



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.

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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].

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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.

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 ($d\rho/dx$) in the shock tube [14], which are related to the chemical reactions occurring through Eq. 1 [14]. Simulation of the density gradients yields rates of reactions and mechanistic details.

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

(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 h. 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 $\sim 30\%$ 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 $R_{CC} > 3 \text{ \AA}$ and quite large

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