Organophosphorus Chemistry. Part XV.[1] Kinetics and Mechanism of the Gas-phase Thermal Reaction of Dimethylphosphine with Tetrafluoroethylene

By **Rodney Brandon, Robert N. Haszeldine,*** and **Peter J. Robinson,** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Reaction of tetrafluoroethylene with an excess of dimethylphosphine (mole ratio 1 : 2 to 1 : 9) in the gas phase at 212—288 °C and total pressures of 67—337 Torr leads to near-quantitative formation (i) of the 1 : 1 adduct, dimethyl-1,1,2,2-tetrafluoroethylphosphine, with a rate expression (ii) where $\log_{10} [k/(\text{dm}^3\ \text{mol}^{-1})^{1\cdot1}\ \text{s}^{-1}] = (8\cdot63 \pm 0\cdot06) - (88\cdot4 \pm 0\cdot6)\ \text{kJ mol}^{-1}/2\cdot303RT$. These and other results are consistent with a homogeneous

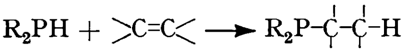
$$Me_2PH + C_2F_4 \longrightarrow Me_2P{\cdot}CF_2{\cdot}CHF_2 \qquad \text{(i)}$$

$$d[Me_2P{\cdot}CF_2{\cdot}CHF_2]/dt = k[Me_2PH]^{0\cdot5}[C_2F_4]^{1\cdot6} \qquad \text{(ii)}$$

$$Me_2PH + C_2F_4 \longrightarrow Me_2P^{\cdot} + {}^{\cdot}CF_2{\cdot}CHF_2 \qquad \text{(iii)}$$

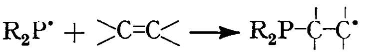
free-radical chain mechanism initiated by an unusual type of reaction, the bimolecular abstraction (iii) of H from dimethylphosphine by tetrafluoroethylene for which the approximate rate equation $\log_{10} k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 11\cdot0 - 106\ \text{kJ mol}^{-1}/2\cdot303RT$ is derived. The chain is propagated by dimethylphosphino and dimethylphosphinotetrafluoroethyl radicals, and terminated by combination of dimethylphosphino radicals. Extensions of this mechanism account satisfactorily for the formation of the other products (predominantly at low phosphine : olefin ratios).

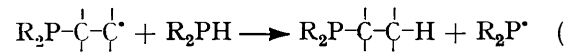
THE addition of phosphines to olefins is a well known preparative reaction proceeding essentially according to


$$R_2PH + {>}C{=}C{<} \longrightarrow R_2P{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \qquad (1)$$

equation (1).[2] The photochemically-initiated reactions have been extensively studied, and a free-radical mechanism (2)—(4) is generally accepted, although precise details have not been elucidated by (for example) kinetic studies. Suitable reactions can also be initiated

$$R_2PH \longrightarrow R_2P^{\cdot} + H \qquad (2)$$


$$R_2P^{\cdot} + {>}C{=}C{<} \longrightarrow R_2P{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{\cdot} \qquad (3)$$


$$R_2P{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{\cdot} + R_2PH \longrightarrow R_2P{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H + R_2P^{\cdot} \qquad (4)$$

thermally, although relatively few details have been reported. Thus dimethylphosphine and tetrafluoroethylene in 1 : 1 mole ratio gave a 25% conversion into the adduct dimethyl-1,1,2,2-tetrafluoroethylphosphine when heated at 100 °C for 6 h.[3] Bis(trifluoromethyl)phosphine and tetrafluoroethylene also gave the 1 : 1 adduct as the main phosphorus-containing product (42% after 24 h at 200 °C),[3] and thermal addition of phosphine itself to a series of olefins has also been reported.[4] In contrast, dimethylphosphine and 1,1,3,3,3-pentafluoropropene or hexafluoropropene gave predominantly alkenylphosphines.[5] In order to clarify the mechanism of the addition reactions, and particularly the mechanism of initiation of the thermal additions, detailed kinetic experiments have now been carried out on the dimethylphosphine–tetrafluoroethylene thermal reaction.

These experiments led to the conclusion that tetramethyldiphosphine is a termination product of the above reaction, and since the thermal addition of diphosphines to olefins is a known reaction [6] it was appropriate also to make a kinetic investigation of the tetramethyldiphosphine–tetrafluoroethylene reaction; this study is reported in Part XVI.[7]

EXPERIMENTAL

Kinetic Apparatus.—This was of conventional design except that special precautions were needed for manipulation of the pyrophoric phosphines. The spherical Pyrex reaction vessel (135 cm³) was heated in a stirred silicone-oil thermostat controlled by a Sirect Mk I proportional controller giving temperatures constant to ±0·1 K during a run and varying by less than ±0·3 K across the reaction vessel. The reaction vessel was connected by heated capillary tubing to a Springham's glass spiral gauge (sensitivity 3·7 mm deflection of the light spot per Torr †) and *via* a Viton-A diaphragm tap to the rest of the system. Mixtures of dimethylphosphine and tetrafluoroethylene were prepared in mixing bulbs (500 cm³) and expanded into the heated reaction vessel. In early experiments the reaction vessel was isolated by a mercury cut-off, in which case reaction mixtures were prepared in the reaction vessel at room temperature, and the vessel heated rapidly to the reaction temperature by raising the thermostat bath. Results obtained in the two systems were identical [*e.g.* $k_6/(\text{dm}^3\ \text{mol}^{-1})^{1\cdot1}\ \text{s}^{-1} = 0\cdot678$, $\sigma = 0\cdot036$ (cut-off) and $0\cdot682$, $\sigma = 0\cdot021$ (diaphragm) for comparable sets of 6 runs at 525 K] and the diaphragm-taps were used for convenience when their satisfactory performance had been established.

As a general check on the apparatus and procedure, results

---

† 1 Torr = (101·325/760) kN m⁻².

[1] Part XIV, F. L. Bowden, A. T. Dronsfield, R. N. Haszeldine, and D. R. Taylor, *J.C.S. Perkin I*, 1973, 516.

[2] See, for example, G. Sosnovsky, 'Free Radical Reactions in Preparative Organic Chemistry,' Macmillan, New York, 1964, p. 153; C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 341; and previous parts of the present series.

[3] R. Fields, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc.* (*C*), 1970, 197.

[4] G. W. Parshall, D. C. England, and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1959, **81**, 4801.

[5] R. Fields, R. N. Haszeldine, and N. F. Wood, *J. Chem. Soc.* (*C*), 1970, 1370; P. Cooper, R. Fields, and R. N. Haszeldine, unpublished results.

[6] (*a*) P. Cooper, R. Fields, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1971, 3031; (*b*) W. Hewertson and I. C. Taylor, *ibid.*, 1970, 1990 and references cited therein.

[7] R. Brandon, R. N. Haszeldine, and P. J. Robinson, following paper.

in good agreement with other work were obtained for the dimerisation of tetrafluoroethylene [10^2k/dm^3 mol^{-1} s^{-1} = 0·724 (2 runs) at 546·5 K and 1·08 (2 runs) at 556·5 K (lit.,[8] 0·730 and 1·10 respectively)] and for the decomposition of trimethyl-1,1,2,2-tetrafluoroethylsilane [10^6k/s^{-1} = 25·5 (3 runs) at 282·8 °C (lit.,[9] 24·0)].

Analysis.—Mixtures for analysis were expanded directly from the reaction vessel into the sampling loop of the gas chromatograph through a Varian–Aerograph valve, to minimise losses of material. Detection was by katharometer (Gow–Mac G-112 glass coated thermistors). Only glass, stainless steel, and Viton were used in the system; exposure to grease, copper, brass, or polyvinyl chloride all resulted in losses of the phosphines. Analysis for the organophosphorus compounds was on a 6·8 m by 5 mm bore Pyrex column packed with 20 wt.% MS 200/50 silicone oil and 1% Carbowax 400 on 60—100 mesh Embacel pretreated with dichlorodimethylsilane and then propanol and operated at 89 °C. The whole gas chromatograph system was similarly treated before use. Fluorocarbon products were analysed on a 5·3 m by 5 mm bore column containing 10 wt. % Kel-F 10, followed by a 2 m by 6 mm bore column containing 30 wt. % oxydipropionitrile, both on Celite, and operated at room temperature. Non-condensable gases were analysed on a 1·5 m by 6 mm bore silica gel column at room temperature. Reasonable straight-line calibrations were eventually obtained for all the materials analysed, although calibrations had to be repeated daily.

Errors in the analysis of synthetic mixtures were greater than expected simply from the calibrations (Table 1).

TABLE 1

Analytical results for typical synthetic mixtures compared with known composition in parentheses

Component pressures/Torr

Me_2PH	C_2F_4	$Me_2P{\cdot}CF_2{\cdot}CHF_2$
68·1(69·5)	15·3(14·0)	
43·2(44·6)	45·9(44·6)	
	34·2(32·9)	32·8(34·1)
	67·6(67·9)	14·0(13·7)
117·2(118·9)	7·8(6·5)	21·6(21·3)

Dimethylphosphine was always underestimated, presumably owing to losses during manipulation, and tetrafluoroethylene was correspondingly overestimated, the percentage error being accentuated by the large excess of phosphine often present. Mixtures containing propane as a non-reactive dummy in place of tetrafluoroethylene were subject to the same errors. Further work on synthetic mixtures is described in the Results section.

Materials.—Dimethylphosphine,[10] essentially pure by g.l.c. and i.r. spectroscopy, was stored in a vessel isolated by a mercury cut-off. Tetramethyldiphosphine [11] and dimethyl-1,1,2,2-tetrafluoroethylphosphine [3] were prepared by known methods. Hydrocarbon and fluorocarbon gases were isolated and/or purified where necessary by preparative g.l.c.

Dimethyl-1,1,2,2,3,3,4,4-*octafluorobutylphosphine* was isolated by fractional condensation from the reaction products of dimethylphosphine with an excess of tetrafluoroethylene, n.m.r. (Perkin-Elmer R10 at 60·00 MHz for ^{1}H and 56·46 MHz for ^{19}F; data quoted are shift in p.p.m. to high field of external benzene or trifluoroacetic acid, intensity, structure, assignment, and derived coupling constant moduli/Hz); ^{1}H: 0·59, 1, tt, CF_2H, J_{HCF} 52·8, J_{HCCF} 6·0; and 5·35, 6, d, PMe_2, J_{HCP} 4·5; ^{19}F: 42·0, d, α-CF_2, J_{FCP} 45·2; 44·2, d, β-CF_2, J_{FCCP} 26·0; and 52·4, α-CF_2; 60·0, d, CHF_2, J_{HCF} 50·8 (further fine structure on most bands).

Reaction of tetramethyldiphosphine (0·79 g, 6·4 mmol) and tetrafluoroethylene (0·50 g, 5·0 mmol) in a Pyrex tube (300 cm^3) for 3 h at 250 °C, followed by fractional condensation, gave 1,2-*bis(dimethylphosphino)tetrafluoroethane* (0·6 g, 2·7 mmol, 54%), $\nu_{max.}$ 671m, 715m, 770s, 807w, 830w, 860m, 879m, 900vs, 953s, 1040s, 1060vs, 1195m, 1280w(sh), 1290w, 1410s, 2800w, 2900w, and 2950w cm^{-1}, n.m.r. ^{1}H: 5·4, complex, PMe_2; ^{19}F: 39, sym. band with major peaks at ±35·4 Hz and smaller peaks at ±5·0 Hz. Mass spectroscopic examination (AEI 902) gave mainly the spectra of oxidation products. The highest peak was *m/e* 223·0066, corresponding to the formula $Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMeO^+$ (Calc. for $C_5H_9F_4OP_2$: *m/e* 223·0064) and in good agreement with the proposed structure. Other compounds of this type have given reasonably strong parent peaks in their mass spectra.[6a]

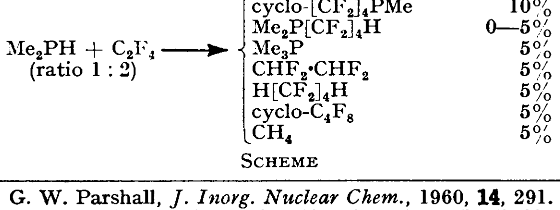
Octafluoro-P-*methylphosphacyclopentane* was also isolated by preparative g.l.c. from the products of reaction of dimethylphosphine and tetrafluoroethylene, $\nu_{max.}$ 699w, 893w, 907w, 973vs, 994vs, 1060w, 1130s, 1160vs, 1200vs, 1240w, 1280s, 1340s, 1420w, 2800w, 2900w, and 2950w cm^{-1}. The strong bands are surprisingly similar to those of perfluorocyclohexene [12] (apart from the double bond absorption) and the C–H vibrations are typical of a methyl group. U.v. and i.r. spectroscopic examination indicated no unsaturation. The mass spectrum provides strong evidence of structure (*m/e*, intensity, and assignment quoted): 245·984, 100%, parent $C_5H_3F_8P^+$ (calc. 245·9845); 146, 13%, $CH_3PC_2F_4^+$; 131, 100%, doublet: 130·967, $C_2F_4P^+$ (calc. 130·967) and 130·992, $C_3F_5^+$ (calc. 130·992); 127, 15%, $CH_3PC_2F_3^+$; 100, 15%, $C_2F_4^+$; 96, 52%, $CH_3PCF_2^+$; 93, 13%, $PC_2F_2^+$; 69, 60%, CF_3^+ and/or PF_2^+; 64·994, 53%, CH_3PF^+ (calc. 64·996, *cf.* $CH_3CF_2^+$, calc. 65·020); 46, 17%, PCH_3^+; 45, 23%, PCH_2^+; 70·7 metastable from $P^+ \longrightarrow 131^+ + 115$.

RESULTS

General Observations.—Reasonable rates of reaction were obtained at 210—280 °C. With dimethylphosphine in excess (mole ratio ⩾ 2 : 1) the main product was the 1 : 1 adduct dimethyl-1,1,2,2-tetrafluoroethylphosphine, with only slight traces of 1,1,2,2-tetrafluoroethane, octafluoro-*P*-methylphosphacyclopentane, and other products; the reaction under these conditions appeared to be essentially (5). With tetrafluoroethylene in excess (up to 5 : 1) the reaction

$$Me_2PH + C_2F_4 \longrightarrow Me_2P{\cdot}CF_2{\cdot}CHF_2 \qquad (5)$$

was much more complex, the product distribution being given approximately by the Scheme. Kinetic studies were



$$\begin{array}{c} Me_2PH + C_2F_4 \\ \text{(ratio 1 : 2)} \end{array} \longrightarrow \left\{ \begin{array}{lr} Me_2P{\cdot}CF_2{\cdot}CHF_2 & 50\% \\ Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2 & 5\text{—}10\% \\ \text{cyclo-}[CF_2]_4PMe & 10\% \\ Me_2P[CF_2]_4H & 0\text{—}5\% \\ Me_3P & 5\% \\ CHF_2{\cdot}CHF_2 & 5\% \\ H[CF_2]_4H & 5\% \\ \text{cyclo-}C_4F_8 & 5\% \\ CH_4 & 5\% \end{array} \right.$$

SCHEME

---

[8] B. Atkinson and A. B. Trenwith, *J. Chem. Soc.*, 1953, 2082.

[9] R. N. Haszeldine, C. Parkinson, and P. J. Robinson, *J.C.S. Perkin II*, 1973, 1018.

[10] G. W. Parshall, *Inorg. Synth.*, 1968, **11**, 157.

[11] G. W. Parshall, *J. Inorg. Nuclear Chem.*, 1960, **14**, 291.

[12] D. G. Wieblen in ' Fluorine Chemistry,' ed. J. H. Simons, Academic Press, New York, 1954, vol. II, p. 478.

therefore restricted to mixtures containing an excess of phosphine.

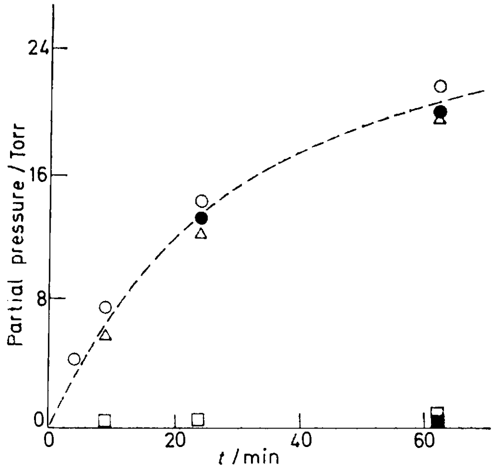


FIGURE 1 Progress curves for dimethylphosphine (140·8 Torr) and tetrafluoroethylene (28·0 Torr) at 250 °C. ○ = Dimethyl-1,1,2,2-tetrafluoroethylphosphine (●, in packed vessel); △ = tetrafluoroethylene consumed; □ = 1,1,2,2-tetrafluoroethane; ■, = cyclo-C_4F_8PMe; broken line = pressure change

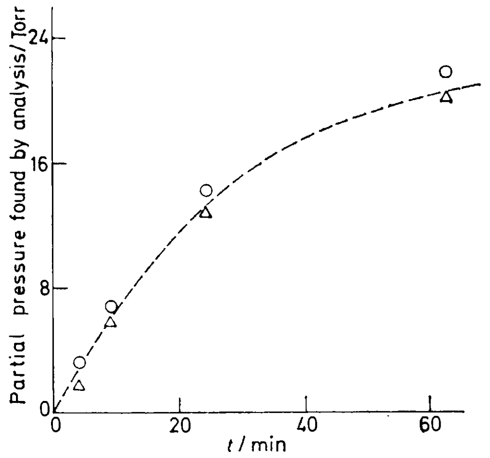


FIGURE 2 Analysis of synthetic mixtures corresponding to analyses in Figure 1 (mixtures made up to correspond to points on the broken line). Symbols as in Figure 1

Analysis of Reaction Mixtures.—In order to test the validity of equation (5) as a basis for the use of pressure measurements in kinetic studies, quantitative analyses were carried out on the products of reaction of 5 : 1 phosphine : olefin mixtures for various times at 498·2, 523·2, and 548·2 K. A typical set of results are shown in Figure 1; data for the consumption of dimethylphosphine are not shown, since they were obtained inaccurately as the difference of two large quantities. The results confirm (*a*) that the minor products are formed only in very small amounts, and (*b*) that the consumption of tetrafluoroethylene and the production of 1 : 1 adduct are both close to the observed pressure change, as expected on the basis of equation (5). The deviations of these latter points from the broken line are in the sense expected from the errors found in the analysis of synthetic mixtures (*q.v.*), and it is therefore a reasonable hypothesis that accurate analysis would give points precisely on the line. This conclusion is strikingly confirmed by the analysis of synthetic mixtures made up to represent the composition of the reaction mixtures in Figure 1, as calculated from the pressure change using equation (5). The results (Figure 2) are virtually indistinguishable from the analyses in Figure 1. It is therefore concluded that, for phosphine : olefin ratios of 5 : 1 or greater, accurate kinetic data can be obtained by interpreting measured pressure changes on the basis of equation (5).

Kinetic Results for Reaction (5).—Since it has been shown that the reaction at high phosphine : olefin ratios is represented by equation (5), kinetic data under these conditions can be obtained simply from pressure measurements. Logarithmic plots of the initial rate of pressure change against total initial pressure at constant reactant ratios gave good straight-line plots corresponding (Table 2) to an overall kinetic order of 2·08 (s.d. 0·04) for the reaction. Separate measurements (Table 3) in which one reactant pressure was varied with the other constant similarly gave linear plots yielding orders of 0·48 for dimethylphosphine (s.d. 0·01) and 1·60 for tetrafluoroethylene (s.d. 0·01), in good agreement with the above overall order. The initial rate of reaction was thus represented with good accuracy by equation (6).

TABLE 2

Total order of reaction from initial rates

T/K	$Me_2PH : C_2F_4$	Total press/ Torr	No. of runs	Order
498·2	5 : 1	67–188	4	2·04
523·2	5 : 1	26–169	6	2·08
523·2	9 : 1	57–282	5	2·08
548·2	5 : 1	36–178	5	2·11

TABLE 3

Orders with respect to individual reactants from initial rates at 523·2 K (error limits are standard deviations)

p_{Me_2PH}/Torr	$p_{C_2F_4}$/Torr	No. of runs	Order
82—254	28	5	(0·48 ± 0·01) w.r.t. Me_2PH
253	28—84	3	(1·60 ± 0·01) w.r.t. C_2F_4

$$d[Me_2P\cdot CF_2\cdot CHF_2]/dt = k_6[Me_2PH]^{0\cdot 50}[C_2F_4]^{1\cdot 60} \quad (6)$$

In order to test whether this equation also described the behaviour throughout the course of the reaction, use was made of the closely related equation (7), which has the integrated form (8).[13] The order 1·50 is significantly different from the experimental value of 1·60 in equation (6), and the two rate-constants are related by equation (9). The quantities $(a - x)$ and $(b - x)$ (where $a = [Me_2PH]_0$, $b = [C_2F_4]_0$, and x = extent of reaction at time t) were computed from the pressure change with allowance for dead-space,[14] and the left-hand-side of equation (8) was plotted against time. With this expression evaluated to high precision by digital computer, it was not necessary to use the limiting algebraic form for $a = b$, even when the initial reactant pressures differed by as little as 0·1 Torr.[13] Straight-line plots were obtained over a wide range of

$$d[Me_2P\cdot CF_2\cdot CHF_2]/dt = k_7[Me_2PH]^{0\cdot 50}[C_2F_4]^{1\cdot 50} \quad (7)$$

$$[2/(a - b)]\{[(a - x)/(b - x)]^{0\cdot 5} - (a/b)^{0\cdot 5}\} = k_7t \quad (8)$$

$$k_6 = k_7[C_2F_4]^{-0\cdot 10} \quad (9)$$

---

[13] P. J. Robinson, *Acta Chim. Acad. Sci. Hung.*, 1970, **66**, 407; please note and quote the errata—*ibid.*, 1971, **68** (4).

[14] P. J. Robinson, *Trans. Faraday Soc.*, 1967, **63**, 2668.

reactant concentrations (Tables 4 and 5), and some typical plots are shown in Figure 3. The slopes (k_7) of the plots varied slightly with the olefin pressure (Table 4), but the corrected rate-constants k_6 were constant within experimental error, thus confirming that the same rate equation (6) applied during the course of the reaction as well as to the initial rates. Runs at seven temperatures in the range 212—288 °C (Table 5) gave a good Arrhenius plot corresponding to the Arrhenius equation (10), in which each rate-constant was given equal weighting and the error limits are the 95% confidence limits.

TABLE 4

Typical rate-constants from equations (6) and (7) at 523·2 K

10^4[reactant]/mol dm^{-3}			
Me_2PH	C_2F_4	k_7/dm^3 mol^{-1} s^{-1}	k_6/(dm^3 mol^{-1})$^{1\cdot1}$ s^{-1}
43·9	4·78	0·284	0·610
43·2	8·56	0·300	0·608
44·7	14·90	0·318	0·610
25·1	8·40	0·301	0·611
34·5	8·56	0·315	0·638
43·2	8·56	0·300	0·608
60·7	8·53	0·299	0·606
77·7	8·57	0·310	0·628

TABLE 5

Rate-constants from equation (6) as a function of temperature (mole ratios 3 : 1 to 9 : 1)

	No. of	Reactant pressures/Torr		k_6/(dm^3 mol^{-1})$^{1\cdot1}$ s^{-1}	
T/K	runs	Me_2PH	C_2F_4	Mean	s.d.
485·7	2	93, 121	18, 24	0·130	0·005
498·2	12	56—136	11—27	0·229	0·012
510·7	3	70—117	14—23	0·393	0·003
523·2	22	22—254	4·4—28	0·628	0·021
535·7	3	72—118	14—23	1·047	0·013
548·2	10	30—148	6·0—29	1·60	0·04
560·7	3	81—131	16—26	2·46	0·12

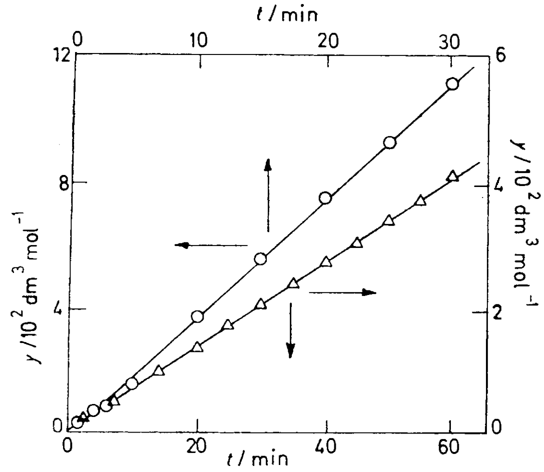


FIGURE 3 Typical kinetic plots for the dimethylphosphine–tetrafluoroethylene reaction; the ordinate y is the l.h.s. of equation (8). ○ = Dimethylphosphine (30·2 Torr) and tetrafluoroethylene (6·0 Torr) at 275 °C; △ = dimethylphosphine (136 Torr) and tetrafluoroethylene (26·9 Torr) at 225 °C

$$\log_{10}[k_6/(\mathrm{dm^3\ mol^{-1}})^{1\cdot1}\ \mathrm{s^{-1}}] = (8\cdot63 \pm 0\cdot06) - (88\cdot4 \pm 0\cdot6)\ \mathrm{kJ\ mol^{-1}}/2\cdot303RT \quad (10)$$

Reaction in a Packed Vessel.—The reaction was also studied in a vessel packed with Pyrex tubes ($S : V = 10\cdot8$ cm^{-1}, *cf.* 1·0 cm^{-1} for the unpacked vessel). Pressure measurements and g.l.c. analysis for the 1 : 1 adduct (*e.g.* Figure 1) both gave results indistinguishable from those in the unpacked vessel [*e.g.* k_6/(dm^3 mol^{-1})$^{1.1}$ s^{-1} = 0·570, 0·588 at 523·2 K, and 1·57 at 548·2 K, *cf.* 0·63 ± 0·02 and 1·60 ± 0·04 respectively in the unpacked vessel]. The reaction is thus concluded to be homogeneous.

Kinetic Results for Minor Products.—Semiquantitative data were obtained for two minor products of particular interest, 1,1,2,2-tetrafluoroethane and octafluoro-*P*-methylphosphacyclopentane (cyclo-$[CF_2]_4PMe$), by g.l.c. analysis at various times of runs with differing reactant concentrations, all at 523·2 K. Orders of reaction were obtained from the extrapolated initial rates of formation. The compounds were formed only in small amounts (*e.g.* 0·2—3 Torr) but the orders were determined within reasonably small error limits as shown in Table 6.

TABLE 6

Orders of reaction for formation of minor products

	Order of formation w.r.t.	
Product	Me_2PH	C_2F_4
$CHF_2{\cdot}CHF_2$	*ca.* 0	1·5—2·0
cyclo-$[CF_2]_4PMe$	−1·0 to −0·5	2·4—2·7

Reaction in the Presence of trans-*But-2-ene.*—In order to throw further light on the mechanism of the addition reaction (5), a number of experiments were performed in which *trans*-but-2-ene was added to reaction mixtures and the products analysed for the presence of *cis*-but-2-ene arising from reversible addition of radicals to the double bond. The results of these and related experiments are given in Table 7. Little or no butene was consumed since the pressure change was unaffected [*e.g.* k_6/(dm^3 mol^{-1})$^{1\cdot1}$ s^{-1} at 523·2 K = 0·556, 0·495 in the presence of butene, *cf.* 0·578, 0·562 for comparable runs in the absence of butene].

Miscellaneous Related Experiments.—Various mechanistic aspects were explored in the following experiments. Dimethylphosphine underwent no detectable change when heated alone at 220—265 °C for 3 h; specifically, no trace of hydrogen or methane could be found. Dimethylphosphine (41 Torr) and ethylene (82 Torr) underwent no change in 90 min at 275 °C (with tetrafluoroethylene the reaction would be largely complete). Trimethylphosphine (35 Torr) and tetrafluoroethylene (35 Torr) underwent no change in 1 h at 250 °C. Reaction of dimethylphosphine and tetrafluoroethylene in the presence of the inert gas carbon tetrafluoride gave rate constants close to the normal values [k_6/(dm^3 mol^{-1})$^{1\cdot1}$ s^{-1} = 0·647 at 523·2 K (3 runs) and 1·64 at 548·2 K (5 runs) *cf.* 0·628 and 1·60 in the absence of CF_4].

Experiments with Low Phosphine : Olefin Ratios.—The reaction under these conditions was complex and was not subjected to detailed kinetic examination. Some typical progress curves are shown in Figure 4 for completeness. Rate constants k_6 obtained as above, from pressure measurements on the basis of equation (5), were constant at phosphine : olefin ratios down to 2 : 1 but thereafter decreased.

DISCUSSION

The thermal reaction between dimethylphosphine and tetrafluoroethylene has been shown to be insensitive to surface : volume ratio and is concluded to be homogeneous. The non-integral orders of reaction [equation (6)], and the complexity of the products at low phosphine : olefin ratios, point strongly to a free-radical mechanism of the general type suggested for the photochemical addition of phosphines to olefins.[2] The initiation process for the thermal reaction is of particular interest, however, and will be discussed first.

Initiation.—The overall kinetic order of about two requires a second-order initiation process, and the order of 1·6 for tetrafluoroethylene requires that this olefin is involved in the initiation. Possible initiation reactions are therefore (11) and (12). To throw further light on this question, qualitative experiments were carried out in

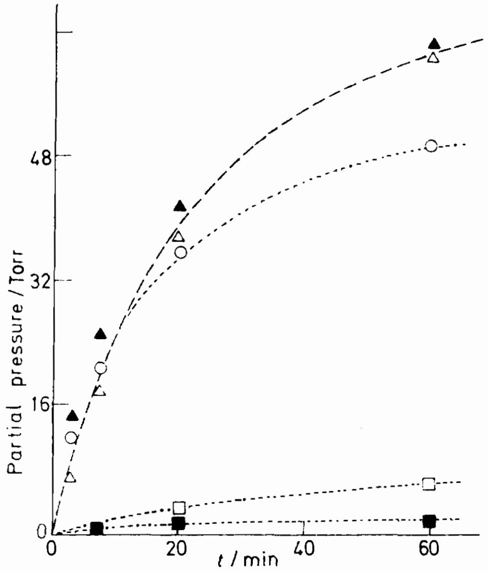


FIGURE 4 Progress curves for dimethylphosphine (85·5 Torr) and tetrafluoroethylene (85·4 Torr) at 250 °C; key as Figure 1, with ▲ = dimethylphosphine consumed

$$2C_2F_4 \longrightarrow \text{radicals} \qquad (11)$$

$$Me_2PH + C_2F_4 \longrightarrow \text{radicals} \qquad (12)$$

which *trans*-but-2-ene was added to various reaction mixtures and the recovered butene analysed for the *cis*-isomer. It has previously been shown [15,3] that a variety of phosphino radicals add reversibly to but-2-ene and so cause geometrical isomerisation. Thus the occurrence of geometrical isomerisation can, in suitable systems, be used as a test for the presence of phosphino radicals. The results of the present experiments are summarised in Table 7. The first two experiments show that radicals produced by decomposition of azobisisobutyronitrile in the presence (but not in the absence) of dimethylphosphine do indeed induce isomerisation of the butene. The radical involved is presumed to be the dimethylphosphino radical. Experiments 3—6 show that, under conditions where the addition reaction readily occurs, neither dimethylphosphine nor tetrafluoroethylene alone induce isomerisation, but that marked isomerisation occurs when both reactants are present. The conclusions are that only radicals from dimethylphosphine (presumably dimethylphosphino) are able to isomerise the butene, and that these radicals are produced only when both dimethylphosphine and tetrafluoroethylene are present. These results, together with the kinetic information, clearly identify the overall initiation process as (12). This overall reaction may be written as any of the following three kinetically equivalent schemes, and the present results provide little ground for choice between them.

TABLE 7

Experiments using *trans*-but-2-ene

Experiment	Reactants [a]	$t/^\circ C$	% *cis* in the recovered butene
1	T + AIBN + NON	80 [b]	0
2	T + AIBN + NON + DMP	80 [b]	12
3	T	250 [c]	0
4	T + DMP	250 [c]	0
5	T + TFE	250 [c]	0
6	T + DMP + TFE	250 [c]	8

[a] T = *trans*-but-2-ene (28—112 Torr), AIBN = azobisisobutyronitrile (0·05 mmol), NON = nonane (10 cm^3) to homogenise the system, DMP = dimethylphosphine (30—90 Torr), TFE = tetrafluoroethylene (60—90 Torr). [b] 2 h in flask (250 cm^3) with greaseless tap; gas and liquid phases present. [c] 3 h in kinetic system; gas phase only.

$$\left.\begin{array}{r} C_2F_4 \overset{\text{eqm}}{\rightleftharpoons} \dot{C}F_2{\cdot}\dot{C}F_2 \\ \dot{C}F_2{\cdot}\dot{C}F_2 + Me_2PH \longrightarrow \dot{C}F_2{\cdot}CHF_2 + Me_2P^{\bullet} \end{array}\right\} \qquad (13a)$$

$$C_2F_4 + Me_2PH \overset{\text{eqm}}{\rightleftharpoons} [C_2F_4{\cdot}Me_2PH] \longrightarrow \dot{C}F_2{\cdot}CHF_2 + Me_2P^{\bullet} \qquad (13b)$$

$$C_2F_4 + Me_2PH \longrightarrow \dot{C}F_2{\cdot}CHF_2 + Me_2P^{\bullet} \qquad (14)$$

Biradicals have been postulated as intermediates in various reactions of halogenated ethylenes [16] but there seems to be no *direct* evidence for their intervention. There is similarly no direct evidence for intermediate complex formation as in (13b), but such a mechanism cannot be ruled out. A single-step initiation analogous to (14) was postulated for the addition of trifluoroacetonitrile to ethylene,[17] and Benson has shown [18] that such reactions would be expected to have high *A* factors. The corresponding reaction involving two unsaturated molecules is also believed to be responsible for the initiation of hydrocarbon olefin pyrolysis.[19]

Complete Mechanism.—A conventional radical chain reaction leading to the production of the 1 : 1 adduct can now be written as (14)—(20) [noting that (14) may be replaced by (13a) or (13b) with the same kinetic predictions]. Steady-state treatment of the scheme leads to a general equation for the rate of formation of 1 : 1 adduct,

---

[15] J. Pellon, *J. Amer. Chem. Soc.*, 1961, **83**, 1915.

[16] P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473.

[17] J. B. Flannery and G. J. Janz, *J. Amer. Chem. Soc.*, 1966, **88**, 5097.

[18] S. W. Benson, *Adv. Photochem.*, 1964, **2**, 1.

[19] M. Simon and M. H. Back, *Canad. J. Chem.*, 1970, **48**, 317, 3313, and references cited therein.

$$\mathrm{CHF_2{\cdot}CF_2^{\bullet} + Me_2PH \longrightarrow CHF_2{\cdot}CHF_2 + Me_2P^{\bullet}} \quad (15)$$

$$\mathrm{Me_2P^{\bullet} + C_2F_4 \rightleftharpoons Me_2P{\cdot}CF_2{\cdot}CF_2^{\bullet}} \quad (16)$$

$$\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2^{\bullet} + Me_2PH \longrightarrow Me_2P{\cdot}CF_2{\cdot}CHF_2 + Me_2P^{\bullet}} \quad (17)$$

$$\mathrm{2Me_2P^{\bullet} \longrightarrow P_2Me_4} \quad (18)$$

$$\mathrm{Me_2P^{\bullet} + Me_2P{\cdot}CF_2{\cdot}CF_2^{\bullet} \longrightarrow Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2} \quad (19)$$

$$\mathrm{2Me_2P{\cdot}CF_2{\cdot}CF_2^{\bullet} \longrightarrow Me_2P[CF_2]_4PMe_2} \quad (20)$$

which for sufficiently high phosphine : olefin ratios reduces to (21), termination then being predominantly by (18). At sufficiently high phosphine concentrations k_{-16} is negligible compared with $k_{17}[\mathrm{Me_2PH}]$ and the

$$\mathrm{d[Me_2P{\cdot}CF_2{\cdot}CHF_2]}/\mathrm{d}t = \frac{(k_{14}/k_{18})^{\frac{1}{2}}k_{16}[\mathrm{Me_2PH}]^{0{\cdot}5}[\mathrm{C_2F_4}]^{1{\cdot}5}}{(1 + k_{-16}/k_{17}[\mathrm{Me_2PH}])]} \quad (21)$$

predicted equation is (22), which is in good agreement with the observed equation (6). The small difference between the two equations can be accounted for at least semiquantitatively by postulating the occurrence of some first-order removal of dimethylphosphino radicals at the walls.

$$\mathrm{d[Me_2P{\cdot}CF_2{\cdot}CHF_2]}/\mathrm{d}t = (k_{14}/k_{18})^{\frac{1}{2}}k_{16}[\mathrm{Me_2PH}]^{0{\cdot}5}[\mathrm{C_2F_4}]^{1{\cdot}5} \quad (22)$$

The present results indicate irreversible addition of dimethylphosphino radicals to tetrafluoroethylene under these conditions, in contrast to the predominantly reversible addition to but-2-ene (see above). The proposed termination product, tetramethyldiphosphine, is known to add to olefins,[6] and this may raise some doubt as to whether (18) can be regarded as a true termination reaction. It is possible to estimate the rate of dissociation of the diphosphine from the estimated rate constant [7] together with an upper limit for the concentration of diphosphine set by the total amount of initiation which has occurred, the initiation rate constant being estimated below. It emerges that the rate of dissociation of the diphosphine was always very small in our experiments compared with the initiation and termination rates (*e.g.* ratio $<10^{-3}$), and that reversibility of reaction (18) was therefore not a significant complication.

Kinetics for Minor Products.—The formation of 1,1,2,2-tetrafluoroethane by reactions (13)—(15) would be first-order in each reactant, and not consistent with the observed kinetic behaviour (Table 6). An alternative mechanism (23) and (24) is thus proposed as the predominant source of the 1,1,2,2-tetrafluoroethyl radical

$$\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2^{\bullet} + Me_2PH \longrightarrow Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}\dot{P}Me_2H} \quad (23)$$

$$\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}\dot{P}Me_2H + C_2F_4 \longrightarrow Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2 + CHF_2{\cdot}CF_2^{\bullet}} \quad (24)$$

and hence 1,1,2,2-tetrafluoroethane. Similar reactions involving phosphoranyl radicals have been postulated for other systems.[20] Steady-state treatment leads to (25),

$$\frac{\mathrm{d[CHF_2{\cdot}CHF_2]}}{\mathrm{d}t} = \frac{k_{23}k_{16}k_{14}{}^{0{\cdot}5}[\mathrm{Me_2PH}]^{0{\cdot}5}[\mathrm{C_2F_4}]^{1{\cdot}5}}{k_{17}k_{18}{}^{0{\cdot}5}} \quad (25)$$

which is reasonably consistent with the approximate orders of reaction obtained experimentally (Table 6). 1,2-Bis(dimethylphosphino)-1,1,2,2-tetrafluoroethane, the other product from (23) and (24), was detected qualitatively in amounts broadly consistent with the above mechanism.

For production of the cyclic product octafluoro-*P*-methylphosphacyclopentane, reactions (26) and (27) are proposed. Only traces of telomer were found, so that cyclisation of the radical formed in (26) appears to predominate over hydrogen abstraction. Methane was produced in about half the amount of the cyclic product, so that the methyl radicals appear to give other products as well, possibly by addition to dimethylphosphine.

$$\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2^{\bullet} + C_2F_4 \longrightarrow Me_2P[CF_2]_4^{\bullet}} \quad (26)$$

$$\mathrm{Me_2P[CF_2]_4^{\bullet} \longrightarrow cyclo\text{-}MeP[CF_2]_4 + Me^{\bullet}} \quad (27)$$

Steady-state treatment gives (28), in good agreement with the approximate experimental orders in Table 6.

$$\frac{\mathrm{d[cyclo\text{-}MeP(CF_2)_4]}}{\mathrm{d}t} = \frac{k_{26}k_{16}k_{14}{}^{0{\cdot}5}[\mathrm{MePH}]^{-0{\cdot}5}[\mathrm{C_2F_4}]^{2{\cdot}5}}{k_{17}k_{18}{}^{0{\cdot}5}} \quad (28)$$

Arrhenius Parameters.—The overall Arrhenius parameters from (10) may be related to those of the elementary steps involved by (22); the derived relationships are (29) and (30). The parameters corresponding to (22) rather than (6) have been used for consistency, although

$$E_{22} = \tfrac{1}{2}E_{14} - \tfrac{1}{2}E_{18} + E_{16} = \tfrac{1}{2}E_{14} + E_{16} = 88{\cdot}4\ \mathrm{kJ\ mol^{-1}} \quad (29)$$

$$A_{22} = (A_{14}/A_{18})^{0{\cdot}5}A_{16} = 10^{8{\cdot}3}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \quad (30)$$

the numerical differences are trivial. It has been deduced [7] that $A_{16} = 10^{8{\cdot}3 \pm 0{\cdot}3}$ dm^3 mol^{-1} s^{-1} and $E_{16} = 50 \pm 15$ kJ mol^{-1}, and these values, together with a typical value of $A_{18} = 10^{11{\cdot}0}$ dm^3 mol^{-1} s^{-1}, give the approximate Arrhenius equation (3) for the initiation reaction (14). The error limits must be wide, but the

$$\log_{10} k_{14}/\mathrm{dm^3\ mol^{-1}\ s^{-1}} = 11{\cdot}0 - 76\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303RT \quad (31)$$

result is indicative of an initiation reaction having little steric requirement and a remarkably low activation energy. If A_{18} is substantially lower than 10^{11} dm^3 mol^{-1} s^{-1} (as now seems to be the case for alkyl radicals other than methyl) [21] A_{14} will be correspondingly lower.

[2/2406 *Received, 23rd October,* 1972]

---

[20] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1963, 1083; J. I. G. Cadogan, *Adv. Free Radical Chem.*, 1967, **2**, 203.

[21] R. Hiatt and S. W. Benson, *J. Amer. Chem. Soc.*, 1972, **94**, 6886; *Internat. J. Chem. Kinetics*, 1972, **4**, 151; R. M. Marshall and J. H. Purnell, *J.C.S. Chem. Comm.*, 1972, 764.