Organophosphorus Chemistry. Part XVI.[1] Kinetics and Mechanism of the Gas-phase Thermal Addition of Tetramethyldiphosphine to Tetrafluoroethylene

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Addition of tetramethyldiphosphine to tetrafluoroethylene in the gas phase at 240—280 °C gives 1,2-bis(dimethylphosphino)tetrafluoroethane [reaction (i)] with a rate expression (ii) where $\log_{10}$ $[k/(\mathrm{dm}^3\ \mathrm{mol}^{-1})^{0{\cdot}6}\ \mathrm{s}^{-1}] = (10{\cdot}87 \pm 0{\cdot}37) - (129{\cdot}_2 \pm 4)\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303RT$. A free radical mechanism is proposed, in which dimethyl-

$$\mathrm{P_2Me_4 + C_2F_4 \longrightarrow Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2} \qquad \text{(i)}$$

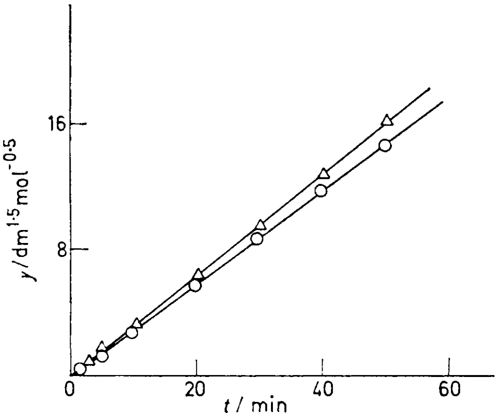
$$\mathrm{d[Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2]}/\mathrm{d}t = k\mathrm{[P_2Me_4]^{0{\cdot}5}[C_2F_4]^{1{\cdot}1}} \qquad \text{(ii)}$$

phosphino radicals are formed by reversible dissociation of the diphosphine. An approximate bond energy $D(\mathrm{Me_2P{-}PMe_2})$ *ca.* 160 kJ mol^{-1} is deduced.

In our study[1] of the thermal addition of dimethylphosphine to tetrafluoroethylene it was postulated that tetramethyldiphosphine was the main termination product. Since diphosphines are known to be able to add to certain olefins[2] it was desirable to study the possibly complicating reaction of tetramethyldiphosphine with tetrafluoroethylene. In addition this study leads to useful Arrhenius data for some of the elementary steps involved in these olefin addition reactions.

RESULTS

The apparatus and materials were as before.[1] Runs were started by expanding the olefin into the vessel already containing the diphosphine at the reaction temperature. In the temperature range 240—280 °C tetramethyldiphosphine and tetrafluoroethylene reacted cleanly and reproducibly to give the 1 : 1 adduct 1,2-bis(dimethylphosphino)tetrafluoroethane as the sole observed product, as reported previously.[2] No other products were detected except for some solid deposits when mixtures containing an excess of olefin were allowed to react for long times. Pressure measurements on a series of runs were thus analysed kinetically on the assumption that the reaction was quantitatively represented by equation (1).



Typical kinetic plots for the tetramethyldiphosphine–tetrafluoroethylene reaction at 250 °C. The ordinate y is the l.h.s. of equation (4) or (5) as appropriate. ○ = Equation (5) for tetramethyldiphosphine (41·1 Torr) and tetrafluoroethylene (21·1 Torr), △ = equation (4) for tetramethyldiphosphine (13·6 Torr) and tetrafluoroethylene (48·7 Torr)

$$\mathrm{Me_2P{\cdot}PMe_2 + C_2F_4 \longrightarrow Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2} \qquad (1)$$

Logarithmic plots of initial rates against reactant concentrations (mole ratios 2 : 1 to 1 : 3·6) gave orders of 0·49 (s.d. 0·02) for tetramethyldiphosphine and 1·13 ± 0·02 for tetrafluoroethylene, the initial rate therefore being given within experimental error by equation (2). Integrated plots (*e.g.* the Figure) were constructed from the closely related equation (3), which has the integrated forms (4) and (5) (where $a = [\mathrm{P_2Me_4}]_0$, $b = [\mathrm{C_2F_4}]_0$, and x = the extent of reaction at time t, corrected for dead-space[3]).[4] Rate constants k_2 were obtained from the slopes k_3 of the linear plots using equation (6), and were independent of reactant pressures at a constant temperature of 523·2 K.

$$\mathrm{d[Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2]}/\mathrm{d}t = k_2\mathrm{[P_2Me_4]^{0{\cdot}5}[C_2F_4]^{1{\cdot}1}} \qquad (2)$$

$$\mathrm{d[Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2]}/\mathrm{d}t = k_3\mathrm{[P_2Me_4]^{0{\cdot}5}[C_2F_4]^{1{\cdot}0}} \qquad (3)$$

$$(b > a) \quad [2/(b-a)^{0{\cdot}5}]\left[\tan^{-1}\{[(b-a)/(a-x)]^{0{\cdot}5}\}\right]_0^t = k_3t \qquad (4)$$

$$(a > b) \quad [1/(a-b)^{0{\cdot}5}]\left[\ln\{[(a-b)^{0{\cdot}5} + (a-x)^{0{\cdot}5}]/[(a-b)^{0{\cdot}5} - (a-x)^{0{\cdot}5}]\}\right]_0^t = k_3t \qquad (5)$$

$$k_2 = k_3\mathrm{[C_2F_4]^{-0{\cdot}1}} \qquad (6)$$

Measurements with a constant composition at five temperatures gave the rate constants in Table 1, from which the Arrhenius equation (7) was computed, giving equal weight to each run; the error limits are 95% confidence limits.

TABLE 1

Rate constants k_2 from equations (4)—(6) as a function of temperature

T/K	Reactant pressures/Torr $\mathrm{P_2Me_4}$	 $\mathrm{C_2F_4}$	$10^3k_2/(\mathrm{dm^3\ mol^{-1}})^{0{\cdot}6}\ \mathrm{s^{-1}}$
513·2	13	21	4·64
523·2	7—14	10—49	9·66 [a]
534·9	14	22	16·8
545·1	14	22	30·2
555·2	15	22	51·8

[a] Mean of seven runs.

$$\log_{10}\,[k_2/(\mathrm{dm^3\ mol^{-1}})^{0{\cdot}6}\ \mathrm{s^{-1}}] = (10{\cdot}87 \pm 0{\cdot}37) - (129{\cdot}_2 \pm 4)\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303RT \qquad (7)$$

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[1] Part XV, R. Brandon, R. N. Haszeldine, and P. J. Robinson, preceding paper.

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

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

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

DISCUSSION

The reaction of tetramethyldiphosphine with tetrafluoroethylene appears to be a clean homogeneous addition reaction (1), and the orders of reaction [equation (2)] indicate a non-molecular mechanism. The production of phosphino radicals from tetramethyldiphosphine at the reaction temperature was confirmed by the observation of 8% isomerisation of *trans*- to *cis*-but-2-ene when heated with an equimolar amount of the diphosphine in the kinetic system for 3 h at 250 °C (*cf.* ref. 1); unlike dimethylphosphine, tetramethyldiphosphine caused isomerisation even in the absence of tetrafluoroethylene. Initiation thus appears to be by reaction (8), and the addition will proceed by (9) and either (10) or (11). If (10) is operative, the scheme is a non-chain mechanism

$$\mathrm{Me_2P{\cdot}PMe_2} \rightleftharpoons \mathrm{2Me_2P{\cdot}} \qquad (8), (-8)$$

$$\mathrm{Me_2P{\cdot}} + \mathrm{C_2F_4} \longrightarrow \mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}} \qquad (9)$$

$$\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}} + \mathrm{Me_2P{\cdot}} \longrightarrow \mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2} \qquad (10)$$

$$\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}} + \mathrm{P_2Me_4} \longrightarrow \mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2} + \mathrm{Me_2P{\cdot}} \qquad (11)$$

analogous to that postulated for the addition of tetrafluorohydrazine to olefins.[5] Reaction (11) offers a plausible alternative in the present case, however, proceeding possibly through an intermediate phosphoranyl radical (such radicals having been postulated previously [6,1]).

Steady state treatment of the two schemes gives the same kinetic behaviour. Taking (8)—(10) [and ignoring (−9) and termination by combination of $\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}}$ radicals by analogy with the reaction of dimethylphosphine with tetrafluoroethylene [1]], equation (12) is obtained, while (8), (−8), (9), and (11), with the same assumptions, lead to the same equation since (9) is rate-controlling. The prediction (12) is in good agreement with the experimental equation (2).

$$\mathrm{d}[\mathrm{Me_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PMe_2}]/\mathrm{d}t = k_8^{0{\cdot}5}k_9[\mathrm{P_2Me_4}]^{0{\cdot}5}[\mathrm{C_2F_4}]/k_{-8}^{0{\cdot}5} \qquad (12)$$

Arrhenius Parameters.—On the basis of the above mechanism the experimental Arrhenius parameters [equation (7)] can be interpreted as combinations of those for the elementary rate constants according to (12). The resulting relationships are (13) and (14); in (14) the A factor corresponding to (3) has been used for consistency although the numerical difference is trivial for present purposes. Unfortunately the parameters for the individual steps cannot be evaluated without additional knowledge which is not available. The dissociation energy $D(\mathrm{Me_2P{-}PMe_2}) = E_8$ is not known. $\mathrm{D(Et_2P{-}PEt_2)}$ has been quoted [7] as 360 kJ mol^{-1} but this is far too high for consistency with (13). Thermochemical data for phosphine and diphosphine, together with an electron-impact figure for $D(\mathrm{PH_2{-}H})$, lead [8] to $D(\mathrm{PH_2{-}PH_2}) = 256 \pm$ *ca.* 12 kJ mol^{-1}, which is probably more reliable. If $D(\mathrm{Me_2P{-}PMe_2}) = D(\mathrm{H_2P{-}PH_2})$, this value leads to $E_9 = 129 - \frac{1}{2}(256) \approx 0$ kJ mol^{-1}. Reported Arrhenius parameters for addition of free radicals to olefins indicate (Table 2) activation energies of 20—40 kJ mol^{-1} for the more reactive radicals and 35—65 kJ mol^{-1} for the more selective radicals. Since $\mathrm{Me_2P{\cdot}}$ belongs more probably to the latter class, it seems likely that $E_9 = 50 \pm 15$ kJ mol^{-1} and thus $D(\mathrm{Me_2P{-}PMe_2}) = 160 \pm 30$ kJ mol^{-1}, *i.e.* substantially less than $D(\mathrm{H_2P{-}PH_2})$, and also lower than the average P–P bond energy in $\mathrm{P_4}$, *viz.*[9] 201 kJ mol^{-1}. Even if $\mathrm{Me_2P{\cdot}}$ is more comparable with alkyl radicals, $D(\mathrm{Me_2P{-}PMe_2})$ can only be *ca.* 200 ± 20 kJ mol^{-1}.

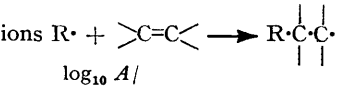
$$E_{12} = \tfrac{1}{2}E_8 - \tfrac{1}{2}E_{-8} + E_9 = \tfrac{1}{2}E_8 + E_9 = 129\ \mathrm{kJ\ mol^{-1}} \qquad (13)$$

$$A_{12} = (A_8/A_{-8})^{0{\cdot}5}A_9 = 10^{10{\cdot}6}\ \mathrm{dm^{1{\cdot}5}\ mol^{-0{\cdot}5}\ s^{-1}} \qquad (14)$$

The A factor A_9 may be estimated from (14) by putting A_{-8} equal to a typical collision number, $10^{11{\cdot}0}$ dm^3 mol^{-1} s^{-1}, and A_8 in the range 10^{15}—10^{16} s^{-1} expected [10] for a unimolecular dissociation reaction. In this case A_9 is in the range $10^{8{\cdot}1}$—$10^{8{\cdot}6}$ dm^3 mol^{-1} s^{-1}, which is reasonable for addition of a radical to an olefin (see Table 2 and ref. 11).

TABLE 2

Reported Arrhenius parameters for some radical addition reactions



$$\mathrm{R{\cdot}} + \mathrm{{>}C{=}C{<}} \longrightarrow \mathrm{R{\cdot}\overset{|}{\underset{|}{C}}{\cdot}\overset{|}{\underset{|}{C}}{\cdot}}$$

Radical	$\log_{10} A$/ dm^3 mol^{-1} s^{-1}	E/kJ mol^{-1}	Ref.
$\mathrm{CH_3{\cdot}}$	8·0—9·0	24—34	*a*
$\mathrm{CCl_3{\cdot}}$	8·1—9·7	26—38	*b*
[$\mathrm{CF_3{\cdot}}$	5·1—6·2	−11—+15	*c*]
$\mathrm{NF_2{\cdot}}$	9·0—10·6	35—65	5
$\mathrm{(CF_3)_2NO{\cdot}}$	5·8—7·6	45—63	*d*

[a] R. J. Cvetanovic and R. S. Irwin, *J. Chem. Phys.*, 1967, **46**, 1694; J. M. Sangster and J. C. J. Thynne, *Internat. J. Chem. Kinetics*, 1969, **1**, 571; J. C. J. Thynne, *ibid.*, 1970, **3**, 155. [b] Parameters for addition to the more reactive end; H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Internat. J. Chem. Kinetics*, 1972, **4**, 249. [c] Relative measurements of J. M. Pearson and M. Szwarc, *Trans. Faraday Soc.*, 1964, **60**, 553, 564, and of G. E. Owen, J. M. Pearson, and M. Szwarc, *ibid.*, 1965, **61**, 1722, combined with data of G. O. Pritchard, H. O. Pritchard, H. J. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849, and P. B. Ayscough, *J. Chem. Phys.*, 1956, **24**, 944; clearly at least one set of measurements is faulty. [d] P. E. Coles, R. N. Haszeldine, and P. J. Robinson, to be published.

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

[7] N. N. Grishin, G. M. Bogolyubov, and A. A. Petrov, *Zhur. obschei Khim.*, 1968, **38**, 1683.

[8] T. McAllister and F. P. Lossing, *J. Phys. Chem.*, 1969, **73**, 2996.

[9] T. L. Cottrell, 'The Strengths of Chemical Bonds,' Butterworths, London, 1958, 2nd edn., p. 254.

[10] See, for example, P. J. Robinson and K. A. Holbrook, 'Unimolecular Reactions,' Wiley, London, 1972, section 7·3.

[11] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, p. 106.