Kinetics of the Caro's Acid Oxidation of Dimethylanilines

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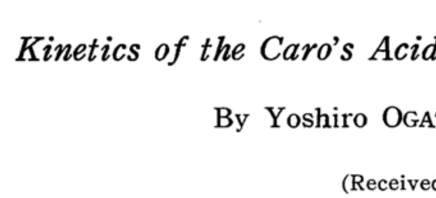
It has been reported that Caro's acid (peroxymonosulfuric acid), presumably contained in a mixture of aqueous sulfuric acid and sodium persulfate, converts aniline (or *N*-monomethylaniline) into phenylhydroxyamine, nitrosobenzene, nitrobenzene and azobenzene1), while *N*-dimethylaniline (abbreviated as DMA) produces a stable amine oxide on oxidation with Caro's acid2).



$$\mathrm{Ph{-}N}\begin{matrix}\mathrm{Me}\\ \mathrm{Me}\end{matrix} + \mathrm{H_2SO_5} \rightarrow \mathrm{Ph{-}}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{N}^+}}\mathrm{{-}O^-} + \mathrm{H_2SO_4}$$

The amine oxide can also be obtained from other tertiary amines, e. g. pyridine, and other oxidizing agents such as hydrogen peroxide3).

The rate of hydrogen-peroxide oxidation of trimethylamine was measured by Ross4) only in neutral aqueous solutions. It was found that the rate was proportional to the concentration of the reactants. However, the effects of amine structure and pH of the solution on the rate have not yet been investigated in detail. The present paper describes the data and the probable mechanism of the oxidation of unsubstituted and ring-substituted DMA with Caro's acid in aqueous media.

Experimental

Materials. — DMA was purified by duplicate fractional distillations, b. p. 193°. *p*-Methyl-(b. p. 133°/55 mm.) and *p*-methoxy-dimethylaniline (m. p. 49°) were prepared by the dimethyl-sulfate methylation of *p*-toluidine and *p*-anisidine, respectively5). *p*-Chlorodimethylaniline was synthesized by the chlorination of DMA6), m. p.7) 35.5°. Caro's acid was prepared by the reaction of potassium persulfate (10 g.) and concentrated sulfuric acid (11 g.) and stored in the form of a dilute solution.

Rate Measurements. — A known amount of acidic aqueous solution of DMA with sulfuric acid or a mixture of potassium hydroxide and borate was mixed in a brown flask and kept at a constant temperature. The solution was mixed with a known amount of aqueous Caro's acid solution maintained at a constant temperature and the reaction was caused to start. Aliquots were taken out at appropriate intervals of time and their peroxide contents were determined iodimetrically. The data of the iodometry were corrected for hydrogen peroxide and peroxydisulfate by another iodometry with cuprous iodide

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1) E. Bamberger and F. Tschirner, *Ber.*, **31**, 1675 (1899); E. Bamberger and M. Vuk, ibid., **35**, 703 (1902).

2) E. Bamberger and P. Leyden, ibid., **34**, 12 (1901); E. Bamberger and F. Tschirner, ibid., **32**, 342 (1899).

3) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

4) S. D. Ross, *J. Am. Chem. Soc.*, **68**, 1484 (1946).

5) H. Wieland, *Ber.*, **43**, 712 (1910).

6) D. V. Tischtschenko, *J. Russ. Phys. Chem. Soc.*, **60**, 153 (1928).

7) T. Heidelberg, *Ber.*, **20**, 149 (1887).

as a catalyst[8]. The rate constants were calculated by means of the usual second-order rate equation or pseudo-first-order equation.

The Equilibrium Constants for the Protonation of Substituted DMA.—The equilibrium constant in aqueous solution, $K'=[BH^+]/([B][H^+])$ was determined spectrophotometrically in buffer solutions at various pH's. The spectral data for free and protonated amines were obtained from those in 0.1 N potassium hydroxide and 0.1 N hydrochloric acid, respectively. The used absorption maxima of free and protonated *p*-substituted dimethylanilines were as follows, respectively: MeO, 237 and 223 mμ; Me 237 and below 210 mμ; H, 240 and below 210 mμ; Cl, 250 and 215 mμ.

Since ordinary organic acids showed interference in UV spectra, 0.5 N ammonium chloride solution containing various amounts of ammonium hydroxide, hydrochloric acid or sodium borate was used as a buffer agent. The measurements were carried out at spectral regions of longer wave lengths to avoid the interference of inorganic materials. The results obtained from experiments carried out at more than one kind of wave length agreed well.

The K' values for substituted DMA are listed in Table I. These values are in accord with the Hammett equation. The values are somewhat different from those obtained by Davies[9] probably because of the difference of his solvent, 50% ethanol.

Supplementary Notes. — (1) A method of volumetric analysis of tertiary amine is suggested, in which an excess of Caro's acid is titrated by iodometry after oxidation of the amine sample at an appropriate pH (pH 4∼5 for DMA). The method may be suitable for the analysis where acidimetry is difficult, e. g. in a buffer solution.

(2) Hall's pK values[10] for anilines are of most systematic ones, but his datum on dimethylaniline somewhat differs from the present datum and seems to be too small on the basis of the following considerations. The increase of pK by the introduction of a second methyl group into monomethylaniline is unusually small, if compared with that of an ethyl group into monomethylaniline or that of a methyl group into monoethylaniline.

$PhNH_2$	4.62	
PhNHMe	4.85,	$\Delta^{0}_{Me}=0.23$
$PhNMe_2$	5.06,	$\Delta^{Me}_{Me}=0.21$
PhNHEt	5.11,	$\Delta^{0}_{Et}=0.49$
$PHNEt_2$	6.26,	$\Delta^{Et}_{Et}=1.15$
PhNMeEt	5.98,	$\Delta^{Et}_{Me}=0.87$
		$\Delta^{Me}_{Et}=1.13$

On the other hand, our datum on dimethylaniline leads to a reasonable increment ($\Delta^{Me}_{Me}=0.52$).

TABLE I

EQUILIBRIUM CONSTANTS FOR THE PROTONATION OF DIMETHYLANILINE

Substituent	pH	K' a)	pK'	pK b)
p-MeO	5.21	0.920×10^6	-5.964	
	5.73	1.03×10^6	-6.013	
	6.00	1.01×10^6	-6.004	
(av.)		0.967×10^6	-5.96	8.04
p-Me	5.50	4.93×10^5	-5.693	
	5.70	5.02×10^5	-5.701	
	5.90	5.06×10^5	-5.705	
(av.)		5.00×10^5	-5.70	8.30
None	5.41	2.52×10^5	-5.402	
	5.67	2.66×10^5	-5.425	
	5.80	2.39×10^5	-5.378	
(av.)		2.52×10^5	-5.40	8.60
p-Cl	3.99	4.71×10^4	-4.673	
	4.50	4.82×10^4	-4.683	
(av.)		4.76×10^4	-4.68	9.32

a) $K'=\dfrac{[BH^+]}{[B][H^+]}$ b) $K=\dfrac{[BH^+][OH^-]}{[B][H_2O]}$

Results

The rate data show that the second-order kinetics are satisfied.

$$dx/dt = k(d-x)(p-x) \qquad (1)$$

Here $(d-x)$ and $(p-x)$ represent the concentrations of dimethylaniline and Caro's acid, respectively. Tables II and III list the effect of initial concentration and acidity on the rate with various substituted DMA's, respectively.

It was reported that some deviation of the apparent rate constant k was observed in the persulfate oxidation in alkaline solution[11] probably owing to the radical reaction, but no indication of the deviation was observed in this case, even if a relatively large excess of DMA was used.

TABLE II

SECOND-ORDER RATE CONSTANT k AT VARIOUS INITIAL CONCENTRATIONS FOR THE CARO'S ACID OXIDATION OF DMA

Temp. 20°C, pH 1.35, Solvent, water

Initial concn. of Caro's acid (M)	Initial concn. of DMA (M)	k (l. mole^{-1} sec.$^{-1}$)
3.93×10^{-3}	0.0167	3.84×10^{-3}
3.67×10^{-3}	0.0308	4.02×10^{-3}
3.76×10^{-3}	0.0600	3.64×10^{-3}
3.96×10^{-3}	0.0800	3.85×10^{-3}

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[8] M. A. Bodin, *Zavodskaya Lab.*, **7**, 1248 (1938).

[9] W. C. Davies and H. W. Bddis, *J. Chem. Soc.*, **1937**, 1622.

[10] N. F. Hall and M. R. Spinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

[11] L. S. Levitt and E. R. Malinowski, ibid., **77**, 4517 (1955).

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE CARO'S ACID OXIDATION OF DIMETHYLANILINES

Unsubstituted DMA

pH	Temp. °C	$k\times10^2$ (l. mole^{-1} sec.$^{-1}$)	$k_4=k\cdot[H^+]\cdot K_2$
1.00	25.0	0.241	60.6
1.22	25.0	0.384	58.5
1.40	25.0	0.600	60.0
1.80	25.0	1.73	69.0
1.85	25.0	1.80	64.2
1.98	25.0	2.36[a]	62.4
2.04	25.0	3.10	71.1
2.29	25.0	4.70	60.5
2.40	25.0	6.05	60.5
2.99	25.0	41.4	
3.70	25.0	346	
4.81	25.0	3200	
6.00	25.0	4250	
7.30	25.0	4360	
8.10	25.0	3780	
9.10	25.0	2700	
9.44	25.0	2220	
10.00	25.0	680	
10.50	25.0	348	
1.70	30.0	2.91	
1.70	20.0	0.980	
1.80	15.0	0.580	
1.80	25.0	1.65[b]	
1.82	25.0	1.80[c]	

p-MeO-DMA

pH	Temp. °C	$k\times10^2$ (l. mole^{-1} sec.$^{-1}$)	$k_4=k\cdot[H^+]\cdot K_2$
1.50	25.0	0.443	135
1.70	25.0	0.590	114
1.70	15.0	0.255	
2.04	25.0	1.20	101
2.28	25.0	2.64	134
3.11	25.0	18.5	139
4.17	25.0	185	121
7.90	25.0	7090	
9.30	25.0	4470	
10.28	25.0	3080	
11.52	25.0	142	
12.20	25.0	22.9	
12.64	25.0	8.79	

p-Me-DMA

pH	Temp. °C	$k\times10^2$ (l. mole^{-1} sec.$^{-1}$)	$k_4=k\cdot[H^+]\cdot K_2$
1.26	25.0	0.403	111
1.36	25.0	0.490	107
1.75	25.0	1.12	105
2.30	25.0	4.16	104
2.42	25.0	5.99	114
3.00	25.0	32.4	162
3.50	25.0	99.6	157
4.00	25.0	368	
4.70	25.0	3260	
7.30	25.0	5280	
8.00	25.0	5040	
8.95	25.0	5720	
9.93	25.0	1980	
10.30	25.0	944	
10.63	25.0	413	
11.60	25.0	59.4	
12.03	25.0	30.3	
12.59	25.0	10.6	
1.90	15.0	0.782	
1.90	25.0	2.15	

p-Cl-DMA

pH	Temp. °C	$k\times10^2$ (l. mole^{-1} sec.$^{-1}$)	$k_4=k\cdot[H^+]\cdot K_2$
1.38	25.0	2.40	47.6
1.60	25.0	3.22	38.5
2.03	25.0	11.8	52.5
2.50	25.0	36.2	54.3
2.81	25.0	73.6	55.9
3.21	25.0	223	
3.53	25.0	965	
4.32	25.0	3340	
7.13	25.0	4110	
7.80	25.0	4160	
8.81	25.0	3360	
9.40	25.0	2360	
9.95	25.0	969	
11.02	25.0	101	
11.52	25.0	38.7	
11.92	25.0	20.1	
1.89	15.0	1.76	
1.89	25.8	9.25	

a) Na_2SO_4 (100 mg.) was added in 50 ml. of the solution.
b) Benzoyl peroxide (5 mg.) was added in 50 ml. of the solution.
c) Hydroquinone (3 mg.) was added in 50 ml. of the solution.

In strong acid media, the rate constant *k* increases with increasing pH, the plot of log *k* against pH giving a satisfactory straight line with a slope of ca. +1. In the strong acidity the rate constants for substituted DMA at a given pH decrease, in the order: *p*-Cl, *p*-H, *p*-Me and *p*-MeO.

The increase of the *k* value with decreasing acidity diminishes gradually, and then *k* reaches a constant value in the neighborhood of the neutrality, where the accurate rate can not be obtained because of its large value together with the spontaneous decomposition of the oxidizing agent.

In weakly alkaline media, *k* tends to decrease with increasing pH and after reaching a bending point at pH 9.5~10.5 an approximate linear relation is observed between log *k* and pH with the slope of

−1. The k values in neutral and an alkaline region decrease with substituents of DMA in the order p-MeO, p-Me, p-H and p-Cl.

The energies of activation for substituted DMA are shown in Table IV.

TABLE IV
TEMPERATURE COEFFICIENT AND ENERGY OF ACTIVATION FOR THE CARO'S ACID OXIDATION OF DIMETHYLANILINES

Substituent	MeO	Me	H	Cl
k_{25}/k_{15}	2.32	2.75	2.98	4.97[a]
E_a(kcal./mole)	14.5	17.4	18.7	25.6

a) $k_{25.3}/k_{15}$

Discussion

The observed second-order kinetics and the effects of acidity and substituents suggest the following mechanism which involves a rate-determining electrophilic attack of neutral molecules of Caro's acid on the free dimethylaniline.

$$\mathrm{ArNMe_2 + H^+ \rightleftarrows Ar\overset{+}{N}Me_2H} \text{ (rapid)} \qquad (2)$$

$$\mathrm{H_2SO_5 \leftrightarrows HSO_5^- + H^+} \text{ (rapid)} \qquad (3)$$

$$\mathrm{ArNMe_2 + H_2SO_5 \rightarrow Ar\overset{+}{N}Me_2OH + HSO_4^-} \text{ (slow)} \qquad (4)$$

$$\mathrm{Ar{-}\overset{+}{N}Me_2{-}OH \rightleftarrows Ar\overset{+}{N}Me_2{-}O^- + H^+} \text{ (rapid)} \qquad (5)$$

From this mechanism, the following relation between the apparent rate constant k and the rate constant of rate-determining step 4 should be expected.

$$k = \frac{1}{K_2[\mathrm{H^+}]+1} \cdot \frac{[\mathrm{H^+}]}{[\mathrm{H^+}]+K_3} k_4 \qquad (6)$$

where k and K are rate- and equilibrium constant of the steps.

At relatively high acidity, equation 6 will be to

$$k = \frac{1}{K_2[\mathrm{H^+}]} k_4 \qquad (7)$$

and in alkaline media where $[\mathrm{H^+}]$ is very small, equation 6 is reduced to

$$k = K_3[\mathrm{H^+}]k_4 \qquad (8)$$

These two equations 7 and 8 satisfy the observed effect of acidity. In alkaline and neutral solutions, almost none the amine molecules are protonated, hence an electron-releasing group in the amine will facilitate the reaction (the substituent affects k_4 alone in eqation 8). But the protonation equilibria 2 become important at high acidity as is obvious from the substituent effect on K_2 in equation 7, and the reverse substituent effect may appear, if the effect on K_2 is larger than that for k_4. These expectations were actually recognized as described previously.

In the acid media the linearity between $\log k$ and pH breaks when $K_2[\mathrm{H^+}]$ becomes comparable with unity as seen in equation 6. This break (Fig. 1) was actually observed at pH 4∼5 and it depended on the p-substituent of dimethylaniline, i. e.,

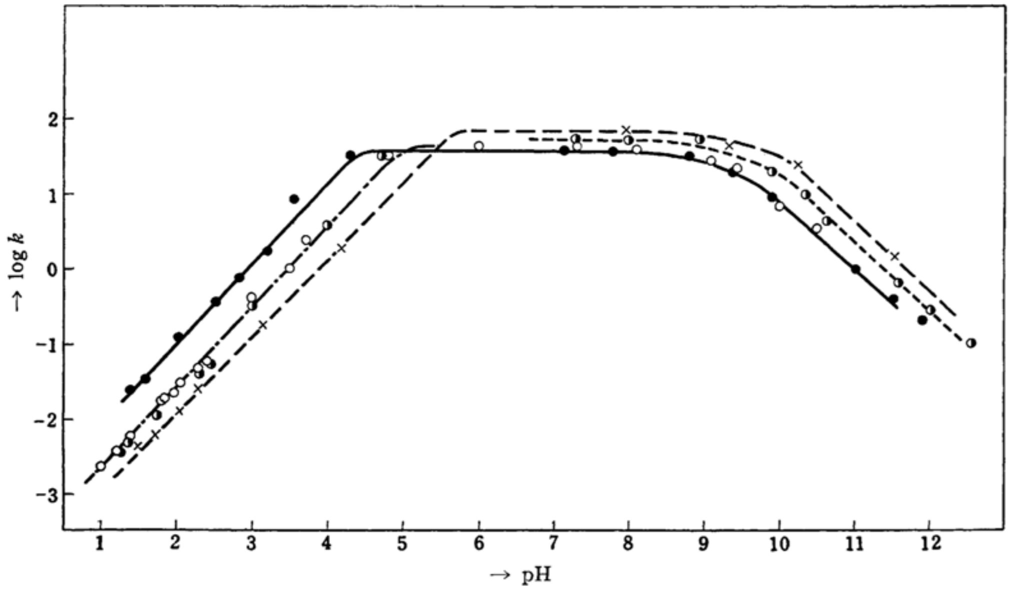

Fig. 1. Plots of $\log k$ vs. pH.
—×— p-MeO, ---◑--- p-Me, —○— p-H, —●— p-Cl

the pH value of this break increased in the order: *p*-Cl, *p*-H, *p*-Me and *p*-MeO. This is natural, since the electron-releasing groups increase the K_2 value in equation 6. On the other hand, the break in alkaline media was observed at pH 9.5~10.5 and was independent of *p*-substituent of DMA. This phenomenon seems to be attributable to a decrease of the concentration of H_2SO_5 because of its dissociation.

On the basis of the prevailing electronic theory, the other mechanisms described below are less probable, but they are discussed briefly. Instead of eq. 4, the rate-determining reaction between

(*a*) $Ar\overset{+}{N}Me_2H$ and HSO_5^-

(*b*) $ArNMe_2$ and HSO_5^-

(*c*) $Ar\overset{+}{N}Me_2H$ and H_2SO_5

leads to the following relation, respectively.

$$(a)\quad k=\frac{K_2[H^+]}{K_2[H]^+ +1}\cdot\frac{K_3}{[H^+]+K_3}k_4'$$

$$(b)\quad k=\frac{1}{K_2[H^+]+1}\cdot\frac{K_3}{[H^+]+K_3}k_4''$$

$$(c)\quad k=\frac{K_2[H^+]}{K_2[H^+]+1}\cdot\frac{[H^+]}{[H^+]+K_3}k_4'''$$

The observed linearity of $\log k$ vs. pH at high acidity is at least unexplicable by the mechanism *c*, and that of $-\log k$ vs. pH in alkaline media is unexplicable by the mechanism *b*. The concentrations of the reactants in *b*, $ArNMe_2$ and HSO_5^-, should be much lower in an alkaline solution, hence the possibility of mechanism *b* is inconceivable over the whole pH range. Similarly, the concentrations of reactants, $Ar\overset{+}{N}Me_2H$ and H_2SO_5, should be much lower in an alkaline solution, hence the mechanism *c* is unlikely.

The mechanism *a* leads to the observed effects of acidity and substituents, and is indistinguishable from eq. 4 with kinetics alone; but the mechanism is less probable, since it involves a reaction between a very weak acid (aminium ion) and a very weak base (peroxysulfate ion) and the possible reaction should be the transfer of a proton from the cation to the anion. Furthermore, the fact that added salt (sodium sulfate) has little effect on the rate, favors the reaction between neutral molecules than that between ions.

It has been reported that the neutralizing equivalent of Caro's acid is a half of its oxidizing equivalent[12], thus the dissociation of its second hydrogen atom is inappreciable. Therefore, the mechanism, in which equilibrium 3 is replaced by

$$HSO_5^- \rightleftarrows SO_5^{2-}+H^+$$

and the attacking agent is HSO_5^- instead of H_2SO_5, is unlikely.

Attempts to isolate pure Caro's acid by way of elimination of sulfuric acid with barium hydroxide or ion-exchange resin failed because of its instability.

No appreciable effect on the rate was recognized on addition of a small amount of hydroquinone or benzoyl peroxide, thus showing the absence of radical intermediates in the main reaction course.

Summary

The rates of the Caro's acid oxidation of dimethylaniline and *p*-substituted dimethylanilines were measured in aqueous solutions of various pH's and temperatures. The rates were found to be proportional to the product of the concentrations of both reactants. The effects of pH and *p*-substituents on the rate constant were estimated. The rate constant in acid media increased with increasing electron-withdrawing power of the *p*-substituent of dimethylaniline, while the constant in alkaline media increased with decreasing pH or increasing electron-releasing power of the substituent. A probable mechanism involving a rate-determining attack of neutral Caro's acid molecule on free amine was proposed and discussed.

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