Kinetics of dimerization of 2-alkylthiopropenals

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The rate constants for cyclodimerization of α-alkylthioacroleins were determined. They are two orders of magnitude higher than those for dimerization of α-alkoxyacroleins.

Key words: 2-alkylthiopropenals, cyclodimerization, reaction rate, 2,5-dialkylthio-3,4-dihydro-2*H*-pyran-2-carbaldehydes, the Diels—Alder reaction.

Unlike 2-alkoxypropenals, their sulfur analogs (2-alkylthiopropenals) are rapidly dimerized to 2,5-dialkylthio-3,4-dihydro-2*H*-pyran-2-carbaldehydes.[1] 2-Alkylselenopropenals behave similarly.[2,3] The experimentally observed regioselectivity and relative reactivity of acrolein and its α-alkoxy and α-alkylthio analogs in thermal cyclodimerization were satisfactorily explained by the Hückel perturbation theory.[4] However, in studying the kinetics of cyclodimerization of acrolein and its α-substituted derivatives, we failed to retard the dimerization of α-alkylthioacroleins to the boundaries appropriate for kinetic monitoring.[4] At that time, it was impossible to confirm the existence of α-alkyhthioacroleins in monomeric state (for example, by "diene traps") and quantitatively compare the dimerization rates of α-alkylthio and α-alkoxyacroleins.

The purpose of the present work is to determine the true rate constants for cyclodimerization of α-alkylthioacroleins. This became possible due to the development of the method of synthesis of α-alkylthioacroleins based not on the Mannich reaction,[5] but on the retro-Diels—Alder decomposition of 2,5-dialkylthio-3,4-dihydro-2*H*-pyran-2-carbaldehydes.[6] The new method makes it possible to obtain α-alkylthioacroleins as mixtures of the monomer and cyclic dimer containing from 25 to 80% of α-alkylthioacrolein. In this case, the formation of minor by-products that accompany the Mannich reaction can be avoided.

The kinetics of dimerization of monomer **1** to cyclic dimer **2** was determined by ^{1}H NMR spectroscopy from a change in the current concentrations of both components (monomer and dimer). It is shown that the formation of adducts involving the carbonyl group of the monomer or dimer (for example, trimers with the trioxane structure) does not occur (Scheme 1).

Cyclodimerization is described by a second-order reaction equation. The rate constant was found by the formula

$$k = \frac{1}{t}\cdot\frac{x}{a\cdot(a-x)},$$

where *a* is the initial molar concentration of monomer **1**, and *x* is the molar concentration of the monomer that is transformed into dimer **2** to the moment *t*. The second order of the reaction is also confirmed by the linear time dependence of $1/(a - x)$ at initial concentrations of α-alkylthioacroleins from 0.15 to 0.9 mol L^{-1}. The method used is based on measuring the ratio of integral intensities of singlets of protons of the aldehyde groups of the monomer and dimer (δ 9.16 and 9.51, respectively). The average values of the rate constants for dimerization ($k\cdot 10^4$ L mol^{-1} s^{-1}) of α-alkylthioacroleins (**1**) in CDCl$_3$ at 27 °C and standard deviations are the following:

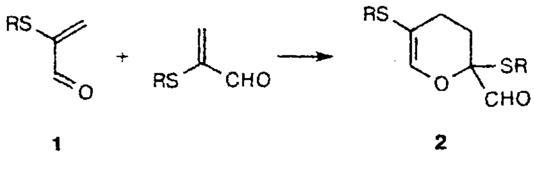
Et	0.70±0.01	Bu	0.75±0.02
Pr	1.4±0.30	C_6H_{13}	0.7±0.1

The found rate constants for dimerization of monomers **1** are alike. This indicates that the steric constant of a substituent has a slight effect on the dimerization rate.

Taking into account that the rate constant for cyclodimerization of α-ethoxyacrolein is equal to $4.6\cdot 10^{-4}$ at 120 °C, and accepting that it increases twofold with a temperature increase of 10°, we may conclude that the cyclodimerization of sulfur analogs is *ca.* 100 times faster.

The result obtained refines the value of the constant for α-alkylthioacroleins that could not previously be determined and agrees with the early assumption[4] that their thermal cyclodimerization occurs through the nonsynchronous mechanism.

Scheme 1



R = Et, Pr, Bu, hexyl

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Experimental

A Jeol FX-90Q spectrometer (89.95 MHz for ^1H) was used for kinetic measurements. Chemical shifts were measured in $CDCl_3$ at 27 °C relative to HMDS as the internal standard with an accuracy of 0.01 ppm, and the accuracy of measurement of the integral intensity was 5%.

General procedure for the preparation of the starting 2-alkylthiopropenals by the retro-Diels—Alder reaction of 2,5-dialkylthio-3,4-dihydro-2*H*-pyran-2-carbaldehydes. A dimer of 2-alkylthiopropenal (3 g) was heated *in vacuo* to 180 °C. The fraction with b.p. 110—140 °C (1 Torr) was collected in a receiver cooled with liquid nitrogen. According to the ^1H NMR spectral data, the obtained mixtures of monomer **1** and dimer **2** contained from 25 to 80% of α-alkylthioacrolein (**1**).

Kinetic measurements were carried out in a tube of an NMR spectrometer in $CDCl_3$ at 27 °C, using freshly distilled mixtures of the monomer and dimer of 2-alkylthiopropenal (C = 0.15—0.9 mol L^{-1}). The calculation of k was performed by monitoring the decrease in time of the relative integral intensity of singlets of protons of the aldehyde group of the monomer. Dimerization constants of 2-alkylthiopropenals were calculated as the average of six to nine values. It is noteworthy that the anamorphoses of the kinetic curves obtained fall well on straight lines (correlation coefficients $r > 0.9845$).

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Long-lived phosphorescence of aqueous solutions of β-cyclodextrin complexes with naphthalene and its derivatives at room temperature

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A long-lived phosphorescence at room temperature (lifetime >1 s) of aqueous solutions of β-cyclodextrin complexes with naphthalene and its derivatives was found. The phosphorescence is observed for aggregated complexes that form in water a light-scattering suspension, and its low intensity is due to predomination of 2 : 2 complexes with efficient excimer fluorescence. Complexes containing isolated aromatic molecules are assumed to be the centers of fluorescence.

Key words: complex, cyclodextrin, naphthalene, long-lived phosphorescence, excimer fluorescence.

It has previously been shown that phosphorescence at room temperature (RTP) of complexes of aromatic molecules with cyclodextrins (CD) occurs only when a third compound (ethanol,[1] dibromoethane,[2] acetonitrile,[3] saturated hydrocarbons,[4—6] and others) is added to an aqueous solution of the complex. The addition of hydrophobic compounds is usually accompanied by the formation of aggregated complexes and appearance of light-scattering microparticles (microcrystals) whose sizes are comparable with wavelengths of visible light, *i.e.*, of an order of one micron. When water-soluble (to some extent) compounds are added, smaller particles are

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