

Kinetics of reactions of *O*-benzoylbenzaldoxime derivatives in acetic acid

J. MOLLIN and A. HOLAKOVSKÁ

*Department of Inorganic and Physical Chemistry, Faculty of Natural Sciences,
Palacký University, CS-771 46 Olomouc*

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The rate of *E*—*Z* isomerization of *O*-acylaldoximes in glacial acetic acid has been followed by using spectral data. The decrease of *O*-acylaldoxime with time was established from the decrease of the limit current of the polarographic wave. Gas chromatography and liquid chromatography were applied to determine the concentration of the reaction products. Conclusions on the reaction mechanism were drawn from the data mentioned above.

С помощью спектральных данных изучена скорость *E*—*Z* изомеризации *O*-ацилальдоксимов в ледяной уксусной кислоте. Убыль *O*-ацилальдоксима со временем определялся по падению предельного тока полярографической волны. Концентрация продуктов реакции определялась газовой и жидкостной хроматографиями. На основе приведенных данных был предложен механизм реакции.

O-Acylaldoximes occur at room temperature in the form of *E*-isomers [1]. Isomerization of these compounds [2], similarly as that of other oximes [3—6], is acid-catalyzed. Cleavage of the formed *Z*-isomers leads to nitriles [2]. By heating to temperatures higher than 100 °C, the *E*-isomers are also cleft to nitriles [7, 8]. Acid-catalyzed reactions of *O*-benzoylbenzaldoximes have been followed qualitatively or at most semiquantitatively [2]. The present communication is devoted to quantitative examination of the reactions of the compounds studied in acid medium.

Experimental

Chemicals

O-Benzoyl-*p*-methoxybenzaldoxime (I) [2], *O*-benzoylbenzaldoxime (II) [2], *O*-benzoyl-*p*-chlorobenzaldoxime (III) [2], *O*-benzoyl-*p*-nitrobenzaldoxime (V) [2], and

O-benzoyl-*p*-dimethylaminobenzaldoxime (VI) [9] were prepared according to the respective literature. The method described in [2] was used to prepare a new derivative, *O*-benzoyl-*m*-bromobenzaldoxime (IV). Recrystallization of this compound from ethanol—water resulted in white crystals (m.p. 118—120 °C) scarcely soluble in diluted ethanol.

For $C_{14}H_{16}BrNO_2$ (IV) (304.15) calculated: 55.29 mass % C, 3.31 mass % H, 4.66 mass % N; found: 55.02 mass % C, 3.25 mass % H, 4.72 mass % N.

p-Methoxybenzotrile, prepared after [10], benzotrile (BDH-Chemicals Ltd., pure), *p*-chlorobenzotrile (Fluka, pure), *p*-nitrobenzotrile [11], *p*-dimethylaminobenzotrile [12], and *p*-dimethylaminofornanilide [13] were used as standard compounds. Melting points and analyses of the prepared compounds were in agreement with the literature data. *m*-Bromobenzotrile was prepared by heating the compound IV in glacial acetic acid for 4 days. The reaction mixture after cooling was poured into water and the formed crystals were sucked and dissolved in a small amount of hot ethanol. Into this solution a solution of NaOH (0.1 mol dm^{-3}) was added under stirring until turbidity occurred. Then the solution was cooled and the crystals formed were recrystallized several times from the mixture of water—ethanol. Analysis and melting point of *m*-bromobenzotrile prepared in this way agreed with the literature data [14]. *n*-Propyl alcohol (Lachema, Brno, anal. grade) and acetic acid (Lachema, Brno, anal. grade) were used as solvents. In order to prevent decomposition of acetic acid into water and acetic anhydride, acetic anhydride (Lachema, Brno, anal. grade) was added into acetic acid to 3 mass % concentration.

Kinetic measurements and analyses

For kinetic studies the ampoule technique has been chosen. The ampoules were filled with the solution, sealed, and immersed into a thermostat bath maintained at $\theta/^\circ\text{C} = 58, 67, 78,$ and 90 with the accuracy of $\pm 0.1^\circ\text{C}$. The spectra of the compounds were recorded on a Pye-Unicam SP 8-100 apparatus using $3.2 \times 10^{-5} \text{ mol dm}^{-3}$ solutions in *n*-propyl alcohol or acetic acid. The concentration decrease of *O*-acylaldoximes in acetic acid was followed on an E 7 polarograph (Laboratory Instruments) with a capillary of drop time interval 2.9 s after diluting the $2 \times 10^{-3} \text{ mol dm}^{-3}$ (in the case of $V 2.5 \times 10^{-4} \text{ mol dm}^{-3}$) solutions with three-fold amount of water. The amounts of the reaction products were established chromatographically from the calibration curve constructed for the standard compounds. Gas chromatograph Chrom 43 (Laboratory Instruments) with a column of 15 % Carbowax 20M on Chromaton N-AW HMDS and a Spectra Physics SP 8700 liquid chromatograph with a Lichrosorp RP 8 column were used for measurements. For chromatographic analyses 0.1 mol dm^{-3} (in the case of $V 2.5 \times 10^{-3} \text{ mol dm}^{-3}$) solutions of *O*-benzoylbenzaldoximes in acetic acid were sealed and heated to temperatures used for kinetic measurements until the concentration of the starting compound decreased to 2 % of the initial value, according to polarographic data. Then the ampoules were withdrawn from the bath and their contents were analyzed with the accuracy of $\pm 4 \%$.

The spectral data of isomerization rate were worked up according to the Guggenheim method [15], the rate constants were calculated from polarographic data after the equation $\ln i_t = -kt + \text{const}$ by the least-square method. The error was less than $\pm 5 \%$.

Results and discussion

Comparison of the spectra of *O*-benzoylaldoximes in *n*-propyl alcohol and acetic acid revealed that these compounds practically did not protonize in acetic acid, except for the compound VI where the $-\text{N}(\text{CH}_3)_2$ group protonized predominantly. The obtained results are presented in Table 1. The shift of the short-wave

Table 1

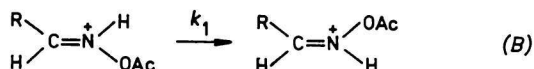
Spectral data of *E*-*O*-benzoylbenzaloxime derivatives in *n*-propyl alcohol and acetic acid

Compound	I	II	III	IV	V	VI	VI	VI
λ/nm	279	258	264	259	281	240	248	340
$\log \{\varepsilon(\textit{n}\text{-propyl alcohol})\}$	4.42	4.39	4.44	4.33	4.39	4.18	—	4.43
$\log \{\varepsilon(\text{CH}_3\text{COOH})\}$	4.38	4.36	4.39	4.59	4.33	—	4.39	4.43

maximum to higher wavelengths with VI due to protonization is not unique and was observed also with other derivatives of *p*-dimethylaminobenzaldehyde [16]. As indicated by the data in Table 1 and the isomerism found with the studied group of compounds [1], the ionization equilibrium in acetic acid, expressed by eqn (A), was shifted to the left to such a degree that it was impossible to observe the protonized form.



Heating of *O*-benzoylaldoximes in acetic acid brought about a rapid change in their spectra at the first stage. Parallel polarographic experiments showed that the changes in the spectra were not accompanied by decrease of the polarographic wave. The spectral changes were within experimental error when the compounds were heated in *n*-propyl alcohol for the same time. Consequently, in neutral medium the compounds are sufficiently stable and do not undergo pyrolysis at the given conditions. It can be assumed in agreement with the literature [2, 3, 5] that the initial rapid change of the spectra in acetic acid is due to acid-catalyzed isomerization. The isomerization reactions are generally reversible, however, the afore-mentioned changes of the spectra followed first-order reaction. Therefore, we assume that, at the given conditions, the compound at equilibrium is present in the form of *Z*-isomer predominantly. Consequently, eqn (B) can be written



The rate constants for the isomerization reaction are presented in Table 2 and graphically plotted in dependence on the σ constants of the Hammett equation [17] (Fig. 1, empty circles). The used method is too slow for direct determination of k_1 for the reaction of the compound *I*. Therefore, this value was obtained by extrapolation of the data found at lower temperatures. It is evident that the found rate constants $\{k_i\}$ suit the Hammett equation well. This experiment proved the hypothesis [2] that the substituent influences the electron density on the nitrogen atom in the oxime group and thus also its basicity and the equilibrium of the reaction after eqn (A), and with increasing concentration of the protonized form also the increasing reaction rate according to eqn (B). With the compound *V* several reactions proceeded simultaneously, therefore, it was impossible to measure $\{k_i\}$. After isomerization followed the establishing of the acid-base equilibrium between the protonized and unprotonized forms of *Z*-*O*-benzoylbenzaldoxime and its derivatives.

Table 2

Rate constants k_1 of *E*-*Z* isomerization of *E*-*O*-benzoylbenzaldoxime derivatives in acetic acid at 90 °C, rate constants k_2 , calculated from decrease of the limit current of polarographic reduction of *O*-benzoylbenzaldoxime derivatives in acetic acid at 90 °C, ΔH^\ddagger and ΔS^\ddagger of the reaction calculated from k_2 , measured at $\theta/^\circ\text{C} = 90, 78, 67,$ and 58 , and yields (%) of the nitriles found chromatographically after the reaction at 90 °C in acetic acid

Compound	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>
$k_1 \cdot 10^5/\text{s}^{-1}$	80	28.4	4.22	2.62	—	51.6
$k_2 \cdot 10^6/\text{s}^{-1}$	81.5	32.2	6.42	3.20	—	26.1
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	61	67	69	70	—	9
$-\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	155	147	156	165	—	115
$w_{\text{R CN}}/\%$	98	98	96	94	70	100

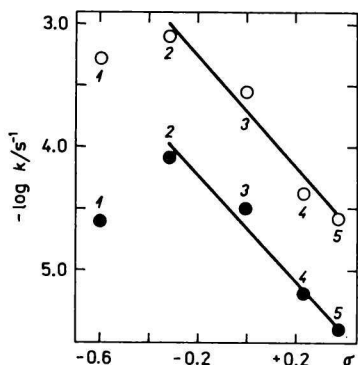


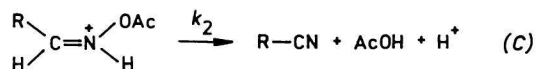
Fig. 1. Correlation of logarithms of numeric values of rate constants with σ constants of the Hammett equation.

Dependence of $\log \{k_1\}$ on σ (○); dependence of $\log \{k_2\}$ on σ (●).

1. *p*-N(CH₃); 2. *p*-OCH₃; 3. H; 4. *p*-Cl; 5. *m*-Br.

Polarographic reduction of *O*-benzoylaldoximes revealed that all compounds, similarly as other oximes [18], afforded a quadrielectron-diffusion wave, the current of which is a linear function of concentration. Moreover, the compound **V** afforded also a separate wave conditioned by the presence of the nitro group in the molecule. The kinetic constants $\{k_2\}$, found polarographically and reflecting the concentration decrease of *O*-benzoylaldoximes in acetic acid with time, are presented in Table 2 which summarizes also the activation parameters calculated from the rate constants $\{k_2\}$ measured at different temperatures, and the yields of nitriles found chromatographically. The rate constants $\{k_2\}$ are correlated with the Hammett equation in Fig. 1 (full circles).

The results of analyses of the solutions after the reaction at 90 °C are presented in Table 2. The results of analyses of the samples heated to lower temperatures were similar and hence are not presented. It is evident from the table that the compounds **I** to **IV** afforded nitriles almost exclusively. The rate constant of these reactions depended on the substituent similarly as that of the isomerization reaction after eqn (A). Consequently, it can be assumed that also the cleavage of the compounds **I** to **IV**, resulting in the formation of nitriles, is acid-catalyzed. Therefore, eqn (C) is valid



The compound **V** afforded the respective nitrile in 70 % yield only. Presumably, **V** enters parallel reactions, some leading to nitriles after eqns (A) to (C), others to other products. By mutual combination of subsequent and parallel reactions the concentration change of the compound **V** with time becomes kinetically confused and $\{k_2\}$ cannot be determined with sufficient accuracy. The anomalous behaviour of the compound **V** can be probably explained by the influence of the nitro group. This suppresses the basicity of the oxime nitrogen significantly and thus shifts the equilibrium of eqn (A) to the left considerably and thus slows the isomerization (B), but simultaneously enables by means of polarization of bonds also other reactions parallel to eqns (A), (B), and (C).

The u.v. spectra indicated that the compound **VI** was protonized to a high degree. The protonized part was probably the dimethylamino group. Spectral measurements cannot exclude small amounts of unprotonized form and hence it is possible that the reactive form was again the molecule protonized on nitrogen of the oxime group and the reaction of the compound **VI** proceeded after eqns (A) to (C). The found high yield of the nitrile proves this assumption. To make clear whether the consideration mentioned above is acceptable with regard to spectral data, we denote the total concentration of the compound **VI** as c , the concentration of the form with the unprotonized dimethylamino group as $c \alpha$. If the afore-mentioned

consideration is valid, the reaction rate is given by the relationship $-dc/dt = k_i \alpha c$, where for the isomerization reaction (B) k_i is equal to $\{k_1\}$, for the formation of nitrile after eqn (C) k_i is equal to $\{k_2\}$. Only the product $k_i \alpha$ is experimentally measurable, $\{k_1\}$ or $\{k_2\}$ can be estimated only, for example from Fig. 1. and then we can calculate α . If we take the σ constant for dimethylamino group equal to -0.60 [19], then we get for α 0.12 (when using the isomerization constants $\{k_1\}$) or 0.04 (when using the constants $\{k_2\}$ for calculation). For σ equal to -0.83 [20] we obtain α even lower. As the fraction with the unprotonized dimethylamino group represents such a small portion in the mixture, it will not appear in the spectrum. Thus, the consideration mentioned above, conditioned by the yield of nitrile, is acceptable also from the view-point of spectral measurements.

The experimental material presented is in agreement with general considerations devoted to the reactions studied [2, 21] and completes the previous communication [2] with quantitative relations and thus enables better understanding of the problem.

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