

PULSE RADIOLYTIC INVESTIGATION OF ALIPHATIC AMINES IN AQUEOUS SOLUTION

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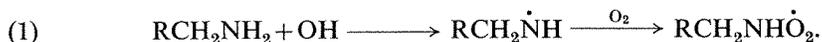
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(Received 31 December 1970)

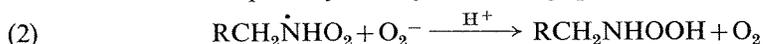
Abstract—The rates of reaction of hydroxyl radicals with various aliphatic amines have been determined as a function of pH. These include methyl, ethyl, isopropyl, *t*-butyl, trimethyl and triethyl amines. Rate constants of $\approx 3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for protonated amines and $\approx 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for unprotonated amines have been obtained. This marked difference is attributed to the electrophilic character of the hydroxyl radical and its unfavorable interaction with the positive center. The transient absorption spectra of the various aminoalkyl and alkyl-amino radicals produced from the reaction of OH radicals with these amines were derived over the pH range 3–13. The transient species produced from trimethyl and triethyl amines have absorption maxima at $\approx 260 \text{ nm}$, all the other amines showed no maxima down to $\approx 230 \text{ nm}$, the limit imposed by experimental conditions. Strong pH dependence of the initial transient absorption is observed for all the amines examined. These changes are caused by the acid–base dissociation of the radicals, and by changes in the site of OH radical attack. Generally, it can be stated that hydrogen atom abstraction by OH radicals from unprotonated amines takes place mainly from an α -position and/or from hydrogen bonded to nitrogen, whereas abstraction from protonated amines occurs mainly at positions β - and/or γ - from the >NH^+ group.

INTRODUCTION

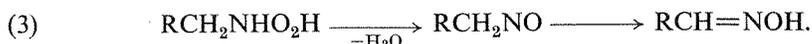
AMINES and the amino group are important basic functional compounds in organic chemistry and biochemistry. Since the early works of J. J. Weiss and co-workers^(1,2) on the radiation chemistry of aliphatic amines in aqueous solution, very little has been done⁽³⁾. Weiss and co-workers^(1,2) determined some of the products produced in the radiolysis of aqueous solutions of amines in presence of oxygen. The formation of oximes from primary and secondary amines was observed only in alkaline solutions at pH above 8.0. While it was clear from these early studies that the free radical mechanisms involving amines were rather complex, they proposed an interesting set of reactions:



The peroxy radical was suggested to be reduced by reaction with O_2^- (formed in the reaction between the primary radiolytic reducing species and molecular oxygen),



and the hydroperoxide decomposed into the oxime



The complexity of these free radical reactions in the presence of oxygen has been fully demonstrated⁽⁴⁾ in the pulse radiolysis of oxygenated aqueous solutions of amines.

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Various aminoalkyl radicals have recently been observed by E.S.R. and were produced in aqueous solutions by the $Ti^{3+} + H_2O_2$ reagent⁽⁵⁾ or by electron radiation⁽⁶⁾, under steady-state conditions. Unfortunately, both methods are limited to the study of the longer-lived radicals, while the primary shorter-lived radicals are often unrecorded.

Pulse radiolysis studies of aqueous solutions of methylamine and aniline have recently been reported⁽⁷⁾, and of the amino group in simple amino acids⁽⁸⁾ and peptides⁽⁹⁾. The reaction rates of OH radicals and e_{aq}^- with various amines have also been determined⁽¹⁰⁾.

In this work, the pulse radiolysis of methyl, ethyl, isopropyl, *t*-butyl, trimethyl and triethyl amines in an air-free aqueous solution has been studied as a function of pH. From the results presented below, some further progress has been made in the elucidation of the complex reaction mechanism which these compounds undergo.

EXPERIMENTAL

Pulse radiolysis was carried out using the Febetron 705 System (Field Emission Corp.). This machine produces pulses of electrons of 2.3 MeV energy and ≈ 30 ns duration. Full experimental details have been published elsewhere⁽¹¹⁾.

The chemicals employed were analytical reagent grade. The gaseous amines were supplied by Matheson and were introduced without further purification into air-free N_2O -saturated water. The liquid amines were supplied by Eastman and were treated with activated charcoal and fractionally distilled before use. The solutions were buffered using perchloric acid, potassium hydroxide, borate and potassium phosphates ($\approx 2-3 \text{ mol m}^{-3}$).

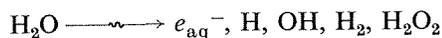
The dose per pulse was determined in N_2O -saturated aqueous solutions of $2 \times 10^{-2} \text{ mol/dm}^{-3}$ KCNS, the O.D. was measured at 500 nm, using

$$\epsilon(\text{CNS})_2^- = 7600 \text{ dm}^3/\text{mol}^{-1} \text{ cm}^{-1} (760 \text{ m}^2/\text{mol})^{(12)}.$$

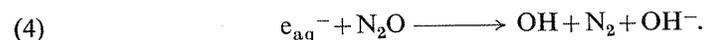
High concentrations of amines were used to ensure complete scavenging of OH radicals at all pH values.

RESULTS

The optical absorption spectra of the transient species produced on pulse radiolysis of aqueous solutions of various amines were derived from reaction with OH radicals. The hydrated electrons produced in the radiation chemistry of water:



were, in our experiments, converted into OH radicals by reaction with N_2O ($25 \text{ mmol dm}^{-3} = 25 \text{ mol m}^{-3}$):



The reactivity of OH radicals with various aliphatic amines was determined in the pH range 3–11 in the presence of N_2O , using the thiocyanate method. These relative rates were determined in 2 mol m^{-3} KCNS solutions by varying the concentration of the amines. The absolute rates were obtained taking⁽¹²⁾

$$k(\text{OH} + \text{CNS}^-) = 1.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The absolute values of $k(\text{OH} + \text{amine})$ for various amines are plotted as a function of pH in Fig. 1. Due to the dissociation of OH radicals ($\text{OH} \rightleftharpoons \text{O}^- + \text{H}^+$, $pK = 11.9$)⁽¹³⁾, these rates could not be correctly determined above $\text{pH} \approx 11.0$. From the known pK_a

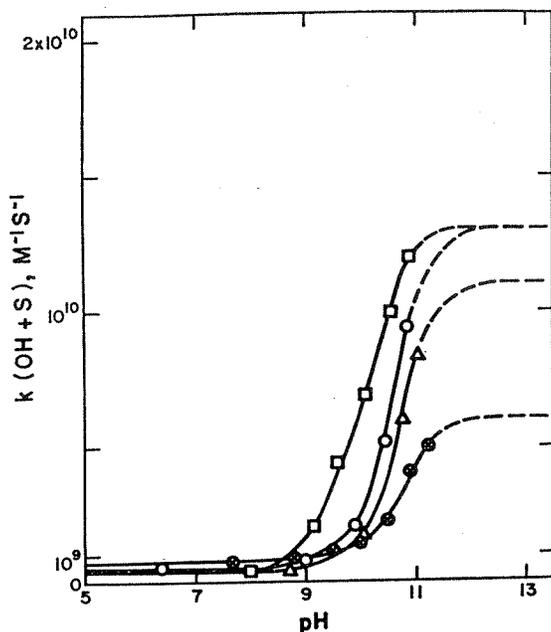


FIG. 1. Dependence upon pH of the reactivity of OH radicals towards some aliphatic amines: trimethyl amine, \square ; isopropyl amine, \circ ; triethyl amine, \triangle ; *t*-butyl amine, \otimes .

values for the amines and the pH at which the relative rates were measured, it was possible to calculate the rates for the reaction of OH radicals with the deprotonated amines using

$$k_{\text{total}} = k_{(\text{OH} + \text{RNH}_3^+)} f_1 [\text{RNH}_3^+] + k_{(\text{OH} + \text{RNH}_2)} (1 - f_1) [\text{RNH}_2],$$

where f_1 and $(1 - f_1)$ represent the fractions of the protonated and deprotonated forms, respectively. The limiting values of OH radicals with the protonated and deprotonated forms of the various amines are presented in Table 1.

The transient absorption spectra of various amino alkyl (and alkylamino) radicals produced from the reaction of OH radicals with methyl, ethyl, isopropyl, *t*-butyl, trimethyl and triethyl amines are shown in Figs. 2-7. These spectra were obtained at various pH values, and the changes in absorbance at specific wavelengths with pH are given in all cases. Experimental difficulties were encountered (low signal-to-noise ratio) in some cases due to the low extinction coefficients of the transients, and their absorption in the far u.v. region. The decay rates of the amino-alkyl radicals observed were determined and the results are given in Table 2.

In the pulse radiolysis of methyl amine, the transient absorption was found (Fig. 2) to be independent of amine concentration in the range $10^{-2} - 1.0 \text{ mol/dm}^{-3}$. The decay rates of the transients were also examined in the wavelength region

TABLE I. RATES OF REACTION OF OH RADICALS WITH ALIPHATIC AMINES IN AQUEOUS SOLUTION, AT VARIOUS pH VALUES

Amine	pH	Form	$k(\text{OH} + \text{amine})$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ *
Methyl amine	8.0	CH_3NH_3^+	$1.1 \times 10^9 \ddagger$
	12.0	CH_3NH_2	$6.9 \times 10^9 \ddagger$
Ethyl amine	3.1	$\text{CH}_3\text{CH}_2\text{NH}_3^+$	3.0×10^8
	11.2	—	1.1×10^{10}
	12.0	$\text{CH}_3\text{CH}_2\text{NH}_2$	$1.3 \times 10^{10} \ddagger$
Isopropyl amine	3.0	$(\text{CH}_3)_2\text{CHNH}_3^+$	5.0×10^8
	10.8	—	9.0×10^9
	12.0	$(\text{CH}_3)_2\text{CHNH}_2$	$1.3 \times 10^{10} \ddagger$
<i>t</i> -Butyl amine	3.2	$(\text{CH}_3)_3\text{CNH}_3^+$	7.0×10^8
	10.9	—	4.0×10^9
	12.0	$(\text{CH}_3)_3\text{CNH}_2$	$6.0 \times 10^9 \ddagger$
Trimethyl amine	7.5	$(\text{CH}_3)_3\text{NH}^+$	4.0×10^8
	10.9	—	1.2×10^{10}
	12.0	$(\text{CH}_3)_3\text{N}$	$1.3 \times 10^{10} \ddagger$
Triethyl amine	3.6	$(\text{CH}_3\text{CH}_2)_3\text{NH}^+$	3.5×10^8
	11.0	—	8.0×10^9
	12.0	$(\text{CH}_3\text{CH}_2)_3\text{N}$	$1.1 \times 10^{10} \ddagger$

* Determined using the thiocyanate method ($2 \times 10^{-3} \text{ mol/dm}^{-3}$), taking
 $k(\text{OH} + \text{CNS}^-) = 1.1 \times 10^{10} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

† From Ref. 7.

‡ Extrapolated values, see Fig. 1.

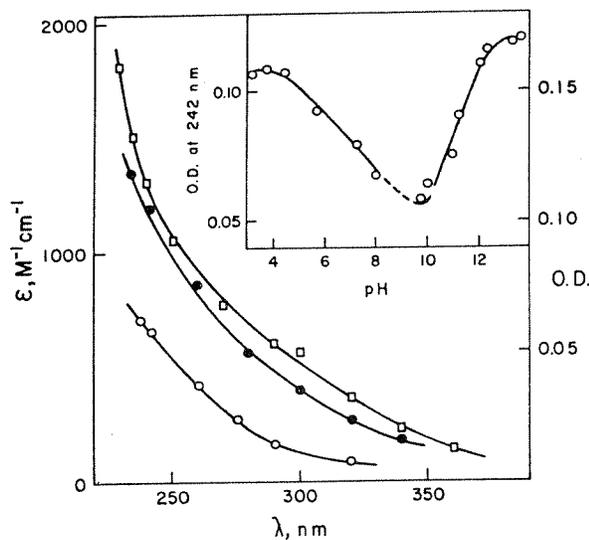


FIG. 2. Transient absorption spectra (ordinates: $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) produced from the reaction of OH radicals with 1.0 mol dm^{-3} methyl amine, in presence of N_2O (1 atm), at various pH values: pH 3.1, ●; pH 9.8, ○; pH 12.3, □. Dose rate 8 krad/pulse. Insert: O.D. at 242 nm as a function of pH.

TABLE 2. ABSORPTION MAXIMA, EXTINCTION COEFFICIENTS, DECAY KINETICS AND pK VALUES OF TRANSIENT SPECIES PRODUCED FROM THE REACTION OF OH RADICALS WITH VARIOUS AMINES IN AQUEOUS SOLUTION

Amine	pKa		pH	Transient spectra		Decay kinetics		
	Parent	Transient		λ_{\max} (nm)	ϵ_{\max} (dm ³ mol ⁻¹ cm ⁻¹)	2k/ε	Measured at λ (nm)	2k (dm ³ mol ⁻¹ s ⁻¹)
Methyl amine, CH ₃ NH ₂	10.62	≈7 ≈11.3	3.8 10.1 12.3	<230 <235 <230	>1350 >700 >1800	1.8 × 10 ⁶ 3.0 × 10 ⁶ 3.4 × 10 ⁶	290 290 290	1.8 × 10 ⁹ 1.9 × 10 ⁹ 4.0 × 10 ⁹
Ethyl amine, CH ₃ CH ₂ NH ₂	10.63	≈5.5 ≈10.4	3.0 7.0 12.2	<240 <240 <235	>100 >650 >1350	— * 2.5 × 10 ⁶	— 265 265	— * 1.8 × 10 ⁹
Isopropyl amine, (CH ₃) ₂ CHNH ₂	10.63	6 10.7	3.0 8.0 12.2	<240 <240 <240	>300 >1600 >2400	— * 1.5 × 10 ⁶	— 250 270	— * 1.6 × 10 ⁹
<i>t</i> -Butyl amine, (CH ₃) ₃ CNH ₂	10.55	4.6 9.8	3.0 7.0 12.2	<220 <220 <235	>650 >550 >1000	7.2 × 10 ⁶ — 2.5 × 10 ⁶	260 — 260	3.0 × 10 ⁹ — 1.5 × 10 ⁹
Trimethyl amine, (CH ₃) ₃ N	9.76	3.5 9.2	3.3 5.1 11.9	≈250 ≈260 ≈260	1900 2600 5200	— — 4.0 × 10 ⁵	270 280 270	8.5 × 10 ⁵ s ^{-1†} 2.7 × 10 ⁵ s ^{-1†} 2.1 × 10 ⁹
Triethyl amine, (C ₂ H ₅) ₃ N	10.65	6 9.5	3.0 7.8 12.0	<250 <240 ≈265	>300 >1500 3400	— 1.1 × 10 ⁶ 6.6 × 10 ⁵	— 270 300	— 1.2 × 10 ⁹ 1.0 × 10 ⁹

* Decay shows mixed components.

† First-order decay of transient.

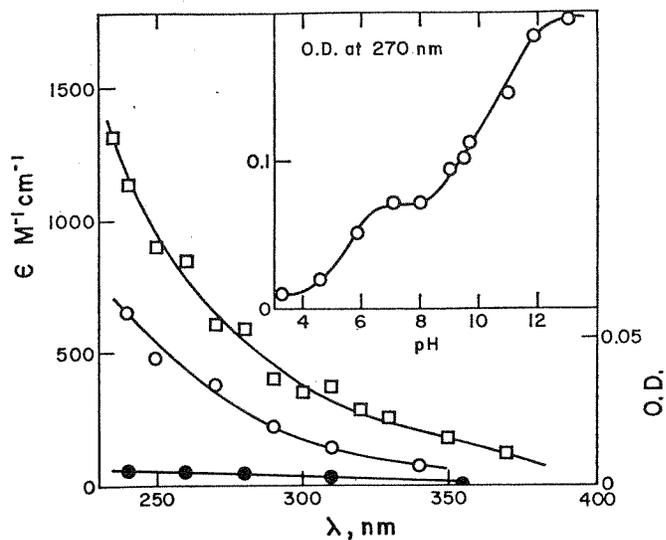


FIG. 3. Transient absorption spectra (ordinates: $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) produced from the reaction of OH radicals with 1.0 mol dm^{-3} ethyl amine, in presence of N_2O (1 atm), at various pH values: pH 3.1, \bullet ; pH 9.8, \circ ; pH 12.3, \square . Dose rate 8 krads/pulse. Insert: O.D. at 270 nm as a function of pH.

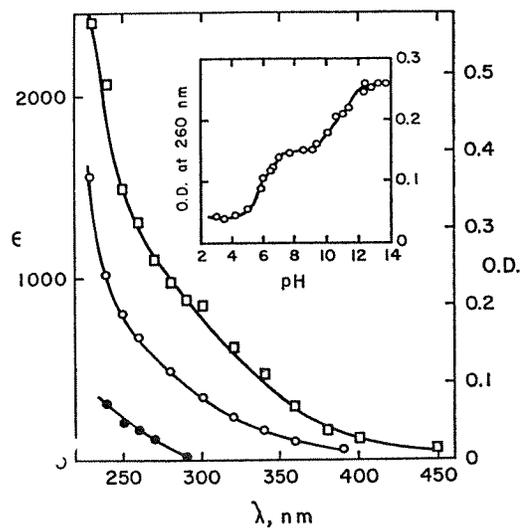


FIG. 4. Transient absorption spectra (ordinates: $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) produced from the reaction of OH radicals with 1.0 mol dm^{-3} isopropyl amine, in presence of N_2O (1 atm), at various pH values: pH 3.0, \bullet ; pH 7.7, \circ ; pH 12.2, \square . Dose rate 19 krads/pulse. Insert: O.D. at 260 nm vs. pH.

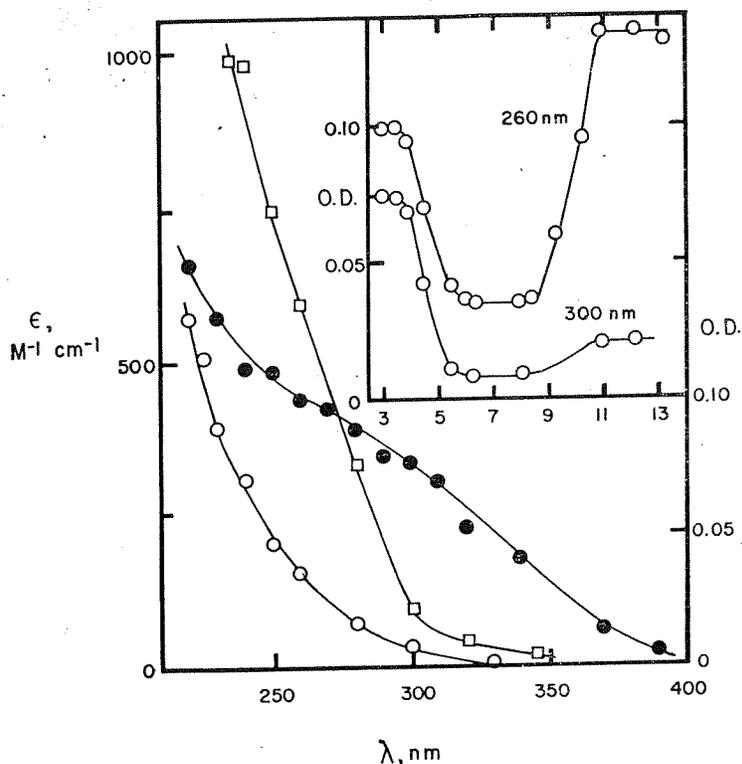


FIG. 5. Transient absorption spectra (ordinates: $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) produced from the reaction of OH radicals with 0.5 mol dm^{-3} *t*-butyl amine, in presence of N_2O (1 atm) at pH 3.0, ●; pH 8.1, ○; pH 12.2, □. Dose rate 19 krad/pulse. Insert: O.D. at 260 nm and 300 nm vs. pH.

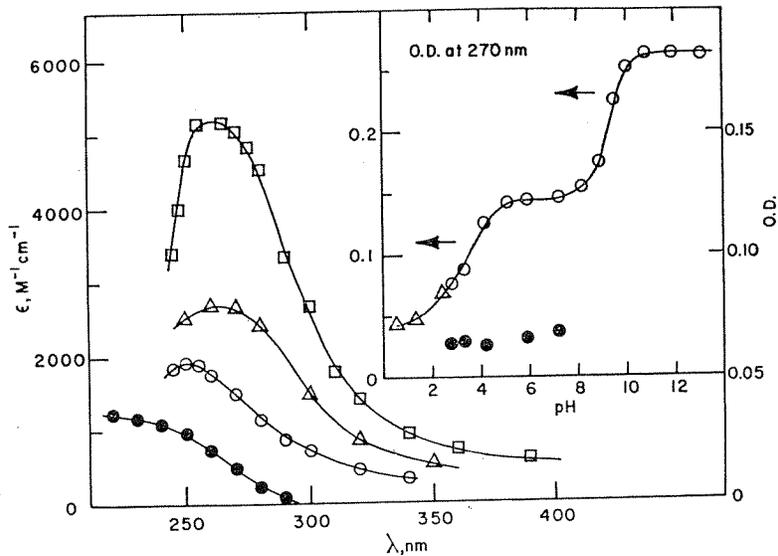


FIG. 6. Transient absorption spectra (ordinates: $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) produced from the reaction of OH radicals with 1.0 mol dm^{-3} trimethyl amine, in presence of N_2O (1 atm) at pH 3.3 (○, initial O.D. ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) measured at $\approx 0.5 \mu\text{s}$ and slow transient ●, measured at $10 \mu\text{s}$); pH 5.1, △; and pH 11.9, □. Insert: O.D. at 270 nm vs. pH.

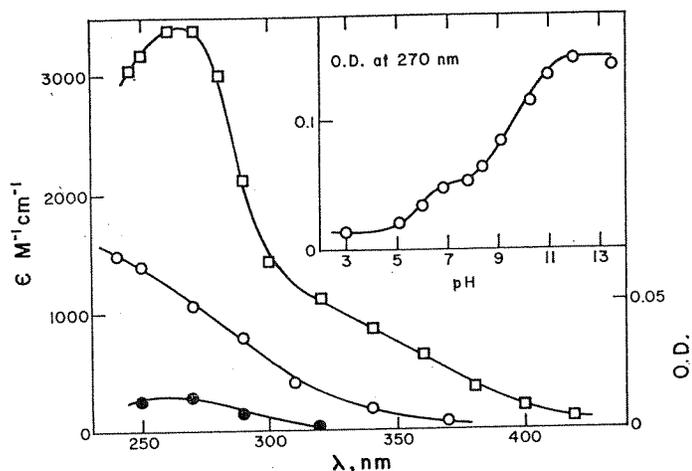


FIG. 7. Transient absorption spectra (ordinates: $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) produced from the reaction of OH radicals with 0.2 mol dm^{-3} triethyl amine, in presence of N_2O (1 atm) at pH 3.0, ●; pH 7.8, ○; pH 12, □. Dose rate 4 krads/pulse. Insert: O.D. at 270 nm vs. pH.

240–290 nm, and were found to be independent of amine concentration. In all cases the transients were found to decay by a second-order process, at doses of 2.4–19.0 krads/pulse. The presence of small amounts of oxygen was found to alter the transient spectra and the decay kinetics. The decay showed⁽⁴⁾ two components, a first-order decay followed by a slow second-order decay. This change in the decay rates was taken as an indication that our solutions were relatively free of oxygen.

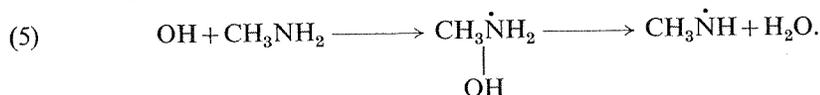
DISCUSSION

The amino group plays a determining role in the reactivity of a number of amino-substituted compounds towards attack by electrophilic or nucleophilic reagents or free radicals. The reactivity of aliphatic amines towards hydrated electrons was found⁽¹⁰⁾ to be rather low, $k(e_{\text{aq}}^- + \text{amine})$ being $\approx 10^6 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ for deprotonated amines, and two to three times faster for protonated amines. This is in marked contrast to the reactivity of the amino group in amino acids and peptides, where rates of $k(e_{\text{aq}}^- + \text{RNH}_3^+) \geq 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ and $k(e_{\text{aq}}^- + \text{RNH}_2) \geq 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ have been found⁽¹⁴⁾. Furthermore, selective reductive deamination by e_{aq}^- was also demonstrated⁽¹⁴⁾.

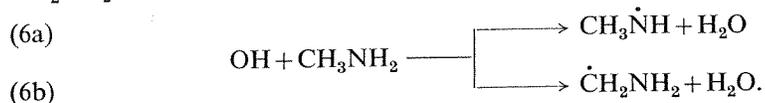
It has already been shown^(9,15) that the reactivity of OH radicals with some amino acids and peptides is strongly pH-dependent. More recently, such a behavior was also reported⁽⁷⁾ for methyl amine and aniline. In Fig. 1 and in Table 1 one can see that other primary amines, as well as tertiary amines, follow the same pattern. Certain differences appear between the values given in Table 1 and those recently reported⁽¹⁰⁾, but no obvious explanation is presently available. In alkaline solutions, at pH values where the amines are deprotonated, the reaction rate constant of OH radicals is greatly increased, and is close to being diffusion controlled,

$$k \approx 10^{10} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}.$$

The protonation of the amino group to give $-\text{NH}_3^+$ is presumably accompanied by transmission of negative charge from the hydrogen through the carbons to the $-\text{NH}_3^+$ group. Since OH radicals are electrophilic, the abstraction of H atoms in an α -position to the $-\text{NH}_3^+$ group is considerably reduced. Indeed, OH radicals preferentially abstract (see below) from β - or γ -positions, i.e. away from the $-\text{NH}_3^+$ group. In its deprotonated form, the amino group enhances radical attack by OH radicals. It was proposed⁽⁷⁾ that OH adds initially to the amino group. This mechanism was suggested on the basis of the observed⁽⁷⁾ first-order decay of the initial transient, followed by unimolecular elimination of water:



This first-order decay was not found in this work, and it is believed that the transients observed (which decay by a second-order process) are $\text{CH}_3\overset{\cdot}{\text{N}}\text{H}$ and $\overset{\cdot}{\text{C}}\text{H}_2\text{NH}_2$:



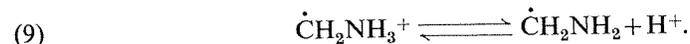
Support for reaction (6a) could be obtained from reactions (1)–(3). More recently, both $\text{CH}_3\text{NHNHCH}_3$ and $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ have been found⁽¹⁶⁾ on γ -radiolysis of air-free alkaline aqueous solution of methylamine. The yield of ethylenediamine was observed⁽¹⁶⁾ to be pH independent, while the yield of 1,2-dimethylhydrazine increased sharply in alkaline solutions. Radical-solute reactions might also occur, their relative importance are expected to be dependent on pH and the state of protonation of the amine and the radical:



In acid solutions, only abstraction of an H atom bonded to carbon takes place:



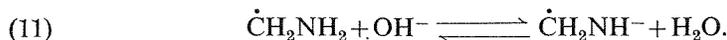
The radical produced is expected to be in equilibrium with its conjugate base:



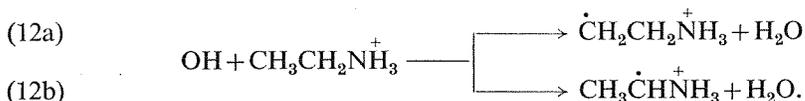
The change in absorbance with pH (insert in Fig. 2) indicates that two intermediates are produced with different acid-base properties, and with apparent $\text{pK} \approx 7.0$ and $\text{pK} \approx 11.3$. Under the experimental conditions used, at $\text{pH} \approx 9.0$ most of the OH radicals react predominantly with the deprotonated form of the parent amine. It is, therefore, suggested that the broad change in absorbance between pH 3 and 10 is associated with equilibrium (9) as well as with a change in the site of attack, reaction (6a). The changes observed at $\text{pH} > 10$ are similar to those which have been seen for amino acids⁽⁸⁾ and peptides⁽⁹⁾, and could be due to the acid-base properties of the radicals:



and possibly

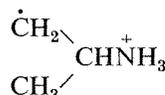


The other primary amines investigated, viz. ethyl, isopropyl and *t*-butyl amines, are considered to follow reaction paths similar to those suggested for CH_3NH_2 . With ethylamine in the protonated form, OH radicals are expected to attack predominantly the β -position reaction (12a), Fig. 3:



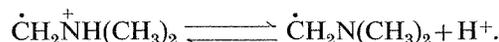
Only $\dot{\text{C}}\text{H}_2\text{CH}_2\text{NH}_3^+$ radicals have been observed by E.S.R.^(5b). At higher pH's, the radicals $\text{CH}_3\dot{\text{C}}\text{HNH}_2$ and $\text{CH}_3\text{CH}_2\dot{\text{N}}\text{H}$ are presumably formed. The O.D._{270 nm} vs. pH curve, Fig. 3, is different from that found for methyl amine. This difference probably reflects the relatively low extinction coefficient of the β -radical $\dot{\text{C}}\text{H}_2\text{CH}_2\text{NH}_3^+$.

With isopropyl amine the



radical is, Fig. 4, predominantly found in acid solutions, and the $(\text{CH}_3)_2\dot{\text{C}}\text{NH}_2$ radical in alkaline solution. The shape of the O.D._{260 nm} vs. pH curve, Fig. 4, is similar to that found for ethyl amine. Again in acidic solutions the extinction coefficient of the β -radical is low. At pH 8.0, the transient appears to decay initially by a first-order process with $k \approx 1.3 \times 10^5 \text{ s}^{-1}$, and subsequently by second order with $2k/\epsilon \approx 8.5 \times 10^4$ at 250 nm. With *t*-butyl amine, Fig. 5, only the $\text{CH}_2(\text{CH}_3)_2\dot{\text{C}}\text{NH}_3^+$ radical can initially be produced in acid solutions; if this is the radical observed, then the $\text{p}K \approx 4.6$ is due to the loss of the proton on the amino group. In alkaline solutions, $(\text{CH}_3)_3\dot{\text{C}}\text{NH}$ radicals are produced with some $\dot{\text{C}}\text{H}_2(\text{CH}_3)_2\text{CNH}_2$.

Two tertiary amines, trimethyl and triethyl amine, were investigated in the hope of eliminating the complexities which arise from the attack of OH radicals on the N—H bond. The three changes observed for trimethyl amine (see insert in Fig. 6 and Table 2) are difficult to explain on the basis of the equilibrium:



Since the decay kinetics are found to be first order at pH 3.3 and 5.1, and second order at pH 11.9, it is suggested that in alkaline solution the radical observed is $\dot{\text{C}}\text{H}_2\text{N}(\text{CH}_3)_2$, and that the radicals observed in neutral and acid solution have $\dot{\text{C}}\text{H}_2\text{N}^+(\text{CH}_3)_2$ and/or $\dot{\text{C}}\text{H}_2\text{N}(\text{CH}_3)_2$ as precursors. Recent E.S.R. results⁽⁶⁾ indicate the presence of $\dot{\text{C}}\text{H}_2\text{N}(\text{CH}_3)_2$ at pH 7–13.5 and a secondary product $\text{CH}_3\dot{\text{N}}\text{HCH}_3$ at pH 1.0.

Similar arguments could be offered for triethyl amine; however, it is likely that only the radical $\dot{\text{C}}\text{H}_2\text{CH}_2\text{NH}(\text{C}_2\text{H}_5)$ decays by a first-order process in acid solution, and that at pH 7–12 one is observing the equilibrium of the radicals $\text{CH}_3\dot{\text{C}}\text{HNH}(\text{C}_2\text{H}_5)$ and $\text{CH}_3\dot{\text{C}}\text{HN}(\text{C}_2\text{H}_5)$, see Fig. 7.

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CONCLUSIONS

The electrophilic character of the hydroxyl radical can be clearly demonstrated on the basis of the rates of reaction of OH radicals with amines, Table 1. The rate of OH with RNH_2 (or R_3N) is about 30–100 times greater than that with RNH_3^+ (or R_3NH^+). This marked difference is attributed to the unfavorable interaction of OH radicals with a positive center. Consequently, hydrogen atom abstraction from protonated amines occurs mainly at positions β - and/or γ - from the >NH^+ group, whenever possible. With unprotonated amines, H atom abstraction takes place mainly from an α -position and/or from hydrogen bonded to nitrogen.

The marked dependence upon pH of the intermediates produced from the reaction of OH radicals with the amines, the changes in the sites of attack and the acid–base equilibrium of the free radicals produced demonstrate the complex sequence of reactions occurring. The apparent similarity in the transient spectra of $\text{R}\dot{\text{C}}\text{H}\text{NH}_3^+$, $\text{R}\dot{\text{C}}\text{H}\text{NH}_2$ and $\text{RCH}_2\dot{\text{N}}\text{H}$ radicals makes categoric differentiation of these intermediates more difficult. Product analysis is required at this stage.

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Résumé—On a déterminé les vitesses de réaction des radicaux hydroxyles avec des amines aliphatiques diverses en fonction du pH. Il s'agit de méthyl-, éthyl-, isopropyl-, *t*-butyl-, triméthyl- et triéthylamines. Les constantes de vitesse trouvées sont $\approx 3 \cdot 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ pour les amines protonées et $\approx 1 \cdot 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ pour les amines non protonées. On a attribué cette différence marquée au caractère électrophile des radicaux hydroxyles et à son interaction défavorable avec le centre positif. Les spectres d'absorption transitoires des radicaux aminoalkyles et alkylamino produits par la réaction des radicaux OH avec ces amines ont été obtenus pour la gamme de pH de 3 à 13. Les espèces transitoires produites à partir des amines triméthyl- et triéthylamine ont des maximums d'absorption à $\approx 260 \text{ nm}$, toutes les autres ne présentent pas de maximum aux longueurs d'onde supérieures à 230 nm, limite imposée par les conditions expérimentales. L'absorption transitoire initiale dépend fortement du pH pour toutes les amines examinées. Ces variations sont causées par la dissociation acido-basique de ces radicaux et par les changements dans le site des attaques par le radical OH. On peut en tirer la conclusion

générale que l'arrachement des atomes d'hydrogène par les radicaux OH a lieu sur les amines non protonées principalement en position α et/ou touche l'hydrogène lié sur l'azote, alors que l'arrachement à partir des amines protonées a lieu principalement en positions β et/ou γ par rapport au groupement >NH^+ .

Резюме — В зависимости от pH среды были определены скорости реакций гидроксильных радикалов с различными алифатическими аминами, такими как: метиламин, этиламин, изо-пропиламин, трет-бутиламин, триметиламин и триэтиламин. Для протонированных аминов скорости реакций равны $3 \cdot 10^{18} \text{ дм}^3 \text{ мол}^{-1} \text{ сек}^{-1}$ и для непротонированных $1 \cdot 10^{10} \text{ дм}^3 \text{ мол}^{-1} \text{ сек}^{-1}$. Эта разница была объяснена электрофильным характером гидроксильного радикала и его неблагоприятной реакцией с положительным центром. Наблюдали неустойчивые спектры поглощения различных аминалькильных и алкиламинных радикалов, полученных при реакции OH-радикалов с этими аминами в области pH от 3 до 13. Неустойчивые продукты, полученные из триметильных и триэтильных аминов, имеют абсорбционный максимум при 260 нм. В случае других аминов максимума абсорбции не наблюдается до 230 нм, — предела, обусловленного условиями эксперимента. Значительная зависимость начальной неустойчивой абсорбции от pH среды наблюдалась для всех исследованных аминов. Эти изменения объясняются кислотно-основной диссоциацией радикалов и изменением места атаки OH-радикалов. В общем, можно с уверенностью заключить, что отщепление атома водорода радикалами OH от непротонированных аминов происходит, главным образом, из α — положения или же отщепляется атом водорода, связанный с азотом, в то время, как от протонированных аминов отщепляется водород, находящийся в положении β и/или γ по отношению к >NH^+ группе.

Zusammenfassung — Reaktionsgeschwindigkeiten von Hydroxyl-Radikalen mit verschiedenen aliphatischen Aminen wurden als Funktion vom pH bestimmt. Dabei wurden Methyl-, Äthyl-, Isopropyl-, *t*-Butyl-, Trimethyl- und Triäthylamin studiert. Es wurden Geschwindigkeitskonstanten von $\approx 3 \cdot 10^{18} \text{ дм}^3 \text{ мол}^{-1} \text{ s}^{-1}$ für protonisierte Amine, und $\approx 1 \cdot 10^{10} \text{ дм}^3 \text{ мол}^{-1} \text{ s}^{-1}$ für nicht protonisierte Amine erhalten. Dieser bedeutende Unterschied wird dem elektrophilen Charakter des Hydroxylradikals zugeschrieben und seiner ungünstigen Wechselwirkung mit dem positiven Zentrum. Die transienten Absorptionsspektren der verschiedenen Aminoalkyl- und Alkylaminoradikale, die durch die Reaktion der OH-Radikale mit diesen Aminen entstehen, wurden für den pH-Bereich 3 bis 13 angegeben. Die transienten Spezies, welche aus Trimethyl- und Triethylamin entstehen, haben Absorptionsmaximen bei $\approx 260 \text{ nm}$, alle übrigen Amine weisen bis hinab zu $\approx 230 \text{ nm}$ (die durch experimentelle Bedingungen gegebene Grenze) keine Maxima auf. Bei allen untersuchten Aminen wird eine starke Abhängigkeit der anfänglichen transienten Absorption vom pH beobachtet. Diese Änderungen werden von der acido-basischen Dissoziation der Radikale und durch Änderungen in der Lage des Angriffes der OH-Radikale verursacht. Im allgemeinen kann man sagen, dass die Abspaltung des Wasserstoffatoms durch OH-Radikale aus nicht protonierten Aminen hauptsächlich aus einer α -Lage und/oder am Stickstoff erfolgt, während die Abspaltung von protonierten Aminen hauptsächlich in den Lagen β und/oder γ zur >NH^+ Gruppe erfolgt.