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Differential Kinetic Determination of Mixtures of Aniline and Its Derivatives Using N,N-Dimethyl-*p*-phenylenediamine

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The oxidative coupling reaction between the quinonediimine (QDI) of N,N-dimethyl-*p*-phenylenediamine (DMPD) and aromatic amines was utilized for the simultaneous determination of binary mixtures of aniline and its derivatives by the differential reaction rate method. A mixture of oxidant and DMPD was used instead of QDI because QDI was unstable. The effects of pH and the oxidant ($K_3Fe(CN)_6$, $K_2Cr_2O_7$ and their mixture) on the stability of the first oxidation product of DMPD, semiquinone (SQ), and on the equilibrium among DMPD, SQ and QDI, were investigated. The second-order rate constants of two amines reacting with QDI and the overall pseudo first-order rate constant of a mixture were determined from the slope of the straight line (the concentration of SQ *vs.* time) and by simplified complementary tristimulus colorimetry. Mixtures of amines down to 1.0×10^{-4} M were determined. Most relative errors were in the range of 0 to 14%. Among the compounds examined for interference, phenols and carbonyl compounds showed serious effects.

Keywords——aniline and its derivatives; N,N-dimethyl-*p*-phenylenediamine; potassium ferricyanide; potassium dichromate; semiquinone radical; quinonediimine; differential reaction rate method; simplified complementary tristimulus colorimetry

The differential reaction rate method is effective for the *in situ* analysis of mixtures of closely related homologs and isomers, because it can avoid the use of elaborate separation techniques. However, preceding studies have indicated lower accuracy of the method compared to equilibrium methods available, because of the restriction that the low concentrations of the species determined cause the reaction rate to be slow, so that the amount that reacts during measurement is small.[2] It is also known that the semiquinone radicals derived by partial oxidation from aromatic *p*-diamines have intense colors and react with various aromatic amines and phenols to give intensely colored indamine and indoaniline dyes, which can be used as indicators of the degree and rate of reaction.[3] In view of this, semiquinone radicals may represent useful reagents for determining aromatic amine mixtures by the differential reaction rate method. This paper is the first report of such a procedure.

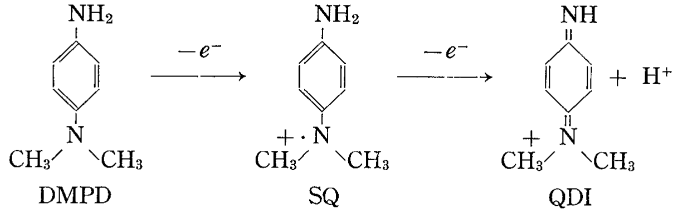

Chart 1

The oxidation of N,N-dimethyl-*p*-phenylenediamine (DMPD) proceeds in two steps, each involving one-electron transfer: first to the semiquinone (SQ) of a stable free radical and

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[1] Location: *5, Nakauchi-cho, Yamashina-ku, Kyoto, 607, Japan.*

[2] *a*) J.G. Hanna and S. Siggia, *J. Pharm. Sci.*, **55**, 541 (1966); *b*) H.B. Mark, Jr. and G.A. Rechnitz, "Kinetics in Analytical Chemistry," Interscience Publishers, Inc., New York, 1968. p. 67.

[3] L. Michaelis, *Chem. Rev.*, **16**, 243 (1935); L. Michaelis, M.P. Schubert, and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

subsequently to a very unstable quinonediimine (QDI) (Chart 1). Under these conditions, aromatic amines react with QDI to yield quantitatively intensely-colored indamine dyes.[4] Based on this reaction, we report here a differential kinetic procedure for the simultaneous determination of mixtures of aniline and its derivatives that is accurate and reproducible, and requires no sample pretreatment for the determination of the total initial concentrations.[2b]

Method

Since the rate of indamine formation follows second-order kinetics (first-order with respect to both QDI and amine),[4b] Eq. (1) holds for a mixture of two amines, C_1 and C_2.

$$-d[\mathrm{QDI}]/dt = d[\mathrm{I_1}]/dt + d[\mathrm{I_2}]/dt = k_2[\mathrm{QDI}][\mathrm{C_1}] + k_2'[\mathrm{QDI}][\mathrm{C_2}] \qquad (1)$$

where I_1 and I_2 are the indamines formed from C_1 and C_2, and k_2 and k_2' are the second-order rate constants of C_1 and C_2 reacting with QDI, respectively. Provided that the initial concentrations, $[C_1]_0$ and $[C_2]_0$, are in large excess over [QDI] (a pseudo first-order condition), the amounts of C_1 and C_2 can be considered constant throughout kinetic measurement. In this case, Eq. (1) can be written as follows:

$$-d[\mathrm{QDI}]/dt = (k_1+k_1')[\mathrm{QDI}] \qquad (2)$$

where $k_1=k_2[C_1]_0$ and $k_1'=k_2'[C_2]_0$. As DMPD is in rapid equilibrium with SQ and QDI, as described later, Eq. (2) can be rewritten as[5]

$$-d[\mathrm{QDI}]/dt = -d[\mathrm{SQ}]/dt = (k_1+k_1')[\mathrm{SQ}]^2/K[\mathrm{DMPD}]_{0(\mathrm{eq})} \qquad (3)$$

where [SQ] and $[\mathrm{DMPD}]_{0(\mathrm{eq})}$ are the concentration of SQ at time t and that of DMPD which is in equilibrium with SQ and QDI at $t=0$, respectively, and K is the equilibrium constant (Eq. (10)). Eq. (3) can be integrated directly to give

$$1/[\mathrm{SQ}] - 1/[\mathrm{SQ}]_{0(\mathrm{eq})} = K^*t \qquad (4)$$

in which

$$K^* = (k_1+k_1')/K[\mathrm{DMPD}]_{0(\mathrm{eq})} \qquad (5)$$

and $[\mathrm{SQ}]_{0(\mathrm{eq})}$ is the concentration of SQ in equilibrium with DMPD and QDI at $t=0$. If A_t is the absorbance of SQ at the stipulated wavelength (515 nm was chosen) at any given time, plots of $1/A_t$ *versus* time should be linear, and the value of K^* can be calculated from the slope.

In addition, a simple relation holds between the concentrations of two indamines at any time, from Eqs. (1) and (2):[6]

$$[\mathrm{I_1}]/[\mathrm{I_2}] = k_1/k_1' \quad ([\mathrm{I_1}]_0=[\mathrm{I_2}]_0=0 \text{ at } t=0) \qquad (6)$$

In the simplified complementary tristimulus colorimetry (SCTS method),[7] as shown in Fig. 1, the color point of a reaction mixture consisting of I_1, I_2 and SQ at any time, M_t, can be resolved into the color points of a mixture of I_1 and I_2 at the same time, m_t, on the straight line connecting those of I_1 and I_2 in the manner described by Flaschka *et al.*[8] The mole fraction of I_1, q, is denoted as

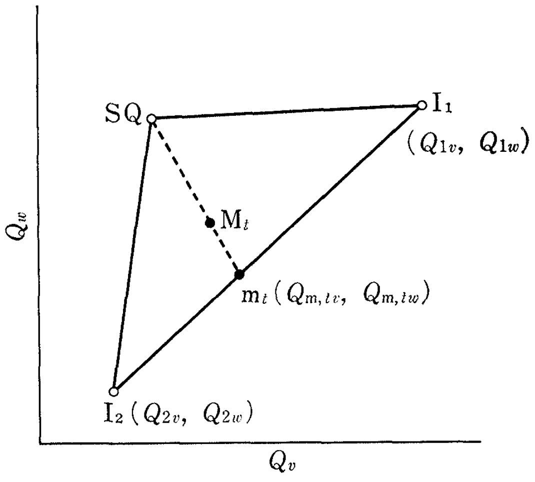

Fig. 1. Q_v–Q_w Plot for I_1, I_2 and Their Mixture

M_t: a mixture of I_1, I_2 and SQ at time t.
m_t: a mixture of I_1 and I_2 at the same time.

$$q = [\mathrm{I_1}]/([\mathrm{I_1}]+[\mathrm{I_2}]) \qquad (7)$$

and the value of q can be calculated from the color point of m_t by the SCTS method:

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4) *a*) O. Heim, *Ind. Eng. Chem., Anal. Ed.*, **7**, 146 (1935); *b*) J.F. Corbett, *J. Chem. Soc.* (*B*), **1969**, 827; *c*) D.N. Kramer and L.U. Tolentino, *Anal. Chem.*, **43**, 834 (1971).

5) B.C. Challis and R.J. Higgins, *J. Am. Chem. Soc.*, **93**, 1597 (1971); A.J. Bard, A. Ledwith, and H.J. Shine, *Adv. Phys. Org. Chem.*, **13**, 155 (1976).

6) A.A. Frost and R.G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley and Sons, Inc., New York, 1961, p. 164.

7) R. Tawa and S. Hirose, *Talanta*, **26**, 237 (1979).

8) H. Flaschka, *Talanta*, **7**, 90 (1960); R. Tawa and S. Hirose, *ibid.*, in press.

$$q = E_2(Q_{2v}-Q_{m,tv})/[E_1(Q_{m,tv}-Q_{1v}) + E_2(Q_{2v}-Q_{m,tv})] \qquad (8)$$

where E_1 and E_2 are the overall absorptivities, and Q_{1v}, Q_{2v} and $Q_{m,tv}$ are the complementary color points of I_1, I_2 and their mixture at time t and wavelength v, respectively (For wavelengths u and w, analogous equations can be written). By considering that $[I_1]/[I_2]$ is given by $q/(1-q)$ [Eq. (7)], k_1 and k_1' can be determined from Eqs. (5), (6) and (8). Therefore, $[C_1]_0$ and $[C_2]_0$ are determined simultaneously from k_1 and k_1' by using k_2 and k_2' determined by individual measurements.

Experimental

Materials——DMPD dihydrochloride was obtained commercially and purified by recrystallization from methanol. A solution was prepared in distilled water before use. Potassium ferricyanide and potassium dichromate were of analytical reagent grade, and were used without further purification. The following amines were used and purified according to the literature:[9] aniline (AA), *o*-toluidine (*o*-TL), *m*-toluidine (*m*-TL), *o*-bromoaniline (*o*-BA), *m*-bromoaniline (*m*-BA), *m*-chloroaniline (*m*-CA), *p*-chloroaniline (*p*-CA), *o*-aminobenzoic acid (*o*-ABA), *p*-aminoacetophenone (*p*-AAP), *o*-anisidine (*o*-AS), α-naphthylamine (α-NA), N-phenylglycine (PG), N-phenylanthranilic acid (PAA), N-methylaniline (MA), N-ethylaniline (EA), N-*n* propylaniline (PA), N,N-dimethylaniline (DMA), N,N-diethylaniline (DEA), N,N-dibenzylaniline (DBA), 3-dimethylaminobenzoic acid (DABA). Other chemicals were of analytical reagent grade. 3-Methoxyindamine (3-MI) ferrocyanide was prepared from DMPD and *o*-AS by the method of Corbett and Gamson.[10] TLC (*sec*-butyl alcohol: acetic acid: water = 2 : 1 : 5) on silica gel layers showed the 3-MI formed to be free from significant impurities.

Apparatus——Absorbance measurements and the calculations of the complementary color points were carried out as described previously.[11] The redox potential measurements were made with a Hitachi-Horiba F-7 pH meter with a Pt electrode and a saturated calomel electrode, equipped with a Takeda Riken TR-6155M digital multimeter and a recorder. Temperature was controlled at 25±0.1° by means of a Sharp TE-10K thermoelectriccirculating bath.

Measurement of the Redox Potential of DMPD——The potential measurements were performed by addition of 4.0 ml of the oxidant solution (a mixture of 3.0×10^{-3} M $K_3Fe(CN)_6$ and 3.2×10^{-3} M $K_2Cr_2O_7$) to 14.0 ml of buffer solution, followed by rapid addition of 2.0 ml of DMPD solution (2.5×10^{-2} M); in every case the extrapolated potential at zero time could be obtained from the potential measurements as a function of time after mixing. All the solutions were purged with nitrogen gas for 10 min and stored under this gas during the measurements.

Hydrolysis of 3-MI——2.0 ml of 3-MI solution (3.0×10^{-3} M) was placed in a 10 ml volumetric flask and the buffer solution was added to make up the volume. An aliquot of the solution was transferred quickly to a 1 cm cell, and the absorbance at 715 nm was recorded as a function of time against the blank solution. The same procedure was followed at each pH. The hydrolysis of 3-MI was followed under first-order kinetics over the pH range studied, and the rate constant, k_{OH}, was determined.[10]

$$k_{OH} = k\alpha[OH^-] + k' \qquad (9)$$

where k and k' are the observed rate constants of the catalyzed and uncatalyzed reactions, respectively, and α is the fraction of indamine as the conjugated acid, which can be calculated from the dissociation constant of 3-MI ($pK_a = 6.07\pm0.38$).

Kinetic Determination of Mixtures——5.0 ml of 0.1 M phosphate buffer (pH 6.1), 1.0 ml of the oxidant solution and a given volume of sample were added to a 10 ml volumetric flask, and the solution was made up to volume with distilled water. The initial time ($t=0$) was taken as the instant when 0.3 ml of DMPD solution (1.0×10^{-3} M) was added to the system. The reaction was followed by measuring the absorbances at 750(u), 695(v) and 515 nm(w) at regular intervals ($t=1.0$ min).

Results and Discussion

The reaction of AA with DMPD under the conditions used involves (a) the oxidation of DMPD to QDI, and (b) the coupling of the latter with AA to give 4-amino-4'-dimethylaminodiphenylamine (leuco-indamine), (c) which is rapidly converted to the indamine by further oxidation (Chart 2).[4b] In this work, a mixture of DMPD and the oxidant solution

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[9] F.E. Critchfield and J.E. Ruch, "Treatise on Analytical Chemistry," Vol. 15, Part II, ed. by I.M. Kolthoff and P.J.E. Elving, A Wiley-Interscience Publication, New York, 1976, p. 187, 194.

[10] J.F. Corbett and E.P. Gamson, *J. Chem. Soc. Perkin II*, **1972**, 1531.

[11] R. Tawa and S. Hirose, *Chem. Pharm. Bull.*, **27** 2515 (1979); R. Tawa, S. Shimizu, and S. Hirose, *ibid.*, **28**, 541 (1980).

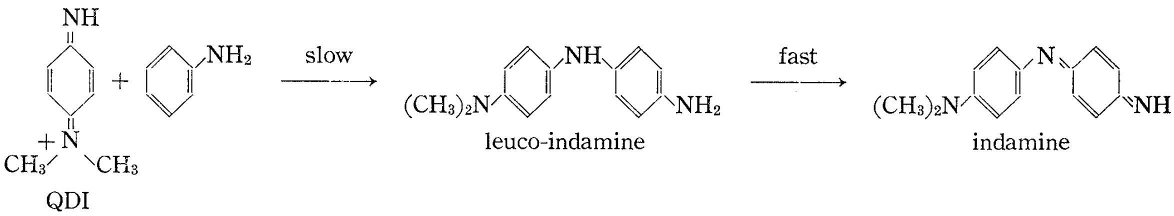

Chart 2

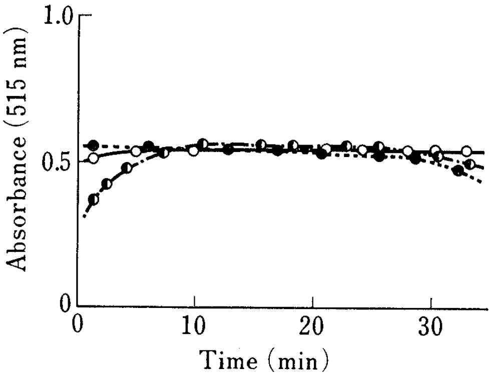

Fig. 2. Compoarison of Oxidants in the Oxidation of DMPD (3.0×10^{-5}M) at pH 6.1

----○----: $K_3Fe(CN)_6$ 3.2×10^{-5} M.
——○——: $K_2Cr_2O_7$ 3.0×10^{-5} M.
——○——: a mixture of $K_3Fe(CN)_6$ 3.2×10^{-5} M and $K_2Cr_2O_7$ 3.0×10^{-5} M.

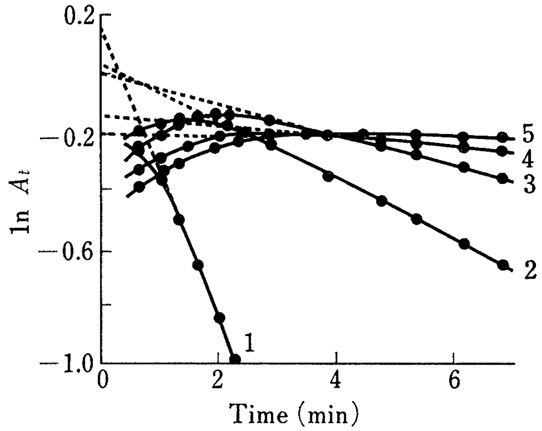

Fig. 3. Extrapolated Absorbance (515 nm)-Time Curves for the Disappearance of SQ at Various pH Values

(1) 4.09, (2) 4.98, (3) 5.19, (4) 5.74, (5) 6.10.
The solutions contained DMPD (3.0×10^{-5} M) and the oxidant (3.2×10^{-5} M $K_3Fe(CN)_6$ and 3.0×10^{-5} M $K_2Cr_2O_7$).

was used as the reagent instead of using QDI, because of the instability of QDI in solution at room temperature.

For an unstable redox system, it is important to choose an oxidizing agent with a high degree of activity and selectivity. Figure 2 shows that the mixture of $K_3Fe(CN)_6$ and $K_2Cr_2O_7$ used here gave more selective oxidation of DMPD to SQ than either agent alone, probably as a result of the acid-base character of the mixed oxidative agent.[12]

As SQ is in rapid equilibrium with both DMPD and QDI, the effect of pH was investigated. Denoting the equilibrium constant as

$$K = [\mathrm{SQ}]^2_{(\mathrm{eq})}/[\mathrm{DMPD}]_{(\mathrm{eq})}[\mathrm{QDI}]_{(\mathrm{eq})} \tag{10}$$

where $[\mathrm{QDI}]_{(\mathrm{eq})}$ is the concentration of QDI in equilibrium, Eq. (13) can be obtained from the initial concentration of DMPD, $[\mathrm{DMPD}]_0$, and the oxidant concentration added, C_{ox}, by using the following stoichiometric relationships[13]

$$C_{\mathrm{ox}} = [\mathrm{SQ}]_{(\mathrm{eq})} + 2[\mathrm{QDI}]_{(\mathrm{eq})} \tag{11}$$

$$[\mathrm{DMPD}]_0 = [\mathrm{DMPD}]_{(\mathrm{eq})} + [\mathrm{SQ}]_{(\mathrm{eq})} + [\mathrm{QDI}]_{(\mathrm{eq})} \tag{12}$$

and by considering that $[\mathrm{SQ}]_{(\mathrm{eq})}$ becomes maximum when $C_{\mathrm{ox}} = [\mathrm{DMPD}]_0$.[14]

$$\sqrt{K} = 2[\mathrm{SQ}]_{(\mathrm{eq})}/([\mathrm{DMPD}]_0 - [\mathrm{SQ}]_{(\mathrm{eq})}) \tag{13}$$

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12) M. Ai, *Yuki Gosei Kagaku Kyokai Shi*, **35**, 201 (1977); J.H. Sinfelt and J.A. Cusumano, "Advanced Materials in Catalysis," ed. by J.J. Burton and R.L. Garten, Academic Press, Inc., New York, **1977**, Chapter I.

13) L.K.J. Tong and M.C. Glesman, *Photogr. Sci. Eng.*, **8**, 319 (1964).

14) G. Pettersson, *Acta Chem. Scand.*, **22**, 3063 (1968).

The value of $[\mathrm{SQ}]_{(\mathrm{eq})}$ could be estimated from the initial absorbance at 515 nm, A_0, which was obtained by extrapolation to zero time in plots of A_t *vs.* time (Fig. 3). The extinction coefficient of SQ at 515 nm was calculated from the initial slope of plots of A_0 *vs.* C_{ox} by Pettersson's method (a value of log $\varepsilon=4.03$ was obtained).[14] The variations of K as a function of pH are shown in Fig. 4. The disappearance of SQ followed first-order kinetics (Fig. 3). SQ was most stable in solution within the pH range of 5.0—6.4 and became unstable outside this range, because of the lability of QDI (Table I). The dissociation constants of SQ are 4.6 and 6.2 (Fig. 5), and only II among the three ionization states (Chart 3) is stabilized by resonance.[15] Therefore, the subsequent reactions were carried out at pH 6.1. The results in Table I also show that SQ is most stable in solution at pH 6.1 when $C_{\mathrm{ox}}=[\mathrm{DMPD}]_0$ under the conditions used.

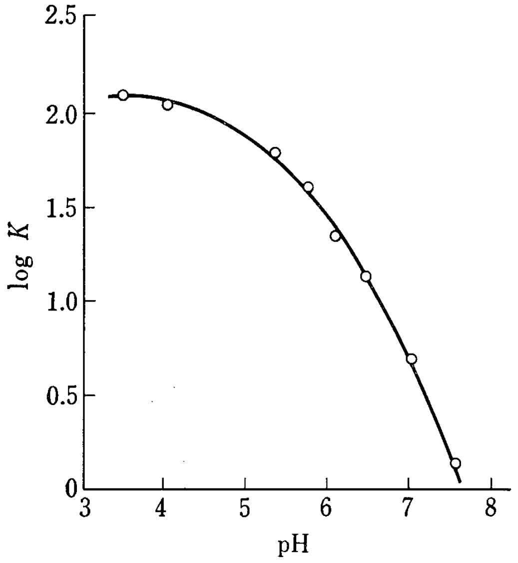

Fig. 4. Change of K for the Formation of SQ as a Function of pH at 25°

DMPD: 3.0×10^{-5} M; oxidant: 3.2×10^{-5} M $K_3Fe(CN)_6$ and 3.0×10^{-5} M $K_2Cr_2O_7$.

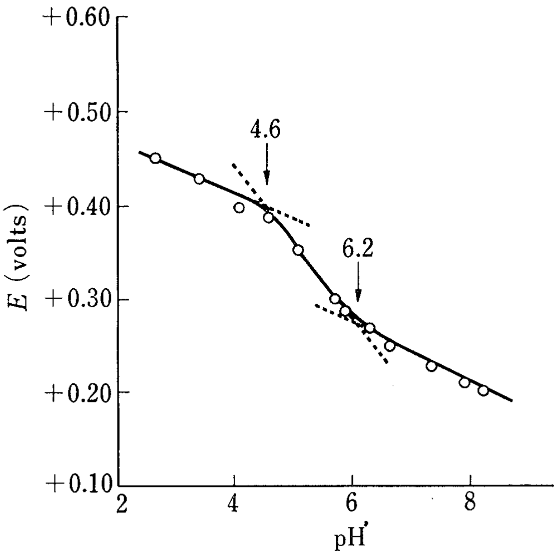

Fig. 5. Oxidation Potential for DMPD at Various pH Values (25°)

DMPD: 2.5×10^{-3} M.
Oxidant: 6.0×10^{-4} M $K_3Fe(CN)_6$ and 6.4×10^{-4} M $K_2Cr_2O_7$.

TABLE I. Observed First-Order Rate Constants, k_1, for the Disappearance of SQ at Various pH Values (25°)

pH	$k_1\times10^3$ (sec^{-1})	
	a)	*b*)
4.09	8.85	—
4.98	1.57	4.75
5.19	0.863	2.74
5.74	0.125	0.855
6.10	Nil	0.308

a) $[\mathrm{DMPD}]_0$: 3.0×10^{-5} M, oxidant: 3.2×10^{-5} M $K_3Fe(CN)_6$ and 3.0×10^{-5} M $K_2Cr_2O_7$.
b) $[\mathrm{DMPD}]_0$: 3.0×10^{-5} M, oxidant: 6.4×10^{-5} M $K_3Fe(CN)_6$ and 6.0×10^{-5} M $K_2Cr_2O_7$.

The concentrations of AA and its derivatives must be kept constant during the measurements (Eq. (2)),[2b] and subsequent kinetic measurements were made with 3.0×10^{-5} M DMPD. The concentration of QDI in equilibrium at time 0, $[\mathrm{QDI}]_{0(\mathrm{eq})}$, was very small, so the reac-

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15) E.S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., New York, 1959, p. 675.

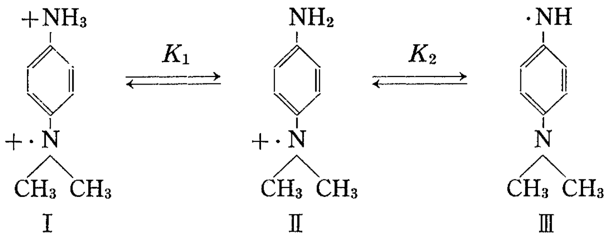

Chart 3

tions could be taken as following pseudo first-order kinetics, and the condensation of QDI to DMPD (auto-coupling)[16] could be ignored (the rate was *ca.* 4.5×10^{-7} $\text{l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$).

The light absorption data and the observed second-order rate constants for coupling reactions of several aromatic amines studied in this work are listed in Table II. *o*-AS, PA and DBA gave the corresponding indamines, but kinetic measurements were unsuccessful under the conditions used. α-NA gave a well-developed indamine color but the solution rapidly formed a precipitate.

Table II. Absorption Maxima and Observed Rate Constants for Indamine Formation of Some Aromatic Amines with DMPD at pH 6.1 and 25°

Amines	$\lambda_{\max}$ (nm)	Observed second-order rate constants $k_2\times10^2$ ($\text{l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$)[a]
AA	695	0.0253 ± 0.010
o-TL	700	0.466 ± 0.085
m-TL	705	0.240 ± 0.032
o-BA	670	$<10^{-4}$
m-BA	700	0.015 ± 0.006
m-CA	690	0.0266 ± 0.015
p-CA	690	0.0007
o-ABA	685	0.0604 ± 0.050
p-AAP	750	0.0441 ± 0.010
o-AS	715	V.L.[b]
α-NA	745	—[c]
PG	710	0.1707 ± 0.055
PAA	720	0.1347 ± 0.210
MA	708	1.102 ± 0.822
EA	715	1.836 ± 0.650
PA	720	V.L.[b]
DMA	725	1.123 ± 0.052
DEA	725	1.039 ± 0.103
DBA	700	V.L.[b]
DABA	735	0.704 ± 0.070

[a] The mean values ±S.D. of five determinations.
[b] V.L.=very large.
[c] The solution rapidly became opaque.

It is well known that an aqueous solution of indamine undergoes hydrolysis to indophenol.[4c,10] The rate of hydrolysis of 3-MI was measured over the pH range of 5.13—6.95, and the observed first-order rate constant was determined to be 0.085 min^{-1}, which was independent of the pH of the solution.

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[16] L.K.J. Tong and M.C. Glesmann, *J. Am. Chem. Soc.*, **79**, 592 (1957).

Table III summarizes the results obtained in analyses of several mixtures of AA and its derivatives at differential ratios. The average relative error, based on the total initial concentration, for all mixtures analyzed except for the *m*-CA—DMA mixture was 1.8%.

TABLE III. Determination of Binary Mixtures of Amines[a)]

Mixture determined	Concentration present (M)	Concentration[b)] found (M)	% error[c)]
p-AAP	3.0×10^{-3}	$2.95 \pm 0.049 \times 10^{-3}$	−1.7(1.7)
PG	2.01×10^{-4}	$1.99 \pm 0.047 \times 10^{-4}$	−1.0(2.4)
	2.0×10^{-3}	$1.89 \pm 0.07 \times 10^{-3}$	−5.5(3.7)
	3.02×10^{-4}	$3.37 \pm 0.05 \times 10^{-4}$	+11 (1.5)
	3.0×10^{-3}	$3.24 \pm 0.162 \times 10^{-3}$	+8.0(5.0)
	5.03×10^{-4}	$4.81 \pm 0.056 \times 10^{-4}$	−4.4(1.2)
o-ABA	2.01×10^{-4}	$2.02 \pm 0.008 \times 10^{-4}$	+0.5(0.4)
PAA	1.5×10^{-3}	$1.56 \pm 0.062 \times 10^{-3}$	+4.0(4.0)
	3.01×10^{-4}	$3.05 \pm 0.022 \times 10^{-4}$	+1.3(0.7)
	1.0×10^{-3}	—	—
AA	5.04×10^{-4}	$4.88 \pm 0.108 \times 10^{-4}$	−3.2(2.2)
DABA	1.0×10^{-4}	$1.14 \pm 0.122 \times 10^{-4}$	+14 (11)
	2.02×10^{-4}	$2.06 \pm 0.142 \times 10^{-4}$	+2.0(6.9)
	3.0×10^{-4}	$3.05 \pm 0.013 \times 10^{-4}$	+1.7(0.4)
o-ABA	5.02×10^{-4}	$4.95 \pm 0.051 \times 10^{-4}$	−1.4(1.0)
DABA	1.0×10^{-4}	$0.93 \pm 0.005 \times 10^{-4}$	−7.0(0.5)
	3.01×10^{-4}	$3.09 \pm 0.012 \times 10^{-4}$	+2.7(0.4)
	2.0×10^{-4}	$2.12 \pm 0.017 \times 10^{-4}$	+6.0(0.8)
MA	1.03×10^{-3}	$1.01 \pm 0.016 \times 10^{-3}$	−1.9(1.6)
DEA	1.01×10^{-4}	$1.05 \pm 0.026 \times 10^{-4}$	+4.0(2.5)
	8.21×10^{-4}	$8.06 \pm 0.040 \times 10^{-4}$	−1.8(0.5)
	2.02×10^{-4}	$2.09 \pm 0.140 \times 10^{-4}$	+3.5(6.7)
m-CA	1.01×10^{-4}	$1.01 \pm 0.002 \times 10^{-4}$	0 (0.2)
DMA	1.07×10^{-4}	$1.01 \pm 0.051 \times 10^{-4}$	−5.6(5.1)
	8.04×10^{-4}	$8.12 \pm 0.018 \times 10^{-4}$	+1.0(0.2)
	2.13×10^{-4}	$1.25 \pm 0.092 \times 10^{-4}$	−41 (7.4)
	5.03×10^{-4}	$4.86 \pm 0.011 \times 10^{-4}$	−3.4(0.2)
	3.2×10^{-4}	$2.85 \pm 0.134 \times 10^{-4}$	−11 (4.7)

a) *u*(750 nm), *v*(695 nm), *w*(515 nm).
b) The mean values ±S.D. of three determinations.
c) Values in brackets are relative standard deviations.

TABLE IV. Determination of AA–DMA Mixtures[a)]

Concentration ratio [AA]/[DMA]	AA			DMA		
	10^4 M Present	10^4 M Found[b)]	% Error[c)]	10^4 M Present	10^4 M Found[b)]	% Error[c)]
0.24	1.01	0.93±0.09	−7.9 (9.6)	4.26	4.25±0.03	−0.23(0.89)
0.68	2.17	2.16±0.12	−0.46(5.6)	3.2	2.71±0.11	−15 (4.1)
1.42	3.02	3.07±0.03	+1.7 (0.98)	2.13	1.62±0.12	−24 (7.4)

a) *u*(750 nm), *v*(695 nm), *w*(515 nm).
b) The mean values±S.D. of five determinations.
c) Values in brackets are relative standard deviations.

There were limitations on the minimum ratios of the rate constants which could be analyzed accurately. As shown in Table IV, the results obtained for the faster reacting component (DMA) involved large errors, which increased as the concentration ratio, [AA]/[DMA], increased. Similar errors were found in the analysis of *m*-CA—DMA mixture (Table III).

The most serious interferences in these analyses were caused by phenols, which reacted with QDI to yield indaniline dyes.[17] Acetone as a solvent and carbonyl compounds also interferred by the formation of Schiff bases with primary or secondary amines (Fig. 6).[9,18] These compounds led to errors of approximately 5 to 10% when present in ten-fold excess over the amines.

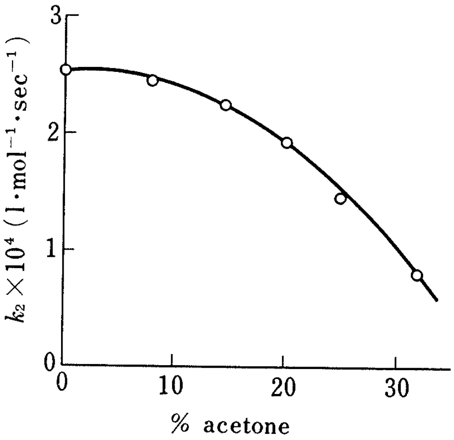

Fig. 6. Change of the Second-Order Rate Constant for AA as a Function of the Reaction Medium at pH 6.1 (25°)

The concentrations in the initial solution were 3.0×10^{-4} M AA, 3.0×10^{-5} M DMPD, 3.2×10^{-5} M $K_3Fe(CN)_6$ and 3.0×10^{-5} M $K_2Cr_2O_7$.

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17) P.W. Vittum and C.H. Brown, *J. Am. Chem. Soc.*, **71**, 2287 (1949).

18) L.J. Papa, J.H. Patterson, H.B. Mark Jr., and C.N. Reilley, *Anal. Chem.*, **35**, 1889 (1963).