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KINETIC HYDROGEN ISOTOPE EFFECTS
ON THE RATES OF IONIZATION OF SOME ACETYLFURANS,
ACETYLTHIOPHENES AND ACETYLPYRIDINES

Progress Report

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Measurements were made of the hydroxide catalyzed rates of T^+ transfer from 2-acetylfuran, 2-acetylthiophene, 2-acetylpyridine, 3-acetylpyridine, 5-methyl-2-acetylfuran, and 5-methyl-2-acetylthiophene over a temperature range. For some of these, namely 2-acetylpyridine, 3-acetylpyridine and 2-acetylthiophene, the rates of H^+ transfer were measured at 25°C. For 2-acetylpyridine the rates of H^+ transfer were measured over a temperature range. The results are summarized in tables I, II, and III. The observed isotope effects agree with the prediction that the primary hydrogen isotope effect for the base catalyzed ionization of an acid (HA) reaches a maximum value when the difference in basicity of B: and A: (ΔpK) is small.

pK values for the compounds used in the present study are not available. However, a rough estimate indicates that pK values decrease in the order 2-acetylthiophene ($pK \approx 18$) > 2-acetylpyridine ($pK \approx 17$) > 3-acetylpyridine ($pK \approx 16$ to 17). The values of k_H/k_T at 25°C in the order of decreasing ΔpK values are 19.8 (2-acetylthiophene), 25.5 (2-acetylpyridine), 30.8 (3-acetylpyridine), which reflects the expected trend.

2-acetylpyridine exhibits the following features which are indicative of tunnelling:

- a) Large isotope effect
- b) $E_T - E_H > 1.8$ kcals/mole
- c) $A_T/A_H > 4$

The difference in pK (ΔpK) between 2-acetylpyridine ($pK \approx 17$) and water ($pK = 15.7$) is around 1.3 and hence the transition state for proton transfer from 2-acetylpyridine to hydroxide ion is almost symmetrical. The above observations support the idea that tunnelling is favored by a symmetrical

barrier. It would be interesting to find out whether or not tunnelling is significant in the proton transfers from 3-acetylpyridine and 4-acetylpyridines to hydroxide ion.

Work on the rates of H^+ , D^+ , and T^+ transfers from several acetylfurans, acetylthiophenes and acetylpyridines is in progress.

Table I Arrhenius parameters for T^+ transfer

Compound	$E_T(\text{kcal.mole}^{-1})$	$A_T(1 \text{ mole}^{-1}\text{sec}^{-1})$
2-acetylfuran	16.11	3.40×10^9
2-acetylthiophene	16.34	4.78×10^9
5-methyl-2-acetylfuran	16.73	4.17×10^9
5-methyl-2-acetylthiophene	16.44	3.05×10^9
2-acetylpyridine	16.74	2.74×10^9
3-acetylpyridine	14.95	1.83×10^9

Table II Isotope effect data at 25°C

Compound	k_H/k_T
2-acetylthiophene	19.8
2-acetylpyridine	25.5
3-acetylpyridine	30.8

Table III Arrhenius parameters for H^+ and T^+ transfer from 2-acetylpyridine

$E_H(\text{kcal.mole}^{-1})$	$E_T(\text{kcal.mole}^{-1})$	$A_H(1 \text{ mole}^{-1}\text{sec}^{-1})$	$A_T(1 \text{ mole}^{-1}\text{sec}^{-1})$	$E_T - E_H(\text{kcal.mole}^{-1})$	$3A_T/A_H$
13.25	16.74	1.85×10^9	2.7×10^9	3.5	4.43