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DUALITY OF MECHANISM IN THE REACTION OF TRIETHYL PHOSPHITE AND CARBON TETRACHLORIDE

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The reaction between triethyl phosphite and carbon tetrachloride to give diethyl trichloromethylphosphonate was first formulated as homolytic by Kamai and Kharrasova,[1,2] mainly on the basis of an "S- shaped rate plot", a view supported by Griffin[3] who observed an acceleration of the reaction by ultra-violet light and by dibenzoyl peroxide. The reaction was formulated[3] as follows:

$$\begin{tikzcd}
\cdot CCl_3 + (EtO)_3P \arrow[r] & (EtO)_3\dot{P}CCl_3 \arrow[d, "CCl_4"] & \text{(i)} \\
(EtO)_2P(O)CCl_3 + EtCl & (EtO)_3\overset{+}{P}CCl_3\overset{-}{Cl} + \cdot CCl_3 \arrow[l] & \text{(ii)}
\end{tikzcd}$$

(Scheme 1)

the alternative route (Scheme 2) suggested by Walling and his co-workers[4] being discounted[3] as a result of the absence of products of disproportionation or dimerisation of the chain carrying ethyl radical.

$$(EtO)_3PCCl_3 \longrightarrow Et\cdot + (EtO)_2P(O)CCl_3 \qquad (iii)$$

$$Et\cdot + CCl_4 \longrightarrow EtCl + \cdot CCl_3 \qquad (iv)$$

(Scheme 2)

Following this, Cadogan and Foster[5] investigated reactions of substituted phosphites with carbon tetrachloride in the presence of dibenzoyl peroxide and, assuming the reactions to be radical, concluded that the products were compatible with the operation of Scheme 1. These workers confirmed the acceleration of the reaction between triethyl phosphite and carbon tetrachloride in ultra-violet light but they also observed that the reaction occurred in the dark in the absence of peroxide. The latter observation, coupled with the later demonstration[6] that dibenzoyl peroxide is very rapidly consumed by triethyl phosphite in carbon tetrachloride in an ionic fashion, and that it does not initiate the formation of diethyl trichloromethylphosphonate, raised the possibility that the reaction between triethyl phosphite and carbon tetrachloride might be heterolytic, at least in the absence of ultra-violet radiation and/or radical initiators. This possibility has now been shown to have substance under certain circumstances.

It has now been shown that:

(1) Carbon tetrachloride (0.26 mole) and triethyl phosphite (0.06 mole) react in the dark at 80° to give diethyl trichloromethylphosphonate, the rate plot being slightly sigmoid. The rate was not significantly reduced by the addition of a radical chain inhibitor (t-butylcatechol).

(2) Addition of increasing amounts of azobisisobutyronitrile (AIBN) leads to increasing overall acceleration of the reaction, with a significantly greater <u>initial</u> acceleration, this acceleration being

greater with the larger amount of AIBN. (See Figure).

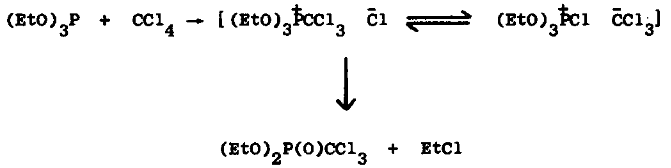
(3) Reactions carried out as under (2) with added radical chain inhibitor (t-butylcatechol) restored the initial rate to that observed under (1).

(4) "Thermal" reactions at 80° between triethyl phosphite (0.006 mole) and carbon tetrachloride (0.05 mole) in the presence of oct-1-ene (0.005 mole) gave diethyl trichloromethylphosphonate (80%) but no 1:1 adduct of oct-1-ene and carbon tetrachloride, whereas a similar reaction in the presence of AIBN gave diethyl trichloromethylphosphonate (80%) and also 1,1,1,3-tetrachlorononane (30%) resulting from the addition of trichloromethyl radicals to oct-1-ene.

(5) The reaction of triethyl phosphite with carbon tetrachloride at 15° was accelerated by irradiation with ultra-violet light, as measured by the rate of formation of diethyl trichloromethylphosphonate (11% after 5 hrs. cf. 1% in absence of u.v.) although this acceleration was not as great as that reported earlier. Products from the photolysis of triethyl phosphite were also observed.

These results permit the following conclusions:

(a) The "thermal" reaction of triethyl phosphite with carbon tetrachloride is heterolytic:

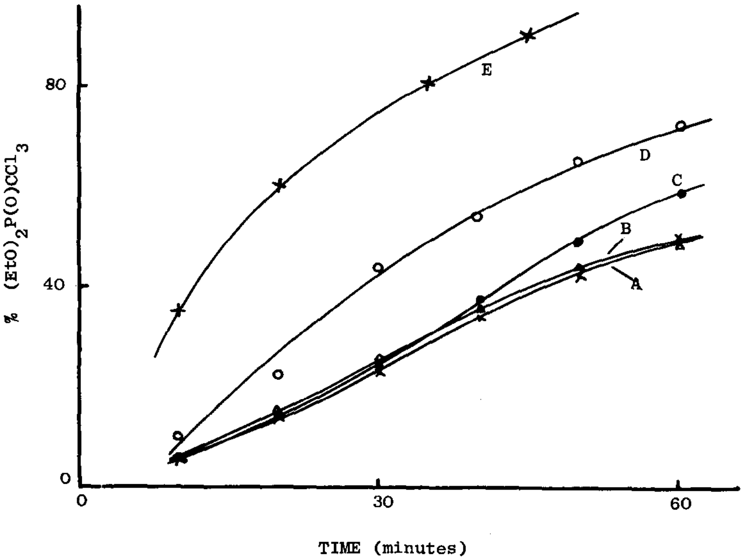


$$(EtO)_3P + CCl_4 \rightarrow [(EtO)_3\overset{+}{P}CCl_3\ \bar{C}l \rightleftharpoons (EtO)_3\overset{+}{P}Cl\ \bar{C}Cl_3]$$

$$\downarrow$$

$$(EtO)_2P(O)CCl_3 + EtCl$$

The sigmoid rate curve observed by us and by Kamai,[2] and assumed by him to be indicative of a radical reaction, is probably due to the change of dielectric constant of the mixture during reaction. A



Carbon tetrachloride (0.26 mole), triethyl phosphite (0.06 mole) plus:

A - t-butylcatechol (0.011 mole).

B - AIBN (0.004 mole), t-butylcatechol (0.015 mole).

C - Nothing added.

D - AIBN (0.005 mole).

E - AIBN (0.029 mole).

Figure

similar sigmoid curve has been obtained by Aksnes and Aksnes[7] in a kinetic study of the Michaelis-Arbuzov reaction.

(b) In the presence of AIBN at least part of the diethyl trichloromethylphosphonate is formed homolytically. The need for relatively large quantities of initiator in order to observe significant acceleration indicates a short kinetic chain length in the reaction. In this connection there is the significant observation that the yield of 1,1,1,3-tetrachlorononane, formed in the radical induced reaction of triethyl phosphite with carbon tetrachloride in the presence of oct-1-ene, was lower (30% after 3 hrs.) than that formed (55% after 3 hrs.) in a comparable reaction in the absence of phosphite. Besides confirming that the phosphite participates in the radical process by trapping trichloromethyl radicals, this observation confirms that oct-1-ene is a valid trapping agent for trichloromethyl radicals in the presence of triethyl phosphite. Hence in the "thermal" reaction of triethyl phosphite and carbon tetrachloride carried out in the presence of oct-1-ene, the absence of 1,1,1,3-tetrachlorononane is indicative of a non-radical reaction.

These results do not permit a choice to be made between Schemes (1) and (2). The short chain length could mean that either of reactions (ii) or (iii) is slow, it being well known that reaction (iv) is fast.

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