Kinetics and thermochemistry of the $C_3H_5 + HBr \rightleftharpoons C_3H_6 + Br$ equilibrium

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The kinetics of the reaction of the allyl radical with HBr has been investigated in a heatable tubular reactor coupled to a photoionization mass spectrometer. The allyl radical, R, was produced homogeneously in the reactor by a pulsed 248 nm exciplex laser photolysis of allyl bromide. The decay of R was monitored as a function of HBr concentration under pseudo-first-order conditions to determine the rate constants as a function of temperature. The reaction was studied at temperatures from 400 to 523 K and in this temperature range the rate constants determined were fitted to an Arrhenius expression (error limits stated as $1\sigma + \text{Student's } t$ values, units in cm³ molecule⁻¹ s⁻¹): $k = (4.6 \pm 3.2) \times 10^{-13} \exp[-(12.6 \pm 4.1) \text{ kJ} \text{ mol}^{-1}/RT]$. The kinetic information was combined with the kinetics of the Br + propene reaction taken from the literature to calculate thermodynamic values for the allyl radical at 298 K using a second-law procedure. The entropy value is $248 \pm 15 \text{ J K}^{-1} \text{ mol}^{-1}$ and the enthalpy of formation is $166.1 \pm 4.3 \text{ kJ} \text{ mol}^{-1}$ in good agreement with previous measurements. The allylic C–H bond energy of propene derived from the enthalpy of reaction value is $363.9 \pm 4.3 \text{ kJ} \text{ mol}^{-1}$, which leads to a value of $59.4 \pm 4.9 \text{ kJ} \text{ mol}^{-1}$ for the resonance stabilization energy of the allyl radical. The resonance stabilization energy calculated by *ab initio* methods is $59.9 \text{ kJ} \text{ mol}^{-1}$.

Introduction

The allyl radical can readily be detected in pyrolysis and combustion processes, which indicates its significant stability against carbon centered alkyl radicals.^{1,2} A possible reason for this is that the allyl radical is a resonance stabilized free radical and it has low reactivity with molecules such as Br₂ and Cl₂ compared to alkyl radicals.³ However, the allyl + $O(^{3}P)$ atom reaction is very fast.⁴ This implies that allyl radical reactions with open shell compounds are important sinks for this radical in combustion reactions. For modelling of high temperature combustion processes, it is very important to know the accurate heat of formation value of the allyl radical. This is necessary in order to estimate the kinetics of the allyl radical reactions with other compounds. Furthermore, conjugation of a C-C double bond is an important factor for changing the chemical nature of molecules. In order to achieve this, it is necessary to have the accurate resonance stabilization energy of the allyl radical for calculating bond strengths of allyl-weakened bonds on complex hydrocarbons.

The current study presents a time-resolved experimental kinetic investigation of the allyl radical with HBr. The reaction has not previously been studied. The approach is the same as that used for other radical + HBr studies.⁵ The study was carried out to investigate the enthalpy of formation and the resonance stabilization energy of the allyl radical. The heat of formation and the resonance stabilization energy of the allyl radical have been investigated previously.^{6–8} Here an *ab initio* approach was also used in the resonance stabilization energy calculations for comparison.

Experimental and kinetics

Description of experiments

The rate constants of the reaction of C_3H_5 with HBr were measured as a function of the temperature range. The experi-

mental apparatus used has been previously described.9,10 Pulsed, unfocused 248-nm radiation from a Lambda Physik EMG 201 MSC exciplex laser operated at 5 Hz was collimated and then directed along the axis of a heatable Pyrex reactor. The 10.5 mm id reactor was coated with Teflon to reduce heterogeneous reactions. Gas flowing through the tube at 5 m s⁻¹ was completely replaced between laser pulses. The flowing gas contained the radical precursor allyl bromide (<0.1%), HBr in varying concentrations and the carrier gas, He, in large excess (>93%). Gas was sampled through a 0.44 mm id hole located at the end of a nozzle in the wall of the reactor and was formed into a beam by a conical skimmer before it entered the vacuum chamber containing the quadrupole mass filter. As the gas beam traversed the ion source, a portion was photoionized by an atomic resonance lamp radiation and then mass selected. Temporal ion signal profiles were recorded from 10-30 ms before each laser pulse and 16-25 ms after the laser pulse with a multichannel scalar. Data from 3000 to 13000 repetitions of the experiments were accumulated before the data were analyzed by a non-linear least-squares analysis program.

The only photolysis wavelength used to generate radicals was 248 nm. At this wavelength it is practically impossible to photodissociate the reactant, HBr, to a measurable extent.¹¹

Kinetic results

The chemical kinetics of the following metathetical reaction was studied in a flow reactor:

$$C_3H_5 + HBr \rightarrow C_3H_6 + Br \tag{1}$$

The kinetics determined was combined with the kinetics of the reverse reaction, (-1), in order to calculate the enthalpy of formation and the experimental entropy value of the allyl radical studied. The results obtained from the experiments to measure reaction (1) are given in Table 1.

T^{a}/K	$[He]/10^{16} \text{ cm}^{-3}$	$[HBr]/10^{15} \text{ cm}^{-3}$	k_2/s^{-1}	$k_1 \ ^{b}/10^{-14} \ \mathrm{cm}^3 \ \mathrm{s}^{-1}$			
400	9.84	1.47–3.48	7.9	0.98 ± 0.25			
444	9.85	1.21-2.99	3.9	1.64 ± 0.36			
500	5.87	0.54-3.10	9.6	2.14 ± 0.18			
523	5.89	1.09-4.54	10.5	2.51 ± 0.10			
$k_1 = (4.6 \pm 3.2) \cdot 10^{-13} \exp \left[-(12.6 \pm 4.1) \text{ kJ mol}^{-1}/RT \right] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$							

^a Temperature uncertainty: \pm 3 K. ^b Teflon used for wall coating, errors are 1 σ + Student's t and based on statistical uncertainties.

Photogeneration of the allyl radical

The allyl radical was photogenerated by photodissociating allylbromide at 248 nm. Up to 7 quartz plates were used to diminish laser influence to a very low level. This ensured that the photon flux did not generate Br atoms from HBr to any measurable extent even though the concentration of HBr was high in some experiments. The allyl radical was formed from the precursor by the C–Br bond rupture. After breaking the bond, the native 3-propenyl radical formed isomerized to the resonance stabilized allyl radical.

Data analysis

Experiments were conducted under pseudo-first-order conditions where HBr existed in great excess compared with the concentration of radicals. Only the following two reactions had significant rates under these conditions:

$$C_3H_5 + HBr \rightarrow C_3H_6 + Br$$

 $C_3H_5 \rightarrow$ heterogeneous loss on the wall (2)

In all sets of experiments the initial radical concentration was adjusted to be so low that radical-radical or radical-atom reactions had negligible rates compared to reactions (1) and (2). This was ensured by comparing the measured first-order wall loss decays, k_2 , of the radical with that produced (in the absence of HBr) at different conditions where precursor concentration was held steady but the laser radiation was attenuated by a factor of 3 using quartz and vycor plates (the radical concentration was changed by the same factor). The decays from these different experiments were equal with respect to their statistical error limits.

Rate constants for reaction (1) were obtained from the slopes of plots of the exponential radical decay constant k' vs. [HBr] {from $[\mathbb{R}^+]_t = [\mathbb{R}^+]_0 \exp(-k't)$ }, where $k' = k_1[\text{HBr}] + k_2$. A representative ion signal decay profile and a decay constant plot from one set of experiments to measure k_1 are shown in Fig. 1. The results obtained from all the experiments to measure reaction (1) are given in Table 1.

Accuracy of measurements

The error limits stated in Arrhenius expressions are 1σ + Student's t and they are based only on the statistical uncertainties. The reactions were studied under pseudo-firstorder conditions when it was needed to know accurately only the concentration of HBr. This was measured before and after the kinetic experiment and the mean value was used for the rate constant calculation.⁵ During some experiments a very large amount of HBr had to be used to obtain large k' decay constants. In these conditions [HBr]/[He] was up to 0.07. However, the gas viscosity of HBr was only 5-15% higher than the viscosity of the carrier gas He in the temperature range used in the current study. This caused about 1% additional error to the large [HBr] (see Fig. 1) when pressure drop along the reactor is considered. The other errors, such as measured temperature and gas flow rates, were always < 1%. All these errors are very small and were thus ignored. The statistical uncertainties of the decay constants were taken into



Fig. 1 Plot of first-order decay constant k' vs. [HBr] for one set of experiments conducted to measure the $C_3H_5 + HBr$ rate constant, k_1 , at 523 K. Inset in the lower right corner is the ion signal profile of $C_3H_5^+$ recorded during one of the experiments shown as a solid circle ([HBr] = 2.78×10^{15} molecule⁻¹ cm⁻³) in the linear regression fit. The line through the data in the insert is an exponential function fitted by a nonlinear least-squares procedure. The first-order decay constant for $C_3H_5^+$ in the displayed ion signal profile is (80.3 \pm 2.0) s⁻¹.



Fig. 2 Arrhenius plot of C_3H_5 + HBr reactions measured in the current study. The line is an Arrhenius expression fitted to the rate constants k_1 . Also shown is the kinetics of Br + C_3H_6 reaction taken from ref. 12.

Species	$\Delta_{\rm f} H_{298}^{\circ}/{\rm kJ}~{\rm mol}^{-1}$	$S_{298}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1}$
$\begin{array}{l} \mathrm{HBr}^{a}\\ \mathrm{Br}^{a}\\ \mathrm{C_{3}H_{6}} \end{array}^{b,c} \end{array}$	- 36.44 111.86 20.2	198.70 175.02 267.1

 a Data taken from ref. 13. b Data taken from ref. 15. c Data taken from ref. 14.

account in data analysis and their effects on the rate constants are shown in Fig. 2. The Arrhenius expression of the reaction was obtained by weighting the measured rate constants with reciprocals of their variances for fitting procedure.

Reagent sources and purification procedures

Allylbromide, 99%, and HBr, 99%, were obtained from Aldrich and helium, 99.995%, from Matheson.

The carrier gas, He, was used as provided. Allyl bromide was degassed by using freeze-pump-thaw cycles. HBr was collected to a flow trap kept at 77 K and was repeatedly distilled to remove any traces of bromine. HBr was stored in a dark Pyrex bulb. The gas handling system, which was used to set up a known HBr flow to the reactor gas inlet, was made from Pyrex glass and Teflon tubes.

Photoionization energies used

Reactants and products of the photolysis as well as the precursors were photoionized using atomic resonance radiation. A chlorine lamp (8.9–9.1 eV) was used to detect C_3H_5 and an argon lamp (11.6, 11.8 eV) to detect HBr, Br_2 and Br.

Thermochemical calculations

Both the enthalpy and entropy changes of the reactions were obtained using a second-law method. This procedure is the same as used previously.⁵ Briefly, at first reaction free energy, enthalpy and entropy were calculated at the mean temperature on a 1/T scale of both reaction directions. Reaction enthalpy change and entropy value were then recalculated at room temperature using heat capacity data. Finally, the enthalpy of formation and entropy of the free radical of interest were obtained from the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values at 298 K.

The Arrhenius expression for the Br + $C_3H_6 \rightarrow C_3H_5$ + HBr reaction, $k_{-1} = (8.2 \pm 4.5) \times 10^{-13} \exp[-(10.4 \pm 1.3)$ kJ mol⁻¹/*RT*] cm³ molecule⁻¹ s⁻¹, was taken from ref. 12. The ratio of rate constants was used to calculate $\Delta_r G^{\circ}$ at 322 K as 3.8 ± 1.7 kJ mol⁻¹. A second-law method was then used to obtain $\Delta_r H_{322}^{\circ}$ to be 2.3 ± 4.3 kJ mol⁻¹ and $\Delta_r S_{322}^{\circ}$ to be $-(5 \pm 14)$ J K⁻¹ mol⁻¹. These thermodynamic functions were then recalculated at 298 K using the heat capacities of the reactant species.^{13,14} Finally, the enthalpy of formation and the entropy of the allyl radical at room temperature were

$$\Delta_{\rm f} H^{\circ}_{298} = 166.1 \pm 4.3 \text{ kJ mol}^{-1}$$

$$S^{\circ}_{298} = 248 \pm 15 \text{ J K}^{-1} \text{ mol}^{-1}$$

The enthalpy of formation can be transplanted to the allylic C–H bond energy of propene to have a value of $363.9 \pm 4.3 \text{ kJ} \text{ mol}^{-1}$.

Computational study

Computation details

Ab initio molecular orbital calculations were carried out with the GAUSSIAN 94 package of programs.¹⁶ All calculations were carried out on an Indigo² IMPACT workstation. Geometries of all open and closed shell species were fully optimized using a second-order Møller-Plesset perturbation theory with the frozen core approximation and 6-31G(d,p) basis set.¹⁷ For the free radicals of interest, expectation values, S^2 , varied in the range of 0.7911 to 0.9591 depending on the type of the radical. The S^2 value was highest for the resonance stabilized allyl radical. All optimized structures were shown to be at the local minimums of the C₃H₅ potential energy surface by frequency calculations at the same level of theory as that for the optimizations. The zero-point energies of the optimized compounds for bond energy studies were obtained from frequency calculations. The zero-point energies were scaled by a factor of 0.9676 as it has been suggested in literature.¹⁷

The energies of the species were calculated at the MP4(SDTQ)/6-311G(d,p) level of theory. The bond energies of propene (RX) were calculated from a homolytic bond dissociation reaction: $RX \rightarrow R + X$, where X = H or open shell C_1 compound and R can be either a radical or a diradical. The calculated bond dissociation energies were temperature corrected simply by 4RT where only translational and rotational contributions have been considered.¹⁸

Optimized geometries of free radicals

Energies and symmetries of the free radicals and the other species are given in Table 3. After photodissociation of the allylbromide or an H atom abstraction reaction of the reverse reaction, the formed native 3-propenyl free radical (*i.e.* perpendicular allyl) will isomerize to the allyl radical, which is a hybrid of the two resonance structures of 3-propenyl radical. The allyl radical is by 60 kJ mol⁻¹ lower in energy at MP4(SDTQ)/6-311G(d,p) level of theory than the 3-propenyl radical. This difference is known as a resonance stabilization energy or a delocalization energy of the allyl radical.

The geometries of the allyl and the 3-propenyl free radicals differ drastically. The allyl radical has C_{2v} symmetry, whereas the 3-propenyl radical has only a reflection plane because of

Table 3 Symmetry point groups, total and zero-point energies. The zero-point energy at the MP2/6-31G(d,p) level and total energies at the MP4(SDTQ)/6-311G(d,p) level are in $E_{\rm h}$

Compound	Symmetry	Multiplicity	Total energy	Zero-point energy
H CH ₂ CH ₃ CH ₂ =CH CH ₂ =CH-CH ₂ CH ₂ CHCH ₂ CH ₃ -C=CH ₂ cH ₃ -C=CH ₂	K_{h} C_{2v} D_{3h} C_{s} C_{2v} C_{s} C_{s} C_{s} C_{s} C_{s}	d t d d d d d d d	-0.499 81 -39.053 05 -39.730 68 -77.692 12 -116.923 98 -116.944 19 -116.913 91 -116.907 62	0.0 0.018 149 0.030 702 0.039 094 0.070 943 0.068 222 0.069 097 0.069 420
trans-CH ₃ -CH=CH CH ₃ -CH=CH ₂	C_{s} C_{s}	d s	- 116.908 31 - 117.598 73	0.069 219 0.081 924

the twisted form of its methylene group. Resonance stabilization causes large changes in the C–C bonds: for the allyl radical the lengths of the hybrid bonds are 1.38 Å and for the 3-propenyl radical they are 1.48 and 1.31 Å, which are typical for single and double C–C bonds.

Two geometrical isomers of the 1-propenyl free radical were considered. The *trans*-conformer in which the dihedral angle between the methyl carbon and the H atom at the radical site is 180°, is 2.3 kJ mol⁻¹ more stable than the *cis*-conformer at the MP4(SDTQ)/6-311G(d,p) level. For comparison the C–C double bond length is 1.29 Å and the C–C single bond length is 1.51 Å for both radicals. The 2-propenyl free radical has the largest C–C–C valence angle of the studied C_3H_5 radicals. It is 138° compared to a typical value of 125° for the other tautomers studied.

Discussion

Kinetics of the reactions

The kinetics of both reactions are shown in Fig. 2. The Br atom abstraction reaction is faster than the forward reaction. Special attention was paid to setting up as low a photon flux as possible to avoid increasing Br atom concentration. If it is too high during measurement of the forward reaction, it will cause a displacement on the monitored C_3H_5 decay signal. Because of the very low [Br] used during experiments, all the exponential decays used for the rate constant measurements were purely single exponential in shapes.

A Br atom can theoretically abstract one of the four different hydrogen atoms on propene. The equilibrium reaction studied requires one of the allylic hydrogens on propene to be abstracted. Concerning this it was shown in the current study by the *ab initio* calculations that the allylic C–H bond is indeed the weakest bond of propene. Both reaction directions of the equilibrium reaction are practically thermoneutral, thus selective Br atom reactions will practically always lead to the abstraction of the allylic H atom on propene. The *ab initio* calculated bond energies of propene are shown in Fig. 3.

Enthalpy of formation of the allyl radical

The enthalpy of formation of the allyl radical was found to be 166.1 ± 4.3 kJ mol⁻¹. This value is in very good agreement with the appearance energy measurement of the allyl cation when various allyl halides and alkenes were used as precursors.¹⁹ Traeger combined the information measured with the adiabatic ionization energy of the allyl radical taken from another source to calculate the heat of formation of the allyl radical as 165.2 ± 3.3 kJ mol⁻¹ at 298 K.

Rossi and Golden derived the heat of formation of the allyl radical to be $164.8 \pm 6.3 \text{ kJ mol}^{-1}$ at 300 K. The authors studied the kinetics of $C_3H_5 + HI$ reaction using a very low-pressure pyrolysis (VLPP) technique in a Knudsen cell.⁶

Fig. 3 Calculated bond energies in kJ mol⁻¹ of propene at 298 K. Values shown are obtained at MP4(SDTQ)/6-311G(d,p)//MP2/6-31G(d,p) level of theory.

Another VLPP investigation of the reaction of allyl radical recombination yielded $\Delta_{f}H^{\circ}_{300}$ to be 163.6 ± 6.3 kJ mol^{-1.7}

The allylic C–H bond energy of propene was calculated as 363.9 ± 4.3 kJ mol⁻¹. This value is about 17 kJ mol⁻¹ lower than the *ab initio* calculated bond energy. A possible reason for the difference is a less accurate temperature correction method used and the fact that the calculated primary C–H bond energies differ typically from the experimental values by about 6 kJ mol⁻¹.²⁰

Resonance energy

The allvl radical is a resonance stabilized free radical. In the current study its resonance energy was calculated to be 59.9 kJ mol⁻¹ by *ab initio* methods at MP4(SDTQ)/6-311G(d,p) //MP2/6-31G(d,p) level of theory. For comparison more accurate calculations at MP4(SDTQ)/6-311G(2d,2p)//MP3/6-311G(d,p) level of theory were also used to obtain the resonance energy to be 58.3 kJ mol⁻¹. The resonance energy was considered as the difference of the calculated (zero-point energy corrected) energies of the allyl and the 3-propenyl free radicals. For more accurate determinations a slight difference in the stretching frequencies of different C-H bonds of the methyl group of propene could be considered. Since frequency is directly related to the dissociation energy of the bond (for a harmonic oscillator), one may also expect slightly different resonance stabilization values for the allyl radical depending on which of the methyl hydrogens is considered.

The calculated allyl resonance energy can be compared to the experimental value of 59.4 ± 4.9 kJ mol⁻¹, which is $E_{d_{298}}(n-C_3H_7-H) - E_{d_{298}}(allyl-H)$. The primary C-H bond dissociation energy of propane is taken from literature.²¹ A previous experiment yielded the allyl resonance energy to be 51 kJ mol^{-1.8} However, this value was calculated using $\Delta_{\rm f} H_{300}^{\circ}(C_3H_5) = 171$ kJ mol⁻¹.

Summary

The kinetics of allyl radical reaction with HBr has been characterized. The rate constants obtained were combined with those for the reverse reaction taken from the literature to obtain the enthalpy of formation of the allyl radical as $166.1 \pm 4.3 \text{ kJ mol}^{-1}$ at 298 K. The enthalpy of formation value was used to determine the resonance stabilization energy of the allyl radical to be $59.4 \pm 4.9 \text{ kJ mol}^{-1}$. The allylic bond of propene was shown by *ab initio* calculations to be the weakest bond of the molecule. *Ab initio* methods were used to calculate a value of 59.9 kJ mol⁻¹ for the resonance stabilization energy of the allyl radical.

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References

- 1 R. D. Smith, J. Phys. Chem., 1979, 83, 1553.
- 2 D. Edelson and D. L. Allara, Int. J. Chem. Kinet., 1980, 12, 605.
- 3 R. S. Timonen, J. A. Seetula and D. Gutman, J. Phys. Chem., 1993, 97, 8217.
- 4 I. R. Slagle, J. R. Bernhardt, D. Gutman, M. A. Hanning-Lee and M. J. Pilling, J. Phys. Chem., 1990, 94, 3652.
- 5 J. A. Seetula, J. Chem. Soc., Faraday Trans., 1996, 92, 3069.
- 6 M. Rossi and D. M. Golden, J. Am. Chem. Soc., 1979, 101, 1230.
- 7 M. Rossi, K. D. King and D. M. Golden, J. Am. Chem. Soc., 1979, 101, 1223.
- 8 W. Tsang and J. A. Walker, J. Phys. Chem., 1992, 96, 8378.
- 9 I. R. Slagle and D. Gutman, J. Am. Chem. Soc., 1985, 107, 5342.



- 10 J. A. Seetula, Ann. Acad. Sci. Fenn., Ser. A2, 1991, 234.
- B. J. Huebert and R. M. Martin, J. Phys. Chem., 1968, 72, 3046.
 Y. Bedianian, G. Poulet and G. Le Bras. J. Phys. Chem. A, 199
- 12 Y. Bedjanian, G. Poulet and G. Le Bras, J. Phys. Chem. A, 1998, 102, 5867.
- M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, J. Phys. Chem. Ref. Data, 1985, 14, Supplement No. 1.
- 14 S. G. Lias, J. F. Liebman, R. D. Levin, S. A. Kafafi and S. E. Stein, Structures and properties, NIST, database 25, 1994.
- 15 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, J. Phys. Chem. Ref. Data, 1988, 17, Supplement No. 1.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y.

Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, GAUSSIAN 94, Revision E.2, Gaussian, Inc., Pittsburgh PA, 1995.

- 17 J. B. Foresman and Æleen Frisch, Exploring Chemistry with Electronic Structure Methods, Gaussian, Inc., Pittsburgh, 2nd edn., 1996.
- 18 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York, 1986.
- 19 J. C. Traeger, Int. J. Mass. Spect. Ion Proc., 1984, 58, 259.
- 20 J. A. Seetula, J. Chem. Soc., Faraday Trans., 1998, 94, 891.
- 21 J. A. Seetula and I. R. Slagle, J. Chem. Soc., Faraday Trans., 1997, 93, 1709.

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