

An E.S.R. Study of Some Reactions of Acylthiyl Radicals

By JEREMY R. M. GILES and BRIAN P. ROBERTS*

(Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ)

Summary U.v. photolysis of diacyl disulphides gives acylthiyl radicals [RC(O)S•] which react with alkenes, trialkyl phosphites, and dialkyl sulphides to give adducts which have been detected by e.s.r. spectroscopy.

Under similar conditions with the less electrophilic alkylthiyl radical, the equilibrium (8) lies sufficiently far to the left that an e.s.r. spectrum of the sulphuranyl adduct cannot be detected.⁹ The *g*-factors of (7) (ca. 2.014) are close to those of CF_3SSR_2 , but lower than those (ca. 2.028) of radicals produced by radiolysis of thiols and disulphides in the solid state and assigned by Symons¹⁰ as RSSR_2 or

$\text{RSS}\cdot$. This suggests that the species with the higher *g*-factor should be identified as a perthiyl radical.⁵ However, the *g*-factor of XSSR_2 could be significantly larger when X is a simple alkyl group than when X is a relatively electronegative CF_3 or RC(O) group.

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