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Addition of Free Radicals to Olefins and Homolytic Aromatic Substitution: a Comparison

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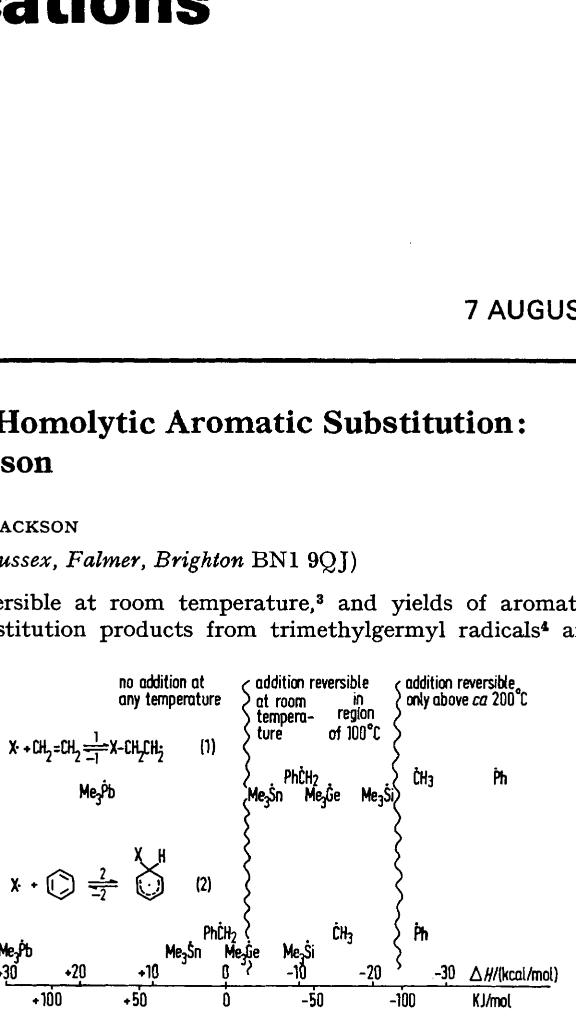
Summary Addition of a particular radical to ethylene is *ca.* 11 kcal mol^{-1} more exothermic than the corresponding addition to benzene to give a cyclohexadienyl radical; use of this difference enables a common pattern of reactivity for the two reactions to be established.

Addition of a free radical to ethylene [reaction (1)] and the first step in homolytic aromatic substitution [reaction (2)] are formally similar, but for a particular radical, reaction (1) will be more exothermic (or less endothermic) than reaction (2) in which some of the delocalization energy of the benzene nucleus is lost. The extent of this difference can be estimated for X=H from known heats of formation of the various species[1] to be 11 kcal† mol^{-1}. On the assumption that this difference applies to radicals other than H$\cdot$, and that $D(\mathrm{XCH_2CH_2{-}H}) = D(\mathrm{C_2H_5{-}H}) = 98$ kcal mol^{-1}, use of the thermodynamic data of refs. 1 and 2 allows the heats of reaction shown in the Scheme to be established for the carbon-centred radicals benzyl, methyl, and phenyl, and for the Group IVB-centred radicals $\mathrm{Me_3M\cdot}$ [M = Si, Ge, Sn, Pb].

Since both reactions (1) and (2) are of the radical + molecule → radical type, the entropy difference will favour the reverse reaction. Unless the forward reaction is significantly exothermic, reaction will not take place at any accessible temperature. For more exothermic reactions, addition will dominate except at very high temperatures. The boundaries for different expected types of behaviour (wavy lines in the Scheme) have been drawn on the basis that the reaction of trialkyltin radicals with alkenes is reversible at room temperature,[3] and yields of aromatic substitution products from trimethylgermyl radicals[4] are extremely low at 40° (left hand line), whereas the right hand line separates processes which are readily reversible below *ca.* 200 °C from those which are not: the addition of $\mathrm{CF_3\cdot}$ (which should be *ca.* 1 kcal mol^{-1} more exothermic than that of $\mathrm{CH_3\cdot}$) to benzene becomes reversible above *ca.* 140 °C,[5] whereas the addition of phenyl is irreversible at 80 °C,[6] and the reverse reaction only becomes significant at *ca.* 210 °C.[7]



Scheme. Comparison between homolytic aromatic substitution and addition to carbon–carbon double bonds.

The known behaviour of other radicals fits their places on the Scheme, as indicated by the following selection of data. Trimethyl-lead radicals do not add to simple olefins.[8]

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† 1 kcal = 4·184 kJ.

Trimethylgermyl radicals add to olefins irreversibly at room temperature, but addition becomes reversible at *ca.* 60—80 °C.[9] The addition of trimethylsilyl radicals to simple olefins is irreversible[9] at 140 °C, but the addition of the somewhat similar trichlorosilyl radical to ethylene becomes reversible[10] at *ca.* 200 °C. In aromatic substitution reactions, no examples of $Me_3Pb^\cdot$ or $Me_3Sn^\cdot$ substituting a benzene ring are known to the author, and benzyl radicals appear to be unreactive in reactions of this type.[11] Trimethylsilyl radicals attack benzene at 45 °C to give 19% of phenyltrimethylsilane,[4] but the yield falls off with increasing temperature.

Diagrams analogous to the one shown in the Scheme can readily be constructed for other radicals or for other types of reaction. For example, addition of free radicals to styrene, which gives a stabilized radical should be more exothermic than the corresponding addition to ethylene by *ca.* 11 kcal mol^{-1}. Aromatic substitution in naphthalene and anthracene which involves less loss in stabilization energy than reaction (2) should lie between (1) and (2) on the energy scale. In accordance with this, benzyl radicals attack the 9-position in anthracene[12] even though there is no reaction with the benzene nucleus,[11] and yields of trimethylgermyl substituted products are significantly greater with naphthalene than with benzene.[4]

Diagrams of this type should be useful in classification of data, in predicting suitable conditions for particular reactions, and in the avoidance of reactions which are inherently unlikely to work.

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