Tetrahedron Letters No. 12, pp 1017 - 1020.
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0040-4039/79/0315-1017$02.00/0

KINETICS OF Z-E ISOMERISATION OF ACETALDOXIME

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The Z(syn) - E(anti) isomerisations of aromatic oximes have been much studied[1-2], and acids[3-4] and bases[4-5] have been found to affect the rates of reaction dramatically. Aliphatic oximes have received less attention[6-8], but Somin and Gindin[8] have reported data for CH_3CHNOH, Me_2NCH_2CHNOH and $Me_3N^+CH_2CHNOH$, in which the rates of isomerisation in aqueous solution are first order in proton concentration, even when the pH is greater than 7. Their results are based on observations of the relatively small changes in isomer ratio when the liquid oxime is diluted by an appropriate solvent mixture (e.g. 39% E in pure acetaldoxime to 46% E in aqueous acid). We have reinvestigated the acetaldoxime case by n.m.r. after isolating pure crystalline Z-acetaldoxime and observing the rate of return to the equilibrium ratio in freshly prepared solutions.

Z-acetaldoxime was prepared by very slow crystallisation of a freshly distilled mixture of the isomers. The rate of isomerisation was measured using the areas of the aldehydic proton n.m.r. quartets of the A and E isomers. Typical spectra are shown in Fig. 1, where it can be seen the E-isomer (downfield quartet) grows steadily with time. In 0.1 N sulphuric acid the equilibrium spectrum is obtained within the one minute required to mix the solution and scan the spectrum in the region of interest, which gives the lower limit for the observed rate constant, k_{obs}, reported in Table 1. In this medium there is no coalescence of either the aldehydic ^1H quartets ($\Delta\nu$ = 53 Hz) or the methine ^{13}C peaks ($\Delta\nu$ = 6.1 Hz) which allows an upper limit for k_{obs} to be calculated.

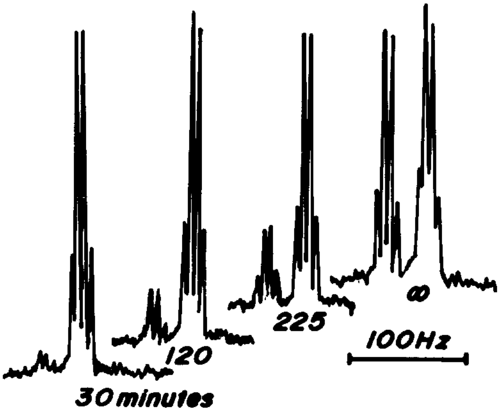
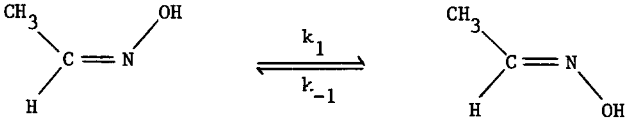


Fig. 1
Acetaldoxime
Z-E isomerisation
in D_2O at 35°C

Table 1 Isomerisation of Acetaldoxime in D_2O Solutions

Temp. °C	Conditions		k_{obs} s^{-1}	k_1 s^{-1}	k_{-1} s^{-1}
29	1×10^{-1}N	H_2SO_4	$> 4 \times 10^{-2}$ < 9.6	$> 1.8 \times 10^{-2}$ < 4.3	$> 2.2 \times 10^{-2}$ < 5.3
29	1×10^{-3}N	H_2SO_4	2.5×10^{-3}	1.1×10^{-3}	1.4×10^{-3}
29	2×10^{-4}N	H_2SO_4	7.0×10^{-5}	3.1×10^{-5}	3.9×10^{-5}
29	1×10^{-5}N	H_2SO_4	3.0×10^{-5}	1.3×10^{-5}	1.7×10^{-5}
35	D_2O		4.5×10^{-5}	2.0×10^{-5}	2.5×10^{-5}
45	D_2O		9.1×10^{-5}	4.0×10^{-5}	5.1×10^{-5}
29	1.3×10^{-2}N	NaOH	5.5×10^{-4}	2.4×10^{-4}	3.1×10^{-4}
29	1.0×10^{-1}N	NaOH	4.2×10^{-3}	1.9×10^{-3}	2.3×10^{-3}

In the other D_2O solutions, where the rate is measurably slow, the approach to equilibrium is first order in oxime and is catalysed by both H^+ and OH^- ions (Table 1). The position of equilibrium (44.4% E isomer) is independent of temperature and the concentration of acid or base. This contradicts the work of Somin and Gindin[9] who claimed that in aqueous solution the Z:E equilibrium ratios were 54:46 for the oxime and 42:58 for its anion. We have no explanation for this difference between our results and those of Somin and Gindin, nor for the fact that we observe both acid and base catalysis, whereas they find only the former. Knowledge of the equilibrium constant ($K = k_1/k_{-1} = 0.80$) for the isomerisation

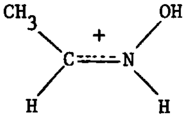


E E

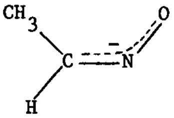
allows calculation of the individual rate constants, since $k_{obs} = k_1 + k_{-1}$. Values for k_1 and k_{-1} are given in Table 1. In pure D_2O $\Delta H^{\ddagger}$ for Z to E isomerisation is approximately 55 kJ mol^{-1} and $\Delta s^{\ddagger}$ is -160 J $mol^{-1} deg^{-1}$.

The results given in Table 1 are consistent with reaction via the cation A and its isomer in acidic solutions and anion B and its isomer in basic media. These species derive their reactivity

A



B



from the decreased double bond character of the C-N bond. Somin and Gindin[8] dismissed the possibility that the carbanion species $CH_3\overline{C}HN = O$ exists in basic solution because it would provide a pathway for deuterium exchange of the methine proton - a process which neither we nor they observe in practice. This objection does not apply to our mechanism since we envisage only a relatively small portion of the negative charge in B residing on the methine carbon atom. The relative effectiveness of protons and hydroxide ions as catalvsts depends on the ease of protonation and deprotonation of the neutral oxime as well as the inherent reactivities of A and B. Using Somin and Gindin's calculations[8] we estimate the equilibrium constant K_p for the reaction

$$CH_3CHNOH + H^+ \underset{}{\overset{K_p}{\rightleftharpoons}} CH_3CHNHOH^+$$

to be 10 M^{-1} whereas that for the deprotonation reaction

$$CH_3CHNOH + OH^- \overset{K_D}{\rightleftharpoons} CH_3CHNO^- + H_2O$$

is 1000 M^{-1}. The reduced sensitivity of the isomerisation rate to base catalysis is therefore due to a much lower reactivity of the anions compared to the cations.

In CCl_4 the situation is more complicated. The first order rate plots of log(isomer concentration) against time are curved, the reaction apparently accelerating as it proceeds, (Fig. 2).

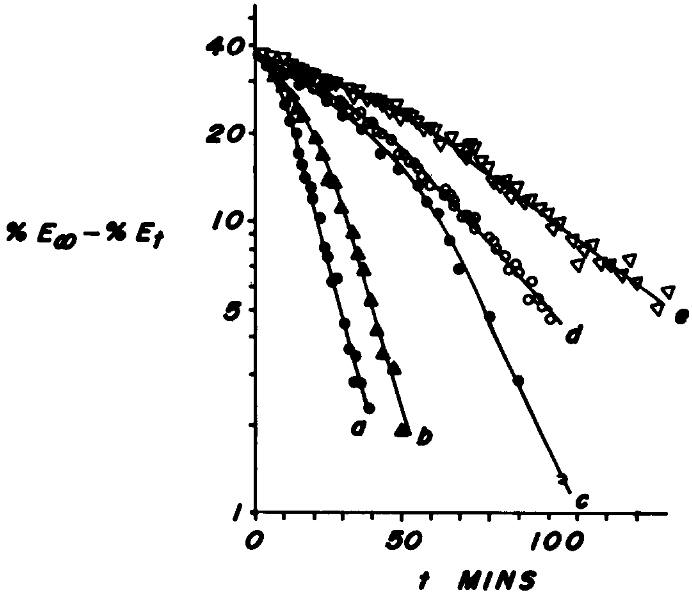


Fig. 2
Acetaldoxime
Z-E isomerisation
in CCl_4.
For conditions
see Table 2.

The reaction rate also appears to be concentration dependent, at least during the initial stages (curves a and b in Fig. 2). Complex kinetics have also been observed by Vassian and Murmann[2] in the isomerisation of phenyl-2-pyridylketoxime in cyclohexane.

Table 2 Isomerisation of Acetaldoxime in CCl_4 Solutions

Run	Temp. °C	Concn. M.	Rate Ms^{-1}
a	45	0.44	1.1×10^{-2}
b	45	0.17	2.5×10^{-3}
c	35	0.20	1.6×10^{-3}
d	24	0.29	3.8×10^{-4}
e	15	0.21	1.9×10^{-4}

However, for a total acetaldoxime concentration of 0.22 ± 0.04 M (runs b to e in Fig. 2) over the limited range of reaction from 92% to 78% Z isomer, plots of [Z isomer] against time are linear and give the rates shown in Table 2. From these rates $\Delta H^{\ddagger}$ for the Z to E isomerisation is estimated as 67 ± 7 kJ mol^{-1}. The complexity of the reaction in CCl_4 can be explained if the reaction proceeds by ionic species as suggested for aqueous solutions. In non-protic solvents these species can be generated via hydrogen bonded interactions and subsequent proton transfer between oxime molecules. Since hydrogen bonding tendencies differ for the two isomers[10], detailed kinetic analysis is unwarranted at this time.

We thank the National Research Council of Canada for financial support of this work.

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(Received in USA 27 November 1978)