

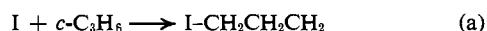
# Homolytic Displacement Reactions on Carbon. I. The Fluorine-Perfluorocyclobutane Reaction

Joseph B. Levy\* and R. Craig Kennedy

Contribution from the Department of Chemistry, George Washington University, Washington, D. C. 20006. Received February 25, 1974

**Abstract:** When fluorine-perfluorocyclobutane mixtures were heated in the range 280–450°, reaction occurred to give perfluoromethane, perfluoroethane, perfluoropropane, and perfluorobutane. Reaction rate measures yielded the expression  $-d(c\text{-C}_4\text{F}_8)/dt = k(c\text{-C}_4\text{F}_8)(\text{F}_2)^{1/2}$ , where  $k = 10^{11.13 \pm 0.2} \exp(-(40,500 \pm 500)/RT) M^{-1/2} \text{ sec}^{-1}$ . The reaction is interpreted in terms of an SH2 attack by a fluorine atom on the ring for which  $k_3 = 10^{8.78 \pm 0.2} \exp(-(21,200 \pm 600)/RT) M^{-1} \text{ sec}^{-1}$ . The observed products are explained on the basis of the decomposition of thermally excited radicals. Mixtures of fluorine with perfluoropropane, perfluorocyclohexane, and trifluoromethyl hypofluorite<sup>1</sup> respectively showed no perceptible reaction at 477° and minimum activation energies for attack by fluorine atom on these species have been calculated.

Free radical displacement reactions on carbon, sometimes designated as SH2 reactions, are seldom encountered. The few cases that have been studied, and have been clearly shown to belong to this class of reactions, have involved displacements of ring bonds in the cyclopropane ring.<sup>2</sup> The only case for which the kinetics have been measured is the reaction



for which

$$k = 10^{9.62} 10^{-17.500/4.57T} M^{-1} \text{ sec}^{-1} \quad (\text{b})$$

is reported.<sup>3</sup> It is clearly desirable that other systems be investigated to try to establish what the barriers to reactions of this class are and what features affect them.

The principal obstacle that arises in the consideration of ordinary organic systems is that displacement by a radical on hydrogen, in a carbon-hydrogen bond for example, proceeds with low activation energy and hence represents a reaction path of such ease that displacement on carbon cannot compete with it. Systems of fluorine and fluorocarbons offer some promise in this area. Since the bond dissociation energy of fluorine is low (38 kcal mol<sup>-1</sup>) and that for the carbon-fluorine bond is high (110–120 kcal mol<sup>-1</sup>) it follows that, for a system containing nothing but carbon-fluorine or carbon-carbon bonds, the only reasonable reaction for attack by a fluorine atom would be the SH2 reaction.

In the present paper the examination of the reaction of fluorine atom with four such species is reported and the results with one, perfluorocyclobutane, for which reaction was obtained and rates were measured, are described in detail. The reaction of interest here is



The particular system has the advantage that: (a) the fluorocarbon is readily available in high purity; (b) its pyrolysis kinetics have been well established<sup>4</sup> and demonstrate that fairly high temperatures can be used

(1) WARNING. Mixtures of fluorine and fluorocarbons other than tetrafluoromethane are capable of thermal explosion and should be handled with care.

(2) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971.

(3) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(4) (a) B. Atkinson and A. B. Trenwith, *J. Chem. Soc.*, 2082 (1953); (b) B. Atkinson and V. Atkinson, *ibid.*, 2086 (1957); (c) J. N. Butler, *J. Amer. Chem. Soc.*, **84**, 1393 (1962); (d) A. Lifshitz, H. F. Carroll, and S. H. Bauer, *J. Chem. Phys.*, **39**, 1661 (1963).

without danger of pyrolysis occurring; (c) the reaction to give perfluoro-*n*-butane proceeds with a pressure drop allowing easy rate measurement.

## Results

The initial result of interest was that reaction was observed for fluorine-perfluorocyclobutane (hereafter abbreviated as PFCB) mixtures at temperatures and reaction times where no perceptible reaction could be observed for PFCB alone. Reaction has been observed with such mixtures (in the general reactant pressure range at 20 to 200 Torr) from 280 to 440°. At 440° a mixture of 20 Torr of each reagent showed 50% reaction in about 10 min. PFCB alone at this temperature showed no reaction over several hours. (The velocity of reaction of PFCB alone at this temperature calculated from literature data<sup>5</sup> is about 0.1% that observed for F<sub>2</sub>-PFCB mixtures containing 10 Torr of fluorine. At lower temperatures the discrepancy is greater.) An experiment in which a mixture of 200 Torr of PFCB and 200 Torr of chlorine was heated at 410° for 3 weeks showed no evidence of ring-opened products at the end of the reaction time. It was thus clear that fluorine molecules or fluorine atoms were attacking PFCB and the reaction was examined in some detail.

**Reaction Rate Measurements.** Rates were measured by premixing reactants in a bulb, expanding the mixture into the reaction bulb, and monitoring the pressure. The nature of the reaction system is such that the rate of PFCB consumption is measured by the rate of pressure independent of the particular stoichiometry.

The absolute pressure drop measures the amount of PFCB consumed but the amount of fluorine consumed depends on the precise nature of the products; thus more fluorine is consumed to give 2 mol of hexafluoroethane than to give 1 mol of perfluoro-*n*-butane. As a consequence it is only at the beginning of the reaction that both the rate of the reaction and the composition of the reacting mixture are known accurately. The procedure adopted here has therefore been to carry out a large number of experiments involving substantial variations in the reactant compositions and a wide temperature range and to rely for kinetic param-

(5) S. W. Benson and A. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21, 295 (1970).

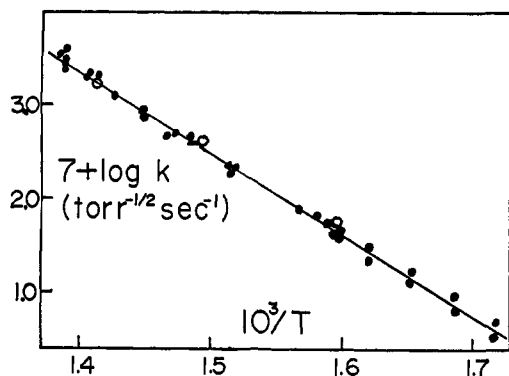


Figure 1. Arrhenius plot for rate constants of expression d. Filled circles are for the bulb reactor,  $A/V = 0.6 \text{ cm}^{-1}$ , and open circles are for the tubular reactor,  $A/V = 8.7 \text{ cm}^{-1}$ .

eters on initial rates. The order of the reaction was established by measuring initial rates, taken as tangents to the pressure-time curves. The data were found to obey the expression

$$v = k(F_2)^{1/2}(PFCB) \quad (d)$$

The data are collected in Table I and plotted in Figure 1.

Support for this expression can be found by comparison of runs 4 and 5, 6 and 7, 10 and 11, 16 and 17, 20 and 21, and 25-29 in Table I. The tabulated rate constants are all in reasonable agreement and substantial variations of compositions and of reaction temperature are illustrated.

The data of Table I and Figure 1 were treated by the method of least squares and yielded the expression

$$k_p = 10^{8.55 \pm 0.2} \exp(-39,800 \pm 500/RT) \text{ Torr}^{-1/2} \text{ sec}^{-1} \quad (e)$$

where the uncertainties shown are the standard deviations. The above corresponds to

$$k = 10^{11.13 \pm 0.2} \exp(-40,500 \pm 500/RT) \text{ M}^{-1/2} \text{ sec}^{-1} \quad (f)$$

It may be noted that the range of rate constant values investigated is about three powers of ten and it is this unusually large range which is responsible for the low uncertainties in the parameters.

The contribution of heterogeneous reaction to the observed results was examined by comparing the results in a tubular reactor ( $A/V = 8.7 \text{ cm}^{-1}$ ) to those in the bulb reactor ( $A/V = 0.6 \text{ cm}^{-1}$ ). Data taken in the tubular reactor are indicated in Figure 1. It is clear that the reaction is homogeneous.

**The Reaction Products.** Examination of infrared spectra of the reaction products indicated the presence of  $n\text{-C}_4\text{F}_{10}$  and  $\text{C}_2\text{F}_6$  (11.1, 13.7, and  $9.0 \mu$ , respectively). Further identification was accomplished by gas chromatography using a 10 ft by 0.25 in. column packed with 60-80 mesh silica gel.<sup>6</sup>

The column was maintained at  $150^\circ$ . Identification was made by comparison with pure samples and the following products were found (retention times in minutes for a helium flow of  $100 \text{ ml min}^{-1}$  are given):  $\text{CF}_4$ , 1.3;  $\text{C}_2\text{F}_6$ , 1.9;  $\text{C}_2\text{F}_4$ , 2.3;  $\text{C}_3\text{F}_8$ , 3.3;  $n\text{-C}_4\text{F}_{10}$ , 5.5. Unfortunately PFCB and  $n\text{-C}_4\text{F}_{10}$  showed ex-

(6) S. A. Greene and F. M. Wachi, *Anal. Chem.*, **35**, 928 (1963).

Table I. Kinetic Data for the  $\text{F}_2$ -PFCB Reaction<sup>a</sup>

Run	Temp, °C	( $\text{F}_2$ )	(PFCB)	$10^7 k$ , Torr <sup>-1/2</sup> sec <sup>-1</sup>
1	309	400	200	5.02
2	320	130	32	6.92
3	320	16	65	9.33
4	332	40	160	15.7
5	332	160	40	16.8
6	345	148	37	30.8
7	345	34	136	22.4
8	353	100	100	56.2
9	353	160	40	46.1
10	354	80	20	38.0
11	354	34	136	41.7
12	357	160	40	56.8
13	386	20	80	212
14	387	80	20	246
15	397	100	100	349
16	401	160	40	392
17	401	16.0	4.0	473
18	409	200	200	502
19	406	80	20	502
20	418	40	160	750
21	418	160	40	875
22	429	16	4	1380
23	433	100	100	1660
24	434	10	10	2138
25	447	69	69	2490
26	447	10	10	2760
27	447	90	23	3312
28	447	27	110	4074
29	449	40	10	3716

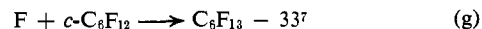
Table II. Analytical Data for the  $\text{F}_2$ -PFCB Reaction (Pressures Given in Torr)

Temp, °K	$\text{F}_2$	PFCB	$\text{CF}_4$	$\text{C}_2\text{F}_6$	$\text{C}_3\text{F}_8$	$\text{C}_4\text{F}_8 + \text{C}_4\text{F}_{10}$	Carbon balance
640	20	10	10.2	4.1	1.5	5.1	1.07
640	20	20	12.5	5.0	1.3	15.0	1.09
680	20	20	12.0	3.8	1.9	14.1	1.02
680	20	200	10.5	5.3	2.0	190	0.98
680	20	380	8.4	4.9	2.1	405	1.13

perimentally indistinguishable retention times. Calibration curves of peak height vs. pressure were linear and the curves for PFCB and  $n\text{-C}_4\text{F}_{10}$  were the same within experimental error. Some representative analyses are shown in Table II.

On the whole the material balances are reasonably satisfactory. There is little doubt that the proportions of the products  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$  are accurately measured.

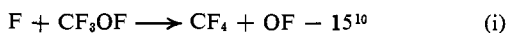
**Attempted Reaction of Fluorine Atoms with Other Molecules.** Experiments were performed in which mixtures containing 900 Torr of fluorine and 100 Torr of a second component were heated at  $750^\circ\text{K}$  for 30 hr and the mixtures then examined on the gas chromatograph for evidence of reaction. The compounds studied in this way were perfluorocyclohexane, perfluoropropane, and trifluoromethyl hypofluorite. The possible reactions and their exothermicities in kilocalories per mole are



(7) The exothermicity is based on assignment of  $82 \text{ kcal}^{-1}$  as the bond dissociation energy of the ring<sup>8</sup> and  $115 \text{ kcal mol}^{-1}$  as the bond dissociation energy of the carbon-fluorine bond in the  $\text{C}_6\text{F}_{13}$  radical.<sup>9</sup>

(8) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

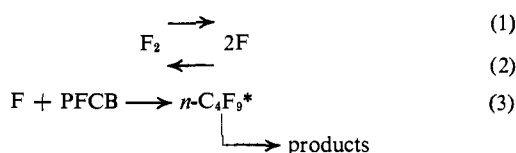
(9) C. R. Patrick, *Advan. Fluorine Chem.*, **2**, 15 (1961).



It would have been possible to detect 0.5 Torr of products expected from reactions g and h and 1 Torr from reaction i. In no case were these amounts detected, and a maximum rate constant based on the hypothesis that the above represented the limiting amount of products formed was calculated in each case. The preexponential figure of rate expression f was then used to allow computation of an overall activation energy and hence values corresponding to reactions g, h, and i above. The minimum values found for the activation energies for (g) and (h) were 44 kcal mol<sup>-1</sup> and that for (i) was 40 kcal mol<sup>-1</sup>.

## Discussion

**Reaction Kinetics and Mechanism of the Fluorine-PFCB Reaction.** The observed kinetic order is most reasonably explained by the steps



Here the perfluoro-*n*-butyl radical is represented as a thermally excited species; such species will be denoted here by an asterisk. The thermochemistry is discussed in further detail below, but it is clear from the natures of the bonds involved in step 3 that the reaction is exothermic.

The above steps determine the kinetics of the reaction so that it is possible to write

$$k = (k_1/k_2)^{1/2} k_3 = (K)^{1/2} k_3$$

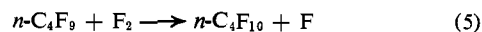
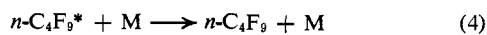
The value for  $K$ , the equilibrium constant for the dissociation of fluorine, has been calculated from literature data<sup>8</sup> at 600°K, a temperature in the middle of the range of the experimental temperatures. The value found was

$$K = 10^{4.70} \exp(-38,600/RT) M$$

The value for  $k_3$  is then

$$k_3 = 10^{8.78} \exp(-(21,200 \pm 600)/RT) M^{-1} \text{ sec}^{-1}$$

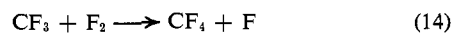
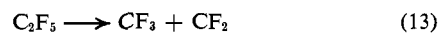
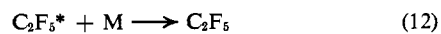
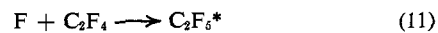
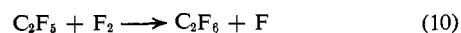
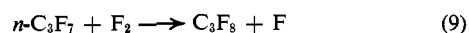
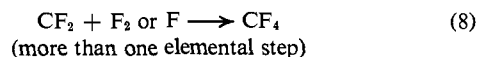
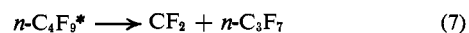
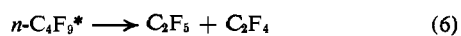
**Product Distribution.** The formation of perfluorobutane follows from



where  $M$  signifies any molecule that can remove energy from the excited radical by a collision.

One way in which  $CF_4$ ,  $C_2F_6$ , and  $C_3F_8$  could have formed was by displacement reactions by fluorine atoms on  $n-C_4F_{10}$ . This possibility was excluded by the observation mentioned earlier that when fluorine-perfluoro-*n*-butane mixtures were heated at reaction temperatures for times considerably in excess of those needed to obtain the above products, no detectable amount of any reaction was observed.

The remaining explanation is that the observed products arise from fragmentation reactions of thermally excited species. These may be written as follows.



Steps 13 and 14 are necessary because the yield of perfluoromethane substantially exceeded that of perfluoropropane.

The most direct test of the presence of thermally excited or hot radicals would be to observe the effect of inert gas or total pressure on the product distribution, that is, to vary the concentration of  $M$  (*cf.* steps 4 and 12). This aspect has not been studied in detail but data can be extracted from the experiments that have been done and will shed some light on this question.

In view of the complexity of the reaction scheme it is desirable to consider pressure effects on product composition in some systematic way. This is done here by defining two fractions:  $R_1$ , which is the fraction of  $n-C_4F_9^*$  that is collisionally deactivated, and  $R_2$ , which is the fraction of  $C_2F_5^*$  which is collisionally deactivated. These fractions can be evaluated by making steady state approximations for  $C_2F_4$  and  $C_2F_5^*$  and the resultant expressions are given below, where  $V_X$  denotes the velocity of formation of species  $X$ .

$$R_1 = \frac{V_{C_4F_{10}}}{V_{C_4F_{10}} + V_{C_3F_8} + 0.5V_{C_2F_6} + 0.25(V_{CF_4} - V_{C_3F_8})} \quad (15)$$

$$R_1 = \frac{k_4[M]}{k_7 + k_6 + k_4[M]} \quad (16)$$

$$R_2 = \frac{V_{C_2F_6} - 0.5(V_{CF_4} - V_{C_3F_8})}{V_{C_2F_6} + 0.5(V_{CF_4} - V_{C_3F_8})} \quad (17)$$

$$R_2 = \frac{k_{12}[M]}{k_{12}[M] + k_{13}} \quad (18)$$

In order to evaluate  $R_1$ ,  $V_{C_4F_{10}}$  must be known. This quantity is not directly available from the analytical data collected since PFCB cannot be distinguished from  $n-C_4F_{10}$  by the gas chromatographic method used here. (Data are not available at present for reaction mixtures containing enough excess fluorine to consume all the PFCB.) Estimates of the perfluoro-*n*-butane can be made by assuming all the fluorine is consumed (since PFCB is in excess), setting up carbon and fluorine material balances, and solving for the unknown, *i.e.*, the yield of perfluoro-*n*-butane. Such data, shown in Table III, are for 640°K, a median temperature and one at which a significant amount of analytical data were taken. Values of  $R_1$  and  $R_2$  are tabulated.

The data clearly support the postulate that fragmentation of hot radicals does display a principal role in determining the product distribution.

**Energetics of SH<sub>2</sub> Reactions.** The F-PFCB reaction reported here is the only SH<sub>2</sub> reaction, except for that between iodine atoms and cyclopropane, for which an

(10) Calculated from thermochemical data taken from ref 8.

**Table III.** The Fragmentations of  $n\text{-C}_4\text{F}_9^*$  and  $\text{C}_2\text{F}_5^*$  at  $640^\circ\text{K}$  (Figures in Reactant and Product Columns Given in Torr)

PFCB	F <sub>2</sub>	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>3</sub> F <sub>8</sub>	C <sub>4</sub> F <sub>10</sub>	R <sub>1</sub>	R <sub>2</sub>
50	50	30.5	13.5	3.7	2.1	0.11	0
50	50	27.5	16.6	4.4	1.0	0.05	0.18
150	50	17.3	13.0	3.4	16.5	0.55	0.30
150	50	17.0	15.8	4.2	13.5	0.47	0.43
350	50	9.5	8.7	2.5	29.5	0.77	0.43
910	50	12.0	13.3	3.5	22.2	0.64	0.51
50 <sup>a</sup>	30	11.0	9.0	2.9	7.5	0.44	0.38
50 <sup>b</sup>	50	14.0	17.2	4.5	15.5	0.50	0.56

<sup>a</sup> 850 Torr of N<sub>2</sub> present. <sup>b</sup> Four atmospheres of helium present.

activation energy has been reported. Some feeling for the energy barriers for such reactions can be gained by considering these activation energies along with the lower limits established for the activation energies for the reactions of fluorine atoms with perfluoropropane, perfluorocyclohexane, and trifluoromethyl hypofluorite.

In comparing the activation energies for the iodine-cyclopropane and fluorine-perfluorocyclobutane reactions, it is clear that there is a profound difference in that the former reaction is thermoneutral while the latter is exothermic by  $60 \text{ kcal mol}^{-1}$ . For similar reactions, the general rule is that the more exothermic reaction proceeds with lower activation energy.<sup>2,11</sup> It thus seems clear that if one were to compare SH2 displacement on cyclopropane and cyclobutane rings where the reactions were of comparable exothermicity, the difference in the activation energies would probably be significantly greater than  $3.7 \text{ kcal mol}^{-1}$ .

What factors determine the magnitudes of these activation barriers? In a recent comprehensive review of free radical substitution reactions, Ingold and Roberts<sup>2</sup> have pointed out that, in the design of a system for an SH2 displacement on carbon, a highly exothermic reaction is desirable, a feature absent in the iodine atom-alkyl iodide systems that have been previously studied. It is evident from the present results with perfluoropropane, perfluorocyclohexane, and trifluoromethyl hypofluorite that strong exothermicity may be a necessary condition for SH2 reactions on carbon but it is not a sufficient one. These authors have also pointed out that the ready occurrence of SH2 displacements on boron, phosphorus, tin, and silicon, *inter alia*, is best explained in terms of an addition-elimination mechanism since for all of these, orbitals are available for bond formation with an attacking radical or atom. The relative ease of reaction with cyclopropanes can thus be related to the established ability of such species to undergo addition reactions, *i.e.*, the degree of  $\pi$  character shown by the ring bonds. The greater difficulty of such reactions with cyclobutanes is consistent with the lessened unsaturated nature of the four-membered ring, while the sharply increased difficulty encountered in the attempts at reaction with perfluoropropane, perfluorocyclohexane, and trifluoromethyl hypofluorite is consistent with the complete lack of unsaturation to be expected in such species.

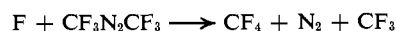
There is one difficulty in the above reasoning that has recently been pointed out by Shea and Skell.<sup>12</sup> It is

(11) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. 1, translated by M. Boudart, Princeton University Press, Princeton, N. J., 1958.

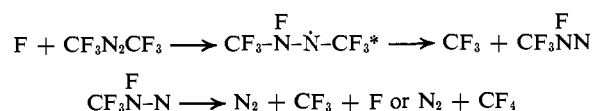
(12) K. J. Shea and P. S. Skell, *J. Amer. Chem. Soc.*, **95**, 6728 (1973).

that the addition-elimination mechanism implies that reaction should occur with retention at the carbon atom which is attacked, while recent studies on the liquid phase photochlorination<sup>13</sup> and photobromination<sup>12</sup> of cyclopropanes have shown that attack occurs with inversion. This is clearly a valid objection and it can only be noted that it has been pointed out<sup>14</sup> that there are some puzzling features about these halogenation reactions. It may be that further study of them will clarify this apparent discrepancy.

In considering whether there are any other factors to be considered in SH2 reactions, it seems reasonable to consider the case of SN2 reactions. For the latter, the nature of the leaving group is a consideration of prime importance.<sup>15</sup> An iodide ion readily displaces iodide ion from an alkyl iodide while displacement of alkoxide ion from an ether by another alkoxide ion does not occur. Both reactions are of course thermoneutral. The question then arises whether, for SH2 reactions, there are good and poor leaving groups and, if so, what determines the nature of such groups. In the consideration of suitable leaving groups, certain factors restrict the range of possibilities. If an atom, such as an iodide atom, is considered, the competing reaction of abstraction of the atom would probably be more favorable than the displacement. Groups containing unsaturation present the possibility of preferential attack at the unsaturation. Thus the reaction of fluorine with perfluoroalkanes to give nitrogen plus the perfluoroalkane<sup>16</sup> can be reasonably presented as an SH2 displacement on carbon.

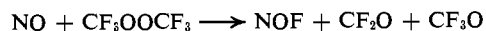


On the other hand fluorine is known to add to such species and the alternative route

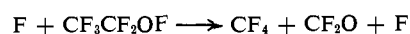


is a strong possibility.

One possibility has suggested itself on the basis of recent work in this laboratory in which a fluorine atom abstraction reaction was demonstrated.<sup>17</sup>



The occurrence of this reaction, since fluorine atom abstractions from carbon are otherwise unknown, may be due to the role COF<sub>2</sub> plays as a leaving group and suggests the possibility of an SH2 displacement as follows



Such reactions are currently being studied in this laboratory.

### Experimental Section

The experiments were carried out in a 500-cm<sup>3</sup> spherical Monel vessel submerged in a molten salt bath thermostated to  $\pm 1.0^\circ$  and connected by 0.25 in. o.d. Monel tubing to a Pace Model V7

(13) J. H. Incremona and C. J. Upton, *J. Amer. Chem. Soc.*, **94**, 301 (1972).

(14) C. Walling and P. Fredericks, *J. Amer. Chem. Soc.*, **84**, 3326 (1962).

(15) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 81.

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pressure transducer. The apparatus and procedure have been described previously,<sup>18</sup> with the exception that all the valves exposed to the F<sub>2</sub>-PFCB mixtures being added to the reactor were changed. The valves initially used had Kd-F sealing seats which became charred and appeared to frequently initiate reaction explosions in many of the early experiments. The explosions were avoided by using only valves having metal-metal sealing surfaces, *i.e.*, eliminating all polymeric material from the manifold used to add the F<sub>2</sub>-PFCB mixtures.

Passivating the Monel bulb surface proved to be quite difficult. Even after being treated several times with fluorine, the most severe treatment being 800 mm of fluorine at 425° for 2 days, the surface appeared to cause a heterogeneous contribution to the observed reaction velocities at the lower temperatures used. The cause of the assumed heterogeneous contribution to the reaction was never isolated. However, the divergence at lower temperatures from the

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straight line Arrhenius plot in Figure 1 steadily decreased with repeated experiments, until the limiting values reported were reproducible. The lack of heterogeneous reaction in the reported results is supported by obtaining comparable results in a Monel tubular reactor ( $A/V = 8.7 \text{ cm}^{-1}$ ) to those in the bulb reactor ( $A/V = 0.6 \text{ cm}^{-1}$ ). Data taken in both reactors are indicated in Figure 1.

Perfluorocyclobutane "Freon C-318" (99.99%) and fluorine (98.0%) were purchased from Matheson Gas Products. Quantities of CF<sub>4</sub>, CF<sub>3</sub>OF, C<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, *n*-C<sub>4</sub>F<sub>10</sub>, and *c*-C<sub>4</sub>F<sub>12</sub> were purchased from Peninsular ChemResearch, Inc. All of the gases were used as received.

**Acknowledgment.** This work was sponsored by the Air Force of Scientific Research under Grant No. ASOSR 70-1939. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright hereon.

## A *p*-Xylene Clathrate of Tris(1,8-naphthalenedioxy)cyclotriphosphazene. X-Ray Crystal and Molecular Structure<sup>1,2</sup>

H. R. Allcock,\* Martha T. Stein, and E. C. Bissell

*Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received December 26, 1973*

**Abstract:** Tris(1,8-naphthalenedioxy)cyclotriphosphazene (III) forms a clathrate inclusion adduct with *p*-xylene. An X-ray single-crystal study has shown that the *p*-xylene molecules are physically trapped in a fixed position within channels that penetrate the lattice. The naphthalenedioxy side groups of the host molecules (III) are bent at the oxygen atoms in such a way that strong host-host interactions stabilize the channel structure. The unit cell is triclinic, with space group *P*1 and with  $a = 8.206 (17) \text{ \AA}$ ,  $b = 14.747 (25) \text{ \AA}$ ,  $c = 13.318 (23) \text{ \AA}$ ,  $\alpha = 101.97 (7)^\circ$ ,  $\beta = 90.77 (7)^\circ$ ,  $\gamma = 109.13 (5)^\circ$ , and  $Z =$  two host molecules and one *p*-xylene. The structure was solved by symbolic addition methods, and refinement to an *R* index of 0.058 was accomplished by Fourier and least-squares techniques. The important mean bond angles and distances within the host molecules are P-N = 1.57 Å, P-O = 1.59 Å, N-P-N = 117.9°, P-N-P = 122.1°, N-P-O = 106.7–110.9°, and O-P-O = 102.2°. The phosphazene ring is puckered in a boat conformation.

We have earlier drawn attention to the unusual crystalline inclusion adducts that are formed by tris(*o*-phenylenedioxy)cyclotriphosphazene (I)<sup>3,4</sup> or tris(2,3-naphthalenedioxy)cyclotriphosphazene (II)<sup>2,5</sup> with organic molecules. In particular it has been shown that the channel inclusion adducts formed by I or II with benzene contain benzene molecules that are free to translate or tumble in the channels. This paper describes a different clathrate arrangement formed between tris(1,8-naphthalenedioxy)cyclotriphosphazene (III) and *p*-xylene.

### Experimental Section

**Preparation of Crystals.** Tris(1,8-naphthalenedioxy)cyclotriphosphazene (III) was prepared by the reaction of hexachlorocyclotriphosphazene with 1,8-naphthalenediol as described previously.<sup>6</sup>

(1) This paper is Part XVIII in a series on phosphorus-nitrogen compounds.

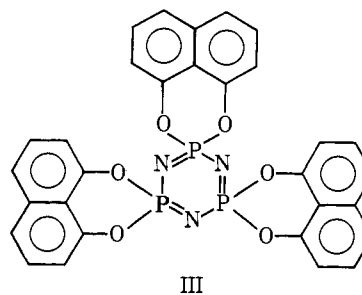
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III

Crystals of III can be grown from a variety of solvents (alcohols, alkanes, cycloalkanes, aromatic compounds), but the crystals for this X-ray study were obtained from *p*-xylene (Fisher, histological grade), which had been dried previously over calcium hydride. The adduct of III with *p*-xylene was stable at room temperature for at least 1 year, but it released *p*-xylene at about 210°. The crystals melted at 360°. *p*-Xylene could also be removed from the adduct at 100–130° (25 mm) to yield a form of III which gave a Debye-Scherrer pattern different from that of the adduct. Subsequent recrystallization from *p*-xylene regenerated the original adduct. Crystals grown from toluene and other solvents produced powder patterns similar to those of the *p*-xylene adduct, and the morphology and color (light orange) were also similar. Thus, it appears likely that the *p*-xylene adduct is typical of several other clathrates formed by III.