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AMINOLYSIS OF *O*-(2,4-DINITROPHENYL)-*p*,*p*′-DISUBSTITUTED BENZOPHENONE OXIMES IN BENZENE: EVIDENCE FOR HIRST'S MECHANISM

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The reactions of *O*-(2,4-dinitrophenyl)-substituted *p*,*p*′-dimethoxybenzophenone oxime, *p*,*p*′-fluorobenzophenone oxime and *p*,*p*′-dichlorobenzophenone oxime with pyrrolidine and piperidine in benzene were found to be third order in amine, with no uncatalytic route. The overall rate is a combined effect of rates of two routes, one of which increases and the other decreases with rise in temperature. The relative contribution of the two routes to overall rate varies with temperature, nucleofugicity of the substrate, nucleophilicity and concentration of amine. As a result, the effect of temperature on the overall rate for some reactions is positive and for others negative. This unusual temperature effect on the overall rate supports Hirst's mechanism.

INTRODUCTION

Aromatic nucleophilic substitution reactions of nitro-activated substrates with amines as nucleophiles have been extensively studied in both dipolar and non-polar solvents. These reactions in dipolar solvents[1–6] normally show a second-order dependence on amine and are explained by Bunnett's mechanism. However, in non-polar solvents these reactions generally show a third-order dependence on amine and exhibit an inverse temperature effect on overall rate (k_A). Four approaches[7] have been adopted to explain this behaviour: (i) Nudelman's mechanism involving attack of amine dimer[8–12] on substrate leading to the formation of a hydrogen-bonded intermediate complex which breaks into products through uncatalysed and catalysed steps; (ii) formation of hydrogen-bonded four-, six- and eight-membered cyclic transition states;[13–16] (iii) an EDA complex mechanism in which Forlani[17,18] considers that the zwitterionic intermediate formed by the attack of nucleophile on substrate–nucleophile complex changes to products through two routes, uncatalysed and nucleophile catalysed; and (iv) Hirst's mechanism involving electrophilic catalysis[19,20] by conjugate and homoconjugated acids. There is a crucial difference in these four mechanisms, although all proceed through two routes. The first three mechanisms involve the participation of hydrogen-bonded species/molecular complexes for both routes whereas in Hirst's mechanism route I invokes electrophilic catalysis by non-hydrogen-bonded conjugate acid and route II by hydrogen-bonded homoconjugated acid. As hydrogen-bonded species/EDA molecular complexes have lower stability at higher temperatures, the rate for a reaction proceeding through the routes involving them is expected to decrease with rise in temperature. As such for the Nudelman, cyclic transition state and EDA complex mechanisms, the difference in the rates for the two routes is expected to decrease with rise in temperature and consequently the overall rate should exhibit an inverse temperature effect (decrease) irrespective of the nature of the substrate and nucleophile. On the other hand, for Hirst's mechanism, the rate for route I is expected to increase and for route II to decrease with rise in temperature. The overall rate may increase or decrease depending on the relative contribution of the two routes. Hence it is evident that a detailed study of the effect of temperature on the separate and overall rates may help in the elucidation of reaction mechanism.

No report is available which shows opposite temperature effects on the reaction rate for the two routes and a correlation between temperature effect (normal or inverse) on the overall rate and concentration and nature of the amine and substrate. Our own earlier study[21] was limited to the effect of temperature on the overall rate only, which decreased with rise in temperature. We have, therefore carried out a detailed study of the effect of temperature on the reaction

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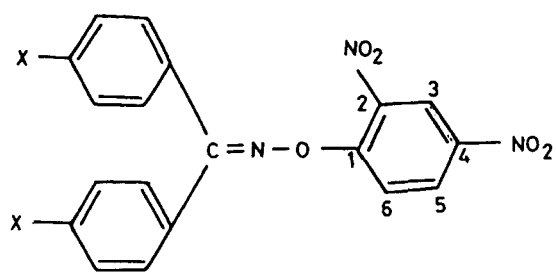


Where X is represented as,
(1) X = OCH_3 ,(2) X = F AND (3) X = Cl

of these newly synthesized substrates, viz. *O*-(2,4-dinitrophenyl)-substituted *p,p'*-dimethoxybenzophenone oxime (**1**), *p,p'*-difluorobenzophenone oxime (**2**) and *p,p'*-dichlorobenzophenone oxime (**3**) with pyrrolidine and piperidine in benzene in order to obtain information on the variations in the rates of the separate routes with temperature so as to provide evidence for the mechanism. The results of these investigations support Hirst's mechanism and also indicate that a normal temperature effect is observed for substrates with good leaving groups and an inverse temperature effect for those with poor leaving groups.

RESULTS AND DISCUSSION

Aminolysis of *O*-aryl oximes results in the formation of *N*-(2,4-dinitrophenyl)amines. The plots (Figure 1) of pseudo-first-order rate constants (k_0) versus [pyrrolidine] for the three substrates are curved, being concave towards the rate axis. This indicates base catalysis with an order of reaction in amine of >1. Further, the plots (Figure 2) of second-order rate constants (k_A), obtained by dividing k_0 by [amine], versus [pyrrolidine] show an upward curvature and pass through the origin, which indicates that the reactions are wholly base catalysed with an order of reaction in amine >2. Similar plots were obtained for pyrrolidinolysis and piperidinolysis at different temperatures for all the substrates.

The k_A values for pyrrolidinolysis and piperidinolysis of all the substrates at different temperatures are given in Table 1. It can be seen that the reactivity decreases in the order **3** > **2** > **1**, which can be explained on the basis of the departure ability of the leaving group. The expulsion of the leaving group involves breaking of a C—O bond, which generates a negative charge on the oxygen. The departure of oximate anion would be facilitated if it can be stabilized by delocalization of the charge towards the benzene rings of the oxime moiety through conjugation. Any substituent X attached to the benzene ring would affect the departure ability of the leaving group depending whether it enhances or hinders delocalization of the charge. Substrate **1** produces the minimum rate because the methoxy group makes the leaving group poorest by a net electron-donating effect[22] towards the ring, which inhibits delocalization. In substrates **2** and **3**, the halogens enhance the departure ability by facilitating delocalization of charge due to a net electron-withdrawing effect. Electrophilic

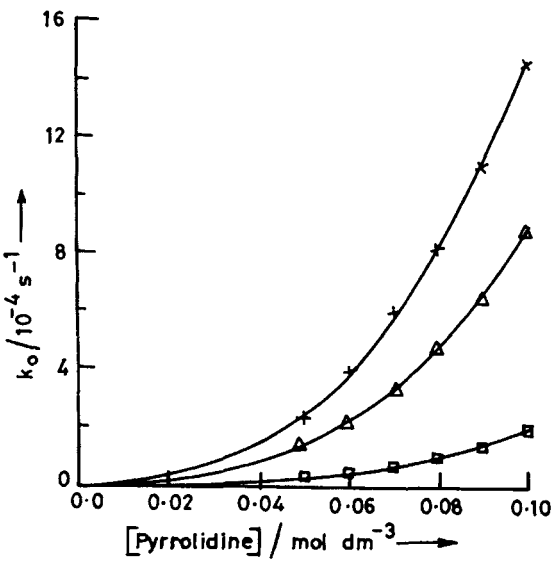


Figure 1. Plots of k_0 versus [pyrrolidine] for the reactions of (□) **1**, (△) **2** and (+) **3** in benzene at 20 °C

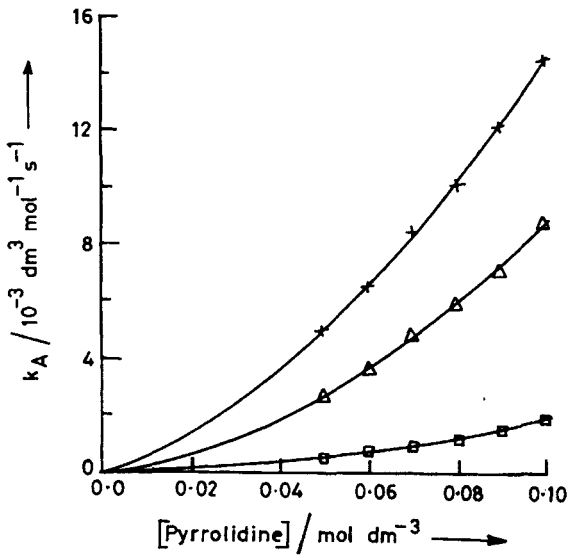


Figure 2. Plots of k_A versus [pyrrolidine] for the reactions of (□) **1**, (△) **2** and (+) **3** in benzene at 20 °C

Table 1. Second-order rate constants (k_A/dm^3 mol^{-1} s^{-1}) for pyrrolidinolysis and piperidinolysis of *O*-aryl oximes in benzene at different temperatures

Substrate	10^2[pyrrolidine] (mol dm^{-3})	$10^4 k_A$ 20 °C	30 °C	40 °C	10^2[piperidine] (mol dm^{-3})	$10^5 k_A$ 20 °C	30 °C	40 °C
1	5	5·9	4·9	4·8	20	7·5	6·7	6·2
	6	7·9	6·6	6·4	25	11·8	10·5	9·8
	7	10·4	8·6	8·0	30	16·8	15·1	13·8
	8	12·8	10·2	9·6	35	22·1	19·6	17·9
	9	16·2	12·8	11·5	40	26·8	23·7	21·4
	10	19·7	15·4	13·6	45	31·1	27·6	25·2
2	5	28·1	26·2	27·1	10	6·3	6·9	8·2
	6	37·2	34·7	34·5	15	11·7	12·5	13·9
	7	49·4	42·5	42·5	20	20·1	19·8	21·6
	8	60·1	54·0	52·8	25	28·8	27·9	29·3
	9	72·0	65·8	60·9	30	39·9	37·5	37·9
	10	88·5	76·7	72·3	35	52·7	47·6	48·9
3	5	50·6	49·2	53·4	10	17·6	21·6	27·2
	6	65·6	65·0	68·1	15	30·3	36·8	44·6
	7	85·1	80·2	82·3	20	46·6	52·5	62·6
	8	102·4	99·5	100·1	25	63·8	72·6	81·9
	9	122·8	115·4	116·5	30	82·8	90·8	105·7
	10	146·2	134·9	134·4	35	107·1	115·8	130·6

substitution studies[23] have indicated that the net electron-withdrawing effect of halogens (due to combined mesomeric and inductive effects) is Cl > F. Thus the rates for halogen substituted substrates should be in the order **3** > **2**.

In order to account for the higher order dependence on amine and the unusual temperature effect observed, we adopted the mechanism of electrophilic catalysis[19] occurring through conjugate and homoconjugated acids (Scheme 1). On applying the steady-state approximation to Scheme 1, the following equation[19] is obtained:

$$k_A = \frac{k_1(k_B K_B[B] + k_D K_D K_B[B]^2)}{k_{-1} + k_B K_B[B] + k_D K_D K_B[B]^2} \quad (1)$$

$$K_B = \frac{[(T^-)][BH^+]}{[(T^\pm)][B]}$$

$$K_D = \frac{[BH^+B]}{[BH^+][B]}$$

With the limiting condition $k_{-1} \gg k_B K_B[B] + k_D K_D K_B[B]^2$, equation (1) is reduced to equation (3).

$$k_A = \frac{k_1 k_B K_B[B]}{k_{-1}} + \frac{k_1 k_D K_D K_B[B]^2}{k_{-1}}$$

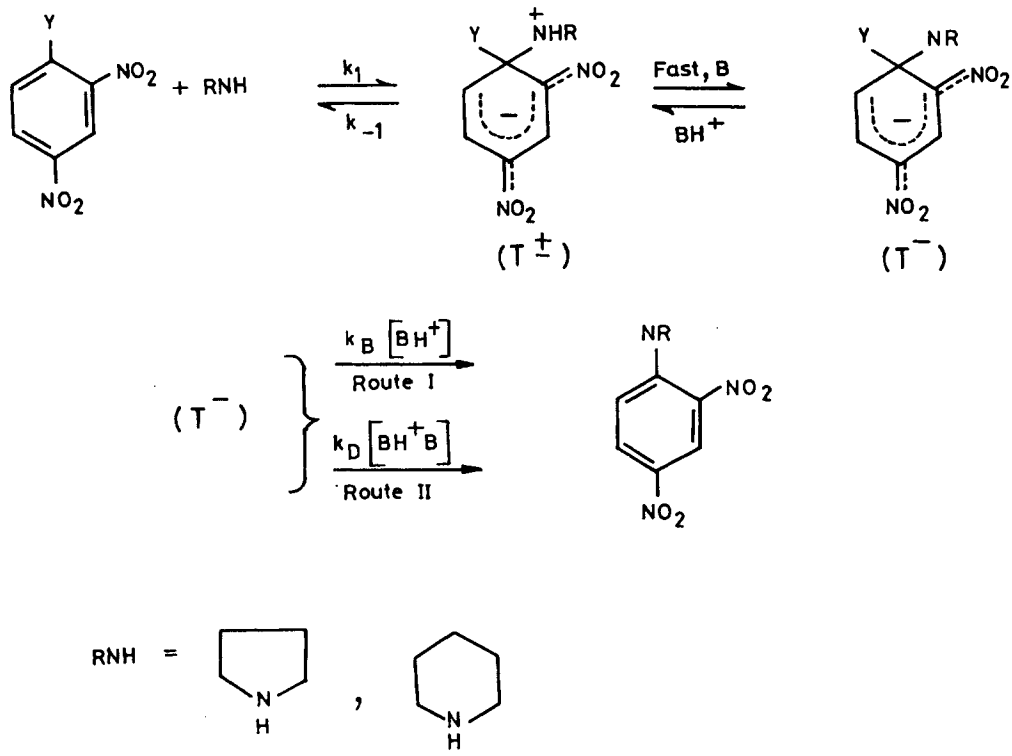
$$k_A = k'[B] + k''[B]^2 \quad (2)$$

$$k_A[B]^{-1} = k' + k''[B] \quad (3)$$

Hence $k_A[B]^{-1}$ should vary linearly with [B] and such plots have been obtained for pyrrolidinolysis (Figure 3) and piperidinolysis (Figure 4). However, in the case of piperidinolysis of **1** the plot deviates from linearity at higher amine concentrations. This indicates that at higher concentrations the limiting condition no longer holds and the curved plot follows equation (1). The piperidinolysis of **1** was not studied at lower concentrations as the rate was slow. The values of k' and k'' were calculated from the intercept and slope of these linear plots for all the substrates except piperidinolysis of **1** and are given in Table 2. It can be seen that at any given temperature, the value of k''/k' depends on the nature of the substrate and decreases as the leaving group becomes better. Further, the values of k''/k' for pyrrolidinolysis are greater than those for piperidinolysis, which is attributed to the smaller size of pyrrolidine than piperidine. BH^+B of pyrrolidine being of smaller size, it will have a higher k_D value than piperidine. Hence higher k_D values for homoconjugated acids of pyrrolidine cause higher k''/k' values for pyrrolidinolysis.

Effect of temperature

It can be seen from Table 2 that k' increases with increase in temperature, i.e. the reaction proceeding through route I shows a normal temperature effect and indicates that hydrogen-bonded species are not involved in this route. Further, k'' decreases as BH^+B tends to break down at higher temperatures, making K_D smaller;



Scheme 1

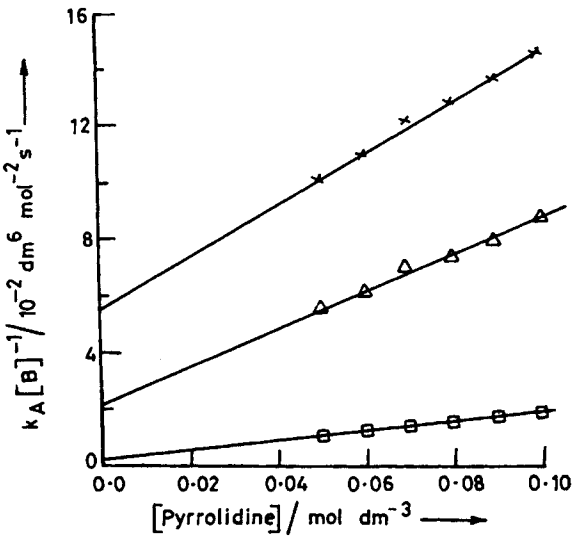


Figure 3. Plots of $k_A[B]^{-1}$ versus [pyrrolidine] for the reactions of (□) **1**, (△) **2** and (+) **3** in benzene at 20 °C

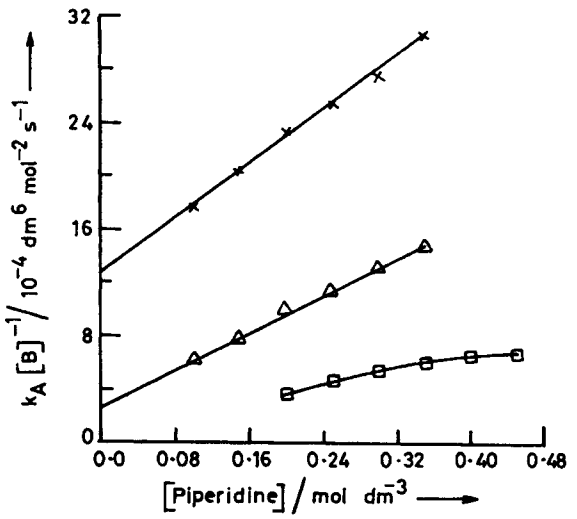


Figure 4. Plots of $k_A[B]^{-1}$ versus [piperidine] for the reactions of (□) **1**, (△) **2** and (+) **3** in benzene at 20 °C

Table 2. Values of third-order rate coefficient (k'/dm^{6}mol^{-2}s^{-1}) and fourth-order rate coefficient (k''/dm^{9}mol^{-3}s^{-1}) for pyrrolidinolysis and piperidinolysis of *O*-aryl oximes in benzene at different temperatures

		20 °C			30 °C			40 °C		
Reaction	Substrate	$10^3k'$	$10^2k''$	k''/k' (dm^{3}mol^{-1})	$10^3k'$	$10^2k''$	k''/k' (dm^{3}mol^{-1})	$10^3k'$	$10^2k''$	k''/k' (dm^{3}mol^{-1})
Pyrrolidinolysis										
	1	3·2	16·3	51·0	4·2	11·2	26·9	5·7	7·9	13·8
	2	22·5	65·2	29·0	28·0	49·1	17·6	35·2	36·2	10·3
	3	55·5	90·0	16·2	64·8	70·2	10·8	78·3	57·4	7·3
		20 °C			30 °C			40 °C		
		$10^5k'$	$10^4k''$	k''/k' (dm^{3}mol^{-1})	$10^5k'$	$10^4k''$	k''/k' (dm^{3}mol^{-1})	$10^5k'$	$10^4k''$	k''/k' (dm^{3}mol^{-1})
Piperidinolysis										
	1	—	—	—	—	—	—	—	—	—
	2	28·0	34·7	12·4	41·0	28·0	6·8	59·0	23·0	3·9
	3	125·4	51·7	4·1	172·5	45·0	2·6	232·5	40·0	1·7

the decrease in k'' supports the participation of hydrogen-bonded species in the rate-determining step of route II. Hence k''/k' decreases with increase in temperature, indicating that the extent of reaction proceeding through route I is relatively greater at higher than at lower temperatures.

Table 1 shows that the effect of temperature on the overall rate (k_A) is of five types : (i) for pyrrolidinolysis and piperidinolysis of **1** it decreases at all the amine concentrations with rise in temperature; (ii) a positive temperature effect is observed in the piperidinolysis of **3** over the whole amine concentration range studied; (iii) for pyrrolidinolysis of **2**, with increase in temperature the rate decreases continuously at all concentrations, except at 0·05 M pyrrolidine, where it first decreases and then increases with rise in temperature; (iv) in the pyrrolidinolysis of **3**, it first decreases (20–30 °C) and then increases (30–40 °C) at all amine concentrations except O·1 M pyrrolidine, where a continuous decrease is observed; and (v) with a rise in temperature from 20 to 30 °C, the rate of piperidinolysis of **2** increases at lower and decreases at higher amine concentrations. However, the rate increases at all concentrations with a rise of temperature from 30 to 40 °C.

These variations of k_A can be explained in terms of equation (2) which shows that the relative contribution of the two routes to the overall rate depends on the values of k', k'' and also amine concentration because of the involvement of the $[B]^2$ term. On this basis, the results can be explained as follows. (i) The values of k''/k' for pyrrolidinolysis of **1** are maximum at all temperatures and so high that the decrease in rate with temperature due to route II ($k''[B]^2$ term) is sufficient to predominate over the rate-increasing effect of route I ($k'[B]$ term) resulting in a decrease in k_A with rise in temperature at all amine concentrations studied. Although k''/k' for piperidinolysis of **1** could not be determined, it is expected to be sufficiently higher to cause a continuous decrease in rate with rise in temperature. (ii) As the values of k''/k' for piperidinolysis of **3** are minimum and so small that in spite of the higher concentration of piperidine used compared with pyrrolidine, the rate-decreasing effect of route II does not overcome the rate-increasing effect of route I and hence a positive temperature effect is observed. (iii) At 20 and 30 °C, for pyrrolidinolysis of **2** and **3** the values of k''/k' are smaller than observed for **1** but still high enough to cause a decrease in rate. However, as at 40 °C the k''/k' values become relatively much smaller, the rate-increasing effect of $k'[B]$ now predominates over the rate-decreasing effect of $k''[B]^2$, resulting in an increase in overall rate with rise in temperature from 30 to 40 °C at lower amine concentrations. At higher pyrrolidine concentrations (0·06–0·1 M for **2** and 0·1 M for **3**), in spite of the same values of k''/k', the rate decreases with increase in temperature from 30 to 40 °C. This is due to the involvement of the $[B]^2$ term in equation (2), which increases the contribution of route II relative to route I at higher amine concentrations. (iv) In the temperature range 20–30 °C, for piperidinolysis of **2** the increase at lower and decrease at higher concentrations can be explained by considering the lower value of k''/k' and concentration effect, respectively. An increase in rate from 30 to 40 °C over the whole concentration range is attributed to the still smaller value of k''/k' at 40 °C.

Table 3. Energy activation (kJ mol^{-1}) for routes I and II

	Pyrrolidinolysis		Piperidinolysis	
Substrate	Route I	Route II	Route I	Route II
1	22·5 ± 0·6	−28·0 ± 0·7	—	—
2	17·4 ± 0·6	−22·3 ± 0·6	28·1 ± 0·8	−15·5 ± 0·5
3	13·2 ± 0·4	−18·0 ± 0·6	23·6 ± 0·7	−10·1 ± 0·4

The energy of activation for pyrrolidinolysis and piperidinolysis proceeding separately through routes I and II was calculated from the temperature effect on k' and k'', respectively and these are given in Table 3. It can be seen that E_a for route I is positive and decreases as the leaving group becomes better from **1** to **3**. The E_a for route II is negative. The overall energy of activation using k_A has not been calculated as it is a function of amine concentration.

The effect of temperature on k' and k'' does not support Banjoko's and Nudelman's mechanisms. The results at any one temperature could have been explained by Banjoko's cyclic transition state mechanism[14,15] invoking six- and eight-membered cyclic transition states in routes I and II, respectively. If this mechanism operates, then the increase in temperature should have decreased both k' and k'' as the two transition states are hydrogen-bonded species and their formation would be hindered[13,14] at higher temperatures. Moreover, a diminution in both k' and k'' with temperature according to this mechanism cannot explain the overall increase in rate that was observed in some cases. Thus increase in k' and decrease in k'' with rise in temperature as determined here rule out this mechanism.

Nudelman's mechanism involving attack of an amine dimer as a nucleophile on the substrate is also not supported by our results, although it predicts[11,12] linear plots similar to those obtained here and shown in Figures 3 and 4, giving the intercept (k') and slope (k''). However, the nature of k' and k'' for dimer mechanism is altogether different from k' and k'' for equation (3). Both k' and k'' of the dimer mechanism[11,12] contain the equilibrium constant K for the formation of a hydrogen-bonded amine dimer ($K = [B \cdots B]/[B_0]^2$). At higher temperatures the value of K will decrease owing to the breakdown of $B \cdots B$, resulting in a decrease in the values of both k' and k'' with increase in temperature. The increase in k', the decrease in k'' and the overall rate increase in some cases with temperature as observed here thus do not support Nudelman's mechanism.

Forlani's EDA molecular complex mechanism[17,18] is also not supported because it (i) predicts $k_A[B]^{-1}(1 + K[B])$ vs [B] plots to be linear whereas we observed linearity for $k_A[B]^{-1}$ vs [B] plots and (ii) gives temperature effects not consistent with our results. Both the intercept and slope obtained from the linear plots for Forlani's mechanism[17,18] contain the formation constant (K) for the molecular complex. At higher temperatures, owing to the lower stability of the molecular complex, the value of K will decrease, resulting in a decrease in both the intercept and slope. This is contrary to our results.

CONCLUSIONS

The results of this investigation thus reveal that the aminolysis reaction of *O*-aryl oximes proceed through Hirst's mechanism, and Nudelman's dimer, Banjoko's cyclic transition state and Forlani's EDA molecular complex mechanisms are not operating. Contrary to earlier reports, aminolysis reactions in non-polar aprotic solvents can exhibit normal or inverse temperature effects depending on the nucleofugicity of the substrate and the nature and concentration of the amine.

EXPERIMENTAL

Reagents and materials. Benzene (Merck) was purified by distillation after drying with $CaCl_2$ and sodium wire. Piperidine (Riedel-de Haën) and pyrrolidine (Merck) were purified by distillation after drying them with sodium metal and kept in the dark under nitrogen. Both benzene and amines were stored over 4 A Linde-type molecular sieves. *p,p'*-Dimethoxy-, -difluoro- and -dichlorobenzophenone oximes were prepared by interacting corresponding disubstituted benzophenones (Aldrich) with hydroxylamine hydrochloride and sodium hydroxide following the procedure described for the preparation of benzophenone oxime.[24] The oximes were crystallized from methanol and the purity was checked by TLC. The substrates, *O*-(2,4-dinitrophenyl)-*p,p'*-disubstituted benzophenone oximes were then synthesized by reacting the appropriate oxime with an equimolar amount of sodium in a methanolic medium followed by treatment with a methanolic solution of 1-chloro-2,4-dinitrobenzene (Fluka) according to the procedure reported for the preparation of *O*-(2,4-dinitrophenyl)anisaldehyde oxime.[25] These were recrystallised from ethyl acetate and the purity was checked by TLC. The substrates synthesized were characterized by ^{1}H NMR spectroscopy (100 MHz) and elemental analysis.

O-(2,4-Dinitrophenyl)-*p,p'*-dimethoxybenzophenone oxime: m.p. 100 °C; ^{1}H NMR, δ_H ($CDCl_3$) 4·0 (two singlets looking like a doublet 6H, $2 \times OCH_3$), 7·0–7·3 (m, 4H, Ar), 7·4–7·7 (m, 4H, Ar), 8·2 (d, 1H, Ar, $J_{6,5} = 9$ Hz), 8·6 (dd, 1H, Ar, $J_{5,6} = 9$ Hz; $J_{5,3} = 3$ Hz), 8·9 (d, 1H, Ar, $J_{3,5} = 3$ Hz); found, C 59·8, H 3·9, N 9·8; calculated for $C_{21}H_{17}N_3O_7$, C 59·6, H 4·0, N 9·9%. *O*-(2,4-Dinitrophenyl)-*p,p'*-difluorobenzophenone oxime: m.p. 124 °C; ^{1}H NMR, δ_H ($CDCl_3$) 7·2–7·5 (m, 4H, Ar), 7·5–7·8 (m, 4H, Ar), 8·2 (d, 1H, Ar, $J_{6,5} = 8$ Hz), 8·5 (dd, 1H, Ar, $J_{5,6} = 8$ Hz, $J_{5,3} = 3$ Hz), 8·9 (d, 1H, Ar, $J_{3,5} = 3$ Hz); found, C 57·0, H 2·8, N 10·6; calculated for $C_{19}H_{11}N_3O_5F_2$, C 57·1, H 2·8, N 10·5%. *O*-(2,4-Dinitrophenyl)-*p,p'*-dichlorobenzophenone oxime: m.p. 145 °C; ^{1}H NMR, δ_H ($CDCl_3$) 7·4–7·9 (m, 8H, Ar), 8·2 (d, 1H, Ar, $J_{6,5} = 8$ Hz), 8·6 (dd, 1H, Ar, $J_{5,6} = 9$ Hz, $J_{5,3} = 3$ Hz), 8·9 (d, 1H, Ar, $J_{3,5} = 3$ Hz); found, C 52·6, H 2·6, N 9·6; calculated for $C_{19}H_{11}N_3O_5Cl_2$, C 52·8; H 2·6, N 9·7%. Stock solutions of the substrates and amines were used within 24 h. The products, *N*-(2,4-dinitrophenyl)amines, were characterized by matching their TLC and spectral data with those of authentic samples obtained by reacting 1-chloro-2,4-dinitrobenzene with amines.

Kinetic procedure. The kinetics were studied on a Shimadzu UV 160 A spectrophotometer fitted with a thermostated multi-cell compartment. All reactions were followed at λ_{max} of the aminolysis product. Precautions were taken to avoid traces of water during the course of the reaction. In all runs, the amine concentrations were in large excess over the substrate concentration ($4·0 \times 10^{-5}$ M) to maintain pseudo-first-order conditions. Pseudo-first-order rate constants (k_0) were calculated numerically by the least-squares method on a Meera PC/AT 286-20 from plots of $\ln(A_\infty - A_t)$ versus time, where A_∞ and A_t are the absorbances at infinite time and time t, respectively. Kinetic runs with correlation coefficients less than 0·999 were rejected. Rate coefficients were reproducible to within 2·5%.

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