[Communication No. 1827 from the Research Laboratories, Eastman Kodak Co.]

The Mechanism of Dye Formation in Color Photography. II. Salt Effects on Deamination Rate of Oxidized *p*-Phenylenediamines

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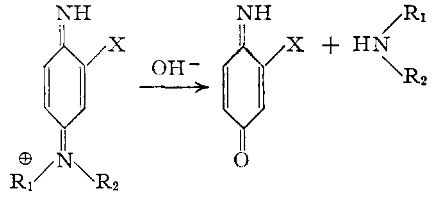
The salt effects on the rate of deamination of oxidized developing agents have been measured. The most probable ionic forms of the quinonediimine were derived from the results.

Introduction

It has been shown in Part I[1] that oxidized N,N-disubstituted *p*-phenylenediamines in alkaline solutions undergo deamination.



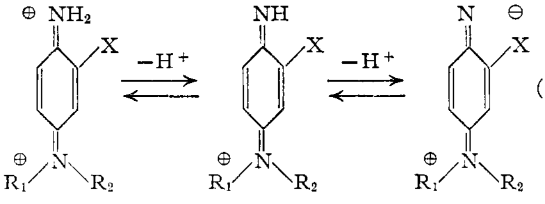
(a)

Quinonediimine (QDI) Quinonemonoimine (QMI)

The reaction is of second order. The rates are proportional to the products of the concentrations of OH^- and quinonediimine, the totally oxidized *p*-phenylenediamine, rather than of the semiquinone.

$$d(QDI)/dt = -k(QDI)(OH^-) \quad (1)$$

The structure QDI given in eq. (a) was assumed for the predominating ionic species of quinonediimine without proof. However, two other structures involving either the loss or the gain of an additional proton are possible.



(b)

(H_2A^{+2}) (HA^{+1}) (A)

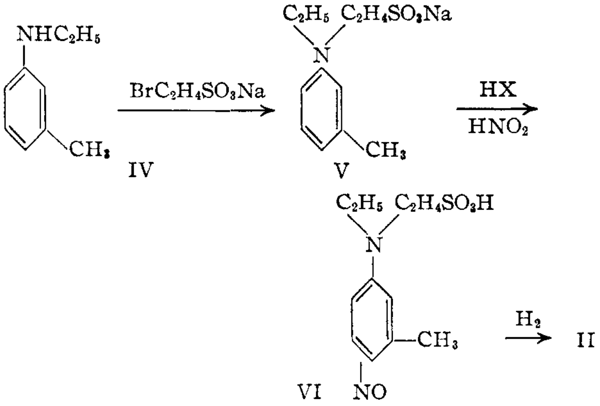
Owing to the instability of the compounds, the ionization constants in eq. b cannot be determined by the usual potentiometric or conductometric titration methods, but conclusions concerning the predominating ionic species of QDI can be based on the *p*H-dependence of, and the salt effects on, the rates of the deamination.

Experimental

1. **Materials.**—The developing agents were prepared by R. L. Bent, of these Laboratories, as follows:

4-Amino-N,N-diethyl-3-methylaniline hydrochloride (I) and ***p*-phenylenediamine dihydrochloride** (III) obtained from the Eastman Organic Chemicals Department, were further purified by recrystallization, as previously described.[2]

4-Amino-N-ethyl-3-methyl-N-(β-sulfoethyl)-aniline (II) was prepared by the following series of reactions



Sodium 2-bromoethanesulfonate (IV) was prepared as described in reference 3.

N-Ethyl-3-methyl-N-(β-sulfoethyl)-aniline, Sodium Salt (V).—Five moles (675 g.) of N-ethyl-*m*-toluidine and 2.5 moles (527.5 g.) of IV were heated in an oil-bath at 175° for approximately 4 hr. After cooling, 1200 ml. of water was added and the mixture made just alkaline with sodium hydroxide solution. The mixture was chilled thoroughly and the filtered solid was washed thoroughly on a funnel with cold acetone and then with cold ether. After drying in steam cabinet, the material was recrystallized from 2500 ml. of 95% ethanol; yield 419.5 g. (63%) of product.

N-Ethyl-3-methyl-4-nitroso-N-(2-sulfoethyl)-aniline (VI).—One mole (265 g.) of V was dissolved in a mixture of 500 ml. of water and 500 ml. of concentrated hydrochloric acid (1.18 sp. gr.). To 250 ml. of water was added 1.05 moles (72.4 g.) of sodium nitrite and the solution added to the mixture with stirring, the temperature being kept below 2°. After addition, the mixture was stirred for another 20 minutes, excess nitrous acid was destroyed with sulfamic acid and the mixture was chilled overnight in a refrigerator. The filtered solid was washed with ice-cold 95% ethanol and then with ice-cold ether; yield 213 g. (78%) (m.p. chars at >190°).

4-Amino-N-ethyl-3-methyl-N-(β-sulfoethyl)-aniline (II).—In a Parr shaker, 120 g. of VI was reduced catalytically in 15-g. portions, together with 280 ml. of 95% ethanol, 50 ml. of water and 1.5 g. of 10% palladium-on-charcoal catalyst for each portion. After reduction (rapid), the mixture was heated on a steam-bath, together with more water, to dissolve all the precipitate, filtered hot to remove the catalyst and finally concentrated to a small volume, using a water-bath and a partial vacuum. The mixture was chilled in a refrigerator and filtered, and the filtered solid was washed successively with small portions of ice-cold water, alcohol and ether and finally dried in a vacuum desiccator; yield 71.5 g. (63%) (m.p. 283–284° dec.) *Anal.* Calcd.: C, 51.2; H, 7.0; N, 10.8. Found: C, 50.8; H, 6.7; N, 10.6.

Reagent grades of inorganic salts were used without further purification. Butyl acetate was Eastman Kodak Co. White Label Grade.

2. **Procedures.**—The general procedures are similar to those already described.[1] The reactions with I and II were followed by the steady-state flow method, using the

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[1] L. K. J. Tong, *J. Phys. Chem.*, **58**, 1090 (1954).

[2] (a) R. L. Bent, J. C. Dessloch, F. C. Duennebier, D. W. Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum and A. Weissberger, This Journal, **73**, 3100 (1951); (b) J. E. LuValle, D. B. Glass and A. Weissberger, *ibid.*, **70**, 2223 (1948).

[3] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 558.

apparatus designed by Ruby[4]; the reactions with III were carried out in bottles and followed by sampling.

4-Amino-3-methyl-N,N-diethylaniline (I).—The solutions were mixed in the following order, starting with the volumes indicated:

Solution	Reactant	Concn., M	Vol., ml.
1	Developing agent	5.00×10^{-4}	7.31
2	$K_3Fe(CN)_6$	3.0×10^{-3}	7.31
3	NaOH	0.0100	14.62
	NaCl	Varied	
4	Phosphate buffer pH 7.5	0.25	29.22

The residual developing agent was determined as follows: 50 ml. of 2.0×10^{-3} M α-naphthol was added to the reaction mixture. The resulting dye was extracted with 50.0 ml. of butyl acetate and the optical density at 600 mμ was measured in a Beckman spectrophotometer.

4-Amino-3-methyl-N-ethyl-N-(β-sulfoethyl)-aniline (II).—The following solutions and volumes were mixed:

Solution	Reactant	Concn., M.	Vol. ratio
1	Developing agent	1.00×10^{-3}	1
2	$K_3Fe(CN)_6$	5.00×10^{-3}	1
3	NaOH	10.0×10^{-3}	2
	NaCl	Varied	
4	Phosphate buffer pH 7.5	0.25	4
	α-Naphthol	5.0×10^{-4}	

α-Naphthol was added with the acid stop solution in this case, since the resulting dyes were water-soluble and did not separate in the apparatus. The dye densities were obtained from the aqueous solution at 600 mμ. Phosphate buffers were used instead of sodium hydroxide in experiments recorded in Table I.

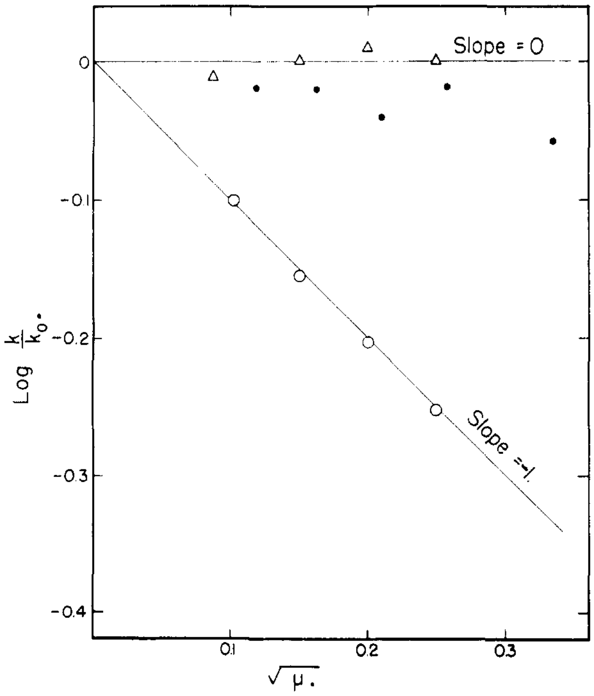


Fig. 1.—Salt effects on the deamination rate of oxidized p-phenylenediamines: ○, developing agent I; ●, developing agent II; △, developing agent III.

p-Phenylenediamine (III).—The deamination of oxidized p-phenylenediamine was carried out in 500-cc. bottles placed in a thermostat at 25 ± 0.1°; the following solutions were mixed: (1) NaOH (5.00×10^{-3} M), NaCl variable, 200 ml.; (2) p-phenylenediamine (0.500×10^{-3} M), 100 ml.; (3) $K_3Fe(CN)_6$ (3.0×10^{-3} M), 100 ml.

At predetermined intervals, up to a maximum of 120 minutes, 50.0-ml. samples were taken and added to a mixture containing 5.0 ml. of α-naphthol (2.0×10^{-3} M) and 20 ml. of phosphate buffer (pH 6). After allowing 3 minutes for coupling to take place, the resulting dyes were extracted with 50.0 ml. of butyl acetate, and absorption measurements were taken.

Table I

Deamination of Oxidized II in Phosphate Buffer, Effect of pH

pH	k, first order, sec.$^{-1}$
8.20	7.5×10^{-3}
9.91	0.63
11.05	7.40
11.91	55.0

Results and Discussion

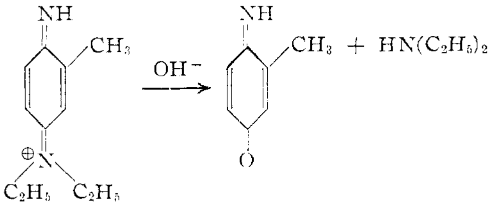
1. Dependence on pH.—The pH-dependence of the reaction involving oxidized II is shown in Table I; similar data for I and III have been published.[1] For the first two developers, the logs of the rates when plotted *vs.* pH were found to be linear, with a slope very near unity; and for III, the rates were found to be independent of pH. Since no breaks were found in the lines, it may be concluded that the solutions contained only one major ionic species in this pH range.

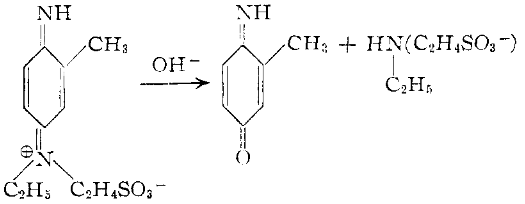
2. Salt Effects.—According to Brönsted[5]

$$\log k/k_0 = 1.0 Z_A Z_B \mu^{1/2} \qquad (2)$$

where k is the second-order rate constant measured at ionic strength μ, k_0 is the limit of k at μ = 0, and Z_A and Z_B are the charges of the reactants. If this equation holds even approximately, then Z_A for QDI can be obtained from the slope of the plot by selecting the nearest integer, since Z_B for OH^- is known to be -1 (see Table II).

Figure 1 shows the integers for I, II and III to be -1, 0 and 0, respectively. These results suggest the predominating species


(c)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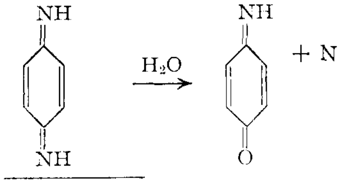
(e)

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[4] W. R. Ruby, *Rev. Sci. Instruments*, **26**, 460 (1955).

[5] J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

Table II

Salt Effect on Deamination of Oxidized Developing Agents

I		II		III	
μ	k,[a] sec.$^{-1}$	μ	k, sec.$^{-1}$	μ	k, sec.$^{-1} \times 10^3$
0.0104	5.56	0.0141	24.0	0.0077	0.280 ± 0.003
.0225	4.90	.0262	24.0	.0225	.287 ± .009
.0400	4.38	.0437	22.8	.0400	.294 ± .009
.0625	3.92	.0662	24.0	.0625	.287 ± .010
		.1141	22.0		

[a] k calculated as first-order rate constant since (OH^-) remained essentially unchanged during the reaction.

It should be pointed out that the salt effect is determined by the equilibrium and not the detailed mechanism which produces the critical complex. While we make the plausible assumption that the predominating species and reactive species are identical in representing the reaction by eq. c to e, any other pair of reactive species in rapid equilibrium with those shown would exhibit identical salt effects.[6]

Rochester, New York

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[6] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 260.

[Contribution from the Research Department, Carbide and Carbon Chemicals Company]

N,N-Bis-(2-cyanoethyl)-carboxamic Acids and Esters

By John W. Lynn

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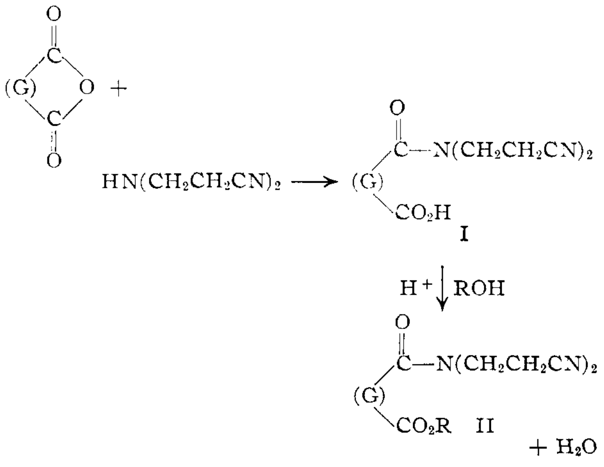
The syntheses of several N,N-bis-(2-cyanoethyl)-carboxamic acids and esters thereof are described starting with cyclic anhydrides, β,β′-iminodipropionitrile and alcohols.

The reaction of β,β′-iminodipropionitrile with cyclic anhydrides gives the corresponding N,N-bis-(2-cyanoethyl)-carboxamic acids (I) in good yield. The only amic acids of this type previously reported are the derivatives of phthalic[1] and succinic anhydrides[2]; the latter by name alone. Esters of N,N-bis-(2-cyanoethyl)-carboxamic acids are hitherto unreported. Several alkyl N,N-bis-(2-cyanoethyl)-carboxamates (II) are useful as plasticizers for vinyl chloride–acrylonitrile resins.

Several cyclic anhydrides were allowed to react with β,β′-iminodipropionitrile in an inert solvent. A slight excess of the anhydride generally resulted in better yields. Physical properties, analyses and yields of the products are given in Table I.

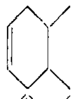
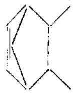
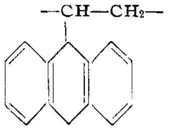
Alkyl N,N-bis-(2-cyanoethyl)-carboxamates (II) are readily prepared by esterification of purified carboxamic acids or, in some cases, by the direct esterification of crude acid reaction mixtures.



Purified esters were not obtainable, except in those cases where the product was a crystallizable solid, owing to thermal degradation during attempted distillations. The products were generally purified by steam distillation to remove volatile by-products. Data on these esters are given in Table II.

Table I

N,N-bis-(2-cyanoethyl)-carboxamic Acids HO_2C-(G)-$CON(CH_2CH_2CN)_2$

(G)	Formula	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
$-CH_2CH_2-$	$C_{10}H_{13}N_3O_3$	92.6	118–119	18.83	18.73
$-CH{=}CH-$(*cis*)	$C_{11}H_{15}N_3O_3$	91.0	140–141	19.0	18.91
$-(CH_2)_3-$	$C_{11}H_{15}N_3O_3$	69.6	85–87.5	17.71	18.10
$-C(CH_3){=}CH-$	$C_{11}H_{13}N_3O_3$	40.0	108–110	17.85	18.16
$-C({=}CH_2)CH_2-$	$C_{11}H_{13}N_3O_3$	32.0	130–131	17.85	17.40
	$C_{14}H_{17}N_3O_3$	95.0	130–133	15.49	15.23
	$C_{15}H_{17}N_3O_3$	92.0	135–136	14.63	15.08
	$C_{23}H_{21}N_3O_3$	83.2	139–141	10.80	10.29

Neither I nor II is thermally stable, particularly in the presence of mineral acid. Attempted distillation of the esters resulted in decomposition, with formation of N-(2-cyanoethyl)-carboximides. Similar pyrolyses have been reported previously for the conversion of N,N-bis-(2-cyanoethyl)-phthalamic acid to β-phthalimidopropionitrile.[1,3] The cyclic imides III were also obtained as a result of the attempted esterification of N,N-bis-(2-cyanoethyl)-4-cyclohexene-1,2-carboxamic acid and N,N-bis-(cyanoethyl)-bicyclo[2.2.1]-5-heptene-2,3-carboxamic acid. The structures of these reaction products were proved by their independent synthesis by means of the cyanoethylation of the respective unsubstituted imides.

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[1] S. Chodroff, R. Kapp and C. O. Beckman, This Journal, **69**, 256 (1947).

[2] R. O. Zerbe, U. S. Patent 2,582,732.

[3] F. E. Küng, U. S. Patent 2,401,429.