Recombination and dissociation of 2-methyl allyl radicals: Experiment and theory

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ABSTRACT

The recombination and dissociation of the resonantly stabilized 2-methylallyl radical has been studied in a diaphragmless shock tube by laser schlieren densitometry (LS) over temperatures of 700-1350 K and pressures of 60-260 Torr. Both 2,5-dimethyl-1,5-hexadiene and the new low temperature precursor 3-methylbut-3-enyl nitrite were used to generate 2-methylallyl radicals under these conditions. Rate coefficients were obtained for dissociation of the precursors, recombination of 2-methylallyl, and dissociation of 2-methylallyl by simulation of the LS profiles. The experiments are complemented by *a priori* theoretical calculations for both the recombination and dissociation of 2-methylallyl. The experimental results and theoretical predictions are in excellent agreement with one another. The calculated high pressure limit rate coefficient for recombination of 2-methylallyl is $\log(k_1) = 14.737 - 0.641\log T + 251.39/(2.303 \times T)$ and that for dissociation of 2-methylallyl is $\log(k_3) = 11.100 - 1.2295\log T - 28545/(2.303 \times T)$. The uncertainties in k_1 and k_3 are estimated as factors of 1.5. Rate coefficients are provided over a broad range of pressures for chemical kinetic modeling.

1. INTRODUCTION

Resonantly stabilized radicals (RSRs) are typically much less reactive than other common combustion radicals such as OH, H, and O. Consequently, RSRs can accumulate in relatively large concentrations and play important roles in combustion. For instance, allyl radicals have been studied extensively ([1–3] and references therein) and recently Curran *et al.* showed the importance of allyl recombination in simulating propene ignition delay times [4,5]. The related RSR, 2-methylallyl, 2MA, plays a similarly important role in the low temperature ignition of isobutene [6] and is responsible for the effectiveness of tert-butyl ethers in suppressing engine knock [7,8].

The literature on recombination and dissociation of 2MA is limited. Roth *et al.* [9] reported rate coefficients for dissociation of 2,5-dimethyl-1,5-hexadiene (25DM15HD), the reverse of reaction 1

(Note: all reaction numbers refer to Tables 1 and S2), from single pulse shock tube (SPST) experiments over 873-1073 K and obtained k_1 from calculated thermochemical quantities and the equilibrium constant. Bayraceken *et al.* [10] obtained k_1 at 295 K from flash photolysis of 2-methylbut-1-ene (1-20 Torr). Tsang studied the dissociation of 2,4-dimethylhex-1-ene [11] by SPST (970-1180 K, 1-5 atm) and reported k_3 for dissociation of 2MA.

Previously we have studied the recombination of allyl radicals using a combination of shock tube methods over a broad range of conditions (10-7600 Torr, 650-1700 K) [1,2]. The current work presents complementary experimental and *ab initio* theoretical treatments of the recombination and dissociation of the related RSR 2-methyl allyl. Together these span conditions relevant to low-temperature ignition and master equation modeling provides rate expressions that encompass the low pressure experimental work (c.f. [1]) and engine relevant pressures. The synthesis and dissociation of a new low temperature precursor for 2MA is also presented.

Table 1. Key reactions for 2,5-dimethyl-1,5-hexadiene and 3-methylbut-3-enyl nitrite pyrolysis

#	Reaction	Log A	<i>n</i>	E_a/R (K)	$\Delta H_{r,298\text{ K}}$	Ref.
1	$2\text{-MA} + 2\text{-MA} + \text{M} \rightarrow 25\text{DM15HD} + \text{M}$	14.737	-0.641	-251.39	-60.7	P.W
2	$\text{C}_5\text{H}_9\text{ONO} + \text{M} \rightarrow 2\text{-MA} + \text{H}_2\text{CO} + \text{NO} + \text{M}$	158.864	-43.95	49108	39.8	P.W 700K<T<1060K
3	$2\text{-MA} + \text{M} \rightarrow \text{CH}_3 + \text{aC}_3\text{H} + \text{M}$	11.100	1.2295	28545	48.7	P.W
4	$\text{C}_2\text{H}_6 + \text{M} \rightarrow \text{CH}_3 + \text{CH}_3 + \text{M}$	28.905	-3.52	47980	28.905	[35]
13	$\text{CH}_3 + 2\text{-MA} + \text{M} \rightarrow \text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3 + \text{M}$	13.0	0	0	-75.2	[11]

Units: kcal, cm, mol, s. $k = AT^n \exp(-E_a/RT)$. k_1 - k_4 , high pressure limit. For the full model see Table S2.

2. EXPERIMENTAL SECTION

Experiments were performed behind incident shock waves in a diaphragmless shock tube (DFST) that created very reproducible and predictable reaction conditions. The DFST has been fully described previously [12]. The temperature, T_2 , and pressure, P_2 , behind the incident shock wave were

calculated from the ideal shock relations, initial loading conditions and incident shock velocity, assuming frozen conditions. The shock velocity, with an estimated error of 0.5% (< 10 K in T_2) was calculated from the time taken for the shock wave to pass between pressure transducers centered around the laser schlieren densitometry (LS) windows.

Reactions were monitored by the LS technique which has also been fully described elsewhere [13,14]. A narrow laser beam traversed the shock tube perpendicular to its long axis, and deflection of the beam in the horizontal plane was measured. The deflection is proportional to axial density gradients (dp/dx) in the shock tube [14], which are related to the chemical reactions occurring through Equation 1 [14]. Simulation of the density gradients yields rates of reactions and mechanistic details.

$$(dp/dx) \propto \sum r_i (\Delta H_{r,i} - C_p T \Delta N_i) \quad (1)$$

(r = rate of reaction i , $\Delta H_{r,i}$ = enthalpy of reaction and ΔN_i = change in number of moles).

Reagent mixtures of 0.5% - 2% dilute in krypton (Airgas, $> 99.999\%$) were prepared manometrically in a pre-evacuated 50 L glass vessel and stirred for at least 1 hour. 2,5-Dimethyl-1,5-hexadiene, 25DM15HD, (TCI America, $> 98\%$) was used for the higher temperature experiments. 3-Methylbut-3-enyl nitrite, C_5H_9ONO , was synthesized from 3-methyl-3-buten-1-ol (Aldrich, $> 97\%$), see supplementary material S1. Reagents were degassed with liquid nitrogen prior to use. The molar refractivities of both reagents, which are necessary for conversion of the LS signals to density gradients [14], were obtained from their refractive indices, η , and densities, ρ . The molar refractivities are: 25DM15HD = $38.288 \text{ cm}^3/\text{mol}$ ($\eta = 1.429$; $\rho = 0.742 \text{ gm/cm}^3$ [15]); $C_5H_9ONO = 29.439 \text{ cm}^3/\text{mol}$ ($\eta = 1.425$; $\rho = 1.0 \text{ gm/cm}^3$ [15]) and Kr = $6.367 \text{ cm}^3/\text{mol}$ [16].

3. THEORY

3.1 Recombination of 2-methylallyl

Variable reaction coordinate transition state theory [17,18] (VRC-TST) was used to calculate the high-pressure-limit, HPL, (capture) rate coefficient for reaction 1. Our procedure was similar to that of

Georgievskii *et al.* [19], who previously considered several RSR + RSR reactions, including the allyl + allyl recombination reaction. Here, a more approximate treatment of fragment relaxation was used in the VRC-TST calculation. We therefore first applied our approximate treatment to the allyl + allyl reaction to validate it against the more detailed calculation of Ref. [19].

In the direct VRC-TST calculations, the interaction potential energy surfaces were evaluated “on-the-fly” using CAS(6e,6o)PT2/cc-pVDZ. This active space correlates asymptotically with the three π orbitals of each of the two reacting radicals. A one-dimensional correction potential (defined for the incipient bond distance R_{CC}) was applied to the CASPT2/cc-pVDZ energies to account for finite basis set and fragment relaxation effects. One could develop independent correction potentials for the two non-equivalent rigid-fragment additions with *cis* or *trans* methyl groups. The calculated correction potentials for these two channels differed by only a few percent, and so a single correction potential was implemented. The basis set correction was defined as the difference in (*trans*) CAS(6e,6o)PT2 energies using the aug-cc-pVTZ and cc-pVDZ basis sets. This correction lowered the interaction potential by ~30% for kinetically relevant R_{CC} . The geometry relaxation correction was defined as the difference in CASPT2/aug-cc-pVDZ energies along two minimum energy paths (MEPs) for association: a rigid-fragment MEP and a fully relaxed MEP, both optimized using M06-2X/cc-pVDZ. This correction was negligible for $R_{CC} > 3$ Å and quite large (−30 kcal/mol) at $R_{CC} = 2$ Å, nearly four times the rigid-fragment interaction energy.

Although similar one-dimensional correction potentials have been previously employed (for examples see Refs. [20,21]), Georgievski *et al.* [19] suggested a more rigorous strategy for reactions involving RSRs due to the increased importance of geometry relaxation for these systems. In their approach, full-dimensional geometry relaxation corrections were calculated on-the-fly during the VRC-TST sampling. This approach was deemed too computationally expensive for the present study. Instead, we first calculated the HPL of the self-recombination reaction of the allyl radical with our procedure,

which we found reproduced the higher-level rate of Ref. [19] to within 10% from 700 - 2500 K, with larger errors at lower temperatures (+100% at 300 K).. Our approach is thus validated for the temperature range of the present experiments (724 - 1336 K). To improve the prediction of reaction 1 at lower temperature where the uncertainties in the calculate values are greater, we scaled the HPL for reaction 1 by the ratio of the capture rate coefficients for allyl + allyl calculated in Ref. [19] and here using the more approximate treatment of fragment relaxation.

The HPL rate coefficient for the unimolecular dissociation of 25DM15HD was obtained from the HPL capture rate coefficient and equilibrium constant, $K_{eq,1}$. The reaction energy ($\Delta H_r = 63.6$ kcal/mol at 0 K) was calculated using $\sim$ CCSD(T)/CBS, where $\sim$ CCSD(T)/CBS = CCSD(T)/cc-pVTZ + MP2/CBS – MP2/cc-pVTZ and the CBS limit was extrapolated using the cc-pVTZ and cc-pVQZ basis sets and a two-point $(l+1)^{-4}$ formula. $K_{eq,1}$ was calculated using the rigid rotor, harmonic oscillator, and one-dimensional hindered rotor approximations for the rovibrational state counts, M06-2X/aug-cc-pVTZ rovibrational properties, and an approximate correction for non-equivalent conformers of 25DM15HD, as described next. The methyl rotor in 2MA is nearly a free rotor and was treated as such.

Using the lowest-energy conformer as a reference, five torsions in 25DM15HD were treated as symmetric one-dimensional hindered rotors [22] with barrier heights (M06-2X/cc-pVDZ) of 3.0 kcal/mol for the central C-C bond, 4.2 kcal/mol for the two equivalent adjacent torsions, and 1.9 kcal/mol for the two equivalent methyl torsions. For symmetric and independent torsions, each internal rotor could be unambiguously assigned a periodicity parameter of 3, implying that the five internal rotors result in 3^5 identical species. Clearly, while internal rotations about the methyl groups give rise to identical species, internal rotations along the C–C backbone do not. In fact, the three backbone torsions are coupled (i.e., are not symmetric and independent) such that 9 unique conformers were found with relative energies differing by as much as 2.6 kcal/mol. We therefore corrected the ideal (symmetric and independent) symmetry number for internal rotations approximately as follows

$$\frac{1}{S_{\text{IR}}^{\text{eff}}} = \frac{1}{S_{\text{IR}}^{\text{ideal}}} \sum_{\substack{i=\text{unique} \\ \text{conformers}}} d_i \exp(-\Delta E_i / k_{\text{B}} T), \quad (2)$$

where d_i is the number of non-superimposable mirror images (1 or 2) of the i^{th} unique conformer, and ΔE_i is its energy relative to the lowest-energy one. This correction increases the effective symmetry number for 25DM15HD by 2.1 at 300 K, 4.0 at 700 K, and 5.6 at 1500 K. The resulting equilibrium constant, $K_{\text{eq},1} = 1.172 \times 10^{-29} (T/298 \text{ K})^{2.141} \exp(32292 \text{ K}/T) \text{ cm}^3$, is only ~30% smaller than values obtained from the thermochemical properties in the chemical kinetic model used to simulate the experimental density gradient profiles.

Low-pressure limit and falloff kinetics for 25DM15HD + Kr were calculated using the one-dimensional (in E) master equation [23] and the exponential down model for collision efficiency. The range parameter, $\alpha = 415 (T/300 \text{ K})^{0.5} \text{ cm}^{-1}$, was calculated using classical trajectories [24,25]. The collision frequency was calculated from Lennard-Jones parameters ($\sigma = 5.02 \text{ \AA}$, $\varepsilon = 206 \text{ cm}^{-1}$) obtained as in Ref. [26]. Both sets of calculations employ the general $\text{C}_x\text{H}_y + \text{Kr}$ potential energy surface of [27]. This approach to predicting the low-pressure-limit has been shown to have an error of up to a factor of ~2, largely due to simplifications in the energy transfer model [28].

3.2 Dissociation of 2-methylallyl

A similar theoretical approach was used to calculate k_3 . The reverse of this reaction has a barrier, and the HPL for k_3 was calculated using variational transition state theory with the Improved Canonical Variational Theory (ICVT) method available in POLYRATE, [29,30] and the dual level ~CCSD(T)/CBS//M06-2X/aug-cc-pVTZ method discussed above. The calculated reaction energy is 44.9 kcal/mol, and the reverse zero-point-inclusive barrier height is 11.1 kcal/mol. The information required for predicting pressure dependence was calculated as discussed above, giving $\alpha = 250 (T/300 \text{ K})^{0.75} \text{ cm}^{-1}$, $\sigma = 4.39 \text{ \AA}$, and $\varepsilon = 153 \text{ cm}^{-1}$.

4. RESULTS AND DISCUSSION

Sample raw LS signals and corresponding semi-log density gradient plots are shown in Fig 1. The chemical signal starts on the falling edge of the large peak which obscures t_0 , Fig. 1a. Consequently, t_0 is located by a well-established procedure to within 0.1 - 0.2 μs and the location of t_0 for one experiment is shown in Fig. 1a. The density gradients due to chemical processes are first observable from the discontinuity around 0.8 μs in each of the main plots in Fig. 1 and the preceding signal is mainly due to interaction of the shock front and laser beam [14]. At longer times the scatter in the experimental points increases as the density gradients become small.

Fig. 1. Semi-log absolute density gradient plots for 25DM15HD/Kr and C₅H₉ONO/Kr. Insets: Raw LS signals; the vertical line in inset (a) shows the approximate location of t_0 for that experiment. Main plot: Lines are simulations and symbols represent experiments. Open circles - positive density

gradients; Filled circles - negative density gradients. (a-d) Solid lines, final model. (a) and (c) Dash $k_1 \times 1.5$; dash-dot $k_1/1.5$; (b) Dash $k_3 \times 1.5$; dash-dot $k_3/1.5$; (d) dash $k_2 \times 1.5$, dash-dot $k_2/1.5$.

To obtain the density gradient at t_0 , $(dp/dx)_0$, from which accurate values for the rate of dissociation of the parent molecule are obtained, the (dp/dx) are extrapolated back to t_0 by simulating the complete experimental profile. The results of simulations based on the methodology of Gardiner *et al.* [31] and a chemical kinetic model are shown in Fig. 1. The key reactions are given in Table 1 and the complete mechanism in S2 of the supplementary material. The C_5H_9ONO experiments were simulated with only reactions 1 and 2 whereas at the higher temperatures of the 25DM15HD studies dissociation of 2MA leads to a more complex but still compact mechanism consisting of reactions 1 and 3-14. All reactions were treated as reversible with reverse rates calculated from the equilibrium constant. Most thermochemical properties were taken from Goos *et al.* [32]. Those of C_5H_9ONO were estimated by group additivity [33] and for 25DM15HD, $\bullet CH_2C(CH_2)C_2H_4C(CH_2)CH_3$, $CH_3C(CH_2)CH(\bullet)CH_2C(CH_2)CH_3$ were obtained from *ab initio* calculations [Personal communication: C. Zhou and H. Curran, NUIG]. The normal assumption is made that the mixture molar refractivity (MMR) remains constant throughout an experiment. This is an excellent approximation for dilute reagent mixtures such as those used here, and any error will be most significant at high temperatures, high concentrations and long times. For example, for 2% 25DM15HD with $T_2 = 1301$ K and $P_2 = 262$ Torr, the change in MMR is $< 2\%$ at $9 \mu s$. For 2% C_5H_9ONO with $T_2 = 917$ K and $P_2 = 141$ Torr, it is $< 6\%$ at $9 \mu s$. In both cases the change is insignificant with respect to determination of the rate coefficients of interest. The majority of the rate coefficients were either fixed at literature values or estimated and are available in S2. However, the simulations were insensitive to all reactions apart from those in Table 1 which were identified by brute force sensitivity analysis. k_1 - k_3 were optimized iteratively. From the 25DM15HD experiments, k_1 was determined from $(dp/dx)_0$ and k_3 , dissociation of 2MA, by fitting the

density gradient profiles. Whereas from the C_5H_9ONO experiments, k_2 , dissociation of C_5H_9ONO , was obtained from $(dp/dx)_0$ and k_1 by fitting the density gradient profiles.

4.1 2,5-dimethyl-1,5-hexadiene

Thirty one experiments were performed with 25DM15HD/Kr over the range 1090 - 1336K at nominal P_2 of 66, 138 and 260 Torr (S3, supplementary material). Figs 1a and b show examples of the 25DM15HD experiments. The density gradients initially fall sharply and then abruptly change to a shallower slope. This behavior is unusual, but well reproduced by the simulations. These indicate that initially 25DM15HD dissociates to two 2MA ($\Delta H_{r,298K} = 60.7$ kcal/mol) by scission of the central C-C bond. The bond dissociation energies of the central C-C bond and the H_3C-C bond, the next weakest were calculated (CBS-QB3) to be 61.6 kcal/mol and 98.2 kcal/mol respectively. Consequently, dissociation of 25DM15HD to 2MA is considered to be the only process at t_0 . After a short period, a sufficient concentration of 2MA is established to maintain reaction 1 close to equilibrium with the parent molecule dissociating to replenish 2MA radicals lost through dissociation, reaction 2, and addition to methyl radicals, reaction 13. Consequently, after the initial drop the signal flattens as the positive contributions to the net density gradient from reaction -1 and dissociation of 2MA ($\Delta H_{r,298K} = 39.8$ kcal/mol) is offset by the negative contributions from reaction of methyl radicals with 2MA, reaction 13, ($\Delta H_{r,298K} = -75.1$ kcal/mol). The sensitivity of the simulations to k_1 and k_3 is shown in Figs. 1a and b respectively. The experiments also showed modest but lower sensitivity to k_{13} . Reaction 13 only becomes significant when there are sufficient CH_3 radicals present to react with 2MA and these are only formed by reaction 3 leading to reduced sensitivity to k_{13} . Initial values of k_3 and k_{13} were taken from Tsang [11]. The best fits over the complete experimental range were obtained when k_{13} was reduced by a factor of 2 and then fixed while k_1 and k_3 were optimized for each experiment. At the higher temperatures and pressures $CH_3 + 25DM15HD$ also plays a minor role. Rate coefficients for abstractions of primary and secondary H-atoms from 25DM15HD to give $\bullet CH_2C(CH_2)C_2H_4C(CH_2)CH_3$

and $\text{CH}_3\text{C}(\text{CH}_2)\text{CH}(\bullet)\text{CH}_2\text{C}(\text{CH}_2)\text{CH}_3$ respectively were estimated [Personal communication: C. Zhou and H. Curran, NUIG].

An Arrhenius plot of k_3 is shown in Fig. 2 along with theoretical values from this work and the HPL from Tsang [11]. The experimental points are in falloff but do not show significant pressure dependence. The theory predicts only a small pressure dependence and tightly bounds the experimental data. The agreement is excellent and within the estimated error of $\pm 50\%$ in the LS results. Tsang's k_3 is 60% lower than the HPL at 1200 K and 10% lower at 900 K. The experimental k_1 and k_{-1} are shown in Figs. 3 and 4 respectively and are discussed later.

We emphasize that no empirical adjustments have been made to the theory to fit the experimental results in Fig. 2. In many similar studies, the range parameter for collisional energy transfer, α , is often used as a fitting parameter, whereas here it was predicted. Low-pressure-limit kinetics can vary nearly linearly with this parameter, and so theoretical studies in which α is adjusted to fit experiment can be of limited value in confirming either the theory or experiment.

Fig. 2. Comparison of experiment and theory for dissociation of 2-methyl allyl ($2MA = CH_3 + \text{allene}$).

Fig. 3. Arrhenius plot of k_1 ($2MA + 2MA = 25DM15HD$). The theoretical rate coefficients have been increased by a factor of 1.5 to improve agreement with the experimental results. This adjustment is reasonable within uncertainties in the calculated capture rate and equilibrium constant due to the treatment of the internal rotors in 25DM15HD.

Fig. 4. Arrhenius plot of k_1 ($25DM15HD = 2MA + 2MA$) for experiments with 25DM15HD. k_1 was calculated from k_1 and $K_{eq,1}$.

4.2 3-Methylbut-3-enyl nitrite

Forty two experiments were performed with mixtures of 0.5, 1 and 2% (C_5H_9ONO) dilute in

krypton over 724 - 1061 K and nominal P_2 of 61, 140 and 260 Torr (see S4 supplementary material). To the best of our knowledge there is no literature on the dissociation of C_5H_9ONO at elevated temperatures. However, this work shows C_5H_9ONO is a clean source of 2MA radicals. The strengths of the O-NO and C-ONO bonds in C_5H_9ONO , by far the weakest bonds, were calculated (CBS-QB3) at 0 K as 42.3 and 60.6 kcal/mol, respectively. Consequently, at the relatively low temperatures of this study cleavage of the C-O bond will not be competitive with scission of the O-NO bond. Breaking the O-NO bond creates the 3-methylbut-3-enyloxy radical that readily eliminates formaldehyde leaving 2MA ($\Delta H_{r,298K} = -0.35$ kcal/mol). For $T > 700$ K the rate coefficient for decomposition of the 3-methylbut-3-enyloxy radical is estimated to be larger than 10^5 s⁻¹. Consequently, the formation of 2MA by dissociation of C_5H_9ONO is treated as a single step in reaction 2. By analogy with dissociation of methyl nitrite [34] a potential alternate route for dissociation of C_5H_9ONO is elimination of HNO either via a five membered transition state or by a roaming transition state. [34] to form 3-methylbut-3-enal. Determination of energetic and kinetic parameters for these processes is a complex theoretical problem, c.f. [34], beyond the scope of this work. However, both roaming and cyclic transition states lead to HNO and the aldehyde and $\Delta H_{r,298K}$ is just 11.0 kcal/mol. Thus $\Delta H_r - C_p T \Delta N$ becomes approximately zero., Eqn. 1. Consequently, even a large flux through the possible HNO elimination channels will generate only a small density gradient. However, flux through these channels will reduce the observed density gradient by reducing the contribution from the strongly endothermic O-NO bond scission channel. Furthermore, at the reaction conditions and short times (<10 μ s) of these experiments the aldehyde can be considered stable and for $T < 900$ K dissociation of HNO is negligible. Thus although a small amount of dissociation of C_5H_9ONO by HNO elimination cannot be entirely eliminated, simulations show that this channel consumes <10% of C_5H_9ONO and that the LS profiles are only sensitive to cleavage of the O-NO bond and recombination of 2MA radicals.

Fig. 5. Arrhenius plot of k_2 ($\text{C}_5\text{H}_9\text{ONO} = 2\text{MA} + \text{H}_2\text{CO} + \text{NO}$).

The experimental data are simulated very well, Figs. 1c and d, by just recombination of 2MA (reaction 1) and dissociation of $\text{C}_5\text{H}_9\text{ONO}$ (reaction 2). At the temperatures of this study 2MA is essentially stable in the 10 μs observation time, in contrast to the 25DM15HD experiments. Initial estimates for k_1 were taken from the 25DM15HD experiments, and those for k_2 by equating the activation energy with the bond dissociation energy. Both rate coefficients were iteratively adjusted to obtain the best fit and the sensitivities to k_1 and k_2 are shown in Figs. 1c and d respectively. The k_2 are shown in Fig. 5. There is little pressure dependence and these data are well represented by $k_2 = 7.31 \times 10^{158} T^{-43.95} \exp(-49108/T) \text{ s}^{-1}$ for $T < 1060 \text{ K}$ which was obtained by a least squares fit (Fig. 5).

Fig. 6. Plot of k_1 from 25DM15HD and $\text{C}_5\text{H}_9\text{ONO}$.

The density gradient plots for $\text{C}_5\text{H}_9\text{ONO}$ show no indication of reaching equilibrium unlike those

from 25DM15HD. Rather, 2MA is simply consumed by reaction 1. The k_1 are plotted in Fig. 3 along with those from 25DM15HD and theoretical prediction. The experimental data show no apparent pressure dependence but are in falloff at higher temperatures. The *a priori* theory is in very close agreement with the experimental results, and agreement can be further improved by increasing the calculated high pressure limit by 1.5 times. This adjustment may be justified by the uncertainties inherent in the present approximate treatment of coupled torsions in 25DM15HD and is well within the expected overall accuracy of the present calculation. The HPL is $\sim$ a factor of 3 greater than the 295 K value of Bayraceken *et al.* [10].

The same information shown in Fig. 3 is plotted for the reverse reaction in Fig. 4, to show the small pressure dependence at higher temperatures and the complete dataset in Fig. 6. The excellent agreement of the *a priori* theory with the experimental results over such a broad temperature range is encouraging. Also shown in Fig. 6 are the results of Roth *et al.* [9] which are about a factor of two lower than the current work.

5. CONCLUSIONS

The recombination of 2-methylallyl radicals has been determined by two sets of experiments that together span a temperature range, 700-1300K, of interest to ignition. The radical is very stable and its chemistry is well-described by only recombination at low temperatures. At higher temperatures, $T > \sim 1100$ K, recombination dominates, although dissociation of 2MA is also significant and addition of CH_3 radicals to 2MA also becomes important. High level theoretical calculations for the dissociation of 2MA are in excellent agreement with the experimental values, and there is very good agreement with the experimental and theoretical recombination rate coefficients. The HPL recombination rate coefficients have been compared with the HPL results for allyl recombination from Georgievski *et al.* [19] and the current results are larger by 25 - 40% for $T < 900$ K. For modelling purposes with $T < 800$ K the current theoretical HPL expression for recombination of 2MA, Table 1, is recommended. At higher

temperatures pressure dependent falloff in both k_1 and k_3 begin to be important and recommended PLOG expressions from the master equation analysis are given in S2.

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Figure Captions:

Fig. 1. Semi-log absolute density gradient plots for 25DM15HD/Kr and C₅H₉ONO/Kr. Insets: Raw LS signals. In (a) t_0 is shown by the vertical line in the inset. Lines are simulations based on the mechanism in Table S2. Symbols represent experiments: Open circles - positive density gradients; Closed circles - negative density gradients (dp/dx). (a-d) Solid lines, final model. (a) and (c) Dash $k_1 \times 1.5$; dash-dot $k_1/1.5$; (b) Dash $k_3 \times 1.5$; dash-dot $k_3/1.5$; (d) dash $k_2 \times 1.5$, dash-dot $k_2/1.5$.

Fig. 2. Comparison of experiment and theory for dissociation of 2-methyl allyl (2MA = CH₃ + allene).

Fig. 3. Arrhenius plot of k_1 (2MA + 2MA = 25DM15HD). The theoretical rate coefficients have been increased by a factor of 1.5 to improve agreement with the experimental results. This adjustment is reasonable within uncertainties in the calculated capture rate and equilibrium constant due to the treatment of the internal rotors in 25DM15HD.

Fig. 4. Arrhenius plot of k_{-1} (25DM15HD = 2MA + 2MA) for experiments with 25DM15HD. k_{-1} was calculated from k_1 and $K_{eq,1}$.

Fig. 5. Arrhenius plot of k_2 (C₅H₉ONO = 2MA + H₂CO+NO).

Fig. 6. Plot of k_{-1} from 25DM15HD and C₅H₉ONO.

Supporting Information

S1: Synthesis of $\text{C}_5\text{H}_9\text{ONO}$.

S2: Complete reaction mechanism, PLOGs and table of molecular structures.

S3: Experimental data from 25DM15HD.

S4: Experimental data from $\text{C}_5\text{H}_9\text{ONO}$.