PERKIN 2

Effect of steric hindrance on the rates and kinetic isotope effects of the reactions of 1-nitro-1-(4-nitrophenyl)alkanes with TBD and MTBD bases in THF

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The rates of the reactions of 1-nitro-1-(4-nitrophenyl)alkanes and their deuteriated analogues with two bicyclic guanidines of comparable basicity, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), in tetrahydrofuran have been measured. The results are discussed in terms of the effects of steric hindrance in the C-acid and the base on the rates and deuterium kinetic isotope effects (KIEs). The reactions of TBD are 118–287 times faster than reactions of MTBD with the same nitroalkanes. The stabilization of the transition state of the TBD reactions by the N–H···O hydrogen bond is plausible. With the most sterically crowded C-acid, the steric hindrance in the base gives a reduced deuterium KIE. Deuterium KIEs for the reactions of MTBD with various C-acids decreases with the steric hindrance in the C-acid but the reverse is true for TBD reactions. Results of this work disagree with the notion that steric hindrance leads to enhanced kinetic isotope effects.

Introduction

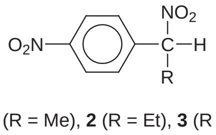
Since hydrogen atoms are usually relatively well exposed to nucleophilic attack, proton transfer reactions in general are not particularly sterically demanding.[1] However, when bulky substituents are crowded around the reaction site the effect of steric hindrance can be observed.[2,3] The effect of steric hindrance on the deuterium kinetic isotope effect (KIE) has been of interest for several decades. Initially it was found that the KIE increased with steric hindrance;[4,5] this was ascribed to removal of the solvent molecules from the vicinity of the reaction site or a steeper energy barrier *i.e.* factors believed to increase proton tunnelling. Since then steric hindrance has been regarded as one of the most important factors leading to increased deuterium KIEs.[6–8] In further studies, even though they were designed to find an increase in the KIE due to steric hindrance, it was found that steric hindrance in both the base and C-acid may actually reduce the KIE.[9,10] However, bulky substituents not only cause repulsive interactions in the transition state, they can also change other parameters influencing the KIE, such as ΔG°, so the discussion of steric effects is doomed to be difficult.

In the last decade some new very strong and sterically crowded bases have become commercially available, among them two bicyclic guanidines of very similar basicity in acetonitrile: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD). These two bases, differing by just one frontal methyl group, have recently been used in several kinetic studies of deprotonation reactions of C-acids in acetonitrile, although KIEs were beyond the scope of these studies. The rates with TBD were always faster than with MTBD. The ratios $k_{\mathrm{TBD}}/k_{\mathrm{MTBD}}$ varied considerably with the structure of the C-acid and were 4–7, 26 and 55 for deprotonation of diarylmethanes,[11] ethyl bis(4-nitrophenyl)acetate[12] and dimethyl (4-nitrophenyl)malonate,[13] respectively. These effects were discussed in terms of greater basicity of TBD than MTBD, steric hindrance in the MTBD molecule and the hypothetical additional hydrogen bond formed in the transition state of the TBD reaction.

However, the first factor must be of secondary importance, since pK_a values for TBD and MTBD are almost equal while the rate ratios are large for some reactions leading to unusual Brønsted β values. Therefore it is of interest to study the effect of steric hindrance brought by both reactants—base and C-acid. As a model of the reaction system we chose TBD and MTBD bases having different crowding in the vicinity of the reaction site and a series of three 1-nitro-1-(4-nitrophenyl)alkanes as C-acids to study changes in the rates and deuterium kinetic isotope effects with the growing bulk of the substituent.

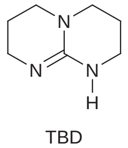
The increase in steric hindrance in the three C-acids caused a decrease in deuterium KIEs for the reactions of the C-acids with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in THF and chlorobenzene.[10] Therefore it is of interest to determine whether this trend will hold with other strong and sterically hindered bases. In this work we chose THF solvent, although pK_a values for the bases in this solvent are not known. The reason for this was in part the earlier study of deprotonation of the same series of C-acids with DBU in acetonitrile[14] in which no effect of steric hindrance on the KIE was found; also an unusual salt effect on the reaction of some nitroalkanes with MTBD in acetonitrile[15] made us think that the MTBD reaction in acetonitrile is complicated in some unknown way. Besides, THF is advantageous because the product exists in this solvent solely as hydrogen bonded ion pairs and one does not expect any side reactions of the strong amine base with the solvent or its impurities that could lead to formation of other anionic bases taking part in the deprotonation of the C-acid. The other bases could exist in small quantities, but show high reactivity with little steric hindrance. This makes acetonitrile potentially unsuitable for studies of steric hindrance involving bases as strong as MTBD and TBD.

The system under study consists of C-acids (**1**–**3**) with

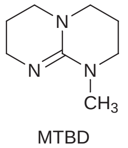


1 (R = Me), **2** (R = Et), **3** (R = Pr^i)

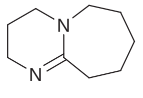
increasing bulk of R substituents and strong cyclic bases with different steric hindrance.



TBD
pK_a = 24.7–26



MTBD
pK_a = 25–25.4



DBU
pK_a = 23.9

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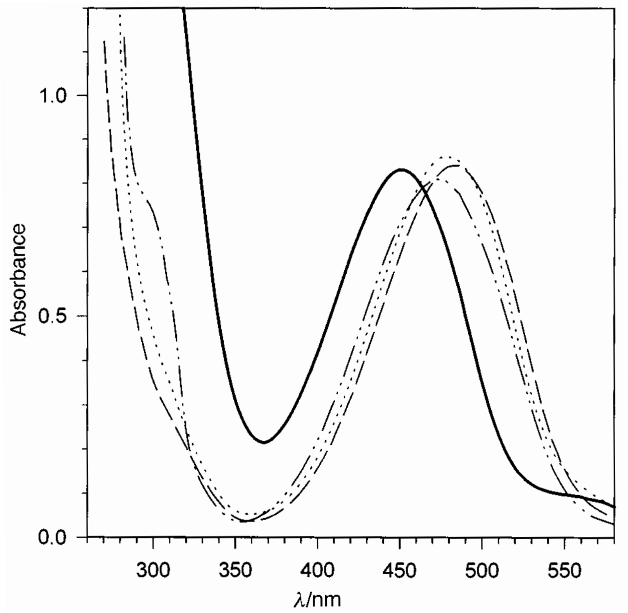
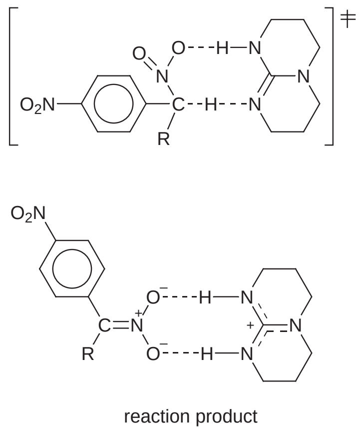


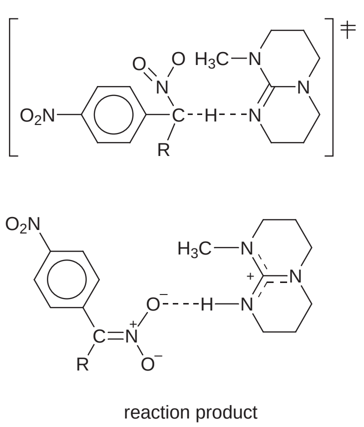
Fig. 1 Spectra of the products of reactions of 1-nitro-1-(4-nitrophenyl)propane (2.5×10^{-5} M) and strong guanidine/amidine bases in THF solvent: TMG (–––), DBU (-----), MTBD (–-–-–), TBD (——)

Results and discussion

In THF solvent, the reaction products of proton transfer reactions between 1-nitro-1-(4-nitrophenyl)alkanes and TBD and MTBD bases are coloured, hydrogen bonded ion pairs (Schemes 1 and 2); λ_{max} are indicated in Fig. 1.



Scheme 1 Transition state and the product of the reaction of TBD with 1-nitro-1-(4-nitrophenyl)alkanes in THF



Scheme 2 Transition state and the product of the reaction of MTBD with 1-nitro-1-(4-nitrophenyl)alkanes in THF

Table 1 Rate constants for the reactions of 1-nitro-1-(4-nitrophenyl)-alkanes with TBD base in THF solvent

T/°C	$c_{TBD}/10^{-3}$ M	k_{obs}/s^{-1}	$k_f/M^{-1}\ s^{-1}$	k_H/k_D
1 H				
10	1–5	12.0–61.7	12 500 ± 300	
15	1–5	14.1–71.0	14 000 ± 300	
25	1–5	19.2–95.6	19 000 ± 200	
35	1–5	25.9–127.6	25 600 ± 200	
1 D				
10	1–5	1.0–5.0	1 010 ± 20	12.3 ± 0.6
15	1–5	1.4–6.6	1 300 ± 20	10.8 ± 0.3
25	1–5	2.1–9.8	1 950 ± 10	9.7 ± 0.1
35	1–5	2.9–14.6	2 930 ± 30	8.7 ± 0.2
2 H				
10	1–5	4.4–23.3	4 720 ± 30	
15	1–5	5.0–27.5	5 650 ± 50	
25	1–5	6.7–34.3	6 800 ± 300	
35	1–5	9.3–44.5	8 700 ± 200	
2 D				
10	1–5	0.35–1.7	332 ± 9	14.2 ± 0.5
15	1–5	0.43–2.1	404 ± 7	14.0 ± 0.4
25	1–5	0.65–3.1	560 ± 5	12.1 ± 0.6
35	1–5	0.97–4.3	830 ± 20	10.4 ± 0.6
3 H				
10	1–5	0.56–2.7	540 ± 10	
15	1–5	0.69–3.2	630 ± 10	
25	1–5	0.94–4.5	880 ± 20	
35	1–5	1.4–6.0	1 140 ± 30	
3 D				
10	1–5	0.034–0.172	35 ± 1	15.4 ± 0.8
15	1–5	0.044–0.215	43 ± 1	14.7 ± 0.6
25	1–5	0.066–0.302	59 ± 1	14.8 ± 0.6
35	1–5	0.0961–0.509	106 ± 5	10.8 ± 0.8

With TBD, the absorption bands of the reaction products are shifted towards shorter wavelengths by 20 nm as compared to the reaction products with MTBD. An even larger difference in λ_{max} of *ca.* 25–30 nm is found when the spectra of TBD and DBU alkanenitronates in THF are compared. The remarkable blue shift observed for TBD salts is consistent with the proposed double hydrogen bonding of the nitronate group by $TBDH^+$. Such blue shifts offer an easy, although not as equivocal as for crystal structures, indication of double hydrogen bonding of the nitronate group.

In analogy to previous studies of the reaction of phenylnitromethane with TBD and MTBD in non-polar aprotic solvents, a larger equilibrium constant is expected for the reactions of TBD compared with MTBD. In acetonitrile, TBD ($pK_a = 25.96$[16] or 24.7[11]) is a slightly stronger or a slightly weaker base than MTBD (25.43[16] or 24.97[11]). However, in benzene, the much higher equilibrium reactivity of TBD with nitroalkanes compared with MTBD, could not be explained by greater 'inherent' basicity of TBD, but rather by the double hydrogen bond complex formed between the $TBDH^+$ cation and nitronate anions.[17,18] This double hydrogen bond was directly observed in the crystalline structure of TBD phenylmethanenitronate.[17,18]

The rate constants for the reaction of 1-nitro-1-(4-nitrophenyl)alkanes with TBD and MTBD in THF are shown in Tables 1 and 2. The kinetic scheme is the same as in a previous study with DBU base.[10] Due to the larger basicity of TBD and MTBD than DBU, reactions with base in excess over C-acid are virtually irreversible, except for the reaction of **3** with MTBD. The plot of k_{obs} *vs.* base concentration for the reaction of MTBD with **3** in THF (Table 2) shows a measurable intercept, while for the reaction of TBD (Table 1) this intercept is zero

Table 2 Rate constants for the reactions of 1-nitro-1-(4-nitrophenyl)-alkanes with MTBD base in THF solvent

T/°C	$c_{\mathrm{MTBD}}/10^{-2}$ M	$k_{\mathrm{obs}}/10^{-2}$ s^{-1}	k_f/M^{-1} s^{-1}	k_H/k_D
1 H				
10	1–5	81–426	86 ± 1	
15	1–5	105–513	103 ± 2	
25	1–5	151–806	161 ± 1	
35	1–5	223–1101	223 ± 7	
1 D				
10	1–5	5.5–33.6	7.0 ± 0.1	12.2 ± 0.2
15	1–5	8.0–40.8	8.3 ± 0.1	12.5 ± 0.3
25	1–5	12.9–71.6	14.8 ± 0.2	10.9 ± 0.1
35	1–5	25.8–125	24 ± 1	9.2 ± 0.6
2 H				
10	1–5	21–125	27 ± 2	
15	1–5	29–139	28 ± 1	
25	1–5	47–211	46 ± 1	
35	1–5	72–319	63 ± 4	
2 D				
10	1–5	1.5–10	2.14 ± 0.08	13 ± 1
15	1–5	1.7–12	2.61 ± 0.04	11 ± 1
25	1–5	3.1–22	4.61 ± 0.06	10.1 ± 0.2
35	1–5	6.0–34	7.01 ± 0.05	8.9 ± 0.6
3 H				
10	1–5	2.5–8.6	1.54 ± 0.04	
15	1–5	4.4–11	1.78 ± 0.05	
25	1–5	9.9–22	3.05 ± 0.09	
35	1–5	23–44	5.3 ± 0.1	
3 D				
10	1–5	0.12–0.69	0.134 ± 0.006	11.5 ± 0.6
15	1–5	0.22–0.94	0.186 ± 0.008	9.6 ± 0.5
25	1–5	0.39–1.84	0.36 ± 0.01	8.5 ± 0.5
35	1–5	0.68–3.19	0.64 ± 0.04	8.2 ± 0.6

within two standard deviations. Then the equilibrium constant for the TBD reaction is larger than 11 000 M^{-1} and is considerably greater than that of 44 M^{-1} for the MTBD reaction, calculated as the ratio of the slope and the intercept. This seems to reflect the double hydrogen bond in the product of the TBD reaction (Scheme 1). The equilibrium constant for the reaction of MTBD with **3**, in turn, is 10 times larger than the equilibrium constant of the faster reaction between **3** and DBU in THF.[10]

This shows that the Brønsted relationship does not hold for the reactions of nitroalkanes with bicyclic guanidines/amidines. Such breakdowns frequently indicate steric hindrance but in the case of TBD base there is another important factor, *i.e.* an additional hydrogen bond both in the transition state and in the product.

Since formation of N–H···O hydrogen bonds, with a hydrogen that was initially attached to a carbon atom of the C-acid, lags behind the proton transfer from carbon, the pK_a values, even though not measured in the same solvent, may actually represent the relative basicity of the bases better than the equilibrium constants for their reactions with nitroalkanes in THF. That is as far as MTBD and DBU bases are considered. With the TBD base, which has one hydrogen atom capable of forming a hydrogen bond, it is likely that there is already one N–H···O hydrogen bond in the transition state (Scheme 1). In this system then, there would be an additional hydrogen bond, both in the transition state and in the product (Scheme 1). Thus the exceptional acceleration of the TBD reaction would be parallel to its enhanced equilibrium constant, which should give a good correlation between the rates of reaction of different bases including TBD and the equilibrium constants in THF.

Table 3 Rate ratios for proton transfer reactions between 1-nitro-1-(4-nitrophenyl)alkanes and various strong bases in THF solvent at 25 °C[a]

	$k_R/k_{\mathrm{Pr^i}}$			
R	DBU[b] pK_a = 23.9	MTBD pK_a = 25–25.4	TBD pK_a = 24.7–26	$k_{\mathrm{TBD}}/k_{\mathrm{MTBD}}$
Me	103.2 (262)	52.8	21.7 (6223)	118
Et	28.2 (71.6)	15.2	7.7 (2222)	146
Pr^i	1 (2.54)	1	1 (287)	287

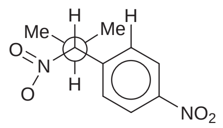
[a] Figures in parentheses are the ratios of second order rate constants k_R and the rate constant for the slowest reaction of **3** with MTBD. [b] Data from ref. 10.

However, for our purpose it is convenient to accept pK_a values as a measure of 'inherent' basicity of all three bases and treat the hypothetical N–H···O hydrogen bond in the transition states for TBD reactions as an additional stabilizing effect.

The reactions of TBD are much faster than the deprotonations with MTBD base of nearly equal pK_a (Table 3). The TBD reactions are also relatively less sensitive to the steric hindrance in the C-acid. It is clear that their $\Delta H^\ddagger$ values (Table 4) are low and do not even increase with the steric hindrance in the C-acid. With MTBD base, the $\Delta H^\ddagger$ values for reactions **1** and **2** are almost identical but they are definitely larger for the reaction of **3**. The reaction with the MTBD base is the slowest, even slower than with DBU, which not only is a weaker base than MTBD by at least one pK_a unit, but also, as already mentioned, its reaction with **3** has a lower equilibrium constant in THF than the reaction of **3** with MTBD. With the steric hindrance in the nitroalkane, the $k_{\mathrm{TBD}}/k_{\mathrm{MTBD}}$ ratios increase from about 120 for proton abstraction from **1** to 290 for **3** (Table 3), and they are much larger than those found in previous studies on reactivity of the two bases. This reflects both steric hindrance and stabilization of the transition state by a relatively strong hydrogen bond (Scheme 1), as compared to the deprotonations of the esters.[12,13]

The reaction with the weakest base, DBU is considerably slower than that with TBD (Table 3), but faster than with MTBD which has 'inherent' basicity comparable to that of TBD. Interestingly, comparison of reactivity of the three bases shows that the replacement of the Me or Et substituent with Pr^i in the C-acid gives the strongest reduction of rate constants with DBU base.

In conclusion, steric hindrance is evident for the reaction of **3** with MTBD and DBU, while in the other cases the increase in the bulk of the alkyl substituent imposes some sterical restraints but repulsive interactions can be avoided. Indeed, analysis of the molecular models of the transition states shows, that at certain configurations the reaction distance can be the same for the reactions of any of the bases with **1** and **2**, and with TBD for the reactions with all three C-acids. In view of the not exceedingly large $\Delta H^\ddagger$ values for the reaction of MTBD with **3** the conformation of **3** in the transition state must be that shown in Scheme 3. This conformation is consistent with the H–H coupling constant found in the NMR spectrum of **3**.[10] If one of the two other conformers obtained by rotation of Pr^i group was to react, large non-bonding interactions would have to be added to $\Delta H^\ddagger$. In the low-energy conformer of **3** shown in Scheme 3, the *ortho*-hydrogen atom of the nitrophenyl ring, one of the oxygen atoms of the nitro group and the two methyl groups are pointed towards the approaching base molecule. To



Scheme 3 Low-energy conformation of 1-nitro-1-(4-nitrophenyl)-2-methylpropane **3**

Table 4 Activation parameters for proton transfer reactions between 1-nitro-1-(4-nitrophenyl)alkanes and various strong bases in THF solvent at 25 °C[a]

	DBU		MTBD		TBD	
R	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
Me	13.8 ± 0.4	−141 ± 2	25.5 ± 0.8	−117 ± 4	18.4 ± 0.8	−101 ± 3
Et	18.0 ± 0.4	−139 ± 1	24 ± 3	−130 ± 10	16 ± 1	−121 ± 4
Pr^i	24.3 ± 0.4	−146 ± 1	34 ± 3	−121 ± 8	19.6 ± 0.4	−123 ± 2

Reactions of deuteriated nitroalkanes

	DBU		MTBD		TBD	
R	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
Me	22.6 ± 0.4	−134 ± 1	34 ± 2	−109 ± 8	30 ± 0.4	−88 ± 2
Et	23.0 ± 0.4	−144 ± 2	33 ± 2	−121 ± 4	24 ± 0.8	−112 ± 4
Pr^i	28.4 ± 0.4	−151 ± 2	43.0 ± 0.4	−109 ± 4	29 ± 3	−110 ± 10

[a] $\Delta H^\ddagger$/kJ mol^{-1}; $\Delta S^\ddagger$/J mol^{-1} K^{-1}.

some extent the structure shown in Scheme 3 resembles sterically crowded triphenylmethanes studied by Terrier *et al.*,[3] where accumulation of *o*-nitro substituents in triphenylmethanes sterically hindered the approach of base to the exocyclic carbon.

The transition state of the TBD reaction is most likely to be stabilized by hydrogen bonding and TBD has relatively good access to the C-acid, even to the most crowded C-acid **3** (Scheme 1). This accounts for the weak sensitivity of these reactions to the steric hindrance in C-acids.

There are two facts that disagree with this concept of stabilization by hydrogen bonding. First, to verify the possible importance of the hydrogen bond in the TS for TBD reactions we can compare k_{TBD}/k_{MTBD} ratios for various C-acids (*i.e.* **1** and **3**) in Table 3. If the hydrogen bond formation in the TS of TBD reactions were a dominant factor, then the effect of the additional hydrogen bond should be the largest for the least crowded C-acid, where the hydrogen bond N–H · · · O could be formed with ease in the transition state of the TBD reaction. As already mentioned, with the steric hindrance in the nitroalkane, the k_{TBD}/k_{MTBD} ratio increases from about 120 for **1** to 290 for **3** reaction. Thus this way the stabilization of the TS for TBD reaction by hydrogen bonding is not confirmed. Secondly, a cyclic rigid structure in the transition state for the TBD reaction due to hydrogen bonding should be reflected in lower $\Delta S^\ddagger$ values for TBD than MTBD reactions. This is not observed (Table 4), since the $\Delta S^\ddagger$ values for MTBD reactions are the same for **3** and lower by about four units for **1** and **2**.

With regard to the first question, molecular models do not predict much steric hindrance for hydrogen bonding of TBD with all three C-acids. Actually, steric crowding in **3** may force the nitro group into a position suitable for hydrogen bonding and this may be the explanation for the nearly equal $\Delta H^\ddagger$ values for the deprotonations of all three acids by TBD (Table 4).

The second disagreement can be explained by the fact that $\Delta S^\ddagger$ is determined by a number of factors and the changes resulting from structural effects can be compensated by solvational changes caused by hydrogen bonding, *i.e.* weaker solvation of charge developing in the transition state stabilized with hydrogen bonding.

The two most sterically hindered reactions of **3** with MTBD and DBU have considerably reduced the KIEs (Table 5). Taking into account that KIEs for the reactions of C-acids with strong amidine or guanidine bases at 25 °C usually range from 10 to 14, this reduction in KIEs for the most hindered reactions is real. It is quite possible that the increase in the KIEs for the relatively unhindered TBD reaction with the bulky alkyl substituent in the C-acid shows the influence of effects other than steric hindrance on the KIE. Should this be true the reduction in the KIE for the reactions of **3** with DBU and MTBD would become even more significant. However, it may be argued that the reactions of TBD with the cyclic transition state cannot be so easily compared to the reactions of MTBD and DBU.

Table 5 Deuterium kinetic isotope effects for the reactions between 1-nitro-1-(4-nitrophenyl)alkanes and various strong bases in THF solvent at 25 °C

	k_H/k_D		
R	DBU[a]	MTBD	TBD
Me	11.4 ± 0.6	10.9 ± 0.1	9.7 ± 0.1
Et	12.1 ± 0.3	10.1 ± 0.2	12.1 ± 0.6
Pr^i	9.7 ± 0.3	8.5 ± 0.5	14.8 ± 0.6

[a] Data from ref. 10.

If KIEs for reactions of different bases with **3** are considered, assuming that the TBD reaction is relatively unhindered, the picture is clear: the steric hindrance in base greatly reduces the KIE. This is not true if reactions of **1** and **2** with TBD and MTBD are compared.

We have to deal with the fact that the KIE for supposedly unhindered TBD reaction is very sensitive to the bulk of the alkyl substituent in C-acid (Table 5). The extent of change comes as a surprise in view of generally moderate variability of KIEs. However, we also observed a similar effect in MeCN solvent[14] so we believe it is real. Clearly KIEs are sensitive to factors other than steric hindrance to a comparable extent. Such an interplay of different factors is going to always happen when one wants to study the effect of steric hindrance on KIEs and this is probably the reason why KIEs sometimes increase but in other cases decrease with the bulk of a substituent irrespective of whether it is positioned in the acid or in the base molecule.[10] This work, in part due to the opposite direction of KIE changes with TBD compared with MTBD and DBU bases, suggests that steric hindrance actually reduces KIEs.

Experimental

A good grade THF was distilled from benzoquinone ketyl and kept under argon. Previously prepared samples of C-acids were used.[10] TBD and MTBD bases (Aldrich) were used without any purification. The purity of the samples of the bases as tested by NMR spectroscopy[11] and titration was satisfactory. The stock solutions of commercial TBD in THF were cloudy, so they were filtered with due caution to protect them from carbon dioxide and moisture and then titrated. The results of the titration were consistent with gravimetric concentration of the base within 1%. The working solutions of bases were made up by dilution of stock solutions.

The rates were measured using an Applied Photophysics stopped flow spectrophotometer at $\lambda_{\max}$ of the product ion-pair (Fig. 1).

At each temperature, observed rate constants were measured for five different concentrations of base (the base was in large excess over C-acid) and the second order rate constants were found from the plots of k_{obs} *vs.* concentration of the base in the normal way.

Acknowledgements

We gratefully acknowledge the financial support from KBN grant 3 TO9A 06914.

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Paper 8/01482E
Received 20*th February* 1998
Accepted 15*th April* 1998