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Preliminary communication

A kinetic ESR study of the reaction of t-butylperoxy radicals with hexaphenylditin and hexaphenyldilead★

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SUMMARY

Absolute rate constants for the reaction of t-butylperoxy radicals with hexaphenylditin and hexaphenyldilead have been found to fit the equations $\log (k_p/M^{-1} \cdot s^{-1}) = (5.5 \pm 0.15) - (3800 \pm 150)/\Theta$ and $\log (k_p/M^{-1} \cdot s^{-1}) \cdot (9.5 \pm 0.3) - (6000 \pm 250)/\Theta$, where $\Theta = 2.303\,RT$ cal mol^{-1}, respectively.

It is now well established that the rate-controlling propagation reaction for the autoxidation of some organometallic compounds (MR_n) involves the rapid bimolecular homolytic displacement of an alkyl radical ($R^{\cdot}$) from the metal (M) by an alkylperoxy radical ($ROO^{\cdot}$)[1,2],

$$ROO^{\cdot} + MR_n \xrightarrow{k_p} ROOMR_{n-1} + R^{\cdot} \qquad (1)$$

where k_p is the absolute rate constant for this reaction. Evidence for this mechanism is that stereoisomeric groups, R, lose their stereospecificity in forming alkylperoxymetallic compounds[1] and that the reaction can be inhibited by free-radical scavengers and accelerated by free-radical initiators[1].

Organometallic compounds are often very susceptible to self-initiated atmospheric oxidation, and are consequently not amenable to the precise kinetic analyses that have been applied to autoxidations of hydrocarbons and their oxygenated derivatives[3]. We report below the preliminary results of a kinetic electron spin resonance study of the reaction of t-butylperoxy radicals with hexaphenylditin and hexaphenyldilead. This study enables us to report the first absolute rate constants for reaction (1) at a true metal centre.

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t-Butylperoxy radicals were generated directly in the cavity of a Varian E-3 ESR spectrometer at temperatures between –70 and –100°, in the presence of either hexaphenylditin or hexaphenyldilead (0.0004–0.04 *M*) by photolysis of azoisobutane in oxygen-saturated cumene. When the initiating light was interrupted the radicals decayed rapidly and rates of radical decay were exactly first-order in the radical concentration and in the substrate concentration, *i.e.*,

$$\frac{-d[\text{t-BuOO}^\bullet]}{dt} = k_p\ [\text{t-BuOO}^\bullet]\ [(C_6H_5)_6M_2]$$

where M is either Sn or Pb. Absolute values of k_p were readily obtained from this equation and plots of log k_p against the reciprocal of the absolute temperature yielded the Arrhenius equations, $\log (k_p/M^{-1}\cdot s^{-1}) = (5.5\pm0.15) - (3800\pm150)/\Theta$ and $\log (k_p/M^{-1}\cdot s^{-1}) = (9.5\pm0.3) - (6000\pm250)/\Theta$, where $\Theta = 2.303\,RT$ cal·mol^{-1}, for $(C_6H_5)_6Sn_2$ and $(C_6H_5)_6Pb_2$, respectively. Thus at 30°, k_p for $(C_6H_5)_6Sn_2 = 5.7 \cdot 10^2$ $M^{-1}\cdot s^{-1}$ and k_p for $(C_6H_5)_6Pb_2 = 1.5 \times 10^5$ $M^{-1}\cdot s^{-1}$ and $(C_6H_5)_6Pb_2$ is therefore approximately 10^3 times more reactive than $(C_6H_5)_6Sn_2$ to t-butylperoxy radicals at this temperature. The absolute value of k_p for $(C_6H_5)_6Sn_2$ is characterized by a low pre-exponential factor and a low activation energy while the value of k_p for $(C_6H_5)_5Pb_2$ has a more normal pre-exponential factor and a somewhat higher activation energy. The lower pre-exponential factor for the ditin compound implies that steric hindrance to attack by a peroxy radical at Sn is more severe than it is at Pb. This steric effect apparently overshadows the lower energy requirement of the Sn compound and renders the Pb compound more reactive to attack by peroxy radicals.

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