

## Relative Rates of Base-catalyzed H-D Exchange in Butan-2-one

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WE have studied the rates of H-D exchange at the 1- and 3- positions of butan-2-one, using n.m.r. spectroscopy.<sup>1</sup> In D<sub>2</sub>O-OD<sup>-</sup> the rates at the two

positions are nearly equal, while for the weaker bases *p*-O<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>O<sup>-</sup> and CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, the methylene group exchanges more rapidly (Table).

The surprising result is that the methyl group at C-3 does not specifically retard HO<sup>-</sup>-catalyzed enolization at that site. The lower overall rate of enolization of butan-2-one, relative to that of

accelerating effect of an  $\alpha$ -alkyl group on the rate of acid-catalyzed enolization.<sup>4</sup>

Our results for base-catalysis by nitrophenoxide and acetate are those predicated from consideration

TABLE

Base (Na <sup>+</sup> salt)	Temp. (°C)	Catalytic Constants <sup>a</sup> (M <sup>-1</sup> sec. <sup>-1</sup> )		$k_2/k_1$
		$k_2$	$k_1$	
OD <sup>-</sup>	0.00 ± 0.05	4.64 ± 0.23 × 10 <sup>-3</sup>	4.59 ± 0.13 × 10 <sup>-3</sup>	1.01 ± 0.09 <sup>b</sup>
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> O <sup>-</sup>	59.2 ± 0.03	1.34 ± 0.07 × 10 <sup>-4</sup>	8.93 ± 0.78 × 10 <sup>-5</sup>	1.50 ± 0.21
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	59.2 ± 0.03	1.18 ± 0.05 × 10 <sup>-6</sup>	5.47 ± 0.70 × 10 <sup>-7</sup>	2.16 ± 0.36

<sup>a</sup> Constants for OD<sup>-</sup> are the average of several determinations. Those for the weaker bases were obtained by an extrapolation technique, since the overall rates in such runs contain a substantial contribution from catalysis by OH<sup>-</sup>.

<sup>b</sup> This is a minimum value for the rate ratio in water. Our medium was 1—2 M-ketone in water and we have found that the ratio  $k_2/k_1$  rises with decreasing ketone concentration.

acetone,<sup>2</sup> is therefore not readily explicable in terms of inductive destabilization of an enolate-like transition state. The results may be accounted for in terms of the termolecular mechanism involving hydroxide as base and water as acid.<sup>3</sup> An enol-like transition state, with very little negative charge in the ketone moiety, should be stabilized by an alkyl substituent at developing *sp*<sup>2</sup>-carbon. Such stabilization is usually invoked to explain the

of the effect that changing the base strength should have on the position of the transition state in the enol-like region of the reaction co-ordinate.<sup>5</sup>

The overall implications of our data are that enolization by dilute HO<sup>-</sup> in H<sub>2</sub>O does not go by a carbanion mechanism and that the polar effect of an alkyl group, on rate of base-promoted enolization in aqueous medium, has been overemphasized or even misinterpreted.

(Received, February 21st, 1966; Com. 107.)

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<sup>4</sup> H. M. E. Cardwell and A. E. H. Kilner, *J. Chem. Soc.*, 1951, 2430.

<sup>5</sup> R. F. W. Bader, *Canad. J. Chem.*, 1964, **42**, 1822.