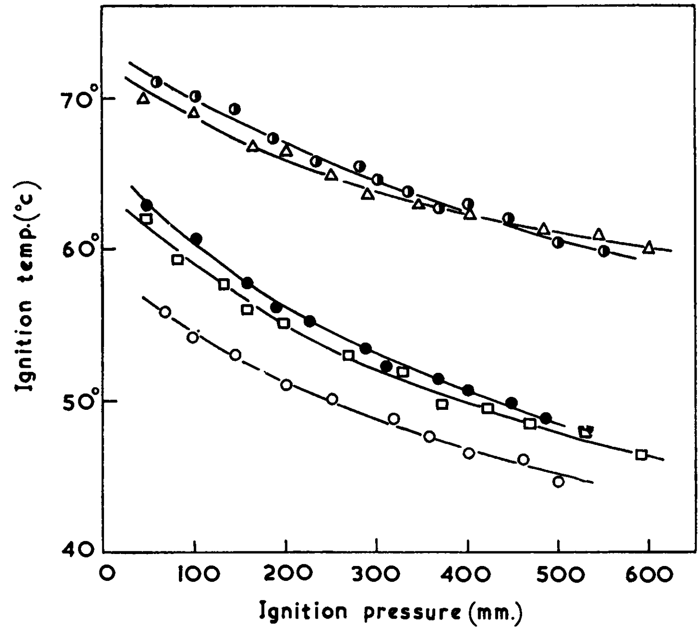
[9] Cf. Banks and Rudge, *J.*, 1950, 191.

RESULTS

General Features.—The influence of pressure and temperature on the ignition limits for a number of chlorine trifluoride–methane mixtures is shown in the Figure. It will be seen that, at a given total pressure, the ignition temperature is lowest for a mixture containing 60% of methane and 40% of chlorine trifluoride.

A striking characteristic of all the systems studied is the extreme suddenness of the transition from immeasurably slow reaction to violent explosion, the change being readily brought about by very small alterations in the experimental conditions. Under conditions near the boundary, explosion was preceded by an appreciable induction period during which there was no detectable consumption of reactants and the length of which was very variable and profoundly affected by the procedure adopted in the previous run. After explosion, the pressure in the system decreased slowly and often reached eventually a value considerably less than the original reactant pressure.



Ignition limits for chlorine trifluoride–methane mixtures.

◑ 25% ClF_3; □ 33% ClF_3; ○ 40% ClF_3; ● 50% ClF_3; △ 60% ClF_3

Packing of the reaction vessel with copper gauze raised the explosion limits to an extent dependent on the resulting surface : volume ratio. As a result of an approximately ten-fold increase in this ratio, the ignition temperature at a given pressure was 10—15° higher (Table 1), but the limits remained as sharp as in an unpacked vessel and no measurable slow reaction could be detected. In the same way, dilution of chlorine trifluoride–methane mixtures with nitrogen also reduced the tendency to explosion, but the suddenness of the transition from negligibly slow to infinitely rapid reaction was little affected.

TABLE 1.

The influence of the surface on ignition limits of 3 : 2 CH_4–ClF_3.

Total pressure (mm.)	150	250	400	500
Ignition temp.: empty vessel	53·0°	50·2°	46·6°	44·9°
packed vessel	67·8°	63·8°	58·5°	55·3°

Since conditions could not be established under which reaction takes place at a conveniently measurable rate, it was not possible to study the kinetics of the slow (non-explosive) reaction in detail. In the circumstances, the only way of deducing something about the sequence of chemical changes occurring was to construct an artificial picture of the progress of the reaction with time by analysis of the products of the explosive reaction of mixtures containing progressively greater proportions of the halogen fluoride.

Reaction Products.—(a) *Qualitative results.* Comparison of the infrared absorption spectra of chlorine trifluoride–methane mixtures with those of the pure reactants and of probable reaction products showed clearly that there was no detectable chemical change under non-explosive conditions. The spectrum of the products of the explosive reaction, although highly complex, yielded some valuable qualitative information. In mixtures containing an excess of methane, considerable amounts of acetylene, ethylene, and ethane were formed and the presence of both fluoro- and chloro-hydrocarbons was suggested by the C–F and C–Cl frequencies observed. On the other hand, after explosion in mixtures containing a large proportion of added nitrogen, no C_2 hydrocarbons could be detected and some partially fluorinated methanes appeared to be present.

(b) *Quantitative results.* The presence of hydrogen fluoride (as SiF_4) and hydrogen chloride could not be demonstrated spectroscopically owing to the masking effect of certain C–F and C–H bonds in the relevant regions of the spectrum. The extent of formation of these two products was, however, readily obtained by volumetric analysis of aqueous solutions of the reaction products. The results in Table 2 show the amounts of the two acids formed after explosion of mixtures containing an excess of methane. A considerable proportion of the combined fluorine in the chlorine trifluoride is converted into hydrogen fluoride. On the other hand, only a very small proportion of the combined chlorine appears as hydrogen chloride, suggesting that nearly all this halogen in fact becomes organically bound. Results similar to those shown in Table 2 were found for other reactant mixtures and after explosion at 65° and 75°.

TABLE 2.

Formation of hydrogen halides during explosion of methane and chlorine trifluoride at 70°.

CH_4 (mm.)	ClF_3 (mm.)	Total acid (mm.)	HCl (mm.)	HF (mm.)	CH_4 (mm.)	ClF_3 (mm.)	Total acid (mm.)	HCl (mm.)	HF (mm.)
384	128	181	13	168	305	202	148	13	135
		187	15	172			148	11	137
		177	12	165			150	12	138
356	178	140	5	135	152	152	209	7	202
		134	4	130			212	8	204
		142	4	138			200	4	196

TABLE 3.

The relative amounts * of volatile products formed after explosion at 70°, as determined by nuclear magnetic resonance spectroscopy.

Chlorine trifluoride pressure, 100 mm.

CH_4 pressure (mm.)	100	150	200	300	CH_4 pressure (mm.)	100	150	200	300
Hydrogen-containing products					*Fluorine-containing products*				
CH_3Cl	(100)	108	118	135	HF	(100)	99	100	100
C_2H_2	34	54	83	128	CF_4	11	8	8	6
C_2H_4	22	26	31	42	CF_3Cl	8	6	6	2
C_2H_6	8	10	13	15	CF_2Cl_2	5	3	4	3
CH_3F	13	12	10	9					

* These are expressed relative to the quantities of methyl chloride and hydrogen fluoride, respectively, formed from an equimolar reactant mixture.

Table 3 gives the amounts of various hydrogen- and fluorine-containing products obtained from the corresponding resonance line intensities; these have been corrected for the numbers of hydrogen and fluorine atoms in the molecules of the various species, so that the figures given represent (within each group) relative molar concentrations. The principal product of the explosive reaction is hydrogen fluoride which is formed together with substantial amounts of methyl chloride, acetylene, and ethylene; smaller quantities of ethane, methyl fluoride, tetrafluoromethane, chlorotrifluoromethane and dichlorodifluoromethane are also present. The formation of the fully halogenated methanes is inhibited and that of the C_2 hydrocarbons is enhanced by the use of mixtures containing initially a high percentage of methane. In the presence of an excess of added nitrogen, the amounts of acetylene and ethylene are markedly reduced and ethane can no longer be detected. At the same time, various partially fluorinated (but no fully fluorinated) methanes were found under these conditions.

Table 4 shows the pressures of the principal organic products formed after explosion of various reactant mixtures. The formation of methyl chloride, acetylene, and ethylene increases and that of the fully halogenated methanes decreases with the proportion of chlorine trifluoride in the initial mixture. Since unchanged methane had to be removed before the other products could be analysed, it was not possible to calculate the proportion of the consumed hydrocarbon converted into the compounds shown. The yields based on methane initially present can, however, readily be determined and are found to be very low. Thus, on any reasonable assumption of the stoicheiometry of the reaction, it is clear that only a small percentage of the methane used appears as the simple products shown. In conformity with the observation that explosion is generally followed by a decrease in total pressure, the remainder of the consumed hydrocarbon is presumably accounted for mainly by the heavy carbonaceous deposits, which are especially noticeable after explosion of methane-rich mixtures, and to a smaller extent by the polymeric material which is found to contain some fluorine.

TABLE 4.

The partial pressures of volatile products formed after explosion at 70°, as determined by gas–liquid chromatography.

Chlorine trifluoride pressure, 100 mm.

CH_4 pressure (mm.)	100	150	200	300
CH_3Cl (mm.)	2·0	2·3	3·1	5·8
C_2H_2 (mm.)	0·7	0·8	1·0	1·4
C_2H_4 (mm.)	0·5	0·6	0·7	1·2
CF_4 (mm.)	0·9	0·7	0·3	0·1
CF_3Cl (mm.)	0·6	0·3	0·4	0·2
CF_2Cl_2 (mm.)	0·3	0·2	0·2	Trace

DISCUSSION

Although it was not possible to control the gaseous interaction of chlorine trifluoride with methane and hence study the kinetic features of the slow reaction, the characteristics of the explosive reaction are consistent with a free-radical chain mechanism. Thus the observed sensitivity to the surface conditions of the reaction vessel, the highly variable induction periods, and the extremely sharp explosion limits are all properties which suggest that a chain reaction is in operation.

In the absence of reliable kinetic data, it is impossible to postulate any detailed reaction mechanism, but certain of the analytical results have important implications. In the first place, the fact that the predominant fluorine- and chlorine-containing products are hydrogen fluoride and methyl chloride, respectively, suggests that substitution reactions of the type:

$$\mathrm{Cl{-}F + C{-}H \longrightarrow C{-}Cl + H{-}F}$$

are much more widespread than the alternative process:

$$\mathrm{Cl{-}F + C{-}H \longrightarrow C{-}F + H{-}Cl}$$

and that the principal action of the halogen fluoride consists in the " stripping off " of hydrogen from the hydrocarbon by fluorine. Secondly, the appearance of relatively large amounts of methyl chloride among the products suggest that this compound is very resistant to attack by chlorine trifluoride, as compared with methane itself. On the other hand, the absence of methyl fluoride and other partially fluorinated compounds from the products of explosion of pure chlorine trifluoride–methane mixtures suggests that these compounds, if formed intermediately, are very rapidly further fluorinated. Only in the presence of an inert gas can the non-stop replacement of hydrogen by fluorine apparently be controlled. Finally, it is clear that the considerable amounts of acetylene, ethylene, and ethane formed must arise as a result of the interaction of C_1 fragments. Binary recombination of CH, CH_2, and CH_3 radicals could scarcely account for the extensive formation of the products mentioned and in any case the operation of processes of this kind would be expected to be favoured by added nitrogen, which would tend to act as a third-body. It is more likely that the C_2 hydrocarbon products arise from attack by high-energy CH and CH_2 radicals on methane itself. There is indirect evidence [10] for the occurrence of reactions of this type and it has been suggested [11] that these radicals are readily deactivated by nitrogen, which would explain the absence of acetylene, ethylene, and ethane in the presence of an excess of an inert gas.

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[11] Arthur, *Nature*, 1950, **165**, 557.