Relative Reactivities of Aliphatic Alcohols and Amines towards Aminyl Radicals

By **Giuseppe Farnia, Renato Tomat,** and **Elio Vianello,*** Institute of Physical Chemistry and Electrochemistry of the University, Via Loredan 2, 35100 Padova, Italy

The relative reactivities for hydrogen abstraction by aminyl radicals from aliphatic alcohols and amines have been determined both by direct kinetic methods and by polarographic measurements. The reactivities increase with increasing chain length as occurs with hydroxyl radicals. A linear correlation exists between the logarithms of the aminyl and hydroxyl reactivities, which indicates the similarity of the mechanism and the relative sensitivity to structural changes for the two reactions.

ALTHOUGH reactions between short-lived free radicals and organic substrates have received increasing attention and several methods have been proposed for the production of the radicals and for the determination of their reactivities, relatively little information is available on reactions involving aminyl radicals.[1-10] In this respect a polarographic method has been proposed for the evaluation of the reactivity of addition of radicals such as OH˙ and NH_2˙ to compounds bearing carbon–carbon double bonds.[11-13] In this paper the method has been extended to the study of hydrogen abstraction by aminyl radicals from aliphatic alcohols and amines. The relative reactivities thus evaluated are compared with those obtained by a direct kinetic procedure [9] and with the reactivities of the same alcohols towards hydroxyl radicals.

As is well known, a suitable source of NH_2˙ radicals

is provided by the redox reaction between Ti^{3+} ions and hydroxylamine in acid media [1] [reactions (1) and (2)].

$$Ti^{3+} + NH_2OH \xrightarrow[H^+]{k_1} NH_2{}^{\bullet} + H_2O + Ti^{4+} \quad (1)$$

$$NH_2{}^{\bullet} + Ti^{3+} \xrightarrow[H^+]{k_2} Ti^{4+} + NH_3 \quad (2)$$

Indirect evidence for the intermediate formation of NH_2˙ radicals is given by their ability to initiate free radical polymerisation [1,9] and to add to unsaturated compounds to give amino-derivatives.[2] They have also been revealed more directly by the e.p.r. spectra of the radicals formed by their addition to vinyl compounds in stationary flux conditions.[3]

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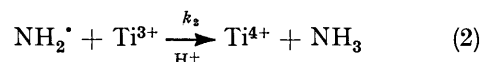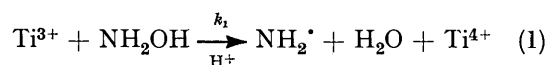
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In the presence of suitable substrates HS, the abstraction (3) of a hydrogen atom is expected to take place, in competition with reaction (2).

$$NH_2^\bullet + HS \xrightarrow{k_3} NH_3 + S^\bullet \qquad (3)$$

On the assumption that the stationary state hypothesis holds for $NH_2^\bullet$ radicals, their formation rate v_1, is equal to their decay rate, $v_2 + v_3$. Thus equation (4) can be readily obtained; the term $k_2[Ti^{3+}]/(k_2[Ti^{3+}] + k_3[HS])$ ($=\alpha$) corresponds to the fraction of $NH_2^\bullet$

$$-d[Ti^{3+}]/dt = k_1[Ti^{3+}][NH_2OH]$$
$$\left(1 + \frac{k_2[Ti^{3+}]}{k_2[Ti^{3+}] + k_3[HS]}\right) \quad (4)$$

radicals which react with the Ti^{3+} ion. It should be noted that in the absence of any substrate or in the presence of an unreactive one, $\alpha = 1$; when practically all the radicals react with the substrate, $\alpha = 0$. Therefore, if one or other of these conditions is fulfilled throughout the reaction, the term in parentheses in equation (4) reduces simply to a stoicheiometric coefficient and the Ti^{3+} decay results a second-order reaction with experimental rate constants equal to $2k_1$ or k_1, respectively. When none of these conditions holds, equation (4) is still easily integrable, provided the reaction is carried out with excess of both NH_2OH and HS, so that their concentrations can be taken as constant throughout the process. Equation (5) is then obtained, where

$$\lg \frac{[Ti^{3+}]_0}{[Ti^{3+}]_t} = \tfrac{1}{2} \lg \frac{2R[Ti^{3+}]_0[HS]}{2R[Ti^{3+}]_t + [HS]} + 0.43\, k'_1\, t \quad (5)$$

$[Ti^{3+}]_0$ and $[Ti^{3+}]_t$ are the concentrations of Ti^{3+} at times zero and t, respectively, $R = k_2/k_3$, and $k'_1 = k_1[NH_2OH]$. Thus the reactivity ratio R can be evaluated by following the change of Ti^{3+} concentration with time, once the value of the pseudo-first-order rate constant k_1' has been determined by a separate experiment in the absence of substrate.[9]

An alternative method for the determination of the relative reactivities of active substrates towards the free radicals produced as intermediates in a redox process, is based on polarographic measurements.[11-14] In the case under consideration, the redox reaction is again the oxidation of Ti^{3+} by NH_2OH in acid media; however Ti^{3+} is not present in the bulk of the solution but is produced at the electrode by reduction of Ti^{4+}, at a potential at which NH_2OH is not reducible because of activation overvoltage. Ti^{3+} is then re-oxidised, as before, in a thin 'reaction layer' adjacent to the electrode surface, producing a 'catalytic current' which is a function of the re-oxidation rate expressed by equation (4). In order to determine the reactivity ratio k_2/k_3, the limiting catalytic current needs to be calculated in a rigorous way through the solution of

the mass transfer problem with respect to the electrode. Whereas this is a simple matter if only reactions (1) and (2) need to be taken into account,[15-17] in the presence of a substrate it involves the solution of a non-linear partial derivative differential equation system.[14] However, for the sake of evaluating relative values of the reactivity of different substrates, with respect to that of an arbitrarily chosen standard, use can be made of the approximate reaction layer method.[15] This gives equation (6) for the limiting catalytic reduction current, where nF is the number of Faradays per mole

$$i_1 = nFq\mu d[Ox]_0/dt \quad (6)$$

of ions reduced at the cathode, q is the average value of the dropping mercury electrode surface area during the life-time of a drop, μ is the thickness of the reaction layer and $d[Ox]_0/dt = -d[Red]_0/dt$ is the rate of re-oxidation of the reduced species at the electrode surface. For the case under consideration, the ratio of the limiting current in the presence (index s) and absence (index c) of substrate results from equations (6) and (4) with the hypothesis that $[NH_2OH]$ is high

$$\frac{i_s}{i_c} = \frac{\mu_s}{\mu_c} \cdot \frac{1 + \alpha_0}{2} \quad (7)$$

enough to be considered independent of the distance from the electrode, i.e. that reaction (1) is pseudo-first-order. In these conditions $\mu_c = (D/2k_1[NH_2OH])^{\frac{1}{2}}$, where D is the diffusion coefficient of Ti^{3+}. It should be noted that for $[HS] = 0$, $\alpha_0 = 1$ and $\mu_s = \mu_c$. On the other hand, for $[HS]$ high enough for reaction (2) to be negligible, $\alpha_0 = 0$ and $\mu_s = (D/k_1[NH_2OH])^{\frac{1}{2}}$. The ratio i_s/i_c will therefore vary between 1 and $1/2^{\frac{1}{2}}$ as the substrate concentration is raised. Let us now consider the case that, for a given value of i_c, the same value of i_s, intermediate between the limits defined above, is obtained with two substrates HS and HS'. This will happen, in general, with different concentrations of the substrates, owing to their different reactivities. One has then $\mu_s(1 + \alpha_0) = \mu'_s(1 + \alpha_0')$. In these conditions it is reasonable to admit that the reaction layer thicknesses are approximately equal, so that $\alpha_0 \simeq \alpha_0'$, i.e., equation (8) applies. This means

$$k_3/k_3' \simeq [HS']/[HS] \quad (8)$$

that, putting the reactivity of one of the substrates arbitrarily equal to unity, the reactivity of any other can be obtained from the ratio of the substrate concentrations necessary to cause an equal decrease in i_c.

EXPERIMENTAL

Materials.—Reagent grade chemicals were used throughout. Solutions were standardised according to classical methods. Titanium tetrachloride solutions were prepared

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by air oxidation in 0·4M-H₂SO₄ of a commercial 15% solution of TiCl₃. The stable yellow complex formed with H_2O_2 in 2M-H₂SO₄ was determined colorimetrically. Titanium trichloride solutions in 0·2M-H₂SO₄ were titrated with standard solutions of Ce^{4+} ions. The end point of the titration was checked either potentiometrically or using N-phenylanthranilic acid as indicator. Hydroxylamine sulphate solutions, *ca.* $10^{-2}M$, were treated with a 20% excess of Ti^{3+} in 0·2M-H₂SO₄. Under these conditions two Ti^{3+} ions react with one molecule of NH_3OH. The Ti^{3+} remaining after completion of the reaction was titrated with Ce^{4+}, as indicated above. The following alcohols and amines were used as substrates: methanol, ethanol, n-propanol, propan-2-ol, n-butanol, t-butyl alcohol, n-pentanol, n-hexanol, methylamine, ethylamine, n-propylamine, n-butylamine, n-pentylamine, n-hexylamine, n-heptylamine, and n-octylamine. Although all the substrates used were reagent grade chemicals, further purification by fractional distillation was carried out in some cases. Solutions were deaerated with electrolytically produced hydrogen, from which the last traces of oxygen had been removed by passing it through a catalytic purifier, Deoxo. The gas was presaturated by bubbling it through a sample of the solution, before introducing it into the measurement cell.

Apparatus.—Polarographic measurements at 30 ± 0·1° were performed by means of an instrument formed by a conventional d.c. polarising unit and a Lange–Nachlauf-schreiber current recorder equipped with a Multiflex galvanometer. H Type polarographic cells were used in which the test solution was in contact with a saturated calomel electrode through a fritted glass disc.

Procedure.—Kinetic runs have been carried out by recording amperometrically, at constant potential, the decay of the anodic diffusion current of Ti^{3+} as follows: solutions of the base electrolyte, 2M-H₃PO₄, with and without the substrate, and previously deaerated, were added with a suitable quantity of Ti^{3+} just before starting the run and the indicator electrode was polarised at the voltage of 0·01 V, corresponding to the limiting diffusion current of Ti^{3+}. A known excess of NH_2OH was then rapidly injected into solution, stirred by hydrogen bubbling. The gas flux was then interrupted and the decrease of Ti^{3+} limiting current was recorded. With this procedure the mixing time could be considered negligible in comparison with the reaction time, so that zero time may be assumed to be the time at which all NH_2OH was injected. Initial concentrations were as follows: $[Ti^{3+}] = 4\cdot00 \times 10^{-4}M$; $[NH_2OH] = 10^{-2}M$; [Substrate] = $4\cdot00 \times 10^{-3}M$.

Concentrations generally used in the polarographic measurement were: $[H_3PO_4] = 2M$; $[NH_2OH] = 0\cdot76$ and 1M; $[Ti^{4+}] = 4\cdot45 \times 10^{-4}$, $1\cdot46 \times 10^{-3}$, and $1\cdot04 \times 10^{-4}M$ with alcohols and $2\cdot25 \times 10^{-4}$, $4\cdot54 \times 10^{-4}$, and $1\cdot62 \times 10^{-3}M$ with amines respectively. Before each series of measurements at variable substrate concentrations the value of the catalytic current in the absence of substrate was checked. Different dropping mercury electrode capillaries were used in the course of the investigations; their characteristics are not reported here, since for our purpose ratios of currents rather than absolute values are needed. However each series of measurements with a single substrate and the determination of the corresponding reference catalytic current i_0, in the absence of substrate, were performed with the same capillary and the same drop-time and mercury flow conditions.

RESULTS

Kinetic Runs.—The kinetics of the reaction between Ti^{3+} and NH_2OH in the absence of substrate have been already investigated, either with stoicheiometric amount of the reagents, so that the process occurs in second-order conditions, or in the presence of an excess of NH_3OH leading to a pseudo-first-order process.[14] The value of k_1 obtained for both conditions, $1\cdot83 \pm 0\cdot05$ 1 mol⁻¹ s⁻¹ at 30°, is in satisfactory agreement with that obtained by polarography.[13]

The addition of a substrate which interacts with NH_2ᐧ modifies the decay rate of Ti^{3+}, since reaction (3) occurs in competition with (2). In order to obtain the value k_2/k_3 according to equation (5), it is necessary that both NH_2OH and the substrate are present in excess with respect to Ti^{3+}, so that their concentration can be considered practically constant during the reaction. On the
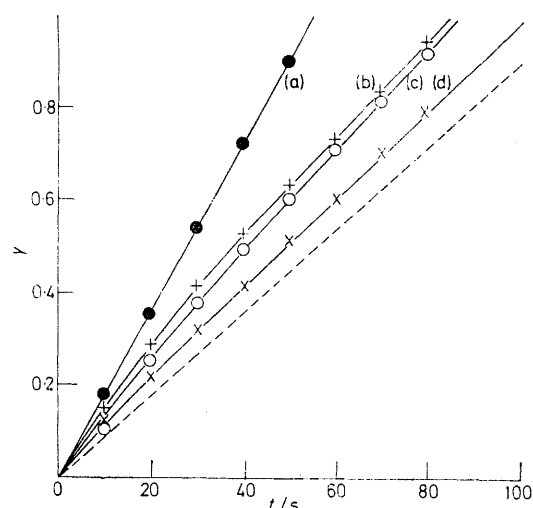

FIGURE 1 Values of $y\{ = \lg([Ti^{3+}]_0/[Ti^{3+}]_t)\}$ against time in the absence (a) and in the presence of some alcohols: (b) ethanol; (c) n-propanol; (d) n-butanol. $[Ti^{3+}] = 4 \times 10^{-4}M$; $[NH_2OH] = 10^{-2}M$; [alcohol] $= 4 \times 10^{-3}M$. The dotted line represents the value of y corresponding to complete suppression of reaction (2)

other hand the substrate concentration must not be so high that reaction (2) is completely suppressed, otherwise the decay of Ti^{3+} would result in a pseudo-first-order reaction $(-d[Ti^{3+}]/dt = k_1'[Ti^{3+}])$. A preliminary series of runs was performed at variable substrate concentrations and constant initial concentration of the other two reagents: $[Ti^{3+}] = 4\cdot00 \times 10^{-4}M$ and $[NH_2OH] = 1\cdot00 \times 10^{-2}M$. It was thus found that reaction (2) occurs appreciably up to $4 \times 10^{-3}M$-hexyl alcohol, which is the most reactive among the substrates studied. Therefore this was the concentration generally employed in kinetic runs.

From the kinetic curves recorded for the different substrates it has been possible to calculate the corresponding reactivity ratio k_2/k_3 by applying equation (5) at different reaction times. Values of k_2/k_3 thus obtained were practically constant for each substrate up to 70% conversion. Furthermore they were practically independent of the initial substrate concentration, in the interval 2—8 × 10⁻³M. Values reported in Table 3 are the averages of the ratios k_2/k_3 determined for each substrate at various reaction times.

Figure 1 shows plots of the term $\lg[Ti^{3+}]_0/[Ti^{3+}]_t$ against time for the reaction in the presence of ethyl, n-propyl, and n-butyl alcohols. The difference between the actual value of the term under the given conditions and the value that it would assume if all the $NH_2^{\cdot}$ radicals were captured (dotted line) represents the value of the term $\frac{1}{2}\lg\{(2R[Ti^{3+}]_0 + [HS])/(2R[Ti^{3+}]_t + [HS])\}$.

amines in Figures 2 and 3, respectively. This ratio decreases with increasing substrate concentration and reaches, in many cases, the theoretical limiting value $1/2^k$, corresponding to total suppression of reaction (2). Only propan-2-ol shows anomalous behaviour, since the i_s/i_c ratio decreases below the limit $1/2^k$ upon increasing the alcohol concentration.

TABLE 1

Relative reactivity of alcohols at different i_s/i_c ratios

i_s/i_c	$(CH_3)_3C-OH$	CH_3-OH	CH_3CH_2-OH	$CH_3[CH_2]_2-OH$	$CH_3[CH_2]_3-OH$	$CH_3[CH_2]_4-OH$	$CH_3[CH_2]_5-OH$
0·95	0·03	0·10	0·48	0·70	1	1·5	1·9
0·925	0·03	0·11	0·49	0·68	1	1·4	1·9
0·90		0·96	0·47	0·68	1	1·4	1·9
0·875		0·98	0·47	0·69	1	1·4	1·8
0·85			0·49	0·68	1	1·3	1·8
0·80			0·48	0·67	1	1·4	1·8

TABLE 2

Relative reactivity of amines at different i_s/i_c ratios

i_s/i_c	$CH_3[CH_2]_2NH_3$	$CH_3[CH_2]_3NH_3$	$CH_3[CH_2]_4NH_3$	$CH_3[CH_2]_5NH_3$	$CH_3[CH_2]_6NH_3$	$CH_3[CH_2]_7NH_3$
0·925	0·12	1	2·7			
0·90	0·11	1	2·6	5·0	8·2	15
0·875		1	2·7	5·1	8·1	14
0·85		1	2·6	5·1	8·2	13
0·80		1	2·5	4·9	8·1	14

TABLE 3

Relative reactivities of alcohols towards $NH_2^{\cdot}$ and $OH^{\cdot}$

Alcohols	(k_3/k_3') $NH_2^{\cdot}$ [a]			(k_2/k_3) $NH_2^{\cdot}$ [b]	(k_3/k_3') $NH_2^{\cdot}$ [b]	(k_3/k_3') $OH^{\cdot}$ [c]
	$[Ti^{4+}]$ $4·45 \times 10^{-4}M$	$[Ti^{4+}]$ $1·46 \times 10^{-3}M$	$[Ti^{4+}]$ $1·04 \times 10^{-2}M$			
CH_3-OH	0·12	0·10	0·13	52	0·11	0·22
CH_3CH_2-OH	0·47	0·48	0·48	11·5	0·50	0·50
$CH_3[CH_2]_2-OH$	0·66	0·68	0·69	8·6	0·67	0·75
$CH_3[CH_2]_3-OH$	1	1	1	5·8	1	1
$CH_3[CH_2]_4-OH$	1·40	1·42	1·47	3·8	1·52	1·25
$CH_3[CH_2]_5-OH$	1·90	1·87	1·85			1·53
$(CH_3)_3-OH$	0·02	0·03	0·03			0·12

[a] Polarographic results. [b] Kinetic results. [c] Ref. 25.

TABLE 4

Relative reactivities of amines towards $NH_2^{\cdot}$ and $OH^{\cdot}$

Amines	$(k_3/k_3')NH_2^{\cdot}$ [a]			$(k_3/k_3')OH^{\cdot}$ [b]
	$[Ti^{4+}]$ $2·25·10^{-4}M$	$[Ti^{4+}]$ $4·50·10^{-4}$	$[Ti^{4+}]$ $1·62·10^{-3}$	
$CH_3-NH_3^+$				0·006
$CH_3CH_2-NH_3^+$				0·09
$CH_3[CH_2]_2-NH_3^+$	0·11	0·13	0·10	0·28
$CH_3[CH_2]_3-NH_3^+$	1	1	1	1
$CH_3[CH_2]_4-NH_3^+$	2·6	2·5	2·6	1·8
$CH_3[CH_2]_5-NH_3^+$	5·0	5·5	5·8	
$CH_3[CH_2]_6-NH_3^+$	8·1	9·6	8·0	
$CH_3[CH_2]_7-NH_3^+$	14	16	15	
$(CH_3)_3-CNH_3^+$				0·15

[a] This work. [b] Ref. 23.

Since kinetic experiments were mainly performed for the sake of comparison with the polarographic results, only a few alcohols were treated in this way.

Polarography.—Values of the ratio i_s/i_c are plotted against the concentration of the various alcohols and

The relative reactivity values, calculated according to equation (8) are reported in Tables 1 and 2, for alcohols and amines respectively and for different values of i_s/i_c. Such results show that the reactivities are satisfactorily independent of the catalytic current ratios. The data of

reactivity reported in Tables 3 and 4 together with the results of the kinetic runs, are averages of the values determined at the different i_s/i_c ratios. These data show
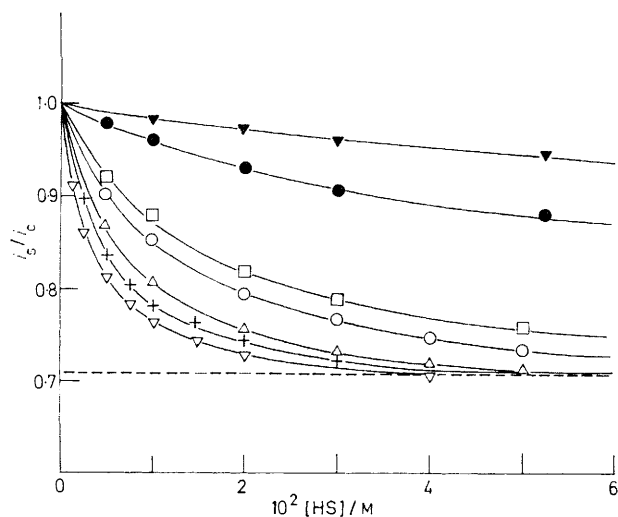

FIGURE 2   Values of the ratio i_s/i_c as a function of alcohol concentration: ▼ t-butyl; ● methyl; □ ethyl; ○ n-propyl; △ n-butyl; + n-amyl; ▽ n-hexyl. [Ti⁴⁺] = 1·46 × 10⁻³M; [NH₂OH] = 0·76M
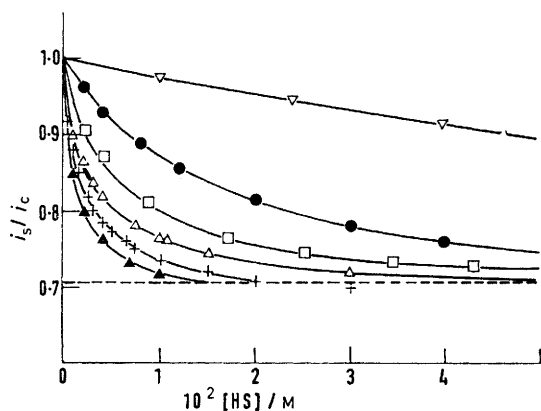
FIGURE 3   Values of the ratio i_s/i_c as a function of amine concentration: ▽ n-propyl; ● n-butyl; □ n-amyl; △ n-hexyl; + n-heptyl; ▲ n-octyl. [Ti⁴⁺] = 4·54·10⁻⁴M; [NH₂OH] = 0·76M

that the reactivities are also satisfactorily independent of [Ti⁴⁺]. The same is true for the hydroxylamine concentration, provided the latter is high enough for reaction (1) to be pseudo-first order.
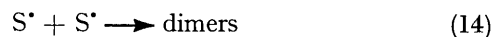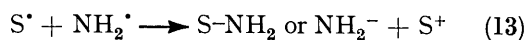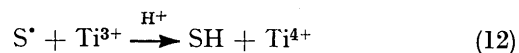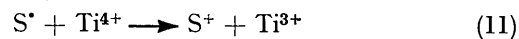
DISCUSSION

Alcohols and amines are known to undergo hydrogen abstraction both with hydroxyl and aminyl radi-

cals [2,3,5,18-26] A condition for the values of reactivities obtained to be attributable to the reaction with aminyl radicals is that reactions such as (9) and (10) are negligible. Literature data show that both reactions can

$$Ti^{3+} + NH_2OH \longrightarrow Ti^{4+} + NH_3 + OH^\bullet \quad (9)$$

$$NH_2^\bullet + H_2O \longrightarrow OH^\bullet + NH_3 \quad (10)$$
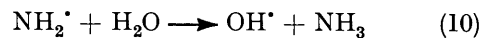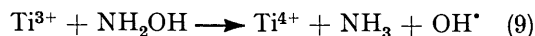
be excluded either on the basis of thermodynamic considerations on the different values of the formation energy of $OH^\bullet$ and $NH_2^\bullet$ radicals [1] or on the basis of e.p.r. results.[3,5]

Other reactions that could occur in our conditions are (11)—(15). If reaction (11) occurred to an appreciable

$$S^\bullet + Ti^{4+} \longrightarrow S^+ + Ti^{3+} \quad (11)$$

$$S^\bullet + Ti^{3+} \xrightarrow{H^+} SH + Ti^{4+} \quad (12)$$

$$S^\bullet + NH_2^\bullet \longrightarrow S-NH_2 \text{ or } NH_2^- + S^+ \quad (13)$$

$$S^\bullet + S^\bullet \longrightarrow \text{dimers} \quad (14)$$

$$S^\bullet + NH_2OH \longrightarrow$$
$$\text{oxidised products} + NH_2^\bullet + OH^- \quad (15)$$

extent during the drop-time the values of the ratio i_s/i_c would decrease below the limit $1/2^{\frac{1}{2}}$ as the substrate concentration is increased, since Ti^{4+} would then be reduced both chemically and electrochemically.

This effect, which has been in fact observed in the presence of alcohols with the catalytic system Fe^{3+}–H_2O_2, which produces $OH^\bullet$ radicals, is due to Fe^{3+} ions oxidising the hydroxyl radicals formed by hydrogen abstraction.[11,18,19] This seems not to happen with the Ti^{4+}–H_3PO_4 complex, probably because of its lower oxidation potential. Propan-2-ol is an exception in this respect. It is known however that radicals derived from secondary alcohols are in fact more easily oxidised by metal ions than those derived from primary alcohols, because of the higher inductive effect which increases the electronegativity at the site of free valence.[18,19]

As for equation (12), it should be noted that, if it were the only possible way for $S^\bullet$ radicals to react, no lowering of catalytic current would be observed by addition of substrate. Although such a reaction may operate under our conditions, it is doubtful that it occurs to an appreciable extent, as is suggested by the fact that values of reactivity are independent of the substrate concentration in the whole range explored, and of the concentration of Ti^{4+} and NH_2OH. Reaction (13) should also not occur appreciably, because of the low stationary concentration of the hydroxyl and

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[26] G. E. Adams, J. W. Boag, J. Current, and B. D. Michael, 'Pulse Radiolysis,' Academic Press, London–New York, 1965, p. 131.

aminyl radicals, which should preferably react according to (2) or (3).

It seems therefore that under our experimental conditions S* radicals should preferably react by equation (14), to give dimers or by (15), owing to the relatively higher oxidation power of hydroxylamine, which is present in large excess. The insensitivity of the i_s/i_c values to the variation of hydroxylamine concentration suggests however that the reactivity values are not substantially affected by reaction (15).

With regard to the conditions for the kinetic runs it should be observed that, in the integration of equation (5) the concentrations of both NH_2OH and substrate have been supposed to be constant. This is true, to a good approximation, for NH_2OH under our experimental conditions. It can be easily calculated that NH_2OH consumption at the end of the reactions is of the order of 5% at the maximum, even taking into account equation (15). The excess of substrate is lower than that of NH_2OH, for the reasons mentioned above; nevertheless, since only the fraction $1 - \alpha$ of the NH_2* radicals reacts with the substrate, its consumption at the end of the reaction is certainly <10%.

Analogous considerations hold for the polarographic conditions, also taking into account that the reaction layer is renewed at each mercury drop so that the reaction times to be considered are the few seconds of the drop-life. This is in agreement with the fact that the values of reactivity are independent of Ti^{4+}, substrate, and NH_2OH concentrations.

E.p.r. spectra show that OH* abstracts a hydrogen atom preferably from C–H group α to hydroxy.[20] The observed high specificity for the α-C–H bonds of alcohols indicates that the resonance effects of the oxygen atom in the resulting free radical must completely outweigh the inductive electron-attracting effect of the hydroxy-group. The increase in reactivity with increasing alkylation of the α-carbon atom must be due to the increasing, inductive, electron-repelling effect associated with the alkyl groups, thus reducing the α-C–H bond energy.

The behaviour of amines is quite different from that of alcohols. The first two compounds in the series, methyl- and ethyl-amine, do not show any appreciable reactivity towards OH*.[21,22] Since these compounds are essentially completely protonated in acid media, their lack of reactivity is attributable to the strong $-I$ effect of the functional group. n-Propylamine is the simplest aliphatic amine from which OH* abstracts an hydrogen atom. The e.p.r. spectrum of the resulting species corresponds to the radical $\dot{C}H_2$–CH_2–$CH_2NH_3^+$,

[27] M. Szwarc and J. H. Binks, ' Theoretical Organic Chemistry,' Butterworths, London, 1959, p. 262.

produced by ω-abstraction.[21,22] For higher amines e.p.r. spectra show that the reaction site is not unique, hydrogen abstraction occurring more from the C–H bond adjacent to the terminal methyl group than from the C–H bonds in the methyl group.[22] The increase of reactivity with chain length suggests that the $+I$ effect of alkyl groups counteracts the opposite $-I$ of NH_3^+.

Relative values of the rate constant for reaction of OH* with the aliphatic alcohols and amines are reported in Tables 3 and 4 respectively, together with those for the NH_2* reactions obtained by us. If the relative reactivities of both radicals towards the same substrate series are compared,[27] one sees the same behaviour for OH* and NH_2*.

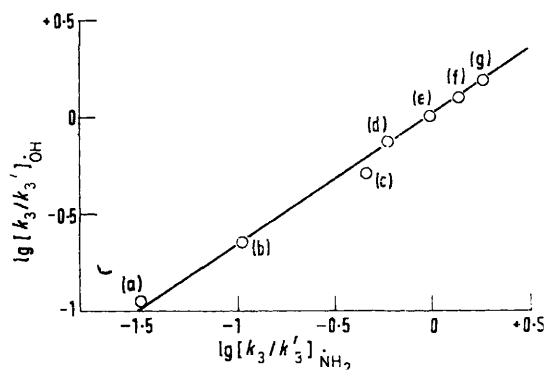The relationship between relative reactivities of these radicals towards alcohols is shown in Figure 4. It

FIGURE 4 Relation between OH* and NH_2* reactivities towards (a) t-butyl; (b) methyl; (c) ethyl; (d) n-propyl; (e) n-butyl; (f) n-amyl; (g) n-hexyl alchohol

may be seen that a linear correlation between the logarithms of the rate constants, and therefore between the free energy of activation of the two reactions, exists when the chain length of the substrate is increased. However the value of the slope: 0·70, i.e. the ' relative selectivity ' of the radicals, indicates that an increase of chain length is more effective in influencing the relative stabilities of the transition state of the NH_2* than of the OH* reaction. On the likely hypothesis that the reaction site is the same for both radicals, namely the carbon α to the hydroxy-group, the greater ' selectivity ' of NH_2* involves a larger amount of bond breaking and of charge separation of the transition state than does the OH* reaction.[28]

[28] W. A. Pryor, ' Free Radicals,' McGraw-Hill, New York, 1966, p. 170.