Generation and Reactions of the Ammoniumyl Radical Cation ($NH_3^{+\cdot}$): an Electron Spin Resonance Investigation

By **Bruce C. Gilbert** * and **Paul R. Marriott**, Department of Chemistry, University of York, Heslington, York YO1 5DD

E.s.r. spectroscopy has been employed to study the reactions of a variety of organic compounds with ammoniumyl ($NH_3^{+\cdot}$) generated in a flow system from the titanium(III)–hydroxylamine couple. Radicals resulting from hydrogen-atom abstraction from certain substrates (*e.g.* alkanols) have been detected and it is concluded that $NH_3^{+\cdot}$ is an electrophilic species with a greater degree of selectivity than hydroxyl. A pseudo steady-state analysis for radicals in the cavity is shown to be appropriate and values have been obtained for the rate constant for the initiating reaction [$k(Ti^{III} + NH_2OH)$ *ca.* 6×10^5 l mol^{-1} s^{-1} at pH 2] and for the relative rates of attack of $NH_3^{+\cdot}$ on different substrates.

It is generally accepted that the titanium(III)–hydroxylamine redox couple is an effective source of $\cdot NH_2$—or, depending on the pH, $NH_3^{+\cdot}$—as shown in reactions (i) and (ii). For example, synthetic applications involving radical addition to alkenes have been described[1] and amino-radical adducts of alkenes and other unsaturated compounds have been detected in continuous flow e.s.r. studies;[2-4] polarographic[5,6] and pulse-polarographic[7]

---

[1] C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Amer. Chem. Soc.*, 1959, **81**, 1489.

[2] (*a*) C. Corvaja, H. Fischer, and G. Giacometti, *Z. Phys. Chem.*, (*Frankfurt*), 1965, **45**, 1; (*b*) C. Corvaja, M. Brustolon, and G. Giacometti, *ibid.*, 1969, **66**, 279.

[3] J. Dewing, G. F. Longster, J. Myatt, and P. F. Todd, *Chem. Comm.*, 1965, 391.

[4] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 182.

[5] K. A. Blazek and J. Koryta, *Coll. Czech. Chem. Comm.*, 1953, **18**, 326.

[6] G. Farnia, D. Anselmi, and E. Vianello, *Ricerca Sci.*, 1968, 1211; G. Farnia, R. Tomat, and E. Vianello, *J.C.S. Perkin II*, 1975, 763.

[7] H. Claus, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 702.

methods have also been employed to study this redox reaction. Evidence has been presented[8] which indicates that, even under acidic conditions, it is NH_2OH rather than the protonated form, $^+NH_3OH$, which reacts with Ti^{III}: most rate constants quoted for the initiating reaction (*e.g.* ref. 7) are ***apparent*** rate constants in that they refer to total hydroxylamine concentration.

Pulse radiolysis of aqueous solutions of hydroxylamine also evidently leads,[9] *via* reactions of e^-_{aq} with NH_2OH, to $\cdot NH_2$ (or $NH_3^{+\cdot}$); the pK_a value for the ammoniumyl radical cation has been determined in this investigation as 6.7, which makes it clear that the reactive species involved in most of the other studies (which employed, typically, acidic solutions) is $NH_3^{+\cdot}$, rather than $\cdot NH_2$ as usually written.

$$Ti^{III} + NH_2OH \longrightarrow Ti^{IV} + \cdot NH_2 + OH^- \quad \text{(i)}$$

$$Ti^{III} + NH_2OH \xrightarrow{H^+} Ti^{IV} + NH_3^{+\cdot} + OH^- \quad \text{(ii)}$$

It has been inferred[1,7,9] that the 'amino' radical can react *via* hydrogen-atom abstraction with suitable substrates [reaction (iii)], as well as *via* addition with alkenes and their derivatives; in all cases it appears that the rapid reduction of $NH_3^{+\cdot}$ (or $\cdot NH_2$) by Ti^{III} [reaction (iv)] provides a competing mode for destruction (see, *e.g.* ref. 7). We have employed e.s.r. spectroscopy in an attempt to detect, directly, radicals formed in reaction (iii) and hence to examine the selectivity with which $NH_3^{+\cdot}$ (and $\cdot NH_2$) attacks different hydrogen atoms (or other reactive sites) in a variety of substrates. It was also our aim to show that the pseudo steady-state analysis demonstrated[10,11] for the Ti^{III}–H_2O_2 reaction under typical flow-system conditions is also applicable for radicals generated by using the Ti^{III}–NH_2OH couple, and therefore that useful kinetic data can be obtained.

$$NH_3^{+\cdot} + RH \longrightarrow NH_3 + R\cdot + H^+ \quad \text{(iii)}$$

$$NH_3^{+\cdot} + Ti^{III} \longrightarrow NH_3 + Ti^{IV} \quad \text{(iv)}$$

RESULTS AND DISCUSSION

Generation and Scavenging of $NH_3^{+\cdot}$.—*E.s.r. results.* We have carried out experiments in which three aqueous solutions, containing titanium(III), hydroxylamine hydrochloride, and an organic substrate, respectively, are mixed shortly before the combined solution enters a sample cell held in the cavity of an e.s.r. spectrometer. The apparatus, similar to that used to study Ti^{III}–H_2O_2–RH reactions (see *e.g.* ref. 12), employed an overall flow-rate of *ca.* 3.5 ml s^{-1} (obtained by gravity feed) which gave a time between mixing and observation of *ca.* 0.08 s. The majority of our experiments have been carried out at pH *ca.* 1.5 (so that $NH_3^{+\cdot}$, rather than $\cdot NH_2$, is generated) with an initial titanium(III) concentration, $[Ti^{III}]_0$, of 2.7 mmol l^{-1} (*cf.* Ti^{III}–H_2O_2).* We usually employed an initial hydroxylamine hydrochloride concentration, $[\text{Hydroxylamine}]_0$, of *ca.* 0.15 mol l^{-1}; concentrations in this range have been found necessary for detecting amino-radical adducts of alkenes[2-4] and proved optimum in our experiments. This concentration is significantly greater (by a factor of 10) than those of hydrogen peroxide employed in typical Ti^{III}–H_2O_2 studies of the generation and reaction of the hydroxyl radical; we believe that this is necessary if radical generation in the cavity in the former reaction is to be fast enough for a sufficiently high steady-state concentration of derived radicals to be obtained. Thus the apparent rate constant for the titanium(III)-hydroxylamine reaction under our conditions (*e.g.* k is[7] 42 ± 2 l mol^{-1} s^{-1} in 0.2M-oxalic acid at 25 °C) is likely to be considerably lower than that for Ti^{III}–H_2O_2 (k is[12] *ca.* 590 l mol^{-1} s^{-1} in aqueous solution and pH *ca.* 1 at room temperature). These concentrations of Ti^{III} and hydroxylamine (total) also ensure that the latter is in considerable excess, so that its decay down the flow-tube is negligible (*i.e.* $[\text{Hydroxylamine}]_0 \simeq [\text{Hydroxylamine}]_t$, the concentration at time t after mixing) and that Ti^{III} decays exponentially after mixing; the relatively low value of $[Ti^{III}]$ should ensure that the effect of reaction (iv) is minimised. The organic substrate (concentration after mixing between 0.03 and 1.5 mol l^{-1}) was contained in the third stream.

Evidence that $NH_3^{+\cdot}$ is effective in hydrogen-atom abstraction was obtained from experiments with a variety of saturated substrates. For example, in the presence of methanol ($[MeOH] >$ *ca.* 0.1 mol l^{-1}) signals from $\cdot CH_2OH$[13] were detected. The height of the signal increased up to a maximum value as [MeOH] was increased to *ca.* 0.8 mol l^{-1}, but increasing the methanol concentration further caused no further increase in the radical concentration (this 'levelling off' was observed in other experiments; see below). We believe that this behaviour is explicable if methanol reacts *via* reaction (v), and that for concentrations greater than 0.8 mol l^{-1} it scavenges all the $NH_3^{+\cdot}$ formed, preventing the occurrence of other reactions which would destroy the intermediate [*e.g.* reaction (iv)]. A full kinetic analysis of a typical abstraction reaction is presented in a subsequent section.

$$NH_3^{+\cdot} + CH_3OH \longrightarrow NH_3 + H^+ + \cdot CH_2OH \quad \text{(v)}$$

$$NH_3^{+\cdot} + CH_2{=}CHCN \longrightarrow H_3\overset{+}{N}{-}CH_2{-}\dot{C}HCN \quad \text{(vi)}$$

We note at this stage that the concentration of methanol necessary to obtain a strong e.s.r. signal is much higher than that necessary for related experiments with alkenes as substrate. For example, when the mixed solution contained propenonitrile (acrylonitrile)

---

* Except where stated otherwise, concentrations are those of components *after* mixing; subscript zero refers to initial concentrations, *i.e.* those obtained immediately mixing has taken place.

[8] R. Tomat and A. Rigo, *J. Electroanalyt. Chem.*, 1972, **35**, 21.

[9] M. Simic and E. Hayon, *J. Amer. Chem. Soc.*, 1971, **93**, 5982.

[10] G. Czapski, *J. Phys. Chem.*, 1971, **75**, 2957.

[11] D. Meisel, G. Czapski, and A. Samuni, *J.C.S. Perkin II*, 1973, 1702.

[12] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174.

[13] R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

at a concentration of only 0.01 mol l^{-1}, the e.s.r. spectrum of $\cdot CH(CN)CH_2NH_3^+$ was detected [a(1H) 2.05, a(2H) 2.36, a(2N) 0.315 mT; see ref. 2a]. We believe that addition [reaction (vi)] is considerably faster than abstraction [reaction (v)] so that smaller concentrations of the alkene, compared with the alkanol, are necessary to scavenge $NH_3^{+\cdot}$ (*cf.* the use of methanol as a solvent for amino-radical addition to alkenes [1]).

Reaction of $NH_3^{+\cdot}$ with ethanol under conditions similar to those indicated for methanol gave strong signals from $\cdot CHMeOH$ and a limiting value of [$\cdot CHMeOH$] was reached for [CH_3CH_2OH] *ca.* 0.15 mol l^{-1} (that this value is less than that for CH_3OH in the related experiment suggests that ethanol is more efficient in scavenging $NH_3^{+\cdot}$). No trace of $\cdot CH_2CH_2OH$ [14] was detected, even in experiments with [CH_3CH_2OH] > 0.15 mol l^{-1}, when the signal-to-noise ratio was *ca.* 100 : 1 (in contrast, reaction with $\cdot OH$ under typical flow conditions gives the isomeric radicals in the ratio [$\cdot CHMeOH$] : [$\cdot CH_2CH_2OH$] *ca.* 10 : 1). Although formation of $\cdot CHMeOH$ from $NH_3^{+\cdot}$ could be the result, at least in part, of abstraction of the hydroxylic hydrogen atom to yield $CH_3CH_2O\cdot$, and its subsequent [15] rearrangement, or of electron abstraction from oxygen to yield $CH_3CH_2OH^{+\cdot}$, and its subsequent deprotonation, results for other substrates (see below) suggest that direct C–H hydrogen-atom abstraction is involved. If this is so, then $NH_3^{+\cdot}$ is a reactive species resembling $\cdot OH$ somewhat in its electrophilic behaviour (kinetic data for $\cdot OH$ have been summarised[16]) but with enhanced selectivity in favour of hydrogen atoms activated by the presence of groups with a $+M$ effect on the attached carbon atom.

Reaction of $NH_3^{+\cdot}$ with propanol led to the detection of $CH_3CH_2\dot{C}HOH$ [a(1H) 1.46, a(2H) 2.16 mT], the major radical (75%), and $CH_3\dot{C}HCH_2OH$ [a(1H) 2.18, a(2H) 1.98, a(3H) 2.52 mT] {with $\cdot OH$ at low $[H_2O_2]_0$, to prevent further oxidation of $CH_3CH_2\dot{C}HOH$ by H_2O_2,[17,18] we detected $CH_3CH_2\dot{C}HOH$ (*ca.* 45%), $CH_3\dot{C}HCH_2OH$ (*ca.* 40%), and $\cdot CH_2CH_2CH_2OH$ (*ca.* 15%)}. The selectivity is again demonstrated. The detection of $CH_3\dot{C}HCH_2OH$, in contrast to the absence of $\cdot CH_2CH_2OH$ in the oxidation of ethanol, presumably reflects the greater reactivity of the secondary as compared with the primary alkyl fragment.

Reaction with propan-2-ol (*ca.* 0.2 mol l^{-1}) led to the detection of $\cdot CMe_2OH$ (with a maximum signal-to-noise ratio of *ca.* 100 : 1), but not $\cdot CH_2CHMeOH$,[17] and similarly in the reaction with tetrahydrofuran only the oxygen-conjugated (α) radical was detected; reaction of $\cdot OH$ with these substrates [17,18] gives both conjugated and non-conjugated radicals.

We have also examined the reaction of $NH_3^{+\cdot}$ with substrates which lack an activating oxygen substituent. For example, inclusion of 2-methylpropan-2-ol in the third stream led to the detection of $\cdot CH_2CMe_2OH$ [19] (the plateau in its concentration was reached at [Me_3COH] *ca.* 1.3 mol l^{-1}); evidently C–H abstraction is preferred to O–H abstraction, which would lead to $Me_3CO\cdot$ and thence $Me\cdot$.[13]

Propanoic acid reacted with $NH_3^{+\cdot}$ to give both $\cdot CH_2CH_2CO_2H$ and $\cdot CHMeCO_2H$ in the concentration ratio 1.8 : 1; provided that the rate coefficients for the three possible bimolecular termination rates for these radicals are similar, then this is also the ratio of the rates of the abstraction reactions at the two sites [*cf.* relative rate constants for [20] $\cdot OH$ (1 : 1.2) and for the relatively nucleophilic Me (1 : 3)]. Reaction with pentan-3-one at pH *ca.* 1.5 (where oxime formation [4] is retarded) gave rise to $\cdot CH_2CH_2COEt$ and $\cdot CHMeCOEt$ in the ratio 2.5 : 1 (*cf.*[20] $\cdot OH$, 1 : 1.7, $Me\cdot$ <1 : 7).

Reaction of $NH_3^{+\cdot}$ with but-3-enoic acid (vinylacetic acid) and with ethoxyethylene (ethyl vinyl ether) led to the detection of signals from $\cdot CH(CH_2CO_2H)CH_2NH_3^+$ [a(N) 0.63, a(1H) 2.24, a(4H) 2.32 mT] and $\cdot CH(OEt)CH_2NH_3^+$ [a(N) 0.99, a(1H) 1.64, a(2H) 1.17, a(2H) 0.189 mT], respectively. No other radicals were detected. This provides further evidence that addition to alkenic bonds is much faster than C–H abstraction, even when the radicals which would be obtained by the latter route possess stabilising features—an allyl substituent and an alkoxy group, respectively.

Effects of pH and complexing reagent. We have carried out preliminary experiments designed to test the effect of pH and of the presence of a complexing reagent, ethylenediaminetetra-acetic acid (EDTA), on the generation of $NH_3^{+\cdot}$ and, in particular, to generate and study the amino radical itself ($\cdot NH_2$).

For example, we have found that when reactions as described in the previous section were carried out at a higher pH (*ca.* 2.2; all other conditions being unchanged) somewhat higher radical concentrations were detected. We believe that this reflects an increased rate of radical generation at higher pH, as would be expected if reaction takes place with NH_2OH (rather than NH_3OH^+).[8] Quantitative aspects of this investigation are described in the subsequent section.

We have also carried out a series of reactions using a three-way flow system, with ethanol (*ca.* 3 mol l^{-1}) in the third stream and with ethylenediaminetetra-acetic acid added to the Ti^{III} stream (to prevent precipitation at pH values >*ca.* 2). At pH 1.5, no signals from the Ti^{III}–EDTA–NH_2OH system with added ethanol were obtained (in contrast with the detection of $\cdot CHMeOH$ in the absence of EDTA). We believe that this reflects the considerable reduction in the rate of the initiating reaction between Ti^{III}–EDTA and NH_2OH as compared with that without the complexing agent: [8] the resulting

---

[14] T. Shiga, *J. Phys. Chem.*, 1965, **69**, 3805.

[15] B. C. Gilbert, R. G. G. Holmes, H. A. H. Laue, and R. O. C. Norman, *J.C.S. Perkin II*, 1976, 1047.

[16] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493.

[17] R. O. C. Norman and P. R. West, *J. Chem. Soc. (B)*, 1969, 389.

[18] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1974, 824.

[19] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

[20] B. C. Gilbert, R. O. C. Norman, G. Placucci, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 885.

steady-state concentrations of $NH_3^{+\cdot}$ and $\cdot CHMeOH$ are thus lowered, and the latter is not detected.[3] However, a strong signal from $\cdot CHMeOH$ was detected from Ti^{III}–EDTA–NH_2OH in the presence of ethanol at pH *ca.* 5. This presumably reflects the increase in the concentration of free, rather than protonated, hydroxylamine and, possibly, the change in the extent of protonation of the complex (this has [21] pK_1 2.02, pK_2 8.64, pK_3 11.61), so that the rate of the initiation reaction is now enhanced.

At pH 6 the spectrum from $\cdot CHMeOH$ was accompanied by a weak signal, which had $a(N) = a(2H) =$ 1.25 mT, g 2.006 4, and which is assigned to [22] $NH_2O\cdot$. At this pH value the reactive entity is still presumably $NH_3^{+\cdot}$ (this has pK_a 6.7) and $\cdot CHMeOH$ probably arises *via* the abstraction reactions described above: the nitroxide $NH_2O\cdot$ probably arises by oxidation of unprotonated NH_2OH (NH_3OH^+ has pK_a 5.96 [23]), present in increasing quantities as the pH is raised [reaction (vii)].

$$NH_2OH + NH_3^{+\cdot} \longrightarrow NH_2O\cdot + H^+ + NH_3 \qquad \text{(vii)}$$

At pH 7 and 8 the spectrum of $\cdot CHMeOH$ was reduced in intensity and the signal from $NH_2O\cdot$ enhanced as compared with the spectra at pH 6; in addition the broad lines associated with the Ti^{III}–EDTA complex [24] were observed and, for experiments in which tap water rather than distilled water was employed, a signal with $a(N)$ 0.90, $a(H)$ 1.26 mT, g 2.006 4 was detected. This radical is evidently $\cdot ONHCO_2^-$.[22]

We suggest that, at least at pH 8, the radicals $\cdot CHMeOH$ and $NH_2O\cdot$ are derived by reactions of ethanol and hydroxylamine, respectively, with the unprotonated amino radical. Since the pK_a values for NH_3OH^+ and $NH_3^{+\cdot}$ are such that the pH cannot be adjusted to give $\cdot NH_2$ from hydroxylamine without also giving appreciable concentrations of $NH_2O\cdot$ and, in addition, because of the appearance of signals from Ti^{III}–EDTA at pH $>$*ca.* 7, it appears unlikely that the Ti^{III}–EDTA system in the presence of hydroxylamine can serve as a suitable source of $\cdot NH_2$ for quantitative work.

Kinetic Studies.—It has recently been shown [10,11] that for typical flow-system experiments with Ti^{III}–H_2O_2 the initiating reaction is incomplete when the reaction stream enters the cavity and also that short-lived radicals $R\cdot$ (from $\cdot OH$ and RH, with $2k_t$ typically *ca.* 10^9 l mol^{-1} s^{-1}) which are detected are formed in the cavity. A quasi steady-state system is established (refs. 11, 12, and 18 describe quantitative applications of this approach); we believe that a similar analysis is appropriate for the titanium(III)–hydroxylamine reaction.

Under conditions such that all $NH_3^{+\cdot}$ formed as in reaction (ii) is scavenged by an excess of added substrate RH [reaction (viii)] and where $R\cdot$ reacts *via* reaction (ix), with no oxidation, reduction, or addition pathways providing significant competition for its destruction, then application of the steady-state approximation for this radical and for $NH_3^{+\cdot}$ leads to equation (x) and (xi) (subscript t refers to concentrations of reagents in the cavity at a time t after mixing, rather than at mixing for which subscript zero is employed; the rate constant for the initiating reaction, $Ti^{III} + NH_2OH$, is referred to as k_{in}). Now $[NH_2OH]$ will depend on the *overall*

$$NH_3^{+\cdot} + RH \longrightarrow NH_3 + R\cdot + H^+ \qquad \text{(viii)}$$

$$2R\cdot \xrightarrow{k_t} \text{molecular products} \qquad \text{(ix)}$$

$$2k_t[R\cdot]^2 = k_{in}[NH_2OH]_t[Ti^{III}]_t \qquad \text{(x)}$$

$$[R\cdot] = \left(\frac{k_{in}[NH_2OH]_t[Ti^{III}]_t}{2k_t}\right)^{\frac{1}{2}} \qquad \text{(xi)}$$

concentration of hydroxylamine added, [Hydroxylamine], and also on the pH, and can be expressed as in (xii) and (xiii), where $K' = K_a/(K_a + [H^+])$. Equation

$$[NH_2OH] = [\text{Hydroxylamine}]K_a/(K_a + [H^+]) \qquad \text{(xii)}$$

$$= K'[\text{Hydroxylamine}] \qquad \text{(xiii)}$$

(xi) now becomes (xiv). For $[\text{Hydroxylamine}]_0 \gg$

$$[R\cdot] = (k_{in}K'[\text{Hydroxylamine}]_t[Ti^{III}]_t/2k_t)^{\frac{1}{2}} \qquad \text{(xiv)}$$

$[Ti^{III}]_0$, then $[\text{Hydroxylamine}]_t \simeq [\text{Hydroxylamine}]_0$ and, since protonation and deprotonation of NH_2OH will be extremely rapid, $[NH_2OH]$ remains essentially constant along the flow tube. The decay of $[Ti^{III}]$ down the flow tube is approximately first-order with $[Ti^{III}]_t = [Ti^{III}]_0\exp(-k_{in}K'[\text{Hydroxylamine}]_0t)$, where t is the time between mixing and observation. Equation (xiv) can now be rewritten as (xv). For experiments in which t, $[\text{Hydroxylamine}]_0$, and $[H^+]$ are kept constant it follows that $[R\cdot]$ should be proportional to the square root of the initial Ti^{III} concentration.

$$[R\cdot] = \{k_{in}K'[\text{Hydroxylamine}]_0[Ti^{III}]_0 \exp(-k_{in}K'[\text{Hydroxylamine}]_0t)/2k_t\}^{\frac{1}{2}} \qquad \text{(xv)}$$

We have tested the applicability of this equation for a series of experiments with ethanol added to the third stream {concentrations *after mixing* were $[EtOH]_0$ 0.6 mol l^{-1}, $[\text{Hydroxylamine}]_0$ 0.16 mol l^{-1}, with $[Ti^{III}]_0$ in the range 1—5 mmol l^{-1} and with t *ca.* 86 ms (see later): the pH was adjusted to be 1.8 (after mixing; see Experimental section)}. As can be seen from Figure 1, the dependence of $[\cdot CHMeOH]$ on $[Ti^{III}]_0^{\frac{1}{2}}$, at least in the range $[Ti^{III}]_0$ 1—3 mmol l^{-1}, is established. At higher concentrations of Ti^{III}, $[\cdot CHMeOH]$ levels off as would be expected if reaction (iv) competes with reaction (viii) (RH = EtOH) for the removal of $NH_3^{+\cdot}$. The rate constant for reaction (iv) must be greater by a factor of *ca.* 10^2 than that for reaction (viii) (RH = EtOH).

It has also been shown that for the Ti^{III}–H_2O_2 reaction in the presence of an efficient scavenger (RH), the observed concentration of $R\cdot$ is maximal, as $[H_2O_2]_0$ is varied, when $[H_2O_2]_0$ is approximately equal (as pre-

---

[21] J. Podlahova and J. Podlaha, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2267.

[22] C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, 1965, 751.

[23] R. A. Robinson and V. E. Bower, *J. Phys. Chem.*, 1961, **65**, 1279.

[24] S. Fujiwara, K. Nagashima, and M. Codell, *Bull. Chem. Soc. Japan*, 1964, **37**, 773.

dicted) to $(k_{in}\,t)^{-1}$, where k_{in} is the rate of the initiating reaction ($Ti^{III} + H_2O_2$) and where t is the mixing time. Similarly it can be shown that, for the Ti^{III}–NH_2OH reaction, $[R\cdot]_{max.}$ for variation of $[\text{Hydroxylamine}]_0$ should be obtained for a value of $[\text{Hydroxylamine}]_0$ given by equation (xvi). Since $K' = K_a/(K_a + [H^+])$ this

$$[\text{Hydroxylamine}]_{max.} = 1/k_{in}K't \qquad \text{(xvi)}$$

predicts that the value of $[\text{Hydroxylamine}]_0$ for which $[R\cdot]$ is maximum will depend on pH. We set out to establish whether this was indeed the case.

We carried out only two series of reactions, with the mixing time invariant and identical in each case [the mixing time was determined by carrying out a similar series of reactions, using the same mixing configuration, with Ti^{III}–H_2O_2–Bu^tOH, to determine $[\cdot CH_2CMe_2OH]$ as a function of $[H_2O_2]_0$: the value of $[H_2O_2]_0$ for $[\cdot CH_2CMe_2OH]_{max.}$ together with [11,12] $k(Ti^{III} + H_2O_2)$ 590 l mol^{-1} s^{-1} gave t 86 ms]. We carried out reactions with Ti^{III}–NH_2OH–EtOH (with concentrations after mixing $[Ti^{III}]_0$ 2.7 mmol l^{-1}, $[EtOH]_0$ 0.2 mol l^{-1}, [Hydroxylamine] 0.08—0.7 mol l^{-1}) at pH 1.8. A maximum in $[\cdot CHMeOH]$ was obtained for $[\text{Hydroxylamine}]_0$ 0.34 mol l^{-1} [see Figure 2(a)]; this, in conjunction with the value of t measured above gives, from equation (xvi) $k_{in}K'$ 34.2 and k_{in} 5.4×10^5 l mol^{-1} s^{-1}. This series of reactions was also carried out at pH *ca.* 2.1; the maximum in the plot of $\cdot CHMeOH$ against $[\text{Hydroxylamine}]_0$ occurred at a lower value of the latter (0.16 mol l^{-1}) than at pH 1.8 [see Figure 2(b)]. This gives, as explained above, $k_{in}K'$ 72.7 and k_{in} 5.8×10^5 l mol^{-1} s^{-1}. These results for k_{in} are in reasonable agreement with each other and with that reported [8] (1.45×10^6 l mol^{-1} s^{-1}). In particular, the results, particularly the dependence on pH of the value of $[\text{Hydroxylamine}]_0$ for maximum $[\cdot CHMeOH]$, suggest that NH_2OH in its *unprotonated* form is responsible for the generation of $NH_3^{+\cdot}$. If reaction between Ti^{III} and $[NH_3OH]^+$ had been dominant, it seems unlikely that the value of $[\text{Hydroxylamine}]_0$ to give $[\cdot CHMeOH]_{max.}$ would have shown as marked a pH dependence.

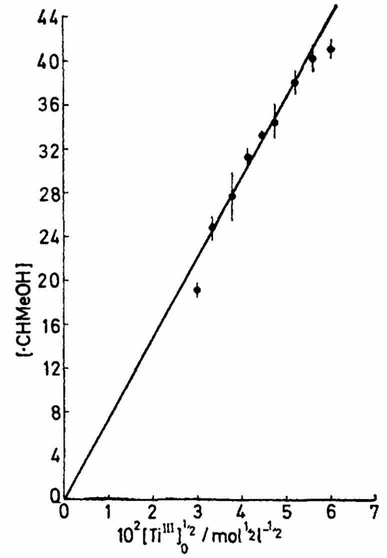

FIGURE 1 Variation of $[\cdot CHMeOH]$ (arbitrary units) with $[Ti^{III}]_0^{\frac{1}{2}}$ in the Ti^{III}–NH_2OH–EtOH reaction at pH 1.8

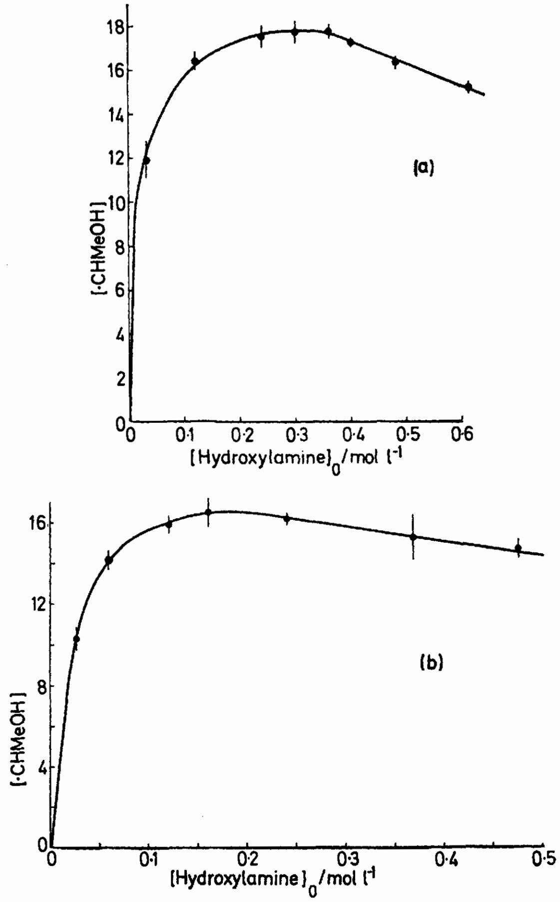

FIGURE 2 (a) Variation of $[\cdot CHMeOH]$ (arbitrary units) with $[\text{Hydroxylamine}]_0$ in the Ti^{III}–NH_2OH–EtOH reaction at pH 1.8; (b) Variation of $[\cdot CHMeOH]$ (arbitrary units) with $[\text{Hydroxylamine}]_0$ in the Ti^{III}–NH_2OH–EtOH reaction at pH 2.1

We have also carried out a series of competitive kinetic experiments in which two substrates were added to the third stream of the flow system (*cf.* refs. 11 and 18 for similar experiments with $\cdot OH$). Equations (xvii)—(xxi) describe the general reaction scheme when two hydrogen donors are present (we have not studied addition reactions because of kinetic complications introduced by reactions of radicals $R\cdot$ with alkenes).

$$NH_3^{+\cdot} + R^1H \longrightarrow R^{1\cdot} + H^+ + NH_3 \qquad \text{(xvii)}$$

$$NH_3^{+\cdot} + R^2H \longrightarrow R^{2\cdot} + H^+ + NH_3 \qquad \text{(xviii)}$$

$$2R^{1\cdot} \longrightarrow \text{molecular products} \qquad \text{(xix)}$$

$$R^{1\cdot} + R^{2\cdot} \longrightarrow \text{molecular products} \qquad \text{(xx)}$$

$$2R^{2\cdot} \longrightarrow \text{molecular products} \qquad \text{(xxi)}$$

If we assume that $2k(\text{xix}) = k(\text{xx}) = 2k(\text{xxi})$, then steady-state analysis of the reaction scheme leads to equation (xxii), which forms the basis for the interpretation of our results.

$$[\mathrm{R}^{2}\cdot]/[\mathrm{R}^{1}\cdot] = k(\mathrm{xviii})[\mathrm{R}^{2}\mathrm{H}]/k(\mathrm{xvii})[\mathrm{R}^{1}\mathrm{H}] \quad (\mathrm{xxii})$$

When mixtures of methanol and ethanol were oxidised, signals from both $\cdot CH_2OH$ and $\cdot$CHMeOH were detected. For these radicals, the termination rates for dimerization are virtually identical (2.4×10^9 and 2.3×10^9 l mol^{-1} s^{-1}, respectively; see ref. 25) and we should expect the rate constant for the combination of the two different radicals [reaction (xx)] to be similar. Thus equation (xxii) should apply. For a series of reactions employing varying [MeOH] and [EtOH], with $[Ti^{III}]_0$ 2.7 mmol l^{-1} and $[\text{Hydroxylamine}]_0$ 0.16 mol l^{-1} (concentrations are those after mixing), the concentrations of $\cdot CH_2OH$ and $\cdot$CHMeOH have been monitored. The results, plotted according to equation (xxii) are shown in Figure 3, from which it can be seen that the predicted behaviour is indeed observed. From the graph we obtain a ratio for the rate constant for hydrogen-atom abstraction from ethanol and methanol as 2.9 : 1 (*cf.*[16] *ca.* 2.4 : 1 for reactions with $\cdot$OH). We have also carried out competitive experiments involving EtOH–Me_2CHOH and MeOH–Me_3COH. Radicals $\cdot CMe_2OH$ and $\cdot CH_2CMe_2OH$ have termination rate constants (1.4×10^9 l mol^{-1} s^{-1} in both cases)[25] similar to those for $\cdot CH_2OH$ and $\cdot$CHMeOH, so that equation (xxii) should still represent a close approximation to the radicals' behaviour; we find that in all cases linear relationships (*cf.* Figure 3) are established. Our results for the relative rate constants are collected in the Table, together with data for $\cdot$OH for comparison. It can be seen that, as deduced above, $NH_3^{+\cdot}$ is more selective than hydroxyl.

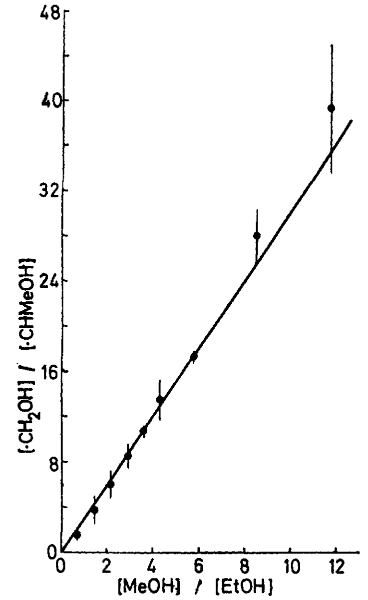

FIGURE 3 Variation of $[\cdot CH_2OH]/[\cdot CHMeOH]$ with [MeOH]/[EtOH] in the Ti^{III}–NH_2OH–EtOH/MeOH system

Relative rates of hydrogen-atom abstraction reactions of $NH_3^{+\cdot}$ and $\cdot$OH with various alkanols

RH	$k(NH_3^{+\cdot})$ [a]	$k(\cdot OH)$ [b]
CH_3OH	1.0	1.0
CH_3CH_2OH	2.9	2.4
$(CH_3)_2CHOH$	6.4	2.4
$(CH_3)_3COH$	0.2	0.8

[a] This work. [b] From ref. 16.

EXPERIMENTAL

The e.s.r. spectrometer and flow system have been described previously.[12] Solution (i) contained, typically, 12.5% w/v titanium(III) chloride solution (*ca.* 10 ml l^{-1}, 8 mmol l^{-1}) together with either 98% sulphuric acid for experiments at low pH, or EDTA (disodium salt) in molar concentration twice that of Ti^{III}, together with sulphuric acid or ammonia (*d* 0.880) added in appropriate quantities to obtain the required pH. This stream was made up in deoxygenated water. Solution (ii) contained hydroxylamine hydrochloride (typically 33 g l^{-1}, *ca.* 0.5 mol l^{-1}) and, for qualitative experiments at low pH, 98% sulphuric acid; for quantitative experiments at controlled pH (1.8 and 2.1), ammonia (*d* 0.880) was added to this stream to achieve the required pH on mixing. Solution (iii) contained the organic substrate (0.1—4 mol l^{-1}) or substrates. All solutions were deoxygenated with a nitrogen purge prior to mixing. All compounds employed were commercially available and were used without further purification.

Relative radical concentrations were obtained by the double-integration procedure.[26]

We thank the S.R.C. for support.

[6/1795 *Received, 24th September,* 1976]

---

[25] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794.

[26] P. B. Ayscough, ' Electron Spin Resonance in Chemistry,' Methuen, London, 1967.