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REACTIVITY OF TRIETHYL PHOSPHITE WITH TETRACHLOROMETHANE : ELECTRON TRANSFER VERSUS IONIC SUBSTITUTION ON "POSITIVE" HALOGEN

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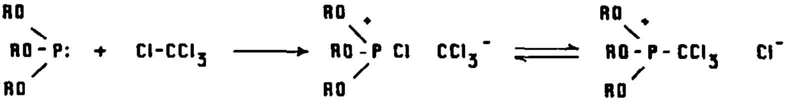
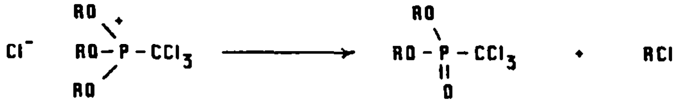
ABSTRACT - The reaction [1] of triethyl phosphite (1) with tetrachloromethane (2) has been studied from a mechanistic point of view. 1 reacts at 80°C with 2 to form diethyltrichloromethanephosphonate (3) (85-90% yield) and chloroethane (4) (80% yield). Several results hint at a radical chain mechanism (like $S_{RN}1$). Trichloromethyl radical is trapped by 2,6-di-t-butyl-4-cresol (BHT), the reaction may be initiated with UV radiation (254 nm) and a charge transfer complex (CTC) is formed between 1 and 2 ; furthermore, the reaction is inhibited by 7,7',8,8' tetracyanoquinodimethane (TCNQ). Tris(cyclopropylmethyl)phosphite (12a) and tri(1-hexene-6-yl) phosphite (7a) are used as potential radical clocks in these reactions. The first leads inter alia to 3-chloro-1-butene (17) and the second to 5-chloro-1-hexene (11), the first therefore suggests a radical mechanism but not the second. However in this particular case even the results obtained with the tris(cyclopropylmethyl)phosphite may be rationalized also by an ionic mechanism. For the photostimulated reaction [1] , the overall quantum yield is 0.1. The electrochemical oxidation of 1 with added CCl_4 does not account for a radical chain process as the main pathway. Furthermore, the application of Marcus analysis to reaction [1] viewed as an electron transfer leads to a calculated rate constant in the range of $10^{-20}\ M^{-1}s^{-1}$. The synergy of the techniques that we used lead us to conclude that the thermal reaction is in fact an S_NCl^+ substitution. The radical intermediates would mainly be derived from the electron-transfer reaction between CCl_3^- and CCl_4 the importance of which increases when special conditions such as hν activation are applied. Reaction [1] therefore provides an example where the observed paramagnetic species during a D/A interaction could deceptively suggest an electron-transfer between D and A whereas they originate from an interaction between A and an electron donor formed after or during the first step of the reaction.

I - INTRODUCTION

Trialkyl phosphites react with tetrachloromethane to give dialkyltrichloromethylphosphonates and haloalkanes[1].

 [1]

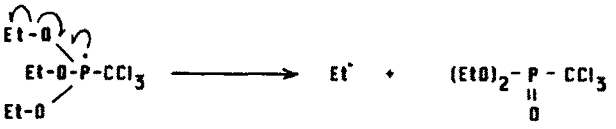
 [2]

When the alkylgroups are different, it is the least hindered haloalcane which is formed[2]. This result supports equation 2 as an S_N2 displacement. Kamai and Kharrasova[3] put forward a radical-chain mechanism for the reaction of triethyl phosphite with tetrachloromethane because the reaction is accelerated by light or benzoyl peroxide and because plots of concentration versus time display a sigmoid shape[4].

$$^{\bullet}CCl_3 \quad + \quad (EtO)_3P: \longrightarrow (EtO)_3\text{-}\dot{P}\text{-}CCl_3 \qquad [3]$$

$$(EtO)_3\text{-}\dot{P}\text{-}CCl_3 \quad + \quad CCl_4 \longrightarrow (EtO)_3\text{-}\overset{+}{P}\text{-}CCl_3 \quad Cl^- \quad + \quad ^{\bullet}CCl_3 \qquad [4]$$

Then the products would result either from S_N2 attack [2] or from radical β homolytic cleavage as advanced by Walling et al.[5]

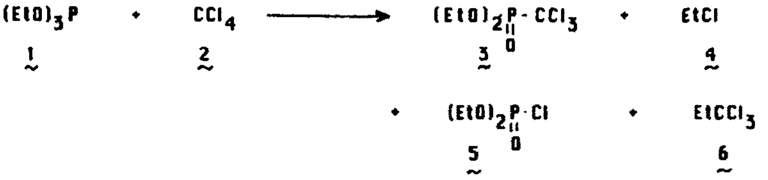

[5]

$$Et^{\bullet} + CCl_4 \longrightarrow EtCl + {}^{\bullet}CCl_3 \qquad [6]$$

Cadogan and Foster[6] proposed another mechanistic scheme which involves simultaneous ionic and radical pathways[7]. They reached the conclusion that the thermal reaction between CCl_4 and $(RO)_3P$ is ionic but becomes partly homolytic under UV irradiation or when azobisisobutyronitrile is added as initiator. These different propositions show the difficulty of rationalizing these types of reactions. Besides the two mechanisms proposed earlier (ionic S_N2 or radical chain), are there other scenarios possible? In particular, if the chain mechanism operates, how is ${}^{\bullet}CCl_3$ formed? We initiated this work with the idea that this coexistence of experimental data hinting at both radical and ionic mechanisms could be indicative of the operation of an $S_{RN}1$ type of mechanism (CCl_4 displays a good electron affinity[8]). Several reports indeed indicated that in $S_{RN}1$ processes the SET pathway may coexist with S_N2 mechanisms[9]. The following results show that the starting idea (i.e., $S_{RN}1$) was wrong but led to interesting insights into the intricacies of the reaction and brought new informations on the origin of ${}^{\bullet}CCl_3$.

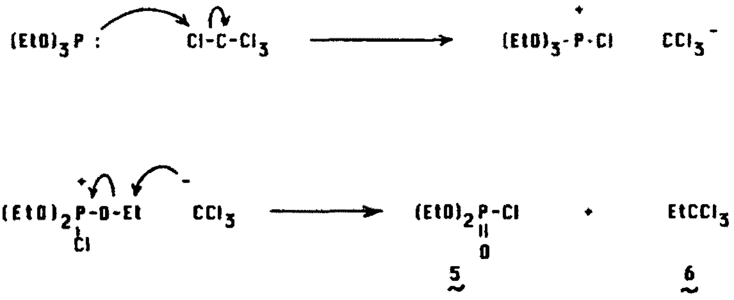
II - DISCUSSION AND RESULTS

Triethyl phosphite (1) reacts at 80°C with tetrachloromethane (2) and leads to diethyl trichloromethanephosphonate (3) in 85-90% yield and chloroethane (4) in 80% yield. Diethyl chlorophosphate (5) (< 1%) and 1,1,1-trichloropropane (6) (< 1%) were formed as very minor by-products.


[7]

$$\underset{1}{(EtO)_3P} + \underset{2}{CCl_4} \longrightarrow \underset{3}{(EtO)_2P(O)\text{-}CCl_3} + \underset{4}{EtCl} + \underset{5}{(EtO)_2P(O)\text{-}Cl} + \underset{6}{EtCCl_3} \qquad [7]$$

Compounds 5 and 6 may result from the earlier proposed nucleophilic attack of phosphorous on positive[10] chlorine followed by an Arbusov rearrangement :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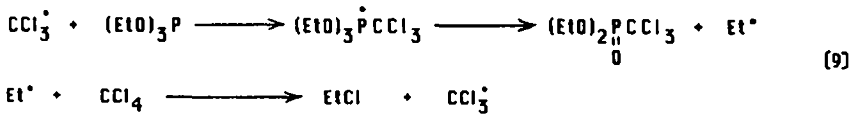
A radical chain process may also operate following Walling's hypothesis[5] ·



$$CCl_3^{\bullet} + (EtO)_3P \longrightarrow (EtO)_3\dot{P}CCl_3 \longrightarrow (EtO)_2\underset{\underset{O}{\|}}{P}CCl_3 + Et^{\bullet}$$

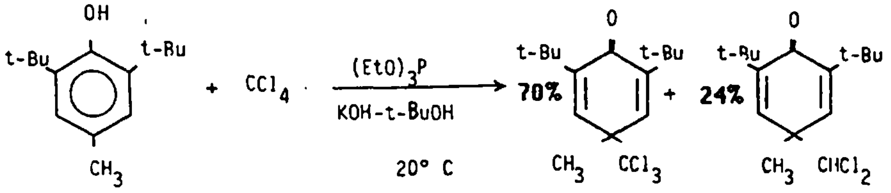
$$Et^{\bullet} + CCl_4 \longrightarrow EtCl + CCl_3^{\bullet} \qquad [9]$$

One possibility for ${}^{\bullet}CCl_3$ generation is CCl_4 homolysis under UV radiations or S_H2 reaction of $(CH_3)_2\dot{C}-CN$ on CCl_4 when azobisisobutyronitrile is used as an initiator .
If we remind the classical criteria of an electron transfer induced chain reaction we can attempt to confirm this later mechanism.

II - 1. Trichloromethyl radical trapping

The results of Meyers et al.[11-12] showed that the anion of the 2,6-di-t-butyl-4-cresol (BHT) is a good trap for ${}^{\bullet}CCl_3$ with which it leads to the formation of a trichloromethylcyclohexadienone product[11]. Meyers et al. also showed with the trap that ${}^{\bullet}CCl_3$ is not formed in a mixture of potassium hydroxide-t-butylalcohol-tetrachloromethane at 20°C. When $CHCl_3$ was used instead of CCl_4 they easily trapped the formed $:CCl_2$ as its adduct with BHT anion, the dichloromethylcyclohexadienone product[11 b,c]. With CCl_4 and $CHCl_3$ present, both the trichloromethyl and dichloromethyl derivatives were formed ($Cl_3C^- + CCl_4 \longrightarrow 2\ Cl_3C^{\bullet} + Cl^-$). With $CBrCl_3$ + BHT anion, the trichloromethyl derivative was formed[11]. They concluded that $CBrCl_3$ but not CCl_4 easily accepts an electron from BHT anion to generate ${}^{\bullet}CCl_3$.

We have now found that when $(EtO)_3P$ was added to a mixture of KOH-t-BuOH-CCl_4 containing



[10]

BHT, the cyclohexadienone adduct of ${}^{\bullet}CCl_3$ as well as $:CCl_2$ (as reported by Meyers et al.) were forme as major products.

Nevertheless the experiment does not specify how ${}^{\bullet}CCl_3$ is formed. It may originate from $CCl_4^{\bullet -}$ formed in the interaction between $(EtO)_3P$ and CCl_4 or from electron transfer between ${}^{-}CCl_3$ and CCl_4:

$$^{-}CCl_3 + CCl_4 \longrightarrow 2\ {}^{\bullet}CCl_3 + Cl^- \qquad [11]$$

II - 2. Activation of the reaction by UV light

In contrast to the thermal reaction which requires heating at 80°C, irradiation with a 254 nm UV lamp leads to the same transformation at 20°C. The rate of formation of $(EtO)_2P(O)CCl_3$ (3) does not depend on the reactants concentration. Moreover a charge transfer complex (CTC) is formed between triethyl phosphite (1) and tetrachloromethane (2).

The formation of a charge transfer complex between ethylphosphonites and CCl_4 has been also shown[13]. In our case the CTC absorbs in the same region as CCl_4, so its association constant cannot be determined by the Benesi-Hildebrand method[14]. Two possibilities exist for the activation of the reaction :

a) The CTC is activated by light and leads to an ion pair. The photochemical initiation step is an electron transfer :

$$(EtO)_3P \;........CCl_4 \xrightarrow{h\nu} (EtO)_3\overset{+}{\dot{P}} + CCl_4^{\bullet -} \qquad [12]$$

b) Under irradiation the C-Cl bond of CCl_4 is homolytically cleaved. This process actually occurs when CCl_4 is photolyzed in heptane as testified by $HCCl_3$ and Cl_3C-CCl_3 isolation.

$$CCl_4 \xrightarrow{h\nu} {}^{\bullet}CCl_3 + {}^{\bullet}Cl \quad . \qquad [13]$$

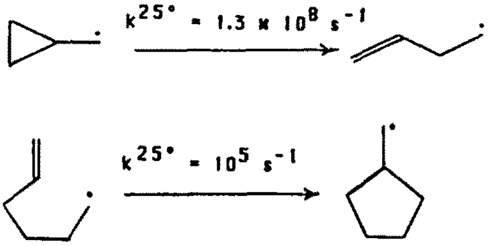
Whatever photoinitiation is, the quantum yield value is 0.1 for 2 formation. It agrees either with a chain mechanism where the primary photochemical act would be inefficient and coupled with a short chain or with an homolysis followed by no chain at all. Wrighton's recent results show that some electron transfer initiated chain reactions may display quantum yields lower than unity[15].

II - 3. Inhibition of the reaction by addition of 7,7',8,8' tetracyanoquinodimethane TCNQ

The use of redox inhibitors as a criterion of $S_{RN}1$ mechanism was proposed by Kornblum[16]. Among the good electron acceptors which can be reduced by the donor and could therefore compete with the formation of $CCl_4^{\bar{\cdot}}$, 7,7',8,8'-tetracyanoquinodimethane (electronic affinity EA = 2.8 eV)[17] is suitable (for CCl_4, EA = 2.1 eV) . Moreover it does not react with 3 under our experimental conditions. Adding small amounts of TCNQ ($\simeq$ 9%) does not inhibit reaction [1] ; however the addition of 44% of TCNQ decreases the rate of formation of 3. These results may be accounted for either as indicative of a short $S_{RN}1$ chain or as a reaction between TCNQ and Cl^- slowering therefore reaction [2].

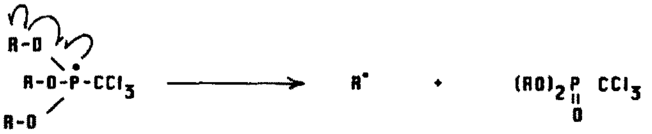
II - 4. Existence of a phosphoranyl radical as intermediate shown with suitable radical clocks

Suitably designed substituents can be used as a mechanistic tool or kinetics standard[18]. Thus a mechanism involving the formation of free radicals may be confirmed by introducing cyclopropylmethyl or 1-hexene-6-yl groups as R in $P(OR)_3$ since the formation of free radicals, via intramolecular rearrangement, leads to 3-butenyl or cyclopentylmethyl radicals[19].



[14]

If a phosphoranyl free radical intermediate with such substituents is formed during the reaction, it could generate rearranged haloalkene and haloalkane provided that no alternative faster reaction of the phosphoranyl free radical is available.

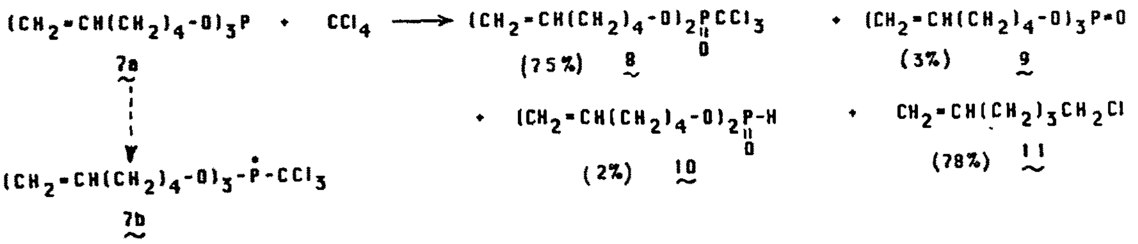


$$(RO)_3\dot{P}-CCl_3 \longrightarrow R^{\bullet} + (RO)_2\underset{O}{\overset{}{P}}\,CCl_3 \qquad [15]$$

$$R^{\bullet} + CCl_4 \longrightarrow RCl + {}^{\bullet}CCl_3 \qquad [16]$$

4. a) Reaction of tri(1-hexene-6-yl) phosphite with tetrachloromethane

In this case, no products indicative of a cyclization of an intermediate like the 1-hexene-6-yl radicals were identified. This result does not support an $S_{RN}1$ type mechanism but it could be that this free radical clock is too slow, we therefore prepared a faster one.

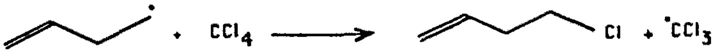

[17]

4\. b) Reaction between tris(cyclopropylmethyl) phosphite and tetrachloromethane

The reaction was performed in toluene to have a dilute medium so that the unimolecular β-cleavage followed by the rearrangement [19] would become competitive with the bimolecular electron transfer reactions[20].


[18]


[19]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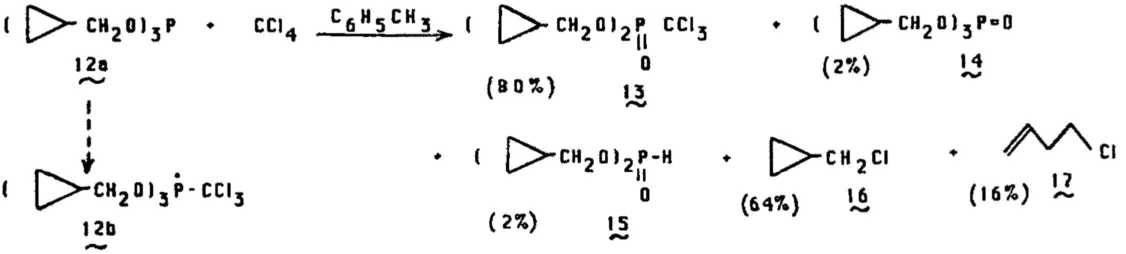
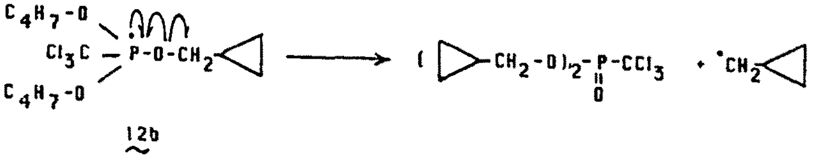
Moreover toluene allows secondary reactions like radical-radical coupling.


[21]

Among the identified products, the formation of 4-chloro-1-butene (17) suggests 12b as one of the intermediates.

Two mechanisms could be involved however with these specific substrates; one involves radical species whereas the second involves only ionic intermediates.

a) β-cleavage of 12b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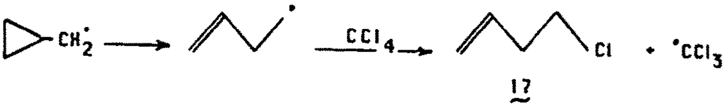
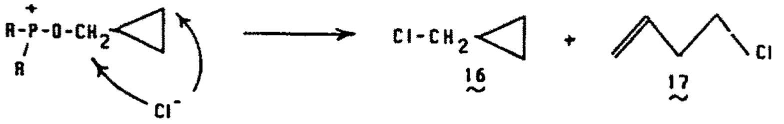
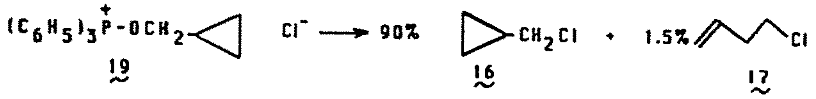

[23]

b) Nucleophilic attack of Cl^- on the phosphonium cation


[24]

Denney has found that the same products 16 and 17 form in the chloromethylcyclopropane synthesis by S_N2 attack of Cl^- on the triphenyl alkoxy phosphonium cation 19[21].



(25)

In contrast with Denney's proportion of 16/17 ratio of 1.2%, our result added to the formation of the coupling product 18 in toluene favors at least some contribution of the β cleavage of 12b.

Let us now examine other experimental results which go against the mechanistic radical-chain possibility and rather favour the ionic mechanism for reaction [1] .

II - 5. Action of oxygen

Solutions of triethyl phosphite (1) and tetrachloromethane (2), if not degassed, form at 80°C triethylphosphate as a byproduct (10% yield).

It has been claimed that oxygen is an efficient $^{\cdot}CCl_3$ trapping agent[22]. By bubbling oxygen into the solution we observed an increase of triethyl phosphate formation, but the relative yields of the other products were not modified.

II - 6. Overall quantum yield

The overall quantum yield value measured at 254 nm is $\Phi = 0.1 \pm 0,002$ and is independent of the concentration of triethyl phosphite.

II - 7. Electrochemical study of the reaction

It is known[23] that the electrochemical reduction of polyhalogenomethane does not lead to $^{\cdot}CX_3$ formation but to anionic species. The electrochemical inducement of the reaction would correspond to a scheme other that the radical one, proposed by Kamai and Kharrasova[2,4]. On the other hand the electrochemical oxidation of trivalent phosphorus compounds is a convenient tool for generating phosphinium cation radicals[24].

With the three solvents (DMF, THF or acetonitrile) and the two types of electrodes (platinum or mercury pool) that we used, we never observed any modification of the intensity-potential curves corresponding to a CCl_4 reduction wave in presence of 1. On the other hand we determined that the half-wave oxidation potential of triethyl phosphite (1) is 2.1 V (vs SCE).

We assumed that $i_L = K_D C$ with i_L current at the limit and C = phosphite concentration; i_L was obtained from the recording of the intensity-potential curves. The proximity of the discharge current of the solvent leads to ill defined diffusion-plateaus. Nevertheless, one can estimate the i_L value at the intercept of the tangents to the plateaus and to the ascendant waves.

Table I - Difference between the introduced and measured concentrations of $(EtO)_3P$ when CCl_4 was added to the medium. $K_D = 4.32 \times 10^{-2}$

$(EtO)_3P$ introduced mole/l x 10^3 Solvent : CH_3CN	CCl_4 added mole/l x 10^3	i_L (A./e) current at the limit	$(EtO)_3P$ calculated from $C = i_L /K$
5	0	216	4.99
4.86	1	204	4.72
4.73	1.97	196	4.53
4.60	2.87	192	4.44
4.48	3.73	184	4.25
4.37	4.55	180	4.16
3.89	8.10	156	3.61

The increasing difference between the calculated and the true concentration of **1** may correspond to a low consumption of **1** rather than a dilution. Nevertheless these variations are too small to be due to an electrochemically induced $S_{RN}1$ process.

We thank Dr Gronchi for fruitful discussions and experimental support during this electrochemical study.

II - 8. Free energy of the electron transfer step

If we retain the results going in the sense of a $S_{RN}1$ scheme, this latter would be induced by electron transfer between **1** and **2** with the possible aid of a CTC viewed as an inner sphere electron transfer without bridge[25]. Moreover a catalytic cycle (or a chain) as proposed by Griffin[3] or Kamai and Kharrasova[4] would follow the initiating electron transfer step.

If we retain the electron transfer as first step, several scenarii are possible for the radical anion-radical cation pair formed in the solvent cage[11,26].

$$(EtO)_3P: \;+\; CCl_4 \longrightarrow \overline{(EtO)_3\overset{+\bullet}{P}\quad \overset{-\bullet}{C}Cl_4} \qquad (26)$$

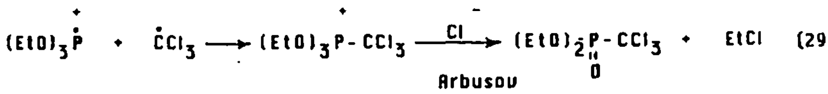
1. Homolytic substitution S_H2 of radical cation on $CCl_4^{-\bullet}$ (i.e. R.A.R.P.)[11]

$$(EtO)_3\overset{+\bullet}{P} \curvearrowright Cl\text{-}\overset{-\bullet}{C}Cl_3 \longrightarrow (EtO)_3\overset{+}{P}\,Cl \;+\; CCl_3^- \qquad (27)$$

2. Cleavage of $CCl_4^{-\bullet}$

$$CCl_4^{-\bullet} \longrightarrow {}^{\bullet}CCl_3 \;+\; Cl^- \qquad (28)$$

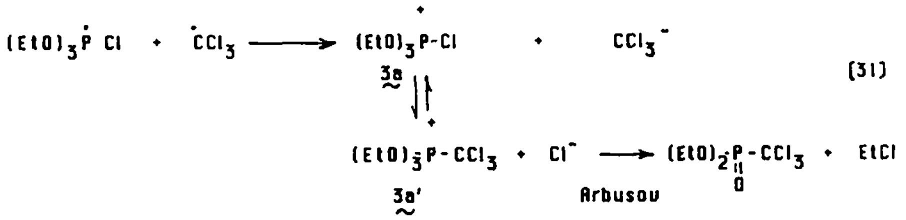
If $(EtO)_3\overset{+\bullet}{P}$ is stable enough it may recombine with the fragments:



$$\text{a)}\quad (EtO)_3\overset{+\bullet}{P} + \overset{\bullet}{C}Cl_3 \longrightarrow (EtO)_3\overset{+}{P}\text{-}CCl_3 \xrightarrow[\text{Arbusov}]{Cl^-} (EtO)_2\underset{\underset{O}{\|}}{P}\text{-}CCl_3 + EtCl \qquad (29)$$

$$\text{b)}\quad (EtO)_3\overset{+\bullet}{P} \;+\; Cl^- \longrightarrow (EtO)_3\overset{\bullet}{P}\,Cl \qquad (30)$$

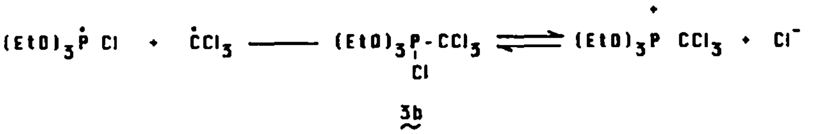
The ${}^{\bullet}CCl_3$ radical is as good electron acceptor as CCl_4[27]. Thus, one could suppose also an electron transfer between ${}^{\bullet}CCl_3$ and $(EtO)_3\overset{\bullet}{P}Cl$ which may lead to CCl_3^- and $(EtO)_3\overset{+}{P}Cl$ (**3a**) :



$$\begin{array}{lll} (EtO)_3\overset{\bullet}{P}\,Cl + \overset{\bullet}{C}Cl_3 \longrightarrow & \underset{\mathbf{3a}}{(EtO)_3\overset{+}{P}\text{-}Cl} & + \; CCl_3^- \\ & \quad\;\upharpoonleft\!\downharpoonright & \qquad\qquad (31) \\ & \underset{\mathbf{3a'}}{(EtO)_3\overset{+}{P}\text{-}CCl_3} + Cl^- & \xrightarrow[\text{Arbusov}]{} (EtO)_2\underset{\underset{O}{\|}}{P}\text{-}CCl_3 + EtCl \end{array}$$

Such an electron transfer is possible within the encounter of two radicals with different electronegativities[28].

Finally the coupling of $(EtO)_3\overset{\bullet}{P}Cl$ and ${}^{\bullet}CCl_3$ cannot be excluded. It would give the pentavalent phosphorus intermediate **3b**.



$$(EtO)_3\overset{\bullet}{P}\,Cl + \overset{\bullet}{C}Cl_3 \;\text{——}\; \underset{\mathbf{3b}}{(EtO)_3\underset{\underset{Cl}{|}}{P}\text{-}CCl_3} \rightleftharpoons (EtO)_3\overset{+}{P}\,CCl_3 + Cl^- \qquad (32)$$

If we would rest on this series of arguments, we would conclude that reaction [1] is an electron transfer induced one. Nevertheless a problem arises when one looks at the thermodynamic feasibility of the electron transfer[29].

The E ½ value of $(EtO)_3P$ allows an approximate calculation of the rate constant which could be expected applying the Marcus approach[30]. In this approach, one calculates the $\Delta G^{\neq}$ of activation for uncharged reactants as :

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2 + w$$

In this expression w is negligible[29a] and the main terms needed are ΔG° and λ. λ is the average reorganization energy associated with the reaction

$$D + A \longrightarrow D^{\dot{+}} + A^{\dot{-}}$$

Taking[31] $\lambda\ CCl_4/CCl_4^{\dot{-}}$ as 70 kcal, $\lambda (EtO)_3P/(EtO)_3P^{\dot{+}}$ as 30 kcal., $\lambda = 50$ kcal/mol.

The $E\frac{1}{2}$ value for CCl_4 reduction is -0.9 V, but it corresponds to an irreversible electron transfer[32] and if one adopts the correction proposed for a similar situation by Eberson[29a] (for $E\frac{1}{2}$ R-X = -2 V, E° R-X = -0.7 V) one finds $E^{\circ}\,CCl_4 = 0.2$ V.

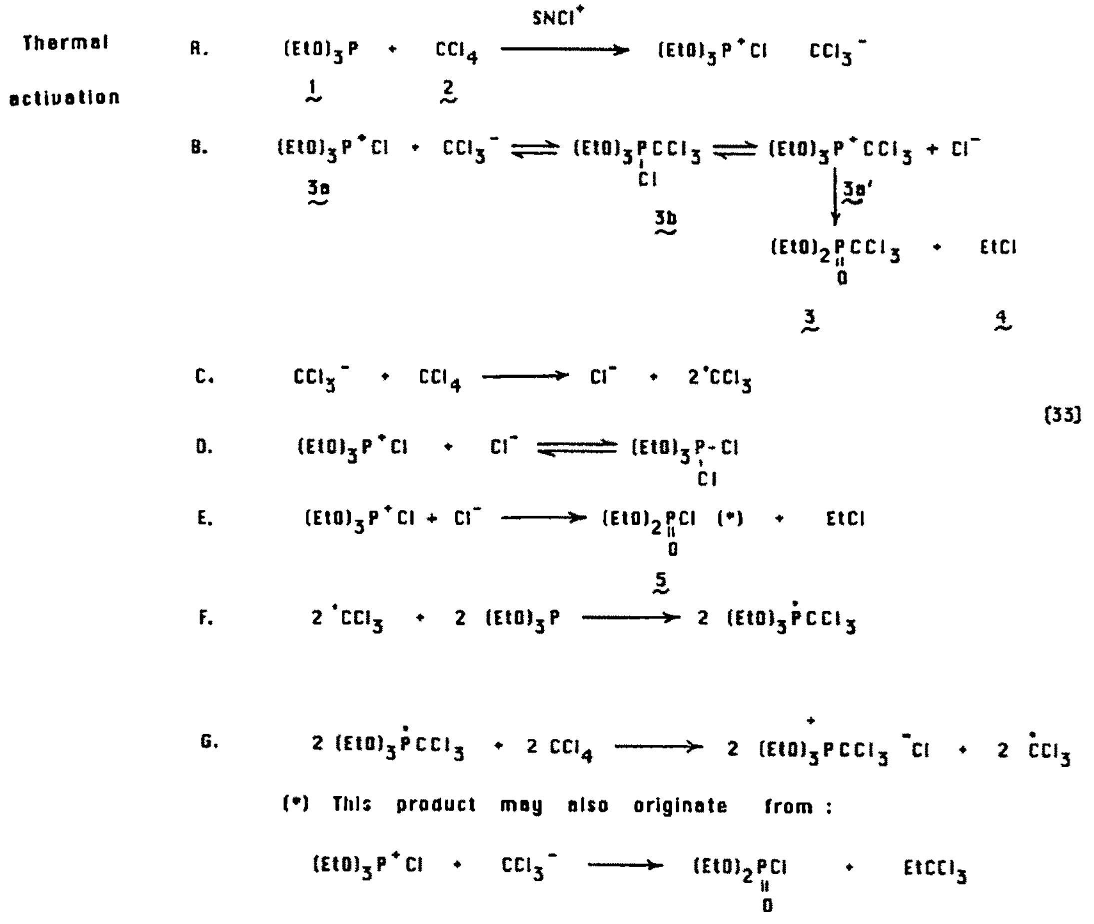
These values lead to :

$\Delta G^{\circ} = 41.5$ kcal/mol. $\Delta G^{\ddagger} = 41.8$ kcal/mol., $k_{e.t.} = 6.7 \times 10^{-20}$
with $k_D = 2 \times 10^{10}\ M^{-1}s^{-1}$
(diffusion constant at 25°C)

This low value clearly shows that an electron transfer between $(EtO)_3P$ and CCl_4 is highly improbable even when one takes E° $(CCl_4/CCl_4^{\dot{-}})$ as a stronger oxidant than its experimental $E\frac{1}{2}$ value would suggest.

We must however recognize that if these calculations discard outer sphere type electron transfer, one possibility still remains (because CTC observation between 1 and 2 see section II.2) that an inner sphere type of electron transfer without atom transfer[33] take place. At this point not much is known about this type of electron transfer mechanism except that it is sensitive to steric effects and that its rate constants cannot classically been predicted with the foregoing Marcus equation.

II - 9. General scheme



Thermal activation

A. $\underset{1}{(EtO)_3P} + \underset{2}{CCl_4} \xrightarrow{SNCl^+} (EtO)_3P^+Cl \quad CCl_3^-$

B. $\underset{3a}{(EtO)_3P^+Cl} + CCl_3^- \rightleftharpoons \underset{3b}{(EtO)_3\underset{Cl}{P}CCl_3} \rightleftharpoons (EtO)_3P^+CCl_3 + Cl^- \xrightarrow{3a'} \underset{3}{(EtO)_2\underset{\overset{\|}{O}}{P}CCl_3} + \underset{4}{EtCl}$

C. $CCl_3^- + CCl_4 \longrightarrow Cl^- + 2\,{}^{\bullet}CCl_3$ (33)

D. $(EtO)_3P^+Cl + Cl^- \rightleftharpoons (EtO)_3\underset{Cl}{P}-Cl$

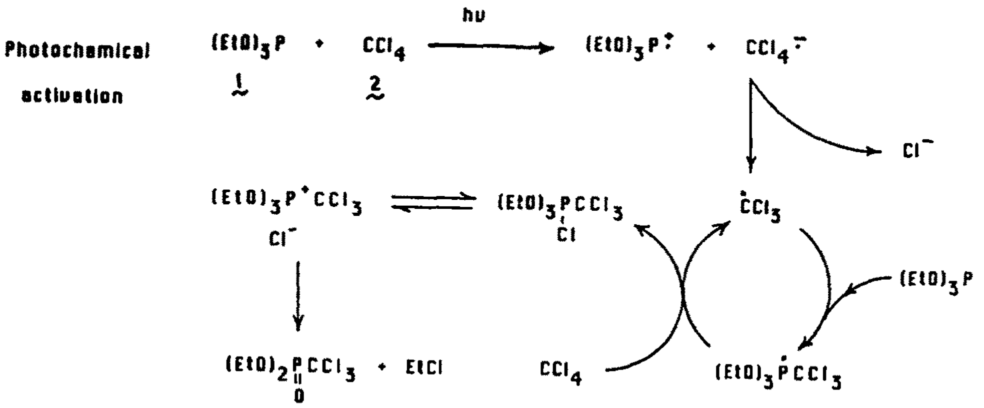
E. $(EtO)_3P^+Cl + Cl^- \longrightarrow \underset{5}{(EtO)_2\underset{\overset{\|}{O}}{P}Cl}\ (*) + EtCl$

F. $2\,{}^{\bullet}CCl_3 + 2\,(EtO)_3P \longrightarrow 2\,(EtO)_3\dot{P}CCl_3$

G. $2\,(EtO)_3\dot{P}CCl_3 + 2\,CCl_4 \longrightarrow 2\,(EtO)_3\overset{+}{P}CCl_3\ {}^-Cl + 2\,\dot{C}Cl_3$

(*) This product may also originate from :

$(EtO)_3P^+Cl + CCl_3^- \longrightarrow (EtO)_2\underset{\overset{\|}{O}}{P}Cl + EtCCl_3$



(34)

We thus retain a scheme which reconciles the duality of ionic and radical intermediates. We propose that the first step of the reaction is not an electron transfer but an ionic displacement on Cl^+ by triethyl phosphite (leaving group Cl_3C^-). Meyers et al.[11b] showed elsewhere that Cl_3C^- anion may transfer its electron to CCl_4[34a] and we confirmed these results[34b]. Thus for the thermal version of reaction [1] there could be competition between reaction [33-B] and electron transfer from Cl_3C^- to CCl_4 eq. 33-C. If the second channel occurs, a short chain could develop following the mechanism given under the photochemical stimulation (eq. 34).

Finally the electron transfer from Cl_3C^- to CCl_4 deserve some comments. The redox potential of the $Cl_3C^{\cdot}/Cl_3C^-$ couple is not known and it was not possible to check its value by polarography since one could not obtain a sufficient concentration of $Cl_3C^{\cdot}$ in the mixture. Its theoretical value was calculated[35] and found equal to -0.83 V (vs SCE). If we retain the -0.73 V (vs SCE) value of Meyers[10a] for the $CCl_4/CCl_4^{\cdot-}$ couple the reaction is thermodynamically allowed but with a less negative value of ΔG = -0.10 eV.

The second step of the chain is possible but the low quantum yield value Φ observed (section II-6.) and its independence on the triethyl phosphite concentration do not agree with a long chain reaction which is usually characterized by $\Phi > 1$ and Φ proportional to the concentration of the nucleophile[36]. The low Φ value could be the result of a low primary quantum yield (e.g. 0.01) followed by a short chain (e.g. 10 cycles). This low chain efficiency may originate from a unfavourable competition for Cl_3C^- between in cage (path 33-B) and out of cage (path 34 or 33-C) reactivity.

III - CONCLUSION

The reaction between triethyl phosphite and tetrachloromethane was the object of several mechanistic proposals in the literature. We studied this reaction using a variety of techniques. Several classical criteria of electron transfer induced chain reactions were positive and could have led to a wrong conclusion if further experiments and thermodynamic considerations of redox potential had not been carried out. The overall set of experimental results that we gathered leads us to propose that the thermal reaction of triethyl phosphite with tetrachloromethane which displays some experimental earmarks of an $S_{RN}1$ reaction is in fact an S_NCl^+ substitution. The radical intermediates observed in the medium would mainly result from an electron transfer between Cl_3C^- and CCl_4. Depending upon the relative concentration of other reagents this trichloromethyl radical may or may not initiate a radical chain reaction whose final products are the same as those obtained in the ionic mechanism. Under usual conditions, the ionic channel is the main one but when special conditions are applied (hν , AIBN) the radical pathway participation increases. These conclusions precise and confirm a previous study performed by Cadogan and draw the attention to the risk of jumping to conclusions when incomplete studies are performed on reactions which include both diamagnetic and paramagnetic intermediates.

EXPERIMENTAL SECTION

GENERAL METHODS

The UV spectra were recorded on a Beckmann 26 spectrometer fitted with 0.5 cm pathlength cell. Gas chromatographic analysis were performed on an Intersmat IGC 121 FL chromatograph fitted with a flame ionization detector. A 2 m x 1/8 in. stainless steel column packed with 10% silicone UCCW 990 on chromosorb WAW DMCS, 80/100 mesh was used with helium as carrier gas. The chromatograph was coupled with a Delsi Instrument Enica 10 integrator-recorder.

The ^{1}H-NMR spectra were obtained on a Varian EM 360 A spectrometer with deuterated benzene as a solvent and tetramethylsilane TMS as internal standard. The chemical shifts are in ppm. The abbreviations are as follows : s : singlet ; d : doublet ; t : triplet ; q : quartet ; m : multiplet.

The ^{31}P-NMR-spectra were recorded on a Bruker AM 200 spectrometer, in C_6D_6 as a solvent. Phosphoric acid 85% in a capillary tube was the internal standard.

Mass spectra were obtained by GC/MS with a Ribermag 10-10 instrument fitted with a silica capillary column (CP Sil 5 ; 25 m x 0.32 mm). The carrier gas was helium. The tension was 70 eV.

The electrochemical set was composed of a Tacussel PRT 30-0.1 potentiostat regulated by a Tacussel UAP 4 unit. The curves were recorded on a Sefram Luxytrace recorder. The working electrode was a rotating platinum disk (2 mm diameter)Tacussel EDI, the auxiliary electrode was a platinum thread. The potentials were controlled with respect to a saturated calomel electrode.

MATERIALS

Solvents : acetonitrile (Merck), dimethylformamide (BDH), tetrahydrofurane (BDH), toluene (Merck) were dried on 4 A° molecular sieves, distilled and stored on molecular sieves.

Triethyl phosphite (Janssen Chimica) was purified as in ref (7), distilled under argon and kept on 4 A° molecular sieves.

Tetrachloromethane (Merck - Spectrosol) was distillated on P_2O_5 with argon bubbling and kept on 4 A° molecular sieves.

2,6-Ditertiobutyl-4-cresol BHT (Fluka, purum) ; 7,7',8,8' tetracyanoquinodimethane (Fluka, purum), 1-hexene (Fluka, purum) ; 6-hexanol (Fluka), hydroxymethylcyclopropane (Fluka, purum), tris(dimethylamino) phosphine were commercial and used without further purification.

Synthesis of tri(cyclopropylmethyl)phosphite (**12a**)

In a 50 ml flask fitted with a water cooled condenser, one introduces 3.22 g (0.02M) tris(dimethylamino) phosphine and 4.36 g (0.06M) hydroxymethylcyclopropane. The mixture was heated to 100°C until dimethylamine no longer evolved. The residual phosphite **12a** was then distilled under vacuum (Bp_{1mm}= 96-98°C) and obtained with 92% yield. RMN ^{1}H ($CDCl_3$, TMS) 0.5 ppm (12 H) 1.25 ppm (3 H) 4.07 ppm (6 H), d-d J_{H-H} : 6 Hz - J_{P-H} : 8 Hz. $C_{12}H_{21}O_3P$ (244.27) calc. C : 59.00, H : 8.66 ; found C : 58.85, H : 8.50.

Syntheses of tri(1-nexene-6-yl)phosphite (**7a**)

The phosphite was synthesized as **12a** by mixing 9 g (0.09 M) 5-hexene-1-ol- and 4.5 g(0.028 M) tris(dimethylamino)phosphite. $Bp_{0.5}$ mm = 109-110°C. 80% yield. RMN ^{1}H ($CDCl_3$, TMS) 1.5 ppm (12 H, m) 1.9 ppm (6 H; m) 3.7 ppm (6 H, d) 4.75 ppm (3 H, d) 4.95 ppm (3 H, d) 5.3-5.7 ppm (3 H, m). $C_{18}H_{33}O_3P$ (328.41) Calc. C : 65.83, H : 10.13 ; found C : 65.90, H : 9.98.

Reaction of $(EtO)_3P$ (**1**) with CCl_4

In a typical experiment 2 g (0.012 M) $(EtO)_3P$ and 6 g (0.038 M) freshly distilled CCl_4 were introduced into a two necked flask fitted with a condenser supplied with a mercury trap. The solution was degassed with argon for 15 min. and heated at 80°C under argon for 4 h. The reaction mixture was then analyzed by G.C. and G.C./M.S. $(EtO)_2PO\ CCl_3$ (**3**) M = 255,5 ; m/e : 137 (0.74) ; 123 (0.02), 121 (0.02), 119 (0.6) ; 109 (1) ; 81 (0.61) ; 65 (0.30).
$(EtO)_2PO\ Cl$ (**5**) M = 184,5 ; m/e : 147 (0.19) ; 145 (0.62) ; 119 (50.31) ; 117 (1) ; 109 (0.13) ; 81 (0.25) ; 65 (0.17) (relative intensities).

Trapping by 2,6-ditertiobutyl-4-cresol

A 50 ml two necked flask fitted with a magnetic stirrer a condenser and a needle crossing through a septum was blown out with argon. CCl_4 (8ml), tertiobutanol (5 ml), 2,6-ditertiobutyl-4-cresol, 2.2 g (0.01 M), KOH, 4 g (powder) were succesively introduced. Then $(EtO)_3P$ 0.67 g (0.004 M) was injected with a syringe. The mixture was stirred for 3 h at room temperature and diluted with water. The organic layer was separated. The aqueous phase was acidified by H_2SO_4, washed three folds with 10 ml ether. The ether fraction was joined together with the organic one, dried over Na_2SO_4 and concentrated. The crude extract was analyzed by GC/MS : 2,6-ditertiobutyl-4-methyl-4-trichloromethylcyclohexadienone M = 336. m/e : 336, 303 (0.07) ; 301 (0.09) ; 219 (0.31) ; 57 (1) ; 41 (0.43). 2,6-ditertiobutyl-4-methyl-4-dichloromethylcyclohexadienone M = 302. m/e : 304 (0.06) ; 302 (0.01) ; 269 (0.02) ; 267 (0.08) ; 219 (0.24) ; 57 (1) ; 41 (0.4) (relative intensities).

Activation by light

The reactants were introduced in a quartz tube closed with a septum and degassed with argon bubbling for 1 h. The tube was irradiated by a low pressure mercury lamp (TQ 150-Hanau) for 4 h. Then the same process as for thermal activation was used.

Activation by azobisisobytyronitrile (AIBN)

The procedure was as for general technique but 20% AIBN was added.

Inhibition by 7,7',8,8' tetracyanoquinodimethane (TCNQ)

The reactants were introduced as for the general case together with a 10–45% ratio of TCNQ in a pyrex tube, sealed under vacuum and heated at 80°C for 4 h. The mixture was then analyzed by GC.

Reaction of tris(cyclopropylmethyl)phosphite (12a) with CCl_4

The reaction was conducted as for the standard procedure. The products were separated by preparative GC and identified by ^{31}P NMR. $(C_4H_8O)_2PO\ CCl_3$ (13) : 5,5 ppm ; $(C_4H_8O)_3PO$ (14) : -0,8 ppm ; $(C_4H_8O)_2POH$ (15) : 6.3 ppm ; J_{P-H} : 683-685 Hz.

Reaction of tri(1-hexene-6-yl)phosphite (7a) with CCl_4

The procedure was the same as for 12a. ^{31}P nmr $(C_6H_{11}O)_2PO\ CCl_3$ (8) : 5.3 ppm ; $(C_6H_{11}O)_3PO$ (9) : –0.6 ppm ; $(C_6H_{11}O)_3POH$ (10) : 6.5 ppm.

Electrochemical measurements :

The cell (25 ml), fitted with the three electrodes, was purged with a dry argon stream purified by successive passes over silicagel, 4 A° molecular sieves, oxygen absorber "Altech associated 4005", P_2O_5. The solution was introduced into the cell with a tight syringe and degassed with argon for 30 min. Then the impulsional voltamperograms were recorded with the following parameters : impulse time : 28 msec., impulse interval : 1 s, rotating disk speed : 150 r.p.m.

QUANTUM YIELD MEASUREMENTS

The quantum yield determinations were performed in a "merry-go-round" apparatus[37] using potassium ferrioxalate as a chemical actinometer[38]. The 254 nm light was obtained from a low pressure mercury lamp Hanau TQ 150. The actinometer tubes were randomly irradiated by 10 fractions of 1 minute. The ferrioxalate concentration was adjusted to 10^{-2}M so that its optical density was > 2 after irradiation. The disappearance of the substrate was obtained by G.C. analysis with dodecane as standard. Since the consumption ratio was small (2-5%) the absorption band of triethyl phosphite at 260 nm remained well resolved and unmasked for all the time.

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