

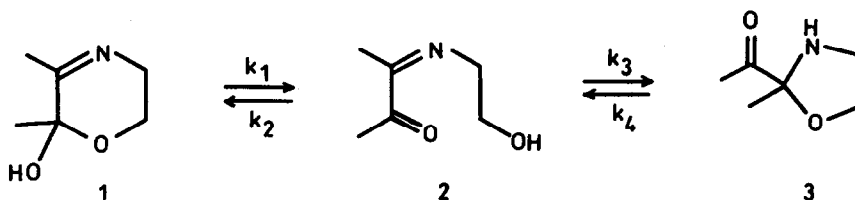
ANATOMY OF A THREE SPECIES TAUTOMERIC PROCESS:  
THE RING-CHAIN TAUTOMERISM IN 5,6-DIHYDRO-2-HYDROXY-2,3-DIMETHYL-2H-1,4-OXAZINE

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**Summary:** A ring-chain tautomerism involving two single processes hydroxyketone-hemiacetal and hydroxyimine-1,3-oxazolidine is kinetically studied.

The ring-chain tautomerism is a well studied process.<sup>1</sup> Among the immense variety of these phenomena, the combinations, in one single process, of two tautomeric equilibria hydroxyketone-hemiacetal and hydroxyimine-1,3-oxazolidine is, to the best of our knowledge, unprecedented in the literature. In this report we account for one case. Reaction of diacetyl with 2-aminoethanol (molar ratio 1:1, in CH<sub>2</sub>Cl<sub>2</sub> at room temperature) affords the 5,6-dihydro-2-hydroxy-2,3-dimethyl-2H-1,4-oxazine 1.<sup>2</sup> In solution of CDCl<sub>3</sub>, compound 1 is in equilibrium with the iminoketone 2 and oxazolidine 3 (Scheme) as indicate the <sup>1</sup>H- and <sup>13</sup>C-nmr spectra. Analogous oxazine derived from benzil is in tautomeric equilibrium only with the 1,2-iminoketone.<sup>2</sup>



Scheme

Attempts of independent synthesis of iminoketone 2 were unsuccessful. However oxazolidine 3 was isolated as an unstable liquid (b.p. 62-64°C/0.05 mm Hg, yield 20%) by reaction of diacetyl with 2-aminoethanol in boiling benzene.<sup>2</sup> Variation of the

concentration of each compound 1-3 with time was obtained by  $^1\text{H}$ -nmr integration of the methyl groups signals at convenient intervals of time (Figure).

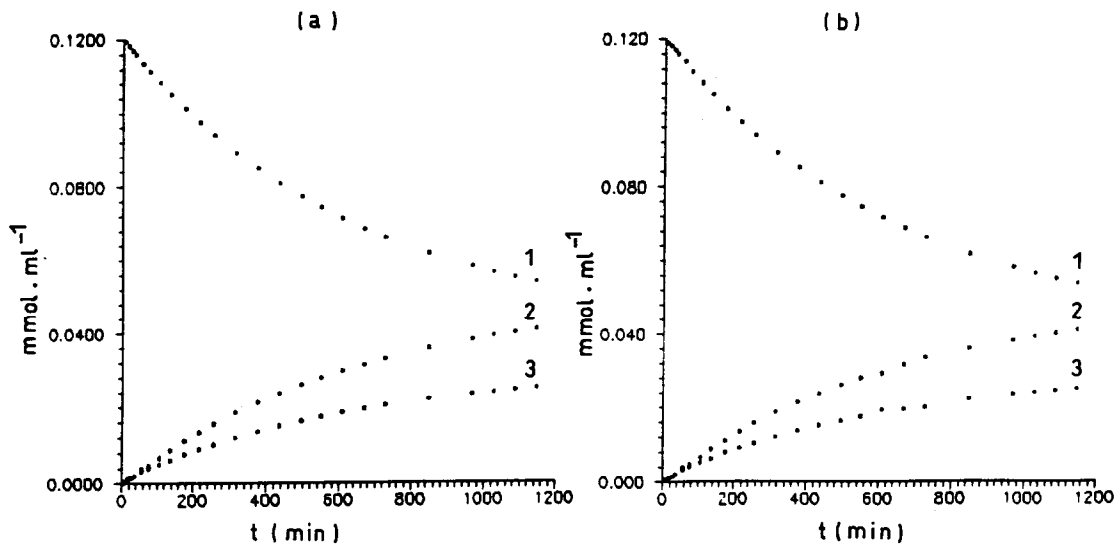
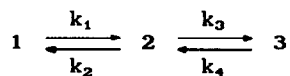


Figure. Calculated (a) and experimental (b) variation of concentration of species 1, 2, and 3 with time.

Kinetic analysis for the process has been performed as follows: for the general kinetic process



and assuming pseudofirst order for each reaction, the system of differential equations:

$$\frac{d[1]}{dt} = -k_1[1] + k_2[2]$$

$$\frac{d[2]}{dt} = k_1[1] - k_2[2] - k_3[2] + k_4[3]$$

$$\frac{d[3]}{dt} = k_3[2] - k_4[3]$$

has been solved by the determinant method<sup>4</sup> leading to:

$$[1] = [1]_0 \left\{ \frac{k_2 k_4}{\lambda_2 \lambda_3} + \left[ \frac{\lambda_2^2 - (k_2 + k_3 + k_4)\lambda_2 + k_2 k_4}{\lambda_2(\lambda_2 - \lambda_3)} \right] e^{-\lambda_2 t} + \left[ \frac{\lambda_3 - (k_2 + k_3 + k_4)\lambda_3 - k_2 k_4}{\lambda_3(\lambda_3 - \lambda_2)} \right] e^{-\lambda_3 t} \right\}$$

$$[2] = k_1 [1]_0 \left\{ \frac{k_4}{\lambda_2 \lambda_3} + \frac{k_4 - \lambda_2}{\lambda_2(\lambda_2 - \lambda_3)} e^{-\lambda_2 t} + \frac{k_4 - \lambda_3}{\lambda_3(\lambda_3 - \lambda_2)} e^{-\lambda_3 t} \right\}$$

$$[3] = k_1 k_3 [1]_0 \left\{ \frac{1}{\lambda_2 - \lambda_3} + \frac{e^{-\lambda_2 t}}{\lambda_2(\lambda_2 - \lambda_3)} - \frac{e^{-\lambda_3 t}}{\lambda_3(\lambda_3 - \lambda_2)} \right\}$$

where  $[1]_0$  means the concentration of oxazine at  $t = 0$  with  $[2]_0 = [3]_0 = 0$  for the present experiment and

$$2\lambda_2 = k_T + (k_T^2 - 4k_F)^{1/2}$$

$$2\lambda_3 = k_T - (k_T^2 - 4k_F)^{1/2}$$

$$k_T = k_1 + k_2 + k_3 + k_4$$

$$k_F = k_1 k_4 + k_2 k_4 + k_1 k_3$$

For the determination of the  $k_i$ 's ( $i = 1-4$ ) we have used a non linear regression method based on the Newton-Gauss algorithm.<sup>5</sup> The  $k_i$ 's values so obtained are:  $k_1 = 10^{-3} \text{ min}^{-1}$ ,  $k_2 = 1.4 \cdot 10^{-3} \text{ min}^{-1}$ ,  $k_3 = 69.0 \cdot 10^{-3} \text{ min}^{-1}$ , and  $k_4 = 42.0 \cdot 10^{-3} \text{ min}^{-1}$ .

Extension of this analysis to other related system are being currently studied in our laboratory.

#### Acknowledgment

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#### References and Notes

1. Walters, R. E.; Fitch, W. in *Ring-Chain Tautomerism*, Plenum, NY, 1985.
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3. Reaction time: 45 min. Selected spectroscopic data for 3: IR (neat)  $\nu$  1720  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  1.50 ( $\text{CH}_3\text{-C2}$ ), 2.25 ( $\text{CH}_3\text{CO}$ );  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  22.4 ( $\text{CH}_3\text{-C2}$ ), 45.6 (C4), 66.2 (C5), 97.2 (C2). Imino ketone 2 (only one diastereomer) was characterized by  $\text{CH}_3\text{-C=N}$  signal at 1.98 ppm.
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5. Berington, P. R. in *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, NY, 1969.

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