Anomalous Kinetic Hydrogen Isotope Effects on the Rate of
Ionization of Some Alkyl Substituted Ketones

MASTER

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Measurements are made on the Kinetics of the hydroxide catalyzed rates of H^+ , D^+ , and T^+ transfer from 2,4-dimethyl-3-pentanone and 3,5-dimethyl-4-heptanone over a temperature range. Both of the compounds exhibit the following features:

- (a) Normal deuterium isotope effects (For 2,4-dimethyl-3-pentanone, k_H/k_D at $25^\circ C.$ = 6.09 and for 3,5-dimethyl-4-heptanone, k_H/k_D at $25^\circ C.$ = 3.67).
- (b) A_D/A_H values within the limit predicted by the absolute rate theory (For 2,4-dimethyl-3-pentanone, A_D/A_H = 0.636 and for 3,5-dimethyl-4-heptanone, A_D/A_H = 0.874).
- (c) $E_D - E_H > 1200 \text{ cal mole}^{-1}$.
- (d) Linear Arrhenius plots.

These results confirm that tunnelling is not significant in these proton transfer reactions.

The rates of H^+ and T^+ transfers from both 2,4-dimethyl-3-pentanone and 3,5-dimethyl-4-heptanone are similar at all temperatures and, apparently, there is no tritium isotope effect. These results are intriguing since a K_H/K_T of 13.55 for 2,4-dimethyl-3-pentanone and 9.82 for 3,5-dimethyl-4-heptanone at $25^\circ C.$ can be expected on the basis of Swain's equation and the observed values of deuterium isotope effects. It is possible that in detritiation, T^+ transfer may not be the rate

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determining step and tritium hydrogen-exchange takes place according to the following mechanism:

It is interesting to investigate the rates of H^+ , D^+ , and T^+ transfers from 3-pentanone and 2,2,4-trimethyl-3-pentanone. If the above interpretation is correct, the rates of H^+ and T^+ transfer should be similar for 3-pentanone whereas 2,2,4-trimethyl-3-pentanone should yield a significant tritium isotope effect. We have now synthesized 2,2,4-trimethyl-3-pentanone and the deuterium and tritium labelled 2,2,4-trimethyl-3-pentanone and 3 pentanone.

Work is in progress on the detritiation of these compounds.