Common intermediates in the OH-radical-induced oxidation of cyanide and formamide†

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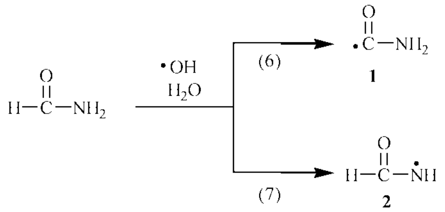
OH radicals generated in the pulse radiolysis of N_2O-saturated water react with formamide (by H-abstraction) and with cyanide (by addition and rearrangement) to give the same radicals, the main radical being the $^{\bullet}CONH_2$ radical **1** (85–95%), the other most likely being the $HC(O)NH^{\bullet}$ radical **2** (5–15%). Quantum-chemical calculations support the preferred formation of **1** from formamide as well as from cyanide. Radical **1** reduces tetranitromethane (TNM) to the nitroform anion (2.8×10^8 dm^3 mol^{-1} s^{-1}). In the presence of oxygen, it rapidly adds oxygen (2.7×10^9 dm^3 mol^{-1} s^{-1}) to give the corresponding peroxyl radical $^{\bullet}OOCONH_2$ (**3**) which absorbs more strongly in the wavelength region 250–400 nm than radical **1** [ε(320 nm) $\approx$ 180 dm^3 mol^{-1} cm^{-1}]. Peroxyl radical **3** deprotonates in basic solution (p$K_a \approx 9.6$), and its anion rapidly eliminates $O_2^{\bullet -}$ (10^6 s^{-1}) to give cyanic acid. Product studies under γ-radiolysis conditions show that in the absence of O_2 less than half of radical **1** decays by disproportionation to produce cyanate and formamide. In basic solution and in the presence of O_2, the *G* values of cyanate and H_2O_2 confirm that all of the peroxyl radical **3** decays by $O_2^{\bullet -}$-elimination.

The radiation chemistry of cyanide in aqueous solution has found considerable interest because of its possible role in prebiotic stages of the chemical evolution on the primitive earth.[1–5] EPR experiments[1] and pulse radiolysis studies[3,4] showed that the reaction of OH radicals with CN^- produces the $^{\bullet}CONH_2$ radical **1**. Additional evidence for the formation of **1** in aqueous cyanide solution was provided by product studies.[5]

For its formation one may assume that first an OH-adduct radical is formed [reaction (1)]. Such three-electron-bonded intermediates are common in the free-radical chemistry of halide and pseudo-halide ions. Subsequent protonation at nitrogen (by water) and subsequent rearrangement of the enolic radical **1a** will yield **1** [reactions (2) and (3)]. Protonation at carbon is kinetically usually slower than that at a heteroatom, and hence the formation of **2a/2** [reactions (4) and (5)] is less likely, although not excluded.

The same radicals may be generated in the reaction of the OH radical with formamide [reactions (6) and (7)]. Indeed, EPR studies[1] and spectral measurements[3] showed that the radicals produced by the reactions of OH radicals with formamide and with cyanide are identical.

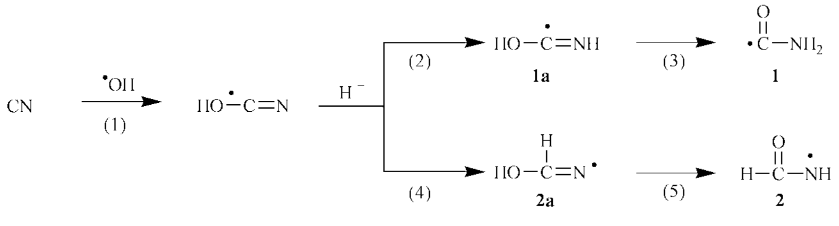
There were disagreements among earlier EPR studies on the site of OH radical attack on formamide. While the spectral parameters had first been assigned to the *N*-centered radical **2**,[6,7] they were later interpreted as belonging to the *C*-centered radical **1**, and this was confirmed by using D_2O as a solvent.[8] The same conclusion was arrived at by using the *in situ* radiolysis–EPR method.[1] These data are in favour that at least the major radical formed by H-abstraction from formamide is radical **1**.



The present paper concentrates on the question, whether in the formamide system radical **1** is the only radical formed upon OH-radical attack, or whether radical **2** is also formed. Special emphasis will be on the reaction of **1** with molecular oxygen and the fate of the corresponding peroxyl radical(s). Some experiments concerning the cyanide system will also be reported.

Experimental

Pulse radiolysis of aqueous solutions of formamide [(1–5) × 10^{-2} mol dm^{-3}; Fluka, p.a.] potassium cyanide (10^{-4}–10^{-3} mol dm^{-3}; Merck, >97%) in Milli-Q-filtered (Millipore) water saturated with either N_2O or with N_2O–O_2 (4 : 1 v/v if not stated



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† Cartesian coordinates and energies of the radicals are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/a9/a909609d. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

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otherwise) was carried out with a 2.8 MeV Van-de-Graaff accelerator delivering electron pulses of 0.4 µs duration. Intermediates were monitored by optical and conductometric detection. The pulse radiolysis set-up has been described previously.[9] For dosimetry, N_2O-saturated 10^{-2} mol dm^{-3} thiocyanate solution was used for optical detection, taking $G \times \varepsilon[(SCN)_2^{\bullet -}] = 4.8 \times 10^{-4}$ m^2 J^{-1} at 480 nm.[10,11] For conductometric detection, N_2O-saturated 10^{-2} mol dm^{-3} dimethyl sulfoxide solution[12] at pH 4 was used as dosimeter, taking $G(H^+) = G(CH_3SO_2^-) = 6.2 \times 10^{-7}$ mol J^{-1}.[13]

γ-Radiolysis was carried out in a ^{60}Co-source at dose rate of 0.15 Gy s^{-1} to total absorbed doses of ~150 Gy. Cyanate in irradiated samples was analysed directly by ion chromatography (Dionex DX-2010i, 4 × 250 mm AS9-SC column with a 4 × 50 mm AG9-SC pre-column, ASRS-I suppressor). The eluent used was an 1.8×10^{-3} mol dm^{-3} Na_2CO_3–1.7×10^{-3} mol dm^{-3} $NaHCO_3$ solution at a flow rate of 1 cm^3 min^{-1}. The retention time of the cyanate anion was 4 min. Hydrogen peroxide in the irradiated formamide solution was determined using molybdate-activated iodide.[14] Formylurea was determined by a spectrophotometric method using diacetylmonoxime.[15] Standard formylurea solution gives a characteristic pink colour reaction with maximum absorption at 540 nm and $\varepsilon = 4140$ dm^3 mol^{-1} cm^{-1}.

We found that an aqueous solution of 10^{-2} mol dm^{-3} formamide at pH 11.3 hydrolyses only slowly (<5% after 2 hours) at room temperature. Thus under our experimental conditions, one can assume negligible hydrolysis of formamide within the time of our measurements. The hydrolysis of cyanic acid/cyanate anion as a product of radiolysis is also negligible under our experimental conditions.[16]

The quantum-chemical calculations consisted of optimization of geometries, followed by the determination of the vibrational frequencies using the restricted SCF method. The final energies were determined by the coupled cluster method including triples corrections, CCSD [T]. The basis set used was the correlation-consistent valence triple-ζ-set,[17] but without d functions on the H atoms. All calculations were performed with the MOLPRO system of programs.[18]

Results and discussion

The radical-generating system

Hydroxyl radicals are generated in the radiolysis of water [reaction (8)]. The radiation-chemical yields (*G* values) of the

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H^+, H_2O_2, H_2 \qquad (8)$$

primary radicals are $G({}^{\bullet}OH) \approx G(e_{aq}^-) = 2.9 \times 10^{-7}$ mol J^{-1}, $G(H^{\bullet}) = 0.6 \times 10^{-7}$ mol J^{-1}, and $G(H_2O_2) \approx 0.7 \times 10^{-7}$ mol J^{-1}. N_2O is used to convert the solvated electron into $^{\bullet}OH$ [reaction (9)] so that a total OH-radical yield of 5.8×10^{-7} mol J^{-1} is

$$e_{aq}^- + N_2O + H_2O \longrightarrow {}^{\bullet}OH + OH^- + N_2 \qquad (9)$$

achieved in a 3×10^{-2} mol dm^{-3} formamide solution [$G({}^{\bullet}OH)$ increases with increasing substrate concentration].[19]

Reactions with the hydroxyl radical

The overall rate constant of OH-radical reaction with formamide [reactions (6) and (7)] has been redetermined by competition kinetics with thiocyanate. From the slope of the linear competition plot the ratio of $k_{6,7}/k({}^{\bullet}OH + SCN^-)$ of 0.034 was obtained. From the established rate constant of the reaction of the OH radical with thiocyanate ($k = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1})[20] it follows that $k_{6,7} = 3.7 \times 10^8$ dm^3 mol^{-1} s^{-1}. This value is in good agreement with the reported value of 5.0×10^8 dm^3 mol^{-1} s^{-1}.[21]

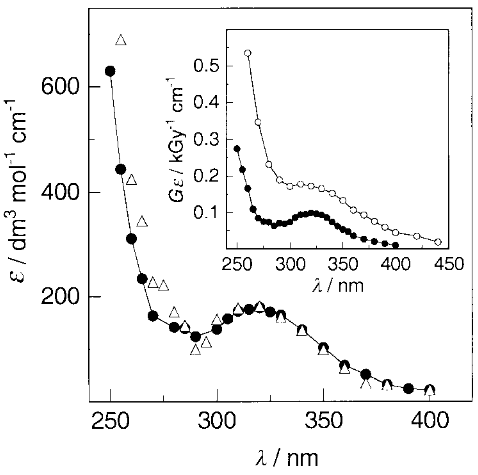


Fig. 1 Comparison of the spectra (5 µs after the pulse) of radicals produced in the pulse radiolysis (of ~5 Gy per pulse) of N_2O-saturated solutions of formamide (5×10^{-2} mol dm^3; ●) and potassium cyanide (2×10^{-4} mol dm^3; Δ) at pH 10. The absorption coefficients (ε) have been calculated on the basis of $G({}^{\bullet}OH) = 5.8 \times 10^{-7}$ mol J^{-1}. Inset: The above formamide spectrum (●), plotted as *G*ε, is compared with that obtained in N_2O–O_2-saturated solution (○) at pH 6.8.

The spectrum of the radicals produced in the pulse radiolysis of N_2O-saturated solution of formamide at pH 10 is shown in Fig. 1 (this is identical to the spectrum taken at pH 6.8). For comparison, the spectrum of radicals produced by OH radicals reactions with cyanide at pH 10 is also shown in Fig. 1. The two spectra are practically identical, as reported previously.[3] However, the absorption coefficient of ε(320 nm) = 180 dm^3 mol^{-1} cm^{-1} determined in this work for the radicals derived from formamide [assuming G(radicals) = 5.8×10^{-7} mol J^{-1}] lies between the reported values of 115 dm^3 mol^{-1} cm^{-1} (ref. 3) and 350 dm^3 mol^{-1} cm^{-1} (ref. 21).

Radical **1** is activated by an α-NR_2 group similar to the radicals derived from OH-radical reactions with uracil[22] and trimethylamine,[23] and is expected to have reducing properties. The *N*-centered radical **2** is not a reducing radical. The reaction of radical **1** with tetranitromethane (TNM) was monitored at 350 nm for the formation of the nitroform anion [reaction (10)].

$$\begin{aligned} &{}^{\bullet}C(O)NH_2\ \mathbf{1} + C(NO_2)_4 \longrightarrow \\ &\qquad OCN^- + 2\,H^+ + C(NO_2)_3^- + {}^{\bullet}NO_2 \qquad (10) \end{aligned}$$

Pulse radiolysis of N_2O-saturated solutions of formamide containing tetranitromethane (TNM) at pH 6.8 showed the formation of the nitroform anion [NF^-, ε(350 nm) = 1.5×10^4 dm^3 mol^{-1} cm^{-1}][24] with a rate constant of $k_{10} = 2.8 \times 10^8$ dm^3 mol^{-1} s^{-1} and total $G(NF^-) = 6.1 \times 10^{-7}$ mol J^{-1} (extrapolated to zero dose to minimise loss due to bimolecular decay of the radicals). This *G* value also includes NF^- from primary H atoms [reaction (8)] scavenged by TNM. This leaves G(radical **1**) = 5.5×10^{-7} mol J^{-1} or 95% of the total OH-radical yield.

The above results show that a small fraction of OH radicals (~5%) might undergo H-abstraction at nitrogen [reaction (7)]. Since the *N*-centered radical **2** could have oxidising properties, we have tried to have this radical react with the strongly reducing agents *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) and hexacyanoferrrate(II). However, in N_2O-saturated solution of formamide (5×10^{-2} mol dm^{-3}) containing TMPD (5×10^{-5} mol dm^{-3}) or $K_4Fe(CN)_6$ (10^{-4} mol dm^{-3}), <3% of radicals were found to oxidise TMPD to $TMPD^{+\bullet}$ (monitored at 565 nm)[22] or $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ (monitored at 410 nm).

Reaction of radical 1 with oxygen

In N_2O–O_2-saturated solution of formamide, radical **1** formed in reaction (6), like other carbon-centered radicals,[25] rapidly adds oxygen to give the peroxyl radical **3** [reaction (11)]. In

$$^{\bullet}C(O)NN_2\ \mathbf{1} + O_2 \longrightarrow {}^{\bullet}OOC(O)NH_2\ \mathbf{3} \qquad (11)$$

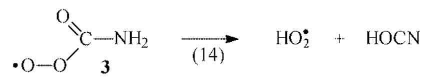
contrast, *N*-centered radicals, such as radical **2**, are known to show a low affinity to oxygen.[26] H atoms formed in the electron pulse [reaction (8)] are mostly scavenged by oxygen [reaction (12)].

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \qquad (12)$$

The transient absorption spectrum (Fig. 1, inset, upper spectrum) obtained in the N_2O–O_2-saturated solution of formamide 1.2 μs after the pulse shows that the peroxyl radical **3** absorbs more strongly than radical **1** (Fig. 1, inset, lower spectrum). Alkylperoxyl radicals with an electron-donating group (OH[27–29] or NH[22,30–33]) at the α-position are known to undergo spontaneous or OH^--induced elimination of $HO_2^{\bullet}/O_2^{\bullet -}$ [$pK_a(HO_2^{\bullet}) = 4.8$; equilibrium (13)].[34] Thus at neutral to basic

$$HO_2^{\bullet} \longrightarrow H^+ + O_2^{\bullet -} \qquad (13)$$

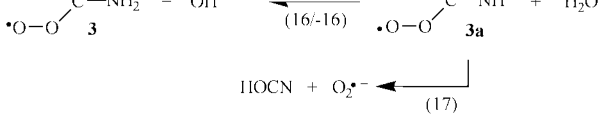
pH where $HO_2^{\bullet}$ is fully dissociated, its formation can be monitored by conductance measurements. In N_2O–O_2-saturated solution of formamide at pH 6.8, a build-up of conductance, whose magnitude [$G(H^+) = 2.6 \times 10^{-7}$ mol J^{-1} at 2 Gy per pulse] decreases and rate increases with increasing doses, was observed. Following this build-up, the conductance subsequently decreased to the original level (*i.e.* no permanent change of conductance) in the course of ~10 ms depending on the dose. The unimolecular $HO_2^{\bullet}$-elimination reaction [reactions (14)] produces, besides $HO_2^{\bullet}$, cyanic acid ($pK_a = 3.5$).[35]



Unlike $HO_2^{\bullet}$, which subsequently disappears *via* reaction with $O_2^{\bullet -}$ [reaction (15)], the cyanic acid will remain in the solution (as a permanent change of conductance). Since the observed increase in conductance subsequently disappears, the main source of proton production ($HO_2^{\bullet}$) must come from the bimolecular decay reactions of radical **3**, which compete against reaction (14). The latter is probably too slow for its rate constant to be determined by pulse radiolysis measurements. Product analysis (*cf.* Table 1 below) shows that reaction (14) is not the prevailing reaction in neutral solution of formamide even at the low dose rate of γ-radiolysis. Similar to the cases of uracil[30] and glycine anhydride[33] peroxyl radical **3** appears to undergo mainly base-induced $HO_2^{\bullet}$-elimination (see below).

$$O_2^{\bullet -} + HO_2^{\bullet} + H^+ \longrightarrow H_2O_2 + O_2 \qquad (15)$$

In N_2O–O_2-saturated solution of formamide at pH 11, immediately following the neutralisation of H^+ and OH^- formed within the electron pulse, the conductance was observed to decrease to a lower and constant level corresponding to $G(-OH^-) = 10.2 \times 10^{-7}$ mol J^{-1}. This can be attributed to the deprotonation of radical **3** induced by OH^- to the corresponding radical anion **3a** [equilibrium (16)], which rapidly eliminates $O_2^{\bullet -}$ [reaction (17)]. In reaction (16), OH^- (limiting equivalent conductivity 180 Ω^{-1} cm^2 $equiv^{-1}$)[36] is replaced by the radical anion **3a** with lower conductivity (~50 Ω^{-1} cm^2 $equiv^{-1}$,



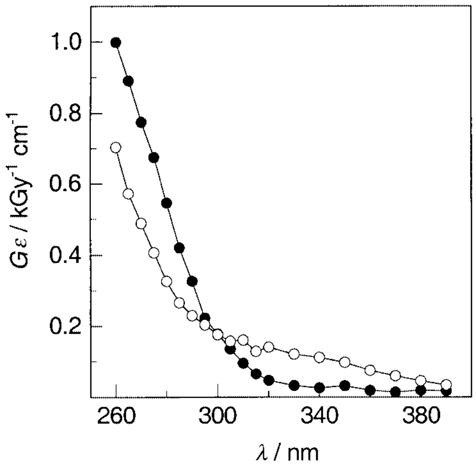


Fig. 2 Initial spectrum (○, 1 μs after the pulse) and final spectrum (▲ 7 μs after the pulse) in the pulse radiolysis of formamide (5×10^{-2} mol dm^{-3}) in N_2O–O_2-saturated solution at pH 10.2.

assumed to be the same as that of $O_2^{\bullet -}$). In basic solution, cyanic acid formed in reaction (17) is neutralised by OH^- to the cyanate anion. Thus a further mol equivalent of OH^- is replaced by the cyanate anion with lower conductivity. From the above yield of OH^- consumption, which also includes the contribution from $H^+/O_2^{\bullet -}$ formation due to the primary H atoms [reactions (8) and (12)], we obtain $G(\mathbf{3}) = G(\mathbf{1}) = 4.8 \times 10^{-7}$ mol J^{-1} or 86% of the total OH radical yield. For cyanide, conductivity experiments under similar conditions showed that the corresponding yield of radical **1** [reactions (1) to (3)] is 94% of the total OH radical yield.

On the other hand, when the formation of $O_2^{\bullet -}$ from reaction (17) was monitored by its fast reaction with tetranitromethane [reaction (18)],[34] we found in N_2O–O_2-saturated

$$O_2^{\bullet -} + C(NO_2)_4 \longrightarrow O_2 + C(NO_2)_3^- + {}^{\bullet}NO_2 \qquad (18)$$

solution of formamide and TNM (10^{-4} mol dm^{-3}) at pH 10.4 (the two solutions were only mixed immediately before the pulse), total $G(NF^-) = 6.0 \times 10^{-7}$ mol J^{-1}. This corresponds to $G(\mathbf{3}) = G(\mathbf{1}) = 5.4 \times 10^{-7}$ mol J^{-1} or 95% of the total OH radical yield.

Reactions (16) and (17) were also monitored optically. Fig. 2 shows that in an N_2O–O_2-saturated solution of formamide at pH 10.2 the spectrum of the peroxyl radical **3** (circles) is transformed in a few μs to a new spectrum resembling that of $O_2^{\bullet -}$.

The observed rate constant of absorption decay at 330 nm (4×10^5 s^{-1}) is identical to that of absorption build-up at 270 nm. The dependence of k_{obs} at 330 nm on pH has a sigmoidal shape with an inflection point at pH 9.7 (Fig. 3). This is an indication that the rate of $O_2^{\bullet -}$ formation might be determined by the equilibrium (16)/(−16) as the rate of oxygen addition (see below) is not the rate determining step. Based on reactions (16), (−16) and (17) and on steady-state conditions, one arrives at the relationship (19) for the rate constant of $O_2^{\bullet -}$ formation:

$$k_{obs}^{-1} = (k_{-16} + k_{17})\, k_{16}^{-1}\, k_{17}^{-1}\, [OH^-]^{-1} + k_{17}^{-1} \qquad (19)$$

From the reciprocal plot (k_{obs}^{-1} *vs.* $[OH^-]^{-1}$) in Fig. 3 inset, the intercept $k_{17}^{-1} = 10^{-6}$ s and the slope $(k_{-16} + k_{17})\, k_{16}^{-1} k_{17}^{-1} = 1.43 \times 10^{-10}$ mol dm^{-3} s are obtained. This gives $k_{17} = 10^6$ s^{-1}. The value of k_{-16} can be calculated from the above value of the slope if for k_{16} a value of 10^{10} dm^3 mol^{-1} s^{-1} is assumed, which is a typical rate constant for the deprotonation of a NH function by OH^-.[37] With this assumption we calculate $k_{-16} = 4.3 \times 10^5$ s^{-1}. From these values for k_{16} and k_{-16}, the pK_a of the peroxyl radical **3** can be calculated. Hence $pK_a(\mathbf{3}) = pK_w - \log(k_{16}/k_{-16}) = 9.6$, which is *ca.* 7 pH units lower than that of formamide. This pK_a value obtained for the peroxyl

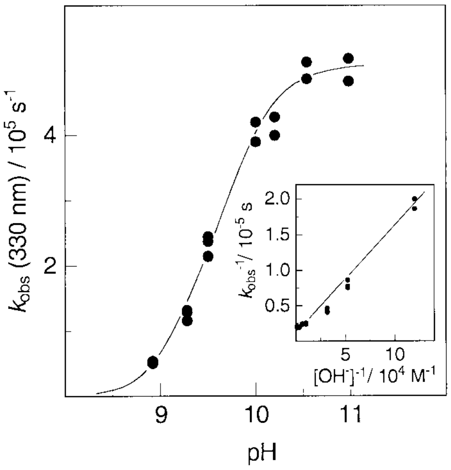


Fig. 3 Observed rate constant of $O_2^{\bullet -}$ formation monitored at 330 nm as function of pH in 3×10^{-2} mol dm^{-3} formamide solution saturated with N_2O–O_2. Dose per pulse ~4 Gy. Inset: plot of k_{obs}^{-1} *vs.* $[OH^-]^{-1}$.

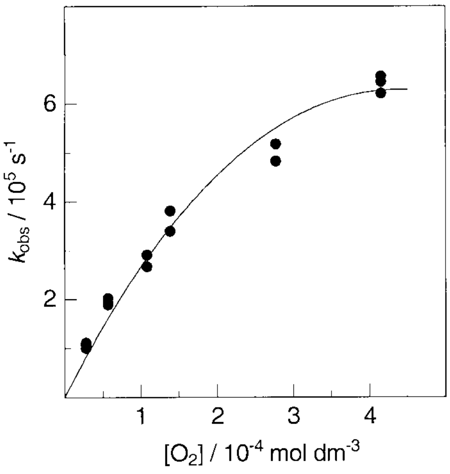


Fig. 4 Oxygen concentration dependence of k_{obs} (330 nm) in N_2O–O_2-saturated solution of 3×10^{-2} mol dm^{-3} formamide at pH 11.

radical **3** essentially agrees with the value predicted by the Taft equation for amides (pK_a for $R^1CONHR^2 = 22.0 - 3.1\ \Sigma\sigma^*$).[38] The two substituents (with their σ^* values) on radical **3** are $-O_2^\bullet$ ($\sigma^* = 3.7$)[39] and –H ($\sigma^* = 0.49$).[38] Hence the predicted $pK_a(\mathbf{3}) = 22.0 - 3.1(3.7 + 0.49) = 9.0$. The pK_a of the peroxyl radical derived from glycine anhydride (10.7)[33] also agrees closely with the value predicted by this Taft equation.

Rate constant of oxygen addition

The rate constant of oxygen addition (k_{11}) was determined by monitoring the rate constant of absorption decay at 330 nm with varying oxygen concentration in N_2O–O_2-saturated solution of formamide at pH 11 where reactions (16) and (17) are both very rapid compared to reaction (11). Fig. 4 shows that at low oxygen concentration ($<1.4 \times 10^{-4}$ mol dm^{-3}) reaction (11) is the rate determining step, k_{obs} is linearly proportional to the oxygen concentration, and from this relationship $k_{11} = 2.7 \times 10^9$ mol dm^{-3} s^{-1} is obtained. This is a typical rate constant for oxygen addition of *C*-centered radicals.

At higher oxygen concentration the situation is more complex. The absorption decay at 330 nm is increasingly determined by the reactions (16)/(−16) and (17) and k_{obs} is no longer linearly dependent on oxygen concentration.

Product analysis

It has been reported[5] that cyanate and formamide were the only products of any importance, produced in equal amounts ($G = 3.4 \times 10^{-7}$ mol J^{-1}), in the γ-radiolysis of N_2O-saturated solution of cyanide at pH 11. It was thus concluded that the radical $^\bullet CONH_2$, **1** resulting from the action of OH radicals with cyanide decays quantitatively by disproportionation to yield equal amounts of cyanate and formamide.

Table 1 *G*(cyanate ion) in units of 10^{-7} mol J^{-1} in the γ-radiolysis of formamide (1×10^{-2} mol dm^{-3}) and potassium cyanide (1×10^{-3} mol dm^{-3}) in N_2O- and N_2O–O_2-saturated solutions

Reaction conditions	Formamide	Cyanide
N_2O, pH 6.8	1.0	n.d.[a]
N_2O, pH 10	1.3	1.8
N_2O–O_2, pH 6.8	2.3 (H_2O_2: 2.1)	n.d.[a]
N_2O–O_2, pH 10	4.8 (H_2O_2: 3.1)	5.4
N_2O–O_2, pH 11	4.6	n.d.[a]

[a] n.d. = not determined.

We have determined the cyanate yields (Table 1) in the γ-radiolysis of formamide and potassium cyanide in N_2O-saturated solution, and found that less than half of radical **1** will decay by disproportionation to produce cyanate and formamide (not determined). Apparently a large fraction of radical **1** also decays by dimerisation.

In the γ-radiolysis of N_2O–O_2-saturated solutions of formamide and potassium cyanide, the yields (Table 1) of the products cyanate and hydrogen peroxide [the sum of primary H_2O_2, $G = 0.7 \times 10^{-7}$ mol J^{-1}, *cf.* reaction (8), and of H_2O_2 from the bimolecular decay of $HO_2^\bullet$, *cf.* reaction (15)] confirmed our above findings in pulse radiolysis. In neutral solution, only about half of the peroxyl radical **3** undergoes $HO_2^\bullet$-elimination [reactions (14) together with (16) and (17)] to give cyanic acid (at this given dose rate). In basic solution, however, all of the peroxyl radical **3** decays *via* reactions (16) and (17) to give cyanate and $O_2^{\bullet -}$. The *G* values of cyanate and H_2O_2 determined in the case of formamide (Table 1) indicate that >85% of OH-radicals react with formamide to give the *C*-centered radical **1** (subsequently the peroxyl radical **3**). Similarly, from the *G* value of cyanate determined for cyanide under similar conditions one calculates that 94% of OH-radicals react with cyanide to give the *C*-centered radical **1**.

From the above pulse radiolysis and product analysis observations one can conclude that OH-radicals reactions with formamide and cyanide lead predominantly to the formation of the *C*-centered radical **1** (85–95% for formamide and ~95% for cyanide).

Direct evidence for the formation of the *N*-centered radical **2** in reactions (4) and (7) has so far eluded our efforts, possibly due to the low yield. However, the existence of **2** can be found in one the products of its bimolecular decay, namely formylurea [reaction (20)]. Indeed, this product was found with a small

$$HC(O)NH^\bullet\ \mathbf{2} + {}^\bullet C(O)NH_2\ \mathbf{1} \longrightarrow HC(O)NHC(O)NH_2 \quad (20)$$

G value of $\sim 0.05 \times 10^{-7}$ mol J^{-1} in the γ-radiolysis of N_2O-saturated solutions of formamide at pH 6.8. Although radical **1** seems to decay by disproportionation [reaction (21), product: cyanate] or by dimerisation [reaction (22), product not deter-

$$2\ {}^\bullet C(O)NH_2\ \mathbf{1} \longrightarrow HC(O)NH_2 + HOCN \quad (21)$$

$$2\ {}^\bullet C(O)NH_2\ \mathbf{1} \longrightarrow (C(O)NH_2)_2 \quad (22)$$

mined] with about equal probability (*cf.* *G* values of cyanate in Table 1), the reaction of radical **2** with radical **1** could still tend to be mostly in favour of disproportionation [reaction (23),

$$HC(O)NH^\bullet\ \mathbf{2} + {}^\bullet C(O)NH_2\ \mathbf{1} \longrightarrow HC(O)NH_2 + HOCN \quad (23)$$

product: cyanate] rather than dimerisation [reaction (20), product: formylurea]. Thus the yield of formylurea found in this case might only reflect a small fraction of the actual yield of radical **2**.

The energetics of radicals 1a, 1, 2a and 2

It has been mentioned above that protonation at carbon is typically slower than protonation at a heteroatom, even when the energetics are in favour of a protonation at carbon. A case in point is the protonation of the uracil radical anion.[40,41] In the present context it is of interest that our quantum-chemical calculations show that (based on radical $\mathbf{1} = 0$) the energy of radical **2** is 134 kJ mol^{-1}. Thus H-abstraction from formamide will preferentially yield **1**, as has been found. In the case of cyanide, the energy of **1a** is at 106 kJ mol^{-1}, while that of **2a** is at 305 kJ mol^{-1}, *i.e.* protonation at carbon [formation of **2a**, reaction (4)] is not only kinetically (*cf.* ref. 37) but also thermodynamically disfavoured.

Hydration of the $^{\bullet}C(O)CH_3$ and the $^{\bullet}C(O)NH_2$ radical

In aqueous solutions, the acetyl radical (non-reactive against mild oxidants) undergoes rapid hydration [reaction (24);

$$^{\bullet}C(O)CH_3 + H_2O \longrightarrow {}^{\bullet}C(OH)_2CH_3 \qquad (24)$$

$k = 2 \times 10^4$ s^{-1})] yielding the strongly reducing $^{\bullet}C(OH)_2CH_3$ radical.[42] There is no spectral evidence that the corresponding $^{\bullet}C(O)NH_2$ radical undergoes hydration [*cf.* reaction (25)]. As

$$^{\bullet}C(O)NH_2\ \mathbf{1} + H_2O \longrightarrow {}^{\bullet}C(OH)_2NH_2 \qquad (25)$$

radical **1** has reducing properties similar to its hydrated form, experimental evidence for the absence/presence of reaction (25) is not readily available.

Quantum-mechanical calculations, however, show that (in the gas phase) reaction (24) is only slightly endothermic (30 kJ mol^{-1}). This does not yet take into account any differences in the solvation energies, and it is very likely that the solvation energy of the hydrated acetyl radical is noticeably higher than that of the acetyl radical itself. On the other hand, our quantum-mechanical calculations (gas phase) show that reaction (25) is noticeably endothermic (85 kJ mol^{-1}). In addition, the solvation energy differences between the two radicals involved may be less, since in water efficient hydrogen bonding at the NH_2 group in $^{\bullet}C(O)NH_2$ will already have reduced its energy. It is noted that these differences are also observed with their parent molecules. While in water acetaldehyde is hydrated to an extent of 55%,[43] formamide is not.

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