

The Production of the Superoxide Radical Anion by the OH Radical-induced Oxidation of Trimethylamine in Oxygenated Aqueous Solution. The Kinetics of the Hydrolysis of (Hydroxymethyl)dimethylamine

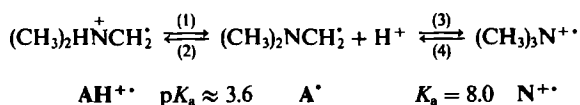
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Received September 22, 1986

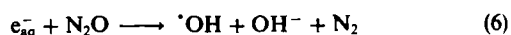
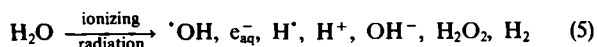
The radiolysis of trimethylamine in N_2O/O_2 (4:1 v/v) saturated basic solutions eventually gives rise to dimethylamine, formaldehyde, and hydrogen peroxide. Pulse radiolysis using conductivity and optical detection permits the observation of the chemical transformations following the generation of the (dimethylamino)methyl radical from trimethylamine upon attack by the hydroxyl radical. The (dimethylamino)methyl radical reacts rapidly with oxygen ($k = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) to give $O_2^{\cdot-}$ and dimethylmonium, possibly via a short-lived ($t_{1/2} < 10^{-6} \text{ s}$) peroxy radical. The dimethylmonium ion adds OH^- to form (hydroxymethyl)dimethylamine ($k = 2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). This is hydrolyzed to dimethylamine and formaldehyde hydrate ($k_{\text{obs}} = 4.0 \pm 0.6 \text{ s}^{-1}$). A mechanism incorporating these reactions is shown to be in good accordance with the experimental data in the pH range from 9 to 11.3.

The reactions of hydroxyl radicals with trimethylamine in deoxygenated aqueous solutions¹⁻⁴ have been extensively studied recently⁵ using pulse radiolysis, combined with ESR and product analysis. Aqueous trimethylamine exists in both the protonated and the unprotonated forms (pK_a 9.76), and hydroxyl radical attack leads to the formation of three radicals, the aminoalkyl radical $(CH_3)_2NCH_2^{\cdot}$ (A^{\cdot}), its conjugated acid $(CH_3)_2HN^+CH_2^{\cdot}$ ($AH^{\cdot+}$), and the alkylamine radical cation $(CH_3)_3N^{\cdot+}$ ($N^{\cdot+}$). These species are linked by acid-base equilibria⁵ as indicated by reactions (1)–(4).



In the present work we study the reactions of these radicals in the presence of oxygen, in the pH range from 9 to 12 where A^{\cdot} is dominant.

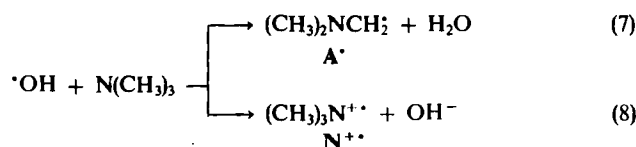
In the radiolysis of N_2O/O_2 (4:1 v/v) saturated aqueous solutions of trimethylamine, OH radicals are generated according to the reactions (5) and (6).



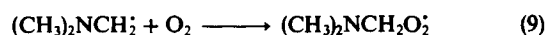
Bildung des Superoxid-Radikalanions bei der OH-Radikal-induzierten Oxidation von Trimethylamin in sauerstoffgesättigter wäßriger Lösung. Kinetik der Hydrolyse von (Hydroxymethyl)dimethylamin

Die Radiolyse von Trimethylamin in N_2O/O_2 (4:1)-gesättigter basischer Lösung führt zur Bildung von Dimethylamin, Formaldehyd und Wasserstoffperoxid. Die Anwendung der Pulsradiolyse in Verbindung mit schneller Leitfähigkeitsmessung und Spektrophotometrie ermöglicht die Beobachtung der chemischen Prozesse, die nach dem Angriff des OH-Radikals am Trimethylamin ablaufen. Das (Dimethylamino)methyl-Radikal reagiert rasch mit Sauerstoff ($k = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), wobei sich Dimethylmonium und Superoxid bildet, möglicherweise über ein kurzlebiges ($t_{1/2} < 10^{-6} \text{ s}$) Peroxyradikal. Das Dimethylmonium-Ion lagert OH^- an und bildet (Hydroxymethyl)dimethylamin ($k = 2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Dieses hydrolysiert in Dimethylamin und Formaldehydhydrat ($k_{\text{obs}} = 4.0 \pm 0.6 \text{ s}^{-1}$). Es wird gezeigt, daß ein Reaktionsmechanismus, der diese Elementarschritte enthält, in guter Übereinstimmung mit den experimentellen Daten (pH von 9 bis 11.3) steht.

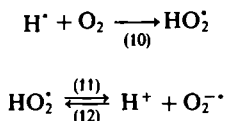
Under such conditions $\cdot OH$ is the major radical (90%, $0.57 \mu\text{mol J}^{-1}$), with a small contribution of the H atom (10%, $0.057 \mu\text{mol J}^{-1}$). Hydroxyl radicals react with trimethylamine thirty times faster ($k_{7,8} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) than with its protonated form ($k = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)⁶. In the present study we deal only with the pH range above 9. This simplifies the situation, because then we may restrict ourselves essentially to the consideration of A^{\cdot} and $N^{\cdot+}$ as the primary amine radicals⁵ [reactions (7) and (8)].



Whereas the aminoalkyl radical A^{\cdot} , like other carbon-centred radicals⁷, is expected to react rapidly with oxygen [reaction (9), for a possible alternative see below], the nitrogen-centred radical cation $N^{\cdot+}$ might perhaps not do so or react to form a labile complex. But, in basic solution through catalysis by OH^- and free amine, it will in any case be quite rapidly converted into A^{\cdot} and hence into the corresponding peroxy radical.



The H atoms from reaction (5) are scavenged by oxygen and form HO₂[•] radicals [reaction (10)] whose transformation into O₂^{-•} is spontaneous as well as base (OH⁻, free amine) catalyzed; pK_a = 4.7, cf. reaction (11)⁸.

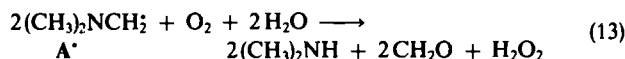


It is the fate of the amine peroxy radical and of its products that we are concerned with in the present study, and it will be shown that the pulse radiolysis technique can also yield valuable information on short-lived non-radical products which otherwise might be difficult to obtain.

Results and Discussion

The Overall Reaction

When OH radicals react with trimethylamine in basic solutions in the presence of oxygen, oxygen is consumed and the products are formaldehyde and dimethylamine as well as hydrogen peroxide, according to the overall reaction (13).



Of the couple formaldehyde/dimethylamine, only the formaldehyde has been measured (Table 1).

Table 1. Products (and *G* values) of the γ -radiolysis of N₂O/O₂ (4:1 v/v) saturated aqueous solutions of trimethylamine (10⁻³ M, pH 10.3). Dose rate 0.27 Gy/s

	<i>G</i> value ($\mu\text{mol}/\text{J}$)
Formaldehyde	0.57
Hydrogen peroxide	0.39
Oxygen consumption	0.31

Considering that in reaction (5) hydrogen peroxide is formed with a *G* value of 0.07 $\mu\text{mol J}^{-1}$ while some additional (0.03 $\mu\text{mol J}^{-1}$) hydrogen peroxide arises from the disproportionation of HO₂[•]/O₂^{-•} from reaction (10), a good material balance between oxygen consumption, formaldehyde, and hydrogen peroxide as well as with respect to the radiolytically formed OH radicals is obtained, which is the basis for some mechanistic conclusions outlined below.

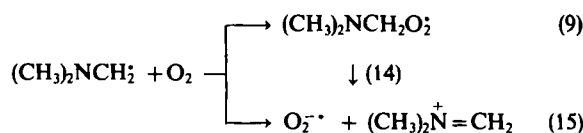
The Reaction of the (Dimethylamino)methyl Radical A[•] with Oxygen

As mentioned above, in basic solution immediately after the pulse, there are essentially only two radical species, the radical A[•] (90%) and O₂^{-•} (10%). A[•] shows a strong absorption near 260 nm with $\epsilon(260 \text{ nm}) = 3400 \text{ M}^{-1} \text{ cm}^{-1}$ ⁹. The reaction of A[•] with oxygen was followed at 260 nm in electron pulse-irradiated N₂O-saturated 10⁻³ M trimethylamine solutions containing oxygen at various concentra-

tions ([O₂] = 7 × 10⁻⁵ to 1.4 × 10⁻⁴ M) at pH 10.4. The absorption at 260 nm was found to decay via a first-order process, the observed rate constants being linearly dependent on the oxygen concentration. From a plot of *k*_{obs} versus [O₂] the rate constant of the reaction of oxygen with the radical A[•] was obtained:

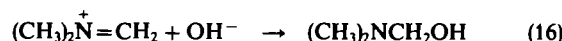
$$k_{9/15} = 3.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

After this fast decay, a product was observed with an absorption spectrum stable on a millisecond timescale and identical to that of O₂^{-•}. Taking the known extinction coefficient of O₂^{-•} ($\epsilon(260 \text{ nm}) = 1940 \text{ M}^{-1} \text{ cm}^{-1}$)⁸, the yield was found to be equal to the primary radical yields [*G*(A[•]) + *G*(HO₂[•])], all of which indicates that the reaction of oxygen with the radical A[•] leads immediately and quantitatively to the formation of O₂^{-•}. Whether such a reaction takes place through the formation of a very short-lived (half-life < 1 μs) peroxy radical [reaction (9)] [which decays to give O₂^{-•}, reaction (14)], or through direct electron transfer from radical A[•] to oxygen [reaction (15)], cannot be distinguished here. Reactions (9) and (14) are written in analogy to other electron-transfer reactions involving free radicals, where short-lived adducts have been found as intermediates (cf. ref.⁹).



Reaction of the Imonium Ion with OH⁻: Formation of (Hydroxymethyl)dimethylamine

In basic solutions, the imonium ion, formed in reaction (9), followed by (14), or (15), reacts with OH⁻ to give the more stable product (CH₃)₂NCH₂OH [reaction (16)].



Since the reactions (14)–(16) involve charged species, pulse radiolysis of N₂O/O₂ (4:1 v/v) saturated 4 × 10⁻⁴ M trimethylamine solutions at pH 9–11.3 was carried out and the conductivity change monitored. At 4–5 μs after the pulse, during which time the reactions (14) and (15) as well as the neutralisation of protons formed in the pulse are essentially complete, an increase in conductivity is observed due to the formation of O₂^{-•} and the imonium ion. On a longer timescale, this is followed by a decrease in conductivity as shown in Figure 1A.

The latter process is found to follow first-order kinetics, and the observed rates are proportional to the OH⁻ concentration (Figure 2).

These results are interpreted on the basis of reaction (16). From the slope of the plot in Figure 2 its rate constant was obtained:

$$k_{(16)} = 2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

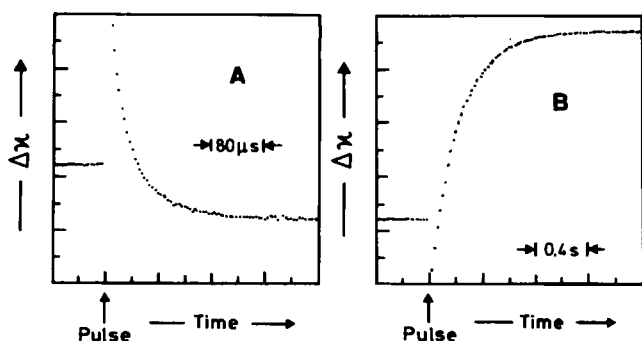


Figure 1. Conductivity change (relative units) in an $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v) saturated 4×10^{-4} M trimethylamine solution (pH 10) following a $1 \mu\text{s}$ electron pulse of ≈ 7 Gy. (A) $400 \mu\text{s}$ total time span; (B) 2 s total time span

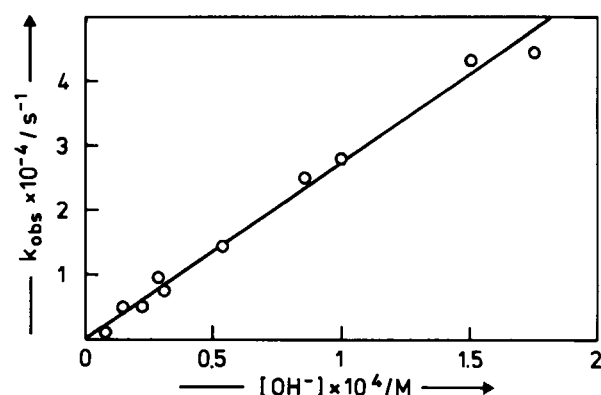


Figure 2. Hydroxide ion concentration dependence of the observed rate constant of the conductivity decrease in pulse irradiated $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v) saturated 4×10^{-4} M trimethylamine solutions

At pH above 11, the net change in conductivity in pulse-irradiated trimethylamine solutions after completion of reaction (16) corresponds essentially to the replacement of one OH^- ($\lambda^\circ = 185 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$) by $\text{O}_2^{\cdot-}$ ($\lambda^\circ = 60 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$). Indeed, at $\text{pH} \geq 11$ the $\Delta\kappa$ values measured after completion of reaction (16) correspond to $G(\text{O}_2^{\cdot-}) =$

$0.62 \mu\text{mol J}^{-1}$, in agreement with the results obtained by optical measurements. At pH below 11 the net conductivity change is smaller and does not fully reflect the yield of $\text{O}_2^{\cdot-}$, due to the buffering effect of trimethylamine ($\text{p}K_a$ 9.76). A plot of the conductivity change taken $300 \mu\text{s}$ after the pulse as function of pH is shown in Figure 3.

Table 2. Reactions and rate constants used in the computer simulation of the conductivity change versus pH shown in Figures 3 and 4. The equivalent ion conductivities employed in the calculations are 323 for H^+ , 185 for OH^- , 60 for $\text{O}_2^{\cdot-}$, 45 for other cations in units of $\Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ (TMA = Trimethylamine)

Reaction	k , unit $\text{M}^{-1} \text{s}^{-1}$ unless stated otherwise	Reference
(1)	$3.0 \times 10^6 \text{ s}^{-1}$	5)
(4)	35 s^{-1}	5)
(7)	0.6×10^{10}	$k(7 + 8) = 1.2 \times 10^{10}$, cf. ref. ⁵⁾
(8)	0.6×10^{10}	
(11)	$1.6 \times 10^5 \text{ s}^{-1}$	from $\text{p}K(\text{HO}_2)$ 4.7, and $k(12) = 1 \times 10^{10}$
(12)	1.0×10^{10}	assumed
(15)	3.5×10^9	this work, see text
(16)	2.7×10^8	this work, see text
(17)	4 s^{-1} ($= k(17)[\text{H}_2\text{O}]$)	this work, see text
(19)	1.0×10^5	from $\text{p}K(\text{DMA}) = 10.72$ and $k(20) = 1.1 \times 10^{10}$
(20)	1.1×10^{10}	assumed
(21) $\text{N}^{\cdot+} + \text{OH}^- \rightarrow \text{A}^{\cdot} + \text{H}_2\text{O}$	1.0×10^{10}	5)
(22) $\text{A}^{\cdot} + \text{H}_2\text{O} \rightarrow \text{N}^{\cdot+} + \text{OH}^-$	1.0×10^2	from $\text{p}K(\text{N}^{\cdot+}) = 8$ and $k(21) = 1.0 \times 10^{10}$
(23) $\text{N}^{\cdot+} + \text{TMA} \rightarrow \text{A}^{\cdot} \text{TMAH}^+$	7.3×10^8	5)
(24) $\text{A}^{\cdot} + \text{TMAH}^+ \rightarrow \text{N}^{\cdot+} + \text{TMA}$	9.9×10^7	from $\text{p}K(\text{N}^{\cdot+}) = 8$, $\text{p}K(\text{TMA}) = 9.76$, and $k(23) = 7.3 \times 10^8$
(25) $\text{HO}_2^{\cdot} + \text{OH}^- \rightarrow \text{O}_2^{\cdot-} + \text{H}_2\text{O}$	1.0×10^{10}	assumed
(26) $\text{HO}_2^{\cdot} + \text{TMA} \rightarrow \text{O}_2^{\cdot-} + \text{TMAH}^+$	1.0×10^{10}	assumed
(27) $\text{O}_2^{\cdot-} + \text{TMAH}^+ \rightarrow \text{HO}_2^{\cdot} + \text{TMA}$	1.1×10^5	from $\text{p}K(\text{HO}_2)$ 4.7, $\text{p}K(\text{TMA})$ 9.76, and $k(26) 1.0 \times 10^{10}$
(28) $\text{OH}^{\cdot} + \text{TMAH}^+ \rightarrow \text{AH}^{\cdot+} + \text{H}_2\text{O}$	1.1×10^8	5)
(29) $\text{OH}^{\cdot} + \text{TMAH}^+ \rightarrow \text{N}^{\cdot+} + \text{H}_2\text{O}$	2.9×10^8	5)
(30) $(\text{CH}_3)_2\text{NCH}_2\text{OH} + \text{H}_2\text{O} \rightarrow$ $[(\text{CH}_3)_2\text{NH}-\text{CH}_2\text{OH}]^+ + \text{OH}^-$	1.0×10^4	assumed
(31) $[(\text{CH}_3)_2\text{NH}-\text{CH}_2\text{OH}]^+ + \text{OH}^- \rightarrow$ $(\text{CH}_3)_2\text{NCH}_2\text{OH} + \text{H}_2\text{O}$	1.1×10^{10}	assumed
(32) $\text{TMA} + \text{H}_2\text{O} \rightarrow \text{TMAH}^+ + \text{OH}^-$	1.2×10^4	from $\text{p}K(\text{TMA}) = 9.76$ and $k(33) = 1.1 \times 10^{10}$
(33) $\text{TMAH}^+ + \text{OH}^- \rightarrow \text{TMA} + \text{H}_2\text{O}$	1.1×10^{10}	assumed
(34) $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	1.4×10^{11}	10)
(35) $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	$2.5 \times 10^{-5} \text{ s}^{-1}$	10)
(36) $\text{N}^{\cdot+} + \text{O}_2^{\cdot-} \rightarrow \text{TMA} + \text{O}_2$	1×10^9	assumed
(37) $\text{HO}_2^{\cdot} + \text{O}_2^{\cdot-} \rightarrow \text{HO}_2^- + \text{O}_2$	1.0×10^8	11)

Dismutation of $\text{O}_2^{\cdot-}$ into H_2O_2 , O_2 , and OH^- by impurities see text and Figures 3 and 4. Symbols see text.

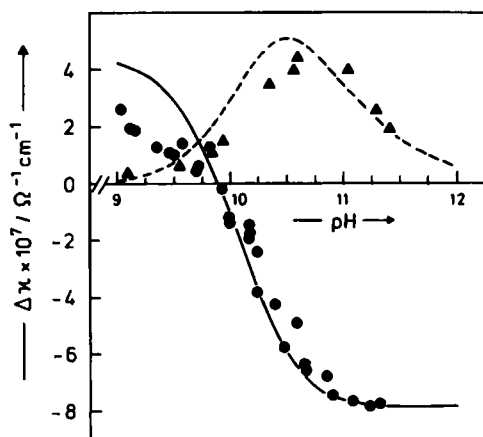


Figure 3. Dependence on pH of the observed conductivity change in $\text{N}_2\text{O}/\text{O}_2$ saturated 4×10^{-4} M trimethylamine solutions irradiated with $1 \mu\text{s}$ electron pulses of 10 Gy. ●, 300 μs after the pulse; ▲, 1 s after the pulse in the presence of superoxide dismutase (10^{-8} M). Curves, computed dependence on pH of the conductivity change: (—) at 300 μs after the pulse, (---) at 1 s after the pulse assuming a rate constant of 10 s^{-1} for the disappearance of $\text{O}_2^{\cdot-}$.

Taking into account the various reactions that may occur in this system, including the hydrolytic processes (cf. ref.¹⁰) and buffering effects, and using the proper rate constants and specific conductivities, the conductivity change at a time of 300 μs after the pulse was computed as a function of pH in the range of pH 9 to 12. The program (written by R. N. Stabler and J. Chesick, Haverford College) performs the integration of the system of differential equations implied by the postulated mechanism, and computes the concentrations of the various species as a function of reaction time. (For rate constants used see Table 2.)

As shown in Figure 3, the result of the simulation (solid line) is seen to reflect the experimental data (full circles) reasonably well.

Hydrolysis of (Hydroxymethyl)dimethylamine

Monitored within two seconds after the pulse, the change of the conductivity in basic $\text{N}_2\text{O}/\text{O}_2$ saturated trimethylamine solutions indicates a second first-order process, this time an increase of the conductivity (at pH > 9.5, cf. Figures 1B and 4).

Following this slow conductivity increase there is a third, even slower, process whose half-life increases from ≈ 1.5 s at pH 9.9 (a decrease in conductivity) to ≈ 7 s at pH 11.1 (an increase in conductivity). According to the published rate constants⁸, $\text{O}_2^{\cdot-}$ should be stable at pH above 9 over many seconds, but there may be disproportionation caused by adventitious transition metal ions (see below). The third process appeared to be such an induced decay of $\text{O}_2^{\cdot-}$. To check this hypothesis, superoxide dismutase (10^{-8} M) was added to accelerate the disappearance of $\text{O}_2^{\cdot-}$ (Figure 3). Indeed, in the presence of superoxide dismutase this process is replaced by a much faster but quantitatively equivalent process complete within 10 ms after the pulse. After the complication due to $\text{O}_2^{\cdot-}$ had been removed the kinetics of the remaining conductivity increase could be measured with fair

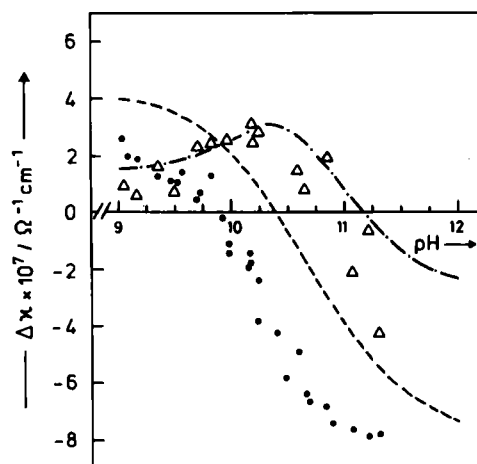
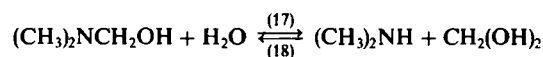


Figure 4. Dependence on pH of the observed conductivity change in $\text{N}_2\text{O}/\text{O}_2$ (4:1) saturated 4×10^{-4} M trimethylamine solutions irradiated with $1 \mu\text{s}$ electron pulses of 10 Gy. Δ , measured 1 s after the pulse. --- curve computed using the published rate constants for the dismutation of $\text{O}_2^{\cdot-}$; - · - · - curve computed assuming a rate constant of 1 s^{-1} for the disappearance of $\text{O}_2^{\cdot-}$. The values measured 300 μs after the pulse have also been included for easy comparison (●).

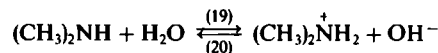
accuracy. The observed first-order rate constant of this process is independent of the OH^- concentration in the pH range between 9 and 11:

$$k_{\text{obs}} = 4.0 \pm 0.6 \text{ s}^{-1}$$

This first-order process is attributed to the hydrolysis of the product of reaction (16), $(\text{CH}_3)_2\text{NCH}_2\text{OH}$, to dimethylamine and formaldehyde [reaction (17)], and is visible because the



dimethylamine formed in reaction (17) is a stronger base ($\text{p}K_{\text{a}} = 10.76$) than the parent compound ($\text{p}K_{\text{a}} = 9.76$) whose hydrolysis leads to the release of some OH^- [reaction (19)].



In Figure 3 the conductivity change in trimethylamine solutions in the presence of superoxide dismutase measured 1 s after the pulse is plotted against the pH (triangles). For this case, the conductivity change at a time of 1 s after the pulse was computed as well. In the presence of superoxide dismutase, i.e. complete removal of $\text{O}_2^{\cdot-}$ within 1 second, the result of the computation (dashed line in Figure 3) mirrors the transformation of the radiolysed part of trimethylamine into dimethylamine. The maximum near pH 10.5 of the conductivity change seen under these conditions reflects the fact that between pH 10 and 11 dimethylamine, being more basic than the starting amine, is largely present in its protonated form whereas for trimethylamine the reverse is true.

As mentioned above, in the absence of superoxide dismutase one must assume some loss of superoxide radicals by dismutation processes, probably caused by adventitious transition metal ions whose overall effect with respect to the conductivity behaviour is the replacement of $O_2^{\cdot-}$ by OH^- . The experiments indicate (Figure 4) that the dismutation is more effective under less alkaline conditions, which seems reasonable in view of the assumption of transition metal participation. A similar phenomenon regarding the disappearance of $O_2^{\cdot-}$ was observed in pulse-irradiated N_2O/O_2 saturated isopropylalcohol solutions under similar conditions. Very rigorous precautions are necessary in order to eliminate the influence of such impurities¹²⁾ which have not been taken in the present case.

Addition compounds of primary and secondary amines to aldehydes are well known. From data given by Le Henaff¹³⁾ in a study of aqueous formaldehyde/amine systems, an equilibrium constant $K_{(17/18)}$ of 1.3×10^{-5} is calculated which, using $k_{obs} = k_{(17)} [H_2O] = 4 s^{-1}$, allows a value of $5.6 \times 10^3 M^{-1} s^{-1}$ for the rate constant $k_{(18)}$ of the reverse reaction to be estimated.

Experimental

Trimethylammonium perchlorate (Alfa) was used as obtained. Solutions were prepared with triply distilled water which was pre-saturated with N_2O/O_2 (4:1 v/v) before the addition of trimethylamine and adjustment to the desired pH by addition of sodium hydroxide. In a few experiments, N_2O/O_2 was also used in other ratios.

For product analysis, solutions were irradiated with ^{60}Co γ -rays at a dose rate of $0.27 Gy s^{-1}$. Formaldehyde was determined spectrophotometrically by the acetylacetone method¹⁴⁾. Hydrogen peroxide was determined iodometrically¹⁵⁾. Oxygen uptake was measured with an oxygen-sensitive electrode (Wissenschaftlich Technische Werkstätten, Weilheim, Germany).

Pulse radiolysis was carried out using a 2.8 MeV van-de-Graaff electron generator. The setup as well as the optical detection tech-

nique have been described previously¹⁶⁾. The conductivity change was monitored by an AC-operated (10 MHz) two-cell bridge as described by Asmus and Janata¹⁷⁾. Dosimetry was performed with a 0.1 M *tert*-butyl alcohol solution saturated with methyl chloride for which $G(HCl)$ is known to be $0.32 \mu mol J^{-1}$ ¹⁸⁾. For the optical measurements, dosimetry was performed with N_2O saturated $10^{-2} M$ KSCN solutions, taking $G = 0.62 \mu mol J^{-1}$ and $\epsilon(480 nm) = 7600 M^{-1} cm^{-1}$ for $(SCN)_2^{\cdot-}$. The electron pulses were of 0.4–2 μs duration, with absorbed doses between 5–40 Gy.

CAS Registry Numbers

O_2 : 7782-44-7 / trimethylamine: 75-50-3 / dimethylamine: 124-40-3 / formaldehyde: 50-00-0 / hydrogen peroxide: 7722-84-1 / (dimethylamino)methyl radical: 30208-47-0 / dimethyliminium: 17000-01-0 / (hydroxymethyl)dimethylamine: 14002-21-2

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