
General Discussion

Prof. Balint-Kurti and **Mr Cole** opened the discussion of Prof. Troe's paper: In his presentation Prof. Troe has stressed the importance of using J -conserving theories within the context of RRKM theory. These J -conserving theories give rise to centrifugal barriers which are absolutely essential in the theory. Prof. Troe's presentation concentrates on the treatment of the transitional modes and stresses their behaviour at large fragment separations. We have been examining this problem for two model systems ($\text{NH}_2 + \text{NO}$ and $\text{CH}_3 + \text{OH}$) within the context of variational J -conserving RRKM theory. We have computed the vibrational frequencies of all the modes at each geometry along the reaction path as the fragments dissociate and have used standard J -conserving variational RRKM theory. As is well known this theory, in which all vibrational modes are treated within a harmonic approximation, breaks down at large fragment separations. In order to allow for this breakdown we have implemented a quantum phase space method in which the fragments are treated as free rotors, but their rotational angular momenta are coupled to their relative orbital angular momentum to give a definite total angular momentum for the systems. This approach also gives a sum-of-states at a particular fragment separation which can be compared with that obtained from the standard J -conserving RRKM theory for the same total angular momentum J , fragment separation R , and total energy, E . In the spirit of variational RRKM theory the lower of the two predictions of the sum-of-states for a given R , J and E should be the more correct of the two and our intention was to use this lower value. This approach would enable us to avoid the major effects of the break-down of the standard RRKM theory at large interfragment separations. The critical distance for a given E and J is that at which the sum-of-states is a minimum. Surprisingly we have found, for the two cases which we have examined, that the critical distances are always relatively small and fall within the range where the standard RRKM theory gives the lower sum-of-states value. Our conclusion is therefore, that the variation of the vibrational frequencies during the bond breaking process is of great importance and must be evaluated as a function of the bond stretching coordinate as the bond is broken.

Prof. Troe responded to Prof. Balint-Kurti and Mr Cole: Apparently you embrace sums-of-states along the reaction path by J -conserving variational harmonic oscillator RRKM and by phase space theory. A more accurate treatment is given by statistical adiabatic channel (SACM) calculations where rovibrational eigenvalues along the reaction coordinate are calculated explicitly (see, *e.g.*, our treatment of the $\text{OH} + \text{OH}$ -system in ref. 1). In this case, neither the harmonic oscillator, nor the J -coupled free rotor limits, but the more correct intermediate case is obtained. Your observation that the channel pattern at the minimum of the sum-of-states corresponds more to an oscillator situation, not only for conserved modes but also for transitional modes, should be taken with caution. Our experience is that the pattern of adiabatic channel maxima, which leads to an activated complex pseudo-sum-of-states, for transitional modes and normal anisotropies of the potential, more corresponds to that of rotors with effectively increased rotational constants (in comparison to those of the corresponding free rotors, see, *e.g.*, ref. 2) than to oscillators. In any case, your final statement about the necessity, of evaluating vibrational frequencies of transitional modes as a function of the length of the breaking bond is an essential element of the SACM concept since its earliest formulation.³

- 1 A. I. Maergoiz, E. E. Nikitin and J. Troe, *J. Chem. Phys.*, 1991, **95**, 5117; A. I. Maergoiz, E. E. Nikitin and J. Troe, *J. Chem. Phys.*, 1995, **103**, 2083; A. I. Maergoiz, E. E. Nikitin and J. Troe, *Z. Phys. Chem.*, 1991, **172**, 129.
- 2 A. I. Maergoiz, E. E. Nikitin, J. Troe and V. G. Ushakov, *J. Chem. Phys.*, 1998, **108**, 5265; A. I. Maergoiz, E. E. Nikitin, J. Troe and V. G. Ushakov, *J. Chem. Phys.*, 1998, **108**, 9987.
- 3 M. Quack and J. Troe, *Ber. Bunsen-Ges. Phys. Chem.*, 1974, **78**, 240.

Prof. Golden asked: The details discussed by Prof. Troe are interesting. What is the sensitivity to this level of treatment in any combustion model? Given the uncertainty in other rate parameters and in the experimental data, does this level of detail make any difference to any quantity that a model would be used to calculate?

Prof. Troe replied: It has been proven useful to characterize falloff curves of dissociation and recombination reactions in terms of limiting low and high pressure rate constants and by broadening factors of the intermediate reduced falloff curves. The present work addresses the question of how broadening factors $F_{\text{cent}}^{\text{SC}}$ at the center of the falloff curves, in the presence of two transitional modes and various numbers of conserved modes, can be estimated quickly. In this sense, it also allows for a check whether an experimental, empirically fitted, $F_{\text{cent}}^{\text{SC}}$ is meaningful or not. In low temperature recombination reactions, where only transitional modes contribute to $F_{\text{cent}}^{\text{SC}}$, correct treatments of rotational effects become particularly important (see, *e.g.*, my treatment of the $\text{HO} + \text{NO}_2 \rightleftharpoons \text{HONO}_2$ system in ref. 1).

1 J. Troe, *Int. J. Chem. Kinet.*, 2001, submitted.

Dr Klippenstein said: I am unclear as to the reason for the concern about the treatment of orbital angular momentum barriers. Microcanonical J -conserving variational transition state theory, which is what we generally use in our single well master equation simulations, correctly treats the rotational dependence of the dissociation rates. With this approach it is not necessary to make separability assumptions or to explicitly consider the orbital barriers and so we do not. We could tabulate rotational barriers as a function of angular momentum, but again it is not necessary for our purposes and so we do not. Instead, such barriers are implicitly considered *via* appropriate determinations of the E and J dependence of the number of available states.

Prof. Troe responded: Microcanonical J -conserving variational transition state theory is not necessarily correct. First, dynamical, nonadiabatic, couplings (see, *e.g.*, ref. 1) generally escape this treatment. Second, it is not clear what sum-of-states should be varied along the reaction coordinate (see, *e.g.*, ref. 2). Finally, just giving the results of a variational transition state/master equation treatment will hide the origin of uncertainties, let it be in the collision model, or in the potential, or elsewhere. The treatment becomes much more transparent and useful for other researchers if the various contributions are separated, *i.e.* if strong and weak collision treatments are compared, if the used potential is given explicitly or, at least, if it is characterized by its centrifugal barriers $E_0(J)$, and if limiting low pressure and high pressure rate constants are given. Otherwise, a reader has just the choice to believe or not to believe the results; he has no chance to judge the quality of the treatment and to transfer parts of it to other applications, *e.g.*, transfer T -averaged to E - and J -resolved rate constants when an inverse Laplace transformation cannot be made.

1 L. B. Harding, J. Troe and V. G. Ushakov, *Phys. Chem. Chem. Phys.*, 2000, **2**, 631.

2 M. Quack and J. Troe, *Ber. Bunsen-Ges. Phys. Chem.*, 1874, **78**, 240.

Dr Klippenstein said: You have stated that it is not possible for variational transition state theory (VTST) to correct for the differences between your classical trajectory simulations and statistical adiabatic channel model calculations of capture rate constants. In fact, this is not true. The statistical adiabatic channel model implicitly assumes that the reaction coordinate is the separation between the centers-of-mass of the two reacting fragments. If one similarly restricts the reaction coordinate within VTST simulations, as in the early work of Wardlaw and Marcus,¹ then you are correct that one would observe similar differences from trajectory simulations. However, the implementation of more general reaction coordinates, as in our variable reaction coordinate VTST formalism, can correct for the non-adiabaticities that you use classical trajectory simulations to study. Thus, there is no inherent reason that your classical trajectory results should differ significantly from the results of optimized variable reaction coordinate VTST simulations, and I know of no evidence to suggest that they do.

1 D. M. Wardlaw and R. A. Marcus, *Adv. Chem. Phys.*, 1988, **70**, (Part I), 231.

Prof. Troe responded: It is certainly true that some problems of early variational transition state theory have been removed by optimized variable reaction coordinate (VRC)-VTST. However, for fundamental reasons, I doubt that all dynamical, non-adiabatic, effects can be accounted for in this way. This is not a problem related to the choice of the reaction coordinate. A comparison with our trajectory calculations for the capture of O₂ in collisions with T, D, H and Mu on an *ab initio* potential¹ would be indicative.

1 L. B. Harding, J. Troe and V. G. Ushakov, *Phys. Chem. Chem. Phys.*, 2000, **2**, 631.

Prof. Golden commented: I would point out that my colleagues and I have found that simple RRKM models based on the Gorin model of bond scission/radical combination reactions are often quite adequate to explain, codify and extrapolate the extant data for systems where little hope exists of finding accurate potential energy surfaces in the next few years. These models include treating the transitional modes as “restricted rotors” and using the Waage–Rabinovitch approximation to account for centrifugal effects, as well as simple pseudo strong collision for energy transfer. Anharmonicities can also be employed in the density of states calculations.

Prof. Troe replied: An RRKM treatment based on a restricted rotor-Gorin model will approach the present treatment if centrifugal barriers are calculated in the same way, *i.e.* not by using Lennard-Jones potential but *ab initio* potentials or at least Morse potentials, and if hindrance parameters are related to our rigidity factors derived from the anisotropy of the potential. On the given level of uncertainty, our approach is not more complicated to use than the Waage–Rabinovitch, restricted rotor, Gorin model; on the other hand, it employs more realistic potentials and provides more realistic predictions of the hindrance parameters and of the apparent moments of inertia of the activated complex.

Prof. Kohse-Höinghaus asked: Of how much value would detailed studies of non-reactive energy transfer (vibrational, rotational) under appropriate (combustion) conditions be in regard of your investigation?

Prof. Troe answered: Non-reactive, vibrational and rotational, energy transfer under combustion conditions can be treated by capture calculations such as used in high pressure unimolecular dissociation/recombination rate theory, if the collisional encounter leads to chemically bound intermediates. Such cases indeed are known, *e.g.* the energy transfer between OH(*v* = 1) and CO involving HOCO complexes¹ where high pressure recombination and vibrational relaxation rates were shown to coincide.

1 D. Fulle, H. F. Hamann, H. Hippler and J. Troe, *J. Chem. Phys.*, 1996, **105**, 983.

Prof. Pilling† asked: For the HO₂ system cited what is the number and nature of the transitional modes? Eqn. (32) implies two, but atom–diatom systems are usually described using one transitional mode.

Prof. Troe answered: The treatment of this work is for atoms, adding to linear molecules of arbitrary numbers of oscillators and forming linear adducts, or for the reverse dissociations. In this case one has two transitional modes. The RRKM calculations of Fig. 12 (of our paper) were made for artificial linear HO₂, *i.e.* for two transitional modes, whereas the trajectory calculations used the true *ab initio* potential. It is indeed a problem to specify the number of transitional modes to be used in simplified models. Only knowledge of the geometry of the true minimum energy path on the accurate potential can help: atom–diatom systems can correspond to one or two transitional modes or to something in between.

† Also Dr S. H. Robertson (Accelrys, Cambridge, UK).

Prof. S. C. Smith said: (1) Two-dimensional (E, J) master equation (ME) solutions are available.¹ These may be useful in determining weak collisional broadening factors with inclusion of angular momentum effects.

(2) Densities of states. HO₂ densities are known exactly from direct quantum mechanical calculation. However, $\rho(E, J)$ models such as that which Prof. Troe has developed are very important for general applications. We are working on another model for densities of states of van der Waals dimer clusters which is based on an extension of the classical Monte Carlo phase space counting algorithms developed for loose (barrierless) transition states.

1 S. J. Jeffrey, K. E. Gates and S. C. Smith, *J. Phys. Chem.*, 1998, **100**, 7090.

Prof. Troe responded: (1) In my view, two-dimensional (E, J) master equation treatments (as your reference and also ref. 1) will only become practically relevant when truly reliable knowledge about rovibrational energy transfer becomes available. This is generally not the case at present.

(2) It is indeed very important to devote more effort to the calculations of accurate rovibrational energy levels on exact potential energy surfaces. Only a few systems have been investigated in sufficient detail such that more empirical approximate models have to be used to estimate anharmonicity contributions. These models, however, urgently need validation.

1 J. Troe, *J. Chem. Phys.*, 1977, **66**, 4745; J. Troe, *Z. Phys. Chem.*, 1987, **154**, 73.

Dr Miller addressed everyone: I agree with Prof. S. C. Smith that it is important to calculate accurate eigenvalues and eigenvectors at low temperature; these contain useful information. However, as long as one only wants the time history of the system, an extremely robust method of solving the problem is simply to integrate the master equation as a set of ODEs (ordinary differential equations) using a stiff ODE integrator such as VODE.¹ I have implemented this approach several times in the past,²⁻⁵ and the method has been included as an option in VARIFLEX.⁶ Also, it is common that the eigenpair that governs the reaction of interest is not one that is computed badly. For example, in the ¹CH₂ + C₂H₂ reaction that Prof. Smith considers, it is the eigenvector $|g_4\rangle$ with the fourth largest eigenvalue λ_4 (*i.e.* the fourth smallest in absolute value) that governs the reaction at low temperature. Our calculations in ordinary precision arithmetic at $T = 300$ K give an accurate value of λ_4 at all pressures, but give good eigenvectors only at higher pressures (*e.g.*, $p = 1$ atm). The situation improves as the temperature increases.

In any event there are two advantages to calculating the eigenvalues and eigenvectors of the transition matrix of the master equation as Prof. Smith (and we) formulates it. The first one is practical. If we have these eigenpairs, we can construct the time evolution operator for the system as

$$\hat{T} = \sum_i e^{\lambda_i t} |g_i\rangle\langle g_i|, \quad (1)$$

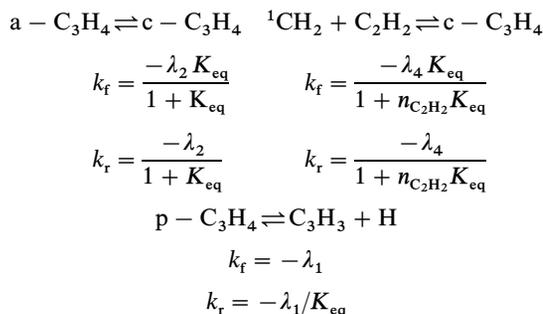
so that the problem is solved for any set of initial conditions corresponding to a given temperature and pressure, *i.e.*

$$|w(t)\rangle = \sum_i e^{\lambda_i t} |g_i\rangle\langle g_i|w(0)\rangle, \quad (2)$$

where $|w(0)\rangle$ may correspond to ¹CH₂ + C₂H₂ or any one of the stabilized C₃H₄ isomers. This is a computational advantage and allows us to study several chemical processes with one set of eigenpairs.

The second advantage is one of physical insight. The eigenvalues and eigenvectors individually have physical meaning. Normally one can associate a transition state with an eigenpair. Note that only four of the multitude of eigenpairs in eqn. (2) describe chemical change. In the present case λ_4 corresponds to the transition state separating ¹CH₂ + C₂H₂ from cyclopropene, λ_3 to that between cyclopropene and propyne, λ_2 to that between cyclopropene and allene, and λ_1 to the transition state connecting propyne to C₃H₃ + H. At low temperature and sufficiently high pressure, the λ s become the 'fundamental relaxation rates' for the reaction between the chemical components that are separated by the corresponding transition states. Under such conditions one can deduce both forward and reverse rate constants from knowledge of the λ s and the corresponding equilibrium constants. Three different types of cases arise, as illustrated for the present reac-

tion by λ_2 (λ_3 is the same), λ_4 and λ_1 :



The number density of acetylene appears above because the addition reaction is only pseudo first order, and the dissociation to $\text{C}_3\text{H}_3 + \text{H}$ is different from the others because the bimolecular products are assumed to be an infinite sink. At lower pressures multiple products appear but the basic idea is the same.

If one follows the time history of the system below 1500 K, as shown in Prof. Smith's movie, one can see four distinct time scales. All three stabilized products, as well as $\text{C}_3\text{H}_3 + \text{H}$, are formed from ${}^1\text{CH}_2 + \text{C}_2\text{H}_2$ on a time scale corresponding to $-1/\lambda_4$ (this is the reaction we are actually interested in). Cyclopropene and propyne equilibrate on a time scale $-1/\lambda_3$, and these two equilibrate with allene on a time scale $-1/\lambda_2$. Dissociation of the three equilibrated isomers takes place on a time scale of $-1/\lambda_1$.

At low temperature the rate constant for the ${}^1\text{CH}_2 + \text{C}_2\text{H}_2$ reaction is equal to $-\lambda_4/n_{\text{C}_2\text{H}_2}$. For a pressure of one atmosphere, at $T \approx 1500$ K the rate constant changes to $-\lambda_3/n_{\text{C}_2\text{H}_2}$, a change that is brought about by a shift in equilibrium of the reaction ${}^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightleftharpoons \text{c} - \text{C}_3\text{H}_4$ in favor of ${}^1\text{CH}_2 + \text{C}_2\text{H}_2$, i.e. $\text{c} - \text{C}_3\text{H}_4$ begins to dissociate as fast as it is formed. This causes the reactant (${}^1\text{CH}_2$) consumption to be controlled by a different transition state, that corresponding to λ_3 . At $T \approx 2500$ K, the $-\lambda_3/n_{\text{C}_2\text{H}_2}$ and $-\lambda_2/n_{\text{C}_2\text{H}_2}$ curves cross with no shift in the rate constant, indicating that the transition state between $\text{a} - \text{C}_3\text{H}_4$ and $\text{c} - \text{C}_3\text{H}_4$ never controls the rate. At still higher temperatures there is another jump of the rate constant from $-\lambda_3/n_{\text{C}_2\text{H}_2}$ to $-\lambda_1/n_{\text{C}_2\text{H}_2}$, caused by a shift in equilibrium analogous to that described above.

- 1 P. N. Brown, G. D. Byrne and A. C. Hindmarsh, *SIAM J. Sci. Stat. Comput.*, 1989, **10**, 1038.
- 2 J. A. Miller and D. W. Chandler, *J. Chem. Phys.*, 1986, **85**, 4502.
- 3 D. W. Chandler and J. A. Miller, *J. Chem. Phys.*, 1984, **81**, 4105.
- 4 J. A. Miller and S. J. Klippenstein, *J. Phys. Chem. A*, 2001, in press.
- 5 D. K. Hahn, S. J. Klippenstein and J. A. Miller, *Faraday Discuss.*, 2001, **119**, 79.
- 6 S. J. Klippenstein, A. F. Wagner, R. C. Dunbar, D. M. Wardlaw, S. H. Robertson and J. A. Miller, Variflex Version 1.08m, 2000.

Prof. S. C. Smith commented: Dr Miller's comments are a useful complement to the discussion in our paper. I note that the analysis of the quality or lack thereof of certain crucial eigenvalues and eigenvectors is not always trivial. Eigenvectors do not always converge accurately under the same conditions as the corresponding eigenvalue, such that one might have a good idea of the overall rate constant without necessarily having good population projections. Whether one can manage with regular double precision calculations, and which aspects of the calculations can be trusted and which cannot, is a matter which may often take careful study from one case to another as conditions are varied. This tedious task is avoided in our high precision algorithm. Our aim in this work has been to try to develop a robust and general algorithm which can be used with confidence under any conditions and can be easily generalized to two-dimensional master equation calculations. Direct time integration is certainly an alternative to high precision matrix diagonalization, but this effectively only gives one access to relatively short timescales, since a very large amount of numerical effort is involved to integrate out to long times.

Prof. Troe continued the discussion of Prof. S. C. Smith's paper: In your system several barrier crossing processes can be studied separately such as the thermal isomerisation of cyclopropene (work by R. Walsh). Have you included that information in your modelling?

Prof. S. C. Smith answered: We have not explicitly considered the results of Dr Walsh's study, but this certainly could be done without further modification of our master equation code.

Dr Kaiser asked: It seems that the schematic potential energy surface of the $\text{CH}_2\text{-C}_2\text{H}_2$ system is a little bit incomplete. Although addition of carbene to acetylene should lead predominantly to cyclopropene, a minor pathway might be the insertion of singlet carbene into a C-H bond of acetylene to form methylacetylene. Could you estimate the role of the addition *vs.* insertion pathways, and possibly the branching ratios? Further, allene is certainly no dead-end species as it can fragment without an exit barrier (except the C-H bond strength) to propargyl plus atomic hydrogen. How will your results change if you include this additional pathway?

Prof. S. C. Smith answered: The possibility of direct insertion of singlet carbene into the C-H bond of acetylene is not included in our present scheme, nor is the loss of H from allene. Our focus has been on solving the challenge of performing accurate calculations at low temperatures with the existing (incomplete) kinetic scheme. We thank Dr Kaiser for his suggestions and will explore the effect of these modifications to the kinetic scheme in future work.

Dr Klippenstein said: In collaboration with Harding we have recently studied the high pressure limit of the rate constant for addition of H atoms to propargyl radical *via* variable reaction coordinate transition state theory employing a multi-reference configuration interaction based potential energy surface.¹ This study suggests that the addition to the CH side to form allene occurs with a rate that is 2/3 of that for the addition to the CH_2 side to form propyne. Thus, in your model the allene potential well should also be directly connected to $\text{C}_3\text{H}_3 + \text{H}$.

1 S. J. Klippenstein and L. B. Harding, *Proc. Combust. Inst.*, 2000, **28**, 1503.

Prof. S. C. Smith responded: We thank Dr Klippenstein for his comments, which support those of Dr Kaiser in connection with the possibility of significant allene dissociation to propargyl plus H. As indicated previously, this will be incorporated into the kinetic scheme in future work.

Prof. Troe commented: When one thinks about where your matrix inversion code would be most useful, one might consider an application to ultrafast multiple well reactions in liquid phase where time scales of collisional stabilization are of similar order of magnitude as time scales of fast intramolecular arrangement processes.

Prof. Pilling said: There is an important aspect of the potential energy surface that requires further consideration. The reaction of $^1\text{CH}_2 + \text{C}_2\text{H}_2$ includes not only the chemical reactions involving the C_3H_4 isomers and $\text{H} + \text{C}_3\text{H}_3$, but also the collision induced intersystem crossing (CIISC) to give $^3\text{CH}_2$. CIISC occurs on collision of CH_2 with inert gases *via* 'doorway' states, of mixed singlet triplet character, coupled with collision induced rotational relaxation. The mechanism that applies in reactive collisions is not clear.

Wagner and coworkers have extensively examined the yield of triplet in reactions of $^1\text{CH}_2$, using LMR, and have shown that for reaction with C_2H_2 at 300 K, 20% of the total rate of removal of the singlet leads to triplet formation.¹ They have also shown that the energy barrier for reaction of $^3\text{CH}_2$ with C_2H_2 is 27 kJ mol^{-1} ,² which is less than the singlet triplet energy difference (37.7 kJ mol^{-1}). Thus there is the possibility of a transition from the attractive $^1\text{CH}_2 + \text{C}_2\text{H}_2$ potential energy surface to the triplet surface correlating with $^3\text{CH}_2 + \text{C}_2\text{H}_2$. Prof. Lin's paper refers to singlet to triplet surface crossing for $\text{CH}_3 + \text{OH}/\text{CH}_2 + \text{H}_2\text{O}$. Is there any clear procedure for introducing such a process into a master equation description of $^1\text{CH}_2 + \text{C}_2\text{H}_2$?

1 W. Hack, M. Koch, H. Gg. Wagner and A. Wilms, *Ber. Bunsen-Ges. Phys. Chem.*, 1988, **92**, 674.

2 T. Boehland, F. Temps and H. Gg. Wagner, *Proc. Twenty-first. Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1986, p. 841.

Prof. S. C. Smith responded: It is relatively straightforward to extend the master equation formulation to incorporate a thermalised triplet methylene population, coupled to the thermalised singlet population *via* an estimated pseudo first order collision induced intersystem crossing (CIISC) rate, and to the propyne isomer with RRKM theory estimates for the association of

triplet methylene with acetylene. The effective CIISC rate (as a function of temperature) would most likely have to be inferred from whatever experimental data is available.

Prof. Balint-Kurti commented: Prof. Pilling has asked if there are ways of treating spin forbidden intersystem crossings which may play a role in the reactions of systems such as $\text{CH}_3 + \text{OH}$. The answer is yes. There are now *ab initio* computer codes (*e.g.* MOLPRO) which permit the calculation of the spin-orbit coupling matrix elements which determine the transition probabilities between the singlet and triplet surfaces. Jeremy Harvey of the University of Bristol has developed interesting new RRKM based methods¹ for computing the rates of such spin forbidden transitions. These methods involve heating the lowest point on the singlet-triplet crossing seam and using this as a critical geometry for the RRKM calculations.

1 J. N. Harvey and M. Aschi, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5555.

Dr Mebel said: In my opinion, the potential energy surface of C_3H_4 used for kinetic calculations of the $\text{CH}_2 + \text{C}_2\text{H}_2$ reaction is not complete.¹ First, allene can also dissociate to form the propargyl radical $\text{C}_3\text{H}_3 + \text{H}$ without an exit barrier. Thus, both allene and propyne can give propargyl + H without an exit barrier in the sense that these decompositions are endothermic but the reverse reactions $\text{H} + \text{C}_3\text{H}_3$ with H addition both to the “head” and “tail” of propargyl have no barriers. The allene $\rightarrow \text{C}_3\text{H}_3 + \text{H}$ channel should certainly be included into kinetic calculations. Additionally, H_2 eliminations from allene and propyne can also play some role in the reaction.

1 A. M. Mebel, W. M. Jackson, A. H. H. Chang and S. H. Lin, *J. Am. Chem. Soc.*, 1998, **120**, 5751.

Prof. Kohse-Höinghaus opened the discussion of Prof. Golden’s paper: Would you have any advice on how to treat higher hydrocarbons, such as those needed in mechanisms for PAH and soot formation, where there may not be experimental evidence? How would you ensure that databases would, while being consistent among themselves, not be off as a whole?

Prof. Golden responded: We have suggested using DFT methods as the only practical calculational procedure. We have offered some group additivity based correction where data exists to allow this. Possibly these can be checked with an occasional very expensive high level calculation. It would also be good if experiments were to be targeted on molecules that could supply the missing groups.

Prof. Lin commented: We have recently attempted to establish an efficient composite scheme for prediction of heats of formation based on B3LYP/aug-cc-pVTZ//B3LYP/cc-pVDZ energies with small ‘higher level corrections (HLC)’.¹ The scheme works well for [C,H,O]-containing species, but it does poorly for N-containing species, such as NH_x , with large errors ($\pm 3 \text{ kcal mol}^{-1}$).

1 Y. M. Choi and M. C. Lin, unpublished work.

Prof. Golden responded: We look forward to seeing the publication. In general we have not found that B3LYP calculations are very sensitive to basis sets. What does ‘work well’ mean? Were these values extracted from isodesmic reactions?

Prof. Troe asked: The described quantum methods still leave substantial uncertainties. Have they led to real improvements over the old fully empirical group additivity based tables?

Prof. Golden answered: Yes and no. The group additivity values come from data. The calculations agree with the data within a few kcal mol^{-1} . Thus we have a certain comfort when using calculated values in cases not measured. (*Caveat emptor!*)

Dr Hessler said: The bootstrap technique, see for example ref. 1, has been used to estimate the uncertainty of predictions by randomly discarding some of the data in a database, re-evaluating

the parameters of the model, and then predicting the values of the discarded data. Have you applied these ideas to estimate the uncertainty of your calibration scheme?

1 B. Efron and R. J. Tibshirani, *An Introduction to the Bootstrap*, Chapman & Hall, New York, 1993.

Prof. Golden answered: No we have not.

Prof. I. W. M. Smith said: Prof. Golden provides extensive comparisons between results of his calculations and the experimental values for the heats of formation for many free radicals. I believe that there are two main sources for the experimental values; first the data obtained by himself and Benson over many years *via* the rates of bromination and iodination, and second a smaller, but significantly different set of values determined chiefly by Gutman and co-workers.¹ Is there anything in these comparisons to suggest that one set is in better agreement with his calculations than the other?

1 J. Berkowitz, G. B. Ellison and D. Gutman, *J. Phys. Chem.*, 1994, **98**, 2744.

Prof. Golden responded: We are not the first to see that calculations yield the higher BDEs for alkane C–H bonds consistent with the work of Gutman and others. We had hoped that the calculations presented here would shed light on this same question with respect to other BDEs. Unfortunately, the uncertainties in the calculations are too large.

Dr Mebel asked: In your paper, you calculated bond dissociation energies based on energies of a molecule and a radical formed after the bond cleavage. Would you expect higher accuracy of the results and their better agreement with experiment if you used isodesmic reactions for the calculations?

Prof. Golden answered: Of course, but these types of reactions can not always be formed with three known values for some of the species considered here.

Prof. Pilling asked: Prof. Golden has commented on inconsistency in thermodynamic databases. What is needed to ensure that such inconsistencies are eliminated?

Dr Hessler responded: Recently Branko Ruscic and his colleagues have generated a mathematical network that describes the enthalpy of formation of CH₂ and the bond dissociation of the methyl radical.¹ They first use this network to identify outliers, *i.e.* results that are not consistent with the other measurements, and then determine the ‘best-fit’ set of thermochemical parameters by a non-linear least squares analysis. Scientists have known about these networks for a long time. However, modern computers now provide an opportunity to put all of the thermodynamic measurements in a single database. As new information is added to the database all of the parameters that depend upon this information may be easily updated. Although it is more complex, this same approach may be extended to kinetic rate measurements.

1 B. Ruscic, M. Litorja and R. L. Asher, *J. Phys. Chem. A*, 1999, **103**, 8625.

Prof. Golden added: I for one have longed for the ‘Great Spreadsheet in the Sky’ that would enable self-consistent evaluation of data. If this is possible, I would love to see it done! Of course funding at a significant level would be necessary.

Prof. S. C. Smith said in conclusion: The microcanonical rate coefficients for dissociation from propyne to propargyl in our present kinetic scheme were obtained by inverse Laplace transform (ILT) of temperature dependent recombination rates for a closely related system, C₃H₅ + H.¹ Dr Klippenstein’s earlier comments indicate unequivocally, however, that in the case of recombination of H plus propargyl there is significant branching to form both allene and propyne. Thus, the microcanonical rate coefficients inferred from the ILT method used previously will likely overestimate the rate constants for dissociation of propyne, while of course the dissociation of allene to propargyl is not represented in our present scheme.

Prof. Golden said in conclusion: One, including me, might have thought that since the C–H bond dissociation energy (BDE) in ethylene is about $110 \text{ kcal mol}^{-1}$ that the correct way to judge the C–H BDE in allene was to subtract the propargyl resonance energy from that number. Likewise, a way to describe the BDE in propyne to give the propargyl radical would be to subtract the propargyl resonance energy from the value of $101 \text{ kcal mol}^{-1}$ that represents a primary C–H BDE. The latter is essentially correct, but allene is apparently not a molecule with two independent π bonds. The heat of hydrogenation of the first π bond to yield propene, is about 10 kcal mol^{-1} less exothermic than the heat of hydrogenation of the bond in propene itself. Thus the two π bonds repel each other by some 10 kcal mol^{-1} and despite what I said earlier, the C–H BDE in allene is less than that in ethylene.

Dr Miller opened the discussion of Prof. Lin's paper: I have three comments.

(1) In one part of your paper you indicate that you use a single exponential down model for $P(E, E')$ with $\langle \Delta E_d \rangle = 40 \text{ cm}^{-1}$, whereas in another part of the paper you say that the grain size in your master equation calculations is 100 cm^{-1} . If this is the case, you do not even come close to resolving the energy transfer function, and it is unlikely that your calculations are very accurate.

(2) The inversion method in VARIFLEX was not intended for high temperatures, and its accuracy there is highly suspect. However your high-temperature calculations on the dissociation of methanol may have benefitted from a cancellation of errors. For methane dissociation (similar to CH_3OH), at $T = 3000 \text{ K}$ I determined using the eigenvector method that the lower limit of the computational domain must be $36\,000 \text{ cm}^{-1}$ below the dissociation limit (*i.e.* $E_{\text{lower}} = -36\,000 \text{ cm}^{-1}$) to calculate an accurate rate constant. If I use this lower limit on E and switch to the inversion method, I calculate a rate constant that is a factor of seven too small. However, if I raise E_{lower} to $-15\,000 \text{ cm}^{-1}$, which you use in your calculation, I make less than a 20% error.

(3) The evidence is overwhelming that the reaction (2) $\text{OH} + \text{CH}_3 \rightleftharpoons {}^1\text{CH}_2 + \text{H}_2\text{O}$ is slightly endothermic (*i.e.* by less than 1 kcal mol^{-1}), and not exothermic by $1.6 \text{ kcal mol}^{-1}$ as you indicate in your paper. At the last DOE-BES Combustion Contractors Meeting¹ Branko Ruscic claimed to have determined all the relevant heats of formation for this reaction to $\pm 0.1 \text{ kcal mol}^{-1}$, from which he deduced that reaction (2) is endothermic by $0.39 \pm 0.2 \text{ kcal mol}^{-1}$ at $T = 0 \text{ K}$. One might argue with this precision, but an exothermic reaction (2) is completely inconsistent with the low-temperature experiments reported in ref. 46–48 of your paper, which include the observation that k_{-2} is almost $10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature. It is worth noting that Ruscic's value of ΔH_2° (0 K) is almost identical to the value of $0.38 \pm 0.48 \text{ kcal mol}^{-1}$ that Pilling and co-workers deduced from their master equation modeling of several experiments. Making the appropriate correction in the thermochemistry should also allow you to predict correctly the product distribution in the dissociation of CH_3OH observed by Dombrowsky, *et al.* (ref. 9 of your paper), since such a correction would make $\text{CH}_3 + \text{OH}$ more accessible energetically than ${}^1\text{CH}_2 + \text{H}_2\text{O}$.

Reaction (2) is extremely important in methane and natural gas flames,² because it is the primary CH_3 -consuming reaction from slightly lean conditions up to an equivalence ratio of roughly $\phi = 1.3$. An increased value of k_2 , as implied by your thermochemistry, would have significant effects on properties of these flames, increasing burning velocities² and yields of prompt NO. The ${}^1\text{CH}_2$ formed produces greater yields of ${}^3\text{CH}_2$ and CH. The reaction of ${}^3\text{CH}_2$ and O_2 is chain branching, thus increasing burning velocities, and the increased CH results in more prompt NO. We should be careful not to confuse the issues concerning reaction (2) with bad thermochemistry.

- 1 B. Ruscic, *Photoionization Studies of Transient Metastable Species, Twenty-Second Annual Combustion Research Conference Book of Abstracts*, U.S. Department of Energy, Office of Basic Energy Sciences, pp. 264–267.
- 2 M. N. Bui-Pham and J. A. Miller, *Twenty-fifth Symp. (Int) Combust.*, The Combustion Institute, Pittsburgh, 1994, p. 1309.

Prof. Lin responded: (1) The grain size used in our calculations depends on the third-body involved. For He, we employed 30 cm^{-1} and for heavier masses such as N_2 , Ar and SF_6 , we used 100 cm^{-1} .

(2) There is an error in the text on the computational domain: $E_{\text{lower}} = -33\,000\text{ cm}^{-1}$, rather than $-15\,000\text{ cm}^{-1}$, was used. The calculation with the lower limit of $-36\,000\text{ cm}^{-1}$ at 1600 and 2500 K showed that the differences between the former and latter limits amount to less than 1% at 1600 K and about 1% at 2500 K. When we switched the inversion method to the eigenvector method, with the $E_{\text{lower}} = -33\,000\text{ cm}^{-1}$, no difference was noted in the predicted rates with both lower limits.

(3) Both G2¹ and G2M² methods over-predict the atomization energy of CH₃OH (by 1.5 and 0.8 kcal mol⁻¹, respectively). On average, the highest-level G2M method predicts heats of formation for the 32 first-row G2 testing species with an absolute error of 0.88 kcal mol⁻¹.² Therefore, one can expect an error of $\pm 1\text{ kcal mol}^{-1}$ for predicted heats of reaction of small molecular systems such as CH₃OH. The relative energies shown in Table 1 and Fig. 2 of our paper are within the expected average error. The G2M method over-predicts $D_0(\text{CH}_3\text{-OH})$ by 1.7 kcal mol⁻¹, comparing with the latest dissociation energy by Ruscic,³ $90.16 \pm 0.18\text{ kcal mol}^{-1}$, although it predicts reasonably the heat of reaction for CH₃OH \rightarrow ¹CH₂ + H₂O (see Table 1 of our paper).

The result of our new calculation with the experimental value of $D_0(\text{CH}_3\text{-OH})$, taking the endothermicity of 0.39 kcal mol⁻¹ for CH₃ + OH \rightarrow ¹CH₂ + H₂O, with and without multiple reflections above the H₂C \cdots OH₂ molecular complex, agrees with experimental rates within the scatter shown in Fig. 9a of our paper.

1 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221.

2 A. M. Mebel, K. Morokuma and M. C. Lin, *J. Chem. Phys.*, 1995, **103**, 7414.

3 B. Ruscic, private communication.

Prof. Pilling commented: I would like to comment further on the central importance of the difference in the energies of CH₃ + OH and ¹CH₂ + H₂O. In a recent experimental paper,¹ we used this energy difference, ΔE , as a variable parameter in fitting the magnitude and pressure dependence of the overall rate coefficient for CH₃ + OH, using a master equation model. We also used the rate coefficient for ¹CH₂ + H₂O and the yield of OH in that reaction.² We obtained $\Delta E = (1.6 \pm 2.0)\text{ kJ mol}^{-1}$. Using all of the fitted parameters, we then found that our model reproduced very satisfactorily the low pressure overall rate coefficients of Deters *et al.*³ for CH₃ + OH, which shows a $\sim 40\%$ fall from the higher pressure limit in the $\sim 1\text{ Torr}$ range. Over this range, the predominant channel changes from stabilization to formation of ¹CH₂ + H₂O; this behaviour is, once again, very sensitive to the value of ΔE .

1 R. De Avillez Pereira, D. L. Baulch, M. J. Pilling, S. H. Robertson and G. Zeng, *J. Phys. Chem. A*, 1997, **101**, 9681.

2 W. Hack, H. Gg. Wagner and A. Wilms, *Ber. Bunsen-Ges. Phys. Chem.*, 1988, **92**, 620.

3 R. Deters, M. Oting, H. Gg. Wagner, F. Temps, B. Laszlo, S. Dobe and T. Berces, *Ber. Bunsen-Ges. Phys. Chem.*, 1998, **102**, 58.

Dr Smith said: In view of the apparent significance of the information presented at the recent DOE-BES Combustion Contractors Meeting in US, it would be helpful to learn just what was said there.

Dr Miller replied: As I mentioned in my initial comment, Branko Ruscic argued convincingly that he had determined the heats of formation for the species involved in the reaction, ¹CH₂ + H₂O \rightleftharpoons CH₃ + OH, to an accuracy of $\pm 0.1\text{ kcal mol}^{-1}$, from which he deduced that this reaction was exothermic by $0.39 \pm 0.2\text{ kcal mol}^{-1}$. This result is consistent with the low-temperature experiments cited in Prof. Lin's paper and with Mike Pilling's previous analysis. It is not consistent with Prof. Lin's electronic-structure calculations.

Prof. Troe said: The recent version of the heat of formation of OH¹ should have some influence on the kinetics of the methanol system, such as it brings rates of the reactions of H + O₂ and of HO + O into much better internal consistency.²

1 B. Ruscic, D. Feller, D. A. Dixon, K. A. Peterson, L. B. Harding, R. L. Asher and A. F. Wagner, *J. Phys. Chem. A*, 2001, **105**, 1.

Prof. Troe asked: Your $\langle \Delta E \rangle_{\text{down}}$ values of 40 cm^{-1} which are much smaller than Pilling's value of 230 cm^{-1} for helium and which correspond to a very unusually small $\langle \Delta E \rangle_{\text{total}}$, might be due to an overestimation of other factors contributing to the low pressure recombination rate constants. Could you guess which factors that could be?

Prof. Pilling‡ said: The figure of 230 cm^{-1} for $\langle \Delta E \rangle_{\text{down}}$ cited by Pilling *et al.* for He is slightly higher than the usual value of $\sim 200 \text{ cm}^{-1}$. The value of 40 cm^{-1} used by the authors seems small by comparison.

Prof. Lin responded to Prof. Miller, Prof. Pilling and Prof. Troe: The value of $\langle \Delta E \rangle_{\text{down}}$, 40 cm^{-1} , for the He-deactivation of the excited CH_3OH formed by $\text{CH}_3 + \text{OH}$ appears to be low. In Fig. 1 presented here we show the results obtained by using higher values (120 and 150 cm^{-1}) for comparison. Although the effect of higher values is small at higher temperatures, it is noticeable at the lowest temperature studied, 290 K , by Pilling and co-workers.¹

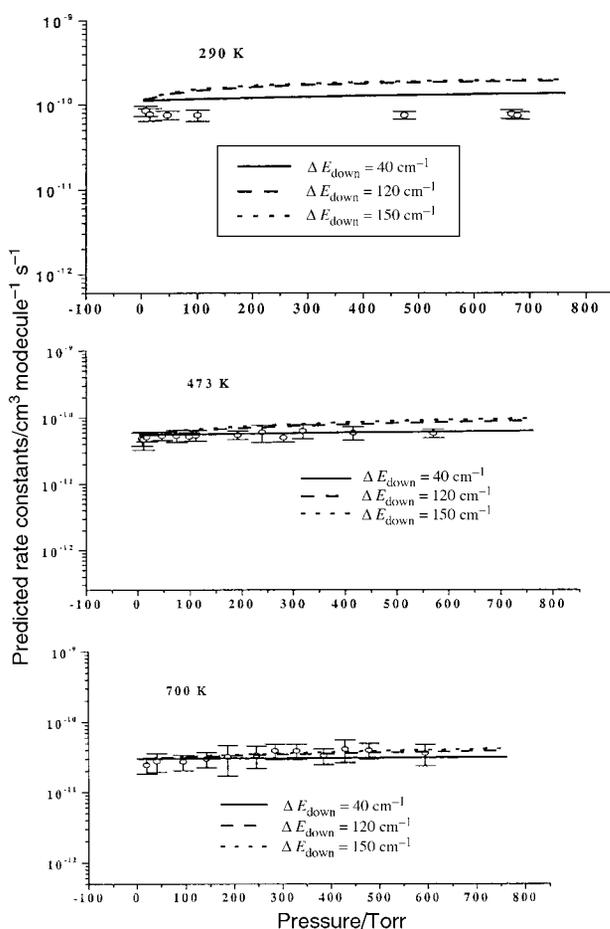


Fig. 1 Predicted rate constants for $\text{CH}_3 + \text{OH} \rightarrow \text{products}$ in comparison with the experimental data at different temperatures and different values of $\langle E \rangle_{\text{down}}$ employed.

‡ Also Dr S. H. Robertson (Accelrys, Cambridge, UK).

It should be mentioned, however, that our recent calculation² for $\text{CH}_3 + \text{O}_2 + \text{He} \rightarrow \text{CH}_3\text{O}_2 + \text{He}$ and that of Tardy³ for $\text{CH}_3 + \text{CH}_3 + \text{He} \rightarrow \text{C}_2\text{H}_6 + \text{He}$ favour $\langle \Delta E \rangle_{\text{down}} = 70 \text{ cm}^{-1}$. Interestingly, for $\text{CH}_3 + \text{O}_2$, Pilling and co-workers⁴ concluded that a broad range of $\langle \Delta E \rangle_{\text{down}}$, 40–285 cm^{-1} , for Ar could reasonably fit experimental data, with 40 cm^{-1} giving the optimal fit.

- 1 R. De Avillez Pereira, D. L. Baulch, M. J. Pilling, S. H. Robertson and G. Zeng, *J. Phys. Chem. A*, 1997, **101**, 9681.
- 2 R. S. Zhu, C.-C. Hsu and M. C. Lin, *J. Chem. Phys.*, 2001, **115**, 195.
- 3 D. Tardy, private communication.
- 4 M. Keiffer, M. J. Pilling and M. J. C. Smith, *J. Phys. Chem.*, 1987, **91**, 6028.

Prof. Plane said: Rollason and I have recently completed a study of FeO recombining with H_2O , CO_2 and O_2 in the presence of either He or N_2 .¹ Application of RRKM theory indicates that $\langle \Delta E \rangle_{\text{down}}$ for He is about 200 cm^{-1} , compared to $\approx 500 \text{ cm}^{-1}$ for N_2 . The He value is obviously much higher than the value of 40 cm^{-1} reported in Prof. Lin's paper. However, the value of $\langle \Delta E \rangle_{\text{down}}$ is rather sensitive to the parameters chosen to estimate the collision frequency with the third body, so this discrepancy may be less than it appears.

- 1 R. Rollason and J. M. C. Plane, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2335.

Dr Miller said: An important point that we all tend to overlook (or ignore) is that the value of $\langle \Delta E_d \rangle$ or $\langle \Delta E \rangle$ that we deduce from any experiment may depend on the form of $P(E, E')$ that we assume. The differences between a single-exponential-down model and a double-exponential-down model are likely to be greatest for chemically activated problems or thermally activated multi-channel reactions. A number of years ago David Chandler and I found significant differences from such models for photo-activated systems,^{1,2} which are very similar to chemically activated ones.

- 1 J. A. Miller and D. W. Chandler, *J. Chem. Phys.*, 1986, **85**, 4502.
- 2 D. W. Chandler and J. A. Miller, *J. Chem. Phys.*, 1984, **81**, 445.

Prof. Balint-Kurti and **Mr Cole** commented: We have also been using *ab initio* methods to study the $\text{NH}_2 + \text{NO}$ reaction. We have used the B3LYP density functional method with a cc-pvdz basis set to compute all the stationary points on the surface, and also to compute the minimum energy reaction and break-up pathways. In addition we have computed the variation of the vibrational frequencies along these paths. At all the critical geometries, such as local minima, transition states and reactants and products, we have computed energies using the quadratic CI method, with a cc-pvqz basis. The energies of the reaction paths and stationary points were scaled so as to fit these quadratic CI values. With this *ab initio* input we have performed *J*-conserving variational RRKM calculations and have used a steady state model to compute overall rate constants. The lower curve in Fig. 2 shows our *ab initio* computed branching ratios for the production of OH as a function of temperature. The upper curve in the figure is an analytic fit to the experimental data taken from the work of Park and Lin.¹

The *ab initio* calculations reproduce the increase of the branching ratio with temperature very well, they are however consistently lower than the experimental values throughout the whole temperature range. At low temperatures around 300 K the experimental branching ratios level off at around 10%. This is hard to reconcile with our theoretical results because we find that the energy of the products $\text{N}_2\text{H} + \text{OH}$ lies above that of the $\text{NH}_2 + \text{NO}$ reactants. This fact implies that the branching ratio must tend to zero as the temperature decreases to zero. A non-zero value of the branching ratio at 0 K would imply that the reaction to give $\text{N}_2\text{H} + \text{OH}$ is exothermic and does not possess any barrier whose energy is higher than the energy of the reactants.

- 1 J. Park and M. C. Lin, *J. Phys. Chem. A*, 1999, **103**, 8906.

Prof. Lin replied: Our recent calculations¹ show that there are low-lying excited states near the $\text{HN}_2 + \text{OH}$ dissociation limit. Their participation in the $\text{NH}_2 + \text{NO}$ reaction may lead to a non-statistical temperature dependence for the OH branching ratio observed experimentally.

- 1 D. Chakraborty and M. C. Lin, unpublished work.

Prof. Van Tiggelen opened the discussion of Dr Klippenstein's paper: I am pleased to see (Fig. 2) that the sigma shape of the curve of the branching ratio *vs.* temperature is predicted nicely from

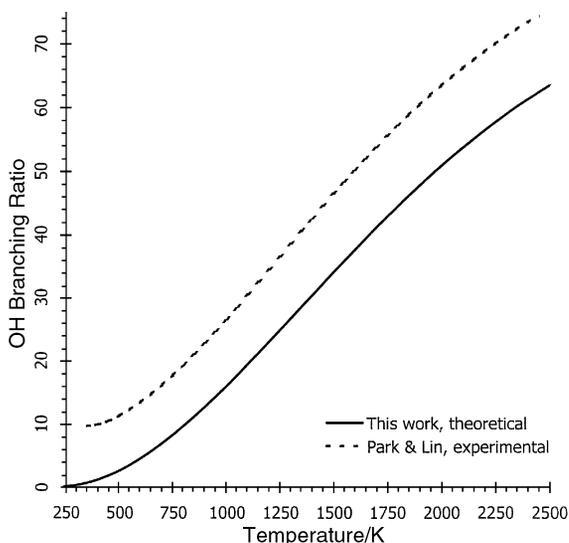


Fig. 2 *Ab initio* branching ratio for OH production from $\text{NH}_2 + \text{NO}$ reaction.

your computation. Would it be possible to get a more steep increase of that ratio? Which thermochemical data are dominant in describing the steepness? What kind of adjustment in the energy barriers are required to obtain an absolute rate constant more flat in the high temperature range (1000–2000 K), but still keeping the rapid decrease in the 400–800 K range. Rather high values of the overall rate constant are necessary to propagate a flame in $\text{NH}_3\text{--NO}$ mixtures, see for instance Brown and Smith's paper¹ well as ref. 13 of your paper.

1 M. J. Brown and D. B. Smith, *Twenty-fifth Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1994, pp. 1011–1018.

Dr Klippenstein responded: As illustrated in the paper, the shape of the branching fraction curve in the intermediate temperature regime depends primarily on the combination of the $\text{HNN} + \text{OH}$ endothermicity and the height of the $\text{ts}_{3/4}$ barriers. The shape also depends on the temperature dependence of the $\text{HNN} + \text{OH}$ association rate constant. However, it is difficult to obtain curves that are significantly steeper at intermediate temperatures (600 to 1500 K) without destroying the flatness at low temperatures. At higher temperatures (*e.g.*, above 1500 K) vibrational anharmonicities (beyond the hindered rotor corrections that were explicitly included in the analysis) and/or non-statistical deviations (since there are then significant contributions from energies for which the dissociation rates of the intermediate complexes exceed 10^{12} s^{-1}) might play a role in yielding somewhat larger branching fractions. There may be similar corrections for the total rate constant. However, it seems unlikely that any such corrections to the total rate constant could be large enough to provide agreement with the values from ref. 13 in our paper.

Prof. Golden said: A new study at Stanford¹ has extended the temperature range for the overall rate constant so that the range is now 1250–2500 K. The values for the branching ratio from 1350 to 17700 K are in agreement with ref. 2.

1 S. Song, R. K. Hanson, C. T. Bowman and D. M. Golden, *Int. J. Chem. Kinet.*, 2001, **33**, in press.

2 J. A. Miller and S. J. Klippenstein, *J. Phys. Chem.*, 2000, **104**, 2061.

Prof. Plane asked: The experimental data plotted in Figs. 9–11 of your paper show that the branching fraction α at 300 K varies by just a few percent, whereas at higher temperatures the spread is much greater. Does this imply accidentally good agreement from a smaller set of measurements at 300 K? Should α be remeasured at this temperature, and perhaps down to 200 K?

Dr Klippenstein answered: It is indeed interesting that the spread of the measurements is smaller at 300 K. Unfortunately, I have no idea as to why that would be. From our perspective, it would indeed be valuable to have further measurements of the branching ratio near room temperature and lower as you suggest.

Dr Smith asked: If the problem is matching the measured branching ratio at low temperatures, is your comment a call for more experiments in that region? If so, over what temperature range?

Dr Klippenstein replied: Yes, we would like to see more experimental measurements of the branching ratio at low temperatures. Precise measurements at any temperature below about 400 K should help to delineate what the HNN + OH endothermicity really is, and thus what the correct low temperature behaviour is.

Prof. Lin said: The OH branching ratio at room temperature is well-established; it has been corroborated by several different experimental methods, including our mass spectrometric measurements for H₂O and CO₂ (formed by OH + CO) which gave the value, 0.10 ± 0.02 .¹

1 J. Park and M. C. Lin, *J. Phys. Chem.*, 1996, **100**, 3317.

Dr Klippenstein replied: While the room temperature branching ratio does appear to be well established, it is difficult for any theoretical model to reconcile the experimental values over the 300 to 500 K range with the also well-established rapid rise at temperatures from 800 to 1800 K. If one allows the room temperature value to be 0.05, which only deviates from your result by 2.5 times your stated error bars, then, as illustrated in Fig. 11 of our paper, one is able to satisfactorily reproduce the remainder of the temperature dependence up to 2000 K.

Dr Taatjes opened the discussion of Prof. Temps's paper: I have a question concerning the carbon balance in your experiments, specifically the ratio of CO production to ketene consumption. In the mechanism of Table 2 (in your paper) nearly every reaction which removes ketene produces CO. The only significant exception is reaction 15.2, OH + CH₂CO → CH₃ + CO₂. However, this represents only 2/7 of the removal of ketene by OH, and OH production represents in turn only ~10% of the ³CH₂ + NO reaction. Yet your ΔCO/−ΔCH₂CO ratios are only ~0.7. What happens to CH₂CO which does not produce CO? Also, are there any contributions from photolysis of reaction products by the Hg lamp?

Prof. Temps responded: The mass balances, including the carbon balance, depend, of course, on the absolute calibrations of the FTIR sensitivities. In response to the question, we note first that due to the strong absorptions, but very small changes in the CH₂CO and NO pressures, the absolute depletions of these compounds could not be determined with high precision. Indeed, within the experimental scatter, the NO profiles were almost flat, which is the reason why we did not even consider them in the experiments at 100 mbar. We therefore specified all product yields with respect to the CO formed. The ΔCO/−ΔCH₂CO ratio is about 0.7 (see Fig. 3 and Table 3 of the paper). As mentioned by Taatjes, only a small part of the extra loss of the CH₂CO is due to the reaction with OH. The main loss term for the CH₂CO is the reaction with HCNO. HCNO is a very unstable species. Its calibration was difficult as one had to work rapidly to avoid excessive decomposition of the prepared pure HCNO samples.

The 'dark' reactions of CH₂CO with HCNO (and possibly also with other acidic products, including HCN or HONO) were very slow, but for photolysis times of 1 h (corresponding to a duration of an experimental run of 2 h), they did play a role. We estimated a loss of HCNO of up to 20%, resulting in an additional loss of CH₂CO of about 18%. Together with the other CH₂CO loss processes, including the reaction with OH, this brings the ΔCO/−ΔCH₂CO ratio to a corrected value close to 0.95, *i.e.* close to unity given the difficulty of determining ΔCH₂CO mentioned above.

We did not observe any evidence for a significant degree of photolysis of the reaction products. We would like to add that we have recently initiated time-resolved product measurements for CH₂ + NO. These experiments were performed using pulsed excimer laser photolysis in a tubular

slow flow reactor in connection with mass spectrometric detection of the HCNO and HCN. The first results are in good agreement with the FTIR data presented here.¹

1 G. Eshchenko, Th. Köcher and F. Temps, to be published.

Prof. Cheskis asked: Could you say something about the reaction of methylene in the single electronic state? What do your calculations predict for branching ratios of different channels of the reaction of singlet methylene with NO?

Prof. Temps answered: The experimental results obtained at a high pressure of $M = \text{Ar}$ (570 mbar) as inert bath gas are for the reaction of triplet methylene ($^3\text{CH}_2$) with NO, as the singlet methylene ($^1\text{CH}_2$) produced by the ketene photolysis is rapidly deactivated to the ground state. However, the measurements conducted with $M = \text{He}$ at a lower total pressure (100 mbar), where more of the $^1\text{CH}_2$ reacts with NO prior to deactivation, gave essentially the same ratio of HCNO to HCN. This indicates little dependence of the product yields on the CH_2 electronic state.

On theoretical grounds, the reactions of both $^3\text{CH}_2$ and $^1\text{CH}_2$ with NO are assumed to proceed on the same (doublet) potential energy hypersurface. In view of the calculated similar threshold energies of the channels to HCNO and HCN and the computed $k(E, J)$ curves given in the paper, we expect rather similar product yields for CH_2 in the two spin states. The extra excitation energy resulting from the electronic excitation of the $^1\text{CH}_2$ should not make a large difference. Although we did not perform full calculations with thermal averaging, these conclusions were confirmed by calculated product distributions of $^1\text{CH}_2$ for selected fixed values of E and J .

Note that the calculated steady state energy distribution functions for $T = 1200 \text{ K}$ (see, *e.g.*, Fig. 7 of the paper) reach well beyond the singlet electronic excitation energy. Nevertheless, the predicted temperature dependence of the product branching ratio (Fig. 10 of the paper) was only weak.

Dr Parker communicated: In Fig. 4 of the paper, have you considered using a weighted linear least squares fit? It is obvious that the fitted line that you have underweighs the smaller-valued data points in H_2CCO and NO decays.

Prof. Temps communicated in response: The full lines in Fig. 4 of the paper are not fitted lines but the results of the numerical simulations of the reaction mechanism detailed in Table 2. Thus, there were no adjustable parameters used in the figure. Corresponding numerical simulations were carried out for the product profiles of all other experimental runs, giving similarly nice pictures.

The experimental results for the branching ratios for HCNO and HCN formation were derived from the experimental data for short reaction times, as explained in the paper. One should keep in mind that the data points at short times show some statistical scatter. However, they were taken for analysis because they are not affected to the same extent by consecutive reactions as the points for long photolysis times. At long times, the (presumably heterogeneous) reaction of HCNO with CH_2CO comes into play.

Prof. S. C. Smith commented: One of the difficulties of modelling chemical activation reactions which are clearly sensitive to angular momentum effects is that it is, to date, very difficult to carry out two-dimensional ME calculations to explore the possible effect of weak collisional relaxation on branching ratios. As a way of rationalising ourselves through this, there are two simple approaches (or scenarios).

(a) We argue that the lifetime of the intermediate is shorter than the mean collision free time, and conclude that collisional relaxation should not be important such that microanonical modelling (master equation or steady state) followed by Maxwell–Boltzmann averaging suffices.

(b) We include strong collisional modelling (possibly with incorporation of a collision efficiency) and look to see if there is any sensitivity to the pressure. If we see no pressure dependence, we again conclude that collisional relaxation is unimportant. Strong collisional modelling can, however, be misleading because it gives qualitatively incorrect time evolution of the population. Branching ratios in reactions with competitive channels can be sensitive to the shape of the population distribution, and we should bear in mind that proper weak collisional simulations might

show pressure effects on the competitive branching ratios which do not show up with the simpler rationalizations summarized above.

Dr Miller responded: For the $\text{NH}_2 + \text{NO}$ reaction (I suspect the same is true for $\text{CH}_2 + \text{NO}$), the mean time between collisions is larger than the RRKM lifetimes for any of the complexes, even for the lowest energy from which the complexes can be formed from $\text{NH}_2 + \text{NO}$.¹ However, I agree that the bimodal energy distribution implied by a pseudo strong-collider model can lead to errors, even very large ones for some reactions. However, here I would like to describe a simple phenomenon that we have observed in master equation calculations at various times, a phenomenon that cannot be described by a pseudo strong-collider model even by adjusting the collision efficiencies.

Fig. 3 is a potential energy profile for the $\text{C}_2\text{H}_5 + \text{O}_2$ reaction. At the collisionless limit the only products are $\text{C}_2\text{H}_4 + \text{HO}_2$. As the pressure is increased, a pseudo strong-collider model predicts that the rate coefficient for the reaction (1) $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$ decreases, because collisions increasingly favor stabilization (2) $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2$.

However, master equation calculations indicate that k_a actually *increases* slightly with pressure. This increase is a consequence of weak collisions that deactivate the $\text{C}_2\text{H}_5\text{O}_2^*$ complexes into the gray region of Fig. 3, from which they can no longer redissociate to $\text{C}_2\text{H}_5 + \text{O}_2$, and in which they do not live long enough to suffer more collisions and end up as stabilized $\text{C}_2\text{H}_5\text{O}_2$. Thus $\text{C}_2\text{H}_5\text{O}_2^*$ complexes that redissociate to $\text{C}_2\text{H}_5 + \text{O}_2$ in the collisionless regime end up forming $\text{C}_2\text{H}_4 + \text{HO}_2$ with a slight increase in pressure.

Fig. 4 shows this effect for $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$ at 298 K. The circles are results from master equation calculations and the solid line is a representation of those calculations in the Troe format, through which F_{cent} was chosen to reproduce the master equation results in the center of the pressure range. The solid line is the same behavior one would get from a strong-collider model

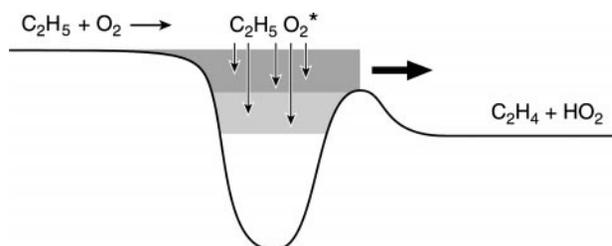


Fig. 3 Schematic diagram of the potential for $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$. $\text{C}_2\text{H}_5\text{O}_2^*$ complexes deactivated into the dark gray region (and light gray region if tunneling is included) cannot return to $\text{C}_2\text{H}_5 + \text{O}_2$ and are not yet 'stabilized.'

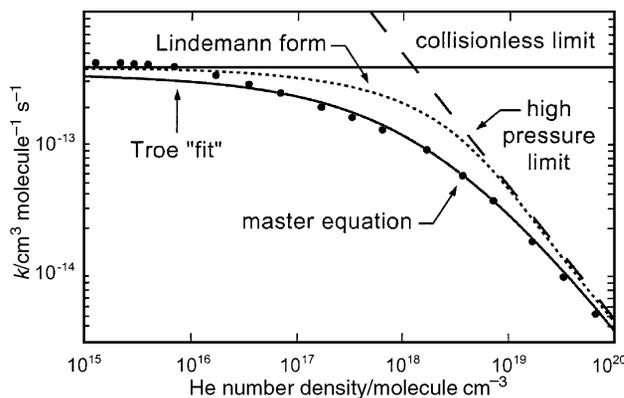


Fig. 4 Pressure dependence of rate constant for $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$ at $T = 298$ K.

in which the collision efficiency was chosen to reproduce the master equation rate constants at intermediate pressures. In the present case, the maximum value of k_a is approximately 10% larger than that at the collisionless limit, but the points deviate from the line in Fig. 4 by about 30%. The latter is a reasonable assessment of the error one might incur in the present case from a pseudo strong-collider model and its associated bimodal energy distribution. However, there is no guarantee that the errors cannot be much larger in other cases.

It is interesting that the same types of collisions were observed by Ian Smith and his collaborators² in their experimental investigation of the CH + H₂ reaction, but with a different effect. At 744 K these investigators observed the total rate coefficient, a combination of the two reactions,



and



to decrease with increasing pressure. They attributed this effect to deactivation of CH₃[‡] complexes with enough energy to go on to CH₂ + H into an energy range where they could only go back to reactants (reaction (4) is slightly endothermic, analogous to the gray region of Fig. 3).

- 1 J. A. Miller, *Twenty-sixth Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1996, p. 461.
- 2 R. A. Brownsword, A. Canosa, B. Rowe, I. W. M. Smith, D. W. A. Stewart, A. C. Symonds and D. Travers, *J. Chem. Phys.*, 1997, **106**, 7662.

Prof. Troe commented: The issue of collisional stabilization in multiple well systems and its treatment by a master equation was raised. On the foundations of the treatment by Seymour Rabinovitch of chemical activation systems, which correspond to the multiple well systems considered here, I have provided simplified solutions of step-ladder models and master equations.¹ They relate collision efficiencies γ_c (which are not identical with collision efficiencies β_c in thermal activation) through an equation $\gamma_c/(1 - \gamma_c^{0.7}) \approx -\langle \Delta E \rangle S / (\langle E_{ac} \rangle - E_o)$ with the average energy $\langle \Delta E \rangle$ transferred per collision, the excess excitation energy $\langle E_{ac} \rangle - E_o$ and the exponent S of the specific rate constants $k(E) \propto (E - E_o)^{S-1}$ of the fastest process depopulating the stabilization well.

- 1 J. Troe, *J. Phys. Chem.*, 1983, **87**, 1800.

Prof. Golden said: The standard methods of dealing with chemical activation systems, pioneered by Rabinovitch involving pseudo strong collision assumptions, seems to be adequate to describe many systems. I think this means that once a system has experienced a single collision, it is deactivated sufficiently that the next most likely event is another collision, rather than product formation.

Prof. Temps responded to Prof. S. C. Smith's comment: As discussed in the paper, we are convinced that our experimental and computational results for the CH₂ + NO reaction apply to the low pressure limit. Collisional effects should not play a role up to pressures below 10 bar (see section 3.2 of the paper).

However, in response to the comment, we would like to point out that the framework for treating chemical activation experiments (including radical-radical-reactions) with collisional deactivation has been well laid out since the work of Kohlmeier and Rabinovitch.¹ Based on master equation modelling, Troe has presented expressions which allow for weak collision effects.^{2,3} It is true that the situation is much more complicated for multiple channel-multiple well reactions, as the CH₂ + NO reaction. That is one of the fascinating aspects of radical-radical reactions and, indeed, a major motivation for our work. In our opinion, two-dimensional master equation models would be very desirable. However, they require allowance for weak collision vibrational and rotational energy transfer (VET and RET), respectively. While RET is in general much faster than VET, little is known experimentally about their combined effect, *i.e.* vibrational-rotational energy transfer (VRET) at the high vibrational energies of the molecules of interest.⁴

- 1 G. H. Kohlmeier and B. S. Rabinovitch, *J. Chem. Phys.*, 1963, **38**, 1709; G. H. Kohlmeier and B. S. Rabinovitch, *J. Chem. Phys.*, 1963, **39**, 490.

- 2 J. Troe, *J. Phys. Chem.*, 1983, **87**, 1800.
- 3 J. Troe, *Proc. Combust. Inst.*, 1998, **27**, 167.
- 4 F. Temps, S. Halle, P. H. Vaccaro, R. W. Field and J. L. Kinsey, *J. Chem. Soc., Faraday Trans 2*, 1988, **84**, 1457.

Prof. Kohse-Höinghaus opened the discussion of Ms Goos's paper: Would any of the adjusted rate coefficients in your paper directly influence the level of propargyl in propene (or other) flames?

In our recent investigations of propene flames¹ and modeling of this system,² there seem to be remaining deviations between measured and simulated propargyl radical concentrations, although benzene is quite well predicted. A similar pattern was recently noted by Lindstedt³ when modeling our pentadiene flame investigated under similar conditions. In this regard, a comment would be much appreciated.

- 1 B. Atakan, A. T. Hartlieb, J. Brand and K. Kohse-Höinghaus, *Twenty-seventh Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1998, p. 435.
- 2 H. Böhm, A. Lamprecht, B. Atakan and K. Kohse-Höinghaus, *Phys. Chem. Chem. Phys.*, 2000, **2**, 4956.
- 3 P. Lindstedt, personal communication (at this meeting).

Prof. Hoyermann responded: The experimental product distribution of the reaction system (propene + CH₃) is well described by the given mechanism (Fig. 2 and Table 3 of our paper) without inclusion of the C₃H₃ radical, thus no direct information on the C₃H₃ chemistry can be deduced. Our similar studies on the systems (1-propyne + CH₃) and (1,2-propadiene + CH₃), where the C₃H₃ is greatly involved with different precursors, gave equal amounts of formed benzene at an otherwise totally different product spectrum. This complements the observations of Kohse-Höinghaus and Lindstedt. In an ongoing evaluation of our experimental results (1-C₃H₄ + CH₃, 1,2-C₃H₄ + CH₃, C₂H₂ + CH₃, and their mixtures) we will consider the suggestions on alternative paths to C₃H₃ to benzene formation.

Prof. Plane asked: This technique clearly produced a steep temperature gradient between the optical axis of the CO₂ laser and the cold reactor walls. Does this affect the estimation of the average temperature at which the reactions are initiated, and perhaps constrain the precursors which can be used?

Dr Desgroux asked: Could you comment on the influence of the radial distribution of temperatures on your measurements? Particularly what kind of 'average' temperature do you use?

Prof. Hippler and **Prof. Hoyermann** replied to Prof. Plane and Dr Desgroux: The radial temperature distribution reflected in the formed C₃H₆ via the isomerization reaction $c\text{-C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_6$ is shown in Fig. 5. The average temperature is essentially that deduced by the chemical thermometer. For a detailed discussion see ref. 30 of our paper. The high activation energy of the decomposition of the precursor di-*tert*-butyl peroxide (156.5 kJ mol⁻¹) leads to the formation of CH₃ radicals mainly at the highest temperatures, switching off the reactions automatically in the cold parts.

Prof. Golden commented: I worry whenever I see that in the formulation of a mechanism, some rate constants are described with two parameters and others with three parameters. This is probably a result of the fact that many values in the literature measured at low to modest temperatures do not reflect Arrhenius curvature. However when these linear fits are extrapolated to higher temperatures they may lead to underestimation of rate constant values. When this is combined with assigning three parameters to other rate constants I wonder if we have created a situation where values cross on the inverse temperature plot, when they should be parallel or close to same.

Prof. Hippler and **Prof. Hoyermann** replied: This general warning has to be taken seriously by any kineticist and modeller. In our particular case we only state agreement between the absolute literature rate coefficients and our model within the limited temperature range of 750–1000 K.

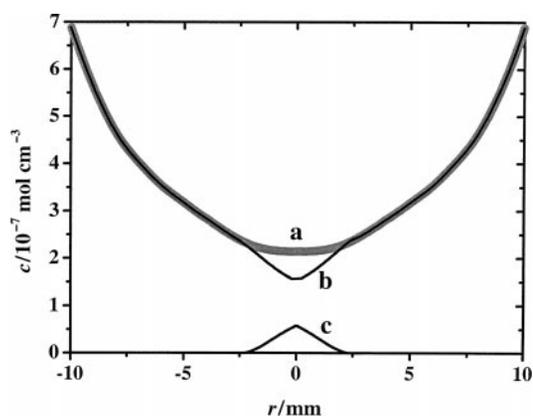


Fig. 5 Radial concentration profiles in the reactor $c\text{-C}_3\text{H}_6$ concentration in the temperature field without (a) and after the isomerization reaction $c\text{-C}_3\text{H}_6 \rightarrow \text{propene}$ (b). The concentration profile of propene is given by (c).

Dr Kaiser commented: The analysis of the $\text{CH}_3\text{-C}_3\text{H}_6$ system looks really interesting. It might be a good idea to investigate how the model predictions will change if you include the reaction of hydrogen poor transient species such as atomic carbon ($\text{C}(^3\text{P}_j)$) with ethylene. Recent crossed beam studies and theoretical investigations of this important reaction suggested the formation of four products: three C_4H_5 isomers and the propargyl radical (Fig. 6).^{1,2} If you investigate the secondary reactions of these radicals, you might form substituted benzenes, cyclopentadienyl radicals, as well as seven and eight membered rings (Fig. 7). The story gets even more fascinating if you could include two C_5H_5 isomers (vinyl propargyl: Fig. 8) which are reaction products of atomic carbon with various C_4H_5 isomers into your model.³⁻⁶ This can bring you to, for example,

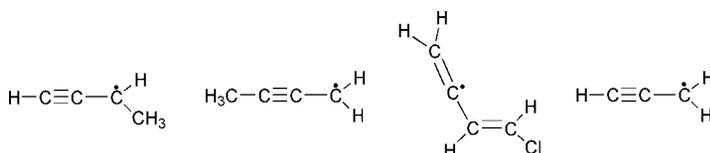


Fig. 6 Four products: three C_4H_5 isomers and the propargyl radical.

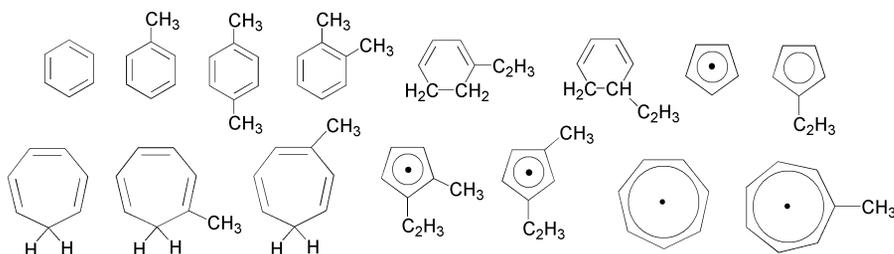


Fig. 7 Secondary reaction products: substituted benzenes, cyclopentadienyl radicals and seven and eight membered rings.

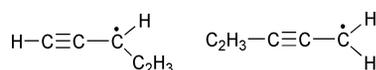


Fig. 8 Two vinyl propargyl (C_5H_5) radicals.

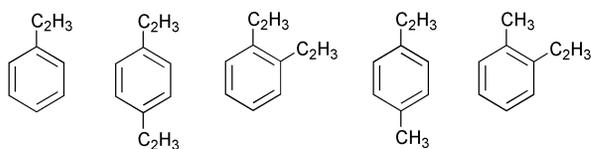


Fig. 9 Mono- and disubstituted benzene molecules.

disubstituted benzene molecules (Fig. 9). In particular, the *ortho*-divinylbenzene is very interesting as this species might undergo ring closure to form a $C_{10}H_{10}$ bicycle.

- 1 R. I. Kaiser, D. Stranges, H. Bevsek, Y. T. Lee and A. G. Suits, *J. Chem. Phys.*, 1997, **106**, 4945.
- 2 R. I. Kaiser, N. Nguyen, H. Le and A. M. Mebel, *Astrophys. J.*, 2001, in press.
- 3 R. I. Kaiser, H. Y. Lee, A. M. Mebel and Y. T. Lee, *Astrophys. J.*, 2001, **548**, 852.
- 4 I. Hahndorf, H. Y. Lee, A. M. Mebel, S. H. Lin, Y. T. Lee and R. I. Kaiser, *J. Chem. Phys.*, 2001, **113**, 9622.
- 5 L. C. L. Huang, H. Y. Lee, A. M. Mebel, S. H. Lin, Y. T. Lee and R. I. Kaiser, *J. Chem. Phys.*, 2001, **113**, 9637.