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HYDROGENOLYSIS OF DICHLOROTETRAFLUOROETHANE ISOMERIC MIXTURES FOR THE FORMATION OF 1.1.1.2 - TETRAFLUOROETHANE.

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SUMMARY

1.1.1.2 - Tetrafluoroethane was prepared from isomeric mixtures of dichlorotetrafluoroethanes through selective hydrogenolysis of CF_3-CCl_2F catalyzed by Pd/C. The other isomer $CClF_2-CClF_2$ appeared more stable to hydrogenolysis and was only converted partially to the monohydrogenated derivative CHF_2-CClF_2.

The influences of the three most important operating parameters were defined on the basis of a statistical testing program.

The mathematical elaboration of the experimental data allowed definition of the relationships by which it is possible to foresee conversion of CF_3-CCl_2F, yield of CF_3-CH_2F and concentration of reaction products, such as CF_3-CH_3, CF_3-CH_2F, $CF_3-CHClF$ and $CClF_2-CHF_2$ in terms of the above parameters.

INTRODUCTION

1.1.1.2 - Tetrafluoroethane (A 134a)*, mixed with other compounds, is useful as a refrigerant, heat transfer medium, gaseous dielectric, expansion agent, aerosol propellant and solvent [1,2].

Chlorofluorocarbons have comparable uses but the problem of their interaction with atmospheric ozone, and the imposition of a ban on their use, is well known.

So far, tetrafluoroethane has been obtained in low yield from trichloroethylene and 1.1.1- trifluoroethylchloride [3,4,5] or from unusual raw materials (trifluoroethyl ester of p-toluene-sulfonic acid and trifluoroethylene) [6,7].

(*) A is an abbreviation for registered Montedison trade mark ALGOFRENE (chlorofluorocarbon).

We had the opportunity of investigating the synthesis starting from 1.1 - dichlorotetrafluoroethane, which is industrially obtained together with 1.2 - dichlorotetrafluoroethane by means of chlorofluorination of ethylene [8-12] . On the basis of what is already found in literature about the hydrogenolysis of the C-Cl bond [13-18] we investigated the hydrogenation on 5% palladium on charcoal. The investigation on the operating parameters was conducted on a statistical basis.

RESULTS AND DISCUSSION

Using palladium on charcoal we found initially that,

- the most important operating parameters for hydrogenolysis are temperature, contact time and molar ratio of the reagents;
- 1.1 - dichlorotetrafluoroethane undergoes hydrogenolysis to 1.1.1.2 - tetrafluoroethane already at 120°C;
- 1.2 - dichlorotetrafluoroethane isomer does not undergo hydrogenolysis to 1.1.2.2 - tetrafluoroethane even at 200°C, but is only converted to 1-chloro-1.1.2.2 - tetrafluoroethane (monohydrogenolysis) to a more limited extent.

The results of the most significant tests at 170°C using isomeric mixtures of dichlorotetrafluoroethanes are illustrated in TABLE 1 :the low reactivity of $CClF_2-CClF_2$ (A 114) is evident. On the other hand the sum of the products from asymmetric dichlorotetrafluoroethane (A 114a) slightly exceeds (by about 2%) the amount of this ispmer in the original mixture : this is due to some isomerization of the symmetric dichlorotetrafluoroethane, as found in a separate test(at 240°C and 22 sec.).

Soon after the completion of this phase of the investigation , summarized in a patent application [19] , similar results appeared in another patent application [20] . Therefore more precise experimentation was carried out.

Dichlorotetrafluoroethane containig 75% of the 1.1-isomer was used; this type of mixture, produced industrially, emphasizes the selectivity of hydrogenolysis upon the two isomers. The test set (eighteen) was planned on a statistico-mathematical basis [21-22] . Independent variables were:

- temperature ranging from 120°C to 240°C
- contact time ranging from 10 to 35 seconds
- molar ratio hydrogen/dichlorotetrafluoroethane ranging from 2 to 4.

The following dependent variables (Y) were considered:

- dichlorotetrafluoroethane conversion (Y_1)
- yield of 1.1.1.2 - tetrafluoroethane (A 134a) (Y_2)
- concentration of 1.1.1.2 - tetrafluoroethane (A 134a) in the organic products (Y_3)

TABLE 1

Hydrogenolysis of $C_2Cl_2F_4$ at different ratio $CF_3CCl_2F/CClF_2-CClF_2$.
Temperature 170°C, contact time 25 sec., molar ratio $H_2/C_2Cl_2F_4$ = 3.5.

N°	$\frac{CF_3-CCl_2F}{CClF_2-CClF_2}$	Vapour composition (% mol.)						
		CF_3-CH_3	CF_3-CH_2F	$CF_3-CHClF$	CHF_2-CClF_2	CHF_2-CHF_2	$C_2Cl_2F_4$	Note
1	96/4	12.3	76.2	9.5	-	-	2.0	
2	78/22	6.5	63.4	8.5	2.2	-	19.4*	*$CClF_2-CClF_2$=89.5%
3	68/32	10.3	48.4	11.3	1.6	-	28.4	
4	6/94	0.5	5.6	1.4	2.9	-	89.5*	*$CClF_2-CClF_2$=100%

- concentration of 1.1.1 - trifluoroethane (A 143a) (Y_4)
- concentration of 1-chloro-1.2,2.2 - tetrafluoroethane (A 124) (Y_5)
- concentration of 1-chloro-1.1.2.2. - tetrafluoroethane (A 124a) (Y_6)

The statistical plan supplied as a mathematical model a complete second degree polynomial of the following type:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 +$$

$$+ b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + e$$

Where: Y is the generic response for one of the dependent variables
x_1 is the temperature
x_2 is the contact time
x_3 is the molar ratio of the reagents
b_0 is a constant
b_1, b_2, b_3 are the coefficents of the linear terms of the polynomial
b_{11}, b_{22}, b_{33} are the coefficents of the square terms of the polynomial
b_{12}, b_{13}, b_{23} are the coefficents of the interaction terms of the polynomial
e is the experimental error

The experimental results of the test set are illustrated in TABLE 2.

The elaboration of these data allowed us to obtain the coefficents and constants reported in TABLE 3.

The high percentage values of the last row show the good fit of the experimental data with the selected mathematical polynomial model.

The equations permitted us to draw the curves representing the trend of the single response as a function of the three independent variables.

In the graphic representation the following values were considered as the extreme values of the range for each variable :

x_1 : 145 - 215°C
x_2 : 15 - 30 sec.
x_3 : 2.4 - 3.6

Outside these ranges in fact one would pass out of the experimental domain. This clearly appears when considering that the experimental plan adopted does not involve any test where the extreme values of the three variables are simultaneously taken into account (see TABLE 2).

TABLE 2

Hydrogenolysis of $C_2Cl_2F_4$* at atmospheric pressure catalyzed by Pd/C (Pd 0.5%)

Test	Experimental conditions			Organic reaction products					(% mol.)
	$H_2/C_2Cl_2F_4$	°C	sec.	A	B	C	D	E	F
1	2.4	144	15	4.85	31.82	58.07	-	-	5.26
2	2.4	216	15	22.69	46.62	17.89	-	1.27	11.52
3	2.4	144	30	5.65	46.66	39.54	-	-	8.14
4	2.4	216	30	19.05	52.40	15.05	-	1.98	11.52
5	3.6	144	15	5.12	41.59	46.60	-	-	6.68
6	3.6	216	15	21.06	51.22	14.97	0.82	1.86	10.06
7	3.6	144	30	5.99	50.89	34.32	-	-	8.81
8	3.6	216	30	16.10	54.85	12.50	0.95	3.64	11.95
9	3.0	240	22	22.66	49.85	11.36	1.17	3.87	11.08
10	3.0	120	22	1.49	16.96	77.96	-	-	3.59
11	3.0	180	35	11.85	57.40	16.15	-	0.61	13.98
12	3.0	180	10	12.93	46.46	33.22	-	0.46	6.92
13	4.0	175	23	12.64	62.99	15.25	-	0.79	8.32
14	2.0	180	22	14.28	52.43	24.59	-	0.43	8.27
15	3.0	180	22	13.52	60.09	16.78	-	0.74	8.87
16	3.0	180	22	13.26	61.14	16.41	-	0.65	8.54
17	3.0	180	22	12.97	61.58	16.26	-	0.73	8.46
18	3.0	180	22	12.88	61.05	16.78	-	0.62	8.67

A = CF_3-CH_3 ; B = CF_3-CH_2F ; C = CF_3-CCl_2F + $CClF_2$-$CClF_2$; D = CHF_2-CHF_2 ; E = $CClF_2$-CHF_2 ;

F = CF_3-CHClF. *CF_3-CCl_2F / $C_2Cl_2F_4$ = 0.75

TABLE 3

Response	Estimated regression equation												
	b_0	b_1	b_2	b_3	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	$\hat{\sigma}_{TOT}$	$\hat{\sigma}_{RES}$	$\left(1-\frac{\hat{\sigma}_R^2}{\hat{\sigma}_T^2}\right)\cdot 100$
y_1 Conversion of $C_2Cl_2F_4$ (°)	-344.5	3.3656	4.8211		-0.0073	-0.063		-0.0109		0.234	19.3	3.2	97
y_2 Yield of CF_3-CH_2F	25.2	0.53	1.233		-0.0021	-0.0275			0.0077		6.9	1.8	93
y_3 CF_3 - CH_2F	-264.4	2.802	2.88		-0.0071	-0.0659				0.199	12.1	3.4	92
y_4 CF_3 - CH_3	- 30.4	0.226	0.589					-0.0035			4.8	0.8	97
y_5 CF_3 - CHClF	- 26.1	0.289			-0.0005	0.0119		-0.0017			3.4	1.0	92
y_6 $CClF_2$ - CHF_2	15.5	-0.1694		-2.654	0.0004				0.0159	0.0114	1.4	0.4	92

$\hat{\delta}_{TOT}$ = standard deviation (total)

$\hat{\delta}_{RES}$ = standard error of estimate (residual)

$\left(1-\frac{\hat{\delta}^2_R}{\hat{\delta}^2_T}\right)100$ = goodness of fit

(°) $\frac{CF_3 - CCl_2F}{C_2Cl_2F_4} = 0.75$

Figure 1 shows that dichlorotetrafluoroethane conversion increases appreciably with temperature up to values almost equal to the percentage of $CF_3\text{-}CCl_2F$ in the feed mixture. However, the reagent molar ratio and contact time also affect the conversion.

Figure 2 shows that yield of 1.1.1.2 - tetrafluoroethane decreases on increasing temperature; it appears slightly higher when intermediate contact times are used, but it is not appreciably affected by the reagent molar ratio.

The trends of the curves of Figures 1 and 2 and the data reported in TABLE 2 (all referring to the isomeric mixture at 75% $CF_3\text{-}CCl_2F$) provide evidence that hydrogenolysis in the operating ranges examined leads mainly to the following selective conversion:

$$CF_3\text{-}CCl_2F \longrightarrow CF_3\text{-}CHClF \longrightarrow CF_3\text{-}CH_2F$$

while the symmetric isomer undergoes only monohydrogenolysis at low conversion levels according to the reaction

$$CClF_2\text{-}CClF_2 \longrightarrow CClF_2\text{-}CHF_2$$

Figures 3-6 show the concentration trends of $CF_3\text{-}CH_3$(A143a), $CF_3\text{-}CH_2F$ (A134a), $CF_3\text{-}CHClF$ (A124) and $CClF_2\text{-}CHF_2$ (A124a) in the organic products in relation to temperature. (Since the molar ratio $H_2/C_2Cl_2F_4$ does not affect yield of A143a and A124, the corresponding Figures 4 and 5 do not report curves at different molar ratios).

Figure 3 shows that the concentration of 1.1.1.2 - tetrafluoroethane in the reaction products rises on increasing temperature up to a maximum at 200°C; it tends to increase on increasing molar ratio and contact time.

In Figure 6 the low concentration of 1-chloro-1.1.2.2 - tetrafluoroethane emphasizes the poor reactivity of symmetric dichlorotetrafluoroethane; this is further supported by the absence of 1.1.2.2 - tetrafluoroethane in the reaction products (TABLE 2). The curve indicates an increase of the symmetric monohydrogenated compound ($CClF_2\text{-}CHF_2$) with contact time and with temperature above 150°C. Moreover, the effect of molar ratio is scarcely meaningful.

By setting three values for the hydrogen/dichlorotetrafluoroethane molar ratio (2.4 - 3.0 - 3.6), three level maps were obtained; they represent the various levels of dichlorotetrafluoroethane conversion, yield of 1.1.1.2 - tetrafluoroethane and 1-chloro-1.1.2.2 - tetrafluoroethane concentration as a function of temperature and contact time.

Such level maps allow the definition of the operating conditions suitable for reproducing (within the limits of experimental error) the three responses and, moreover, the selection of the optimum operating areas.

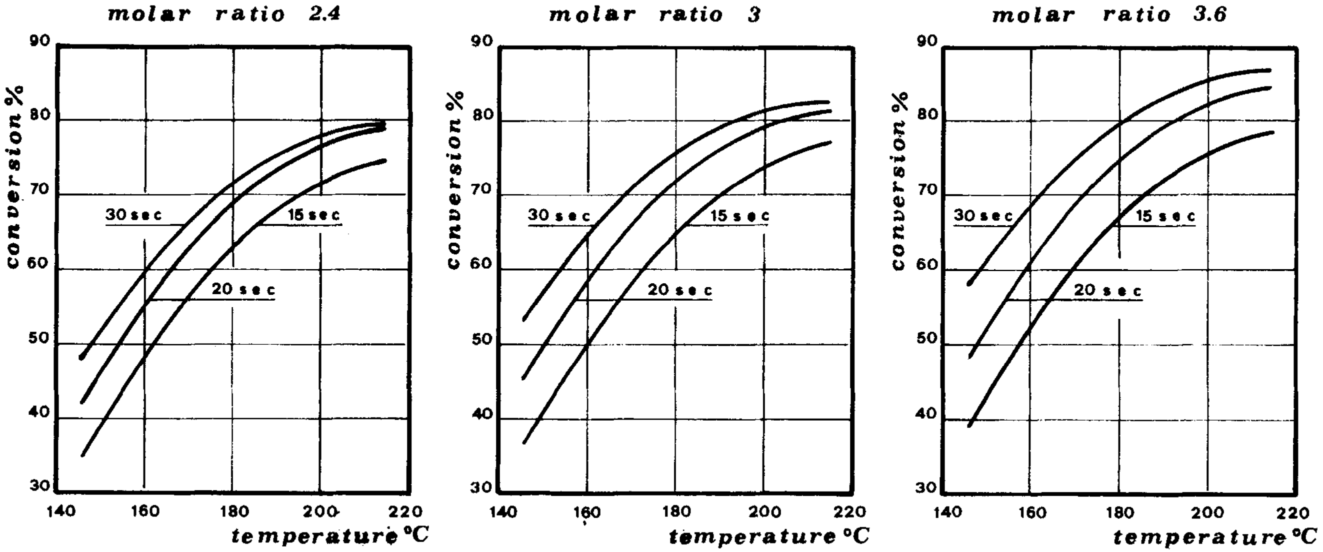

Fig.1 Conversion of $C_2Cl_2F_4$ in the hydrogenolysis on Pd/C

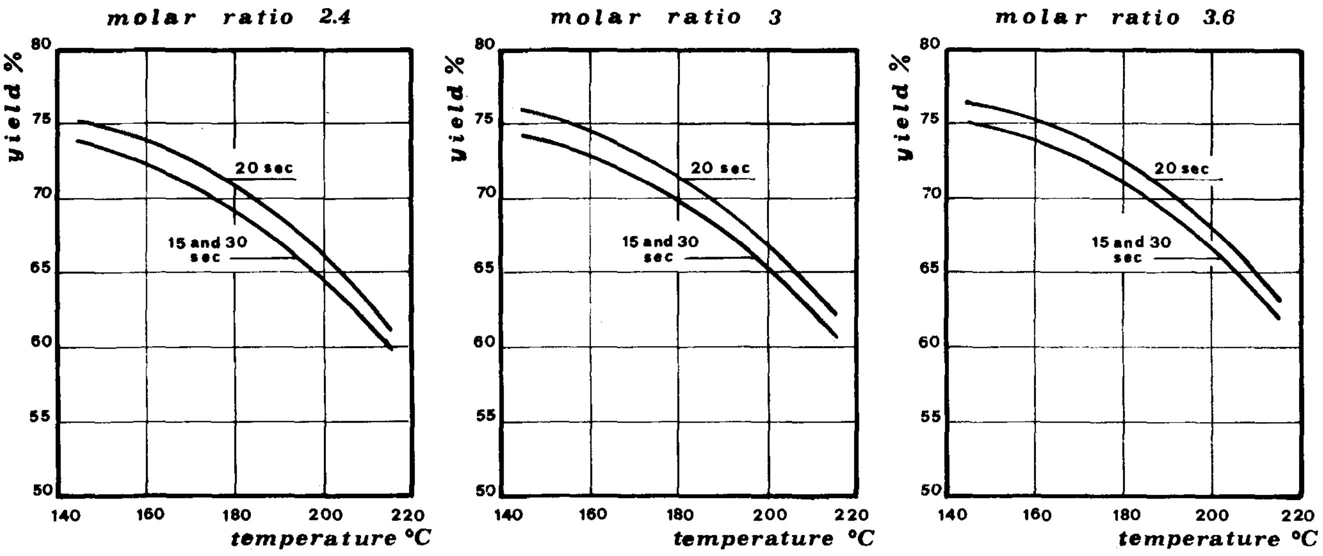

Fig.2 Yield in $CF_3 \cdot CH_2F$ in the hydrogenolysis on Pd/C

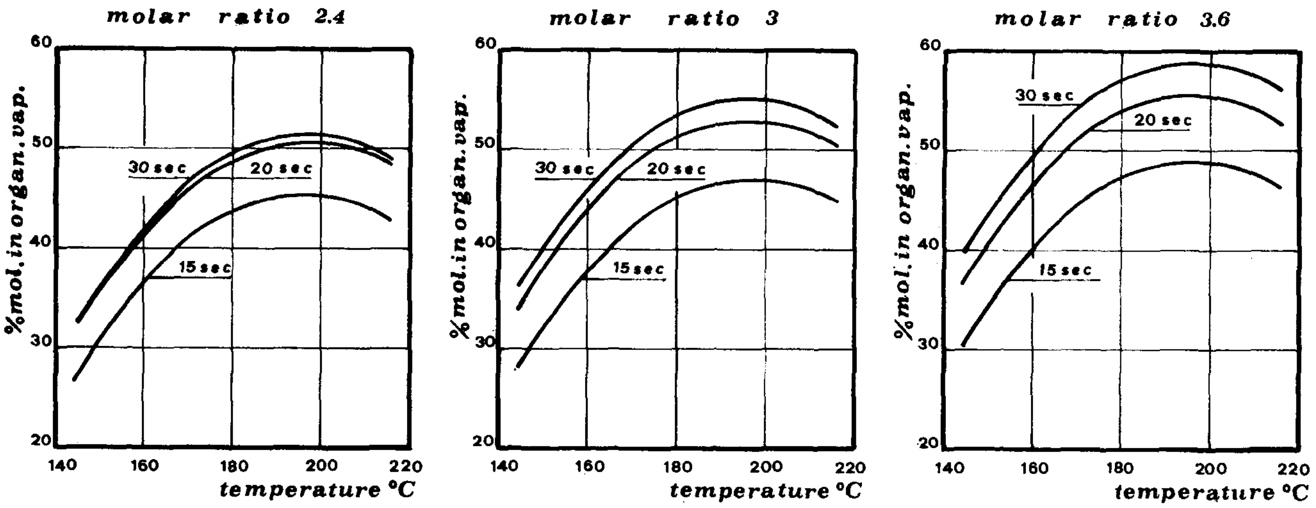

Fig.3 $CF_3{\cdot}CH_2F$ from hydrogenolysis of $C_2Cl_2F_4$ on Pd/C

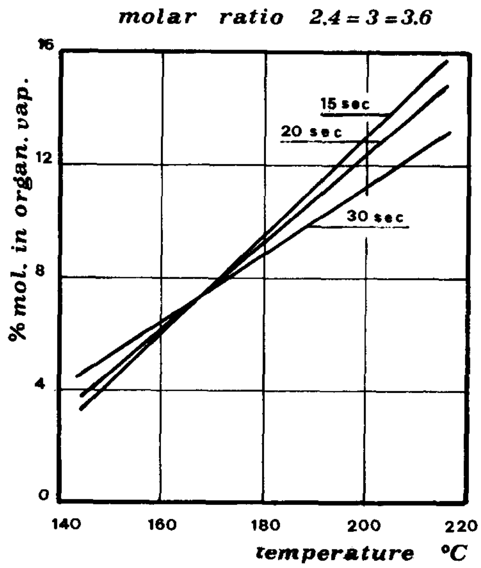

Fig.4 $CF_3 \cdot CH_3$ from hydrogen. of $C_2Cl_2F_4$ on Pd/C

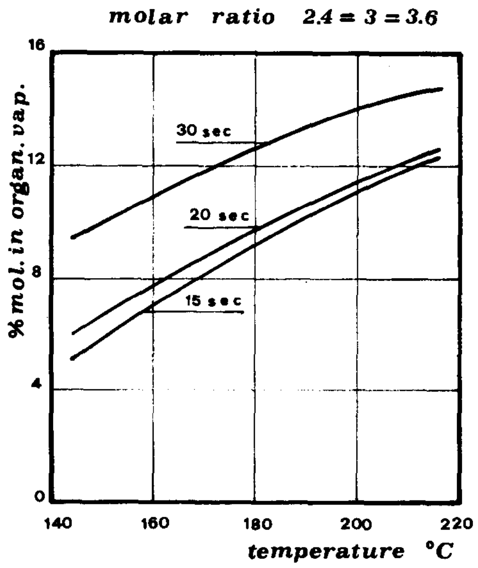

Fig.5 $CF_3 \cdot CHClF$ from hydrogen. of C_2Cl_2F4 on Pd/C

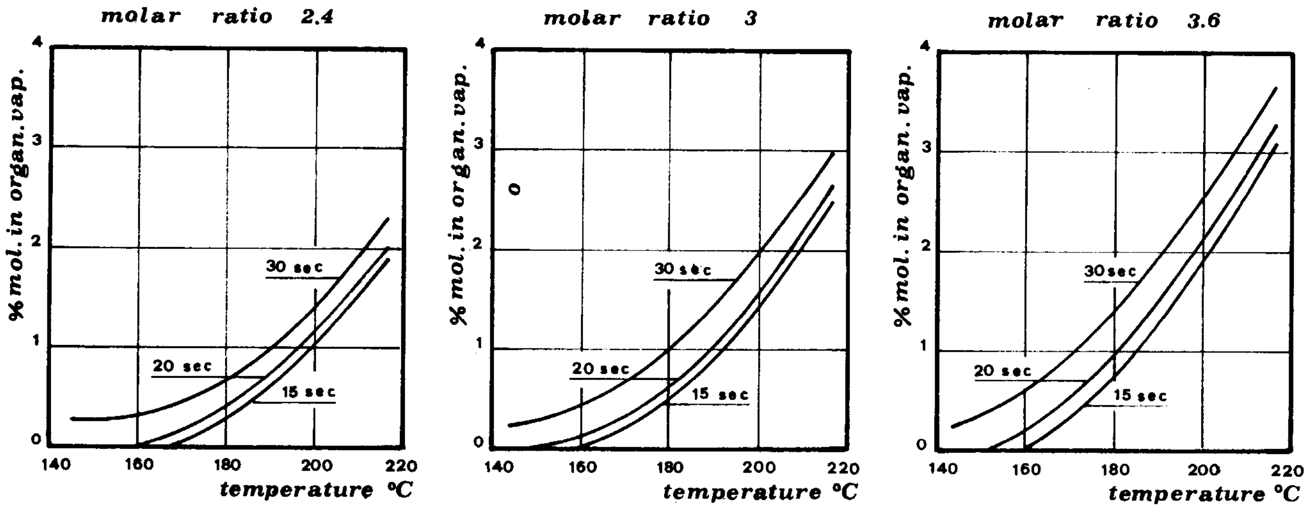

Fig. 6 $CClF_2 \cdot CHF_2$ from hydrogenolysis of $C_2Cl_2F_4$ on Pd/C

For instance (Fig.7, molar ratio 3.6), to reach a conversion of 80% at a yield of 70%, a temperature of 192°C and a contact time of 20 sec. should be adopted: under these conditions a coproduction of 1-chloro-1.1.2.2 - tetrafluoroethane of 1.6% is expected.

Figure 8 and Figure 9 are the other level maps at molar ratios 3.0 and 2.4, respectively.

A mechanism for cleavage of the C-Cl bond in the reported system is not clear on the basis of the data so far available. The following considerations can nevertheless be advanced: the higher reactivity of the group $-CCl_2F$ in CF_3-CCl_2F with respect to the $-CClF_2$ in $CClF_2-CClF_2$ agrees with the experimental findings of other reactions, such as F/Cl substitution, and isomerization and disproportionation of chlorofluorocarbons, where an "abstufung" of reactivity for the $R-CCl_3 > R-CCl_2F \gg R-CClF_2 \gg R-CF_3$ series was observed [23,24,25]. In the reaction $R-CCl_{3-n}F_n + SO_3$, investigated by us [26], a difference in reactivity was shown between CF_3-CCl_3 and $CClF_2-CCl_2F$.

All this could be explained, for the couple CF_3-CCl_2F/$CClF_2-CClF_2$, by the different positive charge on the reagent carbon atom: in one case it is due to the strong effect -I of $-CF_3$ and in the other to the higher number of fluorine atoms which are "kinetically effective in preventing attack by a nucleophile on the carbon to which they are bonded" (Sheppard et al., [27]).

By comparing these hydrogenolysis reactions to the interactions between alkyl halides and transition metals, such as Ti and Pt, investigated by Harrod and Skell, respectively [28, 29], we consider that a rapid dissociative adsorption-associative desorption of the type

$$R-C-C-X + 2S^* \rightleftharpoons R-C-C-S^* + XS$$

(S^* = univalent active site) may be postulated as initial step. The associative desorption of surface alkyl and surface hydride can then lead to the formation of the observed products:

$$R-C-C-S^* + HS^* \rightleftharpoons R-C-C-H + 2S^*$$

Kinetic investigation and a study with high-resolution mass spectroscopy are in progress with a view to clarifying the reaction mechanism.

The fact that, in the case of the system $CClF_2-CClF_2$/CF_3-CCl_2F the second conversion $CF_3-CHClF \rightarrow CF_3-CH_2F$ and not the one $CClF_2-CHF_2 \rightarrow CHF_2-CHF_2$ occurs easily, could be due to kinetic factors deriving from the different concentration of the two intermediates in the reaction products.

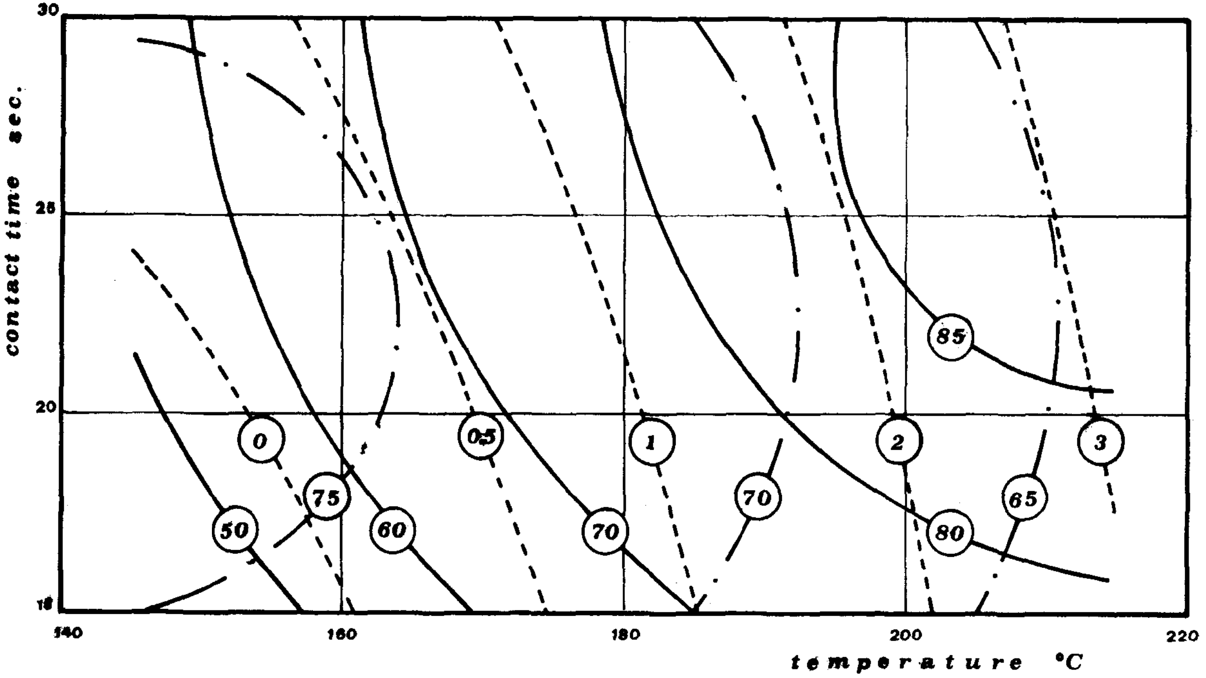

Fig.7 Level map at molar ratio 3.6; $C_2Cl_2F_4$ CONV. % ————; CF_3-CH_2F YIELD % — · — · —; $CClF_2$-CHF_2 CONC. % - - - - - - - -

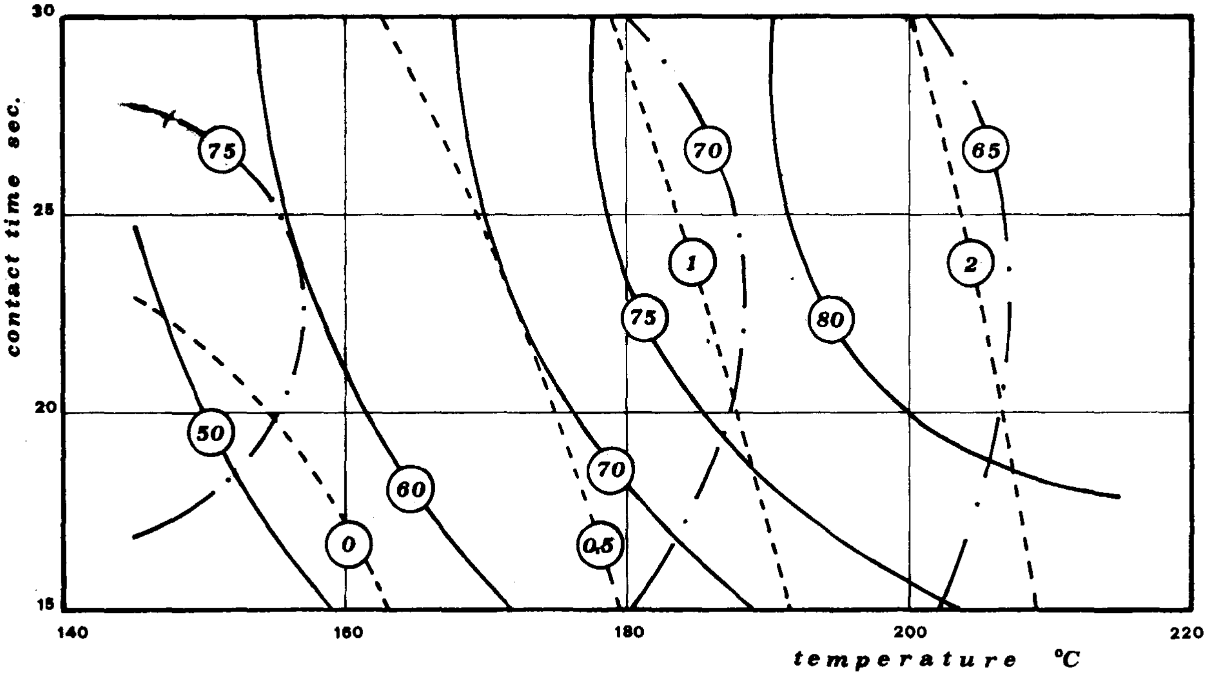

Fig.8 Level map at molar ratio 3; $C_2Cl_2F_4$ CONV. % ————; CF_3-CH_2F YIELD % — · — · —; $CClF_2$-CHF_2 CONC. % - - - - - - - - -

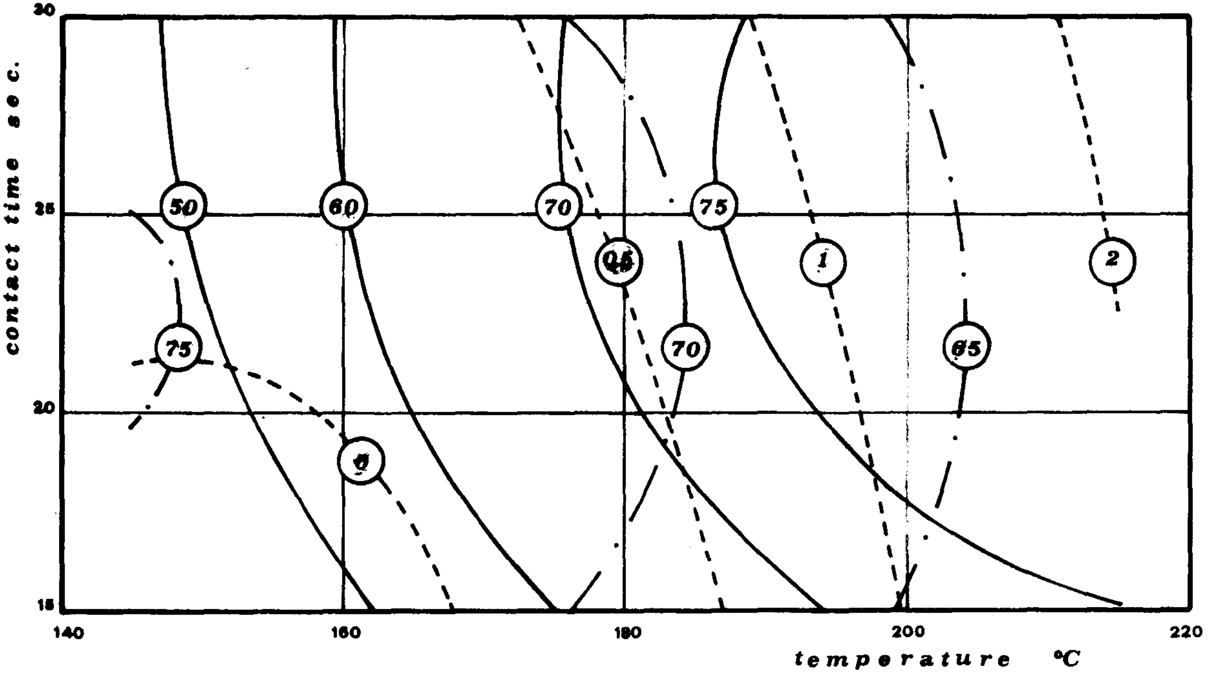

Fig.9 Level map at molar ratio 2.4; $C_2Cl_2F_4$ CONV. % ————————; CF_3-CH_2F YIELD % — · — · —; $CClF_2$-CHF_2 CONC % - - - - - - - - - - -.

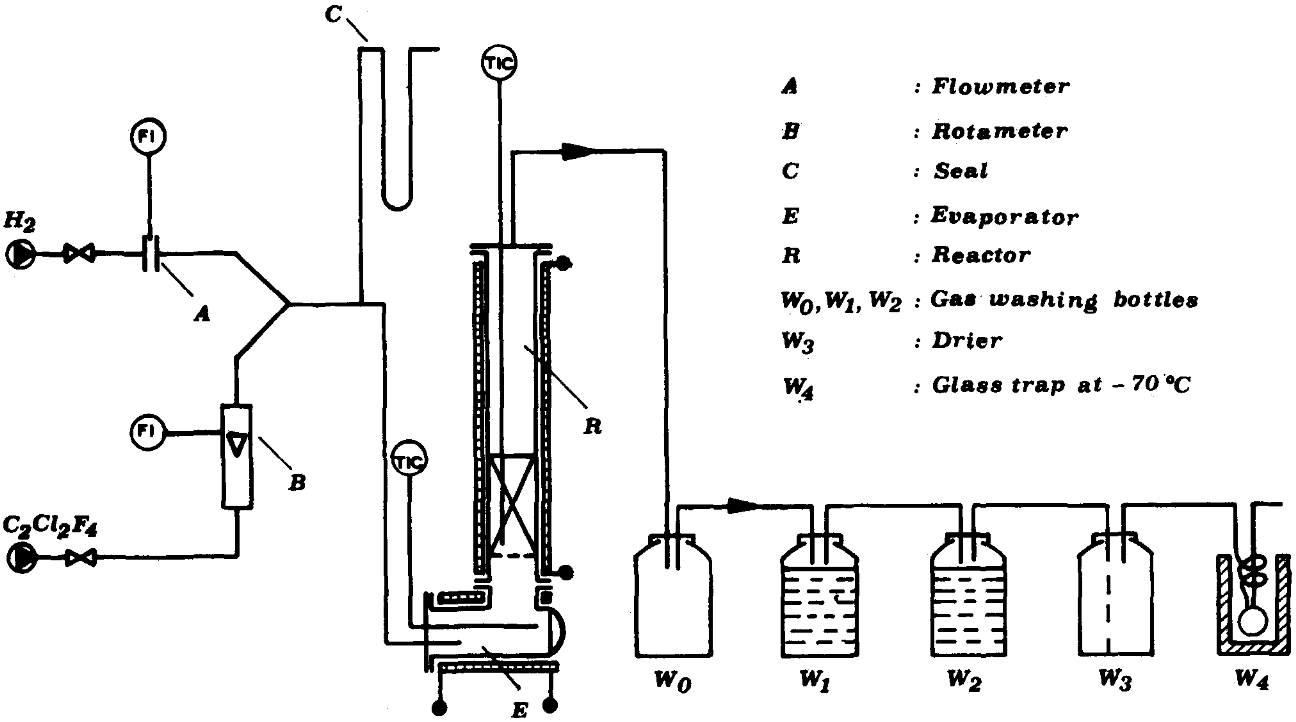

Fig.10 **Miniplant for hydrogenolysis of $C_2Cl_2F_4$**

CONCLUSION

1.1.1.2 -tetrafluoroethane is obtained from 1.1 - dichlorotetrafluoroethane by means of catalytic hydrogenation on palladium on charcoal at atmospheric pressure.

Mixtures of the two isomer dichlorotetrafluoroethanes can also be used since 1.2 - dichlorotetrafluoroethane undergoes only monohydrogenolysis to 1-chloro-1.1.2.2 -tetrafluoroethane in a very limited way. Hydrogenolysis is affected by temperature, contact time and hydrogen/chlorofluorocarbons ratio. The effect of these parameters was quantified and expressed by means of a complete 2^{nd} degree polynomial. By means of the calculation of these polynomials level maps were drawn, by which it proved possible to define the operating parameters, once dichlorotetrafluoroethane conversionn yield of tetrafluoroethane and its concentration in the reaction products were prefixed.

EXPERIMENTAL

The apparatus (Fig. 10) mainly consisted of a stainless steel reactor (R) (length = 700 mm, i.d. = 45 mm), heated outside with electrical resistances connected to an inside thermocouple and containing 235 gr. of Pd/C (pellet form 3 x 1.5 mm, at 0.5% of Pd).

Hydrogenolysis was carried out at atmospheric pressure by feeding hydrogen and dichlorotetrafluoroethane vapour, preheated in E, through the reactor bottom. The organic reaction mixture was gas-chromatographically and spectrometrically analysed.

Analytical GLC work was carried out using a gas-chromatograph equipped with thermal conductivity detector and a 6 m. copper column (i.d. 4 mm) packed with 15% (w/w) Polypropylenglycol UCON LB 550X on Chromosorb P 60/80 mesh. The isomeric ratio of dichlorotetrafluoroethane was determined by Infra Red spectrophotometry using a Perkin-Elmer Model 21 instrument and a glass cell of 10 cm. optical path with sodium chloride windows. Analytical bans used were: 1140 cm^{-1} for the 1.2 - dichlorotetrafluoroethane and 1295 cm^{-1} for the 1.1 - dichlorotetrafluoroethane.

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