MECHANISM OF FORMATION OF PHOSPHONATE CARBANIONS WITH THE USE OF A LITHIUM SALT AND 1,8-DIAZABICYCLO[5.4.0]UNDEC-7-ENE

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The deprotonation reaction mechanism of methyl diethylphosphonoacetate in the presence of lithium salts and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was examined by infrared spectroscopy. It was found that the intermediate species formed by chelation of the bidentate phosphonate with a lithium cation or an ion pair of the salt deaggregated by DBU takes part in the reaction path. The role of the anion X^- is to induce the elimination of a protonated $DBUH^+X^-$ ion pair and that of the solvent is to compete with the bidentate phosphonate in cation solvation. A similar mechanism via a related intermediate is proposed to interpret the results obtained by other workers on the catalysis by $Ba(OH)_2$ of the Wittig–Horner reaction.

INTRODUCTION

We have been interested in the structure and mechanism of the formation of carbanionic species as phosphonoacetate anions for a number of years.[1–3] These compounds are usually generated by the action of a strong organometallic base (n-BuLi, t-BuOK, etc.), on the parent phosphonate in an appropriate solvent such as dimethylether (DME) or tetrahydrofuran, in order to prevent the reaction of the base with the solvent. It has been shown more recently that carbanionic species can be prepared under milder conditions in the presence of a lithium or magnesium salt and an appropriate organic base such as triethylamine or 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU).[4,5] As shown previously, the mechanism of the formation of the carbanionic species in the presence of less than one equivalent of organometallic base proceeds through an intermediate involving an activated parent phosphonoacetate molecule which solvates a carbanionic ion pair or a monomeric organometallic base.[2] This work was aimed at an understanding of the action of the lithium salts in the presence of DBU.[3,6] A reinvestigation by infrared spectroscopy of the complexation of DBU with salts in the absence or presence of water[7] led to a more detailed interpretation of the mechanism of the deprotonation of methyl diethylphosphonoacetate in the presence of DBU and lithium salts.

EXPERIMENTAL

Methyl diethylphosphonoacetate (Janssen) was distilled under reduced pressure and DBU (Janssen) was handled under argon. Acetonitrile (Prolabo, quality for infrared spectroscopy) was dried over Merck molecular sieves 4 Å. The salts LiCl (Merck), LiBr (Koch-Light Laboratories) and LiClO₄ (Aldrich) were dried by slow heating under vacuum and handled under argon.

Solutions were prepared in a dry-box or under argon in a glove-bag.

Infrared spectra were scanned on a Perkin-Elmer 983 spectrometer. The resolution was usually 3 cm^{-1} and the frequencies are given with a precision of at least ±1 cm^{-1}. The cell was equipped with CaF_2 windows and had a thickness of 30 μm.

RESULTS AND DISCUSSION

It has been shown recently that in the presence of water and a lithium or magnesium salt, the DBU molecule dissolved in acetonitrile may be protonated.[7] The increase in the acidity of the water molecule through the cooperative effect of the cation and the anion in a water-separated ion pair is responsible for this deprotonation. When the water molecule is bonded only to a cation or to an anion and to solvent molecules, the protonation of DBU does not take place. The bicyclic DBU molecule [pK_a = 11·6 (Ref. 8)] has two intracyclic nitrogen atoms. Two bands are observed at 1612 and 1313 cm^{-1} for DBU in acetonitrile solution, which correspond to the stretching vibrations of the C=N and C—N bonds, respectively. When a carefully dried lithium salt is added to the acetonitrile solution, the $\nu(C=N)$ vibration is only slightly lowered in frequency (to 1607 cm^{-1}) as a result of complexation of the nitrogen

atom. When water is added to the DBU–LiX solution a new $\nu(C{=}N)$ band appears at 1646 cm^{-1}, which is due to the protonation of the imine nitrogen of the DBU molecule. This 34 cm^{-1} frequency increase arises from a slight coupling of the C=N stretching coordinate with the in-plane bending NH$^+$ coordinate of the protonated imine.[7,9,10] The band at 1646 cm^{-1} was previously erroneously assigned to the complexation of LiCl by DBU,[3] thus the possibility of the protonation of DBU by traces of water present in the salt sample was overlooked.

Figure 1 shows the infrared spectra of an equimolecular solution of methyl diethylphosphonoacetate (Pha) and dried lithium chloride in acetonitrile, with different concentrations of DBU added. As already analysed in detail,[3,6] when the organic base is added the free Pha characterized by the $\nu(C{=}O)$ vibration at 1740 cm^{-1} disappears and the phosphonoacetate anion Pha$^-$ is formed as characterized by the $\nu(C{\doteq}O^-)$ bands or shoulders at 1632, 1594 and 1575 cm^{-1}. These features correspond to a triple anion, a monomeric ion pair and aggregated ion pairs of this bidentate carbanion, respectively. Two bands are related to the addition of DBU to the solution, the band at 1646 cm^{-1} which appears first, showing that DBU acts as a deprotonating agent, and another at 1611 cm^{-1} when larger amounts of DBU are added. The latter band may be due to both unreacted DBU (1612 cm^{-1}) and DBU complexed with the lithium salt (1607 cm^{-1}).[7]

In order to determine the role of the salt and the influence of its anion, a comparison of the effects of

very well dried LiClO$_4$ and LiBr was made (Figure 2). In this case, compared with the results shown in Figure 1, a slight excess of lithium salt and of DBU relative to Pha was used. As seen from the intensity of the $\nu(C{=}O)$ band at 1740 cm^{-1} of the free Pha, the amount of Pha$^-$ formed is less important for LiClO$_4$ than for LiBr. This deprotonation yield is also correlated to the intensity of the $\nu(C{=}NH^+)$ band at 1646 cm^{-1}. The bands at 1605, 1588 cm^{-1} and the shoulder at 1570 cm^{-1} are due to the $\nu(C{\doteq}O^-)$ vibrations of the Pha$^-$ anions involved in triple anions and monomeric and aggregated ions pairs; their frequencies may be slightly influenced by the formation of mixed species with the anions of the added salt in these associated ionic species. The equilibrium between the three forms is different with LiClO$_4$ and LiBr, as shown in Figure 2.

In order to specify the role of the anion, the infrared transmission spectra of these solutions in the 2800–3600 cm^{-1} region, which is shown in Figure 3, was investigated. As the spectrum of the acetonitrile solvent and the added DBU may be perturbed by the salt,[11] an exact subtraction of the solvent spectrum is difficult and was not attempted. In the presence of LiClO$_4$ two new bands appear at 3320 and 3520 cm^{-1} [Figure 3(B)], in addition to the $\nu(CH_2)$ bands of DBU around 2800 cm^{-1}. The new bands may be assigned to the $\nu(NH^+)$ vibration of protonated DBU. The appearance of two components may be due to either a Fermi resonance or the existence of two species in equilibrium. In the presence of LiBr [Figure 3(A)], the intensity of
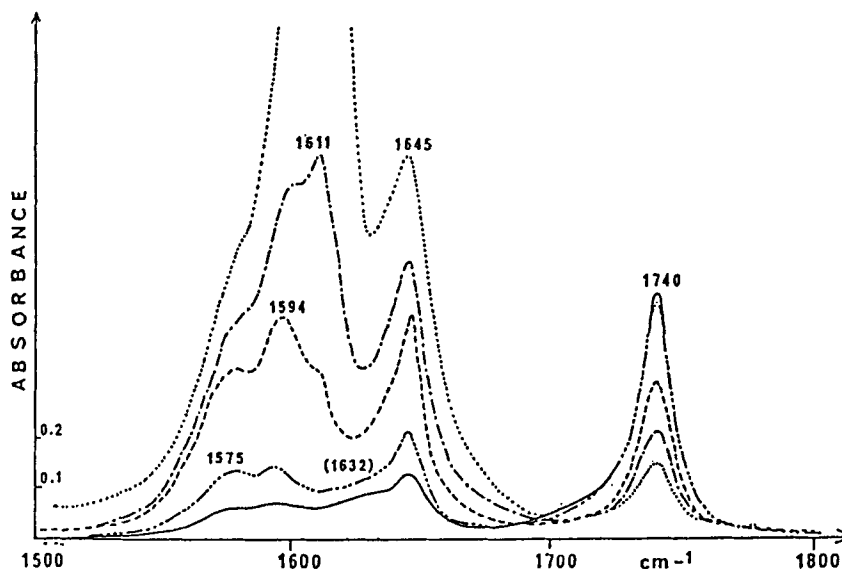

Figure 1. Infrared absorption spectra of an equimolecular solution of methyl diethylphosphonoacetate (Pha) and LiCl in acetonitrile in the presence of DBU at increasing concentrations. DBU/Pha concentration ratio: ———, 0·12; — ··· — ···, 0·25; ----, 0·75; — · — ·, 1·5; ····, 3
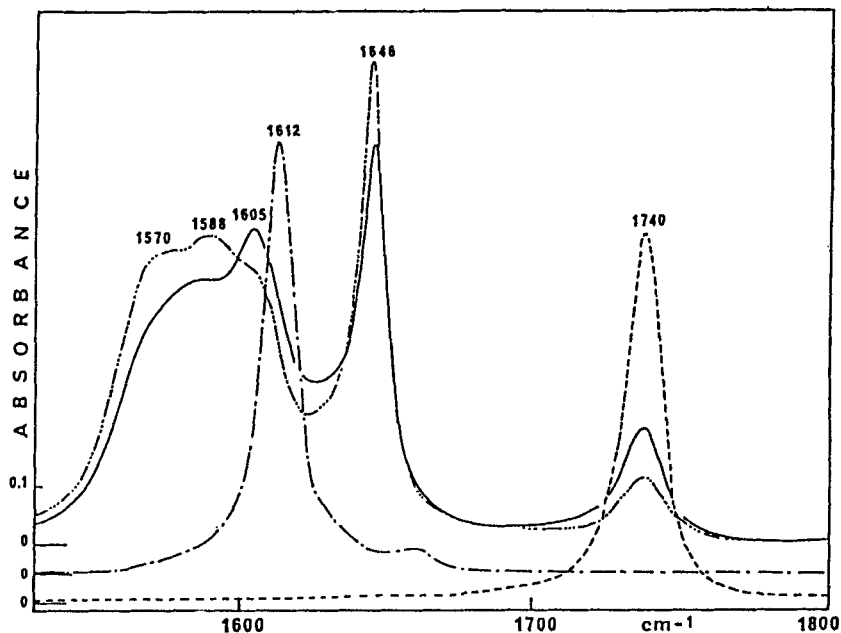
Figure 2. Infrared absorption spectra of a solution of Pha at a concentration of 0·3 M in acetonitrile in the presence of an equimolecular mixture of DBU and of a lithium salt: ——, 1·2 equiv. of LiClO₄ and DBU; —···—···, 1·2 equiv. of LiBr and DBU. Infrared spectra of (---) Pha and (−·−·−) DBU, both 0·3 M in acetonitrile

the 3320 cm⁻¹ band is very low and a new broad band is observed with components at lower frequencies (3080 and *ca* 3000 cm⁻¹), indicating a large shift to lower frequencies of the ν(NH⁺) feature. This result is consistent with the existence of free solvated DBUH⁺···NCCH₃ cation corresponding to the band at 3320 cm⁻¹ and the presence of a low concentration of ion pairs DBUH⁺···ClO₄⁻ corresponding to the band at 3520 cm⁻¹. The high ν(NH⁺) frequency observed in this ion pair is due to the large ClO₄⁻ anion. In the pres-

ence of LiBr, there is a small amount of free solvated DBUH⁺···NCCH₃ cation, the low-frequency band at 3080–3000 cm⁻¹ being assigned to a DBUH⁺···Br⁻ contact ion pair. The lowering of the frequency of the ν(NH⁺) band is due to the N—H⁺···Br⁻ hydrogen bond.

As already discussed from the IR and NMR results,[3,6] the DBU first contributes to the dissolution and the deaggregation of the lithium salt in acetonitrile. It further induces two reaction sequences [equations (1)
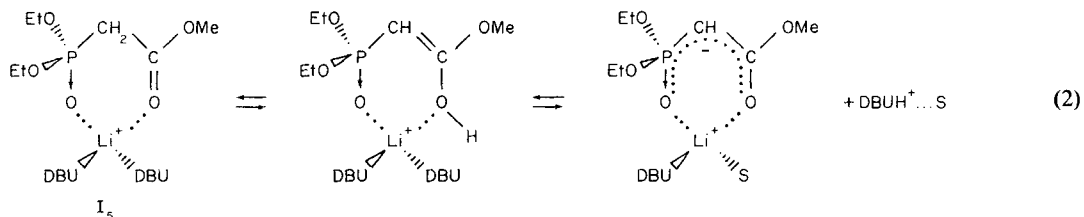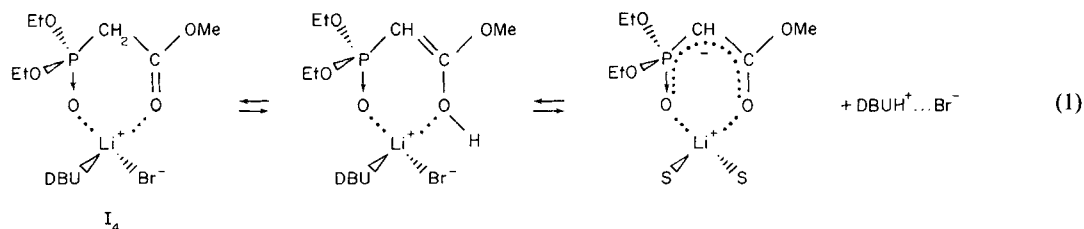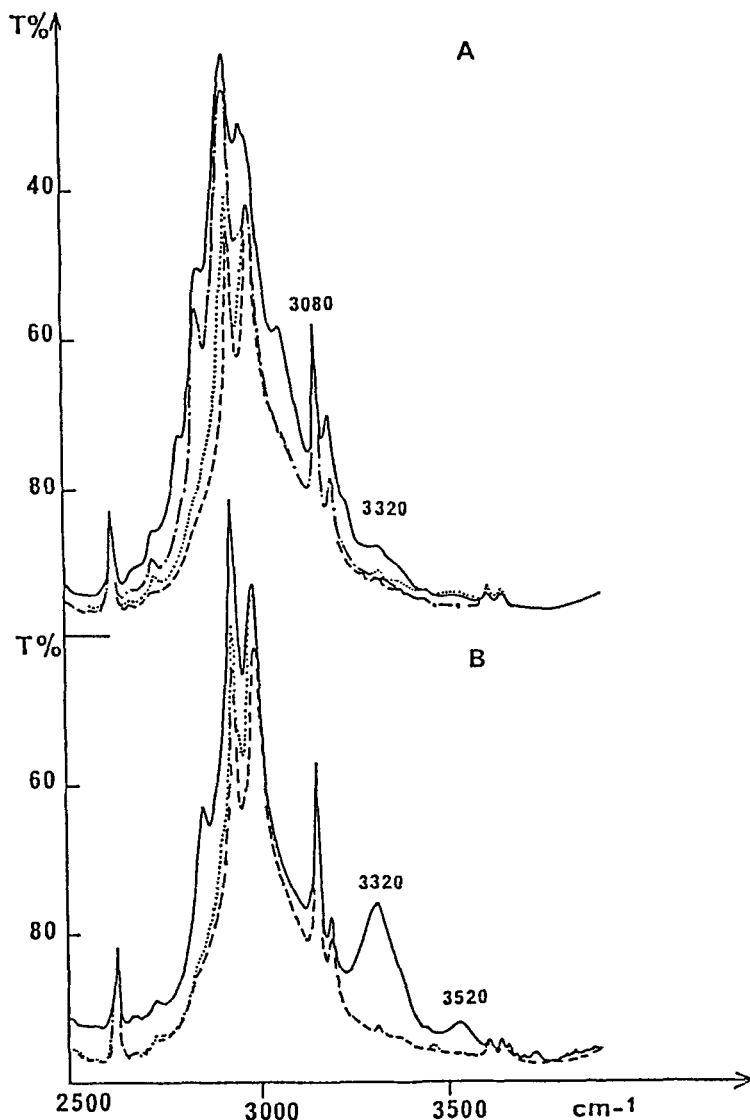
Figure 3. Infrared transmission spectra of solutions of (A) (——) 0·3 M Pha, 0·36 M DBU, and 0·36 M LiBr in acetonitrile and (B) (——) 0·3 M Pha, 0·36 M DBU and 0·36 M LiClO$_4$. The transmission spectra of the pure solvent (----), of the 0·36 M binary salt solvent solution (···) and of the 0·36 M DBU solution in acetonitrile (— · — · —) are shown for comparison

and (2)], depending on the amount of DBU added and the nature of the salt. In these sequences the bidentate phosphonate is coordinated to a lithium ion pair intermediate I$_4$ or a free DBU solvated lithium cation intermediate I$_5$. This coordination induces a lengthening of the carbonyl group as shown by the ν(C=O) frequency shift from 1740 to 1668 cm^{-1} in acetonitrile and a ^{31}P chemical shift variation from 19·1 to 28·1 ppm,[3,6] which shifts the keto $\rightleftharpoons$ enol equilibrium towards the enol form. The enol is promptly deprotonated by elim-

ination of a DBUH$^+$···Br$^-$ ion pair or a DBUH$^+$ solvated cation.

From Figure 2, it is apparent that the yield of the carbanionic species is higher with LiBr than with LiClO$_4$, strongly indicating the importance of intermediate I$_4$, for which the deprotonation may take place through the concerted elimination of a DBUH$^+$···Br$^-$ ion pair. This mechanism is similar to that involved in the protonation of the organic base DBU by a water-separated ion pair[7] [equation (3)]. It is nevertheless not possible to reject

$$\cdots \longrightarrow \mathrm{DBUH^+ \cdots Br^-} + \underline{\mathrm{LiOH}} \rightleftharpoons \mathrm{DBUH^+ \cdots S} + \mathrm{Br^-} \tag{3}$$
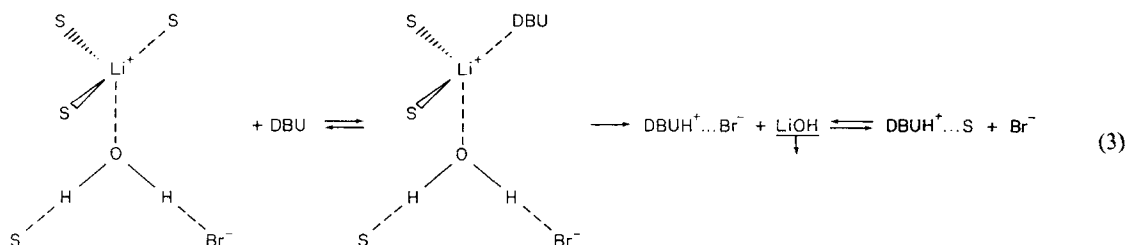
the formation of the anion by direct C deprotonation of the ester, since under these conditions the CH vibrations of the intermediate species, I_4 and I_5, the concentrations of which were always very low, were not observed.

It is important to note that if the salt or the solvent used is incompletely dried, reactions (3) take place at the expense of reactions (1). It has been shown[7] that in the same concentration range, reaction (3) is almost quantitative, whereas the Pha → Pha⁻ reaction is not. On the other hand, the acidity of water is insufficient to protonate DBU in the absence of anionic assistance, while the enol form of the phosphonoacetate molecule may be deprotonated without this anionic assistance. Indeed, in an acetonitrile solution of $LiClO_4$ the DBU molecule is not protonated by water. Finally, the reactivity results of Rathke and Nowak[5] emphasize the importance of intermediates I_4 and I_5 since in dimethylformamide, which forms a very stable $Li^+(DMA)_4$ solvated cation,[12] the deprotonation is much lower than that in the other less coordinating solvents. The dimethylformamide solvent molecule competes strongly with the bidentate Pha molecule, preventing the formation of intermediate I_4 or I_5.

The above mechanism is also in agreement with the experimental observations of Sinisterra Gago and co-workers[13,14] on solid $Ba(OH)_2$ catalysis of the Wittig–Horner reaction. In fact, they observed the formation of an intermediate I characterized by a $\nu(C=O)$ band at 1684 cm⁻¹[3] when ethyl diethylphosphonoacetate is adsorbed on the $Ba(OH)_2$ catalyst C200 in the absence of added water. In this case, in disagreement with their interpretations, only a small amount of carbanionic species (characterized by the $\nu(C \doteq O^-)$ band at 1592 cm⁻¹ and a $\nu(P-O)$ band at 1194 cm⁻¹) is formed. On the other hand, when the adsorption takes place in the presence of water, intense bands at 1570, 1384 and 1194 cm⁻¹ characteristic of ethyl diethylphosphonoacetate carbanion are observed. With this new assignment,[3] it is clear that the formation of a $(Ba^{2+}OH^-)^+$ ion pair at the site where the bidentate phosphonoacetate is adsorbed is needed in order to deprotonate the neutral phosphonate. This interpretation is reinforced by the decrease in the intensity of the $\nu(OH^-)$ band at 3580 cm⁻¹, which is observed simultaneously with the formation of the carbanionic species (Ref. 13, Figure 2). Therefore, either in solution in the presence of lithium salts or on solid $Ba(OH)_2$, the deprotonation by an amine or by OH^- of ethyl

diethylphosphonoacetate requires preliminary coordination of the neutral molecule by a cation.

ACKNOWLEDGEMENT

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