The Reactions of the Ammoniumyl Radical-cation ($NH_3^{+\cdot}$) with Sulphides and Sulphoxides: an Electron Spin Resonance Investigation

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

The results are described of an e.s.r. study of the reactions of $NH_3^{+\cdot}$, generated from the Ti^{III}–NH_2OH couple, with a variety of sulphides and sulphoxides. Signals detected from sulphides include those from dimer radical-cations ($R_2SSR_2^{+\cdot}$), as well as those derived by hydrogen loss (*e.g.* $\cdot CHMeSEt$ from Et_2S) and fragmentation [*e.g.* $\cdot CH_2SCH_2CO_2H$ from $(HO_2CCH_2)_2S$]. Sulphoxides give rise to alkyl and alkanesulphonyl ($RSO_2\cdot$) radicals, the latter of which are evidently derived from sulphinic acids formed *in situ*. Reactions of $NH_3^{+\cdot}$ with both types of substrate are interpreted in terms of the initial formation of radical adducts [$R_2\dot{S}\text{-}NH_3^+$, $R_2\dot{S}(O)NH_3^+$] which can then undergo a variety of reactions, including substitution and fragmentation.

RECENT e.s.r. and pulse-radiolysis investigations have demonstrated that a variety of sulphur-containing compounds (including sulphides and sulphoxides) react very readily with the hydroxyl radical and that attack takes place exclusively at sulphur. For example, e.s.r. investigations showed that [1] reaction of $\cdot OH$ with dimethyl sulphide leads to the dimer radical-cation $Me_2SSMe_2^{+\cdot}$ (now attributed [2] a σ*-structure) at pH 1—2, and that [3] radicals arising from fragmentation processes are formed from some other sulphides [*e.g.* $\cdot CH_2SCH_2CH_2OH$ from $S(CH_2CH_2OH)_2$]; these reactions were initially envisaged as taking place *via* the formation of a sulphur-centred radical-cation ($R_2S^{+\cdot}$). Detailed pulse-radiolysis investigations [4,5] have shown, however, that, for dialkyl sulphides at least, a rather more complicated mechanism is followed. It appears that the dimer radical-cation $R_2SSR_2^{+\cdot}$ derives from reaction of a first-formed adduct [$R_2\dot{S}OH$] with more sulphide [reactions (1) and (2)] and that the radical-cation $R_2S^{+\cdot}$ is then formed by dissociation of the relatively stable ' dimer ' cation [with which it is in equilibrium, reaction (3)]. The adducts $R_2\dot{S}OH$ can also evidently lose water to give sulphur-conjugated radicals of the type $\cdot C\text{–}S\text{–}R$ (which may also derive from deprotonation of $R_2S^{+\cdot}$).

$$R_2S + \cdot OH \longrightarrow R_2\dot{S}OH \qquad (1)$$

$$R_2\dot{S}OH + R_2S \longrightarrow \left[\begin{matrix} HO \\ R_2SSR_2 \end{matrix}\right] \xrightarrow{-OH^-} R_2SSR_2^{+\cdot} \qquad (2)$$

$$R_2SSR_2^{+\cdot} \rightleftharpoons R_2S^{+\cdot} + R_2S \qquad (3)$$

Hydroxyl radicals are also particularly reactive towards sulphoxides, and the formation [6] of alkyl and alkanesulphonyl radicals (*e.g.* $Me\cdot$ and $MeSO_2\cdot$ from $Me_2S{=}O$) has been interpreted in terms of the initial formation of an adduct which rapidly fragments to $R\cdot$ and RSO_2H [reaction (4)]. The reactions between

$$\cdot OH + R_2S{=}O \longrightarrow [R_2\dot{S}(O)OH] \longrightarrow R\cdot + RSO_2H \qquad (4)$$

$$Ti^{III} + NH_2OH \xrightarrow{H^+} Ti^{IV} + OH^- + NH_3^{+\cdot} \qquad (5)$$

$Bu^tO\cdot$ and both sulphides [7] and sulphoxides [8] evidently proceed, at least to some extent, *via* related sulphur-centred radical intermediates.†

We have previously studied [9] some addition reactions (to alkenes) and C–H hydrogen-abstraction reactions of $NH_3^{+\cdot}$, generated in an aqueous flow system from Ti^{III} and hydroxylamine [reaction (5)]; it was shown that $NH_3^{+\cdot}$ is an electrophilic species, somewhat resembling $\cdot OH$ in its behaviour but with an enhanced selectivity. We report here the results of a study of the reactions of $NH_3^{+\cdot}$ with sulphides and sulphoxides, in which we set out to determine whether or not attack is again directed at sulphur and, if so, whether evidence could be obtained for the structure and further reactions of sulphur-centred adducts.

RESULTS AND DISCUSSION

We have studied the reactions of $NH_3^{+\cdot}$ in a three-way aqueous-flow system with mixing time *ca.* 0.1 s.[9] Stream (i) typically contained 12.5% w/v titanium(III) chloride solution (8.3 cm^3 dm^{-3}, 6.3 mmol dm^{-3}), stream (ii) typically contained hydroxylamine hydrochloride (40 g dm^{-3}, *ca.* 0.6 mol dm^{-3}), and the substrate was contained in stream (iii); streams (i) and (ii) also contained sufficient sulphuric acid to yield a combined solution after mixing of the appropriate pH (usually *ca.* 1.5). In order to compare directly the reactions of $\cdot OH$ with those of $NH_3^{+\cdot}$, the reactions of the former were also studied at pH *ca.* 1.5; this was achieved by replacing the hydroxylamine solution in stream (ii) with a solution of hydrogen peroxide (100 volume; 2.5 cm^3 dm^{-3}, 0.02 mol dm^{-3}).

Reactions of $NH_3^{+\cdot}$ *with Sulphides.*—(a) *Dialkyl sulphides.* The inclusion of dimethyl sulphide in the third stream of a Ti^{III}–NH_2OH flow system at pH 1.5 (to give a concentration in the mixed stream ‡ of *ca.* 0.09 mol dm^{-3}) led to the detection of a multiplet spectrum (a 0.66 mT, g 2.0104, ΔH 0.32 mT) of which nine lines could be clearly discerned. This is from $Me_2SSMe_2^{+\cdot}$ (as obtained [1] from $\cdot OH$), the outer lines of the expected 13-line spectrum being masked by the noise. As the sulphide concentration was reduced to *ca.* 10^{-3} mol dm^{-3} the height of the peaks increased as the line-width became less (*ca.* 0.1 mT at this concentration) and the outer lines proved detectable. (The broadening at high sulphide concentration is evidently [1] a consequence of a

---

† The sulphoxide adducts are probably best regarded as sulphur-centred radicals,[8] rather than oxygen-centred intermediates as originally drawn.[6]

‡ All *substrate* concentrations given are for the mixed stream.

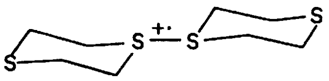
rapid exchange of sulphide between $R_2SSR_2^{+\bullet}$ and 'free' R_2S.) The lower limit for detection of this radical was for $[Me_2S]$ *ca.* 10^{-6} mol dm^{-3}. Similar behaviour was observed at pH 2.0. At higher pHs (*ca.* 3—4), in the presence of disodium ethylenediaminetetra-acetate (Na_2EDTA; to complex Ti^{III}), no signals could be detected; this is perhaps not surprising in view of our previous finding[9] that the presence of EDTA apparently lowers the rate of the reaction between Ti^{III} and NH_2OH. At pH 3.5, $^{\bullet}OH$ reacts with Me_2S to give $^{\bullet}CH_2SMe$, but no detectable dimer radical-cation.[1]

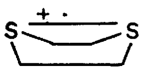
Diethyl sulphide was found to react with $NH_3^{+\bullet}$ in the pH range 1—2 and over a concentration range of *ca.* 10^{-2}—10^{-4} mol dm^{-3} to give signals from the analogous radical-cation $Et_2SSEt_2^{+\bullet}$, accompanied by $^{\bullet}CHMeSEt$[1] for substrate concentrations $<2.5 \times 10^{-3}$ mol dm^{-3}. Both radicals are also formed in the corresponding reaction of $^{\bullet}OH$, with, at any given concentration of Et_2S, the ratio of $[\bullet CHMeSEt] : [Et_2SSEt_2^{+\bullet}]$ greater in this case than for $NH_3^{+\bullet}$ under otherwise identical conditions.

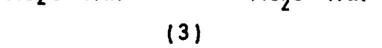
No radicals could be detected from reactions of either $NH_3^{+\bullet}$ or $^{\bullet}OH$ with 1,4-dithian, although pulse-radiolysis evidence indicates[5,10] that reaction with $^{\bullet}OH$ yields the intermolecular radical-cation (1) at high substrate concentrations (*ca.* 10^{-3} mol dm^{-3}) and an intramolecular radical-cation (2) at lower concentrations (*ca.* 10^{-4} mol dm^{-3}). Failure to detect these with e.s.r. spectroscopy may reflect, at least in part, the limited solubility of the substrate, which may similarly account for our failure to detect radicals from di-t-butyl sulphide.

We were also unable to detect signals from radicals $Me_2\dot{S}Cl$ and $Me_2\dot{S}Br$, which may be considered halide-ion analogues of $R_2SSR_2^{+\bullet}$ [see *e.g.* (3)] and which have been characterised *via* pulse radiolysis;[5] thus introduction of chloride ions (0.2 mol dm^{-3}) into a study of the titanium(III) sulphate–H_2O_2–Me_2S system caused a slight increase in the intensity of the signal from $Me_2SSMe_2^{+\bullet}$ (but with no other changes) and in the presence of bromide ions (0.3 mol dm^{-3}) no signals at all could be detected. Since the reactions between $^{\bullet}OH$ and Br^- (to give $Br_2^{-\bullet}$) and between $Br_2^{-\bullet}$ and sulphides are fast (k *ca.*[11] 5.8×10^9 dm^3 mol^{-1} s^{-1}, at pH 1.3, and *ca.*[5] 2×10^9 dm^3 mol^{-1} s^{-1}, respectively), it seems likely that $Me_2\dot{S}Br$ is indeed formed but that extreme broadening (*e.g. via* exchange, with Br^-, or anisotropic or quadrupolar relaxation) renders it undetectable under these conditions.

(b) *Hydroxy- and carboxy-substituted sulphides.* Reaction of $NH_3^{+\bullet}$ with 2,2'-thiodiethanoic acid $[(HO_2CCH_2)_2S]$ in the pH range 1—2 and at concentrations in the range 10^{-1}—10^{-4} mol dm^{-3} led solely to the detection of $^{\bullet}CH_2SCH_2CO_2H$[12] (see Table); $^{\bullet}OH$ behaved similarly. No trace of a dimer radical-cation could be detected; however, we believe that, as with similar dialkyl sulphides, attack at sulphur is implicated. Thus an alternative decarboxylation pathway involving hydrogen-abstraction from the carboxylic acid group and loss of CO_2 from the resulting acyloxyl radical is not a reaction demonstrated by either $NH_3^{+\bullet}$ or $^{\bullet}OH$ with carboxylic acids which do not possess a sulphur substituent (for which C–H abstraction occurs[9]).


(1)


(2)



$$Me_2\dot{S}{-}Hal \longleftrightarrow Me_2S^{+\bullet}\,Hal^-$$

(3)

The reaction of both $NH_3^{+\bullet}$ and $^{\bullet}OH$ with 3,3'-thiodipropanoic acid under similar conditions led to the detection both of a radical assigned the structure[13] $^{\bullet}CH(SCH_2CH_2CO_2H)CH_2CO_2H$ and of[6b] $HO_2CCH_2CH_2SO_2^{\bullet}$ (present in lower concentration). The latter probably derives from formation of $HO_2CCH_2CH_2S^{\bullet}$ (thiyl radicals have been trapped[3] previously in the reaction of sulphides with $^{\bullet}OH$) and its subsequent reaction with $^{\bullet}OH$ or H_2O_2 (*cf.* ref. 14) or $NH_3^{+\bullet}$ (we

E.s.r. parameters for radicals detected during the reactions of $NH_3^{+\bullet}$ with some sulphur-containing compounds[a]

		Hyperfine splittings/mT[b]			
Substrate	Radical	a(α-H)	a(β-H)	a(γ-H)	g[c]
Me_2S	$Me_2SSMe_2^{+\bullet}$		0.66 (12 H)		2.0104
Et_2S	$Et_2SSEt_2^{+\bullet}$		0.66 (8 H)		2.0105
	$^{\bullet}CHMeSEt$	1.70 (1 H)	2.05 (2 H)	0.15 (2 H)	2.0042
$(HO_2CCH_2)_2S$	$\bullet CH_2SCH_2CO_2H$	1.68 (2 H)		0.20 (2 H)	2.0048
$(HO_2CCH_2CH_2)_2S$	$HO_2CCH_2\dot{C}HSCH_2CH_2CO_2H$	1.55 (1 H)	1.70 (2 H)	0.15 (2 H)	2.0045
	$HO_2CCH_2CH_2SO_2^{\bullet}$	0.125 (2 H)	0.25 (2 H)		2.0051
$(HOCH_2CH_2)_2S$	$HOCH_2\dot{C}HSCH_2CH_2OH$	1.69 (1 H)	1.00 (2 H)	0.18 (2 H)	2.0046
	$HOCH_2CH_2SO_2^{\bullet}$		0.40 (2 H)		2.0052
$Me_2CHCH_2SCH_2CH_2OH$	$R^1(R^2)SSR^1(R^2)^{+\bullet}$[d]		0.66 (8 H)		2.0109
	$^{\bullet}CH_2SCH_2CHMe_2$	1.63 (2 H)		0.12 (2 H)	2.0042
Me_2SO	$Me^{\bullet}$	2.26 (3 H)			2.0026
	$MeSO_2^{\bullet}$	0.094 (3 H)			2.0049
Et_2SO	$Et^{\bullet}$	2.19 (2 H)	2.70 (3 H)		2.0027
	$EtSO_2^{\bullet}$	0.10 (2 H)	0.21 (3 H)		2.0053
$(HOCH_2CH_2)_2SO$ $Bu^tS(O)CH_2CH_2OH$	$HOCH_2CH_2SO_2^{\bullet}$		0.40 (2 H)		2.0052
$PhSO_2H$	$PhSO_2^{\bullet}$	0.03 (*o*-H)	0.106 (*m*-H)	0.05 (*p*-H)	2.0046
4-$MeC_6H_4SO_2H$	4-$MeC_6H_4SO_2^{\bullet}$	— (*o*-H)	0.094 (*m*-H)	0.094 (*p*-Me)	2.0047

[a] For substrate concentrations, pH, and relative radical concentrations, see text. [b] ±0.01 mT. [c] ±0.0001. [d] $R^1 = Me_2CHCH_2$, $R^2 = CH_2CH_2OH$.

have found that oxidation of RSH with $NH_3^{+\bullet}$ leads, *via* $RS^{\bullet}$, to $RSO_2^{\bullet}$ in some cases;[15] the mechanism of this will not be discussed further here).

The reaction of 2,2′-dithioethanol [$(HOCH_2CH_2)_2S$] with $NH_3^{+\bullet}$ at pH *ca.* 1.5 over the concentration range 5×10^{-2}—*ca.* 10^{-4} mol dm^{-3} led to the detection of $^{\bullet}CH(CH_2OH)SCH_2CH_2OH$,[2] the signals being particularly intense at a substrate concentration *ca.* 10^{-3} mol dm^{-3}. We also detected an unidentified singlet (*g* 2.0108), at high substrate concentrations, and [6b] $HOCH_2CH_2SO_2^{\bullet}$ for [R_2S] *ca.* 5×10^{-5} mol dm^{-3}. In the reaction of $^{\bullet}OH$ with 2,2′-dithioethanol at pH 1.5, $^{\bullet}CH(CH_2OH)SCH_2CH_2OH$ was also detected as the major radical, although it was accompanied at higher substrate concentrations ($>10^{-3}$ M) by a weaker signal from $^{\bullet}CH_2SCH_2CH_2OH$ (ratio *ca.* 4 : 1 for initial substrate concentration 0.03 mol dm^{-3}). In the same reaction carried out at pH 5, with [$(HOCH_2CH_2)_2S$] similarly 0.03 mol dm^{-3}, a greater proportion of the fragmentation radical $^{\bullet}CH_2SCH_2CH_2OH$ compared to the radical $^{\bullet}CH(CH_2OH)SCH_2CH_2OH$ was noted (*ca.* 1 : 2).

More pronounced differences between the reactions of $NH_3^{+\bullet}$ and $^{\bullet}OH$ occurred with 2-hydroxyethyl isobutyl sulphide ($Me_2CHCH_2SCH_2CH_2OH$), a substrate which showed features in common with both dialkyl sulphides and the substituted sulphides just described in that both the dimer radical-cation and $^{\bullet}CH_2SCH_2CHMe$ could be detected; these reactions were studied in detail as a function of both sulphide concentration and pH.

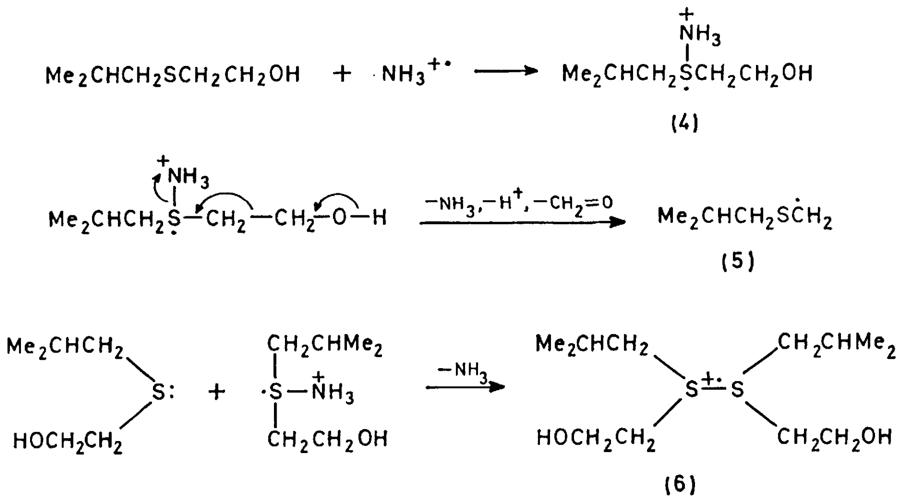
Reaction of $NH_3^{+\bullet}$ with $Me_2CHCH_2SCH_2CH_2OH$ (0.03 mol dm^{-3}) at pH 1.5 yielded exclusively the spectrum of the appropriate dimer radical-cation. A gradual reduction of the substrate concentration led to alterations in the spectra; for [R^1R^2S] 0.002 mol dm^{-3}, signals of equivalent intensity from $Me_2CHCH_2SCH_2^{\bullet}$ and the radical-cation were detected, while for [R^1R^2S] 10^{-3} mol dm^{-3}, only the former radical could be detected. For the reaction with [R^1R^2S] 0.02 mol dm^{-3}, alteration of the pH from 1.5 to 2.1 caused no changes in the spectrum (only the dimer was detected in each case).

The reaction of $^{\bullet}OH$ with $Me_2CHCH_2SCH_2CH_2OH$ (at 0.03 mol dm^{-3} and pH 1.5) led, in contrast to that with $NH_3^{+\bullet}$, to signals from both $^{\bullet}CH_2SCH_2CHMe_2$ and $R^1R^2SSR^1R^{2\,2+\bullet}$ at similar intensities. As the concentration of sulphide was lowered, the signal from the latter radical was reduced in intensity, and, at a concentration of 5×10^{-3} mol dm^{-3}, only $^{\bullet}CH_2SCH_2CHMe_2$ could be detected (*cf.* 10^{-3} mol dm^{-3} for the $NH_3^{+\bullet}$ reaction). Further, the response of this system to change in pH was also different from that for ammoniumyl radical. Thus for [$Me_2CHCH_2SCH_2CH_2OH$] 0.02 mol dm^{-3}, reaction with $^{\bullet}OH$ at pH 1.1 yielded predominantly the dimer radical-cation whereas at pH 2.2 the fragmentation radical was dominant (in contrast to the invariance of the $NH_3^{+\bullet}$ system). At pH 5, reaction of $^{\bullet}OH$ with this substrate (in the range 0.03—10^{-3} mol dm^{-3}) led exclusively to the detection of $^{\bullet}CH_2SCH_2CHMe_2$.

No radicals could be detected in the reaction of $NH_3^{+\bullet}$ with 2-(phenylthio)ethanol present as a saturated solution in the third stream; this may reflect the low solubility of this substrate.

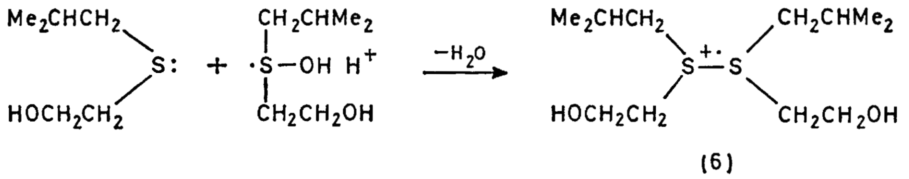
(c) *Mechanistic implications.* The general similarities of the Ti^{III}–NH_2OH and Ti^{III}–H_2O_2 systems in their reactions with dialkyl sulphides (to give dimer radical cations) and the symmetrical hydroxy- and carboxy-substituted sulphides (which give sulphur-conjugated radicals formed by formal loss of H, $CH_2{=}O$ and H, and CO_2 and H) indicate that broadly similar pathways are followed by both $NH_3^{+\bullet}$ and $^{\bullet}OH$. Attack at sulphur in both cases is clearly implied.[3,4] However, some minor differences in behaviour are noted [*e.g.* for $(HOCH_2CH_2)_2S$ and Et_2S] and these, coupled with the rather more striking differences detected for $Me_2CHCH_2SCH_2CH_2OH$ indicate that an identical scheme (*e.g.* *via* a radical-cation $R_2S^{+\bullet}$ which can then react with R_2S, or fragment), is not followed by both radicals. It seems likely that these differences reflect, to some extent at least, the different response to variations in [R_2S] and pH of first-formed ammoniumyl and hydroxyl radical-adducts (considerable evidence exists for the latter [4,5])

The reactions of, for example, $Me_2CHCH_2SCH_2CH_2OH$

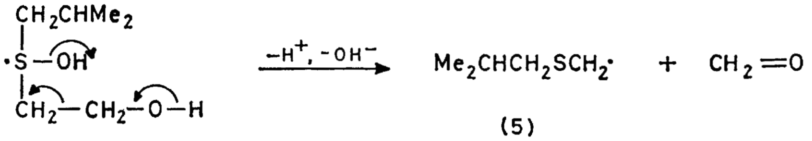


(4) (5) (6)

(6) (7) (8)



(9)

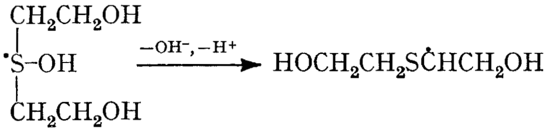


(10)

with $NH_3^{+\cdot}$ at pH 1.5, to give both ${}^\cdot CH_2SCH_2CHMe_2$ (at low sulphide concentrations) and the dimer radical-cation (at higher concentrations) would then be accounted for in terms of the partition of the adduct (4) [formed in reaction (6)] between the fragmentation (7) and the substitution (8).

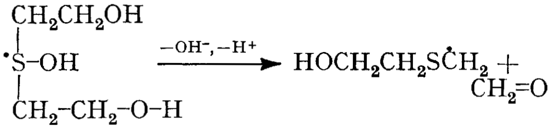
The greater value of the ratio (6) : (5) in the $NH_3^{+\cdot}$ reaction at low pH compared to that observed for ·OH suggests that NH_3 is a particularly good leaving group in reaction (8). The increase in the ratio of [(6)] : [(5)] with decreasing pH for HO· (in contrast with the pH-invariance of $NH_3^{+\cdot}$ suggests that acid-catalysis is necessary for effective dimer radical-cation formation from the ·OH-adduct [reaction (9)].

The ammoniumyl and hydroxyl adducts of unsubstituted dialkyl sulphides evidently preferentially undergo substitution [*cf.* reactions (8) and (9)]; a competing reaction, which may be base-catalysed, is loss of α-hydrogen [4,5] to give a sulphur-conjugated radical (${}^\cdot CH_2SMe$ from $Me_2\dot{S}OH$ at higher pH and ${}^\cdot CHMeSEt$ from $Et_2\dot{S}OH$ and $Et_2\dot{S}NH_3^+$). A similar reaction occurs with the ·OH-adduct from $(HOCH_2CH_2)_2S$ [depicted in reaction (11), although acid- and base-catalysis may be involved], in competition with the fragmentation (12); for the corresponding ammoniumyl adduct, reaction analogous to (11) is evidently favoured.



$$\begin{array}{l} CH_2CH_2OH \\ | \\ {}^\cdot S{-}OH \xrightarrow{-OH^-,-H^+} HOCH_2CH_2S\dot{C}HCH_2OH \\ | \\ CH_2CH_2OH \end{array}$$

(11)



$$\begin{array}{l} CH_2CH_2OH \\ | \\ {}^\cdot S{-}OH \xrightarrow{-OH^-,-H^+} HOCH_2CH_2S\dot{C}H_2 + \\ | \qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2{=}O \\ CH_2{-}CH_2{-}O{-}H \end{array}$$

(12)

Fragmentation reactions analogous to (11) and (12) presumably account for the formation of ${}^\cdot CH(CH_2CO_2H)SCH_2CH_2CO_2H$ and ${}^\cdot CH_2SCH_2CO_2H$ from $S(CH_2CH_2CO_2H)_2$ and $S(CH_2CO_2H)_2$, respectively (with both ·OH and $NH_3^{+\cdot}$).

The results are consistent with an interpretation in which, as with the corresponding ·OH reactions,[4,5] short-lived adducts of the type $R_2\dot{S}{-}NH_3^+$ are important intermediates in the reactions of sulphides with $NH_3^{+\cdot}$ (although a contribution from direct one-electron oxidation to the cation-radical cannot be ruled out). The adducts can evidently undergo a variety of further processes, including substitution and several types of fragmentation, which depend upon the structure of the sulphide concerned, and, in some cases, the presence of acid or base. In the absence of e.s.r. data on such adducts it is impossible to say at this stage whether they resemble the σ* 3-electron-bond species $R_2SSR_2^{+\cdot}$ or the T-shaped sulphuranyl species [16] ${}^\cdot S(OR)_3$ and [17] $R\dot{S}(OR)_2$, both of which have recently been detected at low temperatures in non-aqueous solvents with e.s.r. spectroscopy.

Reactions of $NH_3^{+\cdot}$ *with Sulphoxides*.—(a) *Results*. When dimethyl sulphoxide was included in the Ti^{III}–NH_2OH flow system at concentrations greater than 0.5 mol dm^{-3}, signals from [6a] Me· and $MeSO_2{}^\cdot$ (in comparable concentrations) were detected. No trace of ${}^\cdot CH_2S(O)Me$ could be detected [18] and it can be concluded that, as with sulphides, the presence of the sulphur atom directs attack of $NH_3^{+\cdot}$ away from the alkyl side-chain. In this respect, $NH_3^{+\cdot}$ again resembles ·OH; the reaction of the latter with dimethyl sulphoxide at pH *ca.* 1.5 also yields Me· and $MeSO_2{}^\cdot$,[6b] although two significant differences are noted. First, the ratio of [Me·] : [$MeSO_2{}^\cdot$] in the Ti^{III}–H_2O_2 system (typically *ca.* 5 : 1 under conditions similar to those employed here) is significantly higher than that for $NH_3^{+\cdot}$. Secondly, ·OH is evidently more reactive towards Me_2SO than is $NH_3^{+\cdot}$ since, in the former system, signals from Me· can be detected for much lower concentrations of Me_2SO (*ca.* 0.03 mol dm^{-3}) than the latter.

Reaction of $NH_3^{+\cdot}$ with diethyl sulphoxide (0.15 mol dm^{-3}) led to the detection of Et· and [6b] $EtSO_2{}^\cdot$, in the concentration ratio *ca.* 1 : 1.5. The reactions with bis-(2-hydroxyethyl) sulphoxide [$(HOCH_2CH_2)_2S(O)$] (0.1 mol dm^{-3}) and with 2-hydroxyethyl t-butyl sulphoxide [$Bu^tS(O)CH_2CH_2OH$] both led to the detection of $HOCH_2CH_2SO_2{}^\cdot$ (with signal-to-noise ratios *ca.* 10 : 1), but not alkyl radicals ($Bu^{t\cdot}$ or ${}^\cdot CH_2CH_2OH$). The inclusion of methyl phenyl sulphoxide in the third stream of the flow system gave rise to a very weak spectrum; although individual species could not be identified it seems likely that the signal derives from an $NH_3^{+\cdot}$ adduct (or adducts) on the benzene ring (see later).

Previous studies have shown that reaction of ·OH with Et_2SO yields Et· and $EtSO_2{}^\cdot$ (but with the latter in smaller relative concentrations than that detected here), that $(HOCH_2CH_2)_2SO$ yields $^{\bullet}CH_2CH_2OH$ in addition to the corresponding sulphonyl radical and that $Bu^tS(O)$-CH_2CH_2OH gives $Bu^{t\bullet}$ and $^{\bullet}CH_2CH_2OH$ as well as $HOCH_2CH_2SO_2^{\bullet}$. As with sulphides, the, reactions of $NH_3^{+\bullet}$ and $^{\bullet}OH$ with sulphoxides have features in common, but also exhibit some significant differences: the $NH_3^{+\bullet}$ system, compared with $^{\bullet}OH$, generally gives stronger sulphonyl-radical spectra but weaker or undetectable concentrations of alkyl radicals (the latter observation probably reflects the lower reactivity of $NH_3^{+\bullet}$ towards these substrates under conditions of comparable concentration, as mentioned above for Me_2SO).

It has been shown [6] that $^{\bullet}OH$ adds to sulphoxides to produce adduct radicals [*e.g.* (7) from Me_2SO] which rapidly fragment [$t_{\frac{1}{2}}$ *ca.* 5 μs for (7)] to give alkyl radicals and alkanesulphinic acids, which are further oxidised to alkanesulphonyl radicals [rate constants of 5×10^9 and *ca.* 10^6 dm^3 mol^{-1} s^{-1} have been estimated [6a] for reactions (13) and (15), respectively].

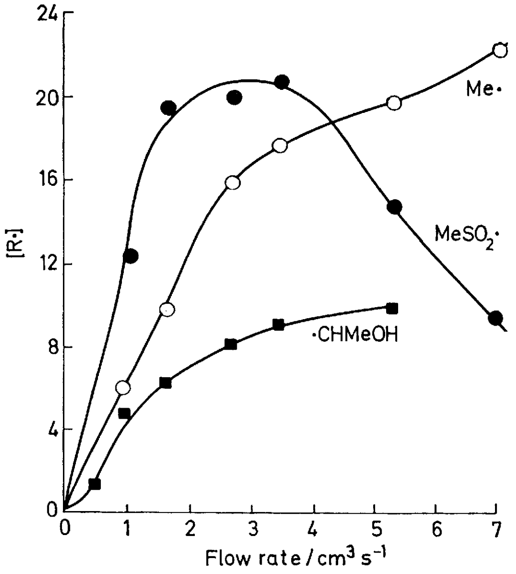
$$HO^{\bullet} + Me_2S{=}O \longrightarrow \underset{(7)}{Me_2\dot{S}(O)OH} \qquad (13)$$

$$Me_2\dot{S}(O)OH \longrightarrow Me^{\bullet} + MeSO_2H \qquad (14)$$

$$Me^{\bullet} + MeSO_2H \longrightarrow MeH + MeSO_2^{\bullet} \qquad (15)$$

A study [6a] of the dependence of $[Me^{\bullet}]$ upon the concentration of Ti^{III} immediately after mixing, $[Ti^{III}]_0$, showed that (provided that $[H_2O_2]_0 \gg [Ti^{III}]_0$) $[Me^{\bullet}]$ is proportional to $[Ti^{III}]_0^{\frac{1}{2}}$; this is consistent with the formation of $Me^{\bullet}$ as a *primary* radical *via* the reactions (13) and (14). $MeSO_2^{\bullet}$ is a *secondary* radical, arising from reaction of $Me^{\bullet}$ with the by-product ($MeSO_2H$) of the latter's formation (at a concentration related to the calculated concentration of $MeSO_2H$ in the cavity); this was demonstrated [6a] by a comparison of the experimentally derived dependence of $[MeSO_2^{\bullet}]$ on $[H_2O_2]_0$ with the calculated extent of reaction before the cavity is reached (and hence the concentration of $MeSO_2H$ reaching the cavity).

We have studied the dependence of $[Me^{\bullet}]$ and $[MeSO_2^{\bullet}]$ on the flow-rate of experiments with Me_2SO and both Ti^{III}–NH_2OH and Ti^{III}–H_2O_2 and find that in both systems $Me^{\bullet}$ is a primary radical and that $MeSO_2^{\bullet}$ is formed in a secondary reaction. It has previously been shown [19] that the concentration of a first-formed short-lived organic radical (with $2k_t$ *ca.* 10^9 dm^3 mol^{-1} s^{-1}) generated by reaction with, *e.g.* hydroxyl, is directly dependent on the rate of the initiating reaction (Ti^{III}–H_2O_2 for $^{\bullet}OH$) in the cavity. Increasing the flow-rate increases the concentrations of initiating reagents in the cavity (Ti^{III} and H_2O_2 or NH_2OH) and, also, therefore, the concentrations of primary species. The concentration of a *secondary* radical in the cavity, on the other hand, will be dependent on the concentrations of both the attacking radical and the substrate (generated by reaction down the flow-tube before the cavity is reached). While the concentration of the former in the cavity should increase with increasing flow-rate, that of the latter would be expected to decrease with the lower extent of reaction before the cavity is reached. These opposing influences upon the concentration of a secondary radical are expected to produce a significantly different concentration dependence on flow-rate compared with that expected for primary radicals.

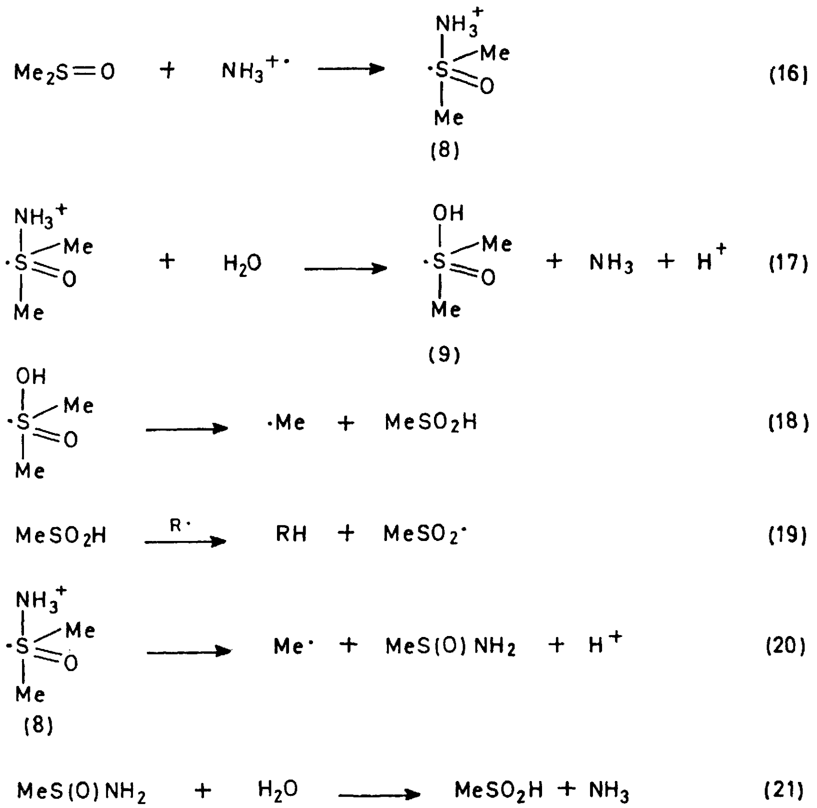


Variation of radical concentration ($[R^{\bullet}]$, arbitrary units) with flow rate, for the radicals from $Me^{\bullet}$ (○) and $MeSO_2^{\bullet}$ (●) (generated by the reaction of $NH_3^{+\bullet}$ with dimethyl sulphoxide) and $^{\bullet}CHMeOH$ (■) (generated from ethanol with $NH_3^{+\bullet}$); for conditions see text

The Figure shows the variation of $[Me^{\bullet}]$ and $[MeSO_2^{\bullet}]$ with flow-rate for the reaction of $NH_3^{+\bullet}$ with Me_2SO. This was obtained for a reaction at pH 1.5 with the concentrations of Ti^{III}, NH_2OH, and Me_2SO in the mixed stream of 2×10^{-3}, 0.2, and 0.85 mol dm^{-3}, respectively; the variation in the flow-rate indicated represents variation in mixing time from *ca.* 0.45 to 0.03 s (*n.b.* most of the experiments reported here employed a flow-rate of *ca.* 1.5 cm^3 s^{-1}, which corresponds to a mixing time of *ca.* 0.11 s). The dependence of the concentration of $^{\bullet}CHMeOH$, a typical primary radical, generated from ethanol and $NH_3^{+\bullet}$ under similar conditions,[9] is included for comparison. The similarity of the variation of $[Me^{\bullet}]$ and $[^{\bullet}CHMeOH]$ suggests that methyl is also a first-formed radical. In contrast, the concentration of $MeSO_2^{\bullet}$ varies as expected for a secondary radical.

This interpretation is supported by our results from a parallel study of the $^{\bullet}OH$–Me_2SO system under similar conditions. The variation of $[Me^{\bullet}]$ was found to resemble closely that of $[Me^{\bullet}]$ in the Ti^{III}–NH_2OH system; similarly, $[MeSO_2^{\bullet}]$ had a maximum at a flow rate of *ca.* 3 cm^3 s^{-1} in the Ti^{III}–H_2O_2 system, but its magnitude was much lower than $[Me^{\bullet}]$ in these reactions and also than $[MeSO_2^{\bullet}]$ in the Ti^{III}–NH_2OH system (by a factor of between 5 and 10).

(b) *Mechanistic implications.* The e.s.r. results are consistent with a reaction mechanism for $NH_3^{+\bullet}$ and sulphoxides which closely resembles that for the corresponding pathway with $^{\bullet}OH$. Thus, it seems likely



that an alkanesulphinic acid serves as the source of $RSO_2^{\bullet}$ in both cases and that this derives *via* initial addition of $NH_3^{+\bullet}$ at sulphur [reaction (16)] to give an adduct.* Two mechanistic schemes may then be envisaged. In the first, rapid hydrolysis of this intermediate [reaction (17), *cf.* the reactions of $R_2\dot{S}OH$ and $R_2\dot{S}NH_3^{+}$ with R_2S] would generate the analogous hydroxy-adduct (9), fragmentation of which would take place as outlined previously [reaction (18)] to give $R^{\bullet}$ and RSO_2H [and ultimately $RSO_2^{\bullet}$, reaction (19)]. The second possibility is that the adduct (8) fragments rapidly to $Me^{\bullet}$ and $MeS(O)NH_2$, the latter being rapidly hydrolysed *in situ* to $MeSO_2H$ before being oxidised [reactions (20), (21), and (19)]. Data concerning the rate of this hydrolytic step do not appear to be available. The failure of $Bu^tS(O)CH_2CH_2OH$ to yield detectable concentrations of alkyl radicals in the $NH_3^{+\bullet}$ system (evidently because of the lower reactivity of sulphoxides towards $NH_3^{+\bullet}$ compared with $^{\bullet}OH$) prevents us establishing the ratio of fragmentation at each of the S–alkyl bonds (as was possible for $^{\bullet}OH$). It is thus not possible to determine whether or not the key intermediate is the same in the two cases, and on the basis of our results we are unable to determine whether fragmentation [reaction (20)] or hydrolysis [reaction (17)] occurs more rapidly.

If either of these pathways accounts for our detection of alkyl and sulphonyl radicals, we must also explain the higher concentrations of $RSO_2^{\bullet}$ found in the $NH_3^{+\bullet}$ system compared with the $^{\bullet}OH$ system. We believe that these arise from reaction of the sulphinic acids generated *in situ* with $NH_3^{+\bullet}$ as well as with $Me^{\bullet}$ (in the Ti^{III}–H_2O_2–Me_2SO system all the $^{\bullet}OH$ generated is believed to be scavenged by the sulphoxide, leaving only $Me^{\bullet}$ to oxidise $MeSO_2H$ to $MeSO_2^{\bullet}$). This is consistent with the lower reactivity of $NH_3^{+\bullet}$ compared with $^{\bullet}OH$ towards sulphoxides (*i.e.* so that all $NH_3^{+\bullet}$ is not scavenged by this substrate) and also with our observation that benzenesulphinic acid (at a concentration of 0.012 mol dm^{-3}) and 4-methylbenzenesulphinic acid (0.016 mol dm^{-3}) are oxidised effectively to the corresponding arenesulphonyl radicals [21] (see Table) in the Ti^{III}–NH_2OH system at pH *ca.* 1.5.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E-104 spectrometer, incorporating 100 kHz modulation and an X-band klystron. The magnetic-field scan was calibrated against the spectrum of $^{\bullet}CHMeOH$, generated by the reaction of either $NH_3^{+\bullet}$ or $^{\bullet}OH$ with ethanol; the e.s.r. parameters of $^{\bullet}CHMeOH$ [a (1 H) 1.51, a (3 H) 2.26 mT] were themselves determined by comparison with those of Fremy's salt [a (N) 1.309 mT].[22] Splitting constants have been measured to within ±0.01 mT and g-values within ±0.0 001 unless otherwise stated. The g-values of radicals detected during the reactions of $^{\bullet}OH$ and $NH_3^{+\bullet}$ were determined by comparison with $^{\bullet}CHMeOH$ (g 2.0033) formed by the introduction of ethanol into the flow-system. The validity of this

---

* It seems possible that the orientation of substituents about sulphur in such an adduct (and the corresponding $HO^{\bullet}$ adduct) will be based on a trigonal bipyramidal structure [*e.g.* (8)] with the amino-group occupying an apical position (*cf.* the proposed intermediate in the reaction of $Bu^tO^{\bullet}$ with dialkyl sulphoxides [8]); alternatively, a σ^*-type structure akin to $Me_2SSMe_2^{+\bullet}$ and [20] $Me_2S(O)S(O)Me_2^{+\bullet}$ may be preferred.

method was confirmed by comparison with Fremy's salt [g 2.0055].[22]

Spectrum simulations were carried out on the Elliot 4130 and the DEC system-10 computers at the University of York; the program, kindly provided by Dr. M. F. Chiu, incorporated Lorenzian line-shapes and second-order effects. Relative radical concentrations were determined using a numerical double integration procedure.[23]

The flow system comprised a modified Varian mixing chamber with an aqueous flow cell, together with a Watson–Marlow H.R. Flow Inducer to pump the reagent solutions through the cavity at a combined flow-rate for a three-way flow-system of *ca.* 1.5 cm^3 s^{-1}. pH Measurements upon the combined solution (*i.e.* after mixing) were made to within ±0.1 pH units, using either an Electronic Instruments model 23A or a Pye–Unicam PW 9410 pH meter, calibrated using commercially available buffer solutions. Concentrations of reagents were as described in the text. In each case the individual solutions were prepared using water previously purged with nitrogen for *ca.* 20 min, and the solutions were then purged with nitrogen during use.

The mixing-time of the flow-system was determined by monitoring the dependence of [$^{\bullet}CH_2CMe_2OH$] (generated using the Ti^{III}–H_2O_2–Bu^tOH system) upon $[H_2O_2]_0$ under conditions where $[Ti^{III}]_0 \ll [H_2O_2]_0$ and all the available $^{\bullet}OH$ is scavenged by the 2-methylpropan-2-ol. The concentration of $^{\bullet}CH_2CMe_2OH$ is found initially to increase to a maximum concentration with increasing $[H_2O_2]_0$ and, having attained this maximum value, to decrease with further increases in $[H_2O_2]_0$. Kinetic analysis of this system has been used to show that the concentration of $^{\bullet}CH_2CMe_2OH$ is maximum when $[H_2O_2]_0$ is approximately equal to $(k_1t)^{-1}$,[24] where k_1 is the rate constant for the Ti^{III}–H_2O_2 redox reaction; since this rate constant is known (k_1 590 dm^3 mol s^{-1}) [25] the mixing time (t) can be derived directly from the value of $[H_2O_2]_0^{max.}$.

Chemicals employed were commercial samples (except where listed below) which were used without further purification, except where stated. 2-Hydroxyethyl isobutyl sulphide was prepared by the reaction of 2-chloroethanol with 2-methylpropane-1-thiol in the presence of ethoxide ions: [26] the reaction mixture was stirred for *ca.* 12 h before the product was recovered in *ca.* 60% yield. The sulphide was purified by distillation under reduced pressure, b.p. 86—88 °C at *ca.* 15 mmHg (lit.,[26] 105—108 °C at 45 mmHg); the ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 6.3 (2 H, t, J 6.0 Hz), 6.9 (1 H, s), 7.3 (2 H, t, J 6.0 Hz), 7.6 (2 H, d, J 6.0 Hz), 8.2 (1 H, m, J *ca.* 6 Hz), and 9.0 (6 H, d, J 6.7 Hz); mass spectroscopic analysis showed M^+ 134 (66%) and prominent ions at m/e 103 (61), 91 (50), 61 (100), and 57 (81).

Diethyl sulphoxide and bis-(2-hydroxyethyl) sulphoxide were prepared by the periodate oxidation of the corresponding sulphides in methanolic solution.[27] The former sulphoxide was recovered in *ca.* 50% yield and purified by distillation under reduced pressure, b.p. 92—96 °C at *ca.* 16 mmHg (lit.,[28] 88—89 °C at 15 mmHg). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 7.3 (4 H, q, J 7.5 Hz) and 8.7 (6 H, t, J 7.5 Hz); the i.r. spectrum of this compound showed $\nu_{max.}$ at 2 970, 2 940, 2 880, 1 460, 1 330, 1 060 (S=O), 1 020, 975, and 890 cm^{-1}. The latter sulphoxide, m.p. 105—109 °C (lit.,[29] 110—111 °C), was recovered in *ca.* 70% yield; the ^1H n.m.r. spectrum in [$^2H_6$]dimethyl sulphoxide showed resonances at τ 6.15 (4 H, t, J 6.5 Hz) 6.5 (2 H, s), and 7.1 (4 H, t, J 6.5 Hz) and the i.r. spectrum showed a strong absorption at 1 060 cm^{-1}. 2-Hydroxyethyl t-butyl sulphoxide was prepared from the corresponding sulphide which itself was prepared by the reaction of 2-chloroethanol with 2-methylpropane-2-thiol in the presence of ethoxide ions.[26] The sulphoxide was obtained *in situ* by stirring an aqueous solution of the sulphide with 10% excess of 100-volume hydrogen peroxide solution (*cf.* ref. 6*b*); the excess of hydrogen peroxide was destroyed before the flow experiments with Ti^{III} and NH_2OH by the addition of sufficient titanium(IV) chloride solution to remove traces of $^{\bullet}OH$-derived radicals when a separate flow experiment was carried out with Ti^{III} itself. When bis-(2-hydroxyethyl) sulphoxide was also prepared *in situ* in this manner, the results were identical with those obtained from the sulphoxide prepared as just described. It was found necessary to distil dimethyl sulphoxide before use (b.p.[30] 84—86 °C at 16 mmHg) in order to obtain reproducible results.

We thank the S.R.C. for a studentship (for P. R. M.).

[8/2174 *Received, 19th December*, 1978]

REFERENCES

[1] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

[2] See, *e.g.*, R. L. Petersen, D. J. Nelson, and M. C. R. Symons, *J.C.S. Perkin II*, 1978, 225.

[3] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 272.

[4] M. Bonifačić, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J.C.S. Perkin II*, 1975, 675.

[5] K.-D. Asmus, D. Bahnemann, and M. Bonifačić, *Faraday Discuss. Chem. Soc.*, 1977, **63**, 213.

[6] (*a*) B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 303; (*b*) B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 308.

[7] J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1976, 407.

[8] W. B. Gara and B. P. Roberts, *J.C.S. Perkin II*, 1977, 1708.

[9] B. C. Gilbert and P. R. Marriott, *J.C.S. Perkin II*, 1977, 987.

[10] D. Bahnemann and K.-D. Asmus, *J.C.S. Chem. Comm.*, 1975, 238.

[11] Z. Draganić, M. M. Kosanić, and M. T. Nenadović, *J. Phys. Chem.*, 1967, **71**, 2390.

[12] H. Taniguchi, H. Takagi, and H. Hatano, *J. Phys. Chem.*, 1972, **76**, 135.

[13] J. Q. Adams, *J. Amer. Chem. Soc.*, 1970, **92**, 4535.

[14] B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 892.

[15] B. C. Gilbert and P. R. Marriott, unpublished observations.

[16] J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1976, 835.

[17] W. B. Gara, B. P. Roberts, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, 1977, (*S*) 152; (*M*) 1748.

[18] P. M. Carton, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 1245.

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

[20] M. C. R. Symons, *J.C.S. Perkin II*, 1976, 908.

[21] C. Chatgilialoglu, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1979, 770.

[22] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462; J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *ibid.*, 1966, **45**, 654.

[23] P. B. Ayscough, 'Electron Spin Resonance in Chemistry,' Methuen, London, 1967, p. 442.

[24] G. Czapski, A. Samuni, and D. Meisel, *J. Phys. Chem.*, 1971, **75**, 3271.

[25] A. Samuni, D. Meisel, and G. Czapski, *J.C.S. Dalton*, 1972, 1273.

[26] C. D. Hurd and K. Wilkinson, *J. Amer. Chem. Soc.*, 1949, **71**, 3429.

[27] C. R. Johnson and J. E. Keiser, *Org. Synth.*, 1966, **46**, 78.

[28] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 4th edn., 1965, vol. 2, p. 1024.

[29] A. H. Ford-Moore, *J. Chem. Soc.*, 1949, 2126.

[30] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 52nd Edition, Chemical Rubber Co., Cleveland, Ohio, 1971, C501.