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CARBONYL-FORMING ELIMINATION REACTIONS. A KINETIC STUDY OF THE DECOMPOSITION OF β-NITROALCOHOLS IN WATER

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Summary: β-Nitroalcohols 1a-g undergo, in aqueous buffered solution, a specific base catalyzed carbonyl-forming elimination. The transition state for the rate-limiting C-C bond breakage step has been estimated to be rather reactant-like.

Carbonyl reactions involving carbanionic nucleophiles (eq [1]) have received sporadic attention, from a mechanistic point of view, notwithstanding the

$$X-\overset{|}{C}^{(-)} + \rangle C=O \rightleftharpoons X-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-O^{(-)} \qquad [1]$$

fundamental importance of C-C bond making-breaking processes in chemistry and biochemistry (1). As far as the Henry reaction is concerned ($X = NO_2$) (2), some data are available on the mechanism of catalysis for the reversible decomposition of β-nitroalcohols both in aqueous (3) and organic (4) solvents, but very little information has been collected on the structure of the transition state, although the "transition state geometry" problem for carbonyl reactions has been long debated and extensive investigation has been carried out for different nucleophiles using various approaches (5,6).

We now report a kinetic study of the carbonyl-forming elimination (eq [2])

$$O_2NC(CH_3)_2CH(Ar)OH \rightleftharpoons O_2NCH(CH_3)_2 + ArCHO \qquad [2]$$

$\underline{1}$

in nitroalcohols $\underline{1}$a-g in buffered aqueous solution. Results are listed in the Table.

Table

Rate constants for decomposition[a] of β-nitroalcohols $\underline{1}$a-g in buffered aqueous solution (T 25.3°C, μ 1.0).

Substr.	Ar	$10^{-4}\cdot k_{OH}$[b]	Substr.	Ar	$10^{-4}\cdot k_{OH}$[b]
$\underline{1}$a	C_6H_5	3.02[c]	$\underline{1}$e	$pNO_2C_6H_4$	4.54
$\underline{1}$b	$pMeC_6H_4$	3.37	$\underline{1}$f	$mClC_6H_4$	3.79
$\underline{1}$c	$pMeOC_6H_4$	5.09	$\underline{1}$g	$mMeOC_6H_4$	3.07
$\underline{1}$d	$pClC_6H_4$	4.22			

[a] Reaction rates were determined spectrophotometrically following the appearance of aldehyde at suitable wavelenghts; [b] $M^{-1}sec^{-1}$; pH range 6.5÷8.4 if not otherwise stated (for each pH a $[buffer]_{tot}$ range $1\cdot10^{-2}\div5\cdot10^{-1}$ was typically examined); k_{OH} values were reproducible to within ±2%; [c] pH range 4.6÷8.4.

Measured reaction rates were not affected, in the pH range indicated in the Table for each substrate, by the nature or, at constant buffer ratio, by the concentration of the buffers employed ($k_{obsd} = k_{OH}\cdot a_{OH^{(-)}}$). This result can be easily accounted for by the mechanism depicted in the Scheme, in which a rate-limiting C-C bond cleavage is preceded by a fast preequilibrium of deprotonation of the substrate alcohol $\underline{1}$. From the pK_a of $\underline{1}$a, which can be reasonably

Scheme

$$\underset{\underline{1}}{O_2NC(CH_3)_2CH(Ar)OH} \underset{k_{-1}[BH^{(+)}]}{\overset{k_1[B]}{\rightleftharpoons}} O_2NC(CH_3)_2CH(Ar)O^{(-)}$$

$$O_2NC(CH_3)_2CH(Ar)O^{(-)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O_2N\overset{(-)}{C}(CH_3)_2 + ArCHO$$

estimated to be about 13 (7), values of $10^3 sec^{-1}$ for k_2 and $10^9 sec^{-1}$ for $k_{-1}[H_2O]$ can be calculated (through eq [3]) (9), which are consistent with the absence of

$$k_{OH} = k_2 \frac{K_{a(\underline{1})}}{K_w} = k_2 \frac{k_{1(OH^{(-)})}}{k_{-1}[H_2O]} \qquad [3]$$

detectable general catalysis within the mechanism of the Scheme (11,12).

Hammett correlations of $\log(k_{OH})$ against σ^n or σ^+ values for the ring substituents give a very poor fit, while the use of the modified Yukawa-Tsuno treatment (eq [4]) (5c,5d) with $\varrho^r/\varrho = -1.5$ ($r = 0.992$) gives values of

$$\log(k_{OH}/k^o_{OH}) = \varrho[\sigma^n + (\varrho^r/\varrho)(\sigma^+ - \sigma^n)] \qquad [4]$$

$+0.24 \pm 0.01$ and -0.36 ± 0.02 respectively for ϱ (polar effects sensitivity) and ϱ^r (through resonance effects sensitivity). If the reasonable assumptions are made that the through resonance effect on the preequilibrium is negligible and that the nature of the leaving group hardly affects the $\varrho^r_{K_2}$ value, then $\varrho^r \simeq \varrho^r_{k_2}$ and $\varrho^r_{K_2}$ can be directly evaluated (13) from literature data (5d,5e,6b,14) as $\simeq -1.1 \div -1.3$ (15). From this, using the ratio ϱ^r/ϱ^r_{eq} as an estimate of transition state hybridization and bond orders (5d), it appears that, for our system, the transition state should lie on the reactant side of the reaction coordinate ($\varrho^r_{k_2}/\varrho^r_{K_2} \simeq 0.3$). This result gives support to the view, derived from recent investigation on carbonyl reactions involving addition of a variety of structurally different nucleophiles (5), that, at least for aromatic carbonyl compounds, the bond order between the carbonyl atom and the nucleophile in the transition state is rather high ($\geqslant 0.5$) and apparently scarcely dependent on the nucleophile itself.

Acknowledgments

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