INVESTIGATION OF METHYLENE GROUP HYDROGEN ATOM REACTIVITY IN SOME AZOLIDINES

IV. Kinetics of the Condensation of Rhodanine With Aromatic Aldehydes*

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UV spectroscopy is used to investigate the kinetics of formation of arylidenerhodanines from rhodanine and various aromatic aldehydes whose benzene ring substitutents differ in nature and position. Hammett's equation is used to determine quantitatively the reactivities of the substituted aldehydes. The order of effect of substituent on reaction velocity is p-NO_2 > p-Cl > H > p-$N(CH_3)_2$, corresponding to a positive value of ρ in the Hammett equation. The position sequence is p-NO_2 > m-NO_2 > o-NO_2, and for chloro derivatives m-Cl > p-Cl, in agreement with views on transmission of inductive and conjugation effects through a benzene ring to a reaction center.

A large number of azolid-4-one derivatives are obtained by condensing the reactive methylene group with carbonyl compounds. The literature contains qualitative correlations between activities of carbonyl compounds and the methylene group of azolid-4-ones [1, 2], iso-oxazolones, and pyrazolones [3], the order of ease of reaction of the methylene group in the latter two compounds being: p-dimethylaminobenzaldehyde > > benzaldehyde, > p-nitrobenzaldehyde [3].

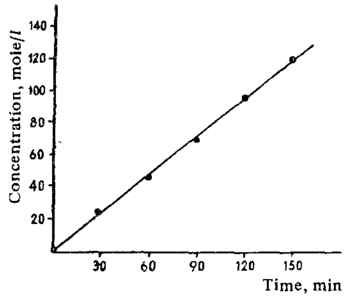
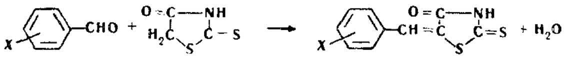


Fig. 1. $(x/(c - x)\cdot 10^3$ mole/l as a function of the time, for the reaction of VI with rhodanine.

Previous research [4] established that of the azolid-4-ones the one with the most reactive methylene group is rhodanine, which we also reacted with aromatic aldehydes to ascertain the effect of the nature and position of the benzene ring substituent on the kinetics of formation of the corresponding arylidenerhodanines.

The reaction between rhodanine and aldehydes was effected in glacial acetic acid in the presence of fused sodium acetate at 60°, 80°, and 100°:



I X=H; II X=m-Cl; III X=p-Cl; IV X=o-NO_2; V X=m-NO_2; VI X=p-NO_2; VII X=p-$N(CH_3)_2$

The amount of alkylidene rhodanine derivative formed was determined spectroscopically. Ranges where the optical density was a linear function of concentration were found, and by special experiments it was shown that the reaction did not give rise to side products to interfere with the spectroscopic determination of 5-arylidenerhodanine.

The velocity constants were calculated from the formula $K = x/t\cdot c(c - x)$, where c is the initial concentration of the starting material, mole/l, and x the concentration of the reaction product after time t, in mole/l.

The known formula [4] showed the reaction to be second order, and this was confirmed by successive insertion of experimental data in the equations found for the various reaction orders. The statistical method was used to determine the accuracy of the quantities obtained (accuracy 0.95).

Table 1 shows a typical experiment on the kinetics of formation p-nitrobenzylidenerhodanine, and Fig. 1 the plot of $x/(c - x)$ against time.

Table 2 gives the combined data for the kinetics of the reaction of aldehydes with rhodanine.

The Arrhenius equation expresses well the reaction investigated, the logarithms of the velocity constants being a linear function of the reciprocal of the absolute temperature (Fig. 2).

The Hammett equation $\lg K/K_0 = \rho\sigma$ enables the reactivities of substituted benzaldehydes to be assessed as a function of their structures in the reaction with rhodanine. K and K_0 are the velocity constants for the substituted and unsubstituted aldehyde, σ is a parameter that depends on the substituent, and ρ is a parameter that depends on the reaction. From the data of Fig. 3, the value of ρ is positive and equal to +1.5.

The numerical value of ρ shows that the reaction is less sensitive to change in polar effects of substituents than in ordinary reactions at carbonyl carbon (e.g. $\rho = +2.5$ for the hydrolysis of ethyl benzoate). [6].

With regard to effect on reaction velocity, the order for the benzaldehyde substituents is p-NO_2 > p-Cl > > H > p-$N(CH_3)_2$, where electron-accepting substituents increase and electron-donating substituents decrease reaction velocity, corresponding to a positive value of ρ. The substituent position effect order is p-NO_2 > m-NO_2 > o-NO_2, for chlorine derivatives m-Cl > p-Cl, which agrees with views regarding transmission of conjugation and inductive effects through the benzene ring to the reaction center. Furthermore,

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*For Part III see [4].

Table 1

Velocity Constants of Formation of 5-Nitrobenzylidenerhodanine at 60° (c = 0.02 mole/*l*)

Time, min	Yield, mole/*l*	K^{2}_{10}
30	0.43646	3.796
60	0.87307	3.804
90	0.22043	3.610
120	1.7274	3.939
150	2.13110	4.092

$K_{av} = 3.848 \pm 0.007835$

Table 2

Kinetics of the Reaction of Aldehydes with Rhodanine

Compound	Aldehyde	$K_{60^\circ} \cdot 10^2$	$K_{80^\circ} \cdot 10^2$	$K_{100^\circ} \cdot 10^2$	E	PZ
I	Benzaldehyde	0.2543±0.0012	1.142 ±0.0082	4.573±0.0088	17.7	9.02
II	m-Chlorobenzaldehyde	0.8906±0.00064	4.133 ±0.0011	16.63 ±0.0921	18.0	9.77
III	p-Chlorobenzaldehyde	0.5149±0.00071	2.388 ±0.00097	12.61 ±0.058	18.1	9.59
IV	o-Nitrobenzaldehyde	1.820 ±0.011	6.880 ±0.0018	22.42 ±0.085	15.9	8.71
V	m-Nitrobenzaldehyde	3.037 ±0.012	11.10 ±0.0042	33.95 ±0.074	15.6	8.72
VI	p-Nitrobenzaldehyde	3.879 ±0.0078	15.16 ±0.023	50.22 ±0.087	16.0	9.12
VII	p-Dimethylaminobenzaldehyde	0.0825±0.00013	0.3997±0.0088	1.523±0.055	16.9	8.00

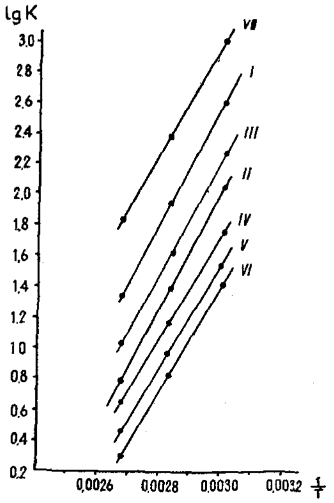

Fig. 2. Change in velocity constant with temperature for reactions of aldehydes I–VII with rhodanine.

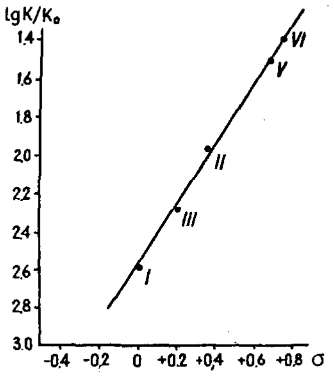

Fig. 3. Relationships between lg K/K_0 and the Hammett constant σ for reactions of I, II, III, V, and VI with rhodanine at 60°.

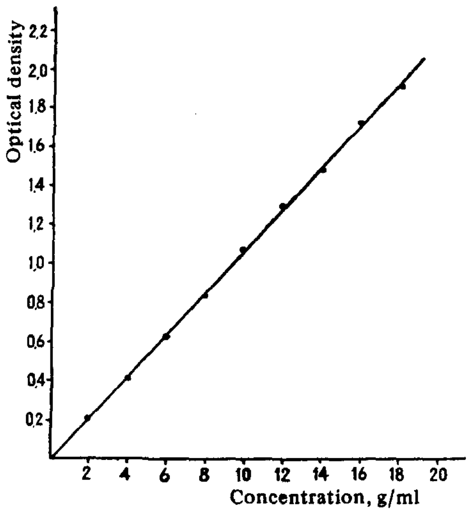

Fig. 4. Calibration plot for p-nitrobenzylidenerhodanine.

constancy of the pre-exponential term is not found for carbonyl carbon, as it is with reactions previously known, and the nature of the substitutent affects both activation energy and pre-exponential term.

EXPERIMENTAL

The compounds required in the research were carefully purified until their constants were steady (mp or bp, and UV spectrum) and agreed with the literature. The method of measuring reaction velocities was similar to that previously used [4].

The amount of 5-arylidenerhodanine formed was found by measuring the optical density for λ corresponding to a wide and intense absorption maximum. Thus investigation of various aldehydes gave the following λ values: I 375; II 376; III 380; IV 375; V 375; VI 372; VII 463 nm.

Figure 4 shows the calibration plot for p-nitrobenzylidenerhodanine.

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