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PREPARATION OF CHLOROPENTAFLUOROETHANE FROM DICHLOROTETRAFLUOROETHANE – Note 1*.

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SUMMARY

Gaseous fluorination with hydrogen fluoride at atmospheric pressure of the two isomers $CClF_2$-$CClF_2$ and CCl_2F-CF_3 was carried out continuously on a chromic oxide based catalyst. The fluorinated derivative , obtained in a yield greater than 90%, was chloropentafluoroethane. Hexafluoroethane and an isomeric mixture of trichlorotrifluoroethane were obtained as by-products. The latter was recycled with unconverted $C_2Cl_2F_4$ for further fluorination . Both conversion of $C_2Cl_2F_4$ and selectivity to the formation of C_2ClF_5 were affected by temperature, contact time and molar ratio of the reagents. The catalytic activity of chromic oxide was adversely affected by small amounts of water in the hydrogen fluoride. A difference was also observed in the reactivity of the two isomers CCl_2F-CF_3 and $CClF_2$-$CClF_2$ The formation of $C_2Cl_3F_3$ as a by-product was due to the disproportionating activity of chromic oxide upon $C_2Cl_2F_4$.

INTRODUCTION

Chloropentafluoroethane is used in the production of the refrigerant F 502 (azeotropic mixture with chlorodifluoromethane 51.2/48.8).

The preparation of chloropentafluoroethane can be carried out in three ways (TABLE 1): chlorofluorination of ethylene [1,2] disproportionation of dichlorotetrafluoroethane [3,4] and fluorination of dichlorotetrafluoroethane [4 - 14].

The first reaction gives low yields (⩽ 63%) together with considerable amounts of dichlorotetrafluoroethane [2] ; in the second reaction the conversion of tetrafluorocompound is somewhat low (⩽ 53%) and involves the unavoidable coproduction of trichlorotrifluoroethane [4] . The fluorination of dichlorotetrafluoroethane is, on the contrary, more specific and advantageous.

The highest yields (95%) reported in the literature are those obtained with catalysts based on tripositive chromium [10]; however, these require particular preparative techniques and handling in order to avoid a rapid loss in their activity. We have studied continuous fluorination of dichlorotetrafluoroethane in the gaseous phase using a particular chromic oxide [15].

TABLE 1

Preparation of CF_3-CClF_2

1. $CH_2=CH_2 + 5Cl_2 + 5HF$	$\longrightarrow$	$CF_3-CClF_2 + 9HCl$
2. $2C_2Cl_2F_4$	$\longrightarrow$	$C_2ClF_5 + C_2Cl_3F_3$
3. $C_2Cl_2F_4 + HF$	$\longrightarrow$	$C_2ClF_5 + HCl$.

RESULTS AND DISCUSSION

The fluorination of dichlorotetrafluoroethane was carried out in a nickel reactor R (Fig. 1) containing the chromic oxide in pellet form. The gaseous hydrogen fluoride and chlorofluoroethane were introduced through the reactor bottom. The reaction products were taken from the top and after aqueous washing and condensation,were analysed from time to time by chromatography.

Various tests were conducted with a single isomer and with mixtures of the two $C_2Cl_2F_4$ isomers (sym- $CClF_2-CClF_2$ and asym- CF_3-CCl_2F) in order to study the amounts of fluorination as a function of:
temperature, contact time, reagent ratio, water content in HF, catalyst ageing resistance, recycle of unreacted dichlorotetrafluoroethane.

a) Reaction temperature

The temperature range studied was 200 to 405°C (contact time 3 sec., linear velocity 11-12 cm $sec.^{-1}$ and molar ratio $HF/C_2Cl_2F_4$ varying from 1 to 1.3). The amount of conversion of dichlorotetrafluoroethane (symmetric/asymmetric isomer=40/60) and the yield of chloropentafluoroethane are illustrated in Fig. 2.

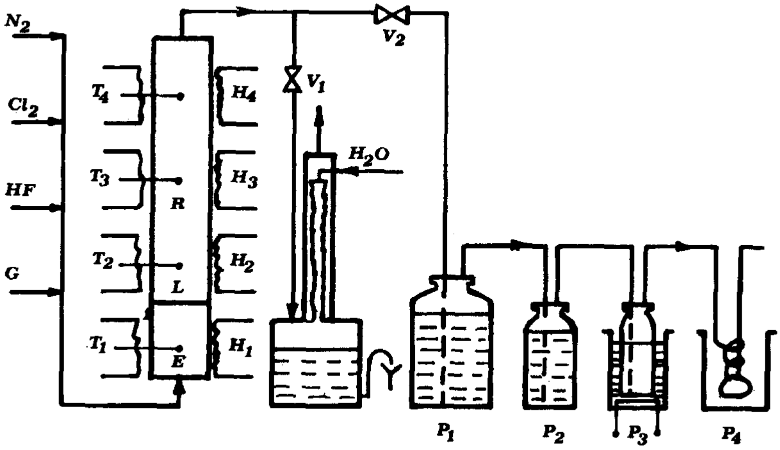

Fig. 1 Diagram of fluorination apparatus

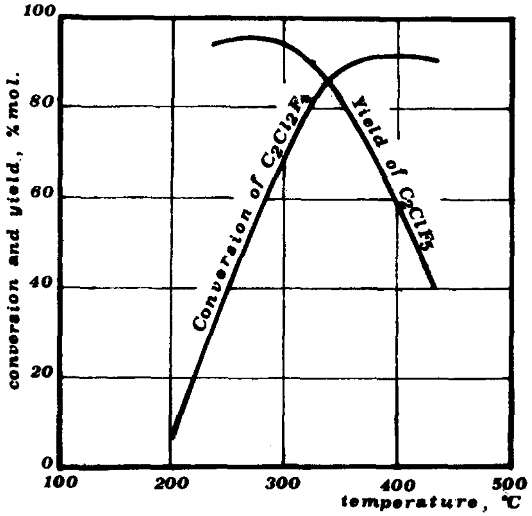

Fig. 2 Conversion of $C_2Cl_2F_4$ and yield of C_2ClF_5 temperature.
Molar ratio $HF/C_2Cl_2F_4$ 1.1, contact time 3 sec.

It is clear that conversion is at a maximum (ca.90%) at about 360°C; on the other hand, the yield of pentafluoroderivative is maximum between 250°C and 300°C, but, at higher temperatures, it decreases owing to the increasing formation of hexafluoroethane (40% at 405°C).

b) Contact time

The contact time range varied from 2.2 to 7 sec. (temperature 300°C, molar ratio HF/$C_2Cl_2F_4$ between 1 and 1.35).
The reaction trends are illustrated in Fig. 3

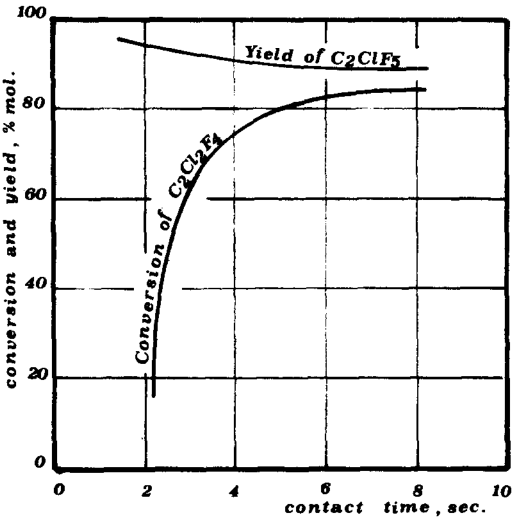

Fig. 3 Conversion of $C_2Cl_2F_4$ and yield of C_2ClF_5 *versus* to contact time.Molar ratio HF/$C_2Cl_2F_4$ 1.1, temperature 300°C.

Only with a contact time of at least 3 sec. does the conversion of tetrafluoroethane (symm/asymm = 40/60) reach ca.65%, while the yields of pentafluoroethane still remain around 90%.

c) Molar ratio HF/dichlorotetrafluoroethane

The molar ratio HF/dichlorotetrafluoroethane ranged from 0 to 1.36 (temperature 300°C and contact time 4 sec.).
The trends of conversion and yields of $C_2Cl_3F_3$ and C_2ClF_5 are illustrated in Fig.4.

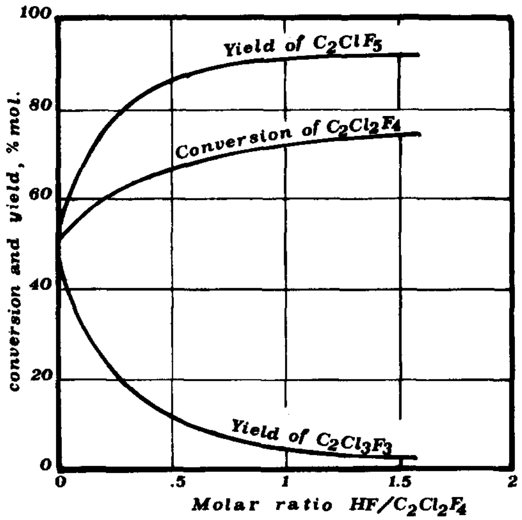

Fig. 4 Conversion of $C_2Cl_2F_4$, yield of C_2ClF_5 and yield of $C_2Cl_3F_3$ *versus* to molar ratio HF:$C_2Cl_2F_4$ Temperature 300°C, contact time 4 sec.

The limited influence of HF on the conversion of dichlorotetrafluoroethane is clearly evident; its effect in decreasing severely the coproduction of trichlorotrifluoroethane thus enhancing the yield of chloropentafluoroethane is nevertheless appreciable. The C_2ClF_5 is higher than 80% even at less than 0.5 mole HF per mole of dichlorotetrafluoroethane and remains around 90% starting from equimolecular ratios HF/$C_2Cl_2F_4$.

It appears that the chromic oxide as fluorinating catalyst also catalyzes simultaneously the disproportionation of dichlorotetrafluoroethane. The disproportionation and isomerization of chlorofluorocarbons on various catalysts are already well known [4, 16, 17, 18, 19]. We have recently shown in experiment with this chromic oxide without HF that:

- dichlorotetrafluoroethane (isomeric mixture 31/69) undergoes 69.5% disproportionation at 350°C with a contact time of 5 sec;
- disproportionation of the asymmetric isomer is 1.8 times greater than that of sym-$C_2Cl_2F_4$;
- the trichlorotrifluoroethane formed by disproportionation consists of 85% 1.1.1 -trichloro-2.2.2-trifluoroethane, even when one stars from dichlorotetrafluoroethane containing 40% of the symmetric isomer;
- there is a slight increase in the amount of symmetric isomer (increases from 12 to 26%) in the unreacted dichlorotetrafluoroethane.

Thus, in addition to fluorination and disproportionation, isomerization of dichlorotetrafluoroethanes is also simultaneously catalyzed by chromic oxide,(see also [4,18]).

(Without such compensation , the high percentage of asymmetric trichlorotrifluoroethane (85%) cannot be explained. Were it derived only by disproportionation of asymmetric dichlorotetrafluoroethane, the amount of disproportionation of symmetric dichlorotetrafluoroethane could not be justified. This disproportionation, at 350°C and 5sec., was at least 31% even on a less active chromic oxide. On the other hand, the higher disproportionation rate of the asymmetric tetrafluorocompound may explain the increase of the symmetric isomer in the undisproportionated dichlorotetrafluoroethane, in spite of the isomerization favouring the asymmetric isomer).

The scheme of conversion reaction of dichlorotetrafluoroethane, taking place simultaneously with fluorination, which in our opinion best represents the above experimental results, is given in TABLE 2, partially drawn from Kolditz's work [18] and in agreement with Vecchio-Groppelli [4] .

Reactivity of the two dichlorotetrafluoroethane isomers to fluorination.

Fluorination was carried out using various mixtures of dichlorotetrafluoroethane in a larger reactor than the one used in the previous tests (i.d. 40mm, catalytic bed height 16mm).

The fluorination trend is shown in Fig. 5 (at 350°C, contact time 3 sec., linear velocity 5-6 cm sec.$^{-1}$). A slight difference in the reactivity between the two isomers is observed from the curves with the asymmetric one showing higher conversion and yield of chloropentafluoroethane by ca.25% and 13%, respectively, than reference to the symmetric isomer. For the asymmetric trichlorotrifluoroethane, we also found a fluorination rate 1.6 times higher than that of the symmetric isomer(72.9% and 47% conversion, respectively, at 350°C and 4 sec.).

Effect of water on the catalyst activity.

Two runs were carried out for comparison using hydrogen fluoride evaporated from cylinders containing reagent with 1.6 or 0.12% water(TABLE 3). The effect of water in reducing the yield of tetrafluorocompound conversion clearly appears from tha data of these tests.

$C_2Cl_2F_4$ mixtures of different isomeric ratios were used in the two runs; from the trends of $C_2Cl_2F_4$ conversion for the isomeric ratios (Fig. 5) it can be calculated that maximum conversion would have been 74% even using the $CClF_2$-$CClF_2/C_2Cl_2F_4$= = 0.2 mixture with HF at 1.6% water (i.e, lower than that at 0.12% water).

TABLE 2

Disproportionation and isomerization of dichlorotetrafluoroethane and trichlorotrifluoroethane on chromic oxide

$C_2Cl_2F_4$	$2CCl_2F{-}CF_3$	$\dashrightarrow$	$CCl_3{-}CF_3 + CClF_2{-}CF_3$	Disproportionation
	$2CClF_2{-}CClF_2$	$\dashrightarrow$	$CCl_2F{-}CClF_2 + CClF_2{-}CF_3$	Disproportionation
	$CCl_2F{-}C\ ClF_2 + CClF_2CF_3$	$\dashrightarrow$	$CClF_2{-}CClF_2 + CCl_2F{-}CF_3$	with isomerization (*)
	$CClF_2{-}CClF_2$	$\dashrightarrow$	$CCl_2F{-}CF_3$	
$C_2Cl_3F_3$	$2CCl_2F{-}CClF_2$	$\dashrightarrow$	$CCl_3{-}CClF_2 + CClF_2{-}CClF_2$	Disproportionation
	$2CClF_2{-}CClF_2$	$\dashrightarrow$	$CCl_2F{-}CClF_2 + CClF_2{-}CF_3$	with isomerization (*)
	$CCl_3{-}CClF_2 + CClF_2{-}CF_3$	$\dashrightarrow$	$CCl_2F{-}CClF_2 + CCl_2F{-}CF_3$	
	$CCl_2F{-}CClF_2 + CCl_2F{-}CF_3$	$\dashrightarrow$	$CClF_2{-}CClF_2 + CCl_3{-}CF_3$	
	$CCl_2F{-}CClF_2$	$\dashrightarrow$	$CCl_3{-}CF_3$	

(*) By L.Kolditz, G.Kauschka and W.Schmidt, Z. anorg. allg. Chem. <u>434</u>, (1977) 41-54.

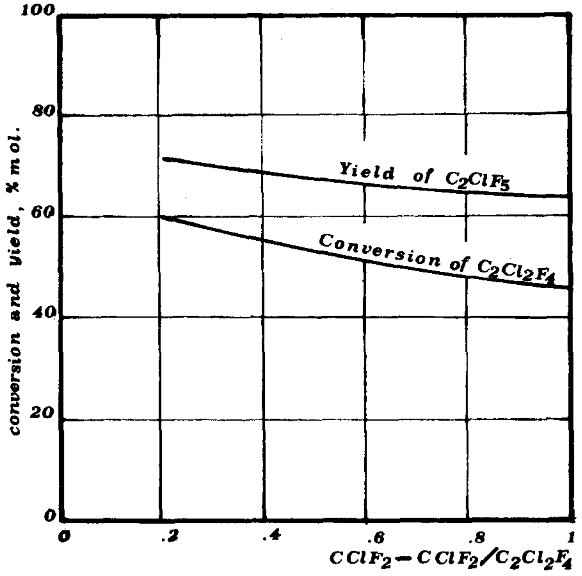

Fig. 5 **Dependence of conversion of $C_2Cl_2F_4$ and yield of C_2ClF_5 upon $C_2Cl_2F_4$ isomeric ratio. Temperature 350°C, contact time 3 sec., molar ratio $HF/C_2Cl_2F_4$ 1.0 .**

TABLE 3 clearly shows the decrease with the time of $C_2Cl_2F_4$ **conversion when using** HF of high water content. After 50 hours it had decreased in the first case to 54.1% from an initial value of 65.2%. When using HF with $<0.12\%$ water, the conversion appeared practically unvaried after 120 hrs. running.

Catalyst life tests

Without recycling dichlorotetrafluoroethane (symm/asymm$\simeq$0.4/0.6)

A 300 hrs. run, under the conditions and with the results given in TABLE 4, did not reveal any decay in the reaction, which remained at the following levels:

- dichlorotetrafluoroethane conversion	72-75%
- chloropentafluoroethane yield	89-92%

Recycling dichlorotetrafluoroethane (symm/asymm.$\simeq$0.2/0.8)

In a further 120 hrs. run, the recycling of unconverted dichlorotetrafluoroethane was also investigated by studying a feed mixture containing 10% $C_2Cl_2F_4$ with 20% of symmetric isomer. The fluorination trend is given in TABLE 5 (during the

TABLE 3

Fluorination of $C_2Cl_2F_4$ with HF on Cr_2O_3.

Effect of H_2O on the catalyst activity

Temperature 350°C, contact time 3 sec., $HF/C_2Cl_2F_4 = 1.1$ (m/m)

roducts of reaction	HF with ≥ 1.6% H_2O $\frac{CClF_2-CClF_2}{C_2Cl_2F_4} = 0.52$		HF with ≥ 0.12% H_2O $\frac{CClF_2-CClF_2}{C_2Cl_2F_4} = 0.2$	
	Composition of organic vapours (%mol.)			
	at beginning	after 50 hrs*	at beginning	after 120 hrs**
C_2F_6	4.4	3.9	4.0	6.2
C_2ClF_5	57.9	47.9	73.6	72.1
$C_2Cl_2F_4$	34.8	45.9	19.5	19.3
$C_2Cl_3F_3$	2.8	2.3	2.9	2.4
Conv. $C_2Cl_2F_4$	65.2%	54.1%	80.5%	80.7%
Yield C_2ClF_5	88.2%	88.5%	91.4%	89.3%

* Kg 2.0 of HF to Kg 0.2 of catalyst

\## Kg 4.8 of HF to Kg 0.2 of catalyst

TABLE 4

Fluorination of $C_2Cl_2F_4$ (*) with HF on Cr_2O_3

Test run (300 hours) at 300°C, 3.8 **sec.**, $HF/C_2Cl_2F_4$ = 1.1 (m/m)

Organic products	% mol.
C_2F_6	3-5
C_2ClF_5	66-70
$C_2Cl_2F_4$	24-28
$C_2Cl_3F_3$	2-3
Others	0.02-0.03
Mean values	
Conversion $C_2Cl_2F_4$	72-75%
Yield of C_2ClF_5	89-92%
Yield of $C_2Cl_3F_3$	2.5-3.0%
Yield of C_2F_6	5-7%
fed $C_2Cl_2F_4$	1.460 Kg/hr • Kg catalyst
produced C_2ClF_5	0.742 Kg/hr • Kg catalyst

(*) $\frac{CClF_2-CClF_2}{C_2Cl_2F_4} = 0.4$

TABLE 5

Fluorination of $C_2Cl_2F_4$ (*) with HF on Cr_2O_3

Test run at 350°C, 3sec., $HF/C_2Cl_2F_4$ = 1.1 (m/m)

Unconverted $C_2Cl_2F_4$ recycled to reactor (**).

Outlet of reactor		Test time (hours)								
		24	36	48	60	72	84	96	108	120
		Vapour composition								
C_2F_6	(% mol)	4.0	5.1	4.8	5.1	5.5	6.1	6.3	6.3	6.2
C_2ClF_5	"	73.6	72.7	73.2	72.6	73.1	72.6	73.0	72.3	72.1
$C_2Cl_2F_4$	"	19.5	19.2	19.1	20.1	18.9	18.8	18.3	18.9	19.3
$C_2Cl_3F_3$	"	2.9	3.0	2.9	2.2	2.5	2.5	2.4	2.5	2.4
$\frac{CClF_2-CClF_2}{C_2Cl_2F_4}$		0.53	0.65	0.62	0.62	0.57	0.53	0.61	0.60	0.62
		Experimental results								
Conversion $C_2Cl_2F_4$ (%)		80.5	80.7	80.9	80.0	81.1	81.2	81.7	81.1	80.7
Yield C_2ClF_5 (% mol)		91.4	90.0	90.5	90.8	90.1	89.4	89.4	89.2	89.3

(*) Fresh feed $\frac{CClF_2-CClF_2}{C_2Cl_2F_4} = 0.2$ (**) $\frac{C_2Cl_2F_4\ \text{fresh}}{C_2Cl_2F_4\ \text{recycl.}} = 9$

test, pure chloropentafluoroethane and unfluorinated dichlorotetrafluoroethane, subsequently continuously recycled to fluorination, were isolated by batch fractional distillation): as can be seen, the conversion of the dichlorotetrafluoroethane remained around 80-81%, and the yield of chloropentafluoroethane around 89-91%. It is worthwhile observing that, as a consequence of its lower activity, the symmetric dichlorotetrafluoroethane in the unconverted compound stabilizes at 60% of the mixture, even though only 20% of it is present in the fresh one.

This is illustrated by the curves of Fig.6

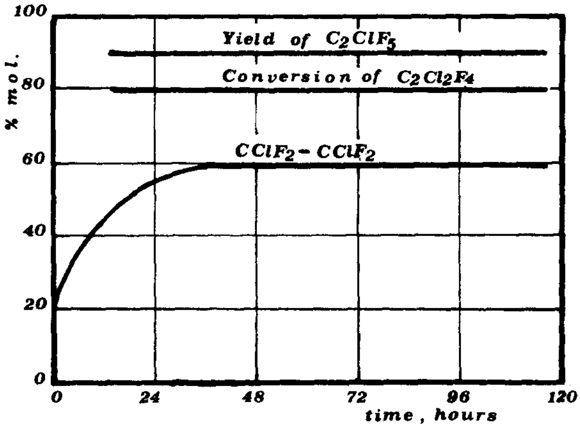

Fig. 6 Fluorination of $C_2Cl_2F_4$
Test run with unconverted $C_2Cl_2F_4$ recycled to reactor

During this run we obtained:

- fed dichlorotetrafluoroethane	1.964 Kg/hr.kg catalyst
- produced chloropentafluoroethane	1.290 Kg/hr.Kg catalyst

CONCLUSION

The catalytic fluorination of the dichlorotetrafluoethane with hydrogen fluoride in the gaseous phase on chromic oxide [20] leads to high yields of chloropentafluoroethane (> 90%).

The reaction is very similar for the two isomeric dichlorotetrafluoroethanes, is affected by temperature, contact time and reagent ratio. The fluorination is also accompained by disproportionation and isomerization of the chlorofluorocarbons. Water adversely affects the catalyst activity.

The uniformity of fluorination and the possibility of carrying out a simultaneous recycling of unconverted dichlorotetrafluoroethane were verified in two test-runs.

EXPERIMENTAL

Fluorination of dichloroetrafluoroethane

The tests were carried out in a miniplant (Fig.1) mainly consisting of a preheater (nickel tube, i.d. 5cm, length 30cm) and a reactor R (nickel tube, i.d. 20mm or 40mm, 50 or 67cm length respectively, fixed catalytic bed 35 or 16cm height, respectively) both heated outside by means of thermoregulated electrical resistances (H_1, H_2, H_3, H_4), with a set of thermocouples (T_1, T_2, T_3, T_4) at different heights along the reactor, in order to avoid any gradient between T_2 and T_3 (catalytic bed). The reactor had an Inconel sintered disc at the bottom.

The reactions were carried out at constant, slightly over atmospheric pressure. HF and dichlorotetrafluoroethane were fed in the gaseous phase through two flowmeters and preheated at 150-200°C in E. The reaction products were washed with water in a PVC column N and sent to a scrubber or to a vent. They were chemically and gas-chromatographically analysed from time to time from polytetrafluoroethylene bottles P_1 (H_2O at $\leqslant 50°C$), P_2/P_3 (NaOH solution 5%) and trap P_4 ($-40 \div -80°C$).

Catalyst

Chromic oxide was prepared from chrome alum $KCr(SO_4)_2 \cdot 12H_2O$ [15] and [20]. The catalyst, prepared in pellet form (diameter 2.5 - 3.0 mm, length 2-4 mm) had a specific surface area ranging from 35 to 75 m^2/g and a sulphate content (impurities) $\leqslant 0.04\%$.

Analysis of products

Analytical GLC work was carried out using a gas-chromatograph equipped with a thermal conductivity detector and a 6meter copper column (i.d. 4mm), packed with 35% silicon oil DC 200/50 on Chromosorb P 30/60 mesh.

The isomer ratio of dichlorotetrafluoroethane and of trichlorotrifluoroethane was determined by GLC analysis and infrared spectroscopy. A GLC fraction of trichlorotrifluoroethane or dichlorotetrafluoroethane was then introduced into the infrared cell and a vapour-phase spectrum measured using a Perkin-Elmer Model 21 spectrophotometer and a gas cell of 10 cm optical path with sodium chloride windows.

Analytical bands used were as follows:

a) determination of $CCl_2F-CClF_2/C_2Cl_3F_3$: 1109 cm^{-1} for $CClF_2-CCl_2F$ and 1255 cm^{-1} for CCl_3-CF_3

b) determination of $CClF_2-CClF_2/C_2Cl_2F_4$: 1140 cm^{-1} for $CClF_2-CClF_2$ and 1295 cm^{-1} for CF_3-CCl_2F.

The isomer ratios were derived from the calibration curves of known mixturs.

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