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# Spectrophotometric Determination and Kinetic Studies of Condensation of Aromatic Aldehydes with 7,9-Dioxo-6,10-dioxaspiro[4.5]decane

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The condensation reaction rates of 7,9-dioxo-6,10-dioxaspiro[4.5]decane with aromatic aldehydes in chloroform in the presence of piperidine has been investigated spectrophotometrically at 25-50 °C. The reaction follows overall second order kinetics, first order in each of the reactants and zero order with respect to piperidine. The rate of condensation increases with the presence of electron withdrawing groups on the aromatic ring of the aldehyde. From the dependence of the rate constants on temperature, activation parameters have been calculated. Plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ for the reaction gave a good straight line with an isokinetic temperature of 367.55 K. Based on this reaction, determination of ten aromatic aldehydes in a concentration range of 2.65-69.2 μg/mL is proposed.

**Keywords:** Aromatic aldehydes; Kinetic; Determination and spectrophotometry.

## INTRODUCTION

Many methods are cited in the literature for kinetic reactions of aromatic aldehydes and comprise reactions with chlorodipentylborane,[1] 5-*N*-benzoylamino-1,3,4-thiadiazole-2-acetonitrile,[2] 1,3-dimethybarbituric acid,[3] 3-methyl-1-phenylpyrazolin-5-one,[4] phenylhydroxylamine,[5] pyridinium chlorochromate,[6] phenylhydrazone,[7] and condensation with *o*-phenylenediamine in the presence of $H_2O_2$[8] with cysteine[9] and with 2,2-dimethyl-1,3-dioxane-4,6-dione.[10] Other methods are available for kinetic oxidation of aromatic aldehydes.[11-23]

This work aims to study the kinetics of the condensation reaction of some aromatic aldehydes with the active methylene compound, 7,9-dioxo-6,10-dioxaspiro[4.5]decane (D) and to study the effect of substituents on the reactivity. This work also aims to be has a spectrophotometric method for determination of some aromatic aldehydes.

## MATERIALS AND METHODS

### Apparatus

Visible absorption spectra were recorded on a Unicam SP 1800 recording spectrometer. An SP 6-200 Pye-Unicam spectrophotometer was used for the kinetic spectrophtometry. IR spectra were recorded (KBr) on a Pye Unicam SP 1000 spectrophotometer. $^1$H NMR spectra were taken at 270 MHz using $CDCl_3$ as a solvent.

### Reagents

All aromatic aldehydes used were of AR grade (BDH). Chloroform (Analar) used as a solvent. The standard solution of piperidine (E. Merck, G. R.) was directly prepared in chloroform. The reagent (D) was prepared by the same procedure of synthesis of some spiro compounds in the literature.[24] To a suspension of 52 g (0.5 mole) of malonic acid in 60 mL (0.6 mole) of acetic anhydride, 1.5 mL of concentrated sulfuric acid and 50 mL (0.55 mole) of cyclopentanone was added while cooling to maintain the temperature at 20-25 ºC. The reaction mixture was allowed to stand overnight in a refrigerator, then filtered and washed by cold water m.p: 90 ºC (Found: C, 56.4; H, 5.85; $C_8H_{10}O_4$ requires C, 56.5; H, 5.9); ν cm$^{-1}$ = 2950 ($CH_2$), 1735 and 1715 (C=O); $^1$H NMR: δ = 0.95-1.22 (m, 8H, $4CH_2$), 4.31 (s, 2H, $CH_2$).

### Kinetic procedure

The rate of reaction of the aldehydes tested (*p*-dimethylaminobenzaldehyde, *p*-nitrobenzaldehyde, *p*-hydroxybenzaldehyde, *p*-methoxybenzaldehyde, *p*-chlorobenzaldehyde, and benzaldehyde) with (D) in the presence of piperidine was followed by monitoring the increase in the absorbance of the product at its wavelength of maximum absorption with time.

Freshly prepared samples of aldehydes ($5 \times 10^{-3}$M), piperidine (0.1 M) and 0.1 M (D) in chloroform were allowed to equilibrate to 25 °C for 10 min in a thermostat. Mixing was carried out by withdrawing 0.5-2.0 mL aliquots of the aldehyde solution to 10 mL flasks containing 1.0 mL of 0.1 M piperidine, 1.0 mL of 0.1 M (D) solution, and the appropriate volume of chloroform. A portion of the reaction mixture was transferred to a quartz cuvette placed in a thermostated (25 ºC) cell compartment. A blank solution was similarly prepared without aldehyde and the absorbance readings were also recorded and followed as a function of time. Another set of runs was carried out in a similar manner using $5 \times 10^{-3}$ M (D) solution and $5 \times 10^{-2}$ M aldehyde solution.

Initial rates were determined by the method of initial rates,[25,26] whereby the absorbance (A) was plotted against time for each run. The initial slopes (dA/dt) for each run were determined and used in the following equation for calculating the rate of the reaction.[25,26]

$$Rate = \frac{dA}{dt} \times \frac{C_\infty - C_i}{A_\infty - A_i}$$

$C_i$ and $C_\infty$ are the initial and final concentrations of the colored reaction products, respectively, calculated by using the molar extinction coefficients ε; $A_i$ and $A_\infty$ are the absorbencies of the colored species at the initial and the end of the reaction. Since both $C_i$ and $A_i$ are nearly equal to zero at the beginning of the reaction, then the above equation reduced to:

$$Rate = \frac{dA}{dt} \times \frac{C_\infty}{A_\infty}$$

The observed rate constants $k_{obs}$ using excess (D) are calculated from the initial rate $R_i$ values by dividing it by the concentrations of the aldehydes. The second order rate constants $k_2 = k_{obs} / [D]$.

### Analytical procedure

A calibration graph for $2.5 \times 10^{-3}$ M each of the aldehydes *p*-nitrobenzaldehyde, *p*-hydroxybenzaldehyde, *p*-dimethylaminobenzaldehyde, *p*-methoxybenzaldehyde, vanillin, syringaldehyde, 2,4-dihydroxybenzaldehyde, *m*-nitrobenzaldehyde, benzaldehyde, *p*-cyanobenzaldehyde and *p*-chlorobenzaldehyde was obtained by transferring (0.1-1.0 mL) aliquots in chloroform to test tubes followed by the addition of 1.0 mL of the (0.1 M) solution of 7,9-dioxo-6,10-dioxaspiro[4.5]decane (D) in chloroform and 1.0 mL of the (0.1 M) piperidine solution in chloroform. The mixtures are thermostated at 50 °C in a water bath for 15 min and then diluted to 10 mL with chloroform and the absorbance of the resulting yellow color is measured at the maximum wavelength of each aldehyde derivative. The points on standard calibration curves each represent the outcome of three determinations.

### Preparation and analysis of reaction products

To a 5 mL solution of (D) (0.004 mol) in chloroform 5 mL. Solution of the aromatic aldehyde (0.004 mol) was added. To the reaction mixture 5 mL of 0.1 M piperidine was added. The reaction mixture was warmed at 50 ºC for 5 min and left at room temperature overnight. The crystals obtained were filtered off, dried and crystallized from chloroform. The physical properties, spectra, and elemental analyses are given in Table 1.

Table 1. Properties, Wave Length, IR and $^1$H NMR Spectral Data and Elemental Analyses of Products from Reaction of Some Aromatic Aldehyde Substituents with (D)

| Substituent | M.P (°C) | λ (nm.) | ν (cm$^{-1}$) | $^1$H NMR [δ (ppm)] in $CDCl_3$ | Molecular formula | Cal. (%) (Found) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | Cl |
| H | 110 | 360 | 2950 ($CH_2$), 1730, 1715 (C=O), 1590 (C=C) | 0.95-1.22 (m, 8H, $4CH_2$), 6.75-7.23 (m, 6 H, aromatic protons) | $C_{15}H_{14}O_4$ | 69.8<br>(69.6) | 5.5<br>(5.49) | - | - |
| *p*-$N(CH_3)_2$ | 142 | 445 | 3100, 3050, 2950 (CH), 1735, 1715 (C=O), 1660, 1620 (C=C) | 0.95-1.22 (m, 8H, $4CH_2$), 2.12 (6H, $CH_3$), 6.73-7.14 (5H, aromatic protons) | $C_{17}H_{19}NO_4$ | 67.8<br>(67.6) | 6.4<br>(6.38) | 4.6<br>(4.59) | - |
| *p*-$OCH_3$ | 125 | 365 | 3050, 2950 ($CH_2$), 1735, 1710 (C=O), 1660 (C=C) | 0.92-1.22 (m, 8H, $CH_2$), 3.52 (s, 3H, $CH_3$), 6.72-7.31 (m, 5, aromatic protons) | $C_{16}H_{16}O_5$ | 66.7<br>(66.6) | 5.6<br>(5.58) | - | - |
| *p*-Cl | 160 | 325 | 2950 ($CH_2$), 1730, 1715 1780 (C=O), 1675 (C=C) | 0.95-1.22 (m, 8H, $4CH_2$), 6.75-7.12 (5H, aromatic protons) | $C_{15}H_{13}O_4Cl$ | 61.5<br>(61.4) | 4.5<br>(4.46) | - | 12.1<br>(12.0) |
| *p*-OH | 136 | 370 | 3450-3390 (OH), 3050, 2950 ($CH_2$), 1630 (C=O) | 0.95-1.22 (m, 8H, $4CH_2$), 3.5 (s, OH), 6.72-7.35 (5H, aromatic protons) | $C_{15}H_{14}O_5$ | 65.7<br>(65.68) | 5.1<br>(5.0) | - | - |
| *p*-$NO_2$ | 135 | 340 | 2950 ($CH_2$), 1735, 1715 (C=O), 1670 (N=O), 1600 (C=C) | 0.95-1.22 (m, 8H, $4CH_2$), 6.75-7.12 (5H, aromatic protons) | $C_{15}H_{13}NO_6$ | 59.4<br>(59.38) | 4.3<br>(4.29) | 4.6<br>(4.59) | - |

## RESULTS AND DISCUSSION

The compound 7,9-dioxo-6,10-dioxaspiro[4.5]decane (D) undergoes condensation with aromatic and heteroaromatic aldehydes furnishing the corresponding arylidene derivatives, which are versatile substrates for different kinds of reactions.[27] They are useful intermediates for cycloaddition reaction and for the synthesis of heterocyclic compounds with potential pharmacological activity.[28] The 1,4-addition of nucleophiles has been widely used synthetically and display some advantages over the acyclic malonate analogous, and the conjugated reduction is the way most often used to prepare 5-monoalkyl Meldrum's acids derivatives or analog and are also applied to obtain deuterated carboxylic acids.[29]

The different reactivity of variously substituted aldehydes could be rationalized taking into account that the reaction occurs in two steps, i.e. the nucleophilic attack and the dehydration (Scheme I). Electron-withdrawing substituents facilitate the first step, meanwhile electron-donor substituents facilitate the loss of water giving a conjugated stabilized olefin.

**Scheme I**

$$—CH_2— \quad + \text{ Ald} \xrightarrow[\text{addition}]{\text{first step}} \left[\ \text{I}\ \right] \xrightarrow[\text{dehydration}]{\text{second step}} \text{Product}$$

From the data compiled in Table 2, it was shown that for all aldehydes studied the kinetics is second order overall, first order with respect to each of the reactants, and zero order with respect to piperidine, according to the simple rate law:

$$d[\text{product}]/dt = k_{obs}\,[\text{aldehyde}][\text{D}]$$

From this equation it can not be distinguished if the rate-limiting step is the nucleophilic attack of the carbanion of (D) on the aldehyde or the dehydration of compound (I), both steps being consistent with a second order equation. The study of the stoichiometry of the reaction indicates that the products have a maximum absorption at a molar ratio of 1:1 (aldehyde:D).

Table 2. Rate Constants of the Reaction of *p*-Methoxybenzaldehyde with 7,9-Dioxo-6,10-dioxaspiro[4.5]decane (D) at 298 K

| [Aldehyde], M | [D], M | [Pip.], M | $10^8$ R, mol. $l^{-1}$.sec$^{-1}$ |
|---|---|---|---|
| $2.5 \times 10^{-4}$ | 0.01 | 0.01 | 4.70 |
| $5.0 \times 10^{-4}$ | 0.01 | 0.01 | 9.78 |
| $7.5 \times 10^{-4}$ | 0.01 | 0.01 | 14.5 |
| $10.0 \times 10^{-4}$ | 0.01 | 0.01 | 19.58 |
| 0.005 | $2.5 \times 10^{-4}$ | 0.01 | 2.45 |
| 0.005 | $5.0 \times 10^{-4}$ | 0.01 | 4.90 |
| 0.005 | $7.5 \times 10^{-4}$ | 0.01 | 7.35 |
| 0.005 | $10.0 \times 10^{-4}$ | 0.01 | 9.80 |
| $5.0 \times 10^{-4}$ | 0.01 | 0.015 | 9.76 |
| $5.0 \times 10^{-4}$ | 0.01 | 0.02 | 9.72 |
| $5.0 \times 10^{-4}$ | 0.01 | 0.03 | 9.75 |

The kinetic results in Table 3 show that the rate of the reaction between different substituted benzaldehydes and (D) decreases in the following order:

$$p\text{-NO}_2 > p\text{-Cl} > \text{H} > p\text{-OCH}_3 > p\text{-OH} > p\text{-N(CH}_3)_2$$

It can be noted that electron-attracting groups increase the rate of reaction, whereas electron-repelling groups suppress it. In fact, the addition of (D) to substituted benzaldehydes (first step) is favored by electron withdrawing groups, and the dehydration step (second step) is favored by electron donating ones. The results for the reaction obtained can then be rationalized considering the first step is the rate-limiting one and the second step is the fast step.

Therefore, the reaction process can be represented by the following equations, where (ald), (D) and (I) refer to the

Table 3. Rate Constants and the Activation Parameters of the Reaction of Substituted Benzaldehydes with (D) Using 0.1 M Piperidine in Chloroform

| Substituent | $10^2$ $k_2$, l.mol$^{-1}$s$^{-1}$ | | | | ΔE$^{\#}$ | ΔH$^{\#}$ | ΔG$^{\#}$ | ΔS$^{\#}$ |
|---|---|---|---|---|---|---|---|---|
| | 298 K | 308 K | 313 K | 323 K | KJ.mol$^{-1}$ | | | J mol$^{-1}$ K$^{-1}$ |
| $p$-NO$_2$ | 4.8 | 10.9 | 19.8 | 33.0 | 63.4 | 60.94 | 80.64 | -65.69 |
| $p$-Cl | 3.1 | 7.6 | 16.5 | 25.0 | 67.7 | 65.18 | 81.61 | -55.10 |
| H | 3.1 | 6.1 | 7.8 | 22.0 | 75.05 | 73.12 | 82.74 | -32.09 |
| $p$-OCH$_3$ | 1.96 | 4.61 | 7.33 | 21.0 | 77.36 | 74.89 | 82.74 | -26.33 |
| $p$-OH | 1.21 | 2.60 | 7.60 | 13.4 | 80.40 | 77.70 | 84.00 | -20.20 |
| $p$-N(CH$_3$)$_2$ | 0.90 | 3.40 | 6.10 | 10.9 | 93.75 | 80.51 | 84.80 | -13.89 |

aldehyde, 7,9-dioxo-6,10-dioxaspiro[4.5]decane and the intermediate (I) in equation (i) respectively:

$$(D) + Pip \underset{fast}{\overset{K_1}{\rightleftharpoons}} (D)^- + \overset{+}{H}Pip \tag{i}$$

$$(Ald) + \overset{+}{H}Pip \underset{fast}{\overset{K_2}{\rightleftharpoons}} (AldH^+) + Pip \tag{ii}$$

$$(D)^- + (AldH^+) \xrightarrow[slow]{k} (I) \xrightarrow[fast]{K_d} Product \tag{iii}$$

The above equations lead to rate expression (iv),

$$Rate = k\,[D^-]\,[AldH^+] \tag{iv}$$

Then,

$$Rate = kK_1K_2\,[D]\,[Ald] \tag{v}$$

From equation (v), one can conclude that

$$k_{obs} = kK_1K_2\,[D] \tag{vi}$$

Equation (v) shows that the reaction follows second order kinetics, first order each in aldehyde and (D). The observed pseudo-first order rate constant $k_{obs}$ is therefore a product of the equilibrium constants of the two steps, the rate constant $k$ of the third step and (D). The rate constant $k$ could not be evaluated since no data are available for the equilibrium constants $K_1$ and $K_2$. The second order rate constants were calculated using the equation, $k_2 = k_{obs} / [D]$.

The rate constants of the reaction of different substituted aldehydes correlate well with Hammett's σ (Hammett's polar substituent constants) values for the aldehydes as shown in Fig. 1. The positive ρ value (0.465) (r = 0.962) means that electron-attracting groups enhance the rate of the reaction.

## Activation Parameters

The rates of the reaction of six different benzaldehydes were determined at three different temperatures, viz., 298, 308, 313 and 323 K. The activation energies $\Delta E^\#$ were determined from the slopes of the Arrhenius plots of log $k_2$ versus $T^{-1}$, as shown in Fig. 2. The other thermodynamic parameters $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$ were calculated[30] at 298 K and are given in Table 3.

The activation parameters show that the entropy of activation values is negative as expected for bimolecular or termolecular reactions. In this study the entropy of activation $\Delta S^\#$ is substituent dependent. Since all the substituents are located in *para* position, direct steric interaction is unlikely, so that resonance and/or inductive effects are the operating factors. Within the series, electron-withdrawing substituents in the aromatic aldehyde, through their resonance and/or inductive effects, localize the formal charge on the T.S. This favours the formation of more ordered transition states reflecting high and negative entropies of activation. On the other hand, the presence of electron donating substituents in the aldehyde alters their nature, leading to much more delocalization of the charge in T.S., and hence reflecting low and negative entropies of activation.

The linear correlation between $\Delta H^\#$ and $\Delta S^\#$ for the reaction of different substituents of benzaldehyde with (D) shows that all the compounds react by the same mechanism.[31] The value of the slope was 367.55 K (r = 0.997), which is the value of the isokinetic temperature β (the temperature at which the substituent effects is supposed to be reversed). This value is not the real temperature used in the kinetic runs.

The constancy of $\Delta G^\#$ may be explained on the basis of an isokinetic relationship that exists for a series of compounds of slightly different structures but undergoing reaction essentially by the same mechanism. The $\Delta G^\#$ may be more or less constant with relative changes in $\Delta H^\#$ and $\Delta S^\#$ as pointed out by Leffler.[31]

The mechanism for the title reaction is common for all members in the series as indicated by (a) the good straight-line plot of $\Delta H^\#$ versus $\Delta S^\#$, and (b) the linear plots of log $k_2$ at 50 °C against log $k_2$ at 25 °C (gradient, 0.658, r = 0.95).

At studied temperatures, an electron-withdrawing sub-

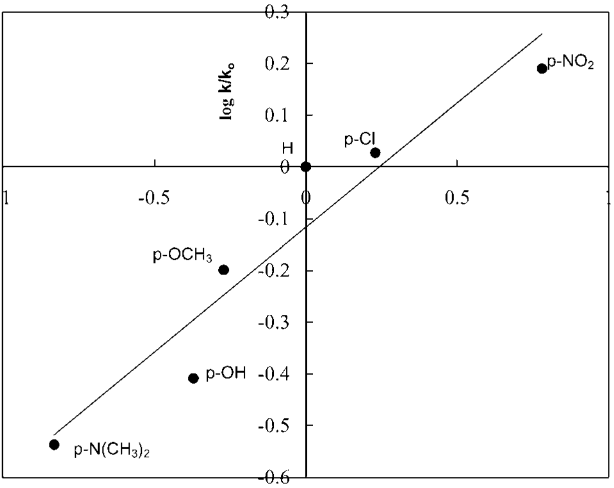


Fig. 1. Hammett plot for the reaction of substituted benzaldehydes with (D).

stituent in the *para* position of the aldehyde increases the reaction rates, while a similarly positioned electron releasing or donating substituent decreases it. This behavior could be explained by the observation that the ratio $k_{p-NO_2} / k_{p-N(CH_3)_2}$ was 5.33, 4.54, 3.25 and 3.03 at 25, 35, 40 and 50 °C, respectively (Table 3). Consequently, the variation of the rate constant depends on the nature of the substituent in the aldehyde. The order of decreasing reactivity of substituted aldehyde in chloroform is $p$-NO$_2$ > $p$-Cl > H > $p$-OCH$_3$ > $p$-OH > $p$-N(CH$_3$)$_2$. This order of decrease in magnitude of the substituent effect is expected on the basis of both inductive and resonance effects.

### Determination of the aldehydes tested

### Effect of time and temperature

The absorbance of the color due to reaction of the aldehydes tested with excess (D) in the presence of 0.1 M piperidine in ethanol reached a maximum intensity after 15 min at 50 °C, as shown in Tables 4 & 5.

Table 4. Effect of Time on the Absorption of the Product of Reaction of the Aldehydes Tested with Excess 7,9-Dioxo-6,10-dioxaspiro[4.5]decane (D)

| Substituent | Absorption at different times (min) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 5 | 10 | 15 | 30 | 60 | 90 | 24 h |
| $p$-OCH$_3$ | 0.7 | 0.88 | 0.87 | 0.87 | 0.86 | 0.86 | 0.86 |
| $p$-OH | 0.9 | 1.00 | 1.10 | 1.11 | 1.12 | 1.12 | 1.11 |
| $p$-NO$_2$ | 0.21 | 0.30 | 0.35 | 0.36 | 0.35 | 0.35 | 0.35 |
| $p$-N(CH$_3$)$_2$ | 1.0 | 1.15 | 1.22 | 1.24 | 1.25 | 1.25 | 1.26 |

Table 5. Effect of Temperature on the Absorption of the Product of Reaction of Aldehydes Tested with Excess 7,9-Dioxo-6,10-dioxaspiro[4.5]decane (D) in Chloroform

| Substituent | Absorption at different temperatueres (°C) | | | |
|---|---|---|---|---|
| | 25 | 30 | 40 | 50 |
| $p$-OCH$_3$ | 0.34 | 0.63 | 0.75 | 0.87 |
| $p$-OH | 0.45 | 0.75 | 0.90 | 1.10 |
| $p$-NO$_2$ | 0.12 | 0.19 | 0.25 | 0.35 |
| $p$-N(CH$_3$)$_2$ | 0.64 | 0.78 | 0.95 | 1.22 |

### Linearity and interferences

Table 6 shows linear regression analysis of the data obtained from calibration graphs of the aldehydes tested from the relation $A = a + bc$, where $A$ is the absorbance at the relevant peak in a 1.0 cm quartz cell, $a$ and $b$ are the intercept and the slope of the calibration graphs, respectively, and $c$ is the

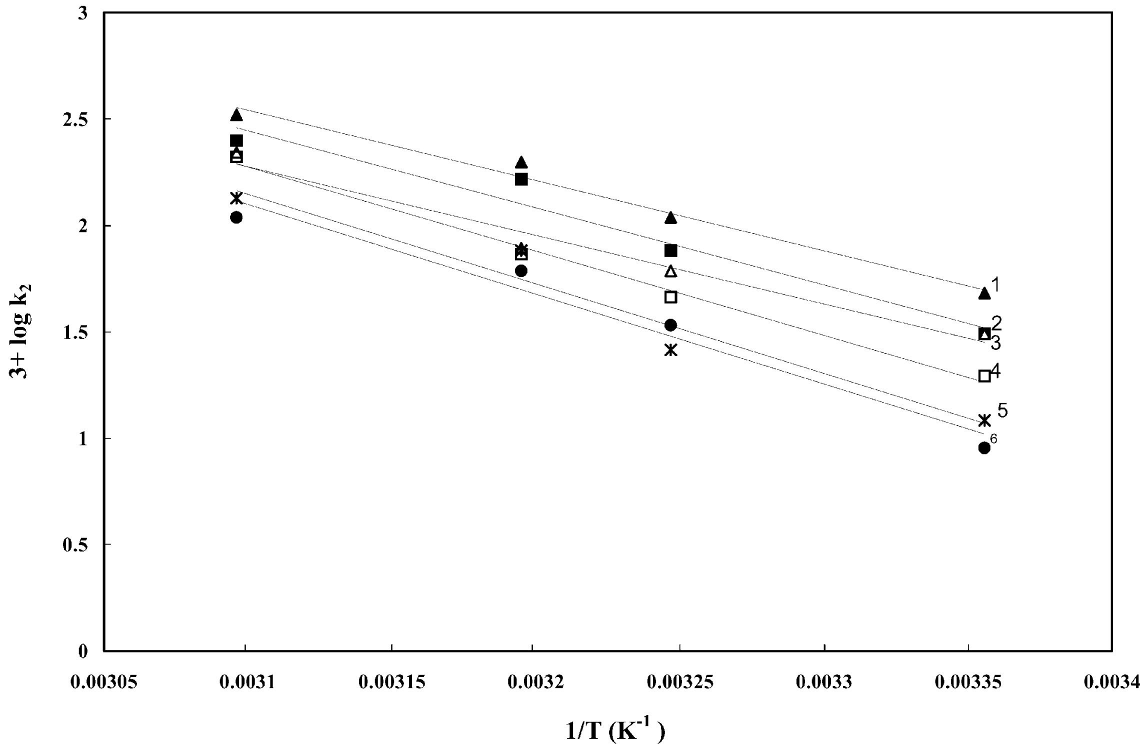


Fig. 2. Arrhenius plots for the reaction of (D) with different substituents of benzadehyde in the presence of 0.1 M piperidine in chloroform: (1) $p$-NO$_2$, (2) $p$-Cl, (3) H, (4) $p$-OCH$_3$, (5) $p$-OH and (6) $p$-N(CH$_3$)$_2$.

Table 6. Statistical Analysis of the Calibration Graphs for the Determination of Some Aromatic Aldehydes by Reaction with 7,9-Dioxo-6,10-dioxaspiro[4.5]decane (D) in Chloroform at 50 °C in the Presence of Piperidine

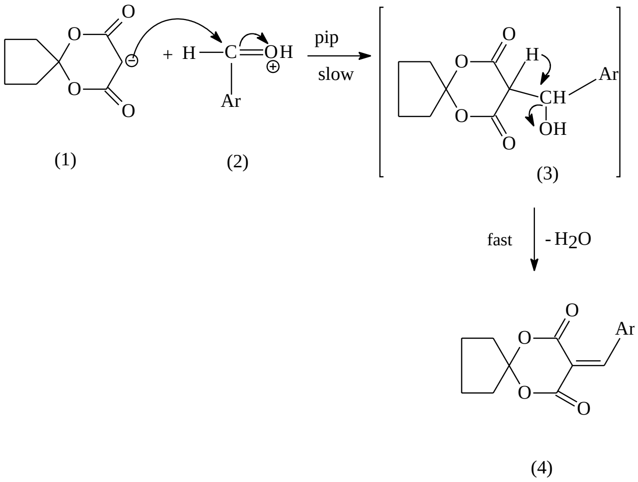
| Aldehydes | $\lambda_{max}$/nm | Concentration range (μg/mL) | ε (l mol$^{-1}$ cm$^{-1}$) | Slope (b) | Intercept (a) |
|---|---|---|---|---|---|
| *p*-Dimethylamino-benzaldehyde | 445 | 3.73-37.25 | 4890 | 0.0333 | 0.012 |
| Syringaldehyde | 365 | 4.55-45.50 | 2580 | 0.0141 | 0.004 |
| *p*-Methoxybenzaldehyde | 365 | 3.40-34.00 | 3510 | 0.026 | -0.005 |
| *p*-Hydroxybenzaldehyde | 370 | 3.05-30.5 | 4430 | 0.0361 | 0.005 |
| *p*-Nitrobenzaldehyde | 340 | 3.78-37.75 | 700 | 0.0093 | 0.000 |
| *m*-Nitrobenzaldehyde | 340 | 3.78-37.75 | 710 | 0.0046 | 0.001 |
| *p*-Chlorobenzaldehyde | 325 | 3.76-37.62 | 600 | 0.0043 | 0.000 |
| *p*-Cyanobenzaldehyde | 340 | 6.90-69.2 | 850 | 0.0071 | 0.002 |
| Vanillin | 370 | 3.80-38.0 | 3440 | 0.141 | 0.004 |
| Benzaldehyde | 360 | 2.65-26.5 | 950 | 0.0093 | 0.00 |

concentration of the aldehyde in μg/mL in the final solution. The points on standard calibration curves each represent the outcome of three determinations. The relative standard deviations (R.S.D%) vary between 0.7 and 1.0% for 10 μg mL$^{-1}$ of each aldehyde used (n = 3), and the reproducibility varies between 95.8 and 101% for each aldehyde.

No interference is caused by the presence of 10 mM formaldehyde, 5.17 mM acetone, 2.46 mM benzoic acid, 6.82 mM acetaldehyde and 3.2 mM aniline. In summary, thirteen aromatic aldehydes have been shown to be assessable with a new simple analytical method.

### The mechanism of the reaction

On the basis of the stoichiometry of the reaction, the nature of the reaction product and the kinetic data, the following mechanism can be suggested:



A piperidine molecule removes a proton from the (D) molecule to yield the carbanion (1), which adds in a slow step to the benzaldehyde molecule (2) to give intermediate (3), which is transformed to product (4) via a fast dehydration step. The observed negative entropy of the activation supports the above mechanism also.

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