The Photolysis of Triphenylmethanethiol

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IRRADIATION of organic sulphur compounds in the form of RSH and RSSR generally leads to production of sulphur radicals.[1] In a recent study of 2,4,6-tri-t-butylthiophenol with ^{33}S isotope, Rundel and Scheffler[2] identified unequivocally the sulphur radical in the form of RS which was found to be stable for some time at room temperature. Because of the stability of the triphenylmethyl radical, photolysis of triphenylmethanethiol could lead to a C–S bond breakage as well as the S–H split. This report presents some preliminary electron paramagnetic resonance (e.p.r.) observations together with a conventional photochemical study.

Triphenylmethanethiol (I) was repeatedly recrystallized from ethanol until free from all paramagnetic contamination. A solution of (I) in benzene exhibits an absorption onset at about 3300 Å. The photochemical reaction was carried out at various temperatures within the microwave cavity of a Varian e.p.r. spectrometer. The light source was a high pressure Hg arc (Bausch and Lomb SP200) equipped with a high intensity monochromator set at 3130 Å. Irradiation of (I) in a degassed benzene solution at 77°K produced the e.p.r. spectrum shown in Figure 1(a). Irradiation of powdered compound (I) in the solid state at 77°K gave a complex spectrum which could not be interpreted. However, at room temperature, the spectrum of the powder became similar to that shown in Figure 1(b). The solution spectrum in Figure 1(a) is a composite of those of two different radicals, a sulphur radical and a hydrocarbon radical. When the sample of the irradiated solution was warmed and allowed to age at −120°C for several hours, the resonance signal due to the hydrocarbon radical decayed, leaving the sulphur radical spectrum shown in Figure 1(b). This asymmetrical spectrum has seven points of inflection resulting from three anisotropic *g* values (1·997, 2·025, 2·053) significantly shifted from the free spin value of 2·003. Because of the characteristic anisotropic *g* values indicating large spin–orbit coupling and the absence of appreciable hyperfine structure, it is concluded that the spectrum is due to $Ph_3CS\cdot$ radical with the unpaired spin localized largely on the S atom. Figure 1(c) gives a triplet spectrum obtained by subtracting Figure 1(b) from 1(a). This calculated spectrum of a triplet is assigned to a cyclohexadienyl radical, $Ph_2\dot{C}_6H_6{\cdot}CSH$, by comparison with the spectra of similar radicals reported in the literature.[3]

While the photolysis of triphenylmethyl alcohol and other derivatives of triphenylmethane produced triphenylmethyl radicals,[4] the present e.p.r. results suggest that the main photochemical process is the breaking of the S–H bond. The formation of cyclohexadienyl radical can be attributed to secondary addition reaction involving a H atom and (I).

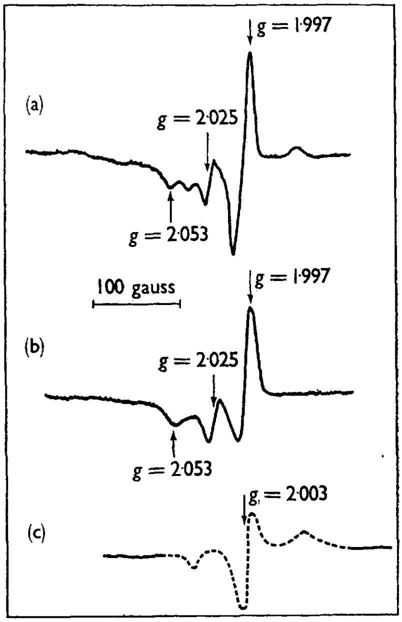

FIGURE 1. *Electron paramagnetic resonance spectra of irradiated triphenylmethanthiol*: (a) *immediately after irradiation at* −196° (b) *after storage at* −120°C *for several hours* (c) *spectrum obtained by subtracting curve* b *from curve* a.

The major reaction products identified from a conventional room temperature photolysis of (I) in a degassed benzene solution are hydrogen, $Ph_3C{\cdot}SPh_3$, triphenylmethane, and sulphur. During photolysis, the concentration of (I) was followed by measuring the relative intensity of the S–H signal at various time intervals in a Varian A60 n.m.r. spectrometer. The quantum yield of the disappearance of (I) was found to be a direct function of its concentration, approaching unity at infinitely high concentrations. A simplified mechanism which accounts for the observed result is:—

$$\begin{array}{lll}
\mathrm{Ph_3C{\cdot}SH} + h\nu & \rightarrow \mathrm{Ph_3C{\cdot}SH^*} & (1)\\
\mathrm{Ph_3C{\cdot}SH^*} & \rightarrow \mathrm{Ph_3C{\cdot}SH} + \text{`energy'} & (2)\\
 & \rightarrow \mathrm{Ph_3C\dot{S}} + \mathrm{H} & (3)\\
\mathrm{H} + \mathrm{Ph_3CSH} & \rightarrow \mathrm{H_2} + \mathrm{Ph_3C{\cdot}\dot{S}} & (4)\\
 & \rightarrow \mathrm{\dot{C}_6H_6{\cdot}Ph_2C{\cdot}SH} & (5)\\
2\ \mathrm{Ph_3C\dot{S}} & \rightarrow \mathrm{Ph_3C{\cdot}CPh_3} + \mathrm{S_2} & (6)\\
\mathrm{Ph_3C{\cdot}CPh_3} & \rightarrow 2\ \mathrm{Ph_3\dot{C}} & (7)\\
\mathrm{Ph_3\dot{C}} + \mathrm{Ph_3C{\cdot}SH} & \rightarrow \mathrm{Ph_3C{\cdot}S{\cdot}CPh_3} + \tfrac{1}{2}\mathrm{H_2} & (8)
\end{array}$$

$$\mathrm{Ph\dot{C}_3} + \mathrm{\dot{C}_6H_6{\cdot}Ph_2C{\cdot}SH} \rightarrow \mathrm{Ph_3CH} + \mathrm{Ph_3CSH} \qquad (9)$$

The absence of a disulphide in the reaction products is due to the back dissociation of $\mathrm{Ph_3C{\cdot}S{\cdot}S{\cdot}CPh_3}$ which is known to occur spontaneously in benzene solution.[5]

Further investigation is in progress in order to establish the nature of the excited (I) molecule, although the preliminary results indicate that it is an excited singlet.

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