Factors controlling reactivity in hydrogen abstractions by free radicals

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Roberts and Steel have proposed an empirical calculation for obtaining energies of activation for hydrogen abstractions by radicals, $A^\bullet + H\text{–}B$. The results of their calculations led them to: (a) conclude that, in identity exchanges ($A = B$ and $\Delta H = 0$), the bond dissociation enthalpy $D(A\text{–}H)$ is a significant factor; and (b) suggest that antibonding between A and B is not an important factor. Both findings are in conflict with our conclusions from results of our model for hydrogen abstractions. It is shown here that an examination of experimental results for several identity hydrogen exchanges does not support (a) and (b). Antibonding is important and, in identity exchanges, $D(A\text{–}H)$ is not an important factor.

A recent article by Roberts and Steel (R&S) in this Journal[1] reported that energies of activation for a selected group of 65 hydrogen abstractions by radicals were fitted by a four-term equation, with a standard error between calculated and experimental values of only ±2.0 kJ mol^{-1}. This unprecedentedly small error is generally somewhat smaller than one finds when comparing E_a determinations from absolute rate measurements in different laboratories for the same reaction. The energy of activation for reaction (1) was calculated from

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

knowledge of bond dissociation enthalpies, $D(A\text{–}H)$ and $D(H\text{–}B)$, Mulliken electronegativities of $A^\bullet$ and $B^\bullet$, and other properties defined by R&S as 'delocalisation term' and 'structural factors'. The coefficients of each of the four terms of the equation were obtained through multiple regression to fit the group of selected E_a values. The first term is $2.017 \times 10^{-4}\,[D(A\text{–}H)][D(H\text{–}B)]$. The second term is $0.2472\,\Delta H$ or, if B is a stabilised carbon radical, $0.1384\,\Delta H$, where ΔH is the enthalpy change. The third term is $-2.084\,\Delta\chi^2$, where $\Delta\chi$ is the difference in electronegativity of $A^\bullet$ and $B^\bullet$ except that $H^\bullet$ is given a χ value of 5.03, as optimised for best fit to the values; this ascribes to hydrogen an electronegativity somewhat greater than that of carbon. The fourth term contains the sum of a 'structural factor' for each $A^\bullet$ and $B^\bullet$, selected from a group of six possible values by multiple regression for best fit; the value of this term can be from 0.0 to 17.06 kJ mol^{-1} or any of 18 values in between, depending on the combination of $A^\bullet$ and $B^\bullet$ and the group into which the radicals were classified for best fitting. This parametric approach was calibrated by fitting known E_a values for 65 reactions, 41 of which were abstractions by carbon radicals.

One of the assumptions built into the model (the first term): 'For a series of thermoneutral identity reactions ($A^\bullet$ + H–A), the activation energy would be expected to decrease as the strength of the A–H bond decreases.' This is in conflict with the conclusions reached from our calculation of energies of activation for H-atom transfer. Our model is based on the standard Morse curve for estimating bonding in A–H and H–B at stretched distances, with the assumption that at the transition structure (TS) such bonding is of equal strength for maximum resonance. Triplet repulsion (antibonding) is assumed between A and B, because of resonance structures such as $A\!\uparrow\!H\!\downarrow\!B\!\uparrow$ at the TS requiring parallel spins on A and B, and the Sato function is used for estimating it.[2] The input data required are D, bond length, and uncoupled IR stretching frequencies for A–H, H–B and A–B. Harshly judged, our model can be considered to have one arbitrary constant, the resonance energy of the TS (−44.35 kJ mol^{-1}) applicable to all reactions. As evaluated by others with 87 hydrogen abstractions,[3] our model was found to have an overall average deviation of ±6.1 kJ mol^{-1} between calculated and experimental values; this evaluation was performed with values of bond dissociation enthalpies that are now known to have had errors of the order of ±6 kJ mol^{-1}. Unlike the R&S model, ours is not parametric but is based on assumed first principles and standard potential energy curves.

Our model does not assume that E_a for thermoneutral identity hydrogen abstractions depends on the strength of the bond involved. There is no basis for making this assumption, reasonable though it may sound. Accurate quantum mechanical results show symmetrical transition states for symmetrical H transfer.[4] The energy lost by stretching one A–H bond is exactly compensated by making the other, even though resonance and other effects change the total energy of the system. With $\Delta H = 0$, the absolute value of A–H is not necessarily an important factor.

This point can be resolved by available experimental information for such identity reactions: E_a values have been reported for five and a minimum E_a value can be estimated for a sixth. Table 1 lists these identity exchanges in decreasing order of experimental E_a. The corresponding $D(A\text{–}H)$ values[5] do not follow the same order and there is no discernible relationship between the two orderings.

An examination of the entries in Table 1 shows that the values of E_a calculated by the algorithm of R&S ($E_{R\&S}$) do not follow the order of experimental E_a. The values calculated by our algorithm (E^*) do.

R&S question the meaning of the experimental value of E_a = 10.9 kJ mol^{-1} for $Bu^tO^\bullet + H\text{–}OBu^t$, because it is much lower than their calculated value of 43.1. The argument given is that the measured value does not pertain to simple hydrogen abstraction, but 'could alternatively be a consequence of hydrogen bonding prior to H-atom transfer', a suggestion previously also made by others to explain the low energies of activation observed in such reactions. If equilibrium (2) is controlling H-atom transfer [eqn. (3)] then the relationship

$$RO^\bullet + HOR' \rightleftharpoons \underset{\text{H-bonded complex}}{[RO^\bullet\cdots HOR']} \qquad (2)$$

$$[RO^\bullet\cdots HOR'] \longrightarrow ROH + {}^\bullet OR' \qquad (3)$$

between the observed activation energy E_{obs}, the enthalpy change in (2) ΔH_2 and the energy of activation of eqn. (3) E_3 is as shown in eqn. (4).

Table 1 Experimental energies of activation (kJ mol^{-1}), D(A–H) values and E_a values calculated by the R&S model, $E_{R\&S}$, and by our model, E^*, and the corresponding triplet repulsion, ^3E

Reaction	E_a	D(A–H)	$E_{R\&S}$	E^*	^3E
$H_3Si^\bullet + H{-}SiH_3$	>62.8[a]	383	44.4	77.4	89.1
$Me^\bullet + H{-}Me$	56.6–60.7[b]	439	55.9	60.7	81.6
$H^\bullet + H{-}H$	40.2[c]	436	38.3	41.0	68.6
$RCH_2S^\bullet + H{-}SCH_2R$	21.8[d]	367	31.1	27.6	57.7
$Cl^\bullet + H{-}Cl$	10.9,[e] 22.6,[f] 27.6[b]	432	37.5	22.2	54.0
$Bu^tO^\bullet + H{-}OBu^t$	10.9[g]	440	43.1	10.9	47.4

[a] Ref. 6. [b] Ref. 7. [c] 'Exact' quantum mechanical calculation at 0 K, ref. 4. For our calculation we used D(H–H) = 432 also at 0 K. [d] Ref. 8. [e] Ref. 9. The average of the three experimental values for this reaction is 20.4. [f] Ref. 10. [g] Ref. 11.

Table 2 Bond data[a] used in the calculation of the E^* values of Table 1

Bond	D/kJ mol^{-1}	r_e/Å	ν/cm^{-1}
$H_3Si{-}H$	383.3[b]	1.4798	2190[c]
$H_3Si{-}SiH_3$	321.7[d]	2.331	432[c]
$CH_3{-}H$	438.9	1.087	2994
$H_3C{-}CH_3$	376.1	1.5351	995
H–H	431.8	1.7414	4159[d]
$RCH_2S{-}H$	367.4	1.350	2600[e]
$RCH_2S{-}SCH_2R$	261.5	2.029	532[f]
Cl–H	431.0	1.2746	2885[d]
Cl–Cl	242.7	1.9878	554[d]
$Bu^tO{-}H$	439.7	0.950	3644[e]
$Bu^tO{-}OBu^t$	159.0	1.480	771[g]

[a] Values from ref. 5, unless otherwise indicated. [b] Ref. 13. [c] Ref. 14. From ΔH_f of disilane in ref. 15, adjusted with the more recent $\Delta H_f(H_3Si^\bullet)$ of ref. 13. [d] Ref. 16. [e] Ref. 17, gas phase values when available. [f] By analogy from propyl disulfide gas, ref. 17. [g] Ref. 18.

$$E_{obs} = 10.9 = E_3 + \Delta H_2 \qquad (4)$$

Since ΔS_2 must be unfavourable for the association of two species, ΔH_2 should be negative for equilibrium (2) to be of any significance, given the usual low concentration of radicals. This would require E_3 to be greater than the value of 43.1 kJ mol^{-1} calculated by R&S for the direct hydrogen abstraction, leaving the question unanswered as to why the system would prefer the higher energy path. Nevertheless, if it is assumed that it is possible for equilibrium (2) to be controlling, in that case reaction of $RO^\bullet$ with D–OR′ should be faster because the equilibrium will be farther to the right than with the natural compound, bonds to deuterium being stronger than bonds to hydrogen. This will generate an inverse isotope effect, $k_H/k_D < 1$. Scaiano and co-workers[12] have determined primary deuterium isotope effects for abstractions of hydroxylic hydrogen (ArO–D) by alkoxyl radicals ($Bu^tO^\bullet$). They found $k_H/k_D = 3.6$ to 4.8 and concluded that 'the breaking of the O–H bond is important at the TS'. Even though the measurements were not performed on the identical reaction as being discussed here, the two systems are sufficiently similar for the isotope effect results to be relevant. Postulating a H-bonded complex in the work of R&S was necessitated by the failure of their algorithm, which gave too high a value of E_a. Our model does not fail, but obtains for the direct abstraction the experimental value observed and is consistent with the isotope effects.

The identity exchange $RCH_2S^\bullet + H{-}SCH_2R$ was not considered by R&S, but application of their model again leads to too high a value (Table 1). Two examples of abstractions from sulfur by carbon radicals were considered by R&S but were not included in the statistics of the 65 successful simulations, because they were considered unsuccessful, giving values that were also too high. It was suggested that in reactions of the type $R^\bullet + H{-}SR' \longrightarrow R{-}H + {}^\bullet SR'$, the actual process may not be a H-atom transfer but may involve 'an assisting interaction between the attacking radical and the polarisable sulfur atom, which is not accounted for' in their model; alternatively, 'it is also possible that a two-step process could be involved, with prior addition of the carbon-centred radical to sulfur'. Although radical addition to divalent sulfur to give sulfuranyl radicals $X_3S^\bullet$ has been postulated previously, the addition presumably occurs with electrophilic radicals. In the two examples treated by R&S, $R^\bullet$ is $Bu^{t\bullet}$ and $PhCH_2^\bullet$, radicals not generally considered electrophilic. Again the only reason, in this R&S work, for postulating alternative possible mechanisms for abstractions from sulfur is that their calculation was judged to fail.

The identity exchange $Cl^\bullet + H{-}Cl$ was not treated by R&S. Their model yields $E_{R\&S} = 37.5$ kJ mol^{-1}, again considerably higher than the three scattered experimental values spanning the range of 11 to 28, for an average of 20.4 ± 6.3. Our model yields $E^* = 22.2$ kJ mol^{-1}.

The identity exchange $H_3Si^\bullet + H{-}SiH_3$ was not treated by R&S and there is no experimental value of E_a reported for it. Attempts to measure it by isotopic studies showed that there are no detectable products of hydrogen abstraction.[6] Instead, displacement is the preferred path, yielding $H_3SiSiH_3 + {}^\bullet H$ despite an endothermicity of 63 kJ mol^{-1} on thermochemical grounds. Thus a reasonable estimate can be made that E_a for H-atom transfer would have a value greater than 63, since it cannot compete with displacement. The R&S calculation yields an energy of activation of 44.4 kJ mol^{-1}, which is much too low. Postulating alternative pathways would not help explain away the failure in this case. Our model obtains $E^* = 77.4$ kJ mol^{-1} for hydrogen abstraction, properly above the estimated minimum.

In summary, for the six thermoneutral identity reactions of Table 1, the R&S algorithm succeeds in two cases; in four cases it fails to match reported E_a values, deviating by at least 9.3 and by as much as 32.2 kJ mol^{-1}. These failures may indeed be due to various complications, possible alternative mechanisms, or errors in the experimental E_a. However, our model does not fail badly in any of the six cases (maximum deviation 5.8 kJ mol^{-1}), especially considering uncertainties in some of the data required as input. The input values used in our calculation are given in Table 2.

Finally, our model places a major emphasis on the importance of antibonding (and so does the semi-empirical BEBO method):[19] R&S compare their calculation to ours and note that 'although (the R&S equation) contains no term which relates to any possible antibonding interaction between groups A and B in the transition state, it is nevertheless generally successful in predicting E_a. . .'. The clear implication is that antibonding is not important.† However, an inspection of Table 1 shows that our calculated antibonding at the TS faithfully parallels the exact ordering of all six experimental

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† It is interesting that this proposal was developed in the context of the alkoxyl–alcohol exchange, where the R&S algorithm fails to match experiment and ours succeeds.

energies of activation.‡ Antibonding can be interpreted to be the cause for the very existence of an energy barrier.

The usefulness of understanding the implications of antibonding can be demonstrated by applying the concept, in a qualitative fashion, to the well studied properties of phenols [tocopherols, 2,6-di-*tert*-butyl-4-methoxyphenol (BHT), *etc.*] as excellent autoxidation inhibitors. The reaction of alkylperoxyl radicals ($ROO^•$, the chain propagating radical in autoxidations) with α-tocopherol is fast, 7×10^6 dm^3 mol^{-1} s^{-1} at 20 °C in air-saturated cyclohexane.[20] To explain measured energies of activation near zero, electron transfer has been postulated to occur prior to H-atom transfer. However, if one considers the A–B bond in this case, one can immediately see that D(ROO–OAr) is so weak that antibonding would be minimal and no substantial energy barrier would be expected. While electron transfer is also possible, it would not be expected to be accompanied by any substantial deuterium isotope effect. For the very similar reaction of $ROO^•$ with 2,4,6-tri-*tert*-butyl[^{2}H]phenol, k_H/k_D values near 10 have been reported.[21]

Note added in proof. Subsequent to acceptance, a refinement of our calculation appeared in: A. A. Zavitsas and C. Chatgilialoglu, *J. Am. Chem. Soc.*, 1995, **117**, 10 645. This does not alter any of the conclusions reached here.

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‡ The magnitude of antibonding depends primarily on the properties of the A–B molecule (bond strength, length and IR stretching frequency), as they shape the antibonding curve. Low values of D(A–B) lead to low antibonding, long bond lengths to high antibonding, and high frequencies to low antibonding; the latter is the 'polar effect', since polar bonds have higher frequencies than non-polar ones of equal strength and high frequency leads to lower antibonding and lower E^*

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