The influence of common cation BH^+ on the products of reactions between C-acids and strong guanidine bases in acetonitrile solvent

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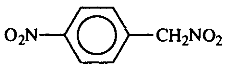
The electronic spectra of the products of reactions between C-acids (4-nitrophenylcyanoalkanes, 4-nitrophenylnitroalkanes and trinitrotoluene) and 1,1,3,3-tetramethylguanidine (TMG), pentamethylguanidine (PMG) and MTBD bases (B) have been recorded in B/BH^+ buffers in acetonitrile at 25 °C. Large BH^+ concentrations had little or no effect on the spectra of the nitrile or trinitrotoluene anions, while the spectra of nitroalkane anions were shifted to the blue by some 50–75 nm. These shifts were ascribed to the formation of hydrogen-bonded ion pairs. In the case of TMG or PMG reactions two types of ion pairs are formed due to homoconjugation of BH^+ cations, which is why an isosbestic point is not observed, while MTBD reactions are free from such complications. The spectra of some ion pair products and ion pair dissociation constants were calculated.

Introduction

In our previous papers we found that the products of reactions between C-acids and strong amine bases in acetonitrile are largely dissociated into free ions at spectrophotometric concentrations of C-acid and a large excess of base.[1–3] However, this large dissociation, which is evident from conductometric studies,[2,3] could not easily be seen in the electronic absorption spectra. The concentration of BH^+ derived from side reactions proved to be much larger than that formed in the deprontonation of C-acid, so that even a pseudo-Benesi–Hildebrand relation was maintained.[2,3] Therefore, we came to the conclusion that in our equilibrium and kinetic studies the concentration of the cation must be controlled. This can be done by carrying out measurements in a BH^+/B buffer solution.[3]

However, a large concentration of BH^+ could cause ion-association of the product, in which case two or more forms of the product must be considered. Those different species would then have to be included in our kinetic scheme. Therefore, it seems to be of interest to find whether a common ion, BH^+, effect on the electronic absorption spectra can be observed.

For our experiments the following C-acids and guanidine bases were chosen.



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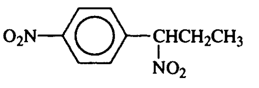

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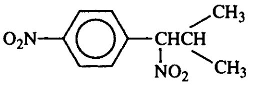

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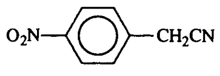

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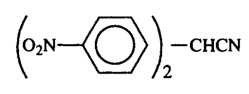

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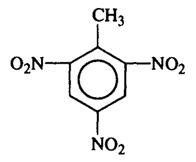
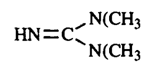
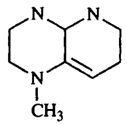


TNT

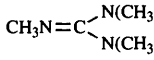


$HN{=}C(N(CH_3)_2)_2$

TMG

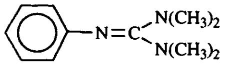


MTBD



$CH_3N{=}C(N(CH_3)_2)_2$

PMG



PhTMG

Experimental

Reagents

1,1,3,3-Tetramethylguanidine (TMG), commercial product (97%) from Aldrich, was stored over KOH pellets, then distilled under vacuum in an atmosphere of dry nitrogen.

1,1,3,3-Tetramethylguanidine perchloride was prepared by mixing stoichiometric amounts of TMG and $HClO_4$ (71%) in methanol. Water and methanol were then removed under reduced pressure. The white crystalline residue was dissolved in methanol and the solvent was evaporated again. This procedure was repeated until the weight of the product corresponded to the calculated amount of the salt.

1,1,3,3-Tetramethylguanidine picrate (TMGHPi) was prepared according to a procedure described by Leffek *et al.*[4] (mp 128.5–129.5 °C).

Pentamethylguanidine was prepared by a modified Bredereck's method.[5,6]

7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), a commercial product (Fluka), was used without purification. Due precautions were undertaken to minimize contact with air.

MTBD perchlorate was prepared in a procedure analogous to TMG perchlorate.

4-Nitrophenylnitromethane **1** was prepared as previously described.[7] 4-Nitrophenyl-1-nitropropane **2** and 2-methyl-1-(4-nitrophenyl)-1-nitropropane **3** were prepared according to a procedure previously described.[2]

2,4,6-Trinitrotoluene (TNT), a commercial product, was purified by repeated crystallization from ethanol (mp 81 °C). The purity parameters were in agreement with the literature.[8]

4-Nitrophenylcyanomethane **4** was a commercial product from Eastman.

Bis(4-nitrophenyl)cyanomethane **5** was prepared according to a previously described procedure.[9]

Acetonitrile (spectroscopic grade solvent from Romil) was stored over CaH_2, distilled over P_2O_5 and, finally, fractionally distilled over CaH_2. The distillate was protected from atmospheric moisture and CO_2.

Solutions of both C-acids and the bases were prepared from freshly purified reagents just before equilibrium experiments.

Spectra and procedures

Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer fitted with a thermostatted cell holder. All spectra were run at 25 °C.

The spectra of the 4-nitrophenylcyanomethane anions were recorded immediately after mixing the reagents. Within 1 h the anion turned into another coloured species, which had a similar spectrum, but the intensity of the absorption band was larger than that of the original product. A slow reaction with TMG leading to colourless products then took place.

Techniques for conductometric measurements and calculations have been described elsewhere.[3,10]

Results and discussion

This study is limited to the products of proton transfer reactions between relatively strong carbon acids and strong guanidine bases. For these reactions proton transfer is complete, provided the concentration of base is reasonably large, and ion association effects on electronic spectra can be easily observed. Guanidine base perchlorates were chosen as a source of common cation, because their solutions are transparent over a broad spectral range and they are presumed to be well dissociated even at concentrations as large as 0.2 mol dm^{-3}.[10] Constant ionic strength was not maintained and activity coefficients, when needed, were calculated using the partially extended Debye–Huckel expression[11] $-\log f = 1.53\ \mu^{1/2}/(1 + 4.8 \times 10^7\ a\mu^{1/2})$. An a value equal to 6 Å was used for all ions.

Chantooni and Kolthoff[10] showed that the spectra of amine–picrate ion pairs are shifted to shorter wavelengths as compared to the picrate ion.

Similar effects have been found in this work for anions of 1-(4-nitrophenyl)-1-nitroalkanes **1–3**. The visible spectrum of 4-nitrophenylmethanenitronate free anion in acetonitrile shows a broad absorption band with a maximum at λ 490 nm. At a large concentration of TMG (c_B = 0.1 and 0.5 mol dm^{-3}), addition of the common cation, $TMGH^+$, to the reaction mixture results in a shift of the band to shorter wavelengths. For a concentration of the cation not exceeding 0.02 mol dm^{-3}, this shift takes place with an isosbestic point at *ca.* 475 nm (in Fig. 1 only selected spectra, and only for one TMG concentration, are shown). For larger concentrations of $TMGHClO_4$ the isosbestic point is no longer observed and the band broadens, losing its maximum intensity. For a concentration of $TMGH^+$ equal to 0.6 mol dm^{-3}, the blue shift reaches ≅50 nm.

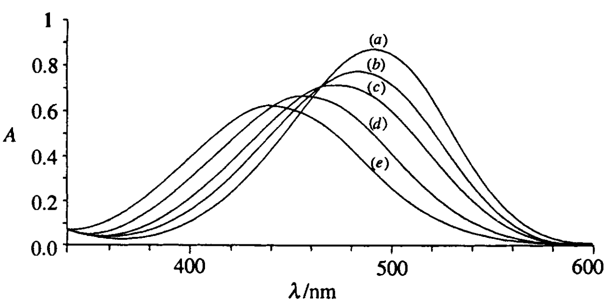
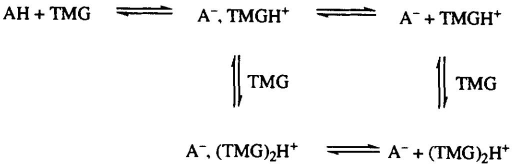


Fig. 1 Visible spectra of the reaction between 4-nitrophenylnitromethane **1** (3×10^{-5} mol dm^{-3}) and TMG (0.1 mol dm^{-3}) with increasing concentration of added $TMGHClO_4$, (BH^+). Concentrations of added BH^+ are: 0 (*a*); 5×10^{-3} mol dm^{-3} (*b*); 2×10^{-2} mol dm^{-3} (*c*); 0.1 mol dm^{-3} (*d*); 0.6 mol dm^{-3} (*e*).



Scheme 1 Equilibria between free ions, ion pairs and homoconjugated ion pairs for the proton transfer reaction between C-acid and TMG base in acetonitrile

The same pattern of spectral changes is observed for the reaction of **1** or **2** with PMG.

Reversibility of the blue shift was demonstrated by dilution of a concentrated solution of the product and BH^+. A 100-fold decrease in $[BH^+]$ resulted in a large red shift in the spectrum of the product.

The spectral shifts shown in Fig. 1 indicate the presence of at least three coloured species and they can be rationalized when homoconjugation of $TMGH^+$ is taken into account. Extensive homoconjugation of $TMGH^+$ in acetonitrile was shown by Kolthoff and Chantooni.[11] Consequently, two types of hydrogen-bonded ion pairs $TMGH^+$, A^- and $(TMG)_2H^+$, A^- can be assumed (see Scheme 1). For this equilibrium, eqn. (1) is fulfilled:

$$[(TMG)_2H^+,A^-]/[TMG^+,A^-] = K_2[(TMG)_2H^+]/[TMGH^+] \quad (1)$$

where K_1 and K_2 are ion association constants for the plain and homoconjugated ion pairs, respectively.

$$K_h = [B_2H^+]/([B] \times [BH^+]) \quad (2)$$

As follows from eqn. (2), when the concentration of B is large, 0.1 or 0.5 mol dm^{-3}, the $[(TMG)_2H^+]/[TMGH^+]$ ratio is approximately constant at low concentrations of added $TMGHClO_4$, up to 0.02 mol dm^{-3}. We can then say that the free nitronate anion is turned into a mixture of ion pairs of a fixed ratio of components and therefore the isosbestic point is observed (Fig. 1). At higher concentrations of BH^+, above 0.02 mol dm^{-3}, the $[B_2H^+]/[BH^+]$ ratio decreases considerably and an isosbestic point should not be observed, as long as the spectra of the two ion pairs are different from each other, which apparently is the case for the reactions of **1–3** with TMG and PMG bases.

When spectra recorded at the same concentration of BH^+ but at different concentrations of TMG or PMG base are overlaid, a bathochromic shift with increasing concentration of base is found. This agrees with the plausible assumption that the homoconjugated ion pair should absorb at longer wavelengths. It is also consistent with greater dissociation of the homoconjugated ion pair.

From these data we were not able to calculate the spectra and accurate dissociation constants for the plain and homoconjugated ion pairs formed in TMG or PMG systems. However, apparent dissociation constants were found for a concentration range over which an isosbestic point is almost observed; these were obtained from the drop in absorbance at wavelengths at which absorbance of ion pairs is negligible. Four such values are shown in Table 1. The value of the apparent dissociation constant for the reaction product of **1** with TMG (entries 1 and 2 in Table 1) depends on the concentration of TMG, but for [TMG] = 0.1 mol dm^{-3} it is not far from the results of more precise methods. This made us believe that the other three values measured at [TMG] = 0.1 mol dm^{-3} give reasonable estimates of the dissociation constants for TMGHA ion pairs and should be quoted in Table 1 along with more rigorously determined values.

The spectrum of the TMGHA ion pair and its dissociation

Table 1 Dissociation constants of the products of reactions between C-acids and guanidine bases in acetonitrile at 25 °C

Reaction system	$k_d/10^{-3}$ mol dm^{-3}	Λ_0	Method[a]	$k_f/10^3$ dm^3 mol^{-1} [d]
1 + TMG	9.0 + 0.6[b]	—	A	
1 + TMG	20 ± 5[c]	—	A	
1 + TMG	8.4 ± 0.4	—	B	60
1 + TMG	6.91	156.9	C	72
1 + PMG	13[b]	—	A	
1 + MTBD	9.7 ± 0.6	—	A	7300
1 + MTBD	10 ± 0.1	—	B	7100
1 + MTBD	11.5	166.3	C	6200
2 + TMG	5 ± 1[b]	—	A	
3 + MTBD	2.4 ± 0.2[e]	—	A	0.16,[f] 0.052,[g] 0.146[h]

[a] A, spectrophotometric study in 1 cm cells, [C-acid] = 3–5 × 10^{-5} mol dm^{-3}, $C_{BH^+} < 0.02$ mol dm^{-3}; B, spectrophtometric study of concentrated equimolar mixtures in thin cells, concentration range 5 × 10^{-4}–1 × 10^{-2} mol dm^{-3}; C, conductometric titration of 0.02 mol dm^{-3} C-acid solution with base, Kraus–Fuoss treatment. [b] A rough apparent value, [B] = 0.1 mol dm^{-3}. [c] A rough apparent value, [TMG] = 0.5 mol dm^{-3}. [d] $K_f = K/K_d$, where $K = f^2[BH^+][A^-]/([B][AH])$. [e] [MTBD] = 0.17 mol dm^{-3}. [f] Calculated using Schwezinger's value of pK_a = 25.44 for MTBD.[18] [g] Calculated using Schroeder's value of pK_a = 24.97 for MTBD.[13] [h] Calculated using spectrophotometric equilibrium constant K = 0.352.

constant were obtained from the absorption spectra of equimolar mixtures of **1** and TMG in thin cells. The product concentration range was 0.0005–0.01 mol dm^{-3}. Due to the sufficient difference in pK_a proton transfer is virtually complete and since there is no excess of TMG base the complications from TMG_2H^+ formation are avoided. The spectrum of the ion pair was calculated by extrapolation of the spectral changes to full conversion of free anion into ion pair. Additive absorbance of ions and ion pairs was assumed. A dissociation constant equal to 8.4 × 10^{-3} mol dm^{-3} was evaluated from the drop in absorbance at 560 nm, where the absorbance of ion pairs can be neglected.

Finally, the dissociation constant was estimated from a conductometric titration of a 0.02 mol dm^{-3} solution of **1** with TMG. The results of Kraus–Fuoss treatment of these data are shown in Table 1.

We presume that the values for the plain and homoconjugated ion pair cannot be dramatically different, although that for the homoconjugated ion pair is certainly larger. Chantooni and Kolthoff[10] assumed that the association of homoconjugated ammonium cations with picrate ion, where dissociation constants for plain ion pairs are smaller than those shown in Table 1, was negligible. One would then expect that B_2HA ion pairs formed from nitroalkanes should be entirely dissociated. However, if this were the case the isosbestic point in experiments with addition of $BHClO_4$ would be over the whole range of [BH$^+$] concentrations.

If both assumptions are valid, there is a significant difference in dissociation constants for homoconjugated ion pairs for picrate and nitroalkane systems, whereas the values for plain ion pairs are not far from each other. This prompted us to study the spectral shifts in the spectrum of TMG picrate in acetonitrile. Although conductometric studies showed that TMGHPi is extensively dissociated in acetonitrile,[11] upon addition of large amounts of $TMGHClO_4$ some spectral shifts due to ion pairing were still observed. The procedure and concentration ranges were exactly the same as described for system **1**; [TMG] = 0.1 mol dm^{-3}. The spectrum of TMGHPi with no $TMGHClO_4$ added was identical to the spectrum of tetrabutylammonium picrate reported by Chantooni and Kolthoff.[10] With addition of the common ion a shift to shorter wavelengths with an isosbestic point at 364 nm occurred. In contrast to the system **1**, an isosbestic point was observed over the whole range of cation concentrations, up to 0.6 mol dm^{-3}. The hipsochromic shift was much smaller than those found for most amine picrates by Chantooni and Kolthoff.[10] Judging from the position of the isosbestic point there is a possibility that the spectrum of the TMGHPi ion pair is similar to that of triethylammonium picrate, reported in the work of Kolthoff and Chantooni, which was the most red-shifted of all the spectra of the amine–picrate ion pairs. The above experiment suggests that the difference between the dissociation constants for the two types of ion pairs might indeed be larger for amine picrates than for amine nitronates.

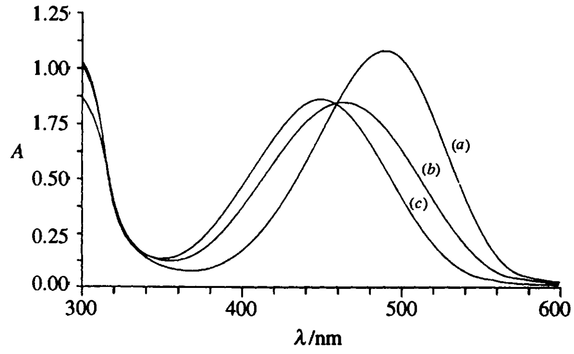


Fig. 2 Visible spectra of the reaction between 2-methyl-1-(4-nitrophenyl)-1-nitromethane **1** (4 × 10^{-5} mol dm^{-3}) and MTBD (0.17 mol dm^{-3}) with increasing concentration of added $MTBDHClO_4$, (BH$^+$). Concentrations of added BH$^+$ are: 0 (*a*); 2.5 × 10^{-3} mol dm^{-3} (*b*); calculated spectrum of the ion pair (*c*).

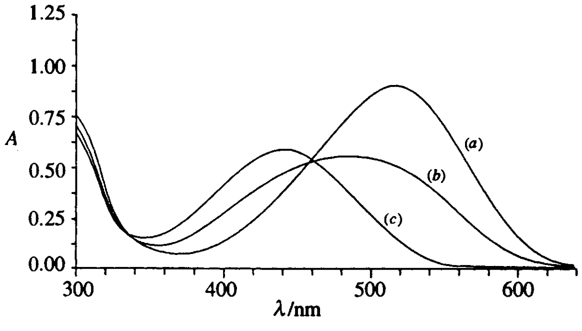


Fig. 3 Visible spectra of the reaction between 2-methyl-1-(4-nitrophenyl)-1-nitropropane **3** (5 × 10^{-5} mol dm^{-3}) and MTBD (0.17 mol dm^{-3}) with increasing concentration of added MTBDH-ClO_4, (BH$^+$). Concentrations of added [BH$^+$] are: 0 (*a*); 4 × 10^{-3} mol dm^{-3} (*b*); calculated spectrum of the ion pair (*c*).

With respect to homoconjugation, the situation seems to be much simpler for the reaction of **1** or **3** with MTBD in acetonitrile (Figs. 2 and 3). In this case an isosbestic point is observed, which indicates that only one ion pair, MTBDH$^+$, A$^-$, is formed. This is in agreement with the infrared spectra of the MTBDH$^+$/MTBD system in acetonitrile, in which homoconjugation of MTBDH$^+$ cannot be seen.[12,13] In addition, the curve for conductometric titration of **1** with MTBD showed no increase after the equivalence point. The dissociation constant resulting from these conductometric data is shown in Table 1.

Despite the fact that for the products of the reactions of **1** and **3** with MTBD we could not bring ion association to completion, the spectrum of the ion pairs and dissociation constant equal to $(9.7 \pm 0.6) \times 10^{-3}$ and $(2.4 \pm 0.2) \times 10^{-3}$ mol dm^{-3}, respectively, were calculated. The values of dissociation constants were established from the drop in absorbance at 540 and 600 nm for systems **1** and **3**, respectively, where the absorption of ion pairs is minimized. The spectra of ion pairs were calculated by extrapolation of spectral changes to full conversion of free anion into ion pair. The spectra of the product without any cation addition were taken as those of free anions.

For the reaction of **1** with MTBD a spectrophotometric study in thin cells, analogous to that described above for system **1** + TMG, gave the ion pair spectrum, shown in Fig. 4 and a dissociation constant which were in satisfactory agreement with the results of other methods (see Table 1). The experiments in thin cells are important, because they were run under entirely different conditions from those with excess BH^+, making it unlikely that the spectral shifts are a result of some unexpected process dependent on the cation concentration.

The spectrum of the ion pair formed by **1** or **3** anions shows a broad band with a maximum at 450 and 445 nm, respectively, which is 45–70 nm less than that for free nitronate ion (for the anion of **3**: $\lambda_{max} = 514$ nm). The intensity of the ion pair absorption bands is considerably lower as compared to the free anion.

It is noteworthy that, with respect to λ_{max}, the spectra obtained by turning free nitronate ions into ion pairs in a concentrated BH^+ cation solution in acetonitrile are similar to those measured in non-polar solvents, where without any BH^+ addition ion pairs are formed.[14–17] The absorption band of the product of the reaction of **1** with TMG in dichloromethane, mesitylene, toluene and THF are characterized by λ_{max} equal 445, 440, 437 and 472 nm.[16] In Caldin and Mateo's paper[16] molar absorptivities of the product ranged from 22 000 in acetonitrile to 33 000 in toluene, while the reduced molar absorptivities of the ion pairs as compared to free anions in acetonitrile are conspicuous (Figs. 1–3). In this paper the molar extinction coefficient of the ion **1** in acetonitrile is 28 500, which is in accord with Rogne and co-workers[17] and the value obtained in the reaction of **1** with DBU.[2] Also, we found that absorption bands of ion pairs in toluene are less intense than those for free ions in acetonitrile (Fig. 5). These findings suggest that molar extinction coefficients of ion pairs, regardless of the solvent, are reduced as compared to free ion.

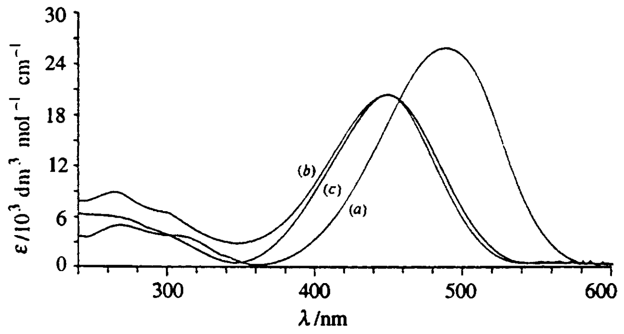


Fig. 4 Spectra of ion pair products of the reactions of **1** with TMG and MTBD, resulting from spectrophotometric experiments in thin cells. The spectra are: (*a*) ions; (*b*) ion pairs (**1** + TMG); (*c*) ion pairs (**1** + MTBD).

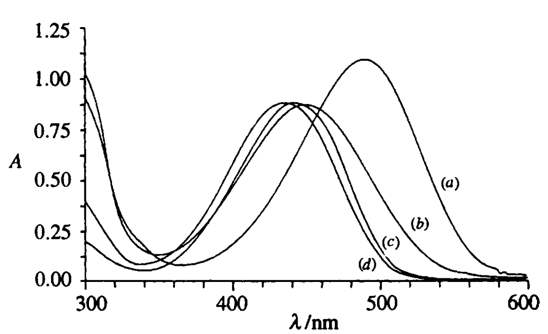


Fig. 5 Spectra of ion and ion pair products of reactions of **1** (4×10^{-5} mol dm^{-3}) with TMG and MTBD in acetonitrile and toluene. The spectra are: (*a*) ions in acetonitrile; (*b*) ion pair product—reaction of **1** with MTBD (7×10^{-3} mol dm^{-3}); (*c*) ion pair product—reaction of **1** with TMG (4.5×10^{-2} mol dm^{-3}) in toluene; (*d*) ion pair product—reaction of **1** with MTBD (7×10^{-3} mol dm^{-3}).

Chantooni and Kolthoff[10] found that the ε_{max} of the undissociated form of anilinium picrate is about 20% less than that of picrate ion, in contrast to all other amine picrates studied. From that they inferred that a small fraction of anilinium picrate might have been present in molecular form. This explanation can be ruled out for most of our nitroalkane systems, since the salt formation constants K_f (Table 1), which can be calculated by dividing equilibrium constant $K = f^2[BH^+][A^-]/([B][AH])$ by K_d, are very large, except that for the **3** + MTBD system, where the ratio $[MTBDH^+,A^-]/[AH]$ derived from data quoted in Table 1 is equal to 27.2, 8.8 or 24.8. The first two values are calculated from a pK_a value for **3** equal to 25.9[2] and two estimates of pK_a for MTBD: 25.44[18] and 24.94.[13] The third value was obtained using an experimental spectrophotometric equilibrium constant $K = 0.352$.[19] The two consistent values seem to be reliable and they lead to a decrease of *ca.* 4%, much less than the values found (Fig. 3). The pK_a values of **1** and TMG needed for calculations of other formation constants K_f are: 20.6[20] and 23.3,[21] respectively.

The difference in λ_{max} between THF and other non-polar solvents observed by Caldin and Mateo was also present for reactions of **1** with benzimidamides[20] and could be explained by assuming that in the ion pair product $TMGH^+$ is hydrogen bonded not only to nitronate anion but also to a THF molecule while the other non-polar solvents are not as good hydrogen bond acceptors as THF. As a result the spectrum in THF should be similar to the spectrum of a homoconjugated ion pair.

The importance of hydrogen bonding in the ion association of nitronates is consistent with the fact that when tetraethylammonium, unable to form hydrogen bonds, was added to products of the reaction of **1** with TMG or PMG, only a slight shift to shorter wavelengths was observed, and that only for $[NEt_4^+] > 0.1$ mol dm^{-3}. This piece of evidence also suggests that the ionic strength effect on the spectra of individual product species is negligible.

The dissociation constant for **3** + MTBD reaction product is about four times smaller than the value for **1** + MTBD reaction product, despite the steric hindrance in molecule **3** that makes the anion bigger. Apparently the hydrogen bond in the latter ion pair is weaker. Perhaps this is due to the weaker coupling of the nitronate group with the 4-nitrophenyl ring in anion **3** than in anion **1**, forced by the steric hindrance. It is noteworthy that the molar absorptivity of anion **3** is considerably smaller than those for less sterically crowded nitronate anions.[21]

In contrast to nitroalkanes, the spectra of nitriles such as 4-nitrophenylcyanomethane **4** and bis(4-nitrophenyl)cyanomethane **5** or trinitrotoluene TNT in concentrated buffer solutions composed of a guanidine such as TMG, PMG or 2-phenyltetramethylguanidine and its perchlorate were identical to those of free anions. It seems plausible that the anions of nitriles and trinitrotoluene simply do not associate with BH^+. The possibility that the spectra of free ions and ion pairs are exactly the same is extremely unlikely, even if the ion pairs were the so-called 'solvent separated ion pairs'.

In conclusion, the relatively strong tendency of alkanenitronates to form hydrogen-bonded ion pairs in acetonitrile must be stressed. The following order of tendency to associate with guanidine bases cations was established: (4-nitrophenyl)-alkanenitronate ~ picrate > anions of nitrophenylcyanoalkanes or TNT.

As far as our kinetic studies of deprotonation of the C-acids in acetonitrile are concerned, one does need to be aware of complications from ion association when the rates or equilibria of deprotonation of a nitroalkane are measured in buffer solutions containing a guanidine base and its salt.

Acknowledgements

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