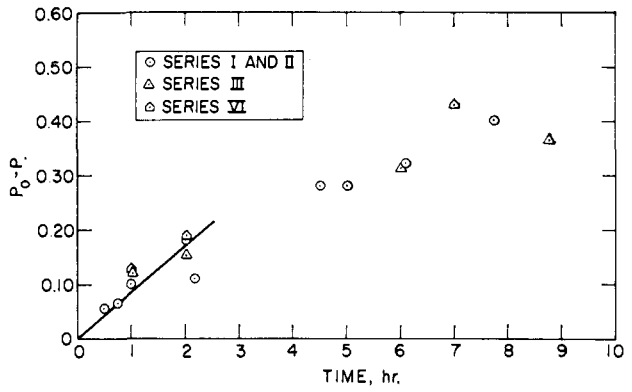

Fig. 1.—Plot of $P_0 - P$ *vs.* time of photolysis.

Since all the radiation incident on the sample is absorbed, the rate of pentoxone removal should be constant during irradiation. Figure 1 is a plot of the change in concentration (P_0-P) *vs.* time of exposure for series I, II, III, and VI. The four series all fit the same plot, and for small times the plot is linear. At longer times, the data lie far below the linear extension of the curve, thus demonstrating that the products inhibit decomposition. The other series were not plotted because results are not available at times short enough to fit the linear portion. However, the higher temperature data (series IV, V) correspond to the plot. The data for the ethanol and allyl alcohol solutions show much greater inhibition, and it is not clear whether the initial rate of decay would be the same as for the other series.

One of the products is mesityl oxide which absorbs radiation in the 3200 Å. region. The radiation absorbed by mesityl oxide is not available to photodecompose the pentoxone, thus giving rise to the observed inhibition.

Since the mesityl oxide absorbs radiation, it also might photodecompose. This possibility was checked by photolyzing mesityl oxide in heptane solutions. The mesityl oxide is remarkably stable; the only product found was a trace of acetone, even after an extended photolysis. This might partially explain the relative increase of acetone observed in the Pentoxone photolysis as irradiation proceeded.

The pyrolysis results give a check to see if the inhibition is really due to absorption by the mesityl oxide. Since there is no radiation, the decomposition should be uninhibited and follow first-order kinetics

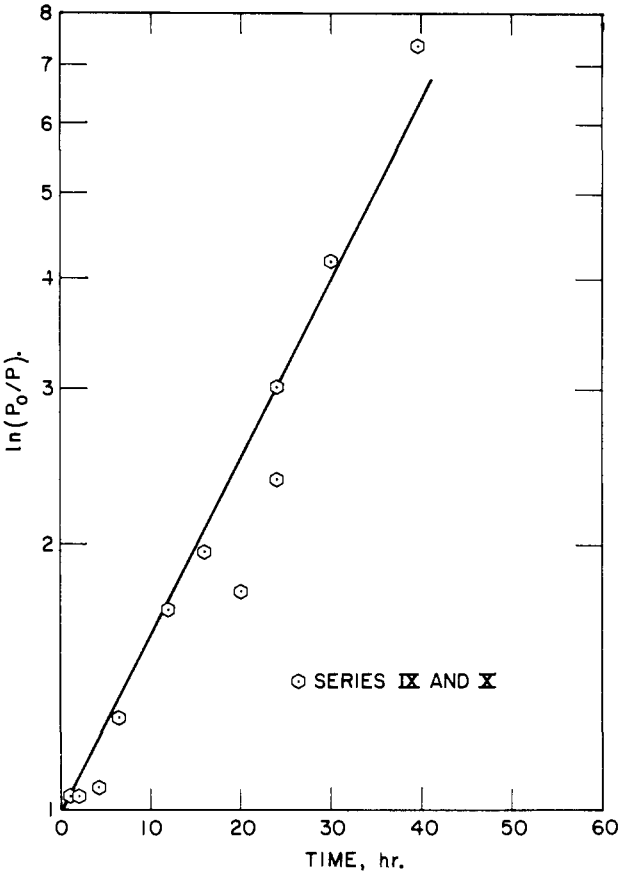

Fig. 2.—Plot of ln (P_0/P) *vs.* time for pyrolysis of Pentoxone.

$$\ln (P_0/P) = kt \qquad (6)$$

where k is the unimolecular rate constant at 200°. Figure 2 is a plot of ln (P_0/P) *vs.* t. The scatter is bad, but the plot shows no indication of inhibition with reaction time. The rate constant k is about 0.045 hr.$^{-1}$.

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[CONTRIBUTION FROM DEPARTMENT OF APPLIED CHEMISTRY, FACULTY OF ENGINEERING, NAGOYA UNIVERSITY, NAGOYA, JAPAN]

Kinetics of the Autoxidation of Phenylhydroxylamines to Azoxybenzenes in Methanol

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RECEIVED DECEMBER 14, 1963

The autoxidation of phenylhydroxylamines in methanol has been studied kinetically by estimating consumed oxygen. The rate is proportional to the product of the concentration of phenylhydroxylamine and the partial pressure of oxygen and is not affected by the addition of radical initiators or inhibitors, but is accelerated by a basic catalyst, methoxide ion. A mechanism was postulated which involves one-electron transfer to oxygen molecule from both free phenylhydroxylamine and its conjugate base, but not from the conjugate acid of phenylhydroxylamine. The substituent effect in pure methanol satisfied the Hammett's law to give a ρ-value of -1.56.

Phenylhydroxylamine in aqueous solution is easily oxidized by oxygen to nitrosobenzene and hydrogen peroxide, and the nitrosobenzene formed condenses rapidly with phenylhydroxylamine to produce azoxybenzene.[1]

$$2C_6H_5NHOH + O_2 \longrightarrow C_6H_5NO{=}NC_6H_5 + H_2O_2 + H_2O \qquad (1)$$

(1) E. Bamberger, *Chem. Ber.*, **27**, 1550 (1894); **33**, 113 (1900).

The hydrogen peroxide formed may also oxidize phenylhydroxylamine to azoxybenzene.[2]

$$2C_6H_5NHOH + H_2O_2 \longrightarrow C_6H_5NO{=}NC_6H_5 + 3H_2O \quad (2)$$

The mechanism of the autoxidation of phenylhydroxylamine has not yet been clarified in detail, although the rate of the autoxidation has been determined in aqueous solutions.[3] As for the autoxidation of aliphatic hydroxylamines in aqueous alkali, a radical mechanism was suggested.[4]

The present paper reports the kinetics of the autoxidation of phenylhydroxylamines studied by measurement of the rate of consumption of oxygen. It was found that the formation of azoxybenzene in methanol follows the stoichiometric equation

$$4C_6H_5NHOH + O_2 \longrightarrow 2C_6H_5NO{=}NC_6H_5 + 4H_2O \quad (3)$$

The reaction products contained no appreciable amount of hydrogen peroxide. The rate is first order with both phenylhydroxylamine and oxygen. The present paper summarizes the data on the kinetic study of the reaction, treats the effect of the basicity of solution, the substituent effect, the effect of radical chain initiators or inhibitors, and derives a probable mechanism presumed from these results.

Experimental

Materials.—Phenylhydroxylamine was synthesized by the reduction of nitrobenzene with zinc powder in aqueous ammonium chloride and recrystallized from a mixture of benzene and petroleum ether[5]; m.p. 82–83° (lit.[6] 82.5°). N-(*p*-Methylphenyl)-hydroxylamine, m.p. 94° (lit.[7] 94°), N-(*p*-chlorophenyl)hydroxylamine, m.p. 87.5–88.0° (lit[8]. 87.5°), N-(*m*-methylphenyl)-hydroxylamine, m.p. 69° (lit.[9] 68.5°), and N-(*m*-chlorophenyl)-hydroxylamine, m.p. 49.6–51.3° (lit.[10] 49°), were obtained by the reduction of the corresponding substituted nitrobenzenes by the same procedure except that a small quantity of methanol was added to the reaction mixture.

Stoichiometry.—To examine the molar ratio of phenylhydroxylamine consumed and azoxybenzene produced, 1.617 g. or 0.01481 mole of phenylhydroxylamine in 30 ml. of methanol was exposed to the air for 12 days until the color changed to black-red. The solvent methanol was then evaporated under vacuum; the residue after being washed with water was filtered and dried under vacuum yielding 1.539 g. or 0.00773 mole of azoxybenzene of m.p. 33°, which rose to 36° (lit.[11] 35.5°) on recrystallization from methanol. Hence 1 mole of phenylhydroxylamine gave 0.511 mole of azoxybenzene in the oxidation.

To determine the stoichiometry of azoxybenzene and oxygen, a 5.5% methanolic solution containing 0.5493 g. or 0.005030 mole of phenylhydroxylamine was kept in a flask shown in Fig. 1 at 40°. After absorption of 0.000884 mole of oxygen for 3 hr., 0.3375 g. or 0.001713 mole of azoxybenzene was obtained. Hence the molar ratio of azoxybenzene *vs.* oxygen was 1.93, or 1 mole of oxygen produced *ca.* 2 moles of azoxybenzene.

Kinetics.—Ten milliliters of 0.15–1.5 *M* methanolic solution of phenylhydroxylamine was placed in one flask of the apparatus shown in Fig. 1 and 10 ml. of methanol in the other. The apparatus was brought to temperature equilibrium in a thermostat. After evacuation of the apparatus, nitrogen gas was introduced and the same procedure was repeated several times to remove oxygen from the vessel completely. Then pure oxygen was introduced to start the reaction with magnetic stirring.

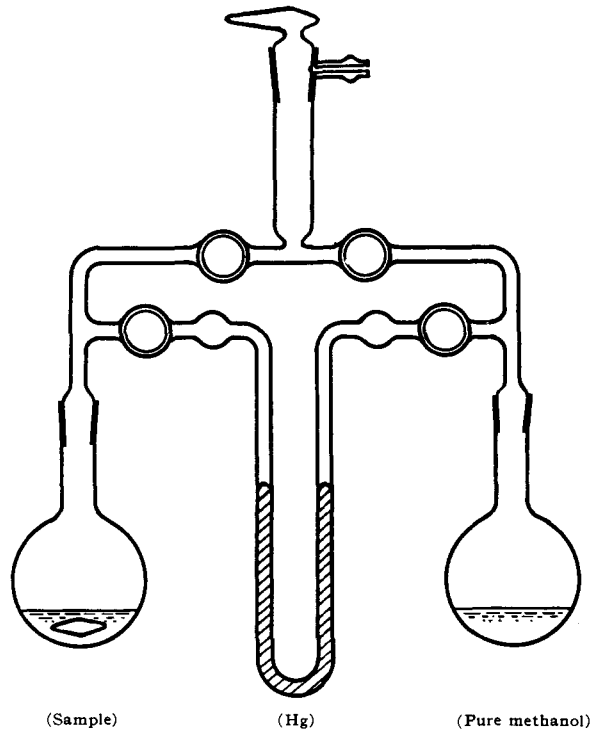

Fig. 1.—Reaction apparatus; sample stirred by a magnetic stirrer.

Assuming oxygen obeys the ideal gas law, the number of moles of consumed oxygen, Δn, is expressed as

$$\Delta n = \Delta p V/RT$$

Here Δp is the partial pressure difference of oxygen and V is the whole volume of gas in the reaction vessel. The stoichiometric eq. 3 gives the concentration of phenylhydroxylamine oxidized as follows, where the volume of the solution is always 10 ml.

$$\Delta[C_6H_5NHOH] = (1000/10)4\Delta n = (400V/RT)\Delta p = f\Delta p \quad (4)$$

Here, f (= $400V/RT$) is constant when a given flask and temperature are used. Therefore, the concentration of phenylhydroxylamine at time t is

$$[C_6H_5NHOH] = [C_6H_5NHOH]_0 - f\Delta p \quad (5)$$

where $[]_0$ represents the initial concentration.

The rate of oxidation, $-dp/dt$, was determined from the tangent of the plots of oxygen pressure *vs.* time.

Results

Rate Equation.—The rate was found to follow second-order kinetics

$$-dp/dt = k[C_6H_5NHOH]p \quad (6)$$

The apparent rate constant increased with proceeding of the reaction probably because of the slight overestimation of the concentration of phenylhydroxylamine owing to neglect of the presence of a small quantity of hydrogen peroxide. The rate constant at the start of reaction, k, was, however, almost constant with various initial concentrations of phenylhydroxylamine and various initial partial pressures of oxygen (Table I).

(2) E. Bamberger, *Chem. Ber.*, **33**, 119 (1900).
(3) M. Kiese and A. von Rückteschell, *Arch. exptl. Pathol. Pharmakol.*, **213**, 128 (1951).
(4) D. H. Johnson, M. A. T. Rogers, and G. Trappe, *Chem. Ind.* (London), 1032 (1953); M. A. T. Rogers, *ibid.*, 1033 (1953).
(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 445.
(6) R. Willstätter and H. Kubli, *Ber.*, **41**, 1936 (1908).
(7) E. Bamberger, *ibid.*, **28**, 245 (1895).
(8) M. D. Farrow and C. K. Ingold, *J. Chem. Soc.*, **125**, 2550 (1924).
(9) E. Bamberger and A. Rizing, *Ann.*, **316**, 283 (1900).
(10) R. D. Haworth and A. Lapworth, *J. Chem. Soc.*, **119**, 773 (1921).
(11) S. Sugden, J. B. Reed, and H. Willkins, *ibid.*, **127**, 1537 (1925).

TABLE I

SECOND-ORDER RATE CONSTANT OF AUTOXIDATION OF PHENYLHYDROXYLAMINE AT ZERO TIME IN METHANOL AT 35°

Init. concn. of C_6H_5NHOH, M	Init. partial press. of O_2, mm.	$k \times 10^4$, M^{-1} min.$^{-1}$	Init. concn. of C_6H_5NHOH, M	Init. partial press. of O_2, mm.	$k \times 10^4$, M^{-1} min.$^{-1}$
0.6669	304	2.20	0.4810	660	2.04
1.1433	304	1.98	.9140	203	6.10[a]
1.4890	311	2.02	.4676	212	6.52[a]
0.6570	203	2.06	.5960	302	6.10[a]
1.1850	500	1.96			

[a] Autoxidation in alkaline methanol buffered at pH 8.2 by the addition of NH_3–NH_4Cl, which was 0.3 pH unit lower than that in water.

Effect of Radical Initiators and Inhibitors.—In general, autoxidation has been regarded as a radical attack of oxygen. To examine the possibility of radical reaction, effects of radical initiators and inhibitors were studied. As shown in Table II, they had no appreciable influence on the rate.

TABLE II

EFFECT OF RADICAL INITIATORS AND INHIBITORS IN METHANOL AT 35°[a]

Added compd.	M	$k \times 10^4$, M^{-1} min.$^{-1}$	Added compd.	M	$k \times 10^4$, M^{-1} min.$^{-1}$
Azobisiso-	0.0052	2.17	Hydroquinone	0.0082	2.19
butyronitrile	.0143	1.90		.0251	2.29
Benzoyl			Benzoquinone	.0095	2.10
peroxide	.0068	2.17	β-Naphthol	.0061	2.23

[a] Initial partial pressure of oxygen is 660 mm. and $[C_6H_5NHOH]_0$ is *ca.* 0.5 *M*.

Effect of the Acidity of Solution.—The effect of the addition of hydrogen chloride was studied in 90% methanol at 25° (Table III). The rate decreased with increasing concentration of the acid for the system of constant initial concentration of phenylhydroxylamine. If the amount of acid surpassed that of phenylhydroxylamine, the oxidation became too slow to measure.

TABLE III

EFFECT OF ACIDITY IN 90% AQUEOUS METHANOL AT 500 MM. INITIAL PARTIAL PRESSURE OF OXYGEN

$[C_6H_5NHOH]_0$, M	[HCl], M	$k \times 10^4$, M^{-1} min.$^{-1}$	$k_{HCl} \times 10^4$,[a] M^{-1} min.$^{-1}$
1.0149	None	0.734	0.734
1.0385	0.0203	.637	.643
1.0635	.1174	.570	.657
1.0299	.5870	.293	.679
0.8827	.4813	.306	.672
1.5431	.9626	.298	.795
0.9802	1.174	Very small	...
0.3997	0.4813	Very small	...

[a] $-dp/dt = k_{HCl}\{[C_6H_5NHOH]_0 - [HCl]\}p$. (6)'

The effect of pH on the rate was examined in methanolic solution buffered with ammonia–ammonium chloride. The pH's of this buffer were determined by a glass electrode, which gave pH values *ca.* 0.3 unit lower than those of the same buffer in water. The rate of the oxidation of phenylhydroxylamines increased with increasing pH, but no linearity was observed in the plot of log k *vs.* pH.

Substituent Effect.—The rates for substituted phenylhydroxylamines were determined at 35° in methanol (Fig. 2 and Table V). The oxidation was accelerated by the introduction of electron-releasing substituents and retarded by electron-attracting substituents. These rates satisfied Hammett's equation with a ρ-value of −1.56.

TABLE IV

APPARENT ENERGY AND ENTROPY OF ACTIVATION FOR THE AUTOXIDATION OF SUBSTITUTED PHENYLHYDROXYLAMINES

Substituent	E_a, kcal. mole^{-1}	ΔS^*, cal. deg.$^{-1}$
p-CH_3	12.22	−29.88
m-CH_3	13.45	−26.57
H	13.06	−28.97
p-Cl	13.53	−28.31

TABLE V

EFFECT OF SUBSTITUENT ON THE RATE OF AUTOXIDATION OF PHENYLHYDROXYLAMINE AT 35°

Initial concn. of ArNHOH, 0.5–0.6 *M*, $p^0 \cong 300$ mm.

	Solvent	
	Methanol	Methanol with NH_3–NH_4Cl (pH 7.97)
Substituent	$k \times 10^4$, M^{-1} min.$^{-1}$	$(k - k_H) \times 10^4$, M^{-1} min.$^{-1}$
p-CH_3	3.70	2.25
m-CH_3	2.44	0.74
H	2.04	2.50
p-Cl	1.04	3.10
m-Cl	0.521	

On the other hand, the oxidation in alkaline media showed a departure from Hammett's plot (Fig. 2), which will be discussed later.

Effect of Temperature.—The effect of temperature was studied at 25, 35, and 45° in methanol. The Arrhenius plots of these results gave straight lines, apparent activation energies and entropies being summarized in Table IV.

Discussion

It was rather surprising to find that no appreciable effect of radical initiators or inhibitors was observed in the autoxidation of phenylhydroxylamine, but that the reaction was affected by acid and base. The substituent effect in pure methanol gave a negative ρ-value.

Neither hydrogen peroxide nor active oxygen was detected on bubbling oxygen into pure or alkaline methanol alone. Hence it is probable that the oxidation proceeds through a one-electron transfer to molecular oxygen from negative nitrogen atom of phenylhydroxylamine. Possible equilibria of phenylhydroxylamine in acidic or alkaline methanol are

$$C_6H_5NHOH + H^+ \underset{}{\overset{K_7}{\rightleftharpoons}} C_6H_5\overset{+}{N}H_2OH \qquad (7)^{12}$$

$$C_6H_5NHOH + OCH_3^- \overset{K_8}{\rightleftharpoons} C_6H_5\overset{-}{N}OH + CH_3OH \qquad (8)$$

If the initial concentration of phenylhydroxylamine is a, consumed oxygen at time t is x and hence the concentration of oxidized phenylhydroxylamine at t is $4x$, the following expressions are obtained at time t.

$$a - 4x = [C_6H_5NHOH] + [C_6H_5\overset{+}{N}H_2OH] + [C_6H_5\overset{-}{N}OH] \qquad (9)$$

$$\left.\begin{aligned} [C_6H_5NHOH] &= \frac{a - 4x}{1 + K_7[H^+] + K_8[OCH_3^-]} \\ [C_6H_5\overset{+}{N}H_2OH] &= \frac{(a - 4x)K_7[H^+]}{1 + K_7[H^+] + K_8[OCH_3^-]} \\ [C_6H_5\overset{-}{N}OH] &= \frac{(a - 4x)K_8[OCH_3^-]}{1 + K_7[H^+] + K_8[OCH_3^-]} \end{aligned}\right\} \qquad (10)$$

(12) Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Am. Chem. Soc.*, **79**, 3397 (1957).

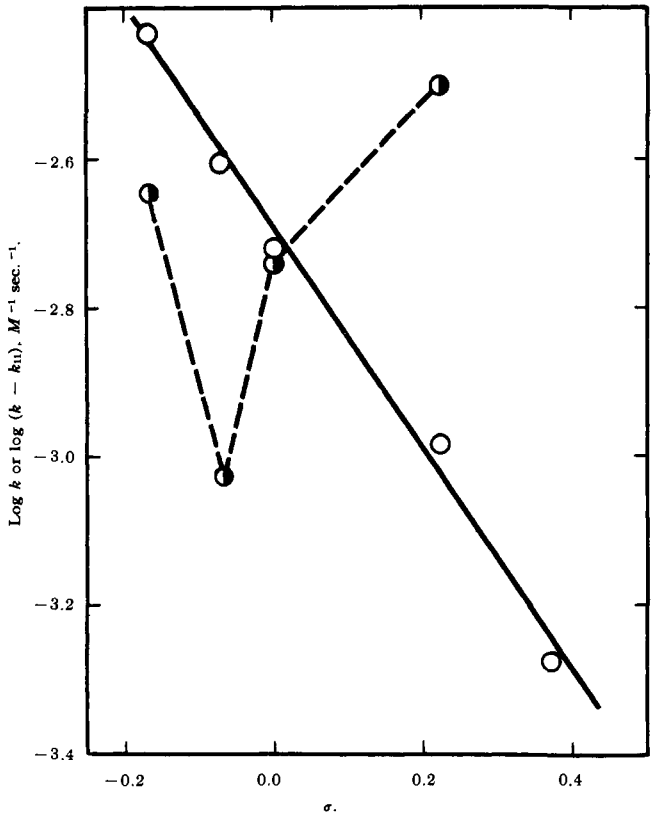

Fig. 2.—Plots of σ (Hammett and Jaffé) *vs.* log k or log $(k - k_{11})$ for the autoxidation of phenylhydroxylamines at 35°: —O—, log k in pure methanol; --◑--, log $(k - k_{11})$ in alkaline methanol of pH 7.97.

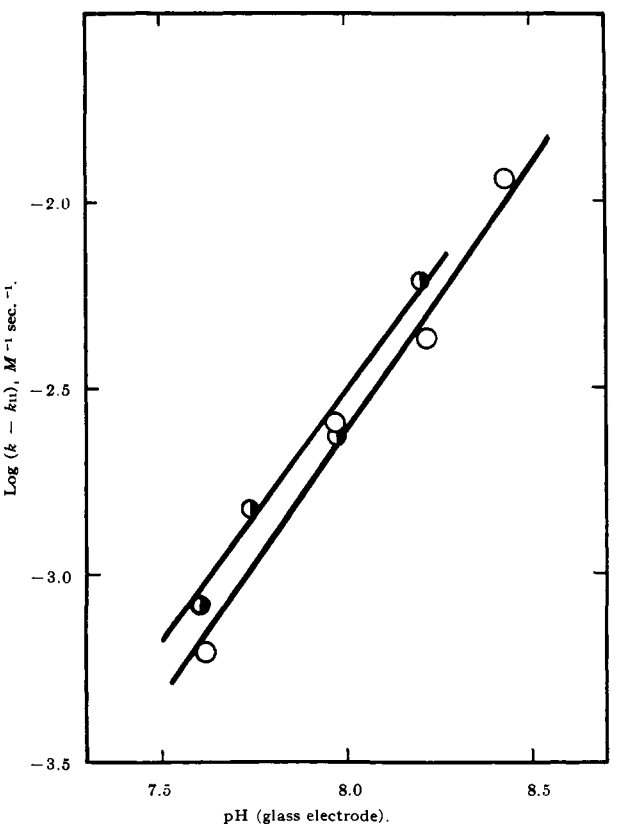

Fig. 3.—Plots of log $(k - k_{11})$ *vs.* pH for the autoxidation in alkaline methanol at 35°: O, phenylhydroxylamine; ◑, *p*-methylphenylhydroxylamine.

The results may be explained by assuming two simultaneous steps 11 and 12, whereas the conjugate acid $C_6H_5\dot{N}H_2OH$ resists oxidation.

$$C_6H_5NHOH + O_2 \xrightarrow[\text{slow}]{k_{11}} C_6H_5\dot{N}HOH^+ + O_2\cdot^- \quad (11)$$

$$C_6H_5\bar{N}OH + O_2 \xrightarrow[\text{slow}]{k_{12}} C_6H_5\dot{N}OH + O_2\cdot^- \quad (12)$$

$$C_6H_5NHOH^+ \xrightarrow{\text{fast}} C_6H_5\dot{N}OH + H^+ \quad (13)$$

$$C_6H_5NHOH + O_2\cdot^- \xrightarrow{\text{fast}} C_6H_5\dot{N}OH + H\dot{O}_2\cdot^- \quad (14)$$

$$2C_6H_5NOH \overset{\text{fast}}{\rightleftharpoons} C_6H_5NO + C_6H_5NHOH \xrightarrow{\text{fast}} C_6H_5NO{=}NC_6H_5 + H_2O \quad (15a)^{12}$$

or

$$2C_6H_5\dot{N}OH \xrightarrow{\text{fast}} C_6H_5NO{=}NC_6H_5 + H_2O \quad (15b)$$

$$C_6H_5NHOH + \left\{\begin{matrix}HO_2^-\\H_2O_2\end{matrix}\right\} \xrightarrow{\text{fast}} C_6H_5NO{=}NC_6H_5 + \left\{\begin{matrix}H_2O + OH^-\\2H_2O\end{matrix}\right\} \quad (16)$$

This mechanism involving short kinetic chains would not interfere with the rate of oxygen absorption which is rate determining. The reversibility of the first step of eq. 15a is assumed from the interconversion of substituted nitrosobenzenes and phenylhydroxylamines.[12]

Thus, the rate equation is

$$-\frac{dp}{dt} = k_{11}\frac{(a - 4x)p}{1 + K_7[H^+] + K_8[OCH_3^-]} + k_{12}\frac{(a - 4x)pK_8[OCH_3^-]}{1 + K_7[H^+] + K_8[OCH_3^-]} = \{k_{11} + k_{12}K_8[OCH_3^-]\}\frac{(a - 4x)p}{1 + K_7[H^+] + K_8[OCH_3^-]} \quad (17)$$

Since the concentration of conjugate acid or base of phenylhydroxylamine in pure methanol is very low, the contribution of $K_7[H^+]$ and $K_8[OCH_3^-]$ and hence the reaction by step 12 seems to be negligible. Therefore, the apparent rate constant in pure methanol may correspond to k_{11}. The rate equation in neutral or acidic media may be expressed as

$$-\frac{dp}{dt} = k_{11} \times \frac{(a - 4x)p}{1 + K_7[H^+]}$$

Since the value of K_7 is very large (2.90×10^3 at 25° in pure methanol),[12] phenylhydroxylamine may be completely protonated by the added acid and deactivated. The constancy of rate constant, k_{HCl}, calculated on the assumption that only free phenylhydroxylamine may be oxidized in acidic media, indicates that the conjugate acid is stable for autoxidation (Table III).

In the presence of methoxide ion, on the other hand, the oxidation occurs by way of eq. 12 as well as eq. 11. Since $K_7[H^+]$ is negligible here, the equation may be

$$-\frac{dp}{dt} = \{k_{11} + k_{12}K_8[OCH_3^-]\}\frac{(a - 4x)p}{1 + K_8[OCH_3^-]}$$

Since phenylhydroxylamine is a strong base and a weak acid, then $K_8[OCH_3^-] << 1$

$$-\frac{dp}{dt} = \{k_{11} + k_{12}K_8[OCH_3^-]\}(a - 4x)p$$

or

$$k = k_{11} + k_{12}K_8[OCH_3^-]$$

If $K_M = [H^+][OCH_3^-]$ is constant in methanol

$$\log (k - k_{11}) = pH + \log (k_{12}K_8K_M)$$

From this equation the plots of log $(k - k_{11})$ *vs.* pH should give straight lines of unit slope. This was realized as shown in Fig. 3, while no linearity was observed in the plot of log k *vs.* pH.

The order of reactivities of substituted phenylhydroxylamines in the presence of alkali was inconsistent with that in pure methanol, resulting in disagreement with Hammett's equation. These results may be explained by taking into account that the substituent effects of k_{12} and K_8 are reversed; *i.e.*, $k_{12} \times K_8$ corresponds to the rate of the oxidation of $C_6H_5\dot{N}OH$, while the substituent effect in pure methanol contains only k_{11} which corresponds to free C_6H_5NHOH. In other words, k_{12} increases with increasing electron-releasing power of substituent, while K_8 behaves reversely.

The plot of log $(k - k_{11})$ *vs.* pH for unsubstituted phenyl hydroxylamine at 35° gave an equation

$$\log (k - k_{11}) = 1.32pH - 10.05$$

Hence

$$\log k_{12}K_8 = -\log K_M - 10.05$$

Assuming the ionic product of methanol is 2×10^{-17} [13]

$$k_{12}K_8 \approx 7.5 \times 10^3$$

Since phenylhydroxylamine is a weak acid, the value of K_8 may be much smaller than 10^6, and then $k_{12} > k_{11}$. Hence, the order of reactivity is $C_6H_5\dot{N}OH > C_6H_5NHOH >> C_6H_5\dot{N}H_2OH$. The increase of the oxidation rate with increasing pH coincides with the decrease of the oxidation potential of phenylhydroxylamine with increasing pH.[14] Moreover, the oxidation potential decreases with decreasing σ-value of substituent on phenylhydroxylamine[15] as observed in the present reaction.

(13) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 256.
(14) J. W. Smith and J. G. Wallen, *Trans. Faraday Soc.*, **46**, 290 (1950).
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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, TOKYO INSTITUTE OF TECHNOLOGY, OHOKAYAMA, MEGUROKU, TOKYO, JAPAN]

Steric Difference between the Substitution Reaction Products of Lithium Alkyls and Grignard Reagents with α-Aminonitriles.[1] An Asymmetric Reproduction

BY JUJI YOSHIMURA, YOSHIAKI OHGO, AND TETSUO SATO

RECEIVED APRIL 3, 1964

Substitution reactions of 3,4-O-isopropylidene N-substituted-D-threosaminonitriles and -D-erythrosaminonitriles with phenylmagnesium bromide and phenyllithium have been investigated. The reaction with phenylmagnesium bromide gave an *erythro* derivative and the reaction with phenyllithium gave *threo* products predominantly, regardless of the configuration of the α-carbon in the substrate. N-Substituted acetone-D-glyceraldimines also gave the same result. Consideration of the steric difference between the Grignard reaction and the phenyllithium reaction leads to two possible explanations for the asymmetric induction of optically active imine-bearing oxygen-like atoms on the α- and β-carbon.

In a pervious paper,[2] one of the authors reported that the substitution reaction of di-O-isopropylidene-N-phenyl-D-glucosaminonitrile with Grignard reagents gave levorotating compounds and that the reaction with lithium alkyls afforded dextrorotating products predominantly. The results prompted the present study of the steric difference between lithium alkyls and Grignard reagents in the substitution reaction.

Materials

3,4-O-Isopropylidene-N-phenyl-D-threosamino- and -erythrosaminonitrile (I-T and I-E), the corresponding N-benzyl derivatives (II-T and II-E),[3] and diastereomeric mixtures of N-ethyl and N-dimethyl derivatives (III-T·E and IV-T·E) were prepared by condensing acetone-D-glyceraldehyde with the corresponding amine and hydrogen cyanide, followed by fractional crystallization.

The Schiff bases, N-phenyl- and N-benzylacetone-D-glyceraldimine (I-S and II-S), were prepared from acetone-D-glyceraldehyde and the corresponding amines. Properties of the materials used are shown in Table I.

N-Substituted Acetone-D-glyceraldimines.—The condensation product of acetone-D-glyceraldehyde and an equivalent amount of benzylamine was distilled at 110° (0.005 mm.). The distillate, however, showed the existence of both the —NH—[4] and the —C=N—[5] groups by an infrared absorption spectrum, but no optical activity in spite of the analytical data which were consistent with the theoretical values for II-S. This fact seems to imply that heat promotes isomeri-

(1) This work was presented at the 15th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1962.
(2) J. Yoshimura, *Bull. Chem. Soc. Japan*, **35**, 536 (1962).
(3) J. Yoshimura, Y. Ohgo, and T. Sato, *ibid.*, **34**, 1197 (1961).
(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London, 1958, p. 2249.
(5) Ref. 4, p. 268.