Electron Spin Resonance of γ-Ray Induced Radicals in Thiourea–Adamantane Solid Solutions

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Thiourea adducts of adamantane are shown to be suitable crystalline matrices for the selective preparation and e.s.r. study of radicals in combination with the γ-irradiation technique. Examples of applications to alcohols, ketones, and vinyl monomers are reported.

WHEN nearly saturated solutions of thiourea and adamantane are kept for a few minutes at 263 K, crystalline precipitates are obtained which, by elemental analysis and g.l.c. are shown to consist of 65—70% thiourea and 30—35% adamantane. The thiourea : adamantane ratio is not appreciably altered by washing the precipitate with n-hexane (which readily dissolves free adamantane) or by prolonged evacuation at 10^{-3} Torr, thus leading to the conclusion that the products obtained are indeed stable solid solutions, presumably clathrates. These clathrates have the property of trapping within the lattice small amounts of solvents, which upon γ-irradiation undergo direct or indirect radiolysis with selective production of radicals. The radicals thus obtained in general show good thermal stability and yield well resolved e.s.r. spectra with line widths at maximum slope of less than 1—2 G. These observations suggest that the thiourea–adamantane system can be used as suitable matrix for the production and e.s.r. study of organic radicals in addition to other methods.[1,2]

EXPERIMENTAL

Test experiments have been performed with clathrates precipitated from alcohols (t-butyl, n-propyl, isopropyl, allyl, and propargyl), ketones (acetone, cyclopentanone, and cyclohexanone) and vinyl monomers (vinyl acetate and acrylonitrile). With the exception of cyclopentanone and cyclohexanone, none of these compounds form stable binary

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[1] O. H. Griffith, *J. Chem. Phys.*, 1964, **41**, 1093; 1965, **42**, 2644; 1965, **42**, 2651; G. A. Helckè and R. Fantechi, *Mol. Phys.*, 1970, **18** 1.

[2] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **53**, 3932; 1970, **52**, 3840.

adducts with thiourea under the experimental conditions employed.

After precipitation the clathrates were washed with n-hexane, to remove free adamantane and then sealed under high vacuum in Pyrex tubes for γ-irradiation and e.s.r. measurement. Irradiations were performed at 77 K in a ^{60}Co source with total dose of *ca.* 5 Mrad. The e.s.r. spectra were recorded with a Varian 4500 X band spectrometer equipped with a variable temperature control accessory. The composition of the clathrates was determined by elemental analysis and g.l.c. at 150 °C on a 2 m GE SE 30 column. The amount of solvents trapped within the clathrates was found to range from $<0.1\%$ (all the alcohols, acetone) to 6—7% (cyclopentanone, cyclohexanone).

RESULTS

Thiourea–Adamantane Clathrate without Solvent trapped within the Lattice.—Samples of solvent-free clathrates have been prepared by sublimation under continuous evacuation of the clathrate obtained by precipitation from propan-2-ol solutions. Following γ-irradiation at 77 K and recording at the same temperature, this system yields a slightly asymmetric doublet of *ca.* 19 G with the centre significantly displaced toward low field (*g ca.* 2.03) (Figure 1a). This signal is not to be confused with that observed by Wood and Lloyd for pure adamantane and attributed to the 2-adamantyl radical,[3,4] because the latter has *g* close to the free spin value; more likely the doublet belongs to some, not yet identified, thiourea radical having one α- or β-proton interacting with the unpaired electron partly localized on sulphur. Such localization is assumed in order to explain, through a spin-orbit coupling mechanism, the large deviation of *g* from the free spin value. The doublet could be assigned to the species $\cdot\mathrm{SCH(NH_2)_2}$ formed by addition of hydrogen atom to the C=S bond. We prefer however to leave this question unsettled. On warming from 77 to 183 K the doublet decays progressively without generating new signals.

Thiourea–Adamantate Clathrates from Alcohols.—The low temperature spectra of thiourea–adamantane clathrates containing alcohols trapped within the lattice are dominated by a doublet identical to that reported in Figure 1a. On warming to 298 K the doublet disappears and is replaced by the e.s.r. signals of hydroxyalkyl radicals formally arising from the parent alcohols by scission of the weakest available C–H bonds: $\cdot\mathrm{CH_2(CH_3)_2OH}$, $\mathrm{CH_3CH_2\dot{C}HOH}$, $\mathrm{(CH_3)_2\dot{C}OH}$ ($6a^{\mathrm{H}}_{\mathrm{OH_3}}$ 19.4 G), $\overline{\mathrm{CH_2CHCH}}\mathrm{OH}$ ($2a^{\mathrm{H}}_{\mathrm{OH_3}} = a^{\mathrm{H}}_{1} = 13.5$, a^{H}_{2} 3.5 G), $\mathrm{CH{\equiv}CH\dot{C}HOH}$ (a^{H}_{3} 10, a^{H}_{1} 16.8 G). The e.s.r. spectra are isotropic and well resolved (line width 1.5—3 G) in the case of isopropyl and allyl alcohols (Figures 1b, c); in the case of n-propyl, t-butyl, and propargyl alcohols the spectra show asymmetric features and significantly larger line widths which prevented accurate determination of the proton hyperfine splitting. The generation of hydroxyalkyl radicals does not seem to be based on direct radiolysis processes but rather on post-irradiation reactions between the parent alcohols and the thiourea radical precursors. This conclusion is inferred from the observed e.s.r. spectra which show a clear correlation between the enhancement of the hydroxyalkyl radical signals and the decay of the doublet. As for the mechanism, only a tentative hypothesis can be made owing to the uncertainty regarding the exact nature of the thiourea radical. If it is accepted, mainly on the basis of the *g* value, that the doublet belongs

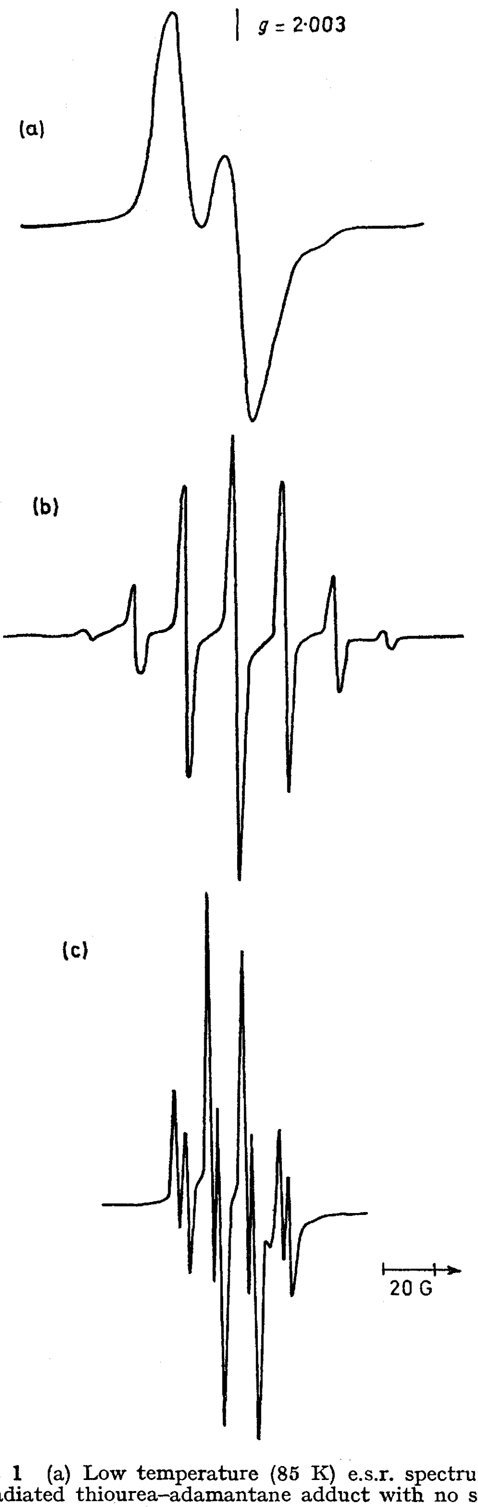

FIGURE 1 (a) Low temperature (85 K) e.s.r. spectrum of the γ-irradiated thiourea–adamantane adduct with no solvent in the lattice; room temperature e.s.r. spectra of γ-irradiated thiourea–adamantane adducts precipitated from (b) isopropyl and (c) allyl alcohols. These spectra develop following the decay of doublets identical to that of Figure 1a

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[3] J. R. Ferrell, G. R. Holden, R. V. Lloyd, and D. E. Wood, *Chem. Phys. Letters*, 1971, **9**, 343.

[4] R. V. Lloyd and M. T. Rogers, *Chem. Phys. Letters*, 1972, **17**, 428.

to a thiyl radical RS·, then a hydrogen abstraction mechanism, $RS\cdot + (CH_3)_2CHOH \longrightarrow RSH + (CH_3)_2\dot{C}OH$, is reasonable especially for isopropyl, allyl, and propargyl alcohols; in fact Huyser and Kellogg[5] have shown that effective hydrogen atom transfer from alcohols to thiyl radicals can take place.

Thiourea–Adamantane Clathrates from Ketones.—γ-Irradiation at 77 K followed by annealing at room temperature of clathrates precipitated from acetone, cyclopentanone, and cyclohexanone yields e.s.r. spectra attributable to the 2-oxoalkyl radicals: $\dot{C}H_2COCH_3$ ($2a^H$ 19.5 G), 2-oxocyclopentyl (a_2^H 18.4, $2a_3^H$ 36.4, $2a_5^H$ 2.4 G), and 2-oxocyclohexyl (a_2^H 17.2, $2a_3^H$ 32.4 G at 293 K) (ref. 6). In the case of acetone the spectrum recorded at 210 K also reveals the presence of a binomial septet which is considered diagnostic of the adduct radical $RO\dot{C}(CH_3)_2$ or the radical anion $^-O\dot{C}(CH_3)_2$; this component is bleached by exposure to u.v. light from an unfiltered high pressure mercury lamp leaving the pure $\cdot CH_2COCH_3$ triplet. As for the origin of the 2-oxoalkyl radicals, the spectra recorded at 87 K are suggestive of a direct radiolysis mechanism in the case of cyclopentanone and cyclohexanone; this result is consistent with the relatively large concentration of these two compounds in the matrix (7.4 and 9.9% respectively). In the case of acetone (whose concentration in the lattice is 0.7%), the mechanism seems to be based mainly on post-irradiation reactions of thiourea radical precursors.

Thiourea–Adamantane Clathrates from Vinyl Monomers.—*Vinyl acetate.* The 89 K spectrum of the clathrate from vinyl acetate is dominated by the thiourea radical doublet; on warming above 150 K the doublet is gradually converted into a composite quartet, *ca.* 1 : 3 : 3 : 1, integrated intensity ratios, and 22 G average hyperfine splitting. This e.s.r. change is reasonably explained in terms of the addition reaction, $R\cdot + CH_2{=}CHCOOCH_3 \longrightarrow RCH_2\dot{C}HCOOCH_3$.

Acrylonitrile. The low temperature spectrum consists of a quintet, 1 : 4 : 6 : 4 : 1, and average hyperfine separation of *ca.* 21 G attributable to the monomer radical $CH_3\dot{C}HCN$ (Figure 2) ($3a^H_{CH_3} = 23.0$ G, $a^H_{CH} = 20.2$ G, $a^N = 4.3$ G). On warming above 220 K the spectrum of $CH_3\dot{C}HCN$ becomes fully resolved and simultaneously the lines of the growing radical $RCH_2\dot{C}HCN$ ($2a^H_{CH_2}$ 22.5, a^H_{CH} 18.2, a^N 3.8 G) are observed; the conversion of monomer into growing radicals is completed in a few minutes at 298 K and is ascribed to the onset of polymerization, $CH_3\dot{C}HCN + CH_2{=}CHCN \longrightarrow CH_3CH(CN)CH_2\dot{C}HCN$. An analogous polymeric radical from acrylonitrile has been recently obtained by Smith and his co-workers[7] in a flow system by using OH radicals from $TiCl_3$–H_2O_2 as initiators. The two radicals show slight differences in the α- and β-proton couplings, probably arising partly from the different conditions employed.

Conclusions.—Judging from the results, the thiourea–adamantane clathrate is a suitable matrix for the radiation-induced preparation and e.s.r. study of organic radicals; for this purpose a necessary condition is that the compounds of interest dissolve sufficient thiourea and adamantane. The mechanism of radical generation apparently depends on the concentrations of trapped compounds. At low concentrations (<1%), the radical are formed mainly *via* post-irradiation reactions initiated by some unidentified thiourea radical precursors. At higher concentrations (6—7%) the direct radiolysis of trapped compound seems to be of major importance. Compared with other clathrate techniques,[1] the present method is of more general application since it does not require the formation of stable binary adducts. Furthermore relative to the cavity isolation method based on pure adamantane[2] a significant advantage is represented by the lower sensitivity to impurities. The intramolecular mobility of radicals within the trapping matrix is often (not always) good enough to lead to nearly complete averaging of anisotropic components. On the other hand, translational diffusion is hindered, but not to the extent of preventing the

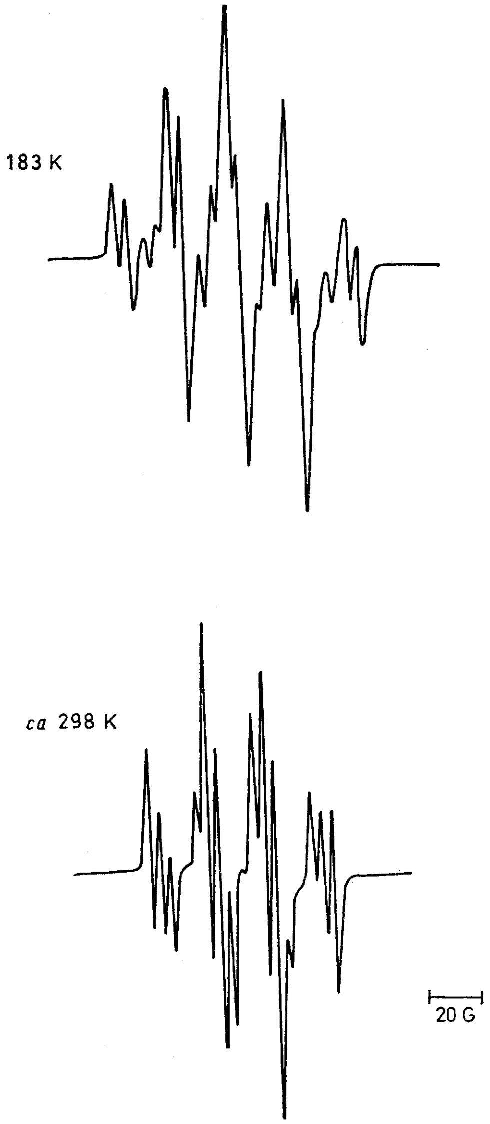

FIGURE 2 E.s.r. spectra of the γ-irradiated thiourea–adamantane clathrate precipitated from acrylonitrile, recorded at 183 and *ca.* 298 K

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[5] E. S. Huyser, R. M. Kellogg, *J. Org. Chem.*, 1966, **31**, 3366.

[6] Detailed work on oxoalkyl radicals in an adamantane matrix has been reported, D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1973, **95**, 7978; see also W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

[7] P. Smith, R. A. Kaba, and J. T. Pearson, *J. Magnetic Resonance*, 1975, **17**, 20.

observation of bimolecular reactions between radicals and parent molecules. These characteristics give the possibility of recording fully resolved spectra of the initiating and growing radicals in the radiation-induced post-polymerization of acrylonitrile, which confirm tentative conclusions based on experiments with the pure monomer.[8]

This investigation has been carried out with financial support from E.N.I., Rome, Italy.

[5/649 *Received, 7th April, 1975*]

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[8] Y. Amagi and A. Shapiro, *J. Chim. phys.*, 1962, 537.