

Spontaneous and Base-catalysed Elimination from 1-Ferrocenylalkyl Cations

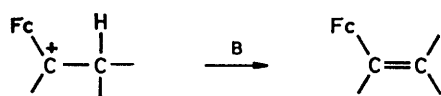
By Clifford A. Bunton,* Nelson Carrasco, and Faegh Davoudzadeh, Department of Chemistry, University of California, Santa Barbara, California 93106, U.S.A.

William E. Watts,* School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland BT52 1SA

The rate constants of proton elimination from 1-ferrocenylalkyl cations $\text{Fc}\overset{+}{\text{C}}(\text{R}^1)\text{CH}_2\text{R}^2$ with unhindered tertiary amines in $\text{H}_2\text{O}-\text{MeCN}$ follow the Brønsted catalysis relation; the values of β are 0.32 for $\text{Fc}\overset{+}{\text{C}}(\text{Ph})\text{CH}_2\text{Bu}^t$ and 0.45 for $\text{Fc}\overset{+}{\text{C}}\text{Me}$. Oxygen bases and sterically hindered amines are much less effective reagents than unhindered amines of similar basicity. The overall kinetic hydrogen isotope effects on elimination from $\text{Fc}\overset{+}{\text{C}}(\text{Ph})\text{CX}_2\text{Bu}^t$ ($\text{X} = \text{H}$ and D) go through maxima with increasing strength of base and $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ values are 4.2, 6.7, and 4.2 for reactions with water, pyridine, and quinuclidine, respectively. Chloride ion speeds the spontaneous reaction of $\text{Fc}\overset{+}{\text{C}}(\text{Ph})\text{CH}_2\text{Bu}^t$ and increases the kinetic isotope effect, but inhibits the reaction with HO^- without affecting the isotope effect. These observations suggest that both ion-pairing and initial-state conformation are important in determining overall reactivity, the Brønsted β value, and $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$.

DEPROTONATION of a carbocation, or an ion-pair, is the fast step in the *E1* mechanism of elimination and only relative rate constants for deprotonation of transient carbocations can be obtained from addition-elimination kinetic product ratios; † but Rappoport has argued² that nucleophilic and base attack on intermediate carbocations in $\text{S}_{\text{N}}1-\text{E1}$ reactions is typically diffusion-controlled. Kinetic study is therefore difficult because relatively long-lived organic carbocations (*e.g.* triaryl-methyl cations) do not undergo deprotonation.

However, a structurally diverse range of carbocations stabilised by an organometallic group is known.³ In particular, there is available a series of 1-ferrocenylalkyl cations which give proton elimination to a base (Scheme 1);⁴ such cations are usually sufficiently stable to be



(Fc = ferrocenyl)

SCHEME 1

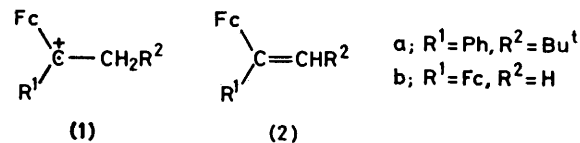
isolated in salts or preformed in solution.^{3b} The base B may be a water molecule of the solvent or an added neutral or anionic proton-acceptor and, in favourable cases, both deprotonation of the carbocation and protonation of the resulting alkene can be studied kinetically.^{4a} Both reactions occur preferentially from the direction *exo* to the ferrocenyl group but this preference may be outweighed by adverse steric-conformational factors.^{3b,4b} Our aim was to examine spontaneous and base-promoted proton elimination from preformed 1-ferrocenylalkyl cations and, in particular, to measure the Brønsted coefficient β and the kinetic β -hydrogen isotope effects.

† For a discussion of the mechanisms of elimination reactions and, in particular, the nature of the transition state in *E2* reactions, see ref. 1.

Some results on spontaneous elimination have been published.^{4a}

Bimolecular *E2* eliminations are believed to encompass a spectrum of mechanisms ranging from *E1cB*-like in which proton loss leads loss of the nucleofugal group, with a carbanion-like transition state, to *E1*-like with a carbocation-like transition state.^{1,5} It has also been suggested that the base may interact with the departing β -proton and the α -carbon atom, and a distinction has been made between this *E2c* mechanism and the *E2h* mechanism in which the dominant interaction in the transition state is between base and proton.⁶ Information concerning the mechanism of proton loss from a preformed carbocation should therefore help our understanding of *E2* mechanisms.

We used two cations, as tetrafluoroborate salts, *viz.* the 1-ferrocenyl-1-phenyl-3,3-dimethylbutylium ion (1a) and the 1,1-diferrocenylethyl cation (1b) which were prepared by reactions of the corresponding alcohols with aqueous HBF_4 . The kinetic hydrogen isotope effect



upon elimination was measured by using the 2,2-dideuterio-derivative of (1a); the corresponding alcohol was obtained by addition of phenyl-lithium to $\text{FcCOCD}_2\text{Bu}^t$ which was prepared from $\text{FcCOCH}_2\text{Bu}^t$ by base-promoted H-D exchange (Experimental). We found earlier that elimination from (1a) gives only one alkene (2a), probably the *E*-stereoisomer.^{4a} Our choice of bases was restricted because nucleophiles add readily to ferrocenylalkylium ions;⁷ for the most part we used tertiary amines, although we also used some oxygen bases and corrected for concomitant nucleophilic addi-

TABLE I
Rate constants for deprotonation of the carbocations (1) ^a

Base	pK _a ^b	Rate constants ^c	
		(1a)	(1b)
1 H ₂ O	-1.43 (-1.75 ^d)	0.000545 ⁱ	0.015
2 Pyridine	4.48 (5.17 ^e)	0.0241	2.63
3 4-Picoline	5.23 (6.02 ^e)	0.0359	2.87
4 MeCO ₂ ⁻	6.19 (4.76 ^e)	0.0250	
5 Quinuclidin-3-one	6.97 (7.27 ^f)	0.0967	47.1
6 N-Methylmorpholine	7.32 (7.38 ^f)	0.0037	
7 3-Chloroquinuclidine	8.19	0.302	222
8 DABCO	8.73 (8.80 ^g)	0.662	382
9 Me ₃ N	9.44 (9.76 ^h)	0.382	448
10 N-Methylpiperidine	9.62 (10.08 ^h)	0.045	
11 Quinuclidin-3-ol	9.92 (9.71 ^f)	0.812	508
12 Et ₃ N	10.18 (10.65 ^h)	0.0098	276
13 Pr ⁱ ₃ NEt	10.64	0.010	59.2
14 Quinuclidine	10.82 (10.88 ^f)	2.23	1480
15 HO ⁻	17.03 (15.75 ^d)	2.54	1120
16 Me ₂ NBu [†]		0.017	

^a In H₂O-MeCN (1:1 w/w) at 25.0°; BF₄⁻ salts of the cations were used. ^b Values in parentheses are for water. ^c Second-order rate constants in l mol⁻¹ s⁻¹ except for the water reaction where the first-order rate constant in s⁻¹ is given. ^d R. P. Bell, 'The Proton in Chemistry,' Chapman and Hall, London, 1973, 2nd edn. ^e H. C. Brown in 'Determination of Organic Structures by Physical Methods,' eds. E. A. Braude and F. C. Nachod, Academic Press, New York, 1955. ^f D. S. Kemp and M. S. Casey, *J. Am. Chem. Soc.*, 1973, **95**, 6670. ^g C. D. Ritchie, D. J. Wright, D.-S. Huang, and A. A. Kamego, *ibid.*, 1975, **97**, 1163. ^h H. K. Hall, *ibid.*, 1957, **79**, 5441. ⁱ A value of 4.9 × 10⁻⁴ s⁻¹ was reported earlier (ref. 4a).

tion. Reactions were conducted in H₂O-MeCN (1:1 w/w) at 25.0° and rates of disappearance of the carbocations were followed spectrophotometrically (Experimental). Acid dissociation constants of the amine hydrochlorides and the oxygen acids were measured potentiometrically in the same solvent.

RESULTS

Base-promoted Eliminations.—The second-order rate constants (*k*^{ene}/*q*) for deprotonation of the carbocations (1a and b) and the pK_a values for the conjugate acids of the bases used are in Table 1. For the reactions with sterically unhindered amines, the results fit the Brønsted catalysis equation, adjusted for statistical factors [equation (1) ⁸

$$\log(k^{\text{ene}}/q) = \beta[\text{p}K_{\text{a}} + \log(p/q)] + c \quad (1)$$

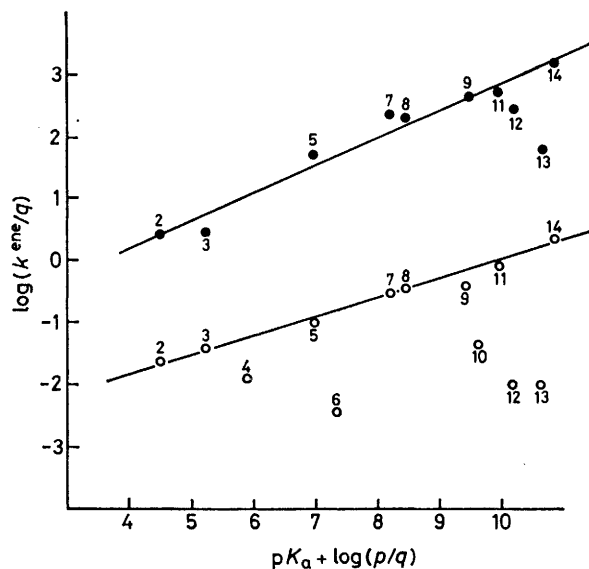
where *c* is a constant, *q* is the number of equivalent sites on the base which can accept a proton in the forward reaction, and *p* is the number of equivalent protons which can be transferred from the acid in the reverse reaction]. For both carbocations, we take *p* = 1 and *q* = 1 for all the bases except acetate ion and DABCO (*i.e.* 1,4-diazabicyclo[2.2.2]-octane) where *q* = 2.

For reactions of the carbocations (1a and b) with unhindered tertiary amines, equation (1) is obeyed over *ca.* 7 log units of basicity (Figure). The slopes β of these plots are 0.32 and 0.45 for reactions of (1a and b), respectively, suggesting that proton transfer is far from complete in the transition states for elimination.^{9a} We see no curvature in these plots, but this may be because we were unable to use a wider range of basicity.

Oxygen bases are much less effective for deprotonation than nitrogen bases of similar basicity. This behaviour is not unusual and probably reflects the differing solvation requirements of a proton-transfer equilibrium of oxygen acids and bases, and a rate-limiting proton transfer (Scheme 2).

The change of solvation in going from the base B to the transition state, relative to that in going from B to BH⁺, will

depend on the charge on the base. Water and hydroxide ion are often less effective as kinetic bases than expected from their nominal basicities, but acetate ion is also relatively ineffective. We also found carbonate ion to be a poor deprotonating agent but we did not obtain a good value for the second-order rate constants for its reactions, in part because the low solubility of Na₂CO₃ in aqueous aceto-

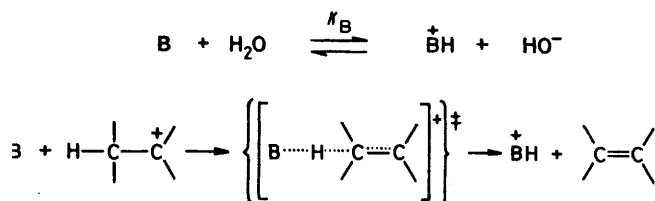


The Brønsted catalysis relation for deprotonation of FcC⁺(Ph)-CH₂Bu⁺ (○) and Fc₂C⁺Me (●); the key to the bases is in Table 1

nitrile limited the concentration. The rate constants for the reactions with the oxygen bases appear to follow a Brønsted relation with β being approximately half that found for reactions with the unhindered amines, but we place little reliance on this observation which is based on only three data points.

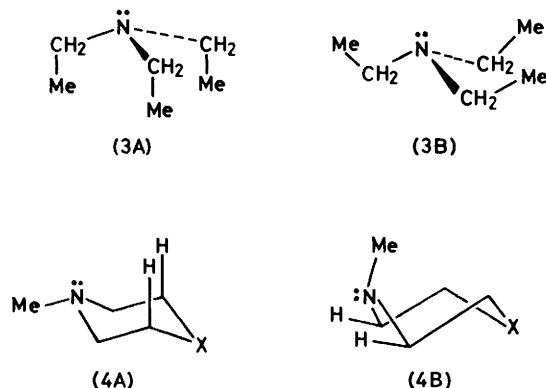
Deprotonations of the carbocations with the sterically

more hindered tertiary amines (bases 6, 10, 12, 13, and 16; Table 1) are all much slower than expected from the pK_a values. The amino-groups in the quinuclidines and DABCO are not screened by adjacent groups. While triethylamine can adopt the conformation (3A) in which the nitrogen atom



SCHEME 2

is similarly exposed, this is energetically unfavourable with respect to other conformations, of which (3B) is an extreme, in which access to the amino-group is hindered. There will be similar unfavourable steric effects upon proton transfer to *N*-methyl-morpholine and -piperidine where access to the



nonbonded electron pair on nitrogen will be hampered by the methyl and methylene groups (*cf.* 4A and B). Deviations of the data points for reactions of the carbocations with these hindered amines (Figure) from the Brønsted relation may then reflect steric hindrance to proton transfer.

TABLE 2

Kinetic hydrogen isotope effects on deprotonation of (1a) (BF_4^-)^a

Base	$10^2 k^{ene}/l \text{ mol}^{-1} \text{ s}^{-1}$ ^b	k_H^{ene}/k_D^{ene}
H ₂ O	0.0545 (0.0130)	4.2
Pyridine	2.41 (0.361)	6.7
4-Picoline	3.59 (0.545)	6.6
Quinuclidin-3-one	9.67 (1.56)	6.2
DABCO	66.2 (12.2)	5.4
Me ₃ N	38.2 (7.67)	5.0
Quinuclidine	223 (53.3)	4.2
HO ⁻	254 (67.0)	3.8

^a In H₂O-MeCN (1:1 w/w) at 25.0°. ^b Second-order rate constants for the dideuterio-derivative are in parentheses. ^c First-order rate constants in s⁻¹.

Hydrogen Isotope Effects.—The overall kinetic isotope effect upon carbocation deprotonation is the product of the primary effect on the transfer of a proton or deuteron and the secondary effect due to the change in hybridisation at the β -carbon atom from sp^3 towards sp^2 .¹⁰ Kinetic hydrogen isotope effects on deprotonation often go through maxima with a monotonic change in strength of base.¹¹

Our results (Table 2) fit this pattern, although we could not use bases with strengths between those of water and pyridine. The maximum overall isotope effect upon deprotonation of (1a) was observed for reaction with pyridine, and the value of $k_H^{ene}/k_D^{ene} = 6.7$ is considerably larger than that of 4.2 for reaction with water. As indicated earlier, these overall isotope effects overestimate the magnitude of the primary isotope effect upon deprotonation. If rehybridisation of the β -carbon atom from sp^3 to sp^2 is complete in the transition state, the secondary isotope effect (k_H^{ene}/k_D^{ene}) would be *ca.* 1.2 and this would decrease with decrease in the extent of proton transfer in the transition state.¹² Application of the Hammond postulate to proton transfer suggests that there would be least transfer (and rehybridisation) with the strongest base,^{9b} which gives the lowest overall isotope effect (Table 2).

If we assume that the maximum observed isotope effect of *ca.* 6.7 for reaction of (1a) with pyridine corresponds to extensive C-H bond-breaking, the primary isotope effect will be *ca.* $6.7/1.2 = 5.6$. The secondary isotope effect should be smallest for reactions with the most reactive bases, where the change in hybridisation in formation of the transition state is least. Therefore, part of the difference in the overall kinetic hydrogen isotope effects for reactions with the least and most reactive amines (pyridine and quinuclidine, respectively) should be due to changes in the secondary isotope effect.

However, the secondary isotope effect for reaction of (1a) with water should be relatively large (*e.g.* close to 1.2, assuming a relatively 'late' transition state), so that the primary kinetic isotope effect should be *ca.* $4.2/1.2 = 3.5$, and much smaller than that for reaction with pyridine.

Salt Effects.—We found earlier that added chloride ion speeds and added perchlorate ion retards spontaneous deprotonation of 1-ferrocenylalkyl cations in aqueous media.^{4a} We now find that added chloride ion slightly increases and added perchlorate ion slightly decreases the overall kinetic hydrogen isotope effect for elimination from (1a) in H₂O-MeCN (1:1 w/w); lithium and sodium chlorides have similar effects (Table 3). Both chloride and perchlorate ions retard elimination with hydroxide ion, but do not change the overall isotope effect.

TABLE 3

Salt effects upon deprotonation of (1a) (BF_4^-)^a

Salt	Reactions with solvent		Reactions with HO ⁻	
	$10^4 k^{ene}/s^{-1}$ ^b	k_H^{ene}/k_D^{ene}	$k^{ene}/l \text{ mol}^{-1} \text{ s}^{-1}$ ^b	k_H^{ene}/k_D^{ene}
None	5.45 (1.30)	4.2	2.54 (0.67)	3.8
0.2M-NaCl	19.4 (3.34)	5.8	1.27 (0.333)	3.8
0.2M-LiCl	16.9 (3.26)	5.2		
0.5M-NaClO ₄	2.83 (0.79)	3.6	0.411 (0.104)	3.95

^a In H₂O-MeCN (1:1 w/w) at 25.0°. ^b Values in parentheses are for the dideuterio-derivative.

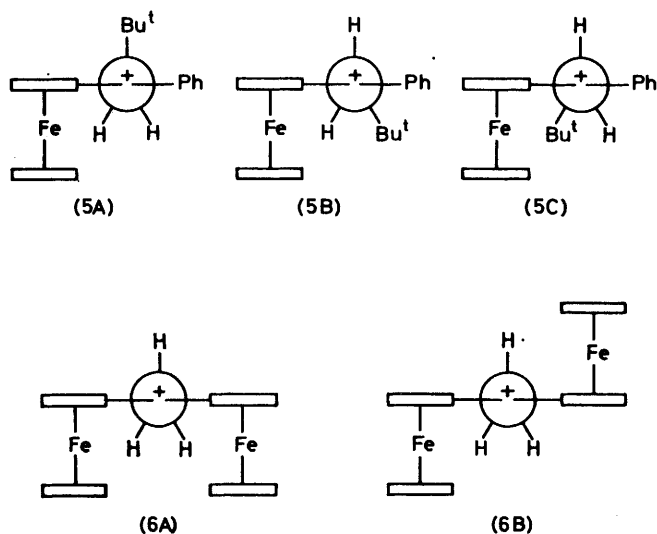
Chloride ion will contribute to the elimination reactions with the least reactive amines (*e.g.* pyridine and 4-picoline) where the reagents are added as the amine-amine hydrochloride buffers. Its contribution is relatively unimportant for reactions with the more reactive amines, however; this was verified by using up to 0.2M-quinuclidine hydrochloride in the reaction of (1b) with 10⁻²M-quinuclidine.

DISCUSSION

Brønsted Coefficients.—The value of the Brønsted coefficient β is regarded as a measure of the extent of proton

transfer in the transition state.^{9a} For reactions of the carbocations (1a and b) with sterically unhindered amines, the values of β of 0.32 and 0.45, respectively, suggest that proton transfer is <50% complete for both cations in the transition states. The finding that the extent of proton transfer in the transition state appears to be greater for the more reactive carbocation (1b) (*cf.* rate constants, Table 1) seems, at first sight, to be in disaccord with the Hammond postulate which predicts a greater extent of proton transfer for the less reactive carbocation (*i.e.* the weaker acid).

The source of this seeming paradox is that cations of the type (1) can adopt various conformations whose reactivities may differ widely because of the steric and/or stereoelectronic preferences for *exo*-proton transfer.⁴ The reaction rate therefore depends upon the reactivity towards deprotonation of each conformer and its population, but it is the reactivity of the individual conformer from which alkene is formed which will be related to the Brønsted β coefficient. Thus, a given carbocation may be relatively unreactive because of a low population of reactive conformer but the transition state for proton transfer from this conformer may be relatively 'early' as reflected in a lower value of β .



The difference in β for deprotonation of the carbocations (1a and b) suggests that the lower reactivity of the former is related to a lower population of reactive conformer rather than to a lower reactivity of an individual conformer. For example, the most populous ground-state conformation of (1a) should be (5A) which lacks an *exo*-oriented β -hydrogen atom and which will therefore be less reactive than conformers (5B and C) from which *exo*-proton transfer can take place. Of these two potentially reactive conformers, the former will be

* These structures are over-simplified in that the exocyclic bonds (C_5H_4)- C^+ are probably displaced from the ring planes towards the iron atom as in the solid-state structure¹³ of the ferrocenylmethyl cation, in accord with the prediction of MO calculations,¹⁴ and steric congestion in (6A) may be relieved by twisting about the exocyclic bonds.^{7b}

strongly preferred in the ground state over the sterically much more congested (5C), and the observation^{4a} of a single stereoisomeric alkene product suggests that (1a) may undergo stereoselective *exo*-deprotonation in the conformation (5B). The diferrocenylethyl cation (1b) could react in either of the conformations (6A or B).^{*} However, the *syn*-conformation (6A) involves considerable interference between the $Fe(C_5H_5)$ residues of the two ferrocenyl groups and its population in the ground state may be so low that the reaction proceeds largely by deprotonation of the *anti*-conformer (6B), even though reaction involves loss of a proton *endo* to one of the ferrocenyl groups.[†]

Another way of looking at this question is to consider differences in β in terms of the relative basicities of the alkenes (2a and b). In the transition state for proton transfer, the position of the proton depends upon the relative basicities of the alkene and the basic reagent (*e.g.* a tertiary amine) from whose conjugate acid the proton is supplied. Alkene (2b) is protonated much more readily^{4a} than (2a), so that the extent of proton transfer from a given acid in the transition state should be correspondingly less for (2b) than for (2a). It follows that, for reactions of the carbocations with a given base, proton transfer should be more advanced, and β larger, for reaction of (1b) as compared with that of (1a), on the presumption that $\alpha + \beta = 1$ where α is the Brønsted exponent for the reverse reaction (*i.e.* alkene protonation).

Steric Effects.—Although steric hindrance is very important in nucleophilic addition or substitution at carbon, it is generally less so in deprotonation[‡] and very bulky tertiary amines are effective bases when nucleophilic reactions at carbon are to be avoided. Unexpectedly, hindered tertiary amines (*e.g.* $EtNPr_2$ and Bu^tNMe_2) are ineffective in deprotonating the carbocations (1a and b) relative to unhindered amines (Table 1; Figure). These large steric effects suggest that the base and the carbocation must be in close proximity in the transition state.

It has been suggested⁶ that the transition states for some *E2* reactions may have a degree of S_N2 character, as in the *E2C* mechanism with an interaction between the incoming base and the α -carbon atom. If such an interaction is important for *E2* eliminations from a non-ionic substrate, it should be even more so for deprotonation of a carbocation. Therefore, the marked steric effect on deprotonation of the ferrocenylalkyl cations may be a consequence of an interaction in the transition state between the tertiary amine and the formal carbocationic centre, *i.e.* there is a four-centre transition state involving base, β -hydrogen atom, and positively charged α -carbon atom. The energy of such a transition state

† Although conformational requirements are important in addition and elimination reactions of 1-ferrocenylalkyl cations,^{3b} we found no deviation from first-order kinetics which suggests that conformational equilibrium [*e.g.* of (5A—C) or (6A, B)] is maintained during the reaction.

‡ However, the steric bulk of the base appears to affect the products of *E2* reactions.^{1b}

would be raised by steric repulsion between a sterically crowded tertiary amine and the bulky groups (ferrocenyl, phenyl) attached to the carbocationic centres of (1a and b).

Nucleophilic additions of bulky amines (*e.g.* Bu^tNH_2) to non-deprotonatable tertiary 1-ferrocenylalkyl cations (*e.g.* $\text{Fc}_2\text{C}^+\text{Ph}$) are sterically hindered,^{7b} and there is the possibility also that the reactive (towards deprotonation) conformers of the carbocations (1a and b) are such that interaction of the base with the β -hydrogen atom may be hindered. For example, if the carbocation (1b) reacts in the conformation (6B), there would be steric interference between a bulky base and a $\text{Fe}(\text{C}_5\text{H}_5)$ group. However, this explanation does not satisfactorily account for the marked steric effects on deprotonation of (1a), which are larger than those for (1b) (Figure), and we favour the first interpretation.

Relation between Hydrogen Isotope Effects and Brønsted Exponents.—The Brønsted exponent (α or β)^{9a} and the primary hydrogen kinetic isotope effect^{9b,11} can both be regarded as a measure of the extent of proton transfer in the transition state. On the simplest assumption that $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ depends upon the loss of zero-point energy of the carbon-hydrogen stretching vibration, a maximum isotope effect of *ca.* 7 corresponds to the proton being approximately midway between its two partners in the transition state.

From this simple model, one would interpret the variation in $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ values (Table 2) in terms of extensive proton transfer to the weaker bases and limited transfer to the stronger bases (HO^- and quinuclidine), suggesting that the Brønsted plots (Figure) should be curved. This explanation is clearly inadequate and one problem, discussed earlier, is the contribution of the secondary isotope effect which means that the overall isotope effects overestimate the variation of the primary kinetic hydrogen isotope effect with base strength. But there is a much more fundamental problem in that, although in many proton transfers the values of $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ go through maxima as the base strength changes, they do not come close to unity even at the extremes of base strength.

The Marcus theory has been applied to acid-base reactions to explain how coupling of proton transfer to other processes, not involving the proton, may make the Brønsted coefficient or the kinetic hydrogen isotope effect an inadequate measure of the extent of proton transfer in the transition state,¹⁵ and would decrease the dependence of $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ and β on base strength. In our reactions, geometrical changes and diffusion of reactants together, or apart, are probably coupled with proton transfer. Despite this coupling, one would expect variations in $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ to be related to changes in β if both depended directly on the extent of proton transfer

* A secondary hydrogen isotope effect upon conformational equilibria seems improbable in view of the dominating steric (and electronic) effects of the ferrocenyl and *t*-butyl moieties, but such an effect would change $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ for reactions of a given carbocation with the various amines to the same extent.

in a 'linear' transition state; the observed maximum in $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ should be related to a monotonic change in β .*

We have no explanation for these observations on $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ and β , although we note that at least part of the variation in $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ in going from quinuclidine to pyridine may be a secondary isotope effect caused by differences in rehybridisation at the β -carbon atom. Two additional factors may be important in these deprotonations of 1-ferrocenylalkyl cations. If the transition state for proton transfer is 'non-linear', there will be changes not only in the hydrogen stretching vibration, which is related to the extent of transfer to the base, but also in the bending vibration. The Brønsted catalysis equation was originally applied only to proton-transfer reactions, but it has also been successfully applied to nucleophilic additions to acyl groups.¹⁶ If in reactions of the carbocations (1a and b) the base interacts with both the proton and the carbocationic centre, β will depend not only on the extent of proton transfer in the transition state, but also on the base-carbon interaction, and both interactions may be described in terms of the Brønsted equation, but only proton transfer will be related to $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$. We note also that it is easier to observe variations in the linear function $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ than curvature in a Brønsted plot because of its logarithmic form.

Catalysis by Chloride Ion.—Deprotonation of 1-ferrocenylalkyl cations in aqueous acetonitrile is catalysed by chloride ion,^{4a} even though chloride ion is a weak base in this solvent.¹⁷ This catalysis is reduced by added perchlorate ion, which ion-pairs with carbocations even in aqueous solvents,¹⁸ and this competition between chloride and perchlorate ions for the carbocations requires that ion-pairs must be involved in catalysis of deprotonation by chloride ion.^{4a}

It has been suggested that chloride ion *in an ion-pair*, formed by ionisation of an alkyl chloride, may be sufficiently basic to abstract a proton from the gegenion.¹⁹ On this hypothesis, elimination from a preformed ion-pair could be responsible for the catalysis by chloride ion (Table 3). In such an ion-pair, the transition state for proton transfer to chloride ion would presumably be 'non-linear' which would lead to the observed increase in the isotope effect (Tables 2 and 3).

The added anion could also affect the reaction rate by changing the conformational populations of the carbocation in an ion-pair such that elimination is more favoured (*cf.* earlier discussion). However, if such a conformational effect were important, chloride ion should have similar effects upon the rates and kinetic hydrogen isotope effect for reaction with both water and hydroxide ion, and this is not so; the isotope effect upon the faster reaction with hydroxide ion is unaffected by added chloride ion whereas its presence increases $k_{\text{H}}^{\text{ene}}/k_{\text{D}}^{\text{ene}}$ for the water reaction (Table 3), and it has opposite effects upon the rates of the two reactions. Thus, it appears that chloride ion introduces a new

reaction path by interacting with the leaving proton. However, this new reaction path will not compete in the reaction of the carbocation with hydroxide ion, and chloride ion has the normal negative kinetic salt effect.

Analogies with the E2C Mechanism.—Although the evidence for the E2C mechanism of elimination from non-ionic substrates is not conclusive, much of it is most economically explained on the assumption that the base interacts with both the departing β -proton and the α -carbon atom in the transition state,⁶ and this interpretation is consistent with the relatively low Brønsted β values for these reactions. These β values, typically for reactions of alkyl halides and tosylates with thiolate ions, are generally 0.5 or less (see Table 10 in ref. 1b, p. 97), as are those for proton transfer from the carbocations (1a and b). Encounter between carbocation and amine must precede reaction, and any interaction between the reactants will keep them together in a pair and so assist reaction.

The nature of the interaction between base and substrate in the E2C mechanism is in doubt. For example, McLennan has suggested²⁰ that there is an electrostatic interaction between the base and the α -carbon atom, and several authors have considered that the base abstracts a proton from an ion-pair rather than from the covalent substrate. There is relatively little bond-making in the transition states for additions of primary and secondary amines to 1-ferrocenylalkyl cations.^{7b} Thus, one might expect interaction between a tertiary amine and the carbocationic centre in (1a and b) to be ion-dipole rather than covalent, which is consistent with McLennan's suggestion.²⁰

EXPERIMENTAL

For general remarks concerning synthetic methods and rate measurements, see refs. 4, 7, and 21. Reagent-grade amines were recrystallised or redistilled, as appropriate, immediately before use and acetonitrile was purified as described previously.^{7a} Preparations of the BF_4^- salts of the carbocations (1a and b) and of the alkenes (2a and b) have been reported.^{4a}

2,2-Dideuterio-3,3-dimethylbutanoylferrocene.—A solution of $\text{FcCOCH}_2\text{Bu}^t$ ²² (0.5 g, 1.8 mmol) in dry dioxan (10 ml) was added to a solution of NaOD in D_2O (from 2.3 g Na and 10 g D_2O), and the two-layer system was heated to 80° and stirred vigorously under nitrogen for 48 h. The mixture was then poured into water (100 ml) and extracted thoroughly with ether. The extract was washed (H_2O), dried (MgSO_4), and evaporated, and the residue was dissolved in light petroleum (b.p. 40–60°) and chromatographed on partially deactivated alumina. Light petroleum-ether (4 : 1) eluted the title compound (0.45 g, 88%) which crystallised from light petroleum as an orange solid, m.p. 53–54° (m.p. of protio-analogue²² is 55–56°); $\tau(\text{CDCl}_3)$ 5.21 and 5.50 ($2 \times t$, C_5H_4), 5.79 (s, C_5H_5), and 8.95 (s, Bu^t); the absence of any absorption around τ 7.5 indicated an isotopic purity > 98%.

2,2-Dideuterio-1-ferrocenyl-3,3-dimethyl-1-phenylbutan-1-ol.—This alcohol was prepared by the addition of PhLi to $\text{FcCOCD}_2\text{Bu}^t$ as described^{4a} for preparation of the protio-analogue (m.p. 99–101°), and was obtained as a yellow

solid, m.p. 99–100°; $\tau(\text{CDCl}_3)$ 2.4–2.9 (m, Ph), 5.6–5.75 and 5.95–6.1 ($2 \times m$, C_5H_4), 5.85 (s, C_5H_5), 7.40 (s, OH), and 9.20 (s, Bu^t); this spectrum was identical with that of $\text{FcCPh(OH)CH}_2\text{Bu}^t$ except for the absence of the CH_2 singlet at τ 7.80.

2,2-Dideuterio-1-ferrocenyl-3,3-dimethyl-1-phenylbutylium Tetrafluoroborate.—Aqueous HBF_4 solution (40%, 1 ml) was added dropwise with stirring to an ice-cold solution of $\text{FcCPh(OH)CD}_2\text{Bu}^t$ (0.5 g, 1.4 mmol) in acetic anhydride-ether (1 : 1, 5 ml). The solution was stirred at 0° for 5 min, then added dropwise with vigorous stirring to dry ether (200 ml), whereupon the title salt precipitated as a dark brown powder (0.51 g, 85%); $\tau(\text{CF}_3\text{CO}_2\text{H})$ 2.1–2.55 (m, Ph), 3.5–3.7, 4.7–4.85, and 5.0–5.2 ($3 \times m$, C_5H_4), 5.20 (s, C_5H_5), and 9.18 (s, Bu^t); this spectrum was identical with that of (1a) (BF_4^-) except for the absence of the AB quartet resonance of the CH_2 group.

Rate Measurements.—Rates were measured for reactions in H_2O -MeCN (1 : 1 w/w) at 25.0° by following spectrophotometrically the disappearance of carbocation at a suitable wavelength, viz. 338 nm for (1a) and 655 nm for (1b), as described previously.^{4,7} Reactions with solvent in the absence of added base were conducted in the presence of 4-picoline ($2 \times 10^{-4}\text{M}$) to suppress the reverse reaction (i.e. alkene protonation); earlier work^{4a} established that this low concentration of 4-picoline has a negligible effect upon the rates of carbocation deprotonation. At least two separate determinations of each rate constant were carried out; results were reproducible. Reactions were followed through at least three half-lives, and the first-order rate constants were calculated by using a least-squares best-fit computer program; correlation coefficients > 0.999 were obtained.

For the base-promoted reactions, we generally used a maximum concentration of base of 0.1M, and a 1 : 1 mixture of base and salt; the counterions were Na^+ for the oxygen acids and Cl^- for the protonated amines. The kinetic hydrogen isotope effects were measured by making several determinations of the first-order rate constants successively with unlabelled and deuterium-labelled substrates, to avoid systematic errors.

For the reactions with bases, the observed first-order rate constants for carbocation consumption were corrected for the contribution of reaction with solvent and separated into deprotonation and nucleophilic addition components by using the alkene : addition product ratios. The spectroscopic method of analysis of the product mixtures in the solutions at the end of the kinetic runs has been described previously.^{4a} Second-order rate constants (k^{ene}), calculated from the observed first-order rate constants for deprotonation and the base concentrations, are in Tables 1–3.

Measurement of Dissociation Constants.—Acid dissociation constants of the oxygen acids and amine hydrochlorides in H_2O -MeCN (1 : 1 w/w) at 25.0° were measured potentiometrically by using a Thomas High pH combination glass electrode. The electrode response was measured by plotting the e.m.f. (mV) against $\log[\text{H}^+]$ for dilute HCl solutions, giving a slope of 57.4 mV/ $\log[\text{H}^+]$ at 25.0° which is close to the theoretical slope of 59.2 mV/ $\log[\text{H}^+]$. The e.m.f. of a dilute solution of KOH was also measured giving an autoprotolysis constant of water in H_2O -MeCN (1 : 1 w/w) of 15.6. These measurements were made in the absence of CO_2 . The dissociation constants of the amine hydrochlorides were determined by using the Henderson-Hasselbach treatment²³ and refer to 10^{-2}M solutions.

The measured pK_a values are in Table 1 which includes for comparison the corresponding values, where available, for solutions in water. The values for the more hydrophobic salts (*e.g.* quinuclidine hydrochloride) in H_2O -MeCN are similar to those in water, whereas for the oxygen acids they are larger in the mixed solvent. These differences are understandable in terms of the solvation requirements of the acids and their conjugate bases.

Support of this work by the National Science Foundation, the Petroleum Research Fund administered by the American Chemical Society, and the S.R.C. is gratefully acknowledged. We thank Miss M. Patton for experimental assistance. N. C. was on leave from the Universidad Técnica del Estado, Santiago, Chile.

[0/1862 Received, 4th December, 1980]

REFERENCES

- ¹ (a) D. V. Banthorpe, 'Elimination Reactions,' Elsevier, New York, 1963; (b) W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley-Interscience, New York, 1973.
- ² Z. Rappoport, *Tetrahedron Lett.*, 1979, 2559.
- ³ (a) L. Haynes and R. Pettit in 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1977, vol. 5; (b) W. E. Watts, *J. Organomet. Chem. Library*, 1979, **7**, 399.
- ⁴ (a) C. A. Bunton, N. Carrasco, N. Cully, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1859; (b) C. A. Bunton, W. Crawford, N. Cully, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2213.
- ⁵ W. H. Saunders, *Acc. Chem. Res.*, 1976, **9**, 19; E. Baciocchi, *ibid.*, 1979, **12**, 430.
- ⁶ J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, 1967, **32**, 11; A. J. Parker, M. Raune, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 1968, 2113; D. Cook and A. J. Parker, *ibid.*, 1969, 4901; G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Am. Chem. Soc.*, 1971, **93**, 4735.
- ⁷ (a) C. A. Bunton, N. Carrasco, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1267; (b) C. A. Bunton, N. Carrasco, F. Davoudzadeh, and W. E. Watts, *ibid.*, 1980, 1520.
- ⁸ W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, p. 173.
- ⁹ (a) A. J. Kresge in 'Proton Transfer Reactions,' eds. E. F. Caldin and V. Gold, Halsted Press, New York, 1975, p. 179; (b) R. A. More O'Ferrall, *ibid.*, p. 201.
- ¹⁰ L. Melander, 'Isotope Effects on Reaction Rates,' Ronald Press, New York, 1960; F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265; C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, 1961, **83**, 3214.
- ¹¹ R. P. Bell and D. M. Goodall, *Proc. R. Soc. London Ser. A*, 1966, **294**, 273; D. J. Barnes and R. P. Bell, *ibid.*, 1970, **318**, 421; F. G. Bordwell and W. J. Boyle, *J. Am. Chem. Soc.*, 1971, **93**, 512.
- ¹² V. J. Shiner in 'Isotope Effects in Chemical Reactions,' eds. C. J. Collins and N. S. Bowman, van Nostrand Reinhold, New York, 1970.
- ¹³ M. Cais, S. Dani, F. H. Herbststein, and M. Kapon, *J. Am. Chem. Soc.*, 1978, **100**, 5554.
- ¹⁴ R. Gleiter and R. Seeger, *Helv. Chim. Acta*, 1971, **54**, 1217; R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, 1976, **98**, 598.
- ¹⁵ *E.g.*, see M. M. Kreevoy and S.-W. Oh, *J. Am. Chem. Soc.*, 1973, **95**, 4805; J. R. Murdoch, *ibid.*, 1980, **102**, 71.
- ¹⁶ D. J. Hupe and W. P. Jencks, *J. Am. Chem. Soc.*, 1977, **99**, 451; C. D. Ritchie, *Pure Appl. Chem.*, 1978, **50**, 1281.
- ¹⁷ C. Moreau and G. Douhéret, *J. Chim. Phys.*, 1974, **71**, 1313.
- ¹⁸ M. J. Postle and P. A. H. Wyatt, *J. Chem. Soc., Perkin Trans. 2*, 1972, 474; C. A. Bunton and S. K. Huang, *J. Am. Chem. Soc.*, 1972, **94**, 3536.
- ¹⁹ M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, 1963, **85**, 1702.
- ²⁰ D. J. McLennan, *Tetrahedron*, 1975, **31**, 2999.
- ²¹ T. D. Turbitt and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1974, 177.
- ²² T. S. Abram and W. E. Watts, *J. Chem. Soc., Perkin Trans. 1*, 1975, 113.
- ²³ See D. D. Perrin and B. Dempsey, 'Buffers for pH and Metal Ion Control,' Chapman and Hall, London, 1974.