

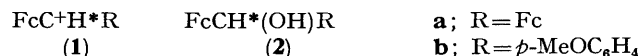
Secondary α -Hydrogen Kinetic Isotope Effects in Nucleophilic Additions to Ferrocenyl-stabilised Carbocations

By CLIFFORD A. BUNTON,* NELSON CARRASCO, and WILLIAM E. WATTS*†

(Department of Chemistry, University of California, Santa Barbara, California 93106
and †School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland BT52 1SA)

Summary The secondary α -hydrogen kinetic isotope effects upon the solvolyses of $\text{Fc}_2\text{C}^+\text{H}$ (**1a**) and $p\text{-MeOC}_6\text{H}_4\text{C}^+\text{HFc}$ (**1b**) (Fc = ferrocenyl) in H_2O , $\text{H}_2\text{O-MeCN}$, and $\text{H}_2\text{O-MeOH}$ ($k_t^{\text{H}}/k_t^{\text{D}} = ca. 0.9$), and upon the acid heterolyses of the corresponding alcohols ($k_t^{\text{H}}/k_t^{\text{D}} = ca. 1.1$), suggest that there is appreciable C...O bond formation in the transition state for carbocation solvolysis; for additions of HO^- , N_3^- , and BH_4^- to (**1a**), $k_t^{\text{H}}/k_t^{\text{D}} = ca. 1.0$, indicating 'early' carbocation-like transition states for these reactions, whereas intermediate values ($k_t^{\text{H}}/k_t^{\text{D}} = ca. 0.96$) are found for additions of primary amines.

SECONDARY α -hydrogen kinetic isotope effects (KIE) are a powerful tool in the elucidation of the mechanisms of nucleophilic substitutions and similar reactions,^{1,2} but they have not been used to date to study nucleophilic additions to preformed carbocations in solution. We have measured these effects upon the rate constants k_t for additions to the cations (**1a, b**)³ and k_r for acid heterolyses of the related alcohols (**2a, b**) (Fc = ferrocenyl; * denotes the position of isotopic replacement by deuterium).



The KIE upon k_t for addition of anionic nucleophiles to (**1a**) are close to unity (Table 1),[‡] suggesting that there is little or no change in the orbital hybridisation of the α -

TABLE 1. α -Hydrogen kinetic isotope effects on nucleophilic additions to (**1a**)^{a, b}

Nucleophile	$k_t^{\text{H}}/1 \text{ mol}^{-1} \text{ s}^{-1}$	$k_t^{\text{H}}/k_t^{\text{D}}$
HO^-	38.7	0.987 ± 0.020
N_3^-	2.61×10^4	1.012 ± 0.013
BH_4^-	1.89×10^3	0.999 ± 0.020
MeNH_2	6.53×10^2	0.955 ± 0.010
Bu^tNH_2	34.7	0.969 ± 0.014
MeONH_2	21.8	0.957 ± 0.004

^a The rate constants and ratios given are each based upon 8–12 determinations, over a tenfold range of nucleophile concentrations; the k_t^{H} values given agree reasonably well with those quoted previously (ref. 3b), except for the hydroxide reaction where the earlier value was in error. ^b In $\text{H}_2\text{O-MeCN}$ (1:1 w/w; mol fraction of $\text{H}_2\text{O} = 0.695$) at 25.0 °C.

carbon in the transition states which, for these anion additions, are therefore akin to ion pairs. However, we found inverse KIE for addition of primary amines to (**1a**) ($k_t^{\text{H}}/k_t^{\text{D}} = ca. 0.96$; Table 1) and of water to (**1a, b**) ($k_t^{\text{H}}/k_t^{\text{D}} = ca. 0.90$; Table 2). In the transition states for these

[‡] Similarly, for the addition of HO^- to (**1b**) in water at 25.0 °C, $k_t^{\text{H}} = 3.66 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_t^{\text{H}}/k_t^{\text{D}} = 0.98 \pm 0.05$.

additions, it follows that there is appreciable bond formation between the reactants with corresponding change in the hybridisation at the reactive site. For the three amines studied, the KIE are of similar magnitude despite differences^{9b} in their nucleophilicities towards (1a) and in their steric bulk.

effect ($k_r^{H^+}/k_r^{D^+} = ca. 0.4$) for acid heterolysis of tri-*p*-anisyl-methanol⁷ and several 1-ferrocenylalkanols^{3a} can be interpreted in terms of a two-step mechanism [equation (3)].

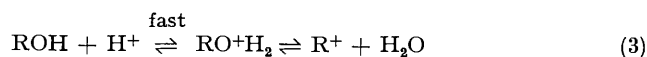
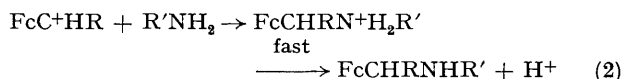
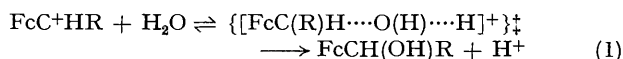


TABLE 2. α -Hydrogen kinetic isotope effects on solvolysis of the cations (1a, b)^a

Cation	k_t^H/s^{-1}	k_t^H/k_t^D	$k_t^H/1 \text{ mol}^{-1} \text{ s}^{-1}$	k_r^H/k_r^D	K_R^H/K_R^D
(1a)	0.0266 ^b	0.915 \pm 0.024	37.2 ^b	1.08 \pm 0.02	0.847
	0.177 ^c	0.896 \pm 0.010			
(1b)	43.2 ^d	0.874 \pm 0.016	1.05 $\times 10^{3d}$	1.15 \pm 0.07	0.760

^{a, b} As for Table 1. ^c In H₂O–MeOH (mol fraction of H₂O = 0.695) at 25.0 °C. ^d In H₂O at 25.0 °C.

The different behaviour of anionic and non-ionic nucleophiles does not depend upon their reactivities but on their charge. Ritchie has suggested⁴ that anion desolvation may provide much of the free-energy barrier to additions of anions to preformed carbocations, and this would involve no significant hybridisation change at the α -carbon of the cation. Additions of both water and a primary amine to a carbocation involve both bond-making and proton loss; for amine addition in aqueous media, one must also consider the process of encounter between reactants, which does not involve rehybridisation at the reaction site. The observation⁵ of general base catalysis of water addition to preformed carbocations suggests that, for this reaction [equation (1)], bond-making and proton loss are concerted. However, catalysis is relatively unimportant for amine addition [equation (2)]. This mechanistic difference



between additions of water and of amines can be rationalised in terms of three-dimensional free-energy diagrams which have been discussed by several authors.⁶

The secondary isotope effects upon cation \rightleftharpoons alcohol equilibria in aqueous acidic media (K_R^H/K_R^D ; Table 2) are as expected¹ for reactions involving $sp^2 \rightleftharpoons sp^3$ change in hybridisation at the reaction centre, and the KIE upon the forward (k_f) and reverse (k_r) reactions are relatively insensitive to solvent changes. The kinetic solvent isotope

These observations are inconsistent with general base catalysis of water addition but it has been pointed out⁸ that values of k_{H_2O}/k_{D_2O} do not necessarily distinguish between concerted and stepwise reactions when a proton is being transferred between electronegative atoms, and a model for conservation of its zero-point energy has been proposed.⁹

Our observed KIE for acid heterolyses (k_r^H/k_r^D) of the alcohols (2a, b) are close to that (1.08) estimated¹⁰ indirectly from the rates of permanganate oxidation of Ph₂CH*OH. The KIE for nucleophilic additions (k_t^H/k_t^D) to the carbocations (1a, b) give no support to the concept¹¹ of 'late' transition states for such reactions. The effects are consistent with the postulate⁴ that water behaves somewhat differently from other nucleophiles, but indicate that HO⁻ behaves like other anionic nucleophiles in its reactions with preformed carbocations in aqueous solutions. The different KIE on addition of anionic and non-ionic nucleophiles suggest that different factors may govern their nucleophilicities towards carbocations and therefore may have a bearing on the interpretation of reactivities in terms of, for example, the N_+ scale.⁴

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