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Reactivity of Some Halogenated Alkanes on 13X Molecular Sieve

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The reactivity of dichlorodifluoromethane, trichlorofluoromethane, dichlorofluoromethane, chlorodifluoromethane, bromotrifluoromethane, and trichlorotrifluoroethane on a 13X Davison molecular sieve at temperatures of 150 and 320°C has been examined. For each of these, the nature and concentration of the resulting products have been determined, the variation of sorption capacity of the sieve for carbon dioxide has been measured, and the amount of acid products resulting from sweeping by means of nitrogen saturated with water vapor has been estimated. All the halogenomethanes decompose at 320°C and only trichlorotrifluoroethane and bromotrifluoromethane do not decompose at 150°C. The main destruction product is always carbon dioxide, except for dichlorofluoromethane and chlorodifluoromethane which give carbon monoxide. When decomposition is extensive, it gives rise to strong acids during the reaction and during sweeping by means of nitrogen saturated with water vapor. The toxics seen are carbon monoxide and phosgene. Sorption capacity is strongly decreased and is not entirely recovered after sweeping by means of nitrogen saturated with water vapor.

I. INTRODUCTION

In laboratory studies carried out on halogenomethane reactivity, we showed that there was extensive decomposition of these compounds over a fixed bed of alumina or platinum alumina (*1*). From the results obtained, a method of complete destruction of dichlorodifluoromethane into carbon dioxide has been developed (*2*). Other authors (*3*) have already noted an action of halogenomethanes on diverse metal oxides. The development of our research has led us to study the reactivity of some perhalogenated hydrocarbons in the presence of aluminosilicates. Measurements of dichlorodifluoromethane and chlorodifluoromethane sorption on a 5A-type molecular sieve have been carried out by Cannon (*4*). These show a reaction of these compounds with the sorbent simultaneously with sorption, the specific area being decreased to half its value. Cannon thinks this reaction involves the constitutional water of the sieve. Moreover, studying dichlorodifluoromethane, fluorodichloromethane, and chlorodifluoromethane sorption at 150°C in chabazite, Barrer and Brook (*5*) showed the existence of a reaction between the sorbent and those of the compounds which are able to be sorbed. So, to study the reactivity of the various chosen halogenoalkanes we selected a type of sieve, the physicochemical structure of which is such that all the compounds could be sorbed. The results of sorption capacity measurements at 25°C in 13X and 5A sieves are shown in Table 1.

Sieve 5A shows notable sorption only for Freons whose dimensions are smaller than those of dichlorodifluoromethane. With

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TABLE 1

Sorption Capacities of Freons

Freon[a]	13X Sieve (g/100 g of sieve)	5A Sieve (g/100 g of sieve)	Molecular dimension (Å)		
			Along longest axis	Critical dimension	Third dimension
F 22	120	20.4	6.11	4.93	4.42 (*5*)
F 12	9	0.02	6.64	4.93	4.90 (*5*)
F 11	7	0	6.9	5.8	4.9

[a] F22, chlorodifluoromethane; F12, dichlorodifluoromethane; F11, trichlorofluoromethane.

freons having larger dimensions than those of Freon 12, the only reactivity seen would occur at surface sites of the sieve. This is observed during the reactivity test of trichlorofluoromethane (F 11) at 320°C with sieve 5A. After 400 min, a relative decomposition (50%) into carbon dioxide and a transhalogenation reaction (25%) producing carbon tetrachloride are seen. Production of HCl, Cl_2, and $COCl_2$ is already noticed. Quantitative measurements of sorption capacity of CO_2 at 25°C, in the sieve, before and after the test with F 11, give nearly the same results. This confirms the suggested theory of the superficial reactivity of the framework, the sieve being undestroyed. Under similar conditions, difluorodichloromethane does not decompose, and dichlorofluoromethane leads to carbon monoxide with a relative decomposition of 80%; traces of HCl and CO_2 are seen. All halogenoalkanes studied here have dimensions smaller than the pore size of 13X sieve. They will be able to be sorbed, and then the observed phenomenon will exhibit the total reactions which can occur either on the surface or inside the sieve cavities. To estimate the degree of destruction of the molecular sieve, its sorption capacity for carbon dioxide is measured before and after 400 min of operation. The amount of halogen fixed on the sieve is also measured. The possibility of recovering the sorption capacity of aluminosilicate is also examined.

II. EXPERIMENTAL

Figure 1 shows a diagram of the apparatus used.

1. *Reactor*

The reactor is a Pyrex tube, 1.10 m long and 5 cm in diameter, which is set in an 80-cm-long horizontal tubular furnace. A 50-g sample of molecular sieve is placed inside the furnace, 40 cm away from the entrance, which allows the gas to be preheated before it reaches the catalyst. The 30-cm-long reactor portion that extends from the furnace is used to cool the effluent gases before passing them to the analyzing equipment.

Temperature control is achieved by means of a platinum temperature probe located in the middle of the catalytic bed and wrapped in a protective glass sleeve. The probe is connected to an electronic thermometer and to a recording device. The furnace is heated by a resistor, which, when fed with 220 V ac, will produce 500 W of power. It is fed by a semiproportional regulator controlled by a platinum probe located between the reactor and the furnace inner wall. Such an arrangement allows constant temperature to be obtained within ±2°C up to 500°C.

5A and 13X Davison molecular sieves are distributed in France by Grace S.A.R.L. (Epernon).

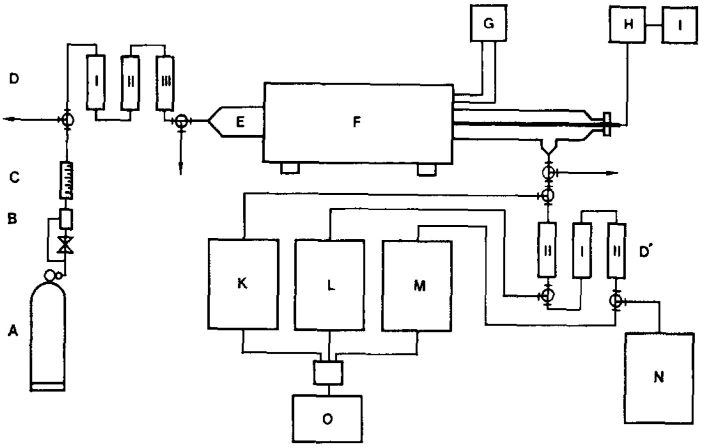

FIG. 1. Diagram of apparatus. A, bottle; B, flow regulator; C, flow meter; D and D', traps: (I) $Ca(OH)_2$, (II) $CaCl_2$, (III) $Mg(ClO_4)_2$; E, reactor; F, furnace; G, regulator; H, thermometer; I, temperature recorder; K, Freon chromatograph; L, CO_2 chromatograph; M, CO_2 analyzer; N, CO analyzer; O, chromatograph and analyzer recorder.

2. *The Feeding System*

The gas mixtures to be studied are prepared in steel bottles, each fitted with a two-stage pressure reducer, a downstream flow regulator, and a ball flow-gauge. The bottles are filled with Freon as follows: A known volume of gaseous Freon, or a known weight of liquefied Freon, is introduced into the previously evacuated bottle; filling is completed with R nitrogen[2] compressed to 100 bars. After temperature equilibrium is achieved, pressure is measured with a precision of 10^{-2} bar.

Taking into account the weight of Freon introduced and the pressure and temperature eventually reached, the concentration can easily be calculated. If compared with various standard gas mixtures, the value of the concentration obtained is checked by gas chromatography. The gas mixture is fed into the reactor at a constant flow rate of 95 liters/hr. Traces of carbon dioxide and water are removed by passing the gases through three traps: $Ca(OH)_2$, $CaCl_2$, and $Mg(ClO_4)_2$. In some tests, these traps are replaced by a water saturator filled with distilled water and intended to saturate the gas mixture with water. Three-way taps located upstream and downstream of the traps allow the gases entering the reactor to be analyzed. At the furnace exhaust end, a water trap is used to decant water that might have formed. Two successive three-way taps direct the gas effluents either toward measuring instruments, to a series of traps, or to the atmosphere.

The traps are designed to protect the CO analyzers ($Ca(OH)_2$ and $CaCl_2$) as well as the CO_2 analyzer ($CaCl_2$), whereas the Freon analyzer is not protected.

3. *Analytical Methods*

The number and nature of the compounds formed, as well as their relative proportions, are determined with a gas chromatograph by determining the various response coefficients as follows.

a. Freon analysis. Halogenoalkanes are analyzed with a gas chromatograph having the following characteristics: double line, two detectors, one column. Columns used are as follows: (i) a 3-m-long, $\frac{1}{8}$-in.-diameter column of 15% dinonylphthalate on 80- to 100-mesh firebrick; (ii) a 2.50-m-long,

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[2] R nitrogen contains $O_2 < 10$ ppm in volume and $H_2O < 10$ ppm in volume. U nitrogen contains $O_2 < 5$ ppm in volume and $H_2O < 5$ ppm in volume.

$\frac{1}{8}$-in.-diameter column of 15% Kel F on 40- to 60-mesh firebrick; (iii) a 6-m-long, $\frac{1}{8}$-in.-diameter column of 20% *N*-hexadecane on 40- to 60-mesh firebrick.

Detectors are as follows: (i) flame ionization detector (H_2–air); (ii) electron capture detector (tritium source); U nitrogen is used as the carrier gas, and the constant flow rate is 30 ml/min.

The columns are operated at room temperature and the detectors at 110°C to prevent water condensation. Gases are injected by means of a valve and bypass loop system, this allowing a constant volume to be introduced and a direct measurement of the concentrations.

Freons 11, 12, 21, 22 are bought at P.C.U.K. (France); freon 113 at Rhone-Poulenc (France); freon 13B1 at Messer-Grieshein G.N.B.H. (Dusseldorf, RFA). F11, trichlorofluoromethane; F12, dichlorodifluoromethane; F21, dichlorofluoromethane; F22, chlorodifluoromethane; F113, trichloro-trifluoromethane; F13B1, bromotrifluoromethane.

b. CO_2 analysis. CO_2 is analyzed with a 2-m, $\frac{1}{8}$-in.-diameter column of Porapak Q (100 to 120 mesh) coated with 0.01% H_3PO_4, operated at room temperature. A thermal conductivity cell is used as a detector, and helium as the carrier gas. This apparatus shows peaks of O_2, N_2, CO_2, and CF_3Cl.

c. Carbon monoxide analysis. CO is present in some mixtures and it sometimes develops as a reaction product. It is analyzed by infrared spectography; as a matter of fact, under the operating conditions used in this work, it has the same retention time for gas chromatography as nitrogen. It is analyzed with a Model UNOR, nondispersive infrared analyzer. (Maihak Cg. Ltd., Hamburg; under ONERA license.)

d. Acid titration. Through a sintered glass, the acid effluent bubbles into 1 *N* soda solution. After reacting, the excess soda is titrated by means of a pH meter coupled with a recording device; this allows the amount of carbon dioxide to be differentiated from that of strong acids.

e. Trace analysis. Reactive Dräger tubes are used to detect traces of $COCl_2$, HF, HCl, Cl_2, and CO.

f. Calibration of analyzers. For CO_2 and CO, standard bottles of gas are used, and the response coefficients of the apparatus are determined after each test. With regard to Freons, calibrated bottles are also used, but in order to reduce handling, a relative response coefficient is determined for each halogenomethane with respect to Freon 12. Later only one calibrated bottle of dichlorodifluoromethane will be used. These response coefficients are calculated by preparation of a standard mixture, of known weight or volume, of a halogenomethane with dichlorodifluoromethane. This calibrated mixture is analyzed by gas chromatography under the operating conditions described before. The proportion between concentrations and peak heights seen on the chromatogram gives a relative response coefficient of the studied halogenomethane with respect to Freon 12. For example, $C_{\mathrm{F}\,11} = k_{11}h_{\mathrm{F}\,11}$, where k_{11} is the response coefficient of the chromatograph for Freon 11.

$$C_{\mathrm{F}\,12} = k_{12}h_{\mathrm{F}\,12},$$

$$\frac{k_{11}}{k_{12}} = \frac{h_{\mathrm{F}\,12} \times C_{\mathrm{F}\,11}}{h_{\mathrm{F}\,11} \times C_{\mathrm{F}\,12}} = K_{\mathrm{F}\,11/\mathrm{F}\,12}.$$

This coefficient is obviously acceptable only for identical conditions of work with the same apparatus. We found the following values: $K_{\mathrm{F}\,22/\mathrm{F}\,12} = 1.30$; $K_{\mathrm{F}\,21/\mathrm{F}\,12} = 2.91$; $K_{\mathrm{F}\,11/\mathrm{F}\,12} = 4.70$; $K_{\mathrm{F}\,13\mathrm{B}1/\mathrm{F}\,12} = 0.532$; $K_{\mathrm{F}\,13/\mathrm{F}\,12} = 0.880$; $K_{\mathrm{CCl}_4/\mathrm{F}\,12} = 6.92$. Freon 113 liquid at room temperature is directly evaluated.

4. Measuring Sorption Capacity for CO_2

A mixture of 3% CO_2 in air is fed into the reactor at a flow rate of 95 liters/hr at room temperature. An ICARE infrared

TABLE 2

Percentage of Freon in Gas Effluent with Respect to Entering Concentration as a Function of Time

Time (min)	Results at 150°C						Results at 320°C					
	F 22	F 21	F 12	F 11	F 13B1	F 113[a]	F 22	F 21	F 12	F 11[b]	F 13B1	F 113
10	0		72	0.6	97	0	0	2.5	8	0	0	62
20	0	38	80	0.6	100	0		3	12		88	67
30	1		87	0.6	100	0	2.5		14	0		
60	5	56	90.5	0.6	100	0		5	20	0	93	89
90	82		93.8	0.6	100	0.3	14		38	0	96	87.5
120	86		97.5				13	6	43	0.3	97.4	97.5
180	92.5	68	98.5			7.1	31	23	46			
240		71	98.8	94		28	30	32	48	6		80
300	92.6	72		93.9		39.5	46		50	11		91.5
360	93.6	73		94		87.4	34		52		98.3	99
400				93.7		99.4	39	33	54	22		

[a] This column corresponds to adsorption.

[b] From 720 to 900 min, F 11 = 45%.

analyzer permits time recording of the concentration of carbon dioxide in effluent gas until complete saturation of the sieve. The breakthrough curve thus obtained allows calculation, by integration, of the amount of CO_2 adsorbed per 100 g of sieve.

5. Measuring Sorption Capacity for Freons

Measurements of sorption for Freons in 5A and 13X sieves are made under the same operating conditions as for carbon dioxide. Freons in gaseous effluents are analyzed by means of gas chromatography.

III. RESULTS AND DISCUSSION

1. Test Operating Mode

A halogenoalkane at a known concentration in nitrogen is sent through the sample of sieve, heated at a temperature of 150 or 320°C, at a flow rate of 95 liters/hr. The qualitative and quantitative analysis of effluent gas, as a function of time, allows determination of the percentage of this halogenoalkane reaction. This reaction may be only a decomposition, in which case it produces carbon dioxide or carbon monoxide with halogen hydrides and sometimes phosgene; alternatively, together with decomposition, a transhalogenation reaction may be observed, which, according to the case, leads to carbon tetrachloride or chloroform formation. After reacting, and cooling the sieve to 25°C, a first carbon dioxide sorption measurement is made. Then the sieve is heated to 320°C under sweeping by nitrogen saturated with water vapor until the effluent gas does not give an acid indication with pH-reactive paper. After this treatment with water vapor, the sieve is swept with dry nitrogen and recooled to 25°C. A second measurement of sorption capacity for carbon dioxide is then made. During the test (between the various analyses) and the sweeping by water vapor, the effluent gas bubbles through an excess known amount of 1 *N* soda solution. An acid–base titration allows the escaped total strong acidity to be determined. The respective amounts of chlorine and fluorine retained on the sieve as halides are determined by analyzing an average sample of the sieve.

All test results obtained according to this procedure are shown in Tables 2 and 3 and Figs. 2 and 3. Note that in some tests, a carbon deposit is seen on the sieve at the end of a reaction. As suggested by Barrer

TABLE 3

Summary of Main Results

Temperature (°C)	Freon	Starting concentration (ppm volume)	Percentage of effluent after		Products formed in descending order	CO_2 capacity (g of CO_2/100 g of sieve)	Time of		2nd CO_2 capacity (g of CO_2/100 g of sieve)	H^+ titration (mole)[a]	Sieve analysis results (g atom of X per 100 g of sieve) (X = Cl, F, Br)
			60 min	400 min			H_2O sweep (hr)	Drying (hr)			
150	F 22	9,950	5	93.6	CO exclusively	3.4	4.5	7	3.8	0.65×10^{-2}	Cl: 0.02 F: 0.77
	F 21	9,600	56	73	CO	—	—	—	—	—	—
	F 12	11,730	90.5	99	CO_2, (HCl)	1.6	1.5	1	2.7	0.24×10^{-2}	Cl: 0.013 F: 0.013
	F 11	12,350	0.6	94	CO_2, CCl_4, (HCl, $COCl_2$)	0.54	16.67	5	0.72	7×10^{-2}	Cl: 0.064 F: 0.021
	F 13B1	4,000	100	100	—	6.1	—	—	—	—	Br: 0.006 F: 0.003
	F 113	1,000	0	99.4	—	6.55	—	8	7.9	—	Cl: 0.02 F: 0.03
320	F 22	10,160	~10	39	CO(HCl, HF, Cl_2, CO_2)	0.8	28.5	4	0.4	3.3×10^{-2}	Cl: 0.02 F: 0.1
	F 21	9,600	5	33	CO, (CO_2, $CHCl_3$)	—	—	—	—	—	—
	F 12	7,700	20	54	CO_2, HCl(HF, CO)	0.5	2.5	0.5	1.3	10.1×10^{-2}	Cl: 0.107 F: 0.105
	F 11	5,000	0	22	CO_2, CCl_4, CO, HCl, $COCl_2$, HF, CF_2Cl_2	0.28	22	7	1.03	10.4×10^{-2}	Cl: 0.022 F: 0.095
	F 13B1	3,700	93	98	CO_2(CO, HF, Br_2)	4.6	3.5	3	5	—	Br: 0.006 F: 0.08
	F 113	7,770	89	99	CO_2, CO	5.4	3	1.5	5.4	—	Cl: 0.03 F: traces

[a] Total amount of effluent acid all through the test and during sweeping with water vapor.

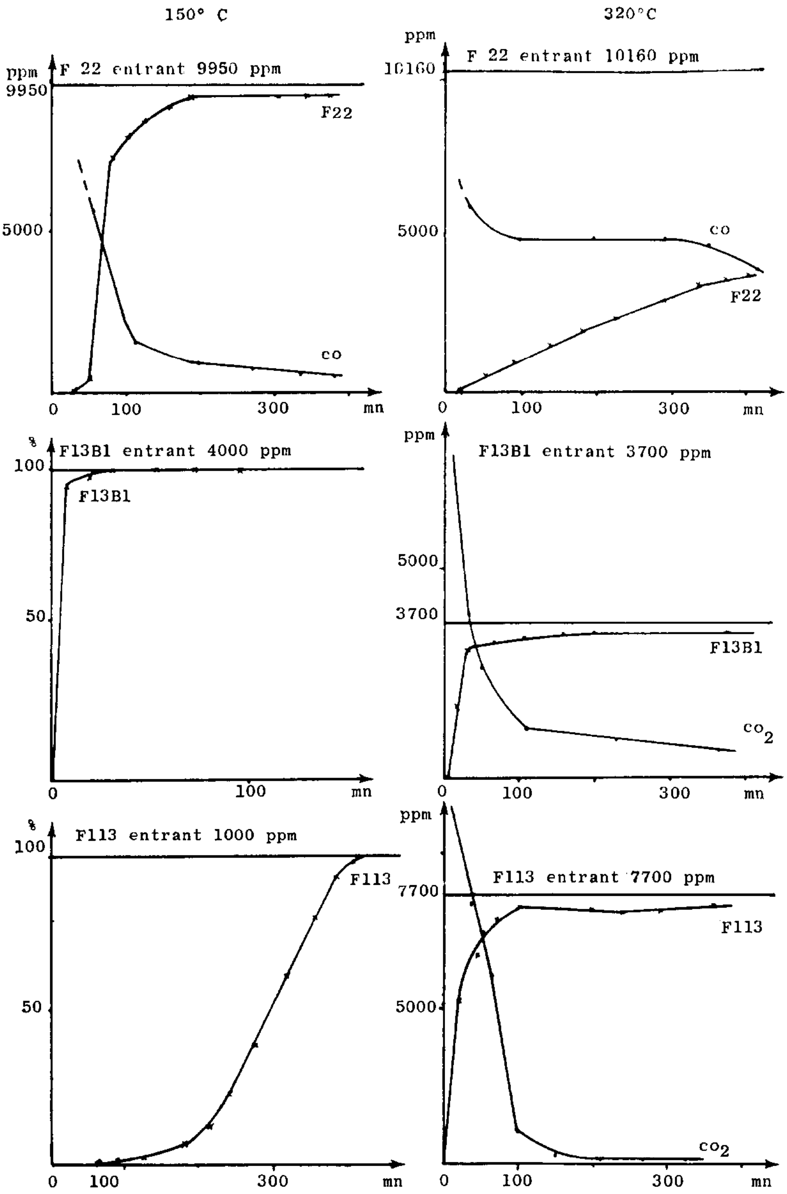

FIG. 2. Effluent behavior of F 22, F 13B1, and F 113 at 150 and 320°C.

and Brook (*5*), it is presumed to have formed during preheating of the sieve.

2. Discussion of Results

a. Results obtained at 150°C. At a temperature of 150°C, all the halogenoalkanes studied, except two, show decomposition. The exceptions are tribromofluoromethane and trichlorotrifluoroethane. The first one is a thermodynamically more stable product (*6*) which does not give any decomposition at this temperature. The second one does not give decomposition, but a notable sorption is seen, corresponding to 3.9 g of Freon per 100 g of sieve. For the other halogenoalkanes, at this temperature, sorption cannot be seen. In the case of Freon 113, the molecule is more strongly occluded, as it needs stronger energy to be excluded. An explanation based on the dimensions of the molecule may be suggested. The size of the Freon 113 molecule, using the usual data relating to bond distances and Van der Waals radii, gives these results: 8 Å along the longest axis, 6 Å as the critical dimension, and 5 Å for the third dimension. Its critical dimension is such that it could easily enter the sieve cavities, but the molecule will take up more space than the molecule of other Freons and so be more strongly occluded.

b. Results obtained at 320°C. At a temperature of 320°C, a considerable increase in the reactivity of all the halogenoalkanes

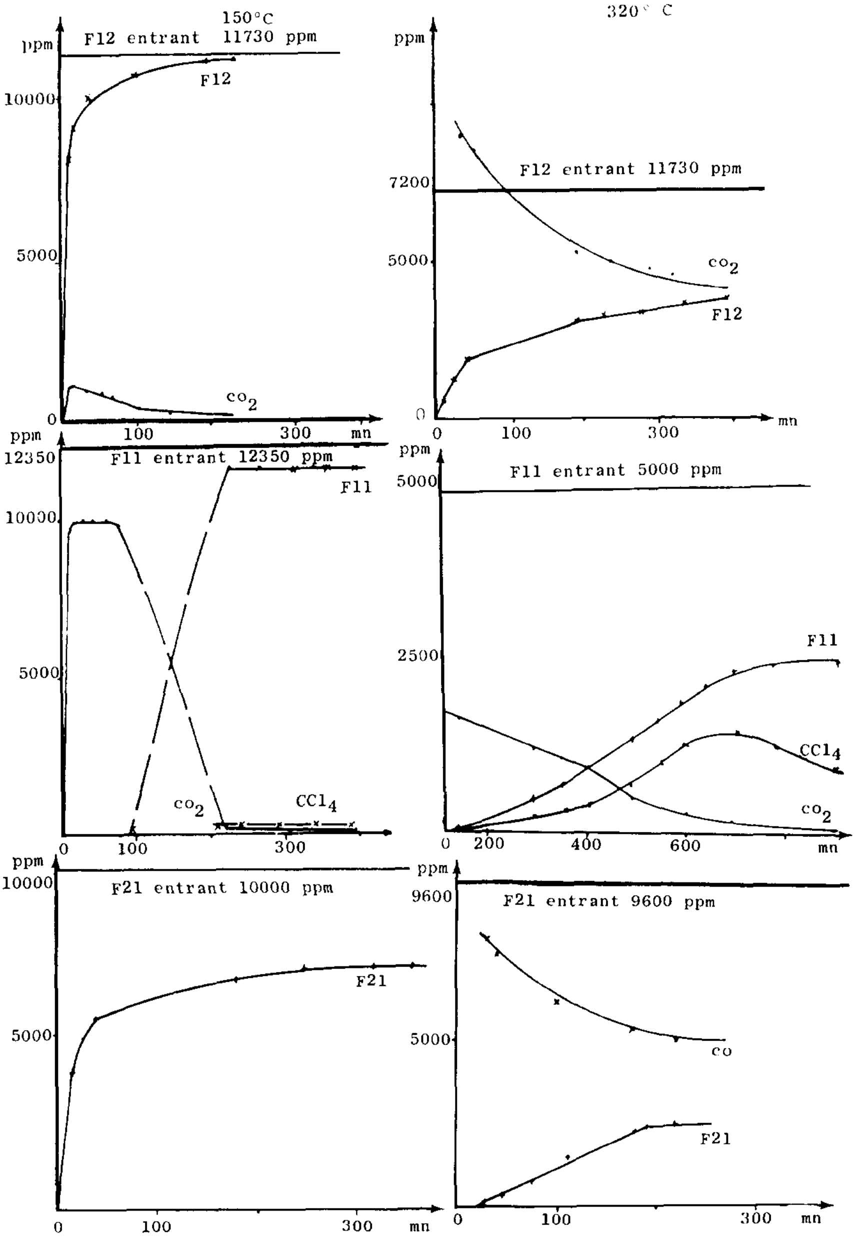

Fig. 3. Effluent behavior of F 12, F 11, and F 21 at 150 and 320°C.

is seen. For Freon 113, the adsorption phenomenon is no longer observed, but a slight decomposition (5%) into carbon dioxide is noticed. Freon 13B1 decomposes only slightly (3%). Decomposition ratios noticed for Freon 22 and Freon 12 after 400 min (when a stable process is established) are, respectively, 51 and 45%.

For Freons 21 and 11 a reaction of transhalogenation is seen simultaneously with the decomposition. The respective percentages of these two phenomena are: for Freon 21, 8 and 59%; for Freon 11, 20 and 35%.

From these experimental results the conclusions below are suggested:

(1) The transhalogenation reaction seen during the tests with Freons 21 and 11 indicates the transient formation, on the framework of the sieve, of halides, which are able to react with additional molecules of Freons to produce CCl_4 and traces of CF_2Cl_2 in the case of Freon 11, and $CHCl_3$ in the case of Freon 21. Parts of these halides are either hydrolyzed by means of water vapor, releasing HX, or fixed on the sieve as $NaX (X = F, Cl)$, the amount of which is determined after the test by analyzing the sieve.

(2) On account of the reactivity of Freons 22, 21, 12, and 11, it appears that the most chlorinated Freons react better: F 21, 67% compared with F 22, 61%; and F 11, 55% compared with F 12, 46%. This may be due to the relative weakness of C–Cl bonds, namely, 73 kcal/mol compared with 102–104 kcal/mol for C–F and about 102 kcal/mol for C–H.

(3) Moreover, Freons containing a hydrogen atom react better: F 22, 61% compared with F 12; 46%, and F 21, 67% compared with F 11, 55%. In this case the relative decomposition ratio for Freon 21 is 59% compared with F 11, 35%. The decomposition of these Freons (22 and 21) releases only carbon monoxide instead of carbon dioxide for the perhalogenated freon. The highest decomposition ratio is seen for Freon 22. The participation of the C–H bond may be understood on the basis of two considerations:

(i) The hydrogen atom can form a hydrogen bond with the oxygen atom of the sieve. This hydrogen bond polarizes the C–H bond and creates a greater reactivity for the molecule of the Freon. This is easier as polarization factors preexist in these compounds: Freons 22 and 21 have dipole electric moments of 1.4 and 1.3 D, whereas those of Freons 12 and 11 are 0.51 and 0.49 D.

(ii) If a mechanism with radical participation, as proposed by Bacmann (*7*), is assumed, among the radicals able to be formed, those whose formation is thermodynamically made easier are $\cdot CHF_2$ and $\cdot CF_2Cl$. Only Freon 22 can give rise to both radicals. This can explain the important relative decomposition of this freon.

To attempt an explanation of carbon monoxide formation from compounds with a C–H bond, the results reported here are compared to those obtained by Vernet *et al.* (*8*) with silica and by G. Fevrier (*9*) with alumina under the same operating conditions. With silica gel, relative decompositions of 3% for F 12 and 10% for F 11 are seen. With alumina the ratios are 15% for F 12 and 25% for F 11. The reactivity observed with the 13X sieve is much greater, because of the important number of active sites regularly distributed. They may cause a reaction in the neighborhood of either silicon atoms or aluminum atoms. In the latter case an attack scheme similar to that proposed by Badré *et al.* (*1*) in agreement with the works of Babad and Zeiler (*10*) and Primet *et al.* (*11*) may be proposed. The authors suggest the formation of an intermediary compound of the $COXX'$ type which may either react on alumina to yield CO and AlX_3 (X = Cl, F) or hydrolyze in the presence of water into CO_2 and HX. In the case of Freons containing a hydrogen atom, one of the presumed intermediary compounds might be of the COH*X* type, an unstable compound that would immediately be destructively changed into CO and H*X* prior to any other reaction. Now, among the degradation products of this Freon, large amounts of hydracids are to be found, besides carbon monoxide. They are responsible for the destruction of the sieve framework.

In the case of Freons 12 and 11, the formation of carbon dioxide according to this same scheme requires the participation of the constitutional water of the sieve, and the formation of by-products such as HCl, CO, and $COCl_2$ is explained too.

It is now understandable that the passage of Freon producing a decomposition reaction deeply affects the sieve structure. The sieve then exhibits very low performance during tests on sorption capacity for carbon dioxide.

IV. CONCLUSION

All the halogenoalkanes studied decomposes on the 13X molecular sieve, except trichlorotrifluoroethane which, at 150°C, is simply adsorbed.

In all cases, the sieve sorption capacity for CO_2 is decreased, and sweeping with water vapor-saturated nitrogen, although it displaces retained halogens, does not allow full regeneration of the sieve.

It is to be noticed that the main decomposition product is carbon dioxide, except in the cases of chlorodifluoromethane and fluorodichloromethane which yield only CO. From the fact that, in these cases, the sieve is less affected than with dichlorodifluoromethane and trichlorofluoromethane, we may deduce that halogenated hydracids are mainly responsible for the sieve destruction. The formation of hydracids from Freons 12 and 11 involves action of the constitutional water of the sieve.

In many cases, toxics and corrosives are released, trichlorofluoromethane being the most noxious.

Progressive formation of stable halogenides on the molecular sieve leads to irreversible destruction of the sieve which loses its sorption capacity.

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