A Study of the Atherton-Todd Reaction Mechanism

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Synopsis. It has been shown that alkylammonium methyl phosphonates $[CH_3OP(O)HO]^-$ $[NCH_3R_3]^+$ and sodium ethyl phosphonate $[CH_3CH_2OP(O)HO]^-$ Na^+ catalyse the Atherton-Todd reaction. It has been established that the alkylammonium salts themself react with carbon tetrachloride to give chloroform, resulting in the postulate that base activation leads to the monoalkyl phosphonate anion.

The Atherton-Todd reaction proceeds, as is well-known,[1-5] only under basic reaction conditions (Eq. 1). It is assumed[4-6] that the first step in this interaction involves proton abstraction from the dialkyl phosphonate in solution (Eq. 2). The active species so formed reacts further with carbon tetrachloride, finally yielding the Atherton-Todd reaction products.

$$(RO)_2P(O)H + CCl_4 \xrightarrow{B} (RO)_2P(O)Cl + CHCl_3 \quad (1)$$

$$(RO)_2P(O)H + B \rightarrow [(RO)_2PO]^-[HB]^+ \quad (2)$$

$(B = Et_3N, NaH, RONa, (RO)_3P)$

It has been otherwise established[7-11] that the treatment of dialkyl phosphonates with amines leads to the formation of the corresponding alkylammonium alkyl phosphonate.[12,13]

$$(RO)_2P(O)H + NR'_3 \rightarrow [RO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O]^-[NRR'_3]^+ \quad (3)$$

Similar products are formed by the reaction of the sodium salt of dialkyl phosphonates with an excess of dialkyl phosphonate itself.[14] Taking into account that these two reactions (Eqs. 3 and 4) can proceed under Atherton-Todd reaction conditions, the interaction of dimethyl phosphonate with carbon tetrachloride was performed in the presence of catalytic amounts of both alkylammonium methyl phosphonate and sodium ethyl phosphonate.

$$(RO)_2P(O)H + [(RO)_2PO]^-Na^+ \longrightarrow [RO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O]^-Na^+ + (RO)_2P(O)R \quad (4)$$

Results and Discussion

The following catalysts shown in Scheme 1 have been used in this study.

$[CH_3O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O]^-$ $[NCH_3R'R''R''']^+$ (1) R′=R″=R‴=CH_3CH_2; (2) R′=R″=H, R‴=n-C_4H_9

$[CH_3CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O]^-$ Na^+ (3)

Scheme 1.

The structures of these salts were established by a combination of ^1H, ^{13}C, ^{31}P NMR, and IR spectroscopy. The ^{31}P NMR chemical shifts are at δ=5.88, 3.93, and 4.91 for **1**, **2**, and **3** respectively, values which are indicative of phosphonium type compounds.[15] The P-H bond is characterized by an approximate 600 Hz coupling due to $^1J(PH)$ in both the ^1H and the ^{31}P NMR spectra. In the IR spectra the P-H and P=O stretching frequencies are lowered by ca. 100 and 30—50 cm^{-1} respectively when compared with the corresponding dialkyl phosphonate-precursor. This shift is probably due to the charge delocalization in the anionic fragment.

The Atherton-Todd reaction was carried out in the presence of catalytic amounts of the salts shown in Scheme 1 (a mole ratio of dimethyl phosphonate: catalyst of 50:1 was used). The mixtures were analyzed by ^1H NMR spectroscopy. In all cases chloroform liberation was established. The yields were estimated from the integral ratio for the chloroform and P-H (of the unconverted dimethyl phosphonate) protons (Table 1). The chemical shift of the chloroform

Table 1. Reaction of Dimethyl Phosphonate with Carbon Tetrachloride in the Presence of Catalytic Amounts of the Compounds **1**, **2**, **3**, and Triethylamine

Catalyst	Temperature / °C	Time	Proton integration ratio PH : $CHCl_3$	Yield / %
1	75	5.5 h	22:15	40.5
3	75	5.5 h	19:2	9.5
Et_3N	75	5.5 h	19:4	17.4
2	75	2.0 h	30:5	14.3[a]
1	25	1 week	22:3	12.0
3	25	1 week	26:1	3.7

Volume of the reaction mixtures are 12.3 cm^3 (4.6 cm^3 of dimethyl phosphonate and 7.7 cm^3 of CCl_4). The catalyst concentrations were 8×10^{-3} mol dm^{-3}.
a) With vigorous stirring.

proton in the product mixture occurs at relative low field (ca. 8 ppm) in comparison with the free chloroform. This is explained[16,17] in terms of hydrogen bond formation with the phosphoryl oxygen from dimethyl phosphonate. In all spectra the $CHCl_3$ signals are verified by addition of a drop of $CHCl_3$ to the sample. The methoxy protons of the reaction product $(CH_3O)_2P(O)Cl$ show as a doublet at δ=3.73 (J(PH)=12 Hz), close to the doublet of the unconverted dimethyl phosphonate at δ=3.76 (J(PH)=12 Hz), hence these two signals are integrated together. Integration of these proton resonances against that of $CHCl_3$ confirms that the conversion of $(CH_3O)_2P(O)H$ into $(CH_3O)_2P(O)Cl$ results in the liberation of one equivalent of chloroform. From Table 1, it is apparent that the yield of $(CH_3O)_2P(O)Cl$ is lowest for **3**, but it is twice as high for Et_3N, and four times as high for **1**. The relative low activity of the sodium salt **3** is probably due to its low solubility in the reaction mixture.

It has been established by an ^1H NMR stydy of the reaction mixture of the alkylammonium salts **1** and **2**, and CCl_4, that both salts react exothermically with CCl_4 to liberate $CHCl_3$. This reaction is carried out under stirred conditions at ambient temperature, and the formation of $CHCl_3$ is verified by the appearance of its growth in the ^1H NMR spectrum. The alkylammonium chlorophosphonates formed are converted to the methyl phosphonate by reaction with methanol, and these final products are confirmed by ^1H, ^{13}C, and ^{31}P NMR.

These experiments show that the alkylammonium or sodium salts of monoalkyl phosphonates catalyze the Atherton-Todd reaction. This leads us to propose that the basic activation in this reaction involves formation of the monoalkyl phosphonate anion $[(RO)PHO_2]^-$, which further catalyses the interaction between CCl_4 and $(RO)_2P(O)H$ (Eq. 5).

$$(RO)_2P(O)H + CCl_4 \xrightarrow{[RO\text{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}\text{-}O]^-K^+} (RO)_2P(O)Cl + CHCl_3 \quad (5)$$

K=alk.M
K=RR′R″R‴N

Our data do not support the earlier proposed mechanisms for this reaction[1-6] in which the three coordinated anion $[(RO)_2PO]^-$, obtained by deprotonation of the dialkyl phosphonate with the basic compound, is postulated to play the key role.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Nuclear magnetic resonance spectra were run on Bruker WM 250 and Tesla BS 467 spectrometers at 250 and 60 MHz for protons, 62.5 for ^{13}C and 101.7 for ^{31}P.

Synthesis of the Catalysts. The alkylammonium salts **1** and **2** were obtained as follows. To a solution of 20.45 g freshly distillated dialkyl phosphonate in MeOH (20 cm^3) was added excess amine. The mixture was refluxed for 2 h, and the MeOH and the excess of amine were removed under reduced pressure. Compound **3** was prepared according to Ref. 18.

Spectroscopic Data: $[(CH_3O)\text{-}P(O)OH]^-[NH_2(CH_3)CH_2\text{-}CH_2CH_2CH_3]^+$ (1). IR (KBr film) 1210 (νP=O) and 2348 (νP-H) cm^{-1}; ^{31}P NMR ($CDCl_3$) 5.88 (^1J(PH)=607 Hz, ^3J(PH)=13 Hz); ^1H NMR (250 MHz, $CDCl_3$) δ=0.94 (t, 3H, J(HH)=7.4 Hz, d-CH_3), 1.40 (sext., 2H, J(HH)=7.4 Hz, c-CH_2), 1.70 (pent., 2H, J(HH)=7.4 Hz, b-CH_2), 2.82 (t, 2H, J(HH)=8 Hz, a-CH_2), 3.33 (s, 3H, NCH_3), 3.52 (d, 3H, J(PH)=12.0 Hz, $POCH_3$), 6.72 (d, 1H, J(PH)=607.1 Hz, P-H), 8.72 (br. s, 2H, NH).

$[(CH_3O)\text{-}P(O)HO]^-[N(CH_3)(CH_2CH_3)_3]^+$ (2). IR (KBr film) 1235 (νP=O) and 2313 (νP-H) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ=1.37 (t, 9H, J(HH)=7.2 Hz, CH_3), 3.13 (s, 3H, NCH_3), 3.48 (q, 6H, J(HH)=7.2 Hz, CH_2), 3.53 (d, 3H, J(PH)=11.9 Hz, $POCH_3$), 6.81 (d, 1H, J(PH)=594.8 Hz, P-H); $^{13}C\{^1H\}$NMR ($CDCl_3$) δ=6.57 (CH_3), 45.48 (CH_2), 48.91 ($POCH_3$), 54.61 (NCH_3); ^{31}P NMR ($CDCl_3$) 3.93 (J(PH)=635 Hz, J(PH)=9 Hz).

$[(CH_3CH_2O)\text{-}P(O)HO]^-Na^+$ (3). IR (KBr) 1222 (νP=O) and 2369 (νP-H) cm^{-1}; ^1H NMR (250 MHz, D_2O) δ=1.26 (t, 3H, J(HH)=7.1 Hz, CH_3), 3.91 (d.q., 2H, J(HH)=7.2 Hz, J(PH)=8.2 Hz, CH_3), 7.21 (d, 1H, J(PH)=633.2 Hz, P-H); $^{13}C\{^1H\}$NMR (D_2O) δ=18.72 (CH_3, 63.18 (CH_2)); ^{31}P NMR (D_2O): 4.91 (^1J(PH)=596.0 Hz, ^3J(PH)=11.6 Hz).

Catalytic Experiments, General Procedure. Dimethyl phosphonate (5.5 g, 50 mmol) and the catalyst (1 mmol) were reacted with an excess of CCl_4 (12.3 g, 80 mmol) under the conditions described in Table 1. Samples were taken after that from the reaction mixture and investigated by ^1H NMR (60 MHz) spectroscopy without addition of any solvent.

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