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Influence of Alkyl Groups in Substituted Tetramethylguanidines on the Rate Constants and Deuterium Isotope Effect for the E2 Elimination Reaction

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The kinetics of the E2 elimination reaction of 1,1,1-trichloro-2,2-di(4-nitrophenyl)ethane promoted by substituted alkyltetramethylguanidine $R{-}N{=}C(NMe_2)_2$ (where R = H, Me, Et, Pr^i and Bu^t) are reported and the influence of alkyl groups on the kinetic isotope effects in tetrahydrofuran is discussed.

Deuterium kinetic isotope effects are frequently used as a tool for determining the mechanism of reactions.[1–3] The values of these effects depend on numerous factors such as temperature, pressure, enthalpy of reaction, solvent and steric hindrance of the reacting molecules.[1–3] The role of steric effects, which seems to be the most interesting factor according to various authors, is controversial.[4–8]

In order to determine the influence of steric hindrance in the vicinity of the reaction site of bases on the rate constants and deuterium isotope effects for elimination reactions, four substituted alkyltetramethylguanidines were used. The substituted alkyltetramethylguanidine $R{-}N{=}C(NMe_2)_2$ (R = H, Me, Et, Pr^i and Bu^t) was prepared using the procedure of Kessler *et al.*[9]

The $pK_A^{H_2O}$ values for $R{-}N{=}C(NMe_2)_2$ are 13.6, 13.9, 13.8, 13.9 and 14.3, where R = H, Me, Et, Pr^i and Bu^t, respectively.[10]

In a previous paper[11] the operation of either an E2H or $(E1cB)_I$ mechanism for the elimination reaction of 1,1,1-trichloro-2,2-di(4-nitrophenyl)ethane promoted by tetramethylguanidine in tetrahydrofuran (THF) was established [eqn. (1)].

$$Ar_2CHCCl_3 + HN{=}C(NMe_2)_2 \longrightarrow Ar_2C{=}CCl_2 + HCl{\cdot}HN{=}C(NMe_2)_2 \qquad (1)$$

The transition states for the E2H and $(E1cB)_I$ mechanisms are shown in Fig. 1. The interaction of the base with the alkane in these transition states is different, but the degree of proton abstraction is similar in both cases, thus the C=C double bond and the strength of the C–Cl bond differentiate the two transition states.

In the present communication the observed rate constants were determined from kinetic runs carried out with an excess of base using a Specord UV-VIS spectrophotometer and then rate constants (k_H, k_D) were determined from the relation $k_{obs} = k_{H(D)}$ [B] by using six different base concentrations: [B] = 0.001–0.02 mol dm^{-3}. The rate constants and deuterium kinetic isotope effects for the elimination reaction are shown in Table 1.

For the elimination reaction examined the alkylated bases show a large increase in the rate constant k_H which then gradually decreases with increasing bulk of the substituted alkyl groups. A distinct decrease in the value of the kinetic isotope effect k_H/k_D is observed for the alkylated bases in comparison with the parent tetramethylguanidine (6.6 to 4.86).

For the reaction with alkylated bases the values of the kinetic isotope effect are virutally the same, with a slight tendency to decrease with increasing bulk of the alkyl substituent (5.3 to 4.9). Therefore, in the transition state there is an elongation of the $C\cdots H\cdots N$ bond. This change in bond length increases the distance of proton transfer and it is responsible for the change of isotope effect for the reaction studied. The structures of the $(E1cB)_I$ transition states for the reaction of the diarylalkane with tetramethylguanidine and *tert*-butyltetramethylguanidine are shown in Fig. 2.

Table 1 Rate constants and deuterium isotope effects (± standard deviations) for the elimination reaction of 1,1,1-trichloro-2,2-di(4-nitrophenyl)ethane promoted by substituted alkyltetramethylguanidine $R{-}N{=}C(NMe_2)_2$ in THF.

$RN{=}C(NMe_2)_2$	$k_H/dm^3mol^{-1}s^{-1}$	$k_D/dm^3mol^{-1}s^{-1}$	k_H/k_D
H	0.461	0.072	6.6
Me	3.86(± 0.08)	0.729(± 0.009)	5.30(± 0.13)
Et	3.47(± 0.11)	0.669(± 0.025)	5.18(± 0.26)
Pr^i	2.07(± 0.09)	0.414(± 0.009)	5.00(± 0.25)
Bu^t	1.75(± 0.04)	0.36(± 0.04)	4.86(± 0.56)

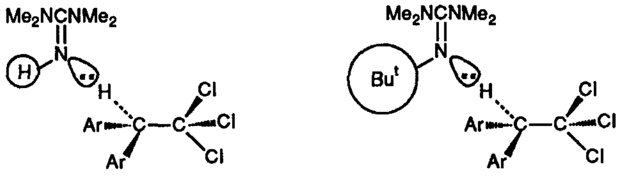
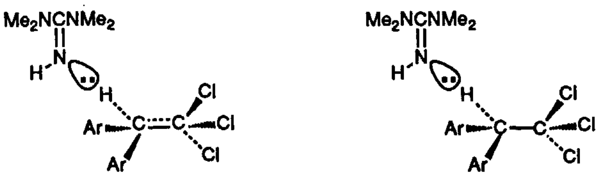


Fig. 2



E2H

$(E1cB)_I$

Fig. 1

The steric effect caused by the bulkiness of the alkyl group is revealed in the decrease of the reaction rate while the strength of the bases remains virtually constant. This effect in $N\text{-}sp^2$ hybridized bases is much smaller than that observed for proton transfer to $N\text{-}sp^3$ hybridized bases, in which there is stronger interaction between the free electron pair and alkyl substituents.

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