

Thermochemical kinetics: does it still give insights?†

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This *tutorial review* revisits the subject of the seminal book written by Sidney Benson in 1968. A short summary of the nature of the subject is presented, including its place in the wider world of quantitative chemistry. A number of themes are selected to illustrate its previous and continuing usefulness in evaluating numerical values of important quantities, and probing ideas of reaction mechanism. These include strain enthalpies for biradical combination, chain reactions, why some reactions don't occur and the involvement of carbenes in hydrocarbon rearrangements.

1. Introduction

Thermochemical Kinetics by Sidney Benson, first published in 1968, was a landmark book.¹ It brought together and focussed many of the ideas that had guided the field of gas kinetics up to that time. In the aftermath of its publication, and for many years following, it exercised great influence. In reviewing it R. M. Noyes² wrote “Dr Benson has attempted to show us how to estimate the rate for any hypothetical reaction involving reasonably conventional compounds. Probably today nobody could do it better”.

The present author wrote an appraisal of the subject, “Thermochemical kinetics: a success story” in 1986,³ in order to demonstrate that the methods of thermochemical kinetics were still as valuable then as they ever had been. In that article I showed how information about the stability and reactivity of silenes (sila-alkenes), silylenes (sila-carbenes) and silyl cations could be obtained, even though (at that time) none of these species had been directly detected. It is now nearly 40 years since the original publication and so it seems worthwhile to

revisit the subject and to attempt a more modern appraisal. However, I do not intend in this article to review the subject matter of the original book chapter-by-chapter, a daunting task, but rather to show how the application of some of the ideas contained in it have led to an understanding of chemical behaviour in some of the reactions we, and others, have encountered in our research, largely in more recent years. By this means I hope to show the underlying ideas are still as relevant today as they were at the time of writing of *Thermochemical Kinetics*.

Before embarking on the details, however, it is worth making a few general observations. Thermochemical kinetics itself should not be regarded as a theory but rather a loose-knit collection of ideas, incorporating the main theories of kinetics (and thermodynamics). It occupies an area between, but overlapping with, several branches of chemistry (not just physical). It may be regarded as being at the interface between “reactivity” and “structure”. Fig. 1 shows its connection with particular branches of chemistry.

As a quick illustration of its use, thermochemical kinetics can take rate measurements and use them to obtain entropies and enthalpies *via* equilibrium constant values. This will be of interest to quantum chemical (*ab initio*) theoreticians.

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† One of a collection of reviews on the theme of gas kinetics.



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His work has been recognised by the 1994 FS Kipping Organosilicon Chemistry award of the American Chemical Society and the 2001 Reaction Kinetics and Mechanism award of the Royal Society of Chemistry.

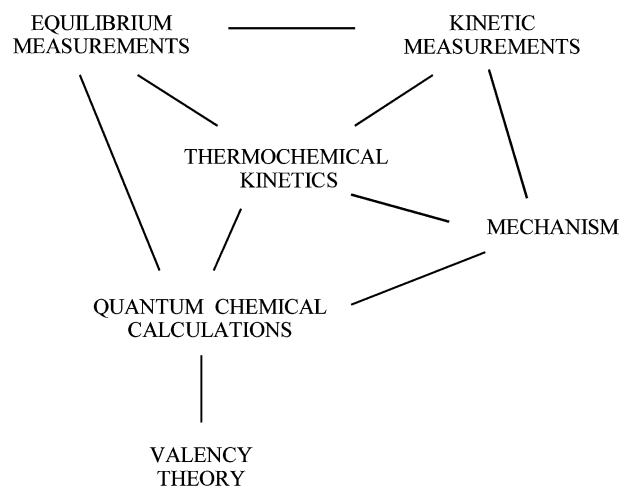
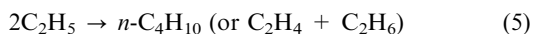
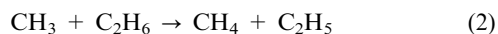
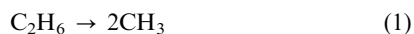


Fig. 1 The linkages between thermochemical kinetics and other subjects.

Alternatively, potential energy surfaces from quantum chemical calculations can be turned into thermodynamic data and be used to predict equilibria and rates in systems of practical interest. Or again, mechanisms in complex systems can be analysed to ask whether the values of rate constants for individual steps are reasonable, in terms of kinetic theories and what is known about the reaction energetics. This can lead to a focus on a key elementary reaction step where kinetic data are lacking, but for which available energetic quantities (*e.g.* a bond dissociation energy) can lead to a reasonable estimate. Sometimes from such considerations new information emerges about the structure and energetics of intermediates which is of interest to valency theory. Thermochemical kinetics tries to paint a broad brush picture, establishing patterns, both in thermodynamic data (entropies, enthalpies of formation) and in kinetic data (A factors, activation energies) and seeking useful generalisations, it tries to keep special cases to a minimum. It has been applied to an enormous range of chemical systems, molecular, free radical, ionic, both in solution and in the gas-phase. Because of the complexities of solvent interactions it works best in the gas-phase. Its strength and merit lies in this broadness since the implication is that patterns *do* exist. This forces questions such as the following: “What should I *expect* for this A factor?” “Is that enthalpy of formation value *reasonable*?” “Why is *this* reaction reversible and *that seemingly similar* one not so?” “Why is *this particular* intermediate involved in the mechanism?”

By looking for patterns this enables “special cases” to be identified. Sometimes they turn out to arise from errors in measurement, in which case thermochemical kinetics has served a useful critical function. However, one may legitimately ask “When should a special case arise?”. In this way thermochemical kinetics guides one to ask the right questions and helps one frame and design experiments.

One should enter a caveat. It is important to recognize that thermochemical kinetics by itself does not offer explanations for chemical phenomena at the deepest level. We may illustrate this by an example. The mechanism of pyrolysis of ethane is well established as involving the main steps:



All of the elementary steps of this scheme have been individually investigated over a wide range of temperature and pressure and are consistent with this mechanism under appropriate conditions. For example we know that the activation energy for step (1) is consistent with the C–C bond dissociation enthalpy in ethane of 376 kJ mol⁻¹. What we do not know is why $H_D^\circ(\text{CH}_3\text{--CH}_3)$ has this particular value. This is a question for theoreticians. The same may be said of the activation energy values for the other steps. A recognition of this is necessary to avoid attributing virtues to thermochemical kinetics to which it does not lay claim.

2. Some basic ideas revisited

A necessary simplification of much of thermochemical kinetics is that rate constants obey the Arrhenius equation, $k = A\exp(-E_a/RT)$. This is, of course, strictly not true. Both simple collision theory, $k = A_{sc}T^{0.5}(\exp(-E_{a,sc}/RT))$ and transition state theory, $k = (k_B T/h)\exp(\Delta S^\ddagger/R)\exp(-(\Delta H^\ddagger/RT))$ have temperature dependences which will show curvature in an Arrhenius plot if the temperature range is wide enough. However the rate constants of many reactions obey the Arrhenius equation extremely closely over the limited temperature range accessible to a single experimental technique and provided the temperature range is specified, the use of the Arrhenius equation has the advantage of simplicity compared with more sophisticated or modified equations.

A word about units. In the original,¹ kcal mol⁻¹ were used for energies and l mol⁻¹ s⁻¹ for second order rate constants. In this article I shall employ kJ mol⁻¹ for energies, overwhelmingly the conventional choice these days, although the calorie habit has been hard to kick (particularly as, for so long, the uncertainties in many bond dissociation enthalpies were close to ±1 kcal mol⁻¹). For second order rate constants, I shall use cm³ molecule⁻¹ s⁻¹, because I sense the majority of practitioners of gas-phase kinetics these days are happier with these units.

(a) A factors

This is a big subject and a central topic of all textbooks on Chemical Kinetics. The emphasis in *Thermochemical Kinetics* is on the estimation of A factors using the macroscopic (thermodynamic) form of transition state theory. To this end Benson supplies practical guidelines for the estimation of entropy, and entropy changes, which can be applied to the calculation of ΔS^\ddagger and thereby A , for any elementary process.‡ Elementary reactions may be divided into unimolecular (spontaneous) and bimolecular (collisional) processes and it is usual to treat each type separately, although some unimolecular and bimolecular processes, *viz.*, dissociation and association reactions, are linked through microscopic reversibility (*vide infra*). In this special (but frequently encountered) case, this means that A factors for forward and reverse reactions are related and the generalisations about magnitudes for one type of reaction direction have implications for the reverse reaction. “Don’t forget the back reaction” was a favourite maxim of Sidney Benson.

For unimolecular reactions, useful generalisations about A factors are summarised in Table 1. These days, of course, it is increasingly possible to calculate ΔS^\ddagger and A , by theoretical (quantum chemical) means and the Gaussian programs include add-ons to do this, but the thermodynamic part of these programs still suffers from inaccuracies arising from failure to treat internal rotations correctly. The gain and loss of internal rotations is very important in many reactions during the passage from reactant to transition state. For bimolecular reactions, the generalisations can be expressed very simply. If we exclude ion–molecule reactions, the upper limit is defined by the collision number, close to 3×10^{-10} cm³

‡ Care has to be exercised with units and standard states. See Appendix 1.

Table 1 Typical magnitudes of activation entropies and A factors for unimolecular reactions

Reaction type	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	Description	$\log(A/\text{s}^{-1})$
Molecular bond fission	+30 to +90	Loose	15–18
Molecular elimination	–20 to +30	Intermediate	13–15
Radical bond fission	–20 to +20	Intermediate	13–14
Concerted (sigmatropic)	–65 to –30	Tight	10–12

molecule^{–1} s^{–1} for many reactions. An A factor of this magnitude implies a *loose* transition state. For many types of bimolecular reaction (radical combination, abstraction, addition, carbene-type insertion) a lower limit is *ca.* 10^{–13} cm³ molecule^{–1} s^{–1}. This value would correspond to a *tight* transition state. For some molecular processes (*e.g.* the Diels–Alder reaction) even lower A factors can occur because of the loss of more rotational entropy when large molecules combine. In calculating values of ΔS^\ddagger for bimolecular reaction care has to be exercised in the choice of standard state and temperature (see Appendix 1). One can still find kinetics papers in the literature where these are not stated.

(b) Activation energies

Energies, or more strictly enthalpies,§ are at the core of thermochemical kinetics. What was assembled together in this book was a set of enthalpy quantities which enormously helped the diagnosis and rationalisation of overall enthalpy changes as well as activation energy values. These include bond dissociation enthalpies, π -bond enthalpies, strain enthalpies and stabilisation enthalpies. Underlying all this is a set of empirical rules,⁴ called Group Additivity¶ which was an extremely successful scheme (although not the only one) for estimating the enthalpy of formation of any compound whatsoever, but mainly organic substances. Even though all of the numbers in this scheme are empirical, it is based strongly on our structural knowledge of chemistry and its rationalisation *via* valency theory. These days the advent of high level quantum chemical calculations may be argued to have diminished the need for all of this. My view is otherwise. Quantum chemical calculations *per se* only provide numbers. They do not provide insight. The only way we know whether they are “correct” is by comparison with experimental data. And if there are no experimental data we need empirical schemes by which to judge the answers. Thus the need for these schemes is still there and because of the diminution of experimental activity in areas of thermochemistry such as calorimetry, one may argue the need is even greater.

These ideas provide the basis for the application of thermochemical kinetics. In what follows I have tried to illustrate its usefulness. Before that a few words about uncertainties. Over the years a useful rule of thumb for the additivity rules has been that enthalpy estimates are uncertain by *ca.* ± 4 kJ mol^{–1} and entropy estimates by ± 4 J K^{–1} mol^{–1}. In my experience, uncertainties can often be a bit larger than this, although they

§ It has been a bad habit in this field for most of my lifetime, to use “energy” when “enthalpy” was meant for many of the quantities of interest. This author will try to use the correct term.

¶ In this article, the values from ref. 1 will be used. Updated versions of these rules and hybrid schemes are listed in Appendix 2.

vary from system to system (for hydrocarbons they can be smaller). Derived uncertainties for A factors and activation energies will depend on these. For rate constant estimates, uncertainties will be temperature dependent. In the end each reaction system needs to be treated on its merits. The existence of margins of uncertainty rarely invalidates the exercise of making thermochemical kinetic estimates. In this article, for simplicity, I have mainly omitted uncertainties.

3. Examples

(a) How do equilibrium measurements help kinetics?

The interlinking of kinetics and thermodynamics occurs *via* the microscopic reversibility principle.⁵ In a reversible reaction represented by;

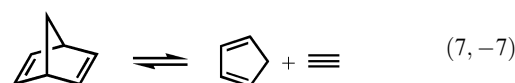


The equilibrium constant K is related to the forward and reverse rate constants as $K = k_6/k_{-6}$. The thermodynamic quantities, ΔH° and ΔS° are linked to the Arrhenius parameters *via*:

$$\Delta H^\circ_{6,-6} = E_a(6) - E_a(-6) \quad \Delta S^\circ_{6,-6} = R \ln(A_6/A_{-6})$$

These equations|| have been used, time and again, to derive thermodynamic quantities from kinetic measurements, for example to obtain enthalpies of formation of free radicals and other reactive intermediates. However the point I wish to illustrate in the example below is that this can be a two way process. Thermodynamic measurements can lead to useful kinetic (and mechanistic) information.

Some years ago⁶ we studied equilibrium process (7, –7):



Kinetic measurements were carried out in both directions to obtain rate constants and Arrhenius parameters for steps (7), (–7). These were combined to yield $K_{7,-7}$, ΔS° and ΔH° . The latter was used in conjunction with the known ΔH_f° values for cyclopentadiene⁷ and ethyne⁸ to give:




$$\Delta H_f^\circ(\text{norbornadiene}) = 243 \pm 3 \text{ kJ mol}^{-1}$$

This value was first of all useful because it corrected an erroneous previous value. But it was also useful because it enabled a value for the strain enthalpy to be worked out. Group Additivity (see Appendix 3) provides a strain free estimate of $\Delta H_f^\circ(\text{norbornadiene})$ of 115 kJ mol^{–1}, leading to a value for the strain enthalpy of 128 kJ mol^{–1}. To put this in context the strain enthalpies of all three of the bicyclo[2.2.1]hydrocarbons obtained in this manner⁹ are given in Table 2. This shows that the introduction of double bonds into norbornane leads to a systematic increase in strain enthalpy (as expected).

This thermochemical bookkeeping assists in the construction of a potential energy surface for the thermal decomposition of norbornadiene and several of its isomers. This is shown in Fig. 2. The ΔH_f° values^{6–8,10,11} for the species involved (both

|| The equations are modified for mole change reactions. For association/dissociation reactions see Appendix 1.

Table 2 Enthalpies of formation and strain enthalpies of the bicyclo[2.2.1]hydrocarbons^a

Molecule	$\Delta H_f^\circ/\text{kJ mol}^{-1}$		$\Delta H_{\text{strain}}/\text{kJ mol}^{-1}$
	Experiment	Strain free ^b	
	-52	-119	67
	88	-2	90
	243	115	128

^a See ref. 9 (Table 4). ^b Values differ slightly from ref. 9 due to use of slightly different additivity increments from ref. 1.

hydrocarbons and diradicals) are listed in Table 3. Those for hydrocarbons are all measured experimentally. For the diradicals, they are estimated. There are several different ways to do this. All are based on the assumption that the radical centres are “non-interacting”, that is the enthalpy of each centre may be calculated separately.** This can be done by using Group Additivity for radicals,¹² or by C–H bond dissociation increments or by directly considering all the thermochemical changes involved in the bond breaking process leading to the diradical. The two possible diradicals involved in these rearrangements are the following:



** Although quantum mechanics tells us that this cannot strictly be true (particularly for trimethylene ($\bullet\text{CH}_2\text{CH}_2\text{CH}_2\bullet$)) it has nevertheless proven an effective and robust approximation.

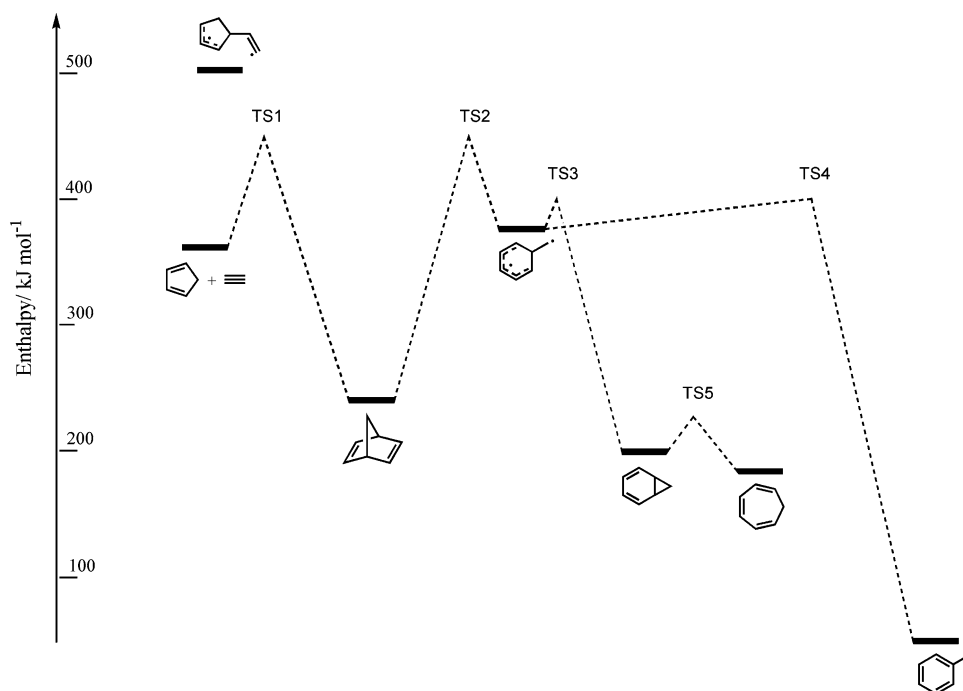
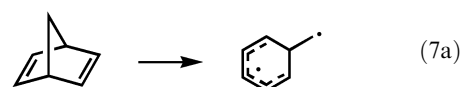


Fig. 2 Thermochemically generated potential energy (enthalpy) surface for part of the C_7H_8 system.

An illustration of the third of the above methods is given in eqn (7a) for the bond breaking process leading to diradical (I):



The enthalpy change for this process is given by:

$\Delta H^\circ = H_D^\circ(\text{C-C}) - \text{cyclohexadienyl stabilisation enthalpy} - \text{strain enthalpy difference.}$

Use of the values for these (see Appendix 3) leads to:

$$\Delta H^\circ/\text{kJ mol}^{-1} = 365 - 102 - 128 = 135$$

Combined with $\Delta H_f^\circ(\text{norbornadiene})$ this yields $\Delta H_f^\circ(\text{diradical (I)}) = 378 \text{ kJ mol}^{-1}$.








$\Delta H_f^\circ(\text{diradical (II)})$ is obtained by a similar operation (see Appendix 3).

The ΔH_f° values for the activated complexes (transition states) were obtained by simply adding ΔH^\ddagger (*viz.* $E_a - R(T)$), obtained from the pyrolysis kinetic studies (of norbornadiene and cycloheptatriene). It is worth noting, in passing, that ΔS^\ddagger (or the A factors) for these processes all have reasonable values. This is always a check that needs to be made.

Two features of this potential energy surface for norbornadiene decomposition are worth pointing out. First the transition state for the retro-Diels–Alder reaction (reaction (–7)) lies significantly below diradical (II) in enthalpy, thus showing that diradical (II) cannot be involved and that this reaction is concerted.†† Secondly for the pathway leading to cycloheptatriene and toluene, diradical (I) is certainly energetically accessible, and overwhelmingly likely to be involved. The potential energy surface also shows us that the 1,5 recombina-

†† This is a classic example of a Woodward–Hoffman symmetry allowed process.¹³

Table 3 Enthalpies of formation of some C₇H₈ hydrocarbon species

Species	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	Ref.
	243	6b
 + \equiv	360	7, 8
	198 ^a	10a
	181	8b
	50	8
	378	See Appendix 2
	505	See Appendix 2
TS1	453	6a
TS2	453	6a
TS3, TS4 ^b	400	11
TS5	229	10a

^a This value is based on an estimated ΔG° for the equilibrium between norbornadiene and cycloheptatriene. ΔH° is assumed equal to ΔG° . Group additivity gives a value of 231 kJ mol⁻¹. The difference (33 kJ mol⁻¹) may be due to homoaromaticity (see ref. 10b). ^b TS3 and TS4 are assumed to have the same value; from experiment (ref. 11) it cannot be determined which is the true reaction transition state.





tion of diradical (I) (*i.e.* reversion to norbornadiene) has a barrier of 79 kJ mol⁻¹, which makes it unfavourable relative to 1,3 recombination to give norbornadiene (which ring opens to give cycloheptatriene). The magnitude of the 1,5 recombination barrier represents *ca.* 60% of the total strain enthalpy of norbornadiene and gives us an idea of the difficulty of single bond formation in such rigid structures. Similar circumstances in other reaction systems have been exploited to inhibit combination (and other reaction channels) to such an extent that particular hydrocarbon diradicals have been directly observed.¹⁴

Although this is an old story, it illustrates how one type of enthalpy increment, a strain enthalpy, can be obtained and used in a simple way to contribute to an understanding of mechanism. It also shows that some quite elaborate potential energy surfaces can be constructed without the need for quantum chemical calculations.

(b) Not all isomerisation/decomposition reactions are unimolecular

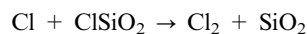
Such a statement should seem obvious to any gas kineticist, and hardly warrant serious discussion. However with the increasing ease of theoretical calculations and proliferation of potential energy surfaces as aids to reaction mechanism, there is a growing temptation to rationalise reaction product formation on the basis of a single energy surface, especially where kinetic information is sparse, or even non-existent. We had a timely reminder of this in a recent high temperature flow

Table 4 Calculated (G3) relative enthalpies of some SiCl₂O₂ species

Species	$\Delta H_{\text{rel}}^\circ/\text{kJ mol}^{-1}$	Ref.
SiCl ₂ + O ₂	0	15a
Cl ₂ SiOO (T)	-2	15b
	-318	15a
 (cis)	-277	15a
SiO ₂ + Cl ₂	-112	15a
 + Cl	-54	15a
 + Cl ₂	+122	15b
SiO ₂ + 2Cl	+126	15a
TS1	+71	15a
TS2	+37	15a

tube study¹⁵ of the reaction of SiCl₂ + O₂, a reaction of significance to the production of SiO₂ films (by CVD). Of surprise to us was the detection of Cl₂ as a reaction product. This was because it indicated the breaking of two Si-Cl bonds, which are normally very strong and have dissociation energies in the range 460–490 kJ mol⁻¹.¹⁶ Experimental thermochemistry for Si-Cl-O species is almost totally lacking and so we undertook a quantum chemical calculation (G3 level) of the structures and enthalpies of some of the likely intermediates involved in this reaction. The ΔH° values obtained are listed in Table 4 and the potential energy surface is shown in Fig. 3. This shows that the product pair, SiO₂ + Cl₂, is exothermic with respect to reactants, as also are Cl₂SiO + O(³P) [Cl₂SiO formation was also observed¹⁵]. The problem was how could SiO₂ + Cl₂ be formed? It seemed likely that the known species¹⁷ dichlorodioxasilirane, cyclo-Cl₂SiO₂, should be formed from the initial (triplet state) Cl₂Si-OO complex, after intersystem crossing. This looks to be the most exothermic pathway available. The next question is how does cyclo-Cl₂SiO₂ decompose? A long search failed to detect any transition state for a direct pathway from cyclo-Cl₂SiO₂ to SiO₂ + Cl₂. Instead two high energy transition states were found for a pathway occurring *via* the intermediacy of the silicon analogue of chlorine chloroformate, ClSi(=O)OCl. Pathways *via* this route would constitute a 1,2 Cl-atom shift with concomitant ring opening, followed by 1,2 Cl₂ elimination *via* a 4-centre activated complex. The trouble with this route is that both these transition states have positive enthalpies with respect to the reactants and so passage *via* them is unlikely to occur on the reaction timescale. Successive Cl-atom elimination is too costly in enthalpy, but single Cl-atom elimination (also with concomitant ring opening) is energetically possible. It is interesting to note that the successive bond breaking enthalpies are 264 and 180 kJ mol⁻¹, *i.e.* much lower than the typical Si-Cl dissociation enthalpies. This is discussed later.

What these relatively low values tell us is that decomposition of cyclo-Cl₂SiO₂ might be possible by other means. A simple one would be for the radicals formed by single bond fission to react together *via* disproportionation, *viz.*



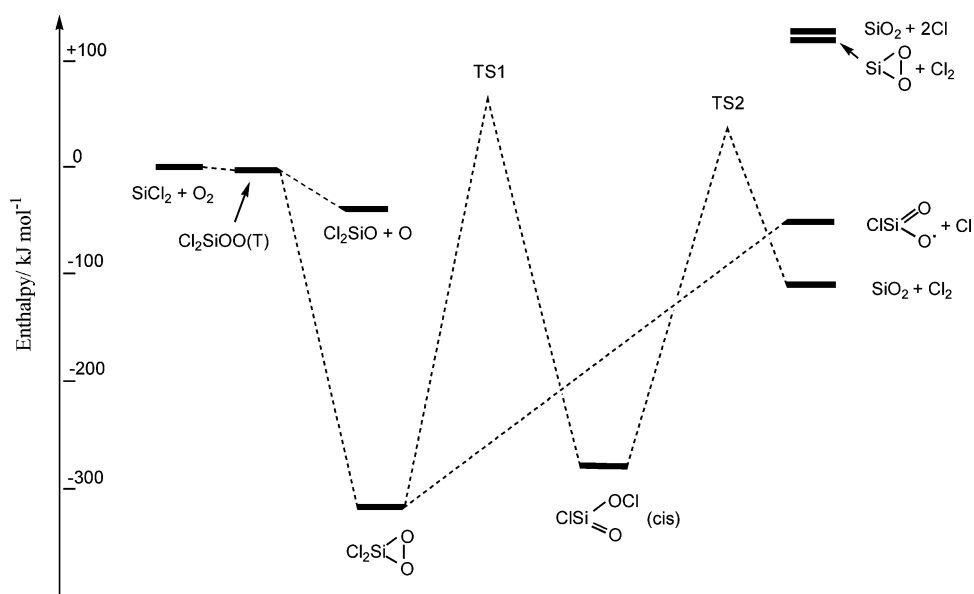


Fig. 3 *Ab initio* (G3) potential energy (enthalpy) surface for reaction of SiCl_2 with O_2 adapted from refs. 15a and 15b.

This is clearly energetically downhill (by 58 kJ mol^{-1}).

Another possibility, is the atomic chain reaction shown in eqn (8)–(11).

This chain reaction should be fairly efficient for the following reasons. Initiation would be by the fission of the relatively weak Si–Cl bond, although in practice, because the cyclo- Cl_2SiO_2 is formed vibrationally hot, some Cl atoms should be formed without collisional activation. Propagation involves (i) abstraction of the weakly bound Cl-atom by a free Cl atom in a nearly thermoneutral process and (ii) dissociation of the weakly bound Cl-atom from the ClSiO_2 radical. The termination step would almost certainly involve a self reaction of the ClSiO_2 radical, either by combination or disproportionation. To make a kinetic model of this scheme requires several rate constant estimates. While this would be relatively easy to do by means of thermochemical kinetics, we can show the feasibility of this mechanism more simply. The overall activation energy for this mechanism^{18‡‡} is given by:

$$E_a = E_a(10) + \frac{1}{2}[E_a(8) - E_a(11)]$$

‡‡ Steady state analytical expressions for chain reactions can be found in many textbooks, e.g. ref. 18.

where each E_a term refers to the appropriate step in the mechanism.

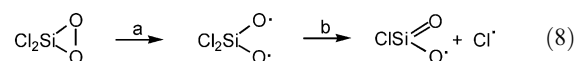
From the data provided:

$$E_a / \text{kJ mol}^{-1} = 180 + \frac{1}{2}(264 - 0) = 312$$

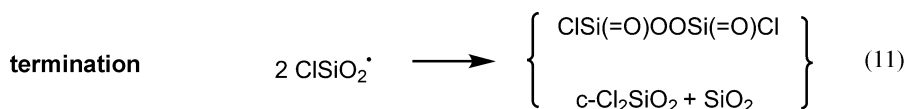
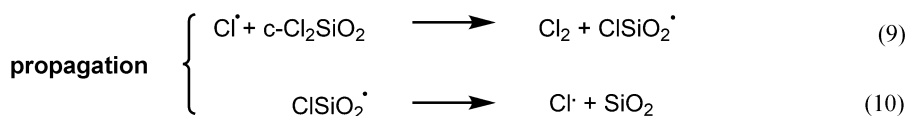
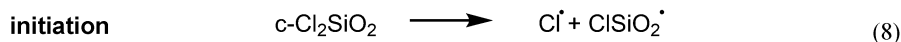
Although this value is quite high for a thermal reaction, it has to be borne in mind that if the initiation is essentially a hot reaction (*i.e.* one assisted by vibrational energy release in the reaction of SiCl_2 with O_2), then the effective activation energy may be as low as 180 kJ mol^{-1} . At a temperature of 673 K ,¹⁵ this makes it a very reasonable possibility.

What further can thermochemical kinetics tell us about this system? We can ask whether the weak Si–Cl bonds in cyclo- Cl_2SiO_2 have reasonable dissociation enthalpies.

The first dissociation process is:



The reaction is shown as passing *via* an intermediate dioxo-diradical (similar to that formed in the decomposition of dioxirane, implicated in the rearrangements of Criegee intermediates¹⁹). The enthalpy change for this process is given by:

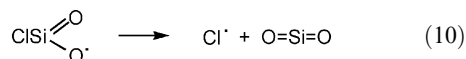


$$\Delta H^\circ = \Delta H^\circ(8a) + H_{D^\circ}(\text{Si-Cl}) - H_{D\pi 1^\circ}(\text{Si=O}) = H_{D^\circ}(\text{O-O}) - \text{strain enthalpy} + H_{D^\circ}(\text{Si-Cl}) - H_{D\pi 1^\circ}(\text{Si=O})$$

Use of the values for these (see Appendix 4) leads to:

$$\Delta H^\circ/\text{kJ mol}^{-1} = 226 - 151 + 501 - 331 = 245$$

The second dissociation process is:



This process can be visualised as a single step and its enthalpy change is given by:

$$\Delta H^\circ = H_{D^\circ}(\text{Si-Cl}) - H_{D\pi 2^\circ}(\text{Si=O})$$

Use of the values for these (see Appendix 4) leads to:

$$\Delta H^\circ/\text{kJ mol}^{-1} = 450 - 285 = 165$$

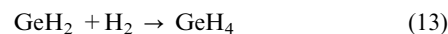
Thus the reason that these Si-Cl bond breaking steps have relatively low enthalpies is that they also involve the release of strain enthalpy and/or the formation of Si=O π -bonds. Both these estimated values lie reasonably close to the G3 calculated values. It should be pointed out that the input data for these also derive from theoretical calculations, so in a sense what has been done here is to use the results of one set of calculations to check another. However in the process we have derived the values for useful quantities, *viz.* the dissociation enthalpies, and π -bond enthalpies for Si=O (in silanoates and silicon dioxide). Considering the reluctance of silicon to form π -bonded species, these latter are quite high in value, although not as high as their carbon analogues (see Appendix 4).

(c) Why are some reactions not observed?

It may reasonably be argued that trying to understand the varied and complex mechanisms of chemical reactions which do occur is a sufficient challenge in itself. Why bother to study those which do not occur? Ever since I first came across and read the book, *Nonexistent compounds* by W. E. Dasent²⁰ with its intriguing title, I have felt there was a place for the subject of “Non-occurring reactions”. The short summary answer given by Dasent to the question “Why can’t certain compounds with plausible chemical structures be made?” is that the proposed synthetic reactions have positive values for ΔG° . His analysis is essentially thermodynamic. But the simple analogous answer to the question, “Why don’t certain plausible reactions occur?” must include the subject of kinetics. One simple answer is that such reactions have activation

energies which are too high. However the answers to both questions are rather more complicated than this and can lead to intriguing questions.

Thermochemical kinetics enters this story because it enables us to obtain limiting values for activation energies of certain attempted reactions which did not go and in some cases to obtain actual estimates. We have found several examples of such reactions in our studies of silylene and germylene reactions.²¹ Three of these^{22–24} are shown in Table 5. In each of these studies lack of an observed reaction enabled us to set an upper limit for the rate constant. Then by means of an estimate of the *A* factor, we could convert this into a lower limit for the value of the activation energy. Details of this are given in the table. For two of these reactions, *viz.*



estimates of their activation energies could be made by consideration of their reverse reactions, *viz.* by making use of microscopic reversibility ($E_a = E_{-a} + \Delta H^\circ + RT$). Values of the activation energies (E_{-a}) for the back reactions (decompositions of CH_3SiH_3 and GeH_4) combined with the known ΔH° values (both these reaction are exothermic, see Appendix 5) lead to values of E_a of 59 (± 12) and 73 (± 12) kJ mol^{-1} , respectively, comfortably in excess of the measured limits. Theoretical values for E_a also exist for these reactions.^{22,24}

The origin of the barrier for reaction (12) is part of the wider difficulty SiH_2 has in inserting into C–H bonds, a fact well known to silicon chemists. Part of the reason for this is the polarity of the $\text{C}^{\delta-}\text{H}^{\delta+}$ bond, which hinders the approach of the positively charged Si atom in SiH_2 .²⁵ The fact that CH_2 (singlet state) can insert readily into C–H bonds (without activation energy) can be attributed to the presence of perturbations from the low lying, nearby triplet state.²⁶ It should be noted however that, whereas the barrier prohibits observation of reaction (12), an intermolecular reaction, its intramolecular counterpart occurs readily as in, for example, the ring closure reaction of ethylsilylene to silirane.²⁷ This illustrates the general proposition that where reactive sites exist in the same molecule, reaction is often favoured, because the timescale can be much shorter than that for the analogous collisional process.

The finding of an energy barrier for reaction (13) contrasts with the lack of barrier for its silicon counterpart, the reaction of $\text{SiH}_2 + \text{H}_2$. It appears that the longer Ge–H bonds in the

Table 5 Rate constant and activation energy limits for some non observed reactions of SiH_2 and GeH_2

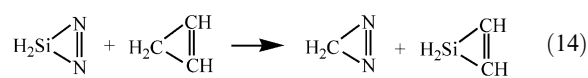
Reaction	<i>T</i> /K	<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	<i>A</i> /cm ³ molecule ⁻¹ s ⁻¹ ^a	<i>E</i> _a /kJ mol ⁻¹	Ref.
$\text{SiH}_2 + \text{CH}_4$	300	$< 3.9 \times 10^{-15}$	3.2×10^{-11}	> 23	22
	610	$< 1.3 \times 10^{-15}$	3.2×10^{-11}	> 45	22
$\text{SiH}_2 + \text{N}_2$	296	$< 3.0 \times 10^{-15}$	2.0×10^{-10}	> 29	23
	417	$< 3.8 \times 10^{-15}$	2.0×10^{-10}	> 39	23
	484	$< 2.6 \times 10^{-15}$	2.0×10^{-10}	> 47	23
$\text{GeH}_2 + \text{D}_2$	293	$< 1.0 \times 10^{-14}$	8.5×10^{-13}	> 11	24
	585	$< 1.7 \times 10^{-14}$	8.5×10^{-13}	> 19	24

^a See original papers^{22–24} for estimation of these values.

transition state require greater extension of the H–H bond (than in the SiH₂ reaction) to get sufficient orbital overlap.²⁴ The extra strain involved gives rise to the barrier.

The remaining reaction of Table 5, that of SiH₂ with N₂, was of interest because it represented a kind of ultimate challenge.²³ SiH₂, because of its highly electrophilic nature, reacts with many molecules, a lot of them at almost the collision rate. Could it react with N₂, one of the most inert molecules known? Before reviewing that system, it is worth noting that earlier we had been able to detect and study the reaction of SiH₂ with CO,²⁸ isoelectronic with N₂. The first attempted kinetic study of this latter reaction, carried out with pressures of up to 10 Torr, reported no reaction.²⁹ When we first considered this system, we knew the probable product, H₂SiCO (silaketene), had been shown to exist in a low temperature matrix and calculated to have a binding energy of 90–100 kJ mol⁻¹. We also knew that SiH₂ exhibited very fast reactions with carbonyl compounds such as acetone³⁰ and acetaldehyde.³¹ Thus our investigation of SiH₂ + CO was carried out at much higher total pressures (up to 500 Torr), on the assumption that the reaction was pressure dependent. Reaction was easily observed and the kinetics findings were consistent with a third body assisted association process close to its low pressure limit. RRKM modelling was fitted to the rate constant pressure dependence and extrapolated to a high pressure limiting value for the second order rate constant close to the collisional value.²⁸

In considering the SiH₂ + N₂ system, we therefore anticipated that pressure dependence might be a problem. However even at pressures of 500 Torr no reaction was observed. With no thermochemistry available we undertook quantum chemical calculations (G3 level) on the structures and enthalpies of some of the likely products and intermediates involved. Apart from a weakly bound complex, H₂Si·N₂, all other plausible species (or molecules we could imagine) were found to be endothermic and there was no process with an energy barrier close to the lower limit obtained by experiment. The complex corresponds to the silicon analogue of diazomethane. Its binding enthalpy is only 26 kJ mol⁻¹. Using a calculated ΔS° to obtain ΔG°, we estimated that, at equilibrium (at 298 K), the conversion of SiH₂ to this complex would be only 0.025%, on the assumption that reaction occurred.²³ Observation of H₂Si·N₂ in a low temperature matrix should be possible but not at room temperature in the gas phase. This appears to be the end of the story, but leaves unanswered the question of why formation of other products was so highly endothermic. It is well known that silicon forms strong bonds with all electronegative elements. For example, single Si–N dissociation energies lie in the range of 408 to 464 kJ mol⁻¹,¹⁶ rather greater than those of C–N bonds (303 to 355 kJ mol⁻¹³²). Can thermochemical kinetics offer any assistance? A check as to whether the Si–N_d bonds of siladiazirine have any special strength (where N_d = double bonded nitrogen) may be made through the thermochemistry of the following isodesmic (group exchange) reaction:



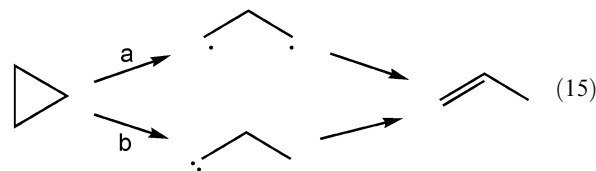
In this reaction, ring strain enthalpies should approximately cancel and the overall enthalpy difference, ΔH°, be given by the following relationship:

$$\Delta H^\circ = [2H_{\text{D}}^\circ(\text{Si}-\text{N}_d) - 2H_{\text{D}}^\circ(\text{Si}-\text{C}_d)] - [2H_{\text{D}}^\circ(\text{C}-\text{N}_d) - 2H_{\text{D}}^\circ(\text{C}-\text{C}_d)]$$

Although these dissociation enthalpies differ in magnitude, some cancellation is to be expected. The only obvious factor which could lead to a ΔH° value significantly different from zero would be the special effect of particularly strong Si–N_d bonds caused by electronegativity difference. In that case a positive value for ΔH° would be expected. Experimental data for ΔH_f° for siladiazirine are lacking, but if the theoretical value is combined with the experimental values of ΔH_f° for the other compounds (see Appendix 6), ΔH° for reaction (14) is found to lie in the range –52 ± 10 kJ mol⁻¹. Our own theoretical (G3) calculation gives –23 kJ mol⁻¹ for this quantity.²³ Thus despite some uncertainty the value is negative rather than positive. This result reveals no special strength for Si–N_d bonds unless there is some other (unknown) factor playing an unexpected role. Thus here we are led to highlight a question about the bonding in particular silicon nitrogen compounds with, as yet, no final conclusion.

(d) Can carbenes compete with diradicals as reactive intermediates?

In 1999, this question was posed^{33,34} in respect of the famous diradical mechanism for cyclopropane isomerisation.³⁵ Specifically, could a mechanism *via* propylidene (reaction (15b)) compete with that *via* 1,3-trimethylene (reaction (15a)), as shown below?



In this case the short answer seemed to be no. Both an experimental test³³ and a theoretical calculation³⁴ failed to provide any evidence or indication of a process *via* propylidene. Thus this brief flurry of activity does not appear to have disturbed the established reaction mechanism. It was, however, interesting to note that the theoretical calculation gave an energy barrier (279 kJ mol⁻¹) for this process only 10 kJ mol⁻¹ higher than that *via* trimethylene (269 kJ mol⁻¹). Interestingly a similar question had arisen some 15 years previously in respect of cyclopropene isomerisation, and in fact the outcome has been different. The analogous question, could a carbene mechanism be involved, focussed on the alternative pathways for propyne formation shown in eqn (16):

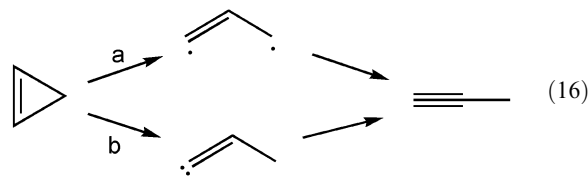


Table 6 Enthalpies of formation (kJ mol⁻¹) of some carbenes

Carbene	Singlet	Triplet
CH ₂	429 ^a	391 ^a
CH ₃ CH	354 ^b	346 ^b
(CH ₃) ₂ C	286 ^b	296 ^b
H ₂ CC	428 ^b	527 ^b

^a Ref. 38. ^b See Appendix 7.

For this case the issue has been settled clearly in favour of reaction *via* propenylidene, *i.e.* the carbene mechanism:³⁶ both theory and experiment are in agreement.³⁷§§ This poses the question, what is the significant difference between these two systems? In order for thermochemical kinetics to address this question, we need information on the thermochemistry of carbenes, particularly in situations where specific stabilisation effects are present. Apart from for methylene, CH₂,³⁸ there is little or no experimental data on carbene thermochemistry. Information on the energetics of carbenes comes largely from theory. The subject is complicated by the fact that carbenes can exist in both singlet (S) and triplet (T) states.

Enthalpies of formation are the prime requirement, and these can be obtained from the calculations of Sulzbach *et al.*³⁹ (ethylidene and 2-propylidene) and the experiments of Ervin *et al.*⁴⁰ (vinylidene). The values are shown in Table 6 for both singlet and triplet states. The derivations of these numbers are shown in Appendix 7. It is, of course, perfectly possible to develop a thermochemistry for both states, but in this article the analysis will be limited to singlets, if only because in thermal rearrangement processes it is reasonable to assume spin conservation and so if carbene involvement is suspected it is the singlet state that is the more likely (even though triplet states may be lower in energy). Because of our interests in the heavy carbenes,²¹ where these species (silylenes, germynes, stannylenes) are particularly stabilised in their ground states (singlets), we developed the concept of Divalent State Stabilisation Enthalpy (DSSE), in order to quantify this concept.^{16,25,41,42} This is defined as follows:

$$\text{DSSE}(\text{MR}_2) = H_{\text{D}}^{\circ}(\text{R}_3\text{M}-\text{R}) - H_{\text{D}}^{\circ}(\text{R}_2\text{M}-\text{R})$$

where M is the Group 14 element and R is the substituent. If substituents are mixed, the definition is similar as long as the first and second dissociation steps involve loss of the same substituent. The values for the appropriate dissociation enthalpies⁴³ and the derived DSSEs are given in Table 7. Here it can be seen that methylene and its methylated homologues have negative DSSE values, while vinylidene has a distinctly

§§ The complete story of the establishment of this mechanism is described in ref. 37.

Table 7 Sequential bond dissociation enthalpies^a and divalent state stabilisation enthalpies for some carbenes

Bond	$H_{\text{D}}^{\circ}/\text{kJ mol}^{-1}$	Bond	$H_{\text{D}}^{\circ}/\text{kJ mol}^{-1}$	Carbene	DSSE/kJ mol ⁻¹
CH ₃ -H	439	CH ₂ -H	500	CH ₂	-61
CH ₃ CH ₂ -H	423	CH ₃ CH-H	451	CH ₃ CH	-28
(CH ₃) ₂ CH-H	413	(CH ₃) ₂ C-H	414	(CH ₃) ₂ C	-1
H ₂ CCH-H	463	H ₂ CC-H	348	H ₂ CC	115

^a From ref. 53 and Table 6.

positive one. This shows clearly that in contrast to the alkylcarbenes, vinylidene is a relatively stable carbene. This points to the greater likelihood of vinylidene and its homologues being energetically accessible in hydrocarbon rearrangements. While this article is not the place to analyse in detail the structural origins of these DSSE values, the lowering of energy of the carbene lone pair orbital with a high degree of s character is a significant factor in vinylidene. This offsets the destabilising effect of electron–electron repulsion, one of the more important factors affecting CH₂ and the alkylcarbenes. Discussion of these and other factors can be found in refs. 44 and 45.

Of course, the question of whether carbenes can compete with diradicals as reaction intermediates in any particular system is not just a question of energetics of the species themselves, but also one of the energetics and structures of the respective transition states involved in their formation and subsequent rearrangement. To address this requires a knowledge of the reactive behaviour of carbenes (and of diradicals). Patterns of mechanistic behaviour for carbenes are qualitatively quite well known (insertion into C–H bonds, addition to π -bonds, reaction with lone-pairs), but quantitative kinetics is fairly sparse (exceptions are CH₂ itself and arylcarbenes⁴⁶). The reason for this is that many substituted carbenes react extremely rapidly (almost certainly on sub-nanosecond time-scales) by intramolecular pathways making direct studies of carbenes by time-resolved means difficult. An example of such a rapid isomerisation would be that of dimethylcarbene to propene, *via* a 1,2 H-atom shift (which can be viewed as a C–H insertion).

The recent finding of the importance of the vinylidene mechanism for cyclopropene thermal rearrangement, has provided a partial handle for probing the quantitative behaviour of carbenes, at least of the vinylidene type. From thermal isomerisation studies of substituted cyclopropenes,^{36,37} it has been possible to obtain relative rate constants for the various reaction pathways of methylethyl- and methylisopropylvinylidenes. These are shown in Table 8. These results permit an evaluation of the relative rate constants of the 1,3 C–H insertion processes into the various different C–H bonds as well as the relative migratory aptitudes of different alkyl groups in the 1,2 shift process to produce alkynes. While the full details are given in the original paper,³⁶ selected information on relative rates (selectivities) for intramolecular C–H insertion is shown in Table 9. This table also includes analogous data for other carbenes^{47,48} obtained by both thermal and photochemical means. The similarity of the selectivities found for different carbenes suggests that their actual rate constants may not be too dissimilar. Nevertheless these data have only been obtained at single temperatures, or over a

Table 8 Relative yields of rearrangement processes of methylethylvinylidene and methylisopropylvinylidene at 500 K

Reactant	Product ^a	Yield (%)	Pathway
		38.2	1,3 C-H _{sec} insertion
		3.5	1,3 C-H _{prim} insertion
		14.2	1,2 Me group shift ^a
		44.1	1,2 Et group shift ^a
		63.8	1,3 C-H _{tert} insertion
		4.1	1,3 C-H _{prim} insertion
		12.8	1,2 Me group shift ^a
		19.2	1,2 iPr group shift ^a

^a The determination of which alkyl group migrates was carried out by ¹³C labelling experiments (ref. 36).

Table 9 Selectivities for various C–H insertion processes

Species	Insertion	<i>k</i> _{prim}	<i>k</i> _{sec}	<i>k</i> _{tert}	<i>T</i> /K	Ref.
Alkylcarbenes	1,2 C–H	1	40	90	400–450	47
Vinylcarbenes	1,2 C–H	1	18	47	500	48
Vinylidenes	1,3 C–H	1	17	46	500	36

narrow temperature range. In order to understand these numbers at a deeper level absolute rate constant measurements over a wide temperature range are required. Up to the present time such information is lacking. Some theoretical calculations of the potential energy surfaces for reactions of dialkylvinylidenes suggest the barriers for their rearrangements lie in the 30–50 kJ mol⁻¹ range.⁴⁹ When combined with reasonable estimates of *A* factors, these correspond to rate constants in the range 10⁵ to 10⁷ s⁻¹. These values are low enough (*i.e.* the isomerisation reactions are sufficiently slow) that bimolecular reactions with efficient trapping agents might be competitive and direct kinetic studies therefore possible. It should be noted that vinylidene itself and vinylidenes with H-atoms at the 2-position undergo very rapid 1,2 H-shifts and would certainly have much shorter lifetimes. The requirements for direct study of these are much more demanding.

All of this suggests that the time is ripe for a further assessment of the possible intervention of carbene or carbene-like intermediates in hydrocarbon chemistry. Thermochemical kinetics can assist in rationalising trends in their stability and in looking for patterns in their reactivity. Direct rate studies of stabilised carbenes look to be eminently possible.

4. Conclusions

In this brief survey of applications of the ideas of *Thermochemical Kinetics* I have tried to touch on a number of the subjects included in Sidney Benson's book, choosing, by and large, recent examples of reaction systems as illustrations. The object has been to demonstrate that the ideas of *Thermochemical Kinetics* are still relevant and can give insights into mechanistic understanding of both a specific and more general kind. The examples chosen range over topics of kinetics and equilibria, unimolecular isomerisation and decomposition reactions, bimolecular association reactions and chain reactions. The reactions considered include not only those involving atoms and free radicals, but also biradicals, carbenes and silylenes as intermediates. They have illustrated the employment of enthalpies of all kinds (dissociation, strain, group increments, DSSE). The increasing contribution of theoretical calculations has been recognised, although I remain at heart an experimentalist. In this world of ever expanding use of computers and computation of all kinds, the numerical basis of thermochemical kinetics is still largely rooted in experimentally determined data. I believe it is important for the health of our subject of gas kinetics that this continues to be so.

Appendices

1. Units and standard states for association processes

Thermodynamic changes for equilibrium processes or activation processes can be a little tricky. This is particularly so for reactions with mole changes, *e.g.* association reactions. The core of the difficulty lies in the fact that in thermodynamics the standard state is the pressure of 1 bar (*ca.* 1 atm) whereas in kinetics, second (and third) order rate constants use concentration units (standard states). Since the link between pressure and concentration ($p = cRT$, assuming ideal gas behaviour) is temperature dependent this introduces complexity into any temperature dependent parameter (*e.g.* ΔH° , ΔS° of thermodynamics, *A* and E_a of kinetics). The appendix provides the useful relationships for mole change reactions ($\Delta n = -1$) and bimolecular reactions ($\Delta n^\ddagger = -1$), not all of which are in Benson's book.¹

(a) Thermodynamic changes

Equilibrium reaction: X + Y \rightleftharpoons XY

$$\Delta H^\circ = \Delta U^\circ - RT_m$$

$$\Delta S_c^\circ = \Delta S_p^\circ - R[1 + \ln(c^\circ R' T_m / p^\circ)]$$

where ΔS_c° is the entropy change for the concentration standard state, c° (either 1 mol dm⁻³ or 1 molecule cm⁻³), ΔS_p° is the entropy change at the pressure standard state, p° (1 bar); *N.B.* the units of R' will be determined by the choices of standard states; T_m is the mean temperature of study.

(b) Thermodynamic quantities of activation

Bimolecular process: $X + Y \rightleftharpoons XY^\ddagger$

$$k = \frac{k_B T_m}{h} e^{+\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

$$A = e^2 \frac{k_B T_m}{h} e^{+\Delta S^\ddagger/R} \left(\frac{R' T_m}{p^\circ} \right)$$

$$E_a = \Delta H^\ddagger + RT_m$$

In Transition State Theory the entropy of activation, ΔS^\ddagger always assumes 1 bar standard state (meaning that the subscript p in ΔS_p^\ddagger is not necessary). The $(e^2 R' T_m / p^\circ)$ term takes care of the unit (standard state) conversion.

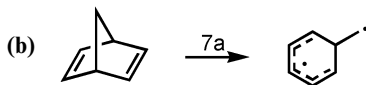
2. Group additivity

The original scheme^{1,4} was updated by Benson and Cohen⁵⁰ in 1993. It was extended to include free radicals by O'Neal and Benson.¹² The hydrogen bond increment method was introduced by Lay *et al.*⁵¹ to extend the range of available data to include resonance stabilised free radicals and incorporated *ab initio* values from theoretical sources. Further versions supplemented by theoretical calculations have been published by Sumathi and Green⁵² and Sabbe *et al.*⁵³ The latter work contains a more comprehensive literature on the subject as well as an extensive set of tables (supporting information).

3. Some group additivity and diradical enthalpy estimates

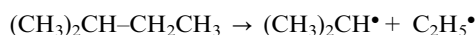
(a) ΔH_f° and strain enthalpy of

Details are given in Table 10.



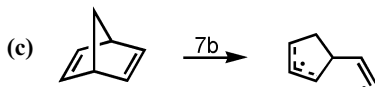
$$\Delta H^\circ = H_D^\circ(\text{C-C}) - \text{cyclohexadienyl stabilisation enthalpy} - \text{strain enthalpy difference}$$

Here the C–C bond dissociation enthalpy is that between alkane CH and CH_2 groups. The reference reaction for this is the following:



Based on ΔH_f° for the hydrocarbon^{8¶¶} and the radicals,⁴³ $H_D^\circ(\text{C-C}) = 365 \text{ kJ mol}^{-1}$. The cyclohexadienyl stabilisation enthalpy is still subject to some uncertainty but based on Sabbe *et al.*⁵³ a value of 102 kJ mol^{-1} is obtained. Assuming the diradical (I) has no strain enthalpy, the strain enthalpy difference is just the value for norbornadiene, 128 kJ mol^{-1} (Table 5).

These numbers generate the value for ΔH° given in the text.



¶¶ Values from refs. 8a and 8b are almost identical in most cases. Where not, 8b was preferred.

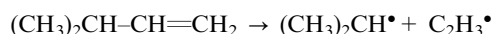
Table 10 Group additivity estimate for ΔH_f° and strain enthalpy for norbornadiene

Groups	Enthalpy contributions ^a	
	kcal mol ⁻¹	kJ mol ⁻¹
$\text{C}_-(\text{C})_2(\text{H})_2$	-4.93	-20.6
$4\text{C}_{d-}(\text{C})(\text{H})$	$4 \times (+8.59) = +34.36$	+143.8
$2\text{C}_-(\text{C}_d)_2(\text{C})(\text{H})^b$	$2 \times (-1.01) = -2.02$	-8.5
Total (strain free value)	+27.41	+114.7
Observed value	+58.0	+243
Strain enthalpy	30.6	+128

^a Values in kcal mol⁻¹ are also given here for ease of back reference to Benson.^{1, b} This group value, not listed in ref. 1, is generated from: $\text{C}_-(\text{C}_d)_2(\text{C})(\text{H}) = \text{C}_-(\text{C}_d)(\text{C})_2(\text{H}) + \text{C}_-(\text{C}_d)_2(\text{H})_2 - \text{C}_-(\text{C}_d)(\text{C})(\text{H})_2$

$$\Delta H^\circ = H_D^\circ(\text{C-C}) - \text{allyl stabilisation enthalpy} - \text{strain enthalpy difference}$$

Here the C–C bond dissociation enthalpy is that between an alkane CH and a vinylic carbon. The reference reaction is the following:



Based on ΔH_f° for the hydrocarbon⁸ and the radicals,⁴³ $H_D^\circ(\text{C-C}) = 416 \text{ kJ mol}^{-1}$. The cyclopentenyl stabilisation enthalpy is assumed to be the same as the allyl stabilisation enthalpy: a value of 51 kJ mol^{-1} is obtained from Ellison's review.⁴³ Assuming the strain enthalpy for diradical (II) is the same as that (25 kJ mol^{-1}) for cyclopentene¹ then the strain enthalpy difference is 103 kJ mol^{-1}

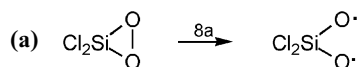
Thus:

$$\Delta H^\circ/\text{kJ mol}^{-1} = 416 - 51 - (128 - 25) = 262$$

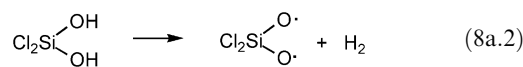
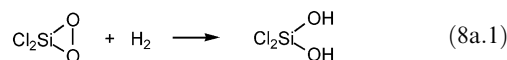
Combined with $\Delta H_f^\circ(\text{norbornadiene})$ this yields $\Delta H_f^\circ(\text{diradical (II)}) = 505 \text{ kJ mol}^{-1}$.

4. Thermochemistry of Si–O–Cl compounds

Very little is known experimentally on this. A good source of theoretical values is provided by Allendorf and Melius⁵⁴ (Si–H–O–Cl system). This was supplemented by an earlier source of theoretical thermochemistry⁵⁵ for non-chlorinated species (Si–O–H system). Some particular ΔH° values were calculated by Dr Pat Cannady.^{15b} These sources were used to obtain enthalpy changes for the following reactions.



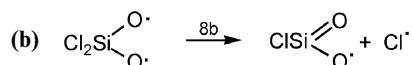
ΔH° for this reaction was obtained by combining the calculated values (G3 level)^{15b} for the reactions;



$$\Delta H^\circ(8a) = \Delta H^\circ(8a.1) + \Delta H^\circ(8a.2)$$

$$\Delta H^\circ(8a)/\text{kJ mol}^{-1} = -519 + 597 = 78$$

This rather small value may be thought of as combining the O–O bond dissociation enthalpy in a silyl peroxide ($H_{\text{D}}^\circ(\text{Cl}_3\text{SiO–OSiCl}_3) = 235 \text{ kJ mol}^{-1}$)⁵⁴ and the strain enthalpy of a typical Si-containing 3-membered ring (157 kJ mol⁻¹).



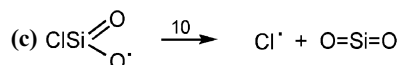
ΔH° for this reaction used the analogy of the Si–Cl bond enthalpy (501 kJ mol⁻¹) in $\text{Cl}_2\text{Si}(\text{OH})_2$ ⁵⁴ and the π -bond enthalpy obtained by considering the dehydrogenation process of $\text{H}_2\text{Si}(\text{OH})_2$ to give $\text{HSi}(=\text{O})\text{OH}$. The enthalpy change for this is given by:

$$\Delta H^\circ = H_{\text{D}}^\circ(\text{Si–H}) + H_{\text{D}}^\circ(\text{O–H}) - H_{\text{D}}^\circ(\text{H–H}) - H_{\text{D}\pi 1}^\circ(\text{Si}=\text{O})$$

$$H_{\text{D}\pi 1}^\circ(\text{Si}=\text{O}) = H_{\text{D}}^\circ(\text{Si–H}) + H_{\text{D}}^\circ(\text{O–H}) - H_{\text{D}}^\circ(\text{H–H}) - \Delta H^\circ$$

$$H_{\text{D}\pi 1}^\circ(\text{Si}=\text{O})/\text{kJ mol}^{-1} = 408 + 515 - 436 - 156 = 331$$

All the above numbers (except that for $H_{\text{D}}^\circ(\text{H–H})$) are from Allendorf and Melius.⁵⁵



ΔH° for this reaction used the analogy of the Si–Cl bond enthalpy (450 kJ mol⁻¹) in $\text{ClSi}(=\text{O})\text{OH}$ ⁵⁴ and the π -bond enthalpy obtained by considering the dehydrogenation process of $\text{HSi}(=\text{O})\text{OH}$ to give SiO_2 . The enthalpy change for this is given by:

$$\Delta H^\circ = H_{\text{D}}^\circ(\text{Si–H}) + H_{\text{D}}^\circ(\text{O–H}) - H_{\text{D}}^\circ(\text{H–H}) - H_{\text{D}\pi 2}^\circ(\text{Si}=\text{O})$$

$$H_{\text{D}\pi 2}^\circ(\text{Si}=\text{O}) = H_{\text{D}}^\circ(\text{Si–H}) + H_{\text{D}}^\circ(\text{O–H}) - H_{\text{D}}^\circ(\text{H–H}) - \Delta H^\circ$$

$$H_{\text{D}\pi 2}^\circ(\text{Si}=\text{O})/\text{kJ mol}^{-1} = 372 + 534 - 436 - 185 = 285$$

All the above numbers (except that for $H_{\text{D}}^\circ(\text{H–H})$) are from Allendorf and Melius.⁵⁵

Using analogous schemes for organic compounds, I obtain the following:⁵⁶

$$H_{\text{D}\pi 1}^\circ(\text{C}=\text{O}) = 372 \text{ kJ mol}^{-1} \text{ (in formic acid)}$$

$$H_{\text{D}\pi 2}^\circ(\text{C}=\text{O}) = 450 \text{ kJ mol}^{-1} \text{ (in carbon dioxide)}$$

5. Activation energies of reactions (12) and (13)

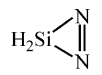
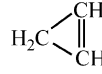
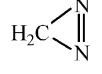
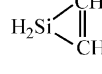
E_a for these reactions is estimated *via* $E_a = E_{-a} + \Delta H^\circ + RT$ (T taken as 298 K). No corrections were made for T dependence of ΔH° . ΔH° and E_{-a} values are given in Table 11. Source references for the data (ΔH_f° and E_{-a} values) are given in refs. 22 and 24.

Table 11 Data^a needed to calculate activation energies of reactions (12) and (13)

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$E_{-a}/\text{kJ mol}^{-1}$	$E_a/\text{kJ mol}^{-1}$
$\text{SiH}_4 + \text{CH}_4 \rightarrow \text{CH}_3\text{SiH}_3$	-227 ± 4	283 ± 12	59 ± 12
$\text{GeH}_2 + \text{H}_2 \rightarrow \text{GeH}_4$	-157 ± 10	227 ± 8	73 ± 13

^a See refs. 22 and 24.

Table 12 Enthalpies of formation (kJ mol⁻¹) of some unsaturated small ring compounds^a

Molecule	$\Delta H_f^\circ/\text{kJ mol}^{-1}$
	331
	276
	266 ± 10
	289

^a See original paper²³ for data sources.

6. Thermochemistry of reaction (14)

ΔH_f° values required to calculate ΔH° are given in Table 12. These are all experimental apart from that for siladiazirine. The available theoretical values for these species are given in the original article.²³ The significant difference between experiment ($-52 \pm 10 \text{ kJ mol}^{-1}$) and theory (-23 kJ mol^{-1}) for ΔH° (see text) is quite likely to be down to the error in the experimental value for ΔH_f° (diazirine) (in my opinion).

7. Carbene thermochemistry

ΔH_f° values for singlet and triplet methyl and dimethyl carbenes were obtained from the group exchange (isodesmic) reactions:



where S and T indicate singlet and triplet states, respectively.

From *ab initio* calculations (Becke3LYP/TZ2P level), Sulzbach *et al.*³⁹ report:

$$\Delta H^\circ(17) = 65.4 \text{ kJ mol}^{-1} (\text{S}) \text{ and } 36.2 \text{ kJ mol}^{-1} (\text{T})$$

$$\Delta H^\circ(18) = 112.4 \text{ kJ mol}^{-1} (\text{S}) \text{ and } 64.8 \text{ kJ mol}^{-1} (\text{T})$$

These were combined with the known^{1,8} values of ΔH_f° for CH_4 , C_2H_6 and C_3H_8 and also those for CH_2 ³⁸ to obtain the ΔH_f° values for $\text{CH}_3\text{CH}(\text{S/T})$ and $(\text{CH}_3)_2\text{C}(\text{S/T})$ listed in Table 6.

The ΔH_f° value for singlet vinylidene comes from ref. 40, that for triplet vinylidene is obtained by combining $\Delta H_f^\circ(S)$ with the S–T splitting of 199 kJ mol^{-1} .⁵⁷

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