[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, PENNSALT CHEMICALS CORP.]

The Thermal Dimerization of Perfluoropropene[1]

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Perfluoropropene has been shown to undergo a mixed head-to-head and head-to-tail cyclic dimerization at elevated temperatures. Three of the four dimers, *cis*- and *trans*-perfluoro-(1,2-dimethylcyclobutane) and *cis*- and *trans*-perfluoro-(1,3-dimethylcyclobutane), are produced. The formation of two of the isomers has been demonstrated to be reversible. The profound effect of time, temperature and pressure on the gross conversion to dimers and on the isomeric distribution of the dimers is illustrated. Physical properties and comparative thermal stabilities of the three isomers are presented.

In the course of the investigation of the thermal synthesis of telomers of perfluoropropene[2-4] a volatile fraction, b.p. 40–50°, $n^{25}\text{D} < 1.3$, containing only carbon and fluorine frequently was obtained, particularly when the reaction was carried out at temperatures above 240°. It was suspected that this product may have been a dimer of perfluoropropene, and consequently an investigation of the thermal reaction of perfluoropropene alone was initiated.

The facile cyclic dimerizations to yield cyclobutanes of a number of fluorinated ethylenes, such as tetrafluoroethylene, chlorotrifluoroethylene and 1,1-dichlorodifluoroethylene among others, are known.[5-7] Such dimerizations have not been reported for the fluorinated C_3 or higher monoölefins.

The present work describes the synthesis and properties of three saturated cyclic dimers of perfluoropropene. This olefin was found to react with itself at elevated temperatures and pressures to yield saturated dimeric products. The reaction conditions required for good conversions are much more vigorous than for the fluorinated ethylenes. Thus, the latter undergo cyclic dimerization readily at pressures as low as atmospheric and temperatures below 200°. The reaction with perfluoropropene, however, was very slow at a temperature as high as 250° under a pressure of several hundred atmospheres. At 350° and at similar pressures, the reaction was fairly rapid, and a 72% conversion to dimers was obtained in five hours. The dimers were the exclusive product under these reaction conditions; thus the yield was quantitative. At still higher temperatures, however, other products started to form in significant amounts, and the principal product isolated at 450°, under pressure, was the highly toxic perfluoroisobutylene.[8]

No reaction was detected when perfluoropropene was passed at a contact time of ten seconds through a hot tube at 510° at atmospheric pressure. At the same temperature and pressure, but in a sealed tube for seven hours, a 6% conversion to dimers was obtained.

In hot tube reactions at temperatures above 700° perfluoroisobutylene was identified among the reaction products and was the principal product at 850° (unpublished work).

That the dimerization of perfluoropropene involves an equilibrium,[9] equation 1, is shown by

$$2C_3F_6 \rightleftarrows C_6F_{12} \qquad (1)$$

$$K_c = [C_6F_{12}]/[C_3F_6]^2 \qquad (2)$$

$$K_p = P_{C_6F_{12}}/P^2_{C_3F_6} = K_c/RT \qquad (3)$$

the experimental data. Thus, the approach to an equilibrium composition from either direction was demonstrated at 430 and 510° (Table IV, Experimental). It can be calculated to a first approximation from these data that the "practical" equilibrium constant K_c, equation 2, has a value of *ca.* 3 at 510° and *ca.* 10 at 430°, and must be several powers of ten in the range of 300°.

For this homogeneous gas phase reaction, it is instructive to rewrite equation 2 in a form in which the pressure dependence of the reaction is explicitly shown. Thus, in equation 3, $P_{C_6F_{12}}$ and $P_{C_3F_6}$ are the equilibrium partial pressures in atmospheres of C_6F_{12} and C_3F_6 at absolute temperature T, and R is the universal gas constant in liter-atmospheres per degree. The marked effect of pressure on equilibrium composition is strikingly illustrated by a calculation which shows that a change in equilibrium total pressure from 0.1 to 100 atm. shifts the equilibrium composition at 430° from 3 wt. % C_6F_{12} to *ca.* 90 wt. % C_6F_{12}.

The perfluoropropene dimer was found to consist of at least three isomers, A, B and C, which proved difficult to separate. By careful fractional distillation pure A, nearly pure B and a fraction substantially enriched in C, were isolated.

Physical properties of these samples of the three isomers are listed in Table I. The infrared wave lengths and absorption intensities for the vapor spectra of these samples are presented in Table II.

From the infrared spectra, the purity of isomer A was assessed at 100%, while B contained 7% of isomer C, and C contained 30% of isomer B. All three isomers show absorption at 7.42, 7.92–7.96, 8.22 and 13.4 μ. Bands at 7.57, 7.80, 9.09, 9.39,

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[1] The work herein reported was carried out under contract between the Office of Naval Research and the Pennsalt Chemicals Corporation. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] M. Hauptschein, M. Braid and F. E. Lawlor, THIS JOURNAL, **79**, 2549 (1957).

[3] M. Hauptschein, M. Braid and F. E. Lawlor, *ibid.*, **79**, 6248 (1957).

[4] M. Hauptschein, M. Braid and A. H. Fainberg, *ibid.*, **80**, 851 (1958).

[5] J. Harmon, U. S. Patent 2,404,374; July 23, 1946.

[6] A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947).

[7] W. T. Miller, Jr., *Nat'l. Nuclear Energy Ser.*, Div. VII, 1, "Prep'n. Properties, and Technol. of Fluorine and Org. Fluorine Compds.," Chapter 32, p. 592 (1951).

[8] T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearlson, THIS JOURNAL, **75**, 2698 (1953).

[9] With respect to isomers A and B. For the calculation of thermodynamic equilibrium constants, the individual equilibria of isomers A and B, respectively, with perfluoropropene would, of course, have to be used. The determination of the equilibrium constants is complicated by concurrent side reactions, including formation of isomer C, at temperatures where dissociation of dimers A and B becomes significant.

TABLE I

PHYSICAL PROPERTIES AND THERMAL STABILITIES OF THE PERFLUORO-(DIMETHYLCYCLOBUTANE) ISOMERS

Isomer	A	B	C
Purity, %	100	93	70
Isomeric impurity	..	7%C	30%B
Temp. of formation,[a] °C.	250	390	450
B.p. (760 mm.), °C.	45.1	43.6	42.8
F.p., °C.	−16.3[b]	*ca.* −50	−115 (glass)
d^{25}_4, g./ml.	1.6730	1.6632	....
$n^{25}D$	1.2622	1.2600	1.2576
$MR^{25}D$ found[c]	29.61	29.55	....
⋗CF resonance, n.m.r.	Doublet	Singlet	Singlet
Thermal stability[d] at 430°, wt. % C_3F_6 formed	26	10	0
Wt. % of isomer decomposed[e]	67	30	0

[a] Reaction temperature at which this isomer is the principal product. [b] F.p. depression, 0.3°. [c] $MR^{25}D$ calculated 29.60, based on the atomic refractions $AR^{20}D$: C, 2.584; F, 1.165; saturated C_4-ring increment +0.10; dMR_D/dt = +0.015% $MR^{20}D$/°C.; proposed by A. H. Fainberg and W. T. Miller, Jr., unpublished work in preparation. [d] Based on sealed tube reaction and reported in Table IV, adjusted to 100% isomer purity. [e] *I.e.*, 100 − wt. % of the isomer recovered.

TABLE II

PRINCIPAL INFRARED PEAKS CHARACTERISTIC OF THE PERFLUORO-(DIMETHYLCYCLOBUTANE) ISOMERS

Wave length, μ	Absorbance[a] Isomer A	Isomer B	Isomer C
7.24	1.4	0.35	..
7.42	1.5	1.5	2.4
7.57	2.5	..	..
7.70	..	5.2	6.0
7.80	2.1[b]	..	..
7.92	6.3	..	5.4
7.96	5.7[b]	7.3	..
8.22	3.8	2.5	2.5
8.34	..	0.7[b,c]	1.6
8.40	2.3	..	..
8.56	..	..	0.6
8.88	..	0.16[c]	1.2
9.09	0.2	..	..
9.20	..	0.06	..
9.39	0.9	..	..
9.46	..	..	0.5
9.59	..	0.7	0.4[b,d]
9.75	..	.2[b]	..
9.89	.2	..	..
10.52	..	.2[c]	1.4
11.01	1.9	1.1	0.4[d]
11.35	1.8	1.0	.4[d]
11.57	..	0.3[b]	.15[d]
11.84	..	.15[c]	1.0
13.4	0.5	.2	0.16
13.63	.7	..	..
13.8	..	.9	.3[d]
14.15	..	.15[c]	1.1
14.5	..	.05[c]	0.3
14.8	..	.05[c]	.3

[a] Absorbance of vapor at 10.0 mm. in a 10.0-cm. cell. [b] Shoulder. [c] Isomer C impurity. [d] Isomer B impurity.

9.89 and 13.63 μ are characteristic only of isomer A; bands at 9.20, 9.59, 11.57 and 13.8 μ are characteristic only of isomer B; bands at 8.56, 8.88, 9.46, 10.52, 11.84, 14.15, 14.5 and 14.8 μ are characteristic only of isomer C.

The isomeric composition of the dimer as determined *via* infrared (see Experimental) was found to vary significantly with temperature of formation as shown in Table III. In the temperature range from 250°, the lowest practicable temperature for dimer formation, to 350°, isomers A and B were formed almost exclusively in nearly equal amounts, isomer A being more favored at the lower temperature. A marked shift in isomer distribution favoring B was observed when the reaction temperature was raised to 390°. At the still higher temperature of 450° isomer C, which had been formed in only very small amounts at the lower temperatures, became the predominant isomer.

The thermal stabilities of the three isomers were determined at 430° (see Table I). In four hours, isomer A underwent 67% decomposition, forming 26% of perfluoropropene and 41% of isomer B. Under identical conditions, isomer B underwent 30% decomposition, producing 10% of perfluoropropene and 20% of isomer A. In contrast, there was no evidence of any decomposition of isomer C under these conditions.

It is clear that for reaction temperatures in the range of 250 to 350° the formation of dimers from perfluoropropene was essentially kinetically controlled. The formation of both isomers A and B in substantial amounts under these conditions suggests that the activation energies of formation are similar, perhaps somewhat lower for A. At 390° the reverse reaction became significant and equilibria in addition to kinetics determined the isomer composition. Thus the relative proportions of the more thermally stable isomers B and C were increased at the expense of A. This effect became much more pronounced at 450° where C became the predominant isomer.

The molecular formula C_6F_{12} for each of the dimers was unequivocally established by elemental analysis, molecular weight, boiling point and molar refraction. Furthermore, the completely saturated nature of these dimers necessitates postulating cyclic structures.

Nuclear magnetic resonance (n.m.r.) spectra[10] of the three isomers were substantially identical, differing only in fine structure. Each of the three isomers shows three main lines, with intensities in the ratio of 3:2:1, and corresponding δ-values[11] of +0.2, −5.2 and −11.5, characteristic, respectively, of $-CF_3$, $>CF_2$ and ⋗CF groups. These spectra are completely consistent with a perfluoro-(dimethylcyclobutane) structure.

The four possible structures are *cis*- and *trans*-perfluoro-(1,2-dimethylcyclobutane), I and II, respectively, and *cis*- and *trans*-perfluoro-(1,3-dimethylcyclobutane), III and IV, respectively.

It is evident, therefore, that perfluoropropene must undergo cyclic dimerization in head-to-tail as

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(10) N.m.r. spectra were taken by Dr. H. S. Gutowsky of the University of Illinois, and Dr. H. C. Beachell of the University of Delaware, and interpreted by Dr. Gutowsky.

(11) $\delta = 10^6(H_r - H_0)/H_r = 0$ for CF_3COOH, where H_r and H_0 are the magnetic field strengths of the reference compound and the observed compounds, respectively.

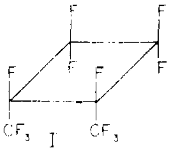
TABLE III

AUTOCLAVE REACTIONS

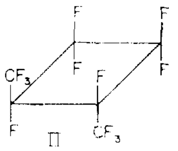
No.	Temp., °C.	Time, hr.	Wt. C_3F_6, g.	Obsd. pressure, p.s.i. Initial[a]	Obsd. pressure, p.s.i. Final	Conversion to dimer, %	Yield, %	Dimer compn., % A	Dimer compn., % B	Dimer compn., % C
1	250 ± 5	19	350	7100	6500	8	100	60	40	Trace
2	265 ± 5	208	317	5800	3700	47	100	55	45	Trace
3	350 ± 5	5	300	[b]	4200	72	100	51	46	3
4	390 ± 10	24	195	[b]	1950	88	98	15	80	5
5	450 ± 10	21	340	[c]	[c]	6[c]	6[c]	Trace	40	60

[a] It is noted that the initial pressures observed in all cases were considerably higher than those calculated from the $pv = nRT$ equation. For example, in run 1, the calculated initial pressure is only 4900 p.s.i., while that measured was 7100 p.s.i. Dissociation of perfluoropropene below 250°, which would account for this apparent deviation from the ideal gas law, is inconsonant with the known chemistry of this olefin. An alternative explanation for this phenomenon is not perceivable at this time. [b] The initial pressure could not be observed, since the pressure had begun to drop before the reaction temperature was reached; a maximum pressure of 6700 p.s.i. and 3700 p.s.i. was reached at 340 and 360°, respectively, for runs 3 and 4. [c] A maximum pressure of 8800 p.s.i. was attained when the temperature reached 310° after a one-hour heating. During the next three hours, while the temperature was raised slowly to 450°, the pressure varied between 6800 and 8800 p.s.i. The temperature was then held at 450 ± 10° for the remainder of the reaction, the pressure dropping from 6950 p.s.i. to a minimum of 6500 p.s.i. after 2.5 hours, and then rising to 7400 p.s.i. after a total of 21 hours. It is clear, therefore, that a very much higher conversion and yield of dimers would have been obtained had this reaction been stopped when the minimum pressure was reached at 450°.

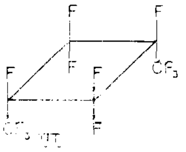
well as head-to-head fashion. This stands in sharp contrast to the previously reported[5-7] cyclic dimerizations of unsymmetrical fluorinated ethylenes, in which the head-to-head cyclic dimers were formed exclusively.



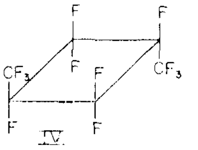
I



II



III



IV

This mixed orientation in the former case may be attributed in part to the higher energy level necessary for dimerization of perfluoropropene to occur, which would favor a more random type of attack.

The chemical evidence clearly favors a perfluoro-(1,2-dimethylcyclobutane) structure for isomer A and a perfluoro-(1,3-dimethylcyclobutane) structure for isomer C. Thus the 1,2-structure would be expected to predominate at the lower temperatures of formation and the 1,3-structure at the higher reaction temperatures. Furthermore, the known[3] increasing order of thermal stability of open chain fluorocarbons, $-CF(CF_3)CF(CF_3)- < -CF_2CF(CF_3)- < -CF_2CF_2-$, confirms the above assignments. The chemical evidence does not adequately distinguish between a 1,2- and 1,3-structure for isomer B, although the relatively small differences in rates of formation and dissociation of isomer A and B favor slightly the 1,2- structure.

The assignments of isomers A and C are supported by n.m.r. fine structure of the $\gg$CF resonances summarized for the three isomers in Table I. For isomer A, this peak was resolved as a symmetrical doublet, with a splitting of 6 c.p.s. For isomers B and C, under similar resolution, the $\gg$CF resonance showed no such splitting. The present interpretation[10] of these data is that isomer A must possess a 1,2-structure and isomers B and C the 1,3-structures.

In conclusion, both chemical and n.m.r. evidence are in agreement with 1,2- and 1,3-formulations for isomers A and C, respectively. The assignment of structure for isomer B, however, is not considered established.

Experimental

Analysis.—The isomeric compositions of the perfluoropropene dimer mixtures were determined from the infrared vapor spectra using reference spectra calculated from the data presented in Table II. For the isomerically pure A, the data therein were employed directly. Assigning the 8.87, 10.53, 11.83, 14.15, 14.5 and 14.8 μ bands to isomer C, and the 11.01, 11.37 and 13.8 μ bands to isomer B, it was estimated that isomer B contained 7% C as impurity, while isomer C fraction actually consisted of 70% isomer C and 30% isomer B. On this basis, reference spectra were calculated for isomerically pure B and C.

By use of these reference spectra, the ratio of isomer A to isomer B was calculated from the ratio of intensities of the 9.39 and 9.59 μ peaks; the 7.24 μ/7.42 μ ratio was useful as a check. However, to determine the A/B ratio in the presence of sizable amounts of perfluoropropene and/or isomer C, the less satisfactory 11.01 μ/11.57 μ and 13.63 μ/13.8 μ ratios had to be employed.

With the A/B ratios established, the particular intrinsic intensity of the 11.01 μ band for this mixture of A + B could then be calculated; this intensity served for the estimation of A + B in the presence of C and/or perfluoropropene. The 10.52 μ band and the 5.56 μ double bond stretching band were satisfactory for the estimation of isomer C and perfluoropropene, respectively.

The ratio of perfluoropropene to total dimers was also determined by vapor–liquid partition chromatography, using a silicone oil column calibrated with synthetic mixtures. These results agreed with infrared analysis within 2%.

Isomers A, B and C could not be separated by vapor-liquid partition chromatography with 6 to 12 ft. columns containing the following stationary liquid phases: di-*n*-decyl phthalate, ethylhexyl sebacate, triethylene glycol dimethyl ether, polyethylene glycol chloride, tetraisobutylene, silicone oil and perfluoropropene telomer oils.[3] A partial separation of the three isomers, however, finally was achieved using a polychlorotrifluoroethylene oil. Chromatographic analysis of the isomer ratios was consistent with the infrared analysis.

Thermal Reactions of Perfluoropropene. (a) In Autoclaves.—Into a 300-ml. Monel autoclave which had been cooled to −75°, perfluoropropene was introduced by gaseous transfer *in vacuo*. The autoclave was then sealed and heated while shaking, the progress of the reaction being followed by the pressure drop. After cooling to room tem-

TABLE IV

SEALED TUBE[a] REACTIONS

Run	Reactant, g.		Initial dimer compn., wt. %			Time, hr.	Temp., °C.	Calcd. init. press., atm.	Prod. comp., wt. % C_3F_6	Final dimer compn., wt. %		
	C_3F_6	$(C_3F_6)_2$	A	B	C					A	B	C
1	..	0.45	49	49	2	2	300	8	0	49	49	2
2	..	0.45	49	49	2	1	410	9	2	50	50	Trace
3	0.50	..	..	..	..	5.5	430	22	51	35	55	10
4	...	0.46	49	49	2	5.5	430	10	25	25	70	5
5	0.24	..	..	..	..	4	430	12	68	30	65	5
6	..	0.24	100	0	0	4	430	6	26	45	55	Trace
7	..	.25	0	91	9	4	430	6	9	20	70	10
8	..	.25	0	33	67	4	430	6	3	Trace	30	70
9	..	.45	49	49	2	1	510	11	52	20	70	10
10[b]	0.50	..	..	..	..	1	510	24	59[b]	15	65	20
11	0.02	..	..	..	..	7	515	1	91	20	55	25

[a] Volume of tubes 7.9 ± 0.3 ml. for runs 5–8; 9.0 ± 0.5 for all other runs. [b] A trace of perfluoroisobutylene was detected in the product.

perature the autoclave was vented through a system of refrigerated receivers.

The data for five autoclave runs, at temperatures ranging from 250 to 450° and reaction times of 5 to 208 hours are summarized in Table III.

At the minimum temperature 250° for the practical operation of the reaction (run 1), kinetic control of the isomeric composition of the products was ensured by stopping the reaction at low conversion.

From the reaction at 265° after a much longer reaction time (run 2), 165 g. of perfluoropropene was recovered and 150 g. of saturated (no C═C absorption in the infrared spectrum, no reaction with potassium permanganate in acetone or with bromine in carbon tetrachloride) dimers C_6F_{12}, b.p. 43.5–45°, f.p. −27 to −28° was obtained; surface tension,[12] dynes/cm. (°C.): 13.7 (0), 12.2 (20), 11.5 (25); viscosity,[12] centistokes (°C.): 0.9 (0), 0.6 (25).

Anal.[13] Calcd. for C_6F_{12}: C, 24.0; H, 0.0; F, 76.0; mol. wt., 300. Found: C, 24.0; H, 0.0; F, 75.7; mol. wt., 301 (gas density balance).

Similarly, at 350° (run 3) where the reaction was very rapid, about half of the pressure drop occurring during the first hour, there were obtained 85 g. of perfluoropropene and 215 g. of dimers, b.p. 43–45°. By careful distillation of the latter in a 2 ft. × 8 mm. dia. Podbielniak Mini-Cal column a pure fraction of isomer A, b.p. 45.1° (physical properties, Table I), was isolated.

Anal. Found: C, 24.1; H, 0.0; mol. wt., 298.

In the reaction at 390° (run 4) the pressure dropped from the observed maximum 3700 p.s.i. to 1950 p.s.i. during 6 hr. but did not decrease during the next 16 hr. Seventeen grams of perfluoropropene was recovered, and there were collected on distillation 4 g. of an intermediate fraction and 174 g. of dimers, b.p. 42.5–45°. By careful redistillation of the dimers there was obtained a fraction greatly enriched in isomer B, b.p. 43.6°, shown by infrared spectroscopic analysis to consist of 93% B and 7% C (physical properties, Table I).

Anal. Found: C, 24.4, 24.1; H, 0.0; mol. wt., 298.

There was recovered from the reaction at 450° (run 5) only 9 g. of perfluoropropene. In addition the following fractions were collected: 103 g., b.p. −30 to 20°, mainly 6.5° shown by infrared spectra to be the highly toxic perfluoroisobutylene[8]; 74 g. of a mixture of olefins b.p. 20–40° (plateau 27–29°); 46 g., b.p. 40–48°, colorless liquid; and 69 g., b.p. 48–102°, a complex olefin-containing mixture not further characterized. Eight grams of higher-boiling residue remained undistilled.

The cut b.p. 40–48° was shown by vapor–liquid partition chromatography and infrared to consist of perfluoropropene dimers and olefinic impurities. Photochemical bromination at 100° failed to remove the latter. Complete oxidation of the olefin with $KMnO_4$ in acetone, however, allowed separation of the dimer as a minimum-boiling azeotrope, b.p. *ca.* 35°, with acetone. After removal of the latter by extraction with iced aqueous $NaHSO_3$ solution, the remaining dimers, 12 g., were carefully fractionated. There was finally obtained 5 g., b.p. 42.8°, shown by infrared spectroscopic analysis to consist of 70% isomer C and 30% of isomer B (physical properties, Table I).

Anal. Found: C, 24.0; H, 0.0; mol wt., 300.

(b) In Sealed Tubes.—Samples of perfluoropropene or of dimers were sealed in thick-wall Pyrex tubes and heated in a Carius tube furnace. The tubes were cooled in liquid nitrogen and the total contents of each tube was analyzed by infrared and vapor–liquid partition chromatography. The results are given in Table IV.

(c) In Hot Tube.—Perfluoropropene was passed at atmospheric pressure through a 0.25 inch i.d. Monel tube heated over an 11-inch section in a tube furnace. The product was condensed in a liquid nitrogen-cooled trap and analyzed by infrared. At 510° using a 10-second contact time, there was no detectable[14] reaction.

PHILADELPHIA 18, PENNA.

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[12] Surface tensions and viscosities were determined by L. P. Muller and A. M. Christofas, Pennsalt Chemicals Corp.

[13] Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and the Analytical Department, Pennsalt Chemicals Corp.

[14] Less than 0.1% C_6F_{12} is readily detectable in perfluoropropene by infrared.