Understanding the rates of hydrogen-atom abstraction reactions: empirical, semi-empirical and *ab initio* approaches

Brian P. Roberts

Christopher Ingold Laboratories, Department of Chemistry, University College London,
20 Gordon Street, London, UK WC1H 0AJ

The performance of the empirical algorithm proposed by Roberts and Steel (*J. Chem. Soc., Perkin Trans. 2*, 1994, 2155), which relates the activation energy for the H-atom transfer reaction (A) to properties of the

$$A^{\bullet} + HB \longrightarrow AH + B^{\bullet} \qquad (A)$$

four molecules involved, is assessed. This approach has been strongly criticised by Zavitsas in two recent papers (*J. Chem. Soc., Perkin Trans. 2*, 1996, 391 and *J. Am. Chem. Soc.*, 1995, 117, 10 645), mainly on the grounds that it performs badly in comparison with his semi-empirical method for estimating E_a. These criticisms are examined and, in the main, are found to be without foundation. The identity reaction $H_3Si^{\bullet}$ + H_4Si is viewed as a test case and it is shown that our empirical approach predicts an activation energy in accord with that estimated here by *ab initio* methods and with published experimental data on related reactions. The value of E_a predicted by Zavitsas' published method (71.5 kJ mol^{-1}) is very much higher than the value deduced from our empirical analysis (37.6 kJ mol^{-1}) or that obtained by the *ab initio* procedure (46.2 kJ mol^{-1}, which itself is probably too high). It is argued that polar effects are important in H-atom abstraction from thiols by alkyl radicals and that hydrogen-bonding interactions between $A^{\bullet}$ and HB can be important, in particular when the leading atoms of A and B are oxygen or nitrogen. It is concluded that empirical models have a role to play in aiding the understanding of radical reactivity and that the approach of Roberts and Steel is relatively successful, given the limitations implicit in the model.

Ab initio methods for computing the potential energy surfaces for simple elementary radical reactions in the gas phase are becoming ever more sophisticated and there seems little doubt that soon it will be possible to achieve 'experimental' accuracy routinely in the calculation of activation energies for hydrogen-atom transfer reactions of the type (1).[1,2] However, even when

$$A^{\bullet} + H\text{–}B \longrightarrow A\text{–}H + B^{\bullet} \qquad (1)$$

such calculations are reliably accurate there will still be a place for more empirical approaches that aim to provide an understanding of reactivity in terms of the interplay between the various factors believed to influence it.

As an extension of the well-known Evans–Polanyi equation, we recently proposed a simple algorithm [eqn. (2)], derived by

$$E_a = E_o f + a\Delta H^{\ominus}(1 - d) + \beta\Delta\chi^2{}_{AB} + \gamma(s_A + s_B) \qquad (2)$$

correlation analysis, which relates the activation energies of 65 selected H-atom transfer reactions of the type (1) to ground-state properties of the four species involved.[3] In eqn. (2), $f = (D_{AH}D_{BH}/D^2{}_{H_2})$, where the quantities D_{AH}, D_{BH} and D_{H_2} are the bond dissociation enthalpies for AH, BH and H_2, respectively. The term $\Delta\chi_{AB}$ is the difference in Mulliken electronegatives of $A^{\bullet}$ and $B^{\bullet}$, the terms s_A and s_B are structural parameters characteristic of the radicals $A^{\bullet}$ and $B^{\bullet}$, and d is the 'delocalisation term,' the value of which measures the extent of unpaired electron delocalisation in the radical $B^{\bullet}$. The parameters E_0, a, β and γ are constants, which were obtained from multiple regression analysis of the experimental data.

For simplicity at this preliminary stage, the delocalisation term d was set equal to a single average value a if $B^{\bullet}$ is a three-coordinate carbon-centred radical in which the unpaired electron is conjugatively delocalised onto an α-substituent (*e.g.* an aryl, cyano, acyl, oxy or amino group); otherwise it was set equal to zero.[3]

The third term in eqn. (2) represents the part played by 'polar effects' in reducing the activation energy for H-atom transfer. In the same way that the strength of the bond between A and B in the molecule A–B is increased by ionic resonance when these two atoms or groups differ in electronegativity,[4] so the transition state (TS) $[A\cdots H\cdots B]^{\bullet}$ for H-atom abstraction from HB by $A^{\bullet}$ should be subject to increasing stabilisation by charge transfer as $\Delta\chi_{AB}$ increases.

The structures of the fragments A and B which are partially bonded to hydrogen in the TS $[A\cdots H\cdots B]^{\bullet}$ will differ to varying extents from their structures in the radicals $A^{\bullet}$ and $B^{\bullet}$. Since the ionisation energies, electron affinities and enthalpies of formation (*via* the bond dissociation enthalpies D_{XH}) used in eqn. (2) relate to the free radicals $A^{\bullet}$ and $B^{\bullet}$, a structural parameter s_X, which is assumed to be a constant for the radical $X^{\bullet}$, is included to reflect any such differences. Thus, the value of s_X would be expected to be smaller the more closely the ground-state structure of a radical resembles that of the corresponding fragment in the TS and would be expected to be close to zero when $X^{\bullet}$ is an atom.

It is clear that eqn. (2) should fail whenever factors that were not included in its derivation, such as steric (van der Waals) and stereoelectronic effects or hydrogen-bonding interaction between $A^{\bullet}$ and HB, are important in the TS. However, the approach based on correlation analysis is highly adaptable and, in principle, eqn. (2) could be extended to account for these and other factors, including[3] the variable position of the TS along the reaction coordinate.

Our empirical approach has been strongly criticised in two recent papers by Zavitsas,[†,5,6] on the grounds that it compares

---

[†] Although ref. 5 appeared before ref. 6, the former makes use of a revised version of Zavitsas' method (see text), while the latter uses the original method. Therefore, quantitative data for comparison with our results are taken from ref. 5.

Table 1 Parameters obtained from multiple linear regression fitting of the data for the 65 reactions cited in ref. 3

	E_o/kJ mol^{-1}	α	β/kJ mol^{-1} eV^{-2}	γ/kJ mol^{-1}	a	$\Delta\chi_H$/ eV	Std. error in E_o/kJ mol^{-1}	Corrln. coeff. (R)
Original	38.337	0.2472	−2.048	3.412	0.44	5.03	2.0	0.988
Revised	37.614	0.2501	−2.045	4.227	0.44	5.03	2.0	0.988

Table 2 Structural parameters (s_X) for radicals X$^•$

	R$^{•a}$	$Cl_3C^•$	$F_3C^•$	$H_2N^•$	YO$^•$,^{b} PhS$^•$	H$^•$, Hal$^{•c}$	$R_3Si^{•d}$	$Cl_3Si^•$	$Bu_3Sn^•$
Original	2.5	0.7	0.0	0.5	0.6	0.0	2.2^e	2.2^e	2.2^e
Revised	2.1	0.7	0.1	0.4	0.6	0.1	1.0	1.9^f	0.5

^{a} Me$^•$, Et$^•$, Pr$^{i•}$, Bu$^{t•}$, c-$C_5H_9^•$, c-$C_6H_{11}^•$, Ph$\dot{C}H_2$, HO$\dot{C}H_2$, MeO$\dot{C}H_2$, Bu^{t}O$\dot{C}H_2$, $\overline{O(CH_2)_3\dot{C}H}$, NC$\dot{C}H_2$, MeC(O)$\dot{C}H_2$. ^{b} Y = H, Me, Bu^t, Ph. ^{c} Hal = Cl, Br. ^{d} R = Me, Et. ^{e} Originally assumed to have the same value. ^{f} Limited date available for this radical.

unfavourably with his semi-empirical method[7,8] which has been used widely for estimating activation energies for H-atom transfer reactions of the type (1). It is the purpose of the present paper to examine these criticisms and to argue that empirical correlation analysis can still play an important part, complementary to the roles of *ab initio* calculations and the various semi-empirical approaches,[7–12] in aiding understanding of the factors that influence the activation energy for H-atom transfer.

The best-fit parameters obtained previously[3] by our method are given in Tables 1 and 2. When obtaining these results, the value of $D(R_3Si–H)$ (R = Me or Et) was taken to be 388 kJ mol^{-1}, the mean of the value obtained for Et_3SiH by photoacoustic calorimetry[13] and the value obtained for Me_3SiH by kinetic methods.[14] It has subsequently become apparent that certain corrections were not applied in the photoacoustic measurements[15] and that, as a consequence, the value obtained by this method is probably too low by *ca.* 20 kJ mol^{-1}; the preferred value of $D(R_3Si–H)$ is now 398 kJ mol^{-1}.[15] The value for $D(Bu_3Sn–H)$ used in our original paper was also determined by photoacoustic calorimetry,[16] in the same laboratory as the work on Et_3SiH was carried out, and it seems quite likely that this bond dissociation enthalpy could also be low by *ca.* 20 kJ mol^{-1}, which would make the revised value about 328 kJ mol^{-1}. In our original analysis the same s-values were ascribed to $X_3Si^•$ and to $X_3Sn^•$, because it was felt at the time that the data did not warrant a more detailed analysis. These radicals are known to be pyramidal and recent *ab initio* calculations by Guerra[17] indicate that the structure of $X_3Si^•$ is very similar to that of the X_3Si moiety in the parent hydride X_3SiH.‡ Consequently, the structure of the X_3M group (X = Si or Sn) should vary rather little on going to the TS and thus we would expect the s-values for silyl and stannyl radicals to be appreciably smaller than for alkyl radicals.

When these increased values of $D(R_3Si–H)$ and $D(Bu_3Sn–H)$ were used, in conjunction with the other data given in our original paper,[3] and the regression analysis was repeated, optimising the s-values for $R_3Si^•$ and $R_3Sn^•$ separately, the revised parameters listed in Tables 1 and 2 were obtained. The correlation coefficient (0.988) and the standard deviation (2 kJ mol^{-1}) for the revised analysis of the 65 reactions are the same as obtained for the original analysis; the difference between calculated and experimental activation energies rarely exceeds 3.5 kJ mol^{-1}. As would be anticipated, the major differences between the original and revised parameters are decreases in the s-values for $R_3Si^•$ and $Bu_3Sn^•$ to 1.0 and 0.5, respectively, which are more in accord with expectations than the original (average) value of 2.2.

In order to facilitate the discussion, it is necessary to give a brief summary of the method developed by Zavitsas for the calculation of activation energies for H-atom transfer.[7,8] In this model, attention is confined to the three-electron three-centre interaction present in the TS [A···H···B]$^•$, one electron coming from A$^•$ and two electrons from the H–B bond; other electronic interactions are not considered explicitly. The strengths of the partial bonds A···H and H···B are assumed to be equal in the TS and the importance of triplet-state electron repulsion between A and B, represented by inclusion of the structure [A↑ H↓ B↑] in a valence-bond description, is emphasised. The total energy of the partially bonded structure [A···H···B]$^•$, relative to that of the separated radicals A$^•$, H$^•$ and B$^•$, is given by eqn. (3). Here, $^1E_{AH}$ and $^1E_{BH}$ are the

$$E_{tot} = 0.5[^1E_{AH} + {}^1E_{BH}] + {}^3E_{AB} + E_R \qquad (3)$$

energies of the partial bonds A···H and B···H (calculated from the Morse equation), $^3E_{AB}$ is the antibonding contribution due to triplet repulsion (calculated by a variant of the Sato equation) and E_R is the delocalisation energy of one electron over three atoms. Originally,[6–8] E_R was somewhat arbitrarily set equal to −44.4 kJ mol^{-1} for all A and B, but recently[5] this assumption has been modified in an *ad hoc* fashion such that E_R is increased to −50.2 kJ mol^{-1} when the leading atom of either A or B has an atomic number greater than that of fluorine.

The procedure used to estimate E_a is as follows. For a given value of the distance r_{A-H}, the value of r_{B-H} is found such that $^1E_{AH} = {}^1E_{BH}$. Since $r_{A-B} = r_{A-H} + r_{B-H}$, the corresponding value of $^3E_{AB}$ can be evaluated and, after correction for zero-point vibrational effects, the value of E_{tot} is obtained. The value of r_{A-H} is varied stepwise until the minimum value of E_{tot} is found, corresponding to the TS, and the activation energy is then given by the difference between E_{tot} and the bond dissociation energy for the reactant molecule BH. As in our empirical method, quantum-mechanical tunnelling is neglected. The data required for the estimation of E_a by Zavitsas' method are D_{AH}, D_{BH} and D_{AB}, the stretching frequencies for the A–H, B–H and A–B bonds in the ground-state molecules, the equilibrium bond lengths r_{A-H}, r_{B-H} and r_{A-B} in these species, and the masses of the leading atoms of the groups A and B.

Zavitsas and Chatgilialoglu[5] contend that this model is not parametric, apart from the *ad hoc* choice of the two values for E_R, and is derived from first principles, based on potential energy curves. The Zavitsas model is certainly successful for very many H-atom transfer reactions,[5–8] but it does fail in cer-

---

‡ High-level *ab initio* calculations were carried out using large basis sets, which include d-orbitals on silicon. In as much as the work represents a straightforward application of the GAUSSIAN92 package of programs,[18] the results regarding the structures of silyl radicals $X_3Si^•$ in relation to those of their silane parents X_3SiH appear to be reliable, particularly in view of the excellent agreement between the calculated and experimental values of the isotropic ^{29}Si hyperfine coupling constants for the radicals. However, the conclusion[17] that there is lack of orbital following (attainment of maximum overlap) in acyclic, unconstrained radicals of the type $X_3Si^•$ is misleading at best, since it is based on comparison of bond angles deduced from a minimal basis set analysis, which includes only s- and p-orbitals, with the bond angles calculated at the *ab initio* level using extended basis sets. Similar inconsistencies are present in the discussions of orbital following in the cases of phosphonyl and alkyl radicals.[19] I thank Dr T. Thirunamachandran for valuable discussions concerning this point.

tain cases, which is worrying because, bearing in mind the claims that are made,[5] it is difficult to see how the model might be modified to rectify these failures without losing much of its simplistic merit.

The criticism of our approach by Zavitsas[5,6] focuses on a series of identity reactions of the type (4). In terms of our

$$A^{\bullet} + H\text{–}A \longrightarrow A\text{–}H + A^{\bullet} \qquad (4)$$

present analysis, the activation energies for such H-atom transfers are given by the simple eqn. (5), since both $\Delta H^{\ominus}$ and $\Delta\chi$

$$E_a = E_o f + 2\gamma s_A \qquad (5)$$

are zero. The identity reactions chosen for consideration by Zavitsas are shown in Table 3, along with the activation energies estimated using eqn. (5), those computed by the method of Zavitsas and Chatgilialoglu[5] and, where available, the experimentally determined values. For entries 1–3, agreement between the two calculated values and experiment is satisfactory, although Zavitsas' method gives marginally better results, which is hardly surprising given the extremely simple form of eqn. (5).

The experimental result for entry 4 actually relates to reaction (6), and Griller and Ingold[20] have reported an approximate

$$Bu^tO^{\bullet} + Bu^t_3COH \longrightarrow Bu^tOH + Bu^t_3CO^{\bullet} \qquad (6)$$

activation energy of 10.9 kJ mol^{-1} for this abstraction of hydrogen from a free (*i.e.* not hydrogen-bonded) OH group in tri-*tert*-butylmethanol. Hydrogen-bonding was not taken into consideration when constructing our empirical algorithm and we proposed[3] that this interaction was responsible for the large discrepancy between the value calculated using eqn. (5) and the experimental result. If the reaction proceeds through a TS of the type $[RO^{\bullet}H{:}OR]^{\ddagger} \longleftrightarrow [RO{:}H^{\bullet}OR]^{\ddagger}$, then hydrogen-bonding would be expected to lower the activation energy below that predicted by eqn. (5). Alternatively, since the hydrogen-bond basicity of $Bu^tO^{\bullet}$ is unlikely to differ appreciably from that of Bu^tOH, the alkoxyl radical could react initially with Bu^t_3COH to give the hydrogen-bonded complex **1**.[21]

$$Bu^tO^{\bullet} + Bu^t_3COH \longrightarrow$$
$$\underset{\mathbf{1}}{Bu^t\dot{O}{:}\cdots H\text{–}OCBu^t_3} \rightleftharpoons \underset{\mathbf{2}}{Bu^tO\text{–}H\cdots{:}\dot{O}CBu^t_3} \qquad (7)$$

Interconversion of **1** with the hydrogen-bonded complex **2** of $Bu^t_3CO^{\bullet}$ should be very rapid, since it corresponds to proton transfer (probably involving tunnelling) accompanied by single-electron transfer between the oxygen atoms. Rapid and irreversible β-scission of **2** gives the *tert*-butyl radical [eqn. (8)],

$$Bu^tOH\cdots{:}\dot{O}CBu^t_3 \longrightarrow Bu^{t\bullet} + Bu^tOH\cdots{:}O{=}CBu^t_2 \qquad (8)$$

the rate of formation of which was used to monitor the H-atom transfer process.[20] In this mechanism, formation of **1** is likely to be rate-controlling and the reaction would then be one of a hydrogen-bond acid with a hydrogen-bond base, which would involve electronic interactions different from those present in the 65 reactions used to establish eqn. (2).

Our explanation was rejected by Zavitsas[6] apparently after consideration of limiting kinetic situations but, we believe, the arguments he offers are invalid. For example, Zavitsas concludes that our interpretation requires the existence of an inverse kinetic deuterium isotope effect ($k_H/k_D < 1$) for the overall reaction of $RO^{\bullet}$ with ROH/D, which he considers unlikely. However, this conclusion is based on consideration of the *equilibrium* deuterium isotope effect for association of $RO^{\bullet}$ with ROH/D, which does not appear to be relevant here. Furthermore, we note that although it turns out that K_H/K_D for the equilibrium association of phenol and of alcohols with hydrogen-bond acceptors can be greater or less than unity, depending on the particular proton acceptor,[22] it is necessary to consider the various zero-point contributions for both[22a] the proton donor and for the hydrogen-bonded complex, not only[6] for the latter.

In Zavitsas' model, the low activation energy for reaction (6) arises mainly because of the relatively small destabilisation of the TS by triplet repulsion, as a result of the weak RO–OR bond. At first sight, it is surprising that Zavitsas' method predicts a value of E_a for $RO^{\bullet}$ + ROH that is in accord with the experimental result, because it does not take explicit account of hydrogen-bonding between the alkoxyl radical and the alcohol.[21] However, the strength of the hydrogen-bonding interaction between $A^{\bullet}$ and HB, the 'tightness' of the TS, and the size of the triplet repulsion between A and B may often be correlated (consider the case of A = B = fluorine). Similar considerations will apply to the abstraction of hydrogen from NH groups and a worthwhile extension of eqn. (2) would be to include the hydrogen-bond basicity of $A^{\bullet}$ and the hydrogen-bond acidity of HB together as a further term in the regression analysis,[23] when the data set contains reactions in which such interactions are likely to be important.

The experimental activation energy for the $Cl^{\bullet}$ + HCl identity reaction (entry 5) is not known with certainty, but appears[24] to be *ca.* 25 kJ mol^{-1}; a recent *ab initio* calculation[25] has given a value of 36.4 kJ mol^{-1}. Zavitsas' value of 16.3 kJ mol^{-1} appears to be too low (perhaps because of unrealistic modelling of triplet state repulsion) and the value obtained with our algorithm is probably too high. Although this reaction was not considered in our original work,[3] the discrepancy is likely to arise mainly because of the neglect of stabilisation of the TS/intermediate by hydrogen-bonding. However, chlorine is a second-row element and the possible consequences of valence-shell expansion must also be considered (see below).

In our original paper,[3] we reported that the activation energies estimated using eqn. (2) for H-atom abstraction from C–H groups by peroxyl radicals (where hydrogen-bonding between $A^{\bullet}$ and BH will not be important) were smaller than the experimental values, unless an unreasonably large *s*-value was ascribed to $ROO^{\bullet}$. For example, if we take χ_{Bu^tOO} to be *ca.* 5.6 eV,§ application of eqn. (2) using the revised parameters and taking $d = 0.44$, predicts the activation energy for reaction (9) to

$$c\text{-}C_5H_9^{\bullet} + Bu^tOOH \longrightarrow c\text{-}C_5H_{10} + Bu^tOO^{\bullet} \qquad (9)$$

be 27.2 kJ mol^{-1} if s is set equal to 0.6 for $Bu^tOO^{\bullet}$.¶ The predicted activation energy for the reverse reaction‖ would then be *ca.* 53 kJ mol^{-1}, in comparison with the experimental value[27] of 70 kJ mol^{-1}. It is tempting to propose that such discrepancies

$$Me^{\bullet} + HOOH \longrightarrow MeH + HOO^{\bullet} \qquad (10)$$

are also a consequence of hydrogen-bonding, this time of the peroxyl radical with the hydroperoxide, since this would be expected to reduce the reactivity of $ROO^{\bullet}$.** Many of the kinetic data for reactions of peroxyl radicals in solution[28] were obtained in the presence of added hydroperoxide and even when this is not purposely added, it could be argued that suf-

---

§ Obtained using our computed estimate of the ionisation energy for $Bu^tOO^{\bullet}$ (10.2 eV) and the experimental[26] electron affinity of $HOO^{\bullet}$ (1.08 eV).

¶ Taking $D(Bu^tOO\text{–}H)^{30} = 374$ and $D(c\text{-}C_5H_9\text{–}H)^{3} = 400$ kJ mol^{-1}.

‖ In our approach, all non-identity reactions must be considered in the exothermic direction.

** We note that full protonation of a peroxyl radical gives a hydroperoxide radical cation, in which the unpaired electron will be more delocalised (symmetrically in the case of $HOOH^{\bullet+}$) than in the corresponding peroxyl radical.

Table 3 Calculated and experimental activation energies for identity H-atom transfer reactions

Entry	$A^\bullet$	AH	D_{AH}[a]/ kJ mol^{-1}	s_A	E_a(calc.)/ kJ mol^{-1}	E_a(Zavitsas)[b]/ kJ mol^{-1}	E_a(expt.)[a]/ kJ mol^{-1}
1	$H^\bullet$	H_2	436	0.1	38.5	41.0	40.2
2	$H_3C^\bullet$	H_4C	439	2.1	55.9	60.7	58.6
3	$Et^\bullet$	EtH	421	2.1	52.8	57.7	54.6[c]
4	$Bu^tO^\bullet$	Bu^tOH	440	0.6	43.4	10.9	10.9[d]
5	$Cl^\bullet$	HCl	432	0.1	37.8	16.3	*ca.* 25[e]
6	$Me(CH_2)_6CH_2S^\bullet$	$Me(CH_2)_4CH_2SH$	365[f]	0.6[g]	31.4	21.3[h]	21.7[i]
7	$H_3Si^\bullet$	H_4Si	384[j]	1.0[k]	37.6	71.5	—

[a] For consistency, taken from ref. 3, unless stated otherwise. [b] Taken from ref. 5. [c] There does not appear to be a recent experimental value for this activation energy. Kerr[44] gives $E_a = 52.7$ kJ mol^{-1} for $Et^\bullet + RCH_3$; Zavitsas[5] prefers $E_a = 56.5$ kJ mol^{-1} for $Et^\bullet$ + EtH; the mean of these values is listed. [d] Refers to $Bu^tO^\bullet + Bu^t{}_3COH$. [e] Ref. 25. [f] Value for MeSH, ref. 30. [g] Assumed to be the same as for $PhS^\bullet$. [h] Zavitsas uses D(S-H) = 367 kJ mol^{-1}. [i] Ref. 31. [j] Ref. 45. [k] Assumed to be the same as for $R_3Si^\bullet$.

Table 4 Polar-effect stabilisation of transition states for $R^\bullet + ZH \longrightarrow RH + Z^\bullet$ according to eqn. (2)

		Polar effect term $(\beta\Delta\chi^2_{RZ})$[b]/kJ mol^{-1}	
$R^\bullet$	χ_R[a]/eV	ZH = MeSH[c]	ZH = Et_3SiH[c]
$Me^\bullet$	4.96	−0.7 (0.60)	−3.1 (1.14)
$Et^\bullet$	4.00	−5.0 (1.56)	0.0 (0.11)
$Pr^{i\bullet}$	3.55	−8.3 (2.01)	−0.2 (0.34)
$Bu^{t\bullet}$	3.32	−10.3 (2.24)	−0.7 (0.57)
$MeO\dot{C}H_2$	3.28	−10.6 (2.28)	−0.8 (0.61)
$MeC(O)\dot{C}H_2$	5.33	−0.1 (0.23)	−4.2 (1.44)

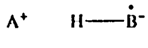
[a] Taken from ref. 3. [b] Taking $\beta = -2.0448$ kJ mol^{-1} eV^{-2}; $\Delta\chi_{RZ}$/eV in parentheses. [c] χ_Z/eV = 5.56 ($MeS^\bullet$), 3.89 ($Et_3Si^\bullet$).

ficient hydroperoxide or other hydroxylic substances are present to deactivate $ROO^\bullet$. Consideration of H-atom abstraction by peroxyl radicals in the gas phase lends some support to this suggestion. Thus, the experimental activation energy for the reverse of reaction (10) is reported[29] to be 103.4 kJ mol^{-1}. Taking[30] D(HOO–H) and D(Me–H) to be 369 and 439 kJ mol^{-1}, respectively, the activation energy for reaction (10) would be *ca.* 33 kJ mol^{-1}. Applying eqn. (2), taking $\chi_{HOO} = 6.22$ eV,[26] $d = 0.44$ and $s_{HOO} = 0.6$, gives an activation energy of 30.4 kJ mol^{-1}, in satisfactory agreement with experiment.

Hypervalency

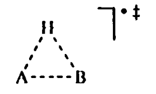
For the (almost) identity reaction of octanethiyl radicals with hexanethiol (Table 3, entry 6), Zavitsas' method (using the increased value of E_R) gives an activation energy in excellent agreement with experiment,[31] while the value obtained using eqn. (5) is too large by *ca.* 10 kJ mol^{-1}. This reaction was not discussed in our original paper. However, it was pointed out that activation energies for H-atom abstraction by carbon-centred radicals from thiols were overestimated by eqn. (2) and we suggested that the propensity of divalent sulfur to undergo valence-shell expansion [not accounted for by eqn. (2)] was responsible for this discrepancy.[3] This explanation has been challenged by Zavitsas,[6] on the grounds that nucleophilic alkyl radicals would not be expected to add to sulfur, and he favours a simple TS of the type $[A\cdots H\cdots B]^\bullet$ for H-atom abstraction from thiols, without any assisting interaction involving valence shell expansion at sulfur.

However, we note that valence-shell expansion, as represented by inclusion of structure **3** in a description of the TS, could be important even for a near-linear TS and a non-linear TS of the type **4** is also feasible. In this context, it is noteworthy that while *ab initio* calculations predicted a near-linear TS for the identity reaction of $HS^\bullet$ with H_2S, semi-empirical AM1 or PM3 calculations for this reaction and for $MeS^\bullet$ + MeSH predicted the preferred course of reaction to involve formation of a sulfuranyl radical $RS\dot{S}(H)R$ followed by 1,2-H-atom migration between the sulfur atoms.[31] We conclude that valence-shell expansion could be important in lowering the energy of the TS



$A^+ \quad H{-}\dot{B}^-$

3



4

for H-atom transfer when B has available orbitals, particularly if it is not coordinately saturated so that it is capable of readily accommodating A or an extra stereochemically active electron. Such a situation could arise when, for example, the leading atom of B is P, As, S, Se, Te, Br, I and (less likely) Cl. In principle, eqn. (2) could be modified to take account of hypervalency.

Polar effects in H-atom abstraction from thiols

Zavitsas and Chatgilialoglu[5] also question our emphasis on the part played by polar effects in H-atom transfer reactions. In particular, they argue that polar effects are unimportant in abstraction of hydrogen atoms from thiols, resting their argument on consideration of the reactions of methyl radicals with thiols and comparison with their reactions with silanes, as modelled by silane itself. However, there is ample evidence of the general importance of polar factors in determining the rates of H-atom abstraction from thiols, and of the opposite response to the polar character of the attacking radical shown by RSH and R_3SnH.[32]

Because of complications arising from hypervalency (see above), discussion of the detailed rates of H-atom abstraction from thiols is not straightforward in terms of our present analysis. Nevertheless, the present model does provide a quantitative measure of the stabilisation afforded to the TS by charge transfer (the polar effect) in the same terms as the argument advanced by Zavitsas and Chatgilialoglu.[5] This stabilisation is represented by $\beta\Delta\chi^2_{AB}$ in eqn. (2) and these quantities are given in Table 4 for H-atom transfer from MeSH and from Et_3SiH.†† As is evident, the polar effect is indeed negligible for the reaction of $Me^\bullet$ with MeSH. However, because χ_R decreases rapidly along the series $R^\bullet = Me^\bullet > Et^\bullet > Pr^{i\bullet} > Bu^{t\bullet}$, the polar effect is predicted to become important for reactions of primary, secondary and tertiary alkyl radicals. On the basis of eqn. (2), the polar effect would be anticipated to be important for other nucleophilic radicals such as $MeO\dot{C}H_2$, but is negligible for an electrophilic radical such as $MeC(O)\dot{C}H_2$. In contrast, negligible stabilisation of the TS is predicted for abstraction from Et_3SiH by primary, secondary or tertiary alkyl radicals; abstraction by the electrophilic $MeC(O)\dot{C}H_2$ is predicted to be favoured by the polar effect.

Considerations of this simple kind have led us to refer to the

---

†† The value (5.56 eV) of χ_{MeS}, which is essentially the same as χ_{PhS},[3] is derived from the ionisation energy[33] of 9.25 eV and the electron affinity[26] of 1.86 eV. The value (3.89 eV) of χ_{Et_3Si} is taken from ref. 3.

catalysis by thiols of the overall H-atom transfer from a silane to an alkyl radical [reactions (11) and (12)] as being an example

$$R^{1\cdot} + R^2SH \longrightarrow R^1H + R^2S^\cdot \qquad (11)$$

$$R^2S^\cdot + Et_3SiH \longrightarrow R^2SH + Et_3Si^\cdot \qquad (12)$$

of polarity-reversal catalysis.[34] Because of their claim that polar effects are unimportant in reaction (11), Zavitsas and Chatgilialoglu have questioned our use of this terminology but, certainly on the basis of the consideration of electronegativity differences, this criticism appears to be unfounded.‡‡ In terms of our model, the smaller *s*-value for $R^2S^\cdot$ compared with $Et_3Si^\cdot$ also favours reaction (11) over the direct abstraction process $R^{1\cdot} + Et_3SiH$. The H-atom transfer reaction (12) is favoured by polar effects ($\beta\Delta\chi^2_{AB} = -5.7$ kJ mol^{-1} when $R^2 = Me$) and, to a lesser extent by the relatively small value of *s* for the thiyl radical.

H-Atom abstraction from silane by silyl radicals

Finally, we consider the identity reaction of $H_3Si^\cdot$ with H_4Si (Table 3, entry 7). As was pointed out by Zavitsas[6] 'postulating alternative pathways would not help explain away failure (of our approach[3]) in this case'! This simple reaction, the second-row congener of $Me^\cdot$ + MeH, should be accounted for by eqn. (5), although it was not included in our original analysis. Our value for E_a is 37.6 kJ mol^{-1}, while Zavitsas calculates the much higher value of 71.5 kJ mol^{-1}; therefore, this reaction becomes an important test case.

Unfortunately, there is no experimental value for the activation energy, but Zavitsas quotes a lower limit of 62.8 kJ mol^{-1}, because, it was claimed[5,6] that 'attempts[36] to measure it by isotopic studies showed that there are no detectable products of hydrogen abstraction.' This is incorrect. In the paper cited, Ring *et al.*[36] reported a study of the pyrolysis of silane using deuterium labelling techniques in order to probe the mechanism. In interpreting their data they state 'we feel that all these results can be explained wholly on the basis of mechanism B (a free-radical chain sequence) with two additional processes: (i) *hydrogen abstraction from silane by silyl radicals* (our italics) [reaction (13)] and most important (ii) the decomposition

$$H_3Si^\cdot + D_4Si \longrightarrow H_3SiD + D_3Si^\cdot \qquad (13)$$

equilibrium of disilanes into silene and silane.' However, to an extent this is academic, because the pyrolysis of silane has been studied on several occasions subsequently. The major processes that occur are evidently non-radical in nature and it is now generally accepted that the reaction is initiated by the elementary step (14).[37] Ring and O'Neal[38] concur with this view and have

$$H_4Si \longrightarrow H_2Si + H_2 \qquad (14)$$

reinterpreted their earlier work.[36] We conclude that the lower limit for the activation energy proposed by Zavitsas is invalid.§§

Gammie *et al.*[40] have reported rate constants of 6.51×10^3 and 4.73×10^2 dm^3 mol^{-1} s^{-1} at 298 K for reactions (15) and (16), respectively and, if we take the rate constant for

$$Me_3Si^\cdot + H_4Si \longrightarrow Me_3SiH + H_3Si^\cdot \qquad (15)$$

$$Me_3Si^\cdot + Me_2SiH_2 \longrightarrow Me_3SiH + Me_2\dot{S}iH \qquad (16)$$

$H_3Si^\cdot + H_4Si$ to be *ca.* 10^3 dm^3 mol^{-1} s^{-1} at 298 K and the Arrhenius *A*-factor to be $10^{8.5}$ dm^3 mol^{-1} s^{-1}, this would imply an activation energy of *ca.* 31.4 kJ mol^{-1}, tolerably close to our value of 37.6 kJ mol^{-1}, but 40 kJ mol^{-1} less than the value estimated by Zavitsas.[5,6]

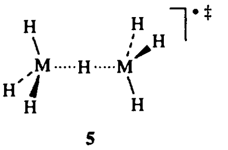
Molecular orbital calculations

In an attempt to resolve the situation, *ab initio* calculations were carried out for the reactants and transition states involved in the H-atom transfers (17)[2] and (18), using the GAUSSIAN92

$$H_3C^\cdot + H_4C \longrightarrow H_4C + H_3C^\cdot \qquad (17)$$

$$H_3Si^\cdot + H_4Si \longrightarrow H_4Si + H_3Si^\cdot \qquad (18)$$

package of programs.[18] Geometries were optimised using the gradient method, in conjunction with the standard 6-31G** basis set, together with Møller–Plesset perturbation theory taken to second-order and excluding the core electrons, to account for electron correlation. For both H-atom transfer reactions, the TS is predicted to adopt the D_{3d} structure **5**, in which the M···H···M grouping is linear (M = C or Si). Spin-restricted calculations were performed for closed-shell molecules and spin-unrestricted calculations for radicals. The set of normal harmonic frequencies was computed for each of these MP2(fc)/6-31G** structures and then used to calculate



5

zero-point vibrational energies (ZPVEs) and thermal contributions ($H_{298} - H_0$) to the enthalpies at 298 K.¶¶ Electronic energies (E_{el}) were determined in single-point calculations at the MP4(full)/6-311++G** level (including single, double, triple and quadruple excitations), using the MP2(fc)/6-31G** geometries. For the open-shell species, account was taken of the small amount of spin-contamination ($\langle S^2 \rangle = 0.75$–$0.79$) by computing the reduction in energy (E_{proj}) after spin-projection of the lowest (quartet state) contaminant. The results are summarised in Table 5.

The enthalpy at 298 K is given[41] by eqn. (19) and hence the

$$H_{298} = E_{el} + E_{proj} + ZPVE + (H_{298} - H_0) \qquad (19)$$

values of $\Delta H^{\ddagger}_{298}$ for reactions (17) and (18) may be calculated to be 68.1 and 43.7 kJ mol^{-1}, respectively. Addition of *RT* to these values yields predicted Arrhenius activation energies of 70.6 and 46.2 kJ mol^{-1}, respectively. Thus, the activation energy for the silyl + silane identity reaction (18) is calculated to be 24.4 kJ mol^{-1} less than that for the methyl + methane identity reaction, although the computed value for the latter reaction is rather higher than the experimentally determined figure (see Table 3; Zavitsas[5,6] cites a spread of experimental values from 56.6 to 60.7 kJ mol^{-1}). Zavitsas and Chatgilialoglu attribute the high value of E_a computed by their method to strong antibonding in the TS due to triplet repulsion.[5] Arguing from their result for reaction (18), they further state that the $H_3Ge^\cdot + H_4Ge$ and $H_3Sn^\cdot + H_4Sn$ identity reactions would also be 'expected to

---

‡‡ In our view, the related consequences[4] of charge-transfer stabilisation (dependent on $\Delta\chi_{RX}$) were overlooked by Rüchardt[35] in discussions of the variations in strength of the R–X bond as the nature of X and of R changes.

§§ Jasinski and Gates[39] state that 'infrared diode laser kinetic studies of silyl demonstrate that it is unreactive with D_4Si at room temperature', citing unpublished results. Without more information it is not possible to assess the significance of this statement.

¶¶ Low frequencies were taken to be associated with molecular vibrations. I am very grateful to Professor J. H. Ridd for providing his computer program for the calculation of thermal contributions to the enthalpy.

Table 5 Results of *ab initio* molecular orbital calculations

Molecule	Point group	Geometrical parameters[a]	Electronic energy (E_{el})/Hartree[b] (U)MP2(fc)/ 6-31G**	(U)MP4(full)/ 6-311++G**[c]	E_{proj}[d]/ kJ mol^{-1}	ZPVE[c,e]/ kJ mol^{-1}	(H_{298} − H_0)[c,e]/ kJ mol^{-1}	$\Delta H^{\ddagger}_{298}$[f]/ kJ mol^{-1}
$H_3C^{\bullet}$	D_{3h}	1.074 (CH)	−39.692 705	−39.751 490	−2.87	75.00	10.86	—
H_4C	T_d	1.086 (CH)	−40.364 626	−40.425 101	—	113.64	10.02	—
$[H_3C\cdots H^*\cdots CH_3]^{\bullet}$	D_{3d}	1.084 (CH), 1.325 (CH*), 105.72 (HCH*)	−80.024 174	−80.146 452	−7.67	187.55[g]	15.71[g]	68.07
$H_3Si^{\bullet}$	C_{3v}	1.473 (SiH), 111.21 (HSiH)	−290.698 252	−290.878 347	−0.82	54.59	10.41	—
H_4Si	T_d	1.474 (SiH)	−291.338 997	−291.526 890	—	79.80	10.57	—
$[H_3Si\cdots H^*\cdots SiH_3]^{\bullet}$	D_{3d}	1.476 (SiH), 1.760 (SiH*), 108.82 (HSiH*)	−582.012 229	−582.384 312	−4.39	127.00[g]	20.72[g]	43.72

[a] At the (U)MP2(fc)/6-31G** level; bond lengths in Å, bond angles in degrees. [b] 1 Hartree = 2625.5 kJ mol^{-1}. [c] At the (U)MP2(fc)/6-31G** geometry. [d] Energy change resulting from annihilation of quartet-state contamination at the MP4 level. In UHF calculations, $\langle S^2\rangle$ was 0.75–0.79 before spin-projection. [e] Vibrational frequencies were scaled by a factor of 0.93 to calculate this quantity. This accounts for the overestimation of frequencies at this level of theory (see ref. 46). [f] Enthalpy difference between reactants and transition state. [g] One negative vibrational frequency, ignored in the calculation.

have high activation energies'.[‖‖] This counter-intuitive conclusion is also at variance with the predictions of our approach and with experimental results for the identity reaction (20),

$$Me_3Sn^{\bullet} + Me_3SnH \longrightarrow Me_3SnH + Me_3Sn^{\bullet} \quad (20)$$

which has been studied by Lehnig using methods based on magnetic resonance lineshape analysis.[43] Two rate constants were obtained, *ca.* 4×10^6 dm^3 mol^{-1} s^{-1} at 298 K from NMR spectroscopy and *ca.* 1×10^7 dm^3 mol^{-1} s^{-1} at 193 K from EPR spectroscopy. Although clearly these values are inconsistent and must be only approximate, they do indicate that reaction (20) is extremely rapid and that its activation energy must be very small, probably $\leqslant$20 kJ mol^{-1}, even if the *A*-factor were as large as 10^{10} dm^3 mol^{-1} s^{-1}. Applying our eqn. (5) in conjunction with $D(Me_3Sn{-}H) = 328$ kJ mol^{-1}, gives $E_a = 25.5$ kJ mol^{-1}; the corresponding estimated value for $Me_3Si^{\bullet}$ + Me_3SiH is 39.8 kJ mol^{-1}. Our approach predicts low activation energies for identity reactions involving stannyl radicals and tin hydrides because of the dependence of E_a on the strength of the Sn–H bond (*via* the *f*-term) and the relatively small *s*-term for $X_3Sn^{\bullet}$, which arises because the structure of the X_3Sn fragment is similar in the radical and in the parent hydride. Of course, the success of both empirical and semi-empirical methods is dependent on the accuracy of the experimental data used as input.

Conclusion

Clearly our empirical approach has some deficiencies in that it does not yet take into account all possible factors. However, an examination of the criticisms of Zavitasas[6] and of Zavitsas and Chatgilialoglu[5] suggests these to be less than objective and, in some instances, based on flawed arguments and incomplete reading of the literature. An objective assessment of the merits of empirical and semi-empirical approaches finds that both have a role to play in promoting a better understanding of the factors that influence the rates of radical reactions and both have value as portable 'rules of thumb' for estimating reaction rates. Our empirical approach,[3] further evaluated here, has the advantage of being based on easily visualised and widely recognised chemical concepts.

The failure of Zavitsas and Chatgilialoglu[5] to reproduce the activation energy for $H_3Si^{\bullet}$ + H_4Si may indicate a deficiency in their procedure, perhaps its inability to model correctly the triplet repulsion between A and B in the TS. Taken together with the arbitrary nature of the choice of the E_R terms that appear in Zavitsas' treatment [eqn. (3)], we believe that there must be doubts concerning the generality of this method in its present form.

Both further experimental work and high level *ab initio* molecular orbital calculations are needed to advance our understanding of the influences of hydrogen-bonding and hypervalency on H-atom transfer reactions.

Acknowledgements

I would like to express my thanks to Professors A. G. Davies, B. C. Gilbert, M. J. Perkins and J. H. Ridd for helpful comments on the manuscript.

References

1 I. H. Williams, *Chem. Soc. Rev.*, 1993, 277.
2 Y. Chen and E. Tschuikow-Roux, *J. Phys. Chem.*, 1993, **97**, 3742.
3 B. P. Roberts and A. J. Steel, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2155.
4 L. Pauling, *The Nature of the Chemical Bond*, Oxford University Press, Oxford, 3rd edn., 1960.
5 A. A. Zavitsas and C. Chatgilialoglu, *J. Am. Chem. Soc.*, 1995, **117**, 10645.
6 A. A. Zavitsas, *J. Chem. Soc., Perkin Trans. 2*; 1996, 391.
7 A. A. Zavitsas, *J. Am. Chem. Soc.*, 1972, **94**, 2779.
8 A. A. Zavitsas and A. A. Melikian, *J. Am. Chem. Soc.*, 1975, **97**, 2757.
9 H. S. Johnson and C. Parr, *J. Am. Chem. Soc.*, 1963, **83**, 2544.
10 R. D. Gilliom, *J. Am. Chem. Soc.*, 1977, **99**, 8399.
11 T. Bèrces and F. Marta, in *Chemical Kinetics of Small Organic Radicals*, ed. Z. B. Alfassi, CRC Press, Boca Raton, 1988, vol. 3, ch. 9.
12 (*a*) A. S. Dneprovskii and E. V. Eliseenkov, *Russ. J. Org. Chem.*, 1988, **24**, 243; (*b*) E. T. Denisov, *Mendeleev Commun.*, 1992, 1.
13 J. M. Kanabus-Kaminska, J. A. Hawari, D. Griller and C. Chatgilialoglu, *J. Am. Chem. Soc.*, 1987, **109**, 5267.
14 A. Goumri, W.-J. Yuan and P. Marshall, *J. Am. Chem. Soc.*, 1993, **115**, 2539; I. J. Kalinovski, D. Gutman, L. M. Krasnoperov, A. Goumri, W.-T. Yuan and P. Marshall, *J. Phys. Chem.*, 1994, **98**, 9551.

[‖‖] The situation here is rather confused because, in our hands, application of Zavitsas' model to the $R_3Sn^{\bullet}$ + R_3SnH identity reaction gives a *relatively small* activation energy. Thus, we obtained an activation energy of 71.9 kJ mol^{-1} (essentially in agreement with the result reported by Zavitsas[5]) for $H_3Si^{\bullet}$ + H_4Si and of 31.6 or 42.7 kJ mol^{-1} [depending on the value taken[42] for D(Sn–Sn)] for $R_3Sn^{\bullet}$ + R_3SnH. The following data (enthalpies in kJ mol^{-1}, bondlengths in Å, stretching frequencies in cm^{-1}, for consistency taken from ref. 5 where available) were used in these calculations: $D(H_3Si{-}H)$ 383, r(Si–H) 1.4798, ν(Si–H) 2190, D(Si–Si) 320, r(Si–Si) 2.331, ν(Si–Si) 432, $M(^{28}Si)$ 28.0; $D(R_3Sn{-}H)$ 322, r(Sn–H) 1.700, ν(Sn–H) 1815, D(Sn–Sn) 234 or 258, r(Sn–Sn) 2.770, ν(Sn–Sn), 192, $M(^{120}Sn)$, 119.9. The calculations were carried out using the program ESTAR written by A. A. Zavitsas.

15 C. Chatgilialoglu, *Chem. Rev.*, 1995, **95**, 1229.
16 T. J. Burkey, M. Majewski and D. Griller, *J. Am. Chem. Soc.*, 1986, **108**, 2218.
17 M. Guerra, *J. Am. Chem. Soc.*, 1993, **115**, 11926; *J. Chem. Soc., Perkin Trans. 2*, 1995, 1817.
18 GAUSSIAN92, Revision C. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh PA, 1992.
19 M. Guerra, *Chem. Phys. Lett.*, 1995, **237**, 61; *J. Phys. Chem.*, 1995, **99**, 81.
20 D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 630.
21 J. S. Francisco and S. P. Sander, *J. Am. Chem. Soc.*, 1995, **117**, 9917 and references cited therein.
22 (*a*) M. D. Joesten and L. J. Schaad, *Hydrogen Bonding*, Marcell Dekker, New York, 1974; (*b*) S. Singh and C. N. R. Rao, *Can. J. Chem.*, 1966, **44**, 2611; (*c*) J. Mendel, A. Mögel and A. Kolbe, *J. Mol. Liquids*, 1984, **29**, 127.
23 M. H. Abraham, P. L. Grellier, D. V. Prior, P. P. Duce, J. T. Morris and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1989, 699; M. H. Abraham, P. L. Grellier, D. V. Prior, J. T. Morris and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1990, 521.
24 F. S. Klein, A. Persky and R. E. Weston, *J. Chem. Phys.*, 1964, **41**, 1799; M. Kneba and J. Wolfrum, *J. Phys. Chem.*, 1979, **83**, 69.
25 N. O. J. Malcolm and J. J. W. McDouall, *J. Phys. Chem.*, 1994, **98**, 12579.
26 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, Suppl. No. 1.
27 J. H. B. Chenier, S. B. Tong and J. A. Howard, *Can. J. Chem.*, 1978, **56**, 3047.
28 J. A. Howard and J. C. Scaiano, in *Landolt–Börnstein; Radical Reaction Rates in Liquids*, ed. H. Fischer, Springer, Berlin, 1984, vol. 13d.
29 D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker and J. Warnatz, *J. Phys. Chem. Ref. Data*, 1992, **21**, 411.
30 *Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, 1993–1994, 74th edn.
31 M. S. Alnajjar, M. S. Garrossian, S. T. Autrey, K. F. Ferris and J. A. Franz, *J. Phys. Chem.*, 1992, **96**, 7037.
32 X. X. Rong, H.-Q. Pan, W. R. Dolbier, Jr. and B. E. Smart, *J. Am. Chem. Soc.*, 1994, **116**, 4521; W. R. Dolbier, Jr. and X. X. Rong, *Tetrahedron Lett.*, 1994, **35**, 6225; C. C. Johnson, J. H. Horner, C. Trouche and M. Newcomb, *J. Am. Chem. Soc.*, 1995, **117**, 1684; J. H. Horner, F. N. Martinez, O. M. Musa, M. Newcomb and H. E. Shahn, *J. Am. Chem. Soc.*, 1995, **117**, 11124; M. Newcomb, J. H. Horner, M. A. Filipkowski, C. Ha and S.-U. Park, *J. Am. Chem. Soc.*, 1995, **117**, 3674.
33 S. Nourbakhsh, K. Norwood, G. Z. He and C. Y. Ng, *J. Am. Chem. Soc.*, 1991, **113**, 6311; B. Ruscic and J. Berkowitz, *J. Chem. Phys.*, 1992, **97**, 1818; L. A. Curtiss, R. H. Nobes, J. A. Pople and L. Radom, *J. Chem. Phys.*, 1992, **97**, 6766.
34 R. P. Allen, B. P. Roberts and C. R. Willis, *J. Chem. Soc., Chem. Commun.*, 1989, 1387; J. N. Kirwan, B. P. Roberts and C. R. Willis, *Tetrahedron Lett.*, 1990, **31**, 5093; S. J. Cole, J. N. Kirwan, B. P. Roberts and C. R. Willis, *J. Chem. Soc., Perkin Trans. 1*, 1991, 103; H.-S. Dang and B. P. Roberts, *Tetrahedron Lett.*, 1995, **36**, 2875.
35 C. Rüchardt, *Angew. Chem., Int. Edn. Engl.*, 1970, **9**, 830.
36 M. A. Ring, M. J. Puentes and H. E. O'Neal, *J. Am. Chem. Soc.*, 1970, **92**, 4845.
37 R. Becerra and R. Walsh, *J. Phys. Chem.*, 1992, **96**, 10856.
38 M. A. Ring and H. E. O'Neal, *J. Phys. Chem.*, 1992, **96**, 10848.
39 J. M. Jasinski and S. M. Gates, *Acc. Chem. Res.*, 1991, **24**, 9.
40 L. Gammie, I. Safark, O. P. Strausz, R. Roberge and C. Sandorfy, *J. Am. Chem. Soc.*, 1980, **102**, 378.
41 C. F. Rodriquez and A. C. Hopkinson, *Can. J. Chem.*, 1992. **70**, 2234.
42 P. G. Harrison, in *Chemistry of Tin*, ed. P. G. Harrison, Blackie, Glasgow, 1989, p. 13.
43 M. Lehnig and K. Dören, *J. Organomet. Chem.*, 1981, **210**, 331; M. Lehnig, *Tetrahedron Lett.*, 1977, 3663.
44 J. A. Kerr, in *Free Radicals*, ed. J. K. Kochi, Wiley, New York, 1973, vol. 1, ch. 1, p. 15.
45 J. A. Seetula, Y. Feng, D. Gutman, P. W. Seakins and M. J. Pilling, *J. Phys. Chem.*, 1991, **95**, 1658.
46 R. H. Nobes and L. Radom, *Chem. Phys. Lett.*, 1992, **182**, 554 and references cited therein.

Paper 6/03124B
Received 3rd *May* 1996
Accepted 22nd *July* 1996