Kinetics of Oxidative Condensation of *p*-Phenylenediamines with Mono- and Poly-substituted Benzoylacetanilides

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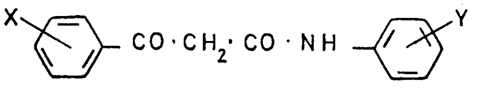
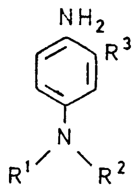
The kinetics of the oxidative condensation of *NN*-dialkyl-*p*-phenylenediamines and mono- and poly-substituted benzoylacetanilides in aqueous alkaline solution, in the pH range 7·5—10·8, have been investigated by the stopped-flow technique. In this pH range the rate is proportional to the concentration of the positively charged *p*-benzoquinone di-imine and of the anion corresponding to the benzoylacetanilide. It is suggested that the rate-determining step is the formation of the leuco-dye. The reactivity of the benzoylacetanilide anions increases with increasing basicity. A linear relationship between log (k_{c-}/k_{0c-}) (where k_{0c-} is the specific rate constant of the unsubstituted benzoylacetanilide) and the σ values of the substituents was obtained for both mono- and poly-substituted benzoylacetanilides.

In the colour photographic process yellow dyes[1] are obtained by oxidative coupling reactions of *NN*-dialkyl-*p*-phenylenediamines (PPD) and benzoylacetanilides (B) Though the kinetics of the oxidative coupling of diamines and phenols have been extensively investigated,[2,3] little work has been devoted to the dye formation from benzoylacetanilides.[4,5]



(1) X = Y = H
(2) X = H, Y = *o*-Cl
(3) X = H, Y = *o*-Br
(4) X = H, Y = *m*-CO_2Me
(5) X = H, Y = *m*-NO_2
(6) X = H, Y = *m*-Ac
(7) X = H, Y = *m*-CN
(8) X = H, Y = *p*-Ac
(9) X = H, Y = *p*-NEt_2
(10) X = H, Y = *p*-OH
(11) X = H, Y = *p*-CO_2H
(12) X = H, Y = *p*-SO_2NH_2
(13) X = 2,4,6-Me_3, Y = H
(14) X = Y = *o*-Cl
(15) X = *o*-Cl, Y = *o*-OMe
(16) X = *p*-OMe, Y = *m*-NO_2
(17) X = *p*-OMe, Y = *m*-CN
(18) X = Y = *p*-OMe
(19) X = *p*-OMe, Y = *o*-NEt_2



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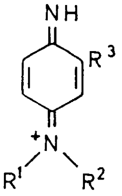


(21)

a; $R^1 = Et$, $R^2 = C_2H_4NHSO_2Me$, $R^3 = Me$
b; $R^1 = R^2 = Et$, $R^3 = H$
c; $R^1 = R^2 = Et$, $R^3 = Me$

Van Brandt and Bruylants[6] investigated the condensation of a group of benzoylacetanilides with *NN*-dialkyl-*p*-nitrosoaniline in ethanol and a relationship between reactivity and the substituent effect σ was obtained.

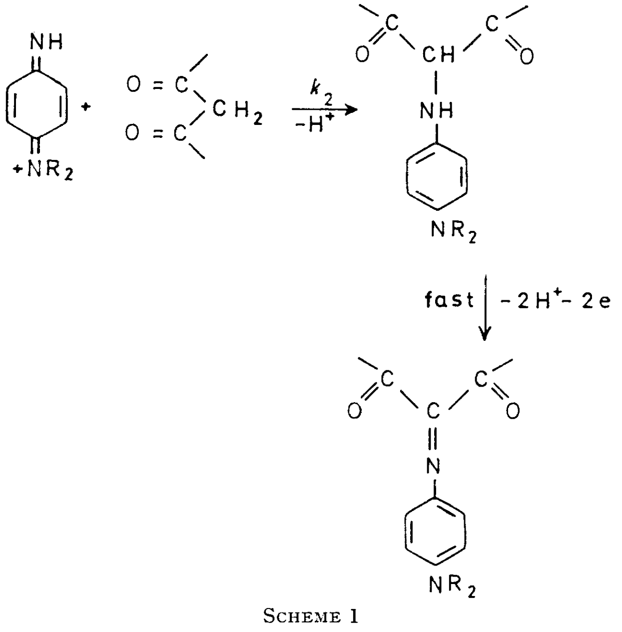
This paper reports the kinetics of the reaction in aqueous alkaline solution (pH 7·5—10·8), in order to ascertain how the reactivity is affected by substituents on the aromatic ring.

The preparation and the acid dissociation constants of the benzoylacetanilides have been described.[7]

Kinetics.—Literature data and the present experiments show that the benzoylacetanilides in aqueous solution and in the pH range investigated are mainly in the ketonic form[8] and that the oxidative coupling needs, at first, two equivalents of oxidant per mole of PPD to form *p*-benzoquinone di-imine (QDI)[9] [reaction (1)].

$$p\text{-phenylenediamine} \xrightarrow[\text{ox}]{k_1} p\text{-di-imine} \quad (1)$$

Two further equivalents of oxidant are then required to oxidize the leuco-dye (L) to the final dye[2] (Scheme 1, which takes account of the structure of the dye[6,10]).



Scheme 1

The reaction was carried out in aqueous alkaline solution (pH 7·5—10·8) at 25 ± 1° with potassium

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[1] C. E. K. Mees, 'The Theory of the Photographic Process,' Macmillan, New York, 1969.

[2] L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.* (*a*) 1957, **79**, 583; (*b*) 1968, **90**, 5154.

[3] (*a*) J. F. Corbett, *J. Chem. Soc.* (*B*), 1970, 1418; (*b*) E. Pelizzetti and G. Saini, *J. Photographic Sci.*, in the press.

[4] B. P. Brand, *J. Photographic Sci.*, 1965, **13**, 248; 1968, **16**, 1.

[5] P. W. Vittum and A. Weissberger, *J. Photographic Sci.*, 1957, **5**, 157.

[6] P. Van Brandt and A. Bruylants, *Bull. Soc. chim. Belges*, 1964, **73**, 843.

[7] E. Pelizzetti and C. Verdi, *J.C.S. Perkin II*, 1973, 808.

[8] L. Hevesi, P. Van Brandt, and A. Bruylants, *Bull. Soc. chim. France*, 1970, **11**, 3971.

[9] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 207.

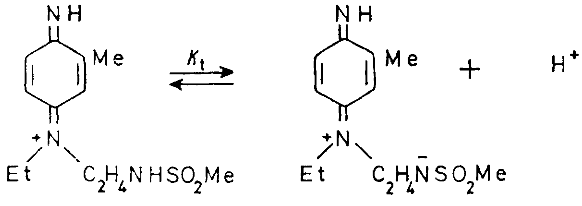
[10] G. H. Brown, J. Figueras, R. J. Gledhill, C. J. Kibler, F. C. McCrossen, S. M. Parmenter, P. W. Vittum, and A. Weissberger, *J. Amer. Chem. Soc.*, 1957, **79**, 2919.

ferricyanide as oxidant. Under these conditions the rate-determining step is the formation of the leuco-dye.[3]

Taking into account the hydrolysis of QDI,[11] Tong [2a] found that equation (2) was obeyed where $m = 1 + (k_d)_{[H^+]}/\{(k_2)_{[H^+]}[B]_0\}$, $[B]_0$ is the initial concentration of

$$(k_2)_{[H^+]} = \frac{2{\cdot}303}{t(m[B]_0 - [QDI]_0)} \log \frac{[QDI]_0([B]_0 - [D])}{[B]_0([QDI]_0 - m[D])} \qquad (2)$$

benzoylacetanilide, irrespective of its ionic form, $[QDI]_0$ is the initial concentration of di-imine, irrespective of its ionic form, [D] is the concentration of dye at time t, obtained from $[D] = A_t/\varepsilon_D$, where A_t and ε_D are respectively the absorbance (at time t) and molar absorptivity at a given wavelength, and $(k_d)_{[H^+]}$ is the overall hydrolysis rate constant for QDI at a given pH. Equation (2) and the expression for m were derived by assuming that four equivalents or more of oxidant are added per mole of PPD. Equation (2) holds for the early part of the reaction or in the presence of a large excess of coupler. Most reactions were carried out with di-imine (21a), for which the $C_2H_4NHSO_2Me$ group can dissociate (Scheme 2).



(21a) (22)

Scheme 2

Previous studies [2,3] of reactions of phenols with di-imines suggest that even benzoylacetanilides should react in their dissociated forms in the pH range investigated; therefore the kinetic expression (3) is obtained where k'_{c^-} and k''_{c^-} are respectively the specific

$$d[D]/dt = k'_{c^-}[B^-][(21a)] + k''_{c^-}[B^-][(22)] \qquad (3)$$

rate constants of the reactions of the benzoylacetanilide anion with the two forms of di-imine [(21a) and (22)].

With $(k_2)_{[H^+]}$ as the observed rate constant at constant pH (Scheme 1) equation (4) holds where K_a is the acid

$$k'_{c^-} = (k_2)_{[H^+]} \frac{K_a + [H^+]}{K_a} \cdot \frac{K_t + [H^+]}{\mu K_t + [H^+]} \qquad (4)$$

dissociation constant of the benzoylacetanilide, K_t the acid dissociation constant of the sulphonamido-group [see Scheme 2; $K_t = 3 \times 10^{-10}$ (ref. 11)] and $\mu = k''_{c^-}/k'_{c^-}$.

For the other di-imines the kinetics are described by equation (5), hence equation (6) applies.

$$d[D]/dt = k_{c^-}[B^-][QDI^+] \qquad (5)$$

$$k_{c^-} = (k_2)_{[H^+]} \cdot \frac{K_a + [H^+]}{K_a} \qquad (6)$$

RESULTS

The $(k_2)_{[H^+]}$ values were evaluated by means of a computer; the calculated absorbances were compared with the experimental ones and $(k_2)_{[H^+]}$ was optimized by successive iterations.

According to Tong,[2b] $(k_2)_{[H^+]}$ increases to a limit as the ratio $[B]_0/[QDI]_0$ decreases (with $[QDI]_0$ constant). The variations are related to the initial concentration of benzoylacetanilide and only indirectly to pH (see Table 1). The values of k_{c^-} [for (21b and c) from equation (6)] and k'_{c^-} [for (21a) from equation (4)] were calculated from the limiting values of $(k_2)_{[H^+]}$.

TABLE 1

Rate data for the reaction of (1) with (21a) at 25°

pH	$10^5[(1)]/M$	$10^5[(21a)]/M$	$10^{-4}(k_2)_{[H^+]}/l\ mol^{-1}\ s^{-1}$
9·0	4·0	4·0	2·8
9·0	8·0	4·0	2·4
9·0	16·0	4·0	1·9
			(2·8) [a]
9·6	4·0	4·0	5·2
9·6	8·0	4·0	4·7
9·6	12·0	4·0	4·4
9·6	16·0	4·0	3·8
			(5·2) [a]
10·0	4·0	2·0	5·6
10·0	8·0	2·0	4·9
10·0	12·0	2·0	3·6
10·0	16·0	2·0	3·2
10·0	4·0	4·0	5·8
10·0	8·0	4·0	5·2
10·0	16·0	4·0	3·9
			(5·8) [a]
10·4	8·0	4·0	5·3
10·4	12·0	4·0	5·0
10·4	16·0	4·0	4·7
			(5·5) [a]
10·8	8·0	4·0	4·8
10·8	16·0	4·0	5·0
			(5·0) [a]

$k'_{c^-} = 1{\cdot}6 \times 10^5$ l mol^{-1} s^{-1}, $\mu = 0{\cdot}28$

Estimated upper limit for the $(k_2)_{[H^+]}$ value.

The assumption of a single μ value for reaction of (21a) with the benzoylacetanilides is unsatisfactory. Therefore an estimate of k'_{c^-} and μ was made for every benzoylacetanilide by trial and error at various pH values. The estimated k'_{c^-} and μ values were fed into a computer to obtain the best fit with the experimental $(k_2)_{[H^+]}$ values. The optimized values of μ ranged from 0·22 to 0·44.

Table 1 collects the $(k_2)_{[H^+]}$ values for the reaction of (1) with (21a); values of $k'_{c^-} = 1{\cdot}6 \times 10^5$ l mol^{-1} s^{-1} and $\mu = 0{\cdot}28$ were obtained from the limiting value of $(k_2)_{[H^+]}$ at every pH.

Table 2 lists the specific rate constants (k'_{c^-} and k_{c^-}) for the reactions of the benzoylacetanilides with (21a—c).

DISCUSSION

Figure 1 shows a plot of log k_{c^-} *vs.* pK_a for the benzoylacetanilides and di-imines. The experimental data lie on a straight line corresponding to equation (7) where,

$$\log k_{c^-} = \log \alpha + \beta pK_a \qquad (7)$$

for (21a), log $\alpha = 0{\cdot}11$ and $\beta = 0{\cdot}55$ were calculated by least square method with correlation coefficient r 0·986 [compound (13) was excluded; the large deviation may

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[11] L. K. J. Tong, *J. Phys. Chem.*, 1954, **58**, 1090.

be due to the steric effect of the two *ortho*-methyl groups). This relationship is valid also for (21b and c) with the same value of β and log $\alpha = 0{\cdot}43$ for (21b) and $-0{\cdot}36$ for (21c).

Correlations of this type are quite common for reactions with nucleophiles;[12] in the present case the reactivity of the benzoylacetanilide anions increases with increasing basicity. Such behaviour is expected from the relation[13] between the charge density on the carbon atom of the methylene group and the pK_a value.

TABLE 2

Specific rate constants for the reaction of benzoyl acetanilides with various di-imines

Anilide	pK_a [a]	pH [b]	10^5[QDI]/M [c]	10^5[B]/M [c]	k'_{c^-}(21a)/ l mol^{-1} s^{-1}	μ	log (k'_{c^-}/k'_{0c^-})	k_{c^-}/l mol^{-1} s^{-1} (21b)	(21c)
(1)	9·4	9·0—10·8	2·0—4·0	4·0—16·0	$1{\cdot}6 \times 10^5$	0·28		$3{\cdot}2 \times 10^5$	$5{\cdot}0 \times 10^4$
(2)	8·9	8·0—10·0	4·0	8·0—20·0	$9{\cdot}1 \times 10^4$	0·44	−0·26	$2{\cdot}0 \times 10^5$	$3{\cdot}8 \times 10^4$
(3)	8·7	8·0—10·0	4·0	4·0—20·0	$7{\cdot}8 \times 10^4$	0·37	−0·31		
(4)	9·2	8·5—10·4	4·0	4·0—20·0	$1{\cdot}2 \times 10^5$	0·37	−0·13		
(5)	8·9	8·0—10·0	4·0	4·0—16·0	$8{\cdot}2 \times 10^4$	0·43	−0·29		
(6)	9·2	8·0—10·0	4·0	4·0—16·0	$1{\cdot}1 \times 10^5$	0·41	−0·16		
(7)	8·9	8·5—10·4	4·0	4·0—20·0	$9{\cdot}0 \times 10^4$	0·39	−0·25		
(8)	9·1	8·5—10·4	4·0	4·0—16·0	$1{\cdot}0 \times 10^5$	0·40	−0·21		
(9)	9·8	9·6—10·4	3·0—4·0	4·0	$3{\cdot}2 \times 10^5$	0·37	+0·30		
(10)	10·2	8·5—10·4	4·0	4·0—20·0	$5{\cdot}5 \times 10^5$	0·24	+0·54	$1{\cdot}0 \times 10^6$	$1{\cdot}8 \times 10^5$
(11)	9·4	9·0—10·4	4·0	4·0—20·0	$1{\cdot}6 \times 10^5$	0·31	0·00		
(12)	8·8	8·5—10·4	4·0	4·0—10·0	$7{\cdot}3 \times 10^4$	0·35	−0·34		
(13)	8·3	8·5—10·4	4·0	4·0—20·0	$4{\cdot}0 \times 10^3$	0·23	−1·86		
(14)	7·4	7·5—9·6	2·5	4·0—10·0	$2{\cdot}1 \times 10^4$	0·30	−0·88		
(15)	7·8	7·5—9·6	2·5	4·0—10·0	$2{\cdot}5 \times 10^4$	0·22	−0·80	$8{\cdot}3 \times 10^4$	$9{\cdot}0 \times 10^3$
(16)	9·6	9·6—10·4	2·0	2·0—8·0	$2{\cdot}1 \times 10^5$	0·24	+0·12		
(17)	9·8	9·0—10·4	2·0	2·0—8·0	$2{\cdot}8 \times 10^5$	0·22	+0·24		
(18)	10·4	8·5—10·4	2·0	2·0	$8{\cdot}0 \times 10^5$	0·31	+0·70		
(19)	10·3	8·5—10·4	2·0	2·0	$7{\cdot}2 \times 10^5$	0·35	+0·64		

[a] See ref. 7. [b] Experimental range of pH. [c] Columns 4 and 5 give the experimental range of di-imine and benzoylacetanilide concentrations respectively.

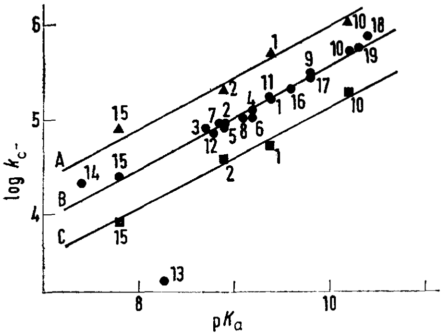

FIGURE 1 Diagram of log (k_{c^-}/k_{0c^-}) as a function of pK_a of the benzoylacetanilides for various di-imines: A, (21b); B, (21a); C, (21c)

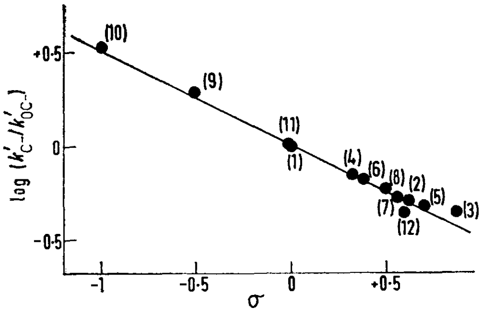

FIGURE 2 Diagram of log (k'_{c^-}/k'_{0c^-}) as a function of the substituent effect for the monosubstituted (Y ≠ H, X = H) benzoylacetanilides

The effect of the substituents on reactivity is shown by Figure 2 which is a plot of log (k'_{c^-}/k'_{0c^-}) [where k'_{0c^-} is the specific rate constant of the unsubstituted benzoylacetanilide (1)] against σ values, for monosubstituted benzoylacetanilides (Y ≠ H, X = H); the experimental data lie on a straight line where $\rho_Y = -0{\cdot}48$ (r 0·987). The σ values were from the literature[14] or were derived from the dissociation constants.[7]

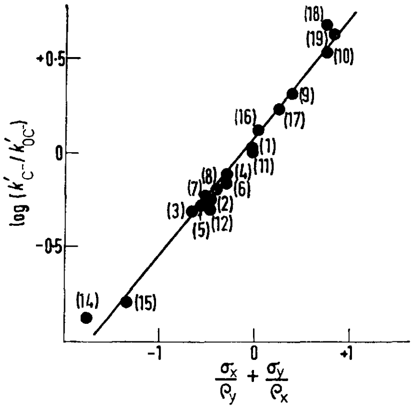

FIGURE 3 Combined effect of the substituents on the reactivity of benzoylacetanilides. The points are the experimental data and the straight line, according to equation (8), has a slope $\rho_X\rho_Y = 0{\cdot}64$ (in order to calculate the abscissa values $\rho_Y = -0{\cdot}48$ and $\rho_X = -1{\cdot}3$ were adopted)

For polysubstituted compounds (Y ≠ H, X ≠ H) equation (8) holds, as shown in Figure 3 where the

$$\log (k'_{c^-}/k'_{0c^-}) = \rho_X\rho_Y\left(\frac{\sigma_X}{\rho_Y} + \frac{\sigma_Y}{\rho_X}\right) \qquad (8)$$

calculated line gave a good fit for $\rho_X = -1{\cdot}3$ (r 0·986).

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[12] J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 1963, **60**, 271; K. M. Ibne Rasa, *J. Chem. Educ.*, 1967, **44**, 89

[13] H. J. Hofmann, M. Scholtz, and C. Weiss, *Z. Chem.*, 1971, **11**, 181.

[14] J. Hine, ' Physical Organic Chemistry,' Holt, New York, 1959.

The monosubstituted compounds are reported for comparison.

The results show that electron-releasing substituents increase the reactivity of the benzoylacetanilides.

Table 2 shows decreasing reactivity of the di-imines in the order (21b) > (21a) > (21c). This result was found previously for the reaction of these di-imines with phenols;[3b] electron-releasing groups decrease the reactivity of the di-imines, while the opposite holds for for coupler.

TABLE 3

Visible spectra of dyes in aqueous alkaline buffer (pH *ca.* 9)

Dye obtained from			$10^{-4}\varepsilon_{max.}$/
Anilide	Di-imine	$\lambda_{max.}$/nm	l mol^{-1} cm^{-1}
(1)	(21a)	460	1·30
(2)	(21a)	460	1·42
(3)	(21a)	461	1·40
(4)	(21a)	461	1·38
(5)	(21a)	462	1·36
(6)	(21a)	464	1·45
(7)	(21a)	462	1·20
(8)	(21a)	462	1·40
(9)	(21a)	458	1·15
(10)	(21a)	458	1·00
(11)	(21a)	464	1·40
(12)	(21a)	466	1·50
(13)	(21a)	474	1·00
(14)	(21a)	472	1·15
(15)	(21a)	462	1·20
(16)	(21a)	456	1·80
(17)	(21a)	457	1·70
(18)	(21a)	453	0·85
(19)	(21a)	447	0·85
(1)	(21b)	456	1·52
(2)	(21b)	456	1·70
(10)	(21b)	468	1·22
(15)	(21b)	450	1·65
(1)	(21c)	456	1·20
(2)	(21c)	456	1·60
(10)	(21c)	470	0·82
(15)	(21c)	456	1·20

EXPERIMENTAL

Benzoylacetanilides.—The preparation and the dissociation constants of the benzoylacetanilides have been given previously.[7] Solutions were prepared in organic solvents (acetone or methanol) and alkaline buffer. The reacting mixture did not contain >1% organic solvent.

p-*Phenylenediamines.*—Reagent grade products were dissolved immediately before use in distilled and deaerated water.

Oxidant.—Reagent grade potassium ferricyanide was added in the amount of four equiv. per mole of PPD.

Buffer Solutions.—Solutions were prepared by mixing 0·0125M-borax with 0·1M-HCl or -NaOH.[15] The pH of the reacting mixture was constant within 0·05 pH unit.

Apparatus.—The absorption spectra of the dyes were recorded with a Hitachi–Perkin-Elmer EPS 3T spectrophotometer. Kinetic measurements were made with a stopped flow Durrum–Gibson apparatus.

Molar Absorptivities.—The molar absorptivities of the dyes at the absorption maxima were evaluated by mixing a constant amount of PPD with a large excess of benzoylacetanilide. The measured absorbance increased till to a limiting value which allowed to estimate ε_D. The measurements were carried out at pH 9, with the stoicheiometric amount of oxidant. The molar absorptivity is given by ε_D = absorbance/[PPD]. Table 3 collects the $\lambda_{max.}$ and ε_D data for the investigated dyes.

Hydrolysis Rate Constants $(k_d)_{[H^+]}$.—These have been previously evaluated and reported.[3b]

Kinetic Experiments.—A mixture of benzoylacetanilide and oxidant in buffer solution was mixed in the stopped-flow apparatus with a buffered solution of PPD and the variation of absorbance with time was taken at the wavelength of maximum absorption of the dye. Since the benzoylacetanilides were previously dissolved into the alkaline buffered solution, no induction periods, as observed from Vittum and Weissberger,[5] were found. The experiments were carried out at 25 ± 1°.

[3/077 *Received, 12th January,* 1973]

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[15] L. Meites, ' Handbook of Analytical Chemistry,' McGraw-Hill, London, 1963, sect. 11-7.