Hydrogen abstractions by radicals. Different approaches to understanding factors controlling reactivity

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This is a response to criticisms expressed by Roberts (B. P. Roberts and A. J. Steel, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 2155) and to reservations regarding the triplet repulsion term of our *a priori* method of calculating energies of activation for hydrogen abstractions by free radicals. It is shown here that this term is related to earlier approaches of London, Eyring and Polanyi, and that our calculation describes satisfactorily reactions for which the empirical approach of Roberts and Steel shows substantial discrepancies. We reply to criticisms and apply our calculation to the understanding of recent experimental results pertaining to the $H^{18}OH$ + $^{\bullet}OH$ identity exchange. We attempt to place in perspective differing views on the factors controlling reactivity.

For hydrogen abstractions by radicals Roberts and Steel[1] have proposed an empirical equation for calculating energies of activation. They noted that no possible antibonding, or triplet repulsion, interaction between the terminal atoms of the three-body system at the transition state (TS) existed in their equation, whereas our *a priori* calculational approach depends heavily on such a term.[2] We have pointed out that their equation yields values with substantial discrepancies from experimental E_a for some reactions, for which our calculation is in better agreement with experiment.[3] Roberts responded[4] that our criticisms were 'less than objective and in some instances, based on flawed arguments and incomplete reading of the literature,' that our description of the experimental results of a report pertaining to the SiD_4 + $^{\bullet}SiH_3$ exchange was 'not correct,' that a particular term in our function was arbitrarily chosen and '*ad hoc*,' that our approach 'fails in certain cases, which is worrying because bearing in mind the claims made,† it is difficult to see how the model might be modified to rectify these failures without losing much of its simplistic merit,' and concluded that 'The failure to reproduce the activation energy for $H_3Si^{\bullet}$ + H_4Si … together with the arbitrary choice of E_R … there must be doubts concerning the generality of this method in its present form.'

The airing of differences of opinion in this case can be beneficial to advancing understanding of the fundamental factors affecting reactivity. This work addresses the criticisms, dispels some misconceptions in ref. 4 regarding our approach, examines recent experimental results for the important identity exchange $H^{18}OH + {}^{\bullet}OH \rightarrow H^{18}O^{\bullet} + HOH$, and attempts to place in perspective varying views on the factors affecting the energy of activation for hydrogen abstractions by radicals.

For reactions of the type shown in eqn. (1), Roberts and Steel

$$X\text{–}H + {}^{\bullet}Y \longrightarrow X^{\bullet} + H\text{–}Y \qquad (1)$$

have reported that energies of activation can be described with an accuracy of ±2.0 kJ mol^{-1} by the four-term equation [eqn. (2)], where energy is in kJ mol^{-1}. *D* denotes bond dissociation

$$E_a = 1.979 \times 10^{-4}[D(X\text{–}H)][D(H\text{–}Y)] + a\Delta H^{\circ} - 2.045\Delta\chi^2_{XY} + 4.227(s_X + s_Y) \qquad (2)$$

enthalpy, ΔH° is the enthalpy of reaction, $\Delta\chi^2_{XY}$ is the square of the Mulliken-type electronegativity difference between the terminal groups X and Y, and *s* is a 'structural factor' characteristic of each $^{\bullet}X$ and $^{\bullet}Y$. The values of the numeric coefficients were obtained by regression analysis to provide the best fit to a selected group of 65 experimentally determined values of E_a. The value of *a* was set to 0.2501, or to 0.1401 if $^{\bullet}Y$ is a three coordinate carbon-centered radical in which the unpaired electron is conjugatively delocalized onto an α-substituent (*e.g.* an aryl, cyano, acyl, oxy or amino group).‡ The values of the constants s_X and s_Y were similarly obtained to provide the best fit to the group of E_a values involving each radical. Roberts and Steel noted that eqn. (2) did not match experimentally determined E_a for hydrogen abstractions by carbon radicals from thiophenols, giving values of 8–9 kJ mol^{-1} higher than observed, and ascribed this discrepancy to the intermediacy of hypervalent sulfur. They also noted that eqn. (2) failed to match the experimentally determined E_a = 10.9 kJ mol^{-1} for $(Bu^t)_3CO\text{–}H + {}^{\bullet}OBu^t$, giving instead 43.1. They ascribed this to hydrogen bonding between reactants prior to hydrogen transfer and possible electron transfer within the complex. They also noted that our calculation of barrier heights to hydrogen abstractions does not fail for the $RO\text{–}H + {}^{\bullet}OR$ reaction and compared eqn. (2) to our approach.

We do not believe that the two approaches are comparable. Eqn. (2) was obtained by regressions analysis for the best fit to experimentally determined energies of activation, with a large number of parameters,§ and reproduces the values from which it was derived quite well. Other parametric approaches fitting known values of E_a have also been proposed.[5] Our approach is totally different in that it does not depend on kinetic information for calibration with each different kind of radical and type of substrate. We have demonstrated that energies of activation can be estimated as follows.[6] The energy barrier separating reactants and products, E^*, is calculated with the requirement that the strength of the bonds being broken and made be equal at the transition state (TS), *i.e.* $^1E(X\text{–}H)^{\ddagger} = {}^1E(H\text{–}Y)^{\ddagger}$ for maximum resonance, as also suggested by Polanyi.[7] The total energy of the TS is given by eqn. (3). $^1E(X\text{–}H)^{\ddagger}$

$$E^{\ddagger} = {}^1E(X\text{–}H)^{\ddagger} + {}^3E(X\text{–}Y)^{\ddagger} + E_R \qquad (3)$$

denotes bonding and $^3E(X\text{–}Y)^{\ddagger}$ denotes triplet repulsion, because the electron spins at the TS must be either X↑H↓Y↑ or X↓H↑Y↓ for simultaneous partial bonding of H to both X and Y, resulting in parallel spins (triplet) on X and Y. A crude and small zero point energy correction is made by assuming

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† It is not clear which claim was meant.

‡ These are the coefficients as revised in ref. 3. Values of 'structural factors' were also revised.

§ The fourth term of eqn. (2) alone can be from 0.0 to 17.75 kJ mol^{-1} or any of 18 values in between. The electronegativity of hydrogen was set to 5.03 in order to fit reactions of $^{\bullet}H$; this value is somewhat greater than the electronegativity of $^{\bullet}CH_3$.

that $ZPE^{\ddagger} = \frac{1}{2}[ZPE(\text{X–H}) + ZPE(\text{H–Y})]$. The energy barrier is $E^* = E^{\ddagger} + D(\text{X–H}) + \Delta(ZPE)$. Low D(X–Y) generally leads to low triplet repulsion, low E^*, and allows Y to approach more closely for a 'tight' TS. E_R is a constant, −44.4 kJ mol^{-1}, when X or Y are from the first two rows of the periodic table, or −50.2 for X or Y beyond fluorine, and we have ascribed it to resonance stabilization of one electron over three atoms.¶ For any stretched r(X–H) there is a corresponding r(H–Y) that meets the equibonding requirement and a corresponding $r(\text{X–Y}) = r(\text{X–H}) + r(\text{H–Y})$, for a linear TS. The most stable such combination of distances is the TS. The Morse function[8] is used to estimate bonding at various stretched r(X–H) and to obtain the r(H–Y) that satisfies the equibonding requirement. The corresponding ^3E(X–Y) is estimated by the anti-Morse (or triplet repulsion) function of Sato.[9] The following properties of X–H, H–Y and X–Y are needed as input data: D, bond length, uncoupled IR stretching frequency, and masses of the bonded atoms. Thus the calculation of E^* does not depend on any information derived from kinetic measurements, but only on properties of bonds in the three stable molecules. The calculation therefore is *a priori* and has been shown to give values of E^* within about 4–5 kJ mol^{-1} of experimentally derived energies of activation near room temperature for over 120 hydrogen abstractions involving radicals on hydrogen, carbon, nitrogen, oxygen, silicon, sulfur, bromine, iodine, tin, germanium, *etc*. However, for abstractions by chlorine, fluorine and hydroxyl radicals from methane, E^* can be as much as 12 kJ mol^{-1} too high relative to experimentally derived values of E_a at 300 to 500 K.

We have pointed out[3] that eqn. (2) fails with some of the simplest types of abstractions, symmetrical ones: $\text{X–H} + {}^{\bullet}\text{X} \rightarrow \text{X}^{\bullet} + \text{H–X}$, with X = H, CH_3, RO, Cl, RCH_2S and SiH_3. Eqn. (2) is successful with the first two, overestimates E_a by 32.2 kJ mol^{-1} for the third, overestimates by about 17 ± 6 for the fourth, and overestimates by 9.3 for the fifth. It was demonstrated that our approach does not fail in these cases. The case of X = $^{\bullet}SiH_3$ is discussed below.

The triplet repulsion term

Although independently derived, our eqn. (3) turns out not to be unrelated to functions derived by others following different reasoning. The first successful application of quantum mechanics to a chemical reaction is due to London,[10] who treated the identity hydrogen exchange $\text{H–H} + {}^{\bullet}\text{H}$. The London equation [eqn. (4)] gives the energy of a reacting 3-electron system,

$$E_{\text{class}} = A + B + C - \{0.5[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\alpha - \gamma)^2]\}^{\frac{1}{2}} \quad (4)$$

$\text{X–H} + {}^{\bullet}\text{Y} \rightarrow \text{X}^{\bullet} + \text{H–Y}$, in terms of coulombic and exchange energies: A and α are the coulombic and exchange energies respectively between X and H, B and β those between H and Y, and C and γ those between X and Y. Bonding between atoms X and H is given by $(A + \alpha)$ and triplet repulsion, or antibonding, by $(A - \alpha)$; similarly $(B \pm \beta)$ for H and Y and $(C \pm \gamma)$ for X and Y. Despite approximations in its derivation, the London equation is still used as the starting point for the construction of accurate potential energy surfaces.[11] For the TS of identity hydrogen abstractions (X = Y) symmetry requires that $A = B$, $\alpha = \beta$, and eqn. (4) simplifies to eqn. (5).

$$E_{\text{class}} = (A + \alpha) + (C - \gamma) + A \quad (5)$$

By definition, $(A + \alpha)$ of eqn. (5) is equal to $^1E(\text{X–H})^{\ddagger}$ of eqn. (3) and $(C - \gamma)$ to $^3E(\text{X–X})^{\ddagger}$. A in eqn. (5) corresponds to E_R of eqn. (3). Eyring and Polanyi estimated that A at the TS is 10–15% of $(A + \alpha)$ or of $^1E(\text{X–H})^{\ddagger}$. London–Eyring–Polanyi (LEP) potential energy surfaces followed,[12] and Sato's anti-Morse equation for triplet repulsion[9] led to LEPS surfaces, still in recent use.[13] For the reaction $\text{H–H} + {}^{\bullet}\text{H} \rightarrow \text{H}^{\bullet} + \text{H–H}$ at 0 K eqn. (3) yields a value of $^1E(\text{X–H})^{\ddagger} = -441.1$ kJ mol^{-1}, 17.2 kJ mol^{-1} away from $D_e(\text{H–H}) = 458.1$, and a value of $E_{\text{class}} = -417.1$, for a classical barrier height of 41.0 kJ mol^{-1} *vs.* 40.2 from the best available high level *ab initio* calculations.[11] Our setting E_R in eqn. (3) equal to −44.4, or 10% of $^1E(\text{X–H})^{\ddagger}$, is consistent with the Eyring–Polanyi estimate and with the resonance delocalization energy of one electron over three atoms noted above. E_R appear to us reasonable, rather than arbitrary and *ad hoc*. While not evident from eqn. (4), eqn. (5) shows clearly the triplet repulsion term of the London equation. Repulsive interactions were also postulated by Evans and Polanyi.[14] The widely used bond energy–bond order (BEBO) method,[15] similar to ours in concept, also uses a triplet repulsion term. The concept that properties of the X–Y bond are indispensable in estimating E_a, even though X–Y is neither reactant nor product, is also evident in the equation of Roberts and Steel, as shown by the $\Delta\chi_{XY}$ term of eqn. (2). The effect of X–Y dipoles was also recognized qualitatively in the formulation of the 'polar effect' concept for radical reactions.[16]

Abstractions by silyl radicals from silane

There is a great discrepancy between the energy barrier calculated by us[6] and by Roberts,[4] 71.5 *vs.* 37.6 kJ mol^{-1}, respectively. We estimated experimental $E_a \geqslant 63$ kJ mol^{-1} by interpreting the results of Ring *et al.*[17] for the pyrolysis of mixtures of silane and [$^2H_4$]silane to mean that they did not see reaction (6), while

$$SiD_4 + {}^{\bullet}SiH_3 \longrightarrow SiD_3^{\bullet} + SiH_3D \quad (6)$$

they had attributed the formation of Si_2H_6 and its isotopomers to reaction (7). Our interpretation was based on the following

$$SiH_4 + {}^{\bullet}SiH_3 \longrightarrow Si_2H_6 + {}^{\bullet}H \quad (7)$$

statement in their section on 'Justification for Reactions': 'Reaction (6) should be as fast and probably faster than reaction (7), since one would estimate that $E_6 \leqslant E_7$ and $A_6 \geqslant A_7$. It should be pointed out that reaction (6) is not essential to the explanation of our data.' We note that reaction (7) is endothermic by 63 kJ mol^{-1} and it was not unreasonable for these authors to *assume* that reaction (6), being nearly thermoneutral, would be faster and must have occurred. However, the authors were careful to note that the assumed reaction was 'not necessary.' We agree with Roberts that the issue of the early work is now academic, since silane pyrolysis has now been reinterpreted as being non-radical in nature.[18] Evidently, reaction (6) does not occur in the thermal decomposition of silane[19] and our estimate of $E_a(6) \geqslant 63$ kJ mol^{-1} based on that report is not valid. We hope that this sets the record straight. However, radical reactions were involved in the mercury photosensitized decomposition of disilane and reactions of photosensitized hydrogen atoms with mixtures of silane and [$^2H_4$]silane.[20] In the reaction schemes proposed for explaining the variety of products obtained, the reaction $SiD_4 + {}^{\bullet}SiH_3 \rightarrow SiD_3^{\bullet} + SiH_3D$, or its reverse, were not invoked. Gammie *et al.*[21] have published a brief communication for the rate constant of $SiH_4 + {}^{\bullet}Si(CH_3)_3 \rightarrow H_3Si^{\bullet} + HSi(CH_3)_3$, $k = 6.5 \times 10^3$ l mol^{-1} s^{-1} at room temperature, from which one can estimate $E_a \approx 27$ kJ mol^{-1} with an assumed Arrhenius A-factor of $10^{8.5}$. After taking into account that the silane–trimethylsilyl reaction is exothermic by 12 kJ mol^{-1} whereas the silane–silyl exchange is thermoneutral, this value of E_a is more in line with the value calculated by Roberts[4] for the silane identity exchange than with our value of E^*.[6] A brief statement also

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¶ 44.4 kJ mol^{-1} is approximately the difference in $D(\text{RCH}_2\text{–H})$ between propane and propene, with the odd electron delocalized over three atoms in the allyl radical. Using −50.2 kJ mol^{-1} for elements beyond fluorine has also been justified in terms of the behavior of the overlap integrals and thus it attempts to reflect known facts. Qualitatively, it is reasonable to expect greater resonance stabilization on spreading of the electron over larger atoms.

exists in the literature to the effect that silyl radicals are unreactive toward [$^2H_4$]silane at room temperature, but experimental details were not given.[22] Thus, there are no experimental studies of the temperature dependence of the rate constant and, worse, there is even conflicting evidence as to the rate at room temperature.

Roberts reports state of the art calculations (U)MP4(full)/6-311++G**, for the barrier of the silane–silyl exchange reaction giving an energy of activation of 46.2 kJ mol^{-1} at 298 K, after ZPE and spin projection corrections. These results are nearer the value of E_a obtained by eqn. (2). However, it is well known that such calculations are not yet fully reliable, especially for transition states. From the *ab initio* results reported by Roberts, we calculate $D(CH_3–H) = 415.1$ kJ mol^{-1} at 298 K, or 23.8 kJ mol^{-1} lower than the currently accepted value.|| Similarly, the *ab initio* values reported give $D(SiH_3–H) = 390.0$ kJ mol^{-1} at 298 K, or 6.7 kJ mol^{-1} higher than the current value.[4] These discrepancies are in opposite directions and give an estimate of errors to be expected of this level of calculation, even when transition states are not involved. There is in the literature another calculation of the energy barrier for the silane–silyl exchange at the 6-31G(2d,p) and 6-31G(d,2p) levels.[23] Energies of activation of 57.3 and 58.2 kJ mol^{-1} were obtained at this lower level of calculation, after the results were empirically corrected for the fraction of correlation energy not captured by MP perturbation theory. These values are nearer our calculated value rather than that of eqn. (2). It would appear that, in the absence of an experimental value for the energy of activation of the silane–silyl exchange, a definitive decision cannot be made. Doubts about the generality of our method because of the value it gives for the silane–silyl exchange should be considered in the context of the 120 or more other reactions we and others have treated successfully so far by the E^* calculation. It should also be noted that E^* is in agreement with experiment for methyl and ethyl radical abstractions from silane and for abstractions by methyl, ethyl and alkoxyl radicals from trialkylsilanes.[6]

Reactions involving thiyl radicals

For abstractions by *tert*-butyl and benzyl radicals from thiophenol, eqn. (2) yields values that are too high by 8–9 kJ mol^{-1} compared to experimental E_a and the intermediacy of hypervalent sulfur was postulated to explain the discrepancy. E^* is in agreement with experiment for abstractions from thiophenol by ethyl, isopropyl, *tert*-butyl and benzyl radicals, the maximum discrepancy being 4.2 kJ mol^{-1}. For abstraction from methanethiol by methyl radicals and by hydrogen atoms we also obtain good agreement, within about ±2.5 kJ mol^{-1}, as we do with abstractions by the same radicals from H_2S.[6] Such reactions are relevant to the explanation of 'polarity reversal catalysis'[24] for the catalytic effect of thiols in the reduction of alkyl halides by trialkylsilanes, postulated to occur *via* reactions (8) and (9), rather than directly as in reaction (10).

$$R'S–H + {}^{\bullet}R \longrightarrow R'S^{\bullet} + H–R \qquad (8)$$

$$Et_3Si–H + {}^{\bullet}SR' \longrightarrow Et_3Si^{\bullet} + H–SR' \qquad (9)$$

$$Et_3Si–H + {}^{\bullet}R \longrightarrow Et_3Si^{\bullet} + H–R \qquad (10)$$

There is no question that adding thiols works well synthetically, but we questioned the effect of 'polar effects' in hydrogen abstraction by methyl radicals from RSH, eqn. (8). Roberts agrees that there is no polar effect for abstraction by $R^{\bullet}$ = methyl in reaction (8), but calculates that there should be such an effect for abstraction by primary, secondary and tertiary alkyl radicals. In reaction (9) with R′ = Me, a 'polar effect' of −5.7 kJ mol^{-1} is estimated by Roberts for reducing the energy of activation. Although this is probably so, a problem remains. E_a [reaction (9)] must be greater than 30 kJ mol^{-1}, the value of the endothermicity of the reaction with the currently accepted values of $D(Me_3Si–H) = 395.4$ kJ mol^{-1} and $D(MeS–H) = 365.3$. E_a [reaction (9)] is probably greater than 36 kJ mol^{-1}, assuming that E_a is only 6 kJ mol^{-1} for the reverse reaction as a minimum. Since E_a [reaction (10)] has been measured as 29–33 kJ mol^{-1}, there would be little to be gained in terms of E_a by the two-step sequence of (8) and (9), unless entropic effects play a major role. We believe that this remains an intriguing problem.

Polar effects

Eqn. (2) accounts for electronegativity differences between X and Y in an explicit fashion in its $\Delta\chi^2$ term. Our E^* calculation incorporates the triplet repulsion between X and Y. Thus both approaches recognize the importance of interactions between the terminal atoms. The X–Y bond properties that we use as input also reflect X–Y electronegativity differences, not explicitly but more subtly. Polar bonds are stronger and have higher stretching frequencies and shorter bond lengths. While a stronger bond leads to greater triplet repulsion, our calculation is more sensitive to the combination of shorter bond length and higher frequency, both of which decrease repulsion. The net effect of polar X–Y is lower E^*. We have shown that measured energies of activation for reactions that would be expected to be subject to strong polar effects are matched quite well by E^*, *e.g.* for $(CH_3)_3C–H + {}^{\bullet}OR$ and $(CH_3)_3Si–H + {}^{\bullet}OR$.[6] In our view, it is reasonable to take under consideration as much of the X–Y interaction as possible, rather than only a part of it, the $\Delta\chi$. As described above, we have postulated that the net X–Y interaction is repulsive. Strong X–Y dipoles simply decrease its magnitude. We have established the significant effect of $\Delta\chi$ on the shape of potential energy curves for diatomics.[25]

The $H^{18}O–H + {}^{\bullet}OH$ reaction

A kinetic study of this reaction in the gas phase was published recently by Dubey *et al.* at 300–420 K.[26] $E_a = 17.5 \pm 2.0$ kJ mol^{-1} and $A = 10^{8.1}$ L mol^{-1} s^{-1}. The gas phase A-factor is a little low compared to the average for hydrogen abstractions often used for more complex species, $10^{8.5}$. The low value of E_a, despite the very strong bond being broken, is consistent with the low value of 10.9 kJ mol^{-1} reported for $(Bu^t)_3CO–H + {}^{\bullet}OBu^t$ in solution, where $A = 10^{6.4}$.[27] Low E_a values for such reactions in the liquid phase have often been rationalized by postulating electron transfer, or by assuming hydrogen bonding between reactants prior to hydrogen transfer, or both. An $[{}^{\bullet}OH \cdots OH_2]$ complex in the gas phase is in fact postulated by Dubey with a fairly long hydrogen bond distance of 2 Å between the hydrogen of the hydroxyl radical and the oxygen of water and stable by 24 kJ mol^{-1} relative to the isolated species. Other hydrogen bonded complexes of lesser stability were also calculated. The complex is assumed to precede the hydrogen abstraction reaction, after appropriate rotation inside its potential well. The TS geometry obtained by UHF//6-31G** for the normal hydrogen transfer step is characterized[26] as being 'very tight' and almost collinear (178.1°).

E^* calculated for normal hydrogen abstraction is 18.8 ± 1.3 kJ mol^{-1}, in perfect agreement with experiment.†† The reason

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|| Since the energy for $H^{\bullet}$ was not given, we take it as −0.5 hartree at 0 K and −0.499 252 at 298 K.

†† The bond properties used to calculate E^* were: $D(HO–H) = 497.9$ kJ mol^{-1}, bond length = 0.958 Å, stretching frequency = 3704 cm^{-1}. $D(HO–OH) = 213$ kJ mol^{-1}, bond length = 1.475 Å, stretching frequency = 943 ± 14 cm^{-1}. The observed stretching frequency is 860 cm^{-1}, but is apparently coupled with O–H bending modes, and the value of 943 cm^{-1} was obtained from the force constant $k_f = 4.322$ mdyn Å^{-1} [L. B. Harding, *J. Phys. Chem.*, 1989, **93**, 8004] by $v = 1303(k_f/\mu)^{\frac{1}{2}}$, where the reduced mass was taken as $\mu = 8.25 \pm 0.25$ amu and this uncertainty causes the uncertainty in E^*.

for this low value is that the X–Y molecule here is HO–OH, with the weak peroxide bond leading to low triplet repulsion. The *ab initio* calculations are in agreement with our prediction of 'tight' TS geometries in such cases. The tightness of the TS is reflected in the somewhat low value found for the *A*-factor in the gas phase. The E^* calculation has shown that the pass between product and reactant valleys is also narrower for RO–H + $^\bullet$OR′, compared with the methane–methyl exchange.[6] This should also lead to lower *A*-factors. In the E^* calculation, the strength of the bond being broken has an almost imperceptible effect in identity exchange reactions.

It is our view that hydrogen bonding in the gas phase should not be a significant factor for the kinetics of the reaction because of the low concentrations involved. For the water–hydroxyl experiments [H^{18}OH] was of the order 7×10^{-5} M and [HO$^\bullet$] was 5–6 orders of magnitude less. Even with an assumed unreasonably high equilibrium constant $K_e = 200$ for formation of hydrogen bonded complexes, their concentration would be of the order of 10^{-11} M or less than 2% of the concentration of HO$^\bullet$. In addition, a hydrogen bonded complex [$^\bullet$OH···^{18}OH$_2$] would have to climb an energy barrier of 41.5 kJ mol^{-1} to be converted to products, whereas the uncomplexed reactants have to overcome a barrier of only 17.5 kJ mol^{-1}. If hydrogen transfer were occurring by tunneling or electron transfer inside the potential well of the complex as the predominant methods of reaction, the observed activation energy would be close to zero, which is not the case. Any small amounts of [$^\bullet$OH···^{18}OH$_2$] that are formed are simply out of action until they re-dissociate; their formation does not remove any significant amounts of reactants. Applying Occam's razor,[28] there appears to be no necessity for postulating a significant role for such complexes in the gas phase kinetics.

The situation is quite different in the liquid phase, as with the RO–H + $^\bullet$OR′ reactions, where hydrogen bonded alcohol dimers and [ROH···solvent] complexes react slower and a very substantial amount of ROH can be in this form. Any complexed R′O$^\bullet$ would have a substantially reduced reactivity and, mostly, would be out of action. We believe that these views are consistent with the conclusions reached by Ingold, Lusztyk and co-workers from their extensive investigations of hydrogen abstractions by Bu^{t}O$^\bullet$ from phenol and from α-tocopherol,[29] which also show very low activation energies consistent with the very low triplet repulsion expected with X–Y = RO–OPh.

Failures of the calculations

Roberts explains discrepancies between experimental E_a and values calculated by eqn. (2) in terms of possible complications such as hypervalent sulfur intermediates for reactions involving thiyl radicals; non-equilibrium hydrogen bonding with possible tunneling or electron transfer for reactions of oxy radicals with alcohols; and possible hydrogen bonding or valence-shell expansion for Cl–H + $^\bullet$Cl. Each of these explanations is not unreasonable. As pointed out,[4] if any such factors are operative, eqn. (2) should fail because such factors were not included in its derivation. Such factors also were not considered in the formulation of the E^* calculation, which should also fail in these cases. It does not.

The E^* calculation does fail with some reactions. For example, for CH$_4$ + $^\bullet$OH, E^* is about 13 kJ mol^{-1} higher than E_a determined experimentally near room temperature. All high level *ab initio* calculations for this reaction also yield high values for the energy of activation near room temperature. The classic explanation for such cases, and invariably invoked, is tunneling, which is probably real in some instances. We prefer to count such cases as failures, to avoid ascribing to our numbers meaning beyond what could be reasonably expected. Another failure of our method that came to our attention recently is PhO–H + $^\bullet$H→PhO$^\bullet$ + H–H,[30] for which we obtain negative E^* using the currently accepted value of D(PhO–H) = 370 kJ mol^{-1}. Substantially higher values of BDE(PhO–H) have been reported[31] and their use would bring E^* to near zero, but these higher values have been questioned,[32] and we avoid entering into the argument solely on the basis of the E^* results.

The advantage of empirical approaches is that one can add terms and parameters to account for various effects such as hydrogen bonding, electron transfer, valence shell expansion, *etc.*,[4] or calibrate for a group of reactions, such as abstractions from phenols, by additional 'structural factors.' Our *a priori* approach is not flexible.

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