THE DETECTION OF THIYL RADICALS BY ESR SPECTROSCOPY

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Thiyl radicals ($R\dot{S}$), formed by radiolysis of rigid solutions of a wide range of thiols at 77 K, are characterised by parallel features with high g-values which are markedly solvent dependent. However, in methanol at 77 K $g_{\parallel} = 2.158$ in all cases and this can be taken as diagnostic of $R\dot{S}$ radicals. Also in methanol, R_2S molecules undergo ready dissociative electron capture to give $R\cdot + RS^-$.

It is now certain that radical species with g-values in the regions of 2.06, 2.025 and 2.00 (species A) frequently detected during the radiolysis or photolysis of organo-sulphur compounds [1] are not $RS\cdot$ radicals as was often supposed, but species containing two sulphur atoms, possibly $RSS\cdot$ [2], or $RSSR_2$ [3]. We have predicted [3] that $RS\cdot$ radicals should have g-values determined largely by the medium, with g_z (z being the carbon—sulphur bond direction) greater than the free-spin value (2.0023), but with Δg_z ($g_z - 2.0023$) becoming smaller as the strength of hydrogen bonding to sulphur by the solvent is increased. Our results for several $RS\cdot$

Table 1
Low-field g-values (g_x) for various thiyl radicals

Substrate	Thiyl radical	Solvent	g_x [a]	$R\cdot$ [b]
MeSH	$MeS\cdot$	CD_3OD	2.158	$\dot{C}H_3$
Me_2S	NIL	CD_3OD		$\dot{C}H_3$ [c]
MeSSMe	NIL [d]			
$HSCH_2CH_2NH_3^+$	$\dot{S}CH_2CH_2NH_3^+$	CD_3OD	2.158	$\dot{C}H_2CH_2NH_3^+$
	$\dot{S}CH_2CH_2NH_3^+$	EtOH	2.159	
		i-PrOH	2.200	
$HSCH_2CO_2^-$	$\dot{S}CH_2CO_2^-$	CD_3OD	2.158	$\dot{C}H_2CO_2^-$
		$NaOH/H_2O$	2.134	$\dot{C}H_2CO_2^-$
cysteine	$\dot{S}CH(NH_3^+)CO_2^-$	CD_3OD	2.158	$\dot{C}H(NH_3^+)CO_2^-$
cysteine hydrochloride	$\dot{S}CH(NH_3^+)CO_2^-$	–	2.321, 2.312	
dithioerythritol	$\dot{S}R$	CD_3OD	2.158	$H_2\dot{C}R$
		–	2.29	
penicillamine	$\dot{S}CMe_2CH(NH_3^+)CO_2^-$	CD_3OD	2.158	$\dot{C}Me_2CH(NH_3^+)CO_2^-$
penicillamine hydrochloride		–	2.295	

[a] Broad unresolved feature, error ca. ±0.003.
[b] Formed by dissociative electron capture (1).
[c] Reaction (1) is relatively inefficient for R_2S compared with RSH compounds.
[d] Other disulphides also gave no $RS\cdot$ radicals, but $RSSR^-$ and $RSSR^+$ radical-ions were detected.

radicals formed by radiolysis of RSH in different environments at 77 K confirm this (table 1). Methanol (CD_3OD) gave a constant value of $g_z = 2.158$, which can be taken as diagnostic of $R\dot{S}$ radicals. It is significant that, whilst $R\dot{S}$ radicals were readily formed from RSH molecules, they were not formed from R_2S or RS–SR molecules. In protic media such as methanol R· radicals were also detected. Thus, for example, methanethiol and dimethylsulphide gave methyl radicals. These were not detected when the pure mercaptans were irradiated. The mercaptans strongly suppress the violet colour characteristic of trapped electrons in methanol and we therefore suggest that the dissociative electron-capture process

$$RSH + e^- \rightarrow R\cdot + SH^- \qquad (1)$$

is favoured by good anion-solvating media. The only alcohol that shows a similar reaction with electrons is *t*-butyl alcohol [4].

Process (1) even occurs for compounds containing the $-NH_3^+$ group in preference to the usual loss of ammonia:

$$RNH_3^+ + e^- \rightarrow R\cdot + NH_3. \qquad (2)$$

Thus, for example, penicillamine gave the readily detectable $Me_2\dot{C}CH(NH_3^+)CO_2^-$ radical in preference to $Me_2C(SH)\dot{C}HCO_2^-$.

References

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