The Oxidation of Trimethylamine by OH Radicals in Aqueous Solution, as Studied by Pulse Radiolysis, ESR, and Product Analysis. The Reactions of the Alkylamine Radical Cation, the Aminoalkyl Radical, and the Protonated Aminoalkyl Radical

Suresh Das and Clemens von Sonntag*

Max-Planck-Institut für Strahlenchemie, Stiftstraße 34—36, D-4330 Mülheim a.d. Ruhr, West Germany

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Introduction

The free radical chemistry of trialkylamines has received considerable attention [1—3]. Owing to their low ionization potentials which centre near 7.5 eV [4] they can serve as electron donors in a number of photo- and thermochemical reactions. In such reactions the formation of nitrogen radical cations (amminium radicals) is often proposed (for a review see ref. [1]). On the other hand, the hydrogen atoms at the α-carbon are only loosely bound and may be readily abstracted by reactive radicals, i.e. trialkylamines are also good hydrogen donors [4—6]. Protonated amines are considerably less reactive. The lone pair at nitrogen is occupied by the proton and electron transfer is no longer feasible. In competition with the abstraction of a carbon-bound hydrogen atom, abstraction of the nitrogen-bound hydrogen atom may also occur which again leads to the radical cation. With trimethylamine one has to consider the possible formation of three radicals, the N-centred radical cation (N\(^+\)), the C-centred radical (A\(^+\)) and the protonated C-centred radical (A\(^{+}\)).

\[
\begin{align*}
(\text{CH}_3)_3\text{N}^+; & \quad (\text{CH}_3)_2\text{NCH}_2^+; \quad (\text{CH}_3)_2\text{HNCH}_2^+ \\
& \quad (\text{N}^+); \quad (\text{A}^+); \quad (\text{A}^{+})
\end{align*}
\]

The reaction of OH radicals with trimethylamine and related compounds have previously been studied using pulse radiolysis [7] and ESR techniques [8, 9]. The pulse radiolysis data cannot be interpreted on the basis of only two intermediates A\(^+\) and A\(^{+}\) as has been suggested [7], since the formation of the third species, the radical cation N\(^+\), has been observed by ESR spectroscopy, at least in acidic solutions (pH 1—3) [9]. ESR evidence for the formation of N\(^+\) in irradiated solid trimethylammonium perchlorate is also well documented [10]. It is worth noting that recently amine radical cations have been postulated as intermediates in the flavin-sensitized [11—13] and in the OH radical-induced [14] decarboxylation of amino acids.

* Reprint requests to Prof. Dr. C. v. Sonntag.
In the present study we look at the reactions of OH radicals with trimethylamine in aqueous solutions, combining pulse radiolysis, ESR and product studies to gain a better understanding of this complex system. For the purpose of getting a better fix on the spectral and redox properties of $\text{AH}^+$, the radical $\text{ACH}_3^+$ ($= [(\text{CH}_3)_3\text{NCH}_2]^+$) was also generated, using tetramethylammonium perchlorate. Hydroxyl radicals have been generated by the radiolysis of $\text{N}_2\text{O}$-saturated aqueous solutions (reactions (i) and (ii)).

\[
\text{H}_2\text{O} \xrightarrow{\text{ionizing radiation}} \text{OH}^- + \text{e}^-_\text{aq}, \text{H}^+, \text{H}_2\text{O}_2 (i)
\]

\[
\text{e}^-_\text{aq} + \text{N}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{OH}^- + \text{OH}^- + \text{N}_2\text{O} (ii)
\]

The primary radicals then are 90% OH and about 10% H atoms. The latter may also undergo H-abstraction reactions, albeit with slower rates. Thus in most of the experiments, i.e. in cases where H atoms are not scavenged by additives, one can reasonably assume that $G(\text{N}^+ + \text{A}^- + \text{AH}^+)$ equals about 6. (The G value is defined as the number of molecules formed per 100 eV of absorbed radiation energy.)

**Experimental**

Trimethyl- and tetramethylammonium perchlorate (Alfa) were used without further purification. The other chemicals were obtained either from Merck or Sigma. All solutions were prepared with triply distilled water which was saturated with $\text{N}_2\text{O}$. After adding the amine, the $\text{N}_2\text{O}$ stream was continued more slowly but sufficiently strongly to prevent both the excessive loss of amine and the access of air. The pH was adjusted by KOH or HClO$_4$. The pulse radiolysis setup has been described before [15]. Dosimetry was performed with $\text{N}_2\text{O}$-saturated 10 mmol dm$^{-3}$ KSCN solutions taking $G(\text{OH}) = 6.0$, and $\varepsilon(\text{SCN})_2^- = 7600$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at 480 nm. In-situ radiolysis ESR measurements were carried out using the method described by Eiben and Fessenden [16]. $^{60}\text{Co-}\gamma$-rays were used for steady-state irradiations. Formaldehyde was measured by the acetylacetone method [17]. H$_2$O$_2$ was determined iodometrically [18].

**Results**

a) Pulse radiolysis

*Transient spectra:* Pulse radiolysis of $\text{N}_2\text{O}$-saturated aqueous solutions of trimethylamine gives rise to a transient absorption with maxima at about 255 nm and 370 nm (Fig. 1). Although the absorbance 2 $\mu$s after the pulse strongly varies with pH (Fig. 2), in good agreement with earlier observations [7], the shape of the spectrum appears to be independent of pH over the range 5.7–11.4 (Fig. 1). As will be discussed below, this is because the spectrum is dominated by the absorbance of A$^+$ even though...
N\(^+\) is present in comparable amounts at pH < 8. The radical cation N\(^+\) has considerably lower extinction coefficients (see inset Fig. 1). The transient absorption above pH 8 disappears in a bimolecular process with a rate constant of \(3.6 \times 10^9\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). Below pH 6 the absorbance disappears by a first-order process with rates dependent upon proton concentration (Fig. 3). The intercept in the \(k_{\text{obs}}\) vs. proton concentration plot reflects the fact that in this case amine concentration was 0.1 mol dm\(^{-3}\). Extrapolation to zero amine concentration would lead to a zero intercept in the \(k_{\text{obs}}\) vs. proton concentration diagram (cf. inset). Absorbances measured for solutions containing 0.5 mol dm\(^{-3}\) phosphate buffer are included in Fig. 2. At such high buffer concentrations, the acid/base equilibria of the short-lived intermediates are practically completely established. At pH 3 there remains a long-lived species (\(t_{1/2} > 20\) ms; this time limit derives from the stability characteristics of the lamp) whose spectrum is shown in the inset of Fig. 1.

**Detection of the reducing radical:** Pulse radiolysis studies of \(N_2O\)-saturated 40 mmol dm\(^{-3}\) trimethylamine solutions containing \(5 \times 10^{-5}\) mol dm\(^{-3}\) p-nitroacetophenone (PNAP) show a buildup at 365 nm (\(k = 4 \times 10^9\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\)) where PNAP\(^+\) has an absorption maximum. The spectrum measured after the completion of the buildup corresponds to the published spectrum of PNAP\(^+\) [19]. The rate of PNAP\(^+\) buildup is of first-order in PNAP concentration and its rate constant is independent of pH in the range of pH 4 – 11. The final yield of PNAP\(^+\), however, increases with increasing pH (Fig. 4).

In the presence of phosphate buffer at pH 7, two time-resolved processes leading to PNAP\(^+\) take place. The PNAP\(^+\) yield due to the fast process which has the same rate constant (\(k = 4 \times 10^9\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\)) as that observed in the absence of buffer decreases with increasing buffer concentration, and a slow PNAP\(^+\) buildup sets in which then dominates in solutions containing 50 mmol dm\(^{-3}\) or more phosphate buffer (Fig. 5). The PNAP\(^+\) yield formed during the slow buildup is quite sensitive to the dose rate; in \(N_2O\)-saturated solutions containing 50 mmol dm\(^{-3}\) trimethylamine, \(2 \times 10^{-4}\) mol dm\(^{-3}\) PNAP and 0.1 mol dm\(^{-3}\) phosphate at pH 7.1, \(G(\text{PNAP}^+)\) increases from 2.7 at 8 Gy per pulse to 5.5 at 0.5 Gy per pulse.

Fig. 6 shows the dependence of the observed rate constant for the slow PNAP\(^+\) buildup on PNAP concentration for solutions containing 50 mmol dm\(^{-3}\) trimethylamine and 0.1 mol dm\(^{-3}\) phosphate buffer at pH 7.13.

**Detection of oxidising radicals:** Using \(\text{Fe(CN)}_6^{4-}\) (\(5 \times 10^{-5} - 4 \times 10^{-4}\) mol dm\(^{-3}\)) as a reducing agent,
Fig. 5. Rate curves of the formation of the P N A P T absorption at 360 nm. 50 mmol dm$^{-3}$ trimethylamine, 0.02 mM PNAP, pH = 7.0; (a) no phosphate buffer 0.13 Gy/pulse; (b) 50 mmol dm$^{-3}$ phosphate buffer 0.2 Gy/pulse. Curves normalized to 1.5 Gy/pulse.

Fe(CN)$_6^{3-}$ formed upon oxidation of the Fe(CN)$_6^{4-}$ is again reduced by radicals A$^\cdot$.

2,2’-Azinobis-(3-ethyl-benzthiazoline-6-sulphonate) (ABTS) was also used to detect the oxidising radical species, as the ABTS$^+$ formed in the oxidation reaction has a strong absorption at 525 nm ($\varepsilon = 3.6 \times 10^6$ dm$^3$ mol$^{-1}$ cm$^{-1}$) [20], far apart from the amine radical absorption. The kinetic behaviour of ABTS$^+$ buildup is very similar to that of Fe(CN)$_6^{3-}$ in the Fe(CN)$_6^{4-}$ system. At pH < 5 the absorption of ABTS$^+$ remains stable over 20 ms. At pH > 5 the buildup of ABTS$^+$ absorption is followed by a fast decay to a lower absorption stable over 20 ms. On including 0.2 mol dm$^{-3}$ phosphate at pH 7.1 in these solutions the fast decay is practically eliminated, ensuring G(ABTS$^+$) = 5.

At pH > 7, N,N,N’,N’-tetramethylphenylenediamine (TMPD) can also be used to monitor the oxidising radical [22]. Pulse radiolysis of N$_2$O-saturated solutions containing 40 mmol dm$^{-3}$ trimethylamine and 0.05 mmol dm$^{-3}$ TMPD at pH 7.2 leads to a fast buildup at 565 nm ($t_{1/2} = 2.9 \mu$s), followed by a slower buildup ($t_{1/2} = 32 \mu$s). The absorption spectrum is identical with that of TMPD$^+$ at all times. It is not yet clear why there are two contributions to TMPD$^+$ formation but it is noted that in the OH/TMPD system a similar phenomenon is observed [21]. Fig. 4 shows the dependence of the TMPD$^+$ yields on pH in pulse radiolysed solutions containing (i) 50 mmol dm$^{-3}$ trimethylamine and 0.05 mM TMPD and (ii) 0.1 mol dm$^{-3}$ trimethylamine and 0.14 mmol dm$^{-3}$ TMPD. The TMPD yields are dose-dependent, and the yields shown in Fig. 4 have been obtained by extrapolation to zero dose.

When 0.25 mol dm$^{-3}$ phosphate buffer at pH 7.3 is included, total G(TMPD$^+$) increases to 5.6. There appear to be two processes, a fast one and a slow one, but they are not as clearly distinguishable as in the absence of phosphate buffer.

Tetramethylammonium perchlorate: Pulse radiolysis of N$_2$O-saturated aqueous solutions yields very weak transient absorptions. Competition kinetics with SCN$^-$ yields $k_{13}(\text{OH}+(\text{CH}_3)_4\text{N}^+)/k(\text{OH}+\text{SCN}^-) = 6.75 \times 10^{-4}$. Using $1.1 \times 10^{10}$ dm$^3$ mol$^{-1}$s$^{-1}$ as the rate constant for OH reaction with SCN$^-$ [23] yields $k_{13} = 7.4 \times 10^6$ dm$^3$ mol$^{-1}$s$^{-1}$. Pulse radiolysis of N$_2$O-saturated solutions containing tetramethylammonium perchlorate and tetranitromethane gives G(nitroform anion) = 0.6. Pulse radiolysis of N$_2$O-saturated

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solutions of tetramethylammonium perchlorate ($5 \times 10^{-2}$ mol dm$^{-3}$) and ABTS ($5 \times 10^{-6}$ mol dm$^{-3}$) leads to the formation of ABTS$^\cdot$. The rate constant of the reaction of ABTS with the ammonium radical is $4 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$. The ABTS$^\cdot$ yield is strongly dose dependent. $G$(ABTS$^\cdot$) increasing from 1.6 at 12.2 Gy per pulse to 4.0 at 3.2 Gy per pulse.

b) ESR studies

In-situ ESR studies on irradiated N$_2$O-saturated solutions of trimethylamine indicates the presence of two radicals. At low pH the ESR spectrum of N$^\cdot$, already well characterised earlier [9], is observed. The signal is most intense at pH 3, decreasing gradually with increasing pH. The ESR spectrum of N$^\cdot$ could be observed, even though very weakly, at a pH as high as 7. Below pH 3 the signal intensity also decreases. At any pH the signal intensity increases with increasing amine concentration.

At pH values $\geq$ 7.8 the ESR spectrum of the unprotonated amine radical A$^\cdot$, also characterized earlier [24], is observed. The signal intensity increases with increasing pH, reaching its maximum value at pH $\geq$ 9.0.

c) Product analysis

A significant product of the radiolysis in N$_2$O-saturated solutions of trimethylamine is formaldehyde. $G$(formaldehyde) increases from 2.6 at pH 10 to 6 when PNAP is included as oxidant. $G$(CH$_2$O) = 2.6 is also found at pH 5, but its yield is not altered in the presence of PNAP. $G$(H$_2$O$_2$) = 0.8 has been found at pH 5 as well as at 10.

Discussion

The following discussion is based on the main reactions (1)–(12)
The OH radicals react with trimethylamine with a rate constant of $k_3 + k_4 = 1.2 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ whereas with the protonated form it reacts 30 times slower with a rate constant of $k_5 + k_6 = 4 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ [7]. With the pK of trimethylamine of 9.76 (reactions (1) and (2)) a "reactivity pK" of 8.3 ensues. At a pH above this value reactions (3) and (4) will predominate, but at pH < 8.3, reactions (5) and (6).

Formation and reactions of the reducing radical:
Above pH 9, OH radicals react mainly with the free amine. The yield of PNAP$^-$ indicates that nearly all the species formed under those conditions are either the reducing radical, or are converted into the latter. The absorption spectrum obtained under these conditions is attributed to that of $A'$ which is known to be strongly reducing [25]. In the absence of any additive the shape of the transient spectrum is independent of pH for pH > 5.7 (Fig. 1). The resemblance of the dependence of both the PNAP$^-$ yield and the transient absorption on pH (Fig. 2 and 4) suggests that $A'$ is the main absorbing species in this system. The absence of a strongly absorbing intermediate in the tetramethylammonium perchlorate solutions is further evidence that the protonated C-centred radical $AH^+$ is weakly absorbing since upon OH radical attack tetramethylammonium can form only the alkyl radical (reaction (13)).

$$\text{OH} + (\text{CH}_3)_3\text{N} \rightarrow (\text{CH}_3)_3\text{NCH}_2^+ + \text{H}_2\text{O} \quad (13)$$

whose spectral to properties would be expected to resemble those of $AH^+$. The reaction of OH radicals with trimethylamine below pH 6 takes place exclusively with the protonated amine. However, a considerable yield of the reducing radical is formed shortly after the pulse as indicated by the transient absorption and PNAP$^-$ yield. As discussed below, the reducing radical $A'$ would be formed by the fast deprotonation of the oxidizing radical $AH^+$ (reaction (7)) which is initially formed (reaction (5)). The first-order disappearance of the thus-formed $A'$ that is observed under these conditions is attributed to its reprotonation at carbon (reaction (10)) which proceeds more slowly, to yield $N^+$. With protons the rate of this process is slightly less than diffusion-controlled ($k_{10} = 2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$) and quite slow with protonated amine ($k_{12} = 2.7 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$). As the above protonation reaction is observed only below pH 7 one would infer that $N^+$ must have a pK$_s > 7$. The change of the transient absorption with pH in solutions containing 0.5 mol dm$^{-3}$ phosphate buffer which increases the rate of reprotonation (Fig. 2) indicates that the radical cation $N^+$ has a pK$_s$ of 8.0.

In solutions containing PNAP, the presence of the oxidant which probes only $A'$ leads, one would expect, to reactions (14)–(16)

$$\begin{align*}
(\text{CH}_3)_2\text{NCH}_2 + \text{PNAP} & \rightarrow \quad \text{AH} + \text{PNAP}^+ \quad (14) \\
(\text{CH}_3)_2\text{N}=\text{CH}_2 + \text{H}_2\text{O} & \rightarrow \quad \text{CH}_3\text{N}=\text{CH}_2 + \text{H}^+ \quad (15) \\
(\text{CH}_3)_2\text{N}^- + \text{CH}_2\text{OH} & \rightarrow \quad \text{CH}_3\text{N}^- + \text{H}_2\text{O} \quad (16)
\end{align*}$$

Bearing in mind that at high pH the radical cation $N^+$ is rapidly converted into the C-centred radical $A'$, this sequence implies that at pH 10 in the presence of PNAP all the radicals are converted into dimethylamine and formaldehyde. $\text{Gr(CH}_3\text{O}) = 6$, as found under such conditions, is in good agreement with this hypothesis.

In neutral solutions in the absence of buffer, the equilibrium (9)/(10) cannot be established, hence PNAP$^-$ yields indicate the yield of $A'$ as formed by reaction (3) and the fast deprotonation reaction (7). In the presence of phosphate buffers, however, equilibrium (9)/(10) is well established. The rate of PNAP$^-$ buildup is then $k_{14} \times k_9[\text{PNAP}] [N^+] / k_{10} [H^+]$, i.e.

$$k(\text{PNAP}^-)_{\text{obs}} = \frac{k_{14} [\text{PNAP}]}{k_{10} [H^+]}$$

$k_9/k_{10} = K_{9/10}$ is the equilibrium constant. From the dependence of $k_{\text{obs}}$ on PNAP concentration (Fig. 6) a value for pK$_{9/10} = 8$ is obtained which is in good agreement with the pK$_s$ value obtained from transient absorption measurements in the presence of 0.5 mol dm$^{-3}$ phosphate buffer. At high PNAP concentration, the rate-limiting step is the buffer-catalysed reaction (9). This causes the curvature (dotted line) in Fig. 6.

In the presence of buffer, equilibrium (9)/(10) is well established and full yields of PNAP$^-$ would be expected. This is indeed the case. The buildup of PNAP$^-$ is much slower at pH 7 (Fig. 5) than at pH 10. The reason for this is that at pH 7 only a fraction of the radical concentration is available as $A'$ because of the buffer-mediated near-equilibrium (9)/(10).
Formation and reactions of oxidising radicals: The formation of the oxidising radicals was followed by means of their reactions with the reductants Fe(CN)$_6^{3-}$ and ABTS at pH $< 7$ and TMPD at pH $> 7$. Below pH 4, oxidising radicals, *i.e.* N$_t^+$ and AH$_t^+$, are primarily formed, their yield decreasing with increasing pH. (The latter radical may fairly be expected to oxidise since the alkyl radical derived from tetramethylammonium, possessing a similar electronic structure, demonstrates oxidising properties.) The reactions of these radicals with reductant lead to the parent amine (reactions (17) and (18)).

With ABTS and TMPD the corresponding reactions yield ABTS$^+$ and TMPD$^+$.

\[
\begin{align*}
(\text{CH}_3)_3\text{N}^+ + \text{Fe(CN)}_6^{4-} & \rightarrow (\text{CH}_3)_3\text{N} + \text{Fe(CN)}_6^{3-} \\
(\text{CH}_3)_3\text{HNCH}_3^+ + \text{Fe(CN)}_6^{4-} & \rightarrow (\text{CH}_3)_3\text{N} + \text{Fe(CN)}_6^{3-}
\end{align*}
\]

(17)

(18)

Above pH 5, some of the Fe(CN)$_6^{3-}$ or ABTS$^+$ so formed is changed back to Fe(CN)$_6^{4-}$ or ABTS by the reducing radical A', before the latter is converted into the oxidising radical N$_t^+$ by the protonation reaction (10). The fact that the reduction reaction occurs between pH 5 and 7 constitutes further evidence for the formation of A' at these pH values.

Unlike ABTS$^+$ and Fe(CN)$_6^{3-}$, the TMPD$^+$ formed is not readily reduced by the radicals A', hence TMPD$^+$ was used to monitor the oxidising species above pH 7. As A' does not react with TMPD$^+$ it will be protonated by the trimethylammonium (reaction (12)) to give the oxidising radical cation. This reaction could account for the slow TMPD$^+$ buildup. The dependence of the yield of TMPD$^+$ on dose is due to the competing bimolecular disproportionation of A' (reaction (19)).

\[
2(\text{CH}_3)_2\text{NCH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{N} + (\text{CH}_3)_2\text{N} = \text{CH}_2 + \text{OH}^-
\]

(19)

Phosphate buffer increases the TMPD$^+$ yield, as the protonation of A' (reaction (10)) becomes more efficient than its disproportionation (19).

**Rate constant of OH + amine:** The rate constant for hydrogen abstraction from (CH$_3$)$_3$N$^+$ by OH is rather low ($k_{13} = 7.4 \times 10^6$ dm$^3$mol$^{-1}$s$^{-1}$). The corresponding reaction for the protonated amine is much higher ($k_1 + k_4 = 4 \times 10^8$ dm$^3$mol$^{-1}$s$^{-1}$), although fewer methyl protons (9 instead of 12) are available. This strongly indicates that in the case of the trimethylammonium ion H abstraction from nitrogen (reaction 6) as well as from carbon (reaction 5) must occur. The rate constant of OH with the neutral amine is very high ($k_3 + k_4 = 1.2 \times 10^{10}$ dm$^3$mol$^{-1}$s$^{-1}$), exceeding the rate constant normally observed for hydrogen abstraction reactions by OH (e.g. formate, $k = 3 \times 10^9$ dm$^3$mol$^{-1}$s$^{-1}$; isopropanol, $k = 3 \times 10^9$ dm$^3$mol$^{-1}$s$^{-1}$; cf. ref. [23]). Hence it is not unlikely that the electron transfer reaction (4) or its equivalent, *i.e.* OH addition at nitrogen and subsequent OH$^-$ loss, may play a role. In basic solutions where this reaction is expected to contribute heavily because of the prevalence of the unprotonated amine, the radical cation would be deprotonated efficiently by both hydroxyl ions and free amine to give A'. Around pH 8—9 there is indeed some buildup of absorption after the pulse. The fact that at pH 10 TMPD$^+$ formation is observed (Fig. 4) is a good indication that reaction (4) takes place. The TMPD$^+$ yield increases with increasing TMPD concentration, as indeed it should considering the competing deprotonation by OH$^-$ and amine. But quantitative data cannot be obtained in more detail under these pH conditions. It is not feasible to increase the TMPD concentrations beyond the concentrations used because its direct oxidation by OH radicals would set in. Nevertheless, the present data allow to conclude that production of N$_t^+$ and A' probably occurs in about equal proportions.

**ESR studies and pK$_a$ value of the AH$_t^+$ species:** ESR studies indicate the presence of radical A' above pH 7, and of N$_t^+$ below pH 7, in support of a pK$_a$ (9/10) not far different from 7. As mentioned above, pulse radiolysis studies in the presence of phosphate buffer (Fig. 2) yield a pK$_a$ of 8.0 for the radical cation N$_t^+$. The dependence of the N$_t^+$ signal intensity on amine concentration between pH 4 and 7 can be explained on the basis of reaction (12). The radical A' formed under these conditions protonates faster with increasing ammonium ion concentration, thus preventing the loss of N$_t^+$ by the disproportionation reaction (20).

\[
(\text{CH}_3)_3\text{N}^+ + (\text{CH}_3)_2\text{NCH}_2 \rightarrow (\text{CH}_3)_3\text{N} + (\text{CH}_3)_2\text{N} = \text{CH}_2
\]

(20)

The corresponding bimolecular reactions between two N$_t^+$ radicals is expected to be much slower. The long-lived absorption observed in pulse radiolysis of solutions of trimethylamine at pH 3 is attributed to the N$_t^+$ radical (Fig. 1, inset). The dependence of the
N\textsuperscript{+} signal on amine concentration below pH 3 can be explained on the basis of increased scavenging, by the ammonium ions, of H atoms which otherwise react with N\textsuperscript{+}. Below pH 3 the H atom contribution becomes relatively more important as protons compete with N\textsubscript{2}O for electrons. The H atom reaction with protonated amines is known to be slow.

In a detailed ESR study on aqueous solutions of trimethylamine, Neta and Fessenden observed only the N\textsuperscript{2} and A\textsuperscript{'} radicals. They attributed the lack of AH\textsuperscript{+} radical signal to a rapid proton exchange at nitrogen, leading to line broadening. However, the present work suggests that this is not the explanation; rather, one expects that AH\textsuperscript{+} is too short-lived to be observed by in situ radiolysis ESR studies. It rapidly deprotonates at nitrogen, and reprotonation at carbon gives the more stable N\textsuperscript{2} radical cation. The pK\textsubscript{a} value of AH\textsuperscript{+} (cf. reactions (7) and (8)) must be around 3.6, roughly indicated by the first hump in the absorbance vs. pH curve in the absence of buffer (Fig. 2). Also, a value of 3.6 is required to obtain a computer fit (see below) for the experimental points in Fig. 2. The pK\textsubscript{a} value of the parent compound is 9.76 whereas that of the corresponding radical, AH\textsuperscript{+} is 3.6. This represents a shift of 6.2 units.

Such a shift is expected considering a similar drop by 4–7 units on going from the alcohol to the α-hydroxyalkyl radical [26, 27]. This value of pK\textsubscript{a}≈3.6 is also very close to that determined for the CH\textsubscript{3}SCH\textsubscript{2}CH\textsubscript{2}CHNH\textsubscript{3} radical (pK\textsubscript{a}=3.85) [28].

Product analysis: The main bimolecular reactions expected of the radicals A\textsuperscript{'} are disproportionation (19) and dimerisation. Disproportionation (an electron transfer reaction) is favoured. Since G(H\textsubscript{2}O\textsubscript{2}) = 0.8 has been found under such conditions, i.e. the full molecular yield (cf. reaction (i)), formaldehyde is not formed by an oxidation of the radicals A\textsuperscript{'} by H\textsubscript{2}O\textsubscript{2}. With G(CH\textsubscript{3}O\textsubscript{2}) = 2.7 it follows that the dimerisation reaction must be negligible (<15\% of reaction (18)). At pH 9.7 in the presence of PNAP electron transfer occurs efficiently leading to an increased formaldehyde yield (reactions (14)–(16)). No such increase has been observed at pH 5. Considerable depletion of PNAP\textsuperscript{−} by N\textsuperscript{2} reforming the amine and PNAP might account for this observation.

Curve fitting: The mechanism suggested in the above discussion was tested using the programme “WR 20” by K. Schmidt [29] which had been modified by F. Schwörer, and in its last version was run on a VAX-11/780 computer.

Table I. Rate constants and extinction coefficients which gave the best fit in the kinetic analysis of the reactions occurring in the radiolysis of N\textsubscript{2}O-saturated aqueous solutions of trimethylamine. For abbreviations see text.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>k(Dimension dm\textsuperscript{3}mol\textsuperscript{−1}s\textsuperscript{−1}) unless shown otherwise</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{OH} + \text{AH}^+ \rightarrow \text{AH}^+ + \text{H}_2 \text{O} )</td>
<td>( 1.1 \times 10^8 ) ( \text{OH} + \text{AH}^+ \rightarrow \text{AH}^+ + \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{OH} + \text{A} \rightarrow \text{N}^+ + \text{H}_2 \text{O} )</td>
<td>( 2.9 \times 10^8 ) ( \text{OH} + \text{A} \rightarrow \text{A}^+ + \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{AH}^+ \rightarrow \text{AH}^+ + \text{H}_2 \text{O} )</td>
<td>( 2.0 \times 10^6 ) ( \text{H}^+ + \text{A} \rightarrow \text{A}^+ + \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{A}^+ + \text{AH}^+ \rightarrow \text{N}^+ + \text{A} )</td>
<td>( 2.7 \times 10^3 ) ( \text{A}^+ + \text{H}^+ \rightarrow \text{AH}^+ )</td>
</tr>
<tr>
<td>( \text{A}^+ + \text{H}^+ \rightarrow \text{N}^+ )</td>
<td>( 2.0 \times 10^3 ) ( \text{A}^+ + \text{AH}^+ \rightarrow \text{N}^+ + \text{A} )</td>
</tr>
<tr>
<td>( \text{A}^+ + \text{AH}^+ \rightarrow \text{AH}^+ + \text{A} )</td>
<td>( 1.0 \times 10^{10} ) ( \text{AH}^+ + \text{OH} \rightarrow \text{A}^+ + \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{A}^+ + \text{A} \rightarrow \text{A}^+ + \text{H}^+ )</td>
<td>( 3.0 \times 10^6 \text{s}^{-1} ) ( \text{N}^+ + \text{OH} \rightarrow \text{A}^+ + \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{N}^+ + \text{A} \rightarrow \text{A}^+ + \text{AH}^+ )</td>
<td>( 1.0 \times 10^{10} ) ( \text{N}^+ + \text{A} \rightarrow \text{A}^+ + \text{AH}^+ )</td>
</tr>
<tr>
<td>( \text{N}^+ \rightarrow \text{A}^+ + \text{H}^+ )</td>
<td>( 35 \text{s}^{-1} ) ( \text{A}^+ + \text{A} \rightarrow \text{Products} )</td>
</tr>
<tr>
<td>( \text{A}^+ + \text{N}^+ \rightarrow \text{Products} )</td>
<td>( 2.0 \times 10^9 ) ( \text{H}^+ + \text{AH}^+ \rightarrow \text{AH}^+ )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{N}^+ \rightarrow \text{AH}^+ )</td>
<td>( 5 \times 10^9 ) ( \text{H}^+ + \text{OH} \rightarrow \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{H}^+ \rightarrow \text{H}_2 \text{O} )</td>
<td>( 6 \times 10^9 ) ( \text{H}^+ + \text{OH} \rightarrow \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{AH}^+ + \text{OH} \rightarrow \text{H}_2 \text{O} )</td>
<td>( 1 \times 10^{11} ) ( \text{AH}^+ + \text{OH} \rightarrow \text{H}_2 \text{O} )</td>
</tr>
<tr>
<td>( \text{A}^+ + \text{H}^+ \rightarrow \text{AH}^+ )</td>
<td>( 2 \times 10^{10} ) ( \text{A}^+ + \text{H}^+ \rightarrow \text{AH}^+ )</td>
</tr>
<tr>
<td>( \text{A}^+ + \text{H}^+ \rightarrow \text{AH}^+ + \text{OH}^- )</td>
<td>( 2.1 \times 10^4 ) ( \text{AH}^+ + \text{AH}^+ \rightarrow \text{H}^+ )</td>
</tr>
<tr>
<td>( \text{AH}^+ + \text{AH}^+ \rightarrow \text{H}^+ )</td>
<td>( 3.5 \text{s}^{-1} ) ( \text{AH}^+ + \text{AH}^+ \rightarrow \text{H}^+ )</td>
</tr>
</tbody>
</table>

Table I shows the rate constants which fitted the data in Fig. 2. Although the fit appears to be acceptable it does not necessarily follow that the pK\textsubscript{a} value of AH\textsuperscript{+} is exactly 3.6, nor that N\textsuperscript{2} and AH\textsuperscript{+} are formed exactly in a 7:3 ratio by OH attack on the trimethylammonium ion. Nevertheless, it is felt that this approach allows to grasp the features of this complicated system whose complexity would make it very difficult to relate the data in any other way.

Conclusion: It has been shown that the main radicals present in steady-state radiolysed solutions are N\textsuperscript{2} and A\textsuperscript{'}

This is due to N\textsuperscript{2} having a higher pK\textsubscript{a} than AH\textsuperscript{+}. Using the equation derived by Eigen et al. [30] for a similar system, the keto-enol tautom-
erism of barbituric acid, the ratio of $N^+$ to $AH^+$ is given by

$$\frac{[N^+]}{[AH^+]} = \frac{10^{-3.6}}{10^{-8}} = 10^{4.4}$$

i.e. the protonated radical will always be more stable in the $N^+$ form. This accounts for the fact that the $AH^+$ radical signal has never been identified in ESR studies.

We would like to thank Drs. G. Koltzenburg and H.-P. Schuchmann for valuable discussions.