PAPER

Ring-opening radical clock reactions: many density functionals have difficulty keeping time†‡

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The ability of several density-functional theory methods to describe the kinetics and energetics of a series of ring-opening reactions of cyclopropyl and cyclobutyl-type radicals was explored. PBE, B971 and B3LYP perform quite well in their ability to replicate experiment, based upon the ring opening of cyclopropylcarbinyl, two α-trialkylsilyloxycyclopropylmethyl radicals, pentamethylcyclopropylcarbinyl, cyclobutylcarbinyl and 1-cyclobutylethylcarbinyl. The other functionals tested, which includes BLYP, CAM-B3LYP, BHandHLYP, B2PLYP and B2PLYP-D, as well as functionals designed for kinetics applications, namely MPW1K, BMK and M06-2X, all perform poorly. The latter of these functionals display some integration grid dependencies.

Introduction

Our recent interest in radical clock species is related to their possible use as a means of measuring hydrogen-abstraction rate constants associated with the formation of ordered organic nanostructure formation on silicon surfaces.[1] We,[2] and others,[3] have shown that silicon surface radicals present on an almost completely hydrogen-terminated silicon(100)-2 × 1 act as initiation sites for the formation of lines of surface-bound molecules. These structures were observed using scanning tunneling microscopy under ultrahigh vacuum conditions.

Using well-understood radical addition chemistry, silicon surface radicals (referred to as dangling bonds (DBs)) will react with double-bond containing molecules like styrene[1] to form a carbon-centred radical addition intermediate that is covalently linked to the surface. The carbon-centred radical then abstracts a surface H atom from a nearby site, thereby passivating itself and generating a new surface DB that is juxtaposed with the newly added molecule (see Fig. 1 of ref. 2a).

The H–Si(100)-2 × 1 surface possesses terraces of parallel rows of silicon dimers. Since the most easily abstractable H atom is the

nearest one on the next dimer in the row, the observed radical-mediated growth on these surfaces generates straight lines of molecules that are aligned with these dimer rows. Controlling the formation of these organic nanostructures on silicon is important for developing technologies that can exploit the unique properties of novel hybrid systems. Fine control over the formation of these nanostructures can only be obtained once we have a good understanding of the kinetics of line formation.

We hypothesize that radical clock precursors could be used to develop some insights into the mechanism/kinetics of line growth processes. (A radical clock precursor is defined as a molecular species that forms a radical clock once it has added to a silicon surface DB.) By using a molecule that is capable of line growth (*i.e.*, that allows radical addition followed by H-abstraction) and alternative chemistry (*e.g.*, ring opening), it should be possible to use nanostructure shape as a reporter of reaction mechanism. For example, cyclobutylmethylketone (*c*-C_4H_7–$C(CH_3)$=O, CBMK) is a radical clock precursor that forms a radical clock (essentially an α-silyloxyl cyclobutylcarbinyl radical) upon addition to the surface, which can then react *via* two pathways.[4] In one pathway, the surface-bound radical can abstract a H atom from a neighbouring surface site, as in the case of styrene. Alternatively, the radical clock can undergo ring opening. In the former case, subsequent addition/H-abstraction events will lead to straight line growth,[5] while the latter results in the formation of a carbon-centred radical on one end of a six atom chain, with its other end anchored to the silicon surface. The longer reach of the ring-opened species allows for H abstraction from a number of surface sites, such that subsequent addition/ring-opening/H-abstraction reactions lead to disordered molecular structures on silicon. Thus, kinetic information about H-abstraction by carbon-centred radicals from silicon surfaces (a critical process for line growth) can be obtained using CBMK. To make use of

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† This work is dedicated to the memory of Athel Beckwith, a teacher and scientist from whom we learned how to study chemistry by example. His pioneering advances in radical chemistry laid the foundation for much of the current radical clock methodology.

‡ Electronic supplementary information (ESI) available: Tables S1–S9: Activation energies and rate constants for ring opening of CPC, SCPC, MSCPC, PMCPC, CBC and CBEC. Tables S10–S16: E_0, ΔE_{therm} and $Q^{\ddagger}/Q$ for ring opening of CPC, SCPC, PMCPC, CBC and CBEC. Table S17: Calculated ring strain enthalpy for cyclopropane and cyclobutane. Tables S18–S37: Optimized Cartesian coordinates. See DOI: 10.1039/c0ob01246g

radical clocks to obtain kinetic information, we can calculate the rate constants for ring opening and for H-abstraction for the surface-bound addition intermediate using quantum mechanics and conventional transition state theory. To ensure that the results of our calculations are in agreement with experiment, we make use of available solution-phase radical clock rate constant data obtained by Beckwith and others.

In this contribution, we present our detailed efforts to understand how different density-functional theory methods treat ring-opening reactions. The radical clock species studied in this work (see Scheme 1) include cyclopropylcarbinyl (CPC), two isomers of α-trialkylsilyloxycyclopropylmethyl radicals (SCPC and MSCPC) and pentamethylcyclopropylcarbinyl (PMCPC). Two clocks with a cyclobutyl framework, namely cyclobutylcarbinyl (CBC) and α-ethylcyclobutylethylcarbinyl (CBEC) are also investigated. The latter of these is used as a model for the more complex 1-cyclobutyldodecyl radical discussed in ref. 10. Collectively, these address an important question posed by Beckwith§ related to delineating the effects of radical clock-substituent on the ring-opening rate constant of the surface species.
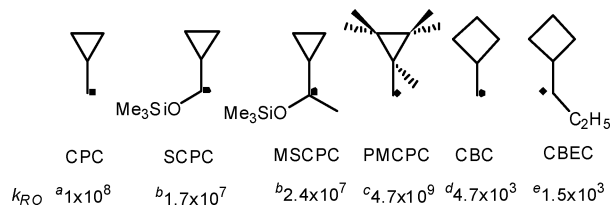
Scheme 1 Representations of the radical clocks studied in this work, with experimentally determined ring-opening rate constants (s⁻¹). [a]Reference 6, [b]Reference 7, [c]Reference 8, [d]Reference 9, [e]Model compound for 1-cyclobutyldodecyl radical (ref. 10).

Computational methods

There is a plethora of computational chemistry methods now available, each of which are better suited to different chemistries and molecular properties. The development of new techniques is often accompanied by testing on benchmark data. Method developers often use high-level wavefunction data (*e.g.*, coupled-cluster singles and doubles with perturbative triples (CCSD(T)) with complete basis set (CBS) extrapolation – considered the computational chemistry "gold standard") on atom-transfer reactions as their benchmark data. This is also true of methods developed specifically for kinetics applications (*e.g.*, MPW1K[11] or BMK[12]) despite the availability of a large amount of very good experimental kinetic data for other reactions.

The radical clocks shown in Scheme 1 were studied using a variety of methods that include traditional and modern density-functional theory (DFT) approaches, implemented in the Gaussian-03[13] and Gaussian-09[14] program packages. Based on works detailing DFTs for thermochemical kinetics,[11,12] and on findings with BHandHLYP, the consensus amongst developers is that large percentages of Hartree–Fock exchange (HFX) in the DTF method is required to give reasonable barrier heights. We

therefore included in our study DFTs that include no HFX in their formulation (B[15]LYP[16] and PBE[17]), hybrid DFTs that include some amount of HFX (B3[18]LYP,[16] B971,[19] and BHandHLYP[16,20]) along with other forms of electron exchange, *e.g.*, B88,[15] and a "range-separated DFT" possessing different HFX at short and long range (CAM-B3LYP[21]). We also included DFT methods specifically developed for kinetics (BMK and MPW1K) and a DFT designed to reproduce dispersion, kinetics and thermochemistry (M06-2X[22]). We thought it might be interesting to assess a "double-hybrid" approach – one that uses Kohn–Sham orbitals in subsequent correlated wavefunction Møller–Plesset calculations with (B2PLYP-D[23]), and without empirical corrections for dispersion (B2PLYP[24]). The basis set dependence of the calculated kinetic parameters for the ring opening of cyclopropylcarbinyl (CPC) was investigated using 6-31+G(d,p), 6-311+G(d,p) and aug-cc-pVTZ and the two former basis sets were used for all of the other species.

We previously showed that DFT methods containing kinetic energy-dependent terms, *viz.*, M06-2X and BMK, produce results that display a significant dependence upon the integration grid used in the calculations.[25] To explore this dependence in the case of ring-opening kinetics, we performed a series of calculations using (300,974), (250,590), (99,302), (49,434) integration grids along with the Gaussian "default" and "ultrafine" integration grids. Unless otherwise specified, default grids were used for all calculations presented *vide infra*.

In the case of CPC, we also performed CCSD(T)/CBS calculations.[26,27]

Kinetic parameters were attained by using data calculated using the methods described above in the rate constant expression obtained from conventional transition state theory (TST):

$$k = \sigma \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q} e^{-\frac{E_0}{RT}} \quad (1)$$

In this expression, σ is the symmetry factor for the reaction (assumed to be 2 for most of the species in Scheme 1), k_B is the Boltzmann constant, h is Planck's constant, T is temperature, $Q^{\ddagger}$ is the partition function of the transition state, Q is the partition function of the radical, E_0 is the zero-point-vibration energy corrected electronic energy barrier height, and R is the ideal gas constant. For MSCPC, $\sigma = 1$ because there is a slight difference in structure and energy for the transition states involved with breaking either C–C bond in the ring. Calculated rate constants for this species are therefore taken as the sum of the rate constants for these two alternate mechanisms.

For SCPC, MSCPC and CBEC, *cisoid* isomers (*viz.*, relative positioning of the substituent and ring groups in the radical) are used to derive the kinetic data since these lie lower in energy than their *transoid* counterparts, albeit with similar barriers to ring opening observed for both isomers. Data for the *transoid* isomers are provided in ESI‡. *cisoid*-SCPC and CBEC are *ca.* 0.8 kcal mol⁻¹ more stable than their *transoid*-isomers, while *cisoid*-MSCPC is *ca.* 1.6 kcal mol⁻¹ lower in energy than *transoid*-MSCPC (calculated by B971/6-31+G(d.p)). In the remainder of the manuscript, discussion is limited to the *cisoid* structures.

The Arrhenius activation energy, E_a, is the electronic energy barrier height corrected for thermal energy (which includes ZPVE), and includes a factor of RT. The Arrhenius pre-exponential factor is evaluated by:
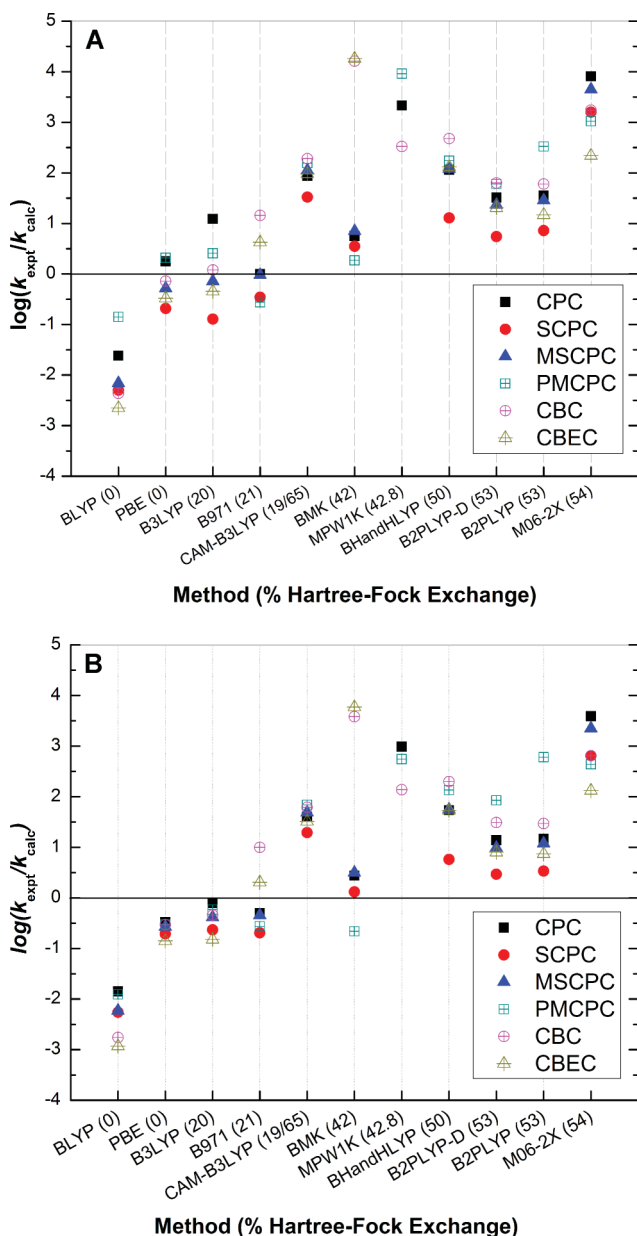
Fig. 1 Ratio of $\log(k_{expt}/k_{calc})$ as a function of density-functional theory method for six ring-opening radical clock reactions. (**A**) 6-31+G(d,p) and (**B**) 6-311+G(d,p) basis sets. Data shown calculated using default integration grid sizes, save those for M06-2X, which employed (300,974).

$$A = \frac{k}{e^{-\frac{E_a}{RT}}} \qquad (2)$$

Results

The plots in Fig. 1 summarize the calculated values of k_{RO} for the ring species shown in Scheme 1, expressed as the logarithm of the ratio of the experimentally determined to calculated k_{RO} values. A full listing of calculated k_{RO} can be found in ESI‡. The computed structures for the ground and transition state structures obtained using B971/6-31+G(d,p) are illustrated in Fig. 2, along with key internuclear separations. Optimized Cartesian coordinates for all species are given in ESI‡.
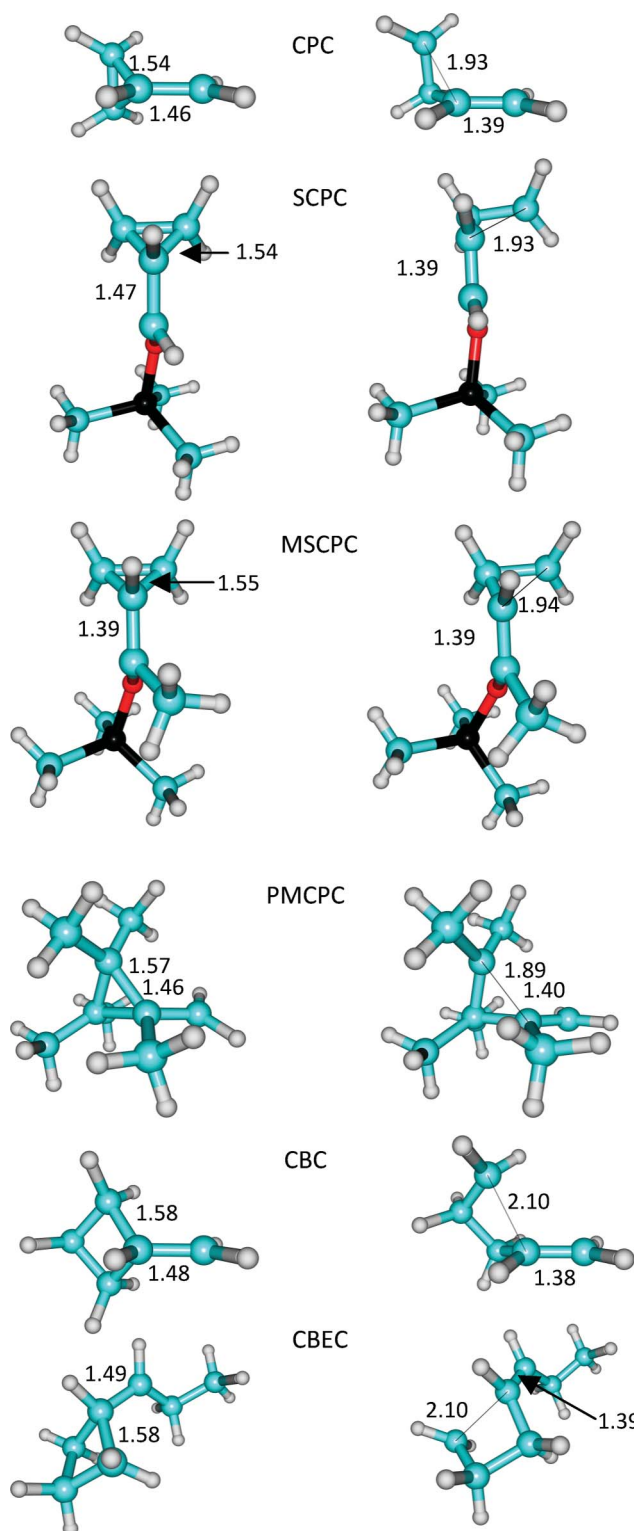
Fig. 2 Perspective views of B971/6-31+G(d,p)-optimized lowest-energy ground (left) and transition state (right) structures for ring-opening radical clock species shown in Scheme 1. Distances in Å.

Fig. 1 conveniently illustrates that different DFT methods vary widely in their ability to predict k_{RO} for the species shown in Scheme 1, with nearly six orders of magnitude separating the extremes in calculated k_{RO}. There is also significant variability in the k_{RO} values

calculated using single approaches for the six radical clocks. For example, the BLYP k_{RO} values range over *ca.* 2.5 orders while BMK values vary by nearly 4 orders of magnitude. PBE, B3LYP and B971 predict k_{RO} in best agreement with experiment, with values for all of the species shown in Scheme 1 clustered together near $\log(k_{Expt}/k_{calc}) = 0$.

Fig. 1 also shows that calculated k_{RO} values vary roughly with the percentage of Hartree–Fock exchange (%HFX) incorporated into the DFT method. k_{RO} values obtained using methods based on B88 exchange decrease in a regular fashion as the proportion of Hartree–Fock exchange increases, *viz.*, BYLP > B3LYP > CAM-B3LYP ≈ BHandHLYP.

Fig. 1A presents the data obtained with 6-31+G(d,p) basis sets and Fig. 1B shows the data obtained with 6-311+G(d,p) basis sets. The B3LYP method shows the largest change in k_{RO} (increase by a factor of *ca.* 15.5) with increasing basis set size, whereas the other approaches demonstrate increases in k_{RO} by a factor of 4.4 or less. Therefore, predicted k_{RO} values vary much less with basis set than with method. In the case of CPC, further increasing the basis set size to aug-cc-pVTZ (for these data, see ESI‡) changes the calculated k_{RO} by less than *ca.* 60% and on average by about 30%, indicating that the benefit to using these large basis sets may not be warranted by the higher computational costs. Based on these findings we did not apply aug-cc-pVTZ basis sets to the other radical clock species, and conclude that for rapid screening of methods small basis sets can be used, but suggest larger basis sets to reduce basis set incompleteness errors.

BMK and MPW1K, as well as M06-2X – *i.e.*, methods that were designed for application to kinetics – do very poorly for the species in Scheme 1. In fact, MPW1K could not find stable structures for either of the isomers of SCPC, MSCPC or CBEC. Errors in k_{RO} with all three of these approaches exceed 4 orders of magnitude in some cases and average nearly 3 orders of magnitude in others. These results suggest that there would be real value to including radical reactions into any training set of reactions used for developing new DFTs for kinetics.

The results obtained using the M06-2X functional display some grid dependence (see ESI‡). Over the range of grids tested, we found that k_{RO} varies by a factor of *ca.* 2, regardless of the basis set employed. The lowest values of k_{RO} were obtained using the default grid size used in the NWCHEM program, *viz.* (49,434),[28] while the highest values were obtained with the Gaussian-03 default grid (75,302). Such errors have been suggested to arise from the kinetic energy density enhancement factor used in the exchange component of this functional.[29] The M06-2X data displayed in Fig. 1, and subsequently discussed in the following sections, were obtained using the large (300,974) grid. In general, calculations using larger grids require more computing time.

As a check on the grid dependence of other functionals, we found that k_{RO} obtained with the BMK also show significant grid dependence, with variation in k_{RO} similar to that found using M06-2X. However, the B971-calculated k_{RO} only vary by *ca.* 5% (see ESI‡), in line with expectations for DFTs that do not have a dependence on kinetic energy density (*i.e.*, non-*meta*-GGA functionals). This check also served as verification that known grid dependencies associated with vibration frequency calculations[30] (and properties derived therein) are negligible for the species under investigation.

Discussion

Three methods, namely PBE, B971 and B3LYP, predict k_{RO} values for the species shown in Scheme 1 that are in very good agreement with experiment.[31] However, many of the other methods tested fare rather poorly. Despite tremendous advances in DFT method development, our results reinforce the importance of benchmarking in the selection of an approach for modelling a particular system. The other methods tested show a large spread in calculated k_{RO} for members of a similar set of radicals, *viz.*, *ca.* 2 orders of magnitude in substituted cyclopropyl rings by the CAM-B3LYP approach, thereby demonstrating that even substituent effects can be poorly predicted.

In order to obtain a better understanding of the variability in calculated k_{RO} values, we examined the components of the rate constants from eqn (1), *viz.*, $Q^{\ddagger}/Q$, E_0 (*i.e.*, the barrier to reaction, neglecting thermal corrections, but including zero-point vibrational corrections), and the thermal corrections to barrier height (ΔE_{therm}), which contribute to E_a. These data for CPC are plotted in Fig. 3 as a function of method/6-31+G(d,p), with similar results found for the other radical clocks in Scheme 1 (see ESI‡).
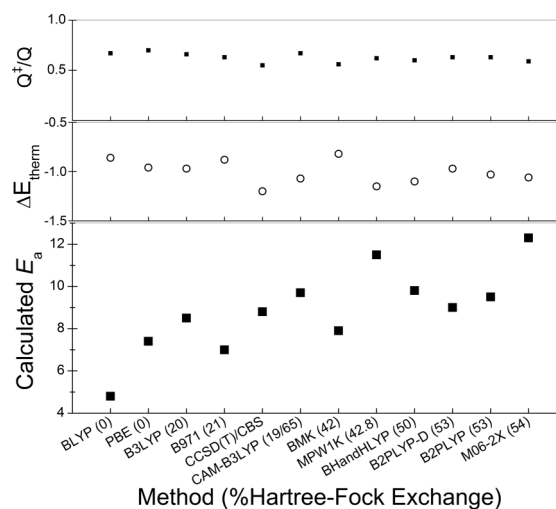

Fig. 3 Plots of $Q^{\ddagger}/Q$ (top), ΔE_{therm} (kcal mol^{-1}, middle) and E_0 (kcal mol^{-1}, bottom) as a function of density functional for ring opening of CPC, calculated using 6-31+G(d,p). Default integration grid sizes were used, save that for M06-2X, which employed (300,974).

Immediately obvious from Fig. 3 is that $Q^{\ddagger}/Q$ (upper frame) and ΔE_{therm} (middle frame) fluctuate very little as a function of method. Values of $Q^{\ddagger}/Q$ range from 0.56 to 0.70, contributing a factor of less than 1.5 to the variability in k_{RO}. Similarly, values for ΔE_{therm} have a narrow range (−1.15 to −0.82 kcal mol^{-1}), which contributes a factor of about 2 (from $\exp(0.33/RT)$) to the variability in k_{RO}. These findings indicate that the vibrational frequencies predicted tend not to be very different from method to method, therefore suggesting that most computational approaches could be used for such calculations.

However, this does not ensure that accurate geometries are obtained using all methods. In fact, there is considerable variability in calculated structure depending on the method employed. For example, for CPC using 6-31+G(d,p) basis sets, the ring C–C bonds adjacent to the radical site have distances that vary

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from 1.51 to 1.56 Å. The calculated lengths for the same bond in the transition state structure vary from 1.90 to 1.98 Å. For comparison, the CCSD/6-311+G(d,p) method predicts these two bonds lengths as 1.53 Å and 1.92 Å, respectively. Yet, there is little correlation between the bond length variability and errors in calculated rate constant.

The lower frame of Fig. 3 reveals that the variability in k_{RO} comes largely from inconsistencies in E_0 and, therefore, by extension, E_a. E_a values are between 4.5 and 12.4 kcal mol^{-1}, which gives a range of *ca.* six orders of magnitude when applied in the expression $\exp(-E_a/RT)$. Clearly, accurate activation energies, at least for the systems studied herein, remain a considerable challenge for many DFT methods.

For CPC, Newcomb and Glenn[6] report an experimental E_a of 6.8 kcal mol^{-1}.[32,33] By calculation, Borden and co-workers[34] recently predicted the temperature dependence of E_a due to tunnelling effects: range 7.6 kcal mol^{-1} (400 K) to 6.0 kcal mol^{-1} (150 K). Such data can be compared to our calculated values of 7.0 kcal mol^{-1} (B971) and 7.4 kcal mol^{-1} (PBE) with 6-31+G(d,p). Using B3LYP/6-31+G(d,p) the barrier is somewhat over-estimated (8.5 kcal mol^{-1}). Jäger *et al.*[35] also recently reported E_a values for CPC (and other radical clocks) using three computational methods. Their best results were generally obtained with the CBS-RAD method,[36] which gives an E_a for CPC of 7.2 kcal mol^{-1}, in good agreement with our B971 and PBE values. Our high-level *ab initio* wavefunction approach gives an E_a of 8.8 kcal mol^{-1}, which may reflect the inappropriate treatment of radical species using an open-shell CCSD approach.

In contrast to B971 and PBE, the E_a for ring opening of CPC, calculated by M06-2X, using the same basis, is 12.3 kcal mol^{-1}, and reflects a general trend for increased E_a with increased HFX (though not a monotonic trend). The fact that PBE and B971 (%HFX = 0 and 21, respectively) do so well for barrier heights contradicts previous conclusions that very high %HFX is required to obtain accurate barrier heights for reactions.[12] However, we note that such conclusions were drawn from data for 22 simple atom transfer reactions (mostly H transfers). Atom and/or group transfer reactions may require DFTs that are better suited to situations where there is a larger degree of electron delocalisation. In the present case, there is inherently less delocalisation because the atoms involved in the reaction are covalently bonded to each other. Given this, it may be that BMK, MPW1K and M06-2X will perform much better for radical clock ring-closing reactions.

The influence of α-trialkylsiloxyl groups on the ring opening of a CPC-type molecule was explored using isomers of SCPC and MSCPC. B971- and PBE/6-31+G(d,p)-calculated E_a for these species compare favourably to available experiment. For ring opening of SCPC we calculate an E_a of 7.3 (B971) and 7.2 (PBE) kcal mol^{-1}, while for MSCPC we find the barrier to be 8.3 (B971) and 8.2 (PBE) kcal mol^{-1}. In comparison, Nonhebel *et al.*[7] found experimental activation energies of 7.48 ± 1.20 kcal mol^{-1} (SCPC) and 7.24 ± 1.20 kcal mol^{-1} (MSCPC). BMK/6-31+G(d,p) predicts E_a's that are *ca.* 1.3 and 1.4 kcal mol^{-1} higher than B971 using equivalent basis sets.

Sterics can play a role in reducing the E_a associated with ring opening of CPC, such as, for example, in PMCPC. For this molecule, B971/6-31+G(d,p) predicts an E_a of 4.1 kcal mol^{-1}, with $\log(A) = 12.03$. The experimental values were measured as 4.9 kcal mol^{-1} and 13.15,[8] further indicating the capability of

the aforementioned basis and density functional for ring-opening reactions. The MPW1K and M06-2X functionals provide E_a's of 8.4 and 8.1 kcal mol^{-1}, respectively, with associated $\log(A)$ values of 11.52 and 12.31. In other words, these functionals exhibit E_a's that are over-estimated by at least 65% in relation to experiment.

Cyclobutyl rings, such as that contained within CBC, open much more slowly than equivalent cyclopropyl species. For CBC, Beckwith *et al.*[37] reported a k_{RO} of 2.35 ± 0.1 × 10^3 s^{-1}. This was later revised by Walton[9] to 4.7 × 10^3 s^{-1}, with which our B971/6-31+G(d,p) value (6.2 × 10^2 s^{-1}) is in reasonable agreement. Acceptable agreement is also reached between experiment and calculated E_a: 12.2 kcal mol^{-1} (experiment) *cf.* 14.9 kcal mol^{-1} predicted by B971/6-31+G(d,p). A better match to experiment can be found when larger basis sets are employed. For example, with B971/6-311+G(d,p), E_a = 14.2 kcal mol^{-1}. Using only E_a as a measure of ability, the best performing method for CBC is PBE/6-311+G(d,p), which gives an E_a of 12.9 kcal mol^{-1}. The calculated k_{RO} for this combination of basis and functional is 1.8 × 10^4 s^{-1}.

Ring opening of 1-cyclobutyldodecyl radical was observed experimentally to proceed with k_{RO} = 1.5 × 10^3 s^{-1},[10] whereas methylcyclobutyl radical opens with k_{RO} = 0.12 ± 0.1 × 10^3 s^{-1} (scaled, see ref. 37). For CBEC we calculate k_{RO} = 3.6 × 10^2 s^{-1} and E_a = 14.2 kcal mol^{-1} by B971/6-31+G(d,p), with the 6-311+G(d,p) basis providing k_{RO} = 7.4 × 10^2 s^{-1} and E_a = 13.7 kcal mol^{-1}, close to that measured for methylcyclobutyl carbinyl (12.5–13.5 kcal mol^{-1}).[37]

The influence of dispersion interactions on the reaction kinetics and energetics has been modelled in this work using corrections to B2PLYP and through the use of M06-2X. Detailed in the ESI‡ is our utilisation of another approach, developed by us, to treat these weak non-covalent interactions within conventional DFTs that otherwise perform very poorly in describing the interaction between non-covalently bound dimers. This methodology incorporates dispersion-correcting potentials (DCPs)[38] on carbon and silicon atoms into a calculation in order to alleviate the known problems associated with many DFTs (including B3LYP, PBE, B971 and BHandHLYP, among others) in predicting dispersion binding. This approach has been shown by us[25b,39] and others[40,41] to work well for a number of different chemical species. For barrier heights calculated in this work, we found that DCPs on B971/6-31+G(d,p) always reduce E_a, but that DCPs on B3LYP/6-31+G(d,p) do not always do so. For example, for CPC, B971/6-31+G(d,p)-DCP predicts an E_a that is 1.4 kcal mol^{-1} lower than when dispersion is not accounted for, while the E_a for CBC calculated by B3LYP/6-31+G(d,p)-DCP is 1.2 kcal mol^{-1} higher than the equivalent non-DCP case. But, it can also be seen that there is negligible effect on E_a for all species upon correcting B2PLYP for dispersion, thus suggesting that these interactions are of minimal importance. Allied to the findings of Shamov *et al.*[42] regarding the improvement in stability of cyclophane and polyhedrane molecules found upon using DCPs, it suggests that DCPs alter both the exchange and correlation behaviour of the functional, which will therefore affect the E_a of radical clock ring opening.

Attempts to explain the discrepancies between calculated and experimental rate constants led us to ponder the influence of ring strain enthalpy on these errors. We therefore calculated the ring strain within cyclopropane and cyclobutane[43] for a number of the functionals listed *vide infra* (see ESI‡). However, overall we

find that there is poor correlation between ring strain for these molecules and the magnitude of $\log(k_{Expt}/k_{calc})$ for CPC and CBC, or indeed to errors in E_a.

Despite this, we note that for the cyclopropyl species (CPC, SCPC and MSCPC) there is good agreement between calculated and experimental rate constants using the BMK approach, but that for the cyclobutyl structures, CBC and CBEC, $\log(k_{Expt}/k_{calc})$ vary by nearly 4 orders of magnitude using this method. Calculated errors in ring strain enthalpies by BMK/6-31+G(d,p) are only −1.70 kcal mol⁻¹ for cyclopropane, but are +3.03 kcal mol⁻¹ for cyclobutane, compared to experiment.[43] However, M06-2X/6-31+G(d,p) predicts the lowest error in ring strain enthalpy for cyclopropane, yet it is poor at describing the rate constant for ring opening of CPC ($\log(k_{Expt}/k_{calc}) \approx 3.91$); thereby underlining our belief that ring strain is only one of several possible explanations for the poor performance of some density functionals in predicting experimental energetics and rate constants. Rather, the discrepancies between calculated and experimental k_{RO} appear to be a manifestation of some combination of factors.

Conclusions

The ability of several density functionals to describe the kinetics of ring opening for a series of small cyclic carbinyls has been tested. PBE, B971 and B3LYP provide excellent agreement to experimentally determined rate constants for the ring opening of cyclopropylcarbinyl (CPC), two isomers of α-trialkylsilyloxycyclopropylmethyl radicals (SCPC and MSCPC), pentamethylcyclopropylcarbinyl (PMCPC), cyclobutylcarbinyl (CBC) and ethylcyclobutylcarbinyl (CBEC). The former two of these functionals also predict activation energies (E_a) for these reactions that closely match experiment. Other density functionals tested included BLYP, CAM-B3LYP, BMK, MPW1K, BHandHLYP, B2PLYP, B2PLYP-D and M06-2X.

Of the DFTs listed, many do rather poorly in replicating experimental rate constants for these simple reactions. We note the particularly poor performance of MPW1K, BMK and M06-2X, which were designed for application to kinetics problems, among others. Furthermore, the latter of these show noteworthy integration grid dependencies, such that larger grids than the default should be used with these functionals. Combined, these points illustrate the importance of benchmarking theoretical approaches to appropriate model systems in order to have confidence in conclusions derived from their use.

B971/6-31+G(d,p)-calculated activation barriers for ring opening are calculated to be 7.0 (CPC), 7.8 (SCPC), 8.0 and 8.3 (MSCPC), 4.1 (PMCPC), 13.3 (CBC) and 14.2 kcal mol⁻¹ (CBEC). Associated k_{RO} for these species were predicted to be 1.0×10^8, 4.9×10^7, 2.5×10^7, 2.3×10^9, 3.2×10^2 and 3.6×10^2 s⁻¹. These data agree well with experiment.[6,7,8,9,37]

We caution that the good performances illustrated here by B971, PBE and B3LYP for k_{RO} do not imply good general performance and *vice versa*. However, further calculations are in progress to determine if these functionals can be successfully applied to simple ring-closing and rearrangement radical clock reactions. Preliminary results suggest that many DFT methods will have difficulty "keeping time" in those cases as well.

Notes and references

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