Deuterium Isotope Effect in Vinyl Radical Combination/Disproportionation Reactions

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The deuterium isotope effect for the vinyl radical combination and disproportionation reactions have been investigated. Protonated or deuterated vinyl and methyl radicals are produced from the 193 nm photolysis of protonated or perdeuterated methyl vinyl ketone. On the basis of product yield measurements, no isotope effect for the combination reactions of either vinyl-vinyl or vinyl-methyl has been observed. From the relative yields of ethylene, an isotope effect of $k_{\rm H}/k_{\rm D} = 1.20$ is determined for the vinyl-vinyl disproportionation reaction.

Introduction

Combination/disproportionation reactions of small hydrocarbon free radicals have been the subject of many studies for many decades. However, in the modern world of direct measurement of kinetic parameters, these reactions have proven to be difficult to study as evidenced by the date of the most recent complete review, which appeared in 1973.¹

The reaction processes of interest are kinetically second order and require an absolute measurement of the initial radical concentrations for a rate constant determination. Common experimental techniques that are used in kinetics such as laserinduced fluorescence are not applicable since fluorescence from small hydrocarbon radicals has not been observed and the strong electronic absorptions of the radicals are frequently in the vacuum ultraviolet, a spectral region which may not overlap with common lasers. However, rate constants for second-order reactions may be obtained through vacuum ultraviolet absorption spectroscopy in conjunction with an appropriate analytical technique such as optical actinometry, mass spectroscopy, or gas chromatography for concentration determinations of reactant species. Product analysis, in addition, provides information on branching ratios: information that is usually difficult to obtain with time-resolved spectroscopic techniques. The approach of real-time absorption spectroscopy with gas chromatographic product analysis has been successfully applied to several hydrocarbon systems, most recently the combination and disproportionation reactions of unsaturated vinyl radicals, C₂H₃.²

The combination and disproportionation reactions of vinyl radicals are remarkably rapid, with rate constants reported to be 1.0×10^{-10} cm³ molecule⁻¹ s⁻¹ and 0.3×10^{-10} cm³ molecule⁻¹ s⁻¹, respectively.² The fast combination reaction has been attributed to the presence of an energetically accessible triplet state of the combination product, 1,3-butadiene.^{2b} The accessible state provides a reaction channel that will allow the combination reaction to proceed at a rate faster than the canonical one out of four effective collisions for doublet species. The disproportionation/combination ratio, $k_d/k_c = 0.3$, indicates that the disproportionation reaction of vinyl itself is about 5-6times faster than might be expected for similar reactions of saturated radicals, e.g., C₂H₅. In an effort to better understand the mechanism of the vinyl-vinyl reactions, we have undertaken a study of the effect of deuteration on both the combination and disproportionation reactions. Similar studies have been reported previously for gas-phase ethyl radical reactions^{4a} and tert-butyl radicals in solution.4b

Experimental Section

The procedures used in these experiments have been described thoroughly in previous publications from this laboratory³ and will be mentioned only very briefly here. The photolysis of the radical precursor, methyl vinyl ketone, in a Suprasil¹¹ cell was performed by an excimer laser whose output at 193 nm was perpendicular to the long axis of the photolysis cell. As shown in Tables 1 and 2, the photolysis sample consisted of a small amount of radical precursor in the presence of a large amount of inert He quencher. Gas chromatographic analysis of the reaction products was performed in the manner previously described.³ A nonreactive and nonabsorbing⁵ tracer gas, cyclopropane, was added to the gas mixtures to provide a calibrant of sample size. In this way each product, relative to the tracer, could be determined by a simple technique that provided more accurate absolute product yields.

Deuterated methyl vinyl ketone was obtained from Cambridge Isotope Laboratories, Inc.¹¹ The chemical purity of the material was determined by the manufacturer to be 98%, and the isotopic purity was 97%.

Results and Discussion

The photolysis of protonated methyl vinyl ketone at 193 nm has been investigated previously,³ where the quantum yields of the primary dissociation processes and the subsequent reaction chemistry of the photofragments have been described. Therefore, several of the conclusions of that work will be described only briefly here. In the earlier work it was determined by utilizing a combination of direct time-resolved optical detection of reaction products, product analysis by gas chromatography, and modeling of the system that the quantum yields of vinyl and methyl radical formation were nearly equivalent and close to unity. The CH₃COC₂H₃ photolysis system could be described simply by consideration of the reactions of the primary photolytic products, CH₃ and C₂H₃, and H atoms formed from the secondary dissociation of excited vinyl radicals. On the time scale of the earlier experiments, as well as those described here, there was no evidence of the presence of a stabilized intermediate CO-containing radical.

We do not observe any significant differences between the photolytic processes of protonated and perdeuterated methyl

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 TABLE 1: Comparison of the Products from the 193 nm

 Photolysis of Protonated Methyl Vinyl Ketone

	C_2H_2/C_2H_6	C_2H_4/C_2H_6	$C_{3}H_{6}/C_{2}H_{6}$	C_4H_6/C_2H_6
$P_{\rm MVK} = 30 \rm Pa$	1.59	0.53	1.36	0.58
$P_{\rm He} = 1.3 \rm kPa$	1.58	0.53	1.32	0.43
	1.69	0.52	1.35	0.60
	1.56	0.55	1.38	0.63
$P_{\rm MVK} = 300 \rm Pa$	1.24	0.46	1.16	nd
$P_{\rm He} = 100 \rm kPa$	1.25	0.46	1.46	nd
	1.22	0.48	1.22	0.55
$P_{\rm MVK} = 190 \rm Pa$	1.16	0.45	1.42	0.41
$P_{\rm He} = 105 \rm kPa$	1.14	0.45	1.42	0.45
	1.16	0.47	nd	0.47
average	1.36 ± 0.22^a	0.49 ± 0.04^a	1.34 ± 0.10^a	$0.52\pm0.10^{\circ}$

^a Measurement uncertainty, 1*o*.

TABLE 2: Comparison of the Products of 193 nmPhotolysis of Deuterated Methyl Vinyl Ketone

	C_2D_2/C_2D_6	C_2D_4/C_2D_6	C_3D_6/C_2D_6	C ₄ D ₆ /C ₂ D ₆
$P_{\rm MVK} = 33 \rm Pa$	1.17	0.36	1.40	0.44
$P_{\rm He} = 6.6 \rm kPa$	1.17	0.35	1.33	0.47
	0.98	0.40	1.34	0.52
	0.97	0.41	1.32	0.56
$P_{\rm MVK} = 150 \rm Pa$	0.97	0.41	nd	0.44
$P_{\rm He} = 93 \rm kPa$	0.96	0.41	nd	0.53
	0.97	0.44	1.34	0.69
	0.90	0.45	1.34	nd
	0.88	0.45	1.38	0.66
	0.89	0.46	1.34	0.44
average	0.98 ± 0.10^{a}	0.41 ± 0.04^{a}	1.35 ± 0.03^{a}	$0.53 \pm 0.09^{\circ}$

^a Measurement uncertainty, 1σ .

vinyl ketone, as is seen by comparison of the product yields shown in Tables 1 and 2. As noted above, the 193 nm photolysis produces equal quantities of vinyl and methyl radicals, both with quantum yields of about one.³ The photolytically produced vinyl radicals react through both combination and disproportionation to produce 1,3-butadiene, acetylene, and ethylene. Vinyl and methyl radicals react through a crosscombination process to yield propylene (C₃H₆). Rate constants, at room temperature, for the cross-combination reactions of vinyl have been previously reported³ to be 1.5×10^{-10} cm³ molecule⁻¹ s⁻¹. Methyl radicals also react through selfcombination to yield ethane, viz.,

$$CH_3COC_2H_3 \rightarrow CH_3 + CO + C_2H_3$$
 (1)

$$C_2H_3 + C_2H_3 \rightarrow C_4H_6$$
 (1,3-butadiene) (2a)

$$- C_2 H_2 + C_2 H_4 \tag{2b}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{3}$$

$$C_2H_3 + CH_3 \rightarrow C_3H_6 \tag{4}$$

It has been shown previously that the combination rate constant for methyl radicals, at room temperature, is unaffected by isotopic substitution.⁶ For the present comparative studies we have used the methyl-methyl combination process as a reference reaction and the yields of all the products are compared with yields of ethane in both the protonated and deuterated systems.

The comparisons of the relative yields of products for the 193 nm photolysis of protonated and deuterated methyl vinyl ketone are presented in Tables 1 and 2. No measurable pressure dependencies of the product yields beyond the experimental uncertainties are observed. A slightly larger value for the $C_2H_4/$

C₂H₆ ratio, at lower pressure, is not statistically significant, as the difference nearly compares with the uncertainty of these measurements. In addition, a similar increase has not been observed for C₂D₄/C₂D₆ at low pressure. The absence of a pressure effect indicated the reactive radical species were thermally equilibrated. Analysis of these results suggests there is no isotope effect in the combination reactions of either vinylvinyl, as derived from the ratio of C₄H₆/C₂H₆ vs C₄D₆/C₂D₆, or vinyl-methyl combination (C₃H₆/C₂H₆ vs C₃D₆/C₂D₆) reactions. This is in agreement with earlier direct observations of no isotope effect in the combination process for methyl radicals.⁶

The effect of isotopic substitution on the disproportionation process may be approximated from the relative yields of ethylene.

$$k_{\rm H}/k_{\rm D} = [(C_2H_4/C_2H_6)/(C_2D_4/C_2D_6)] = 1.20 \pm 0.15$$

or from the relative yields of acetylene,

 $k_{\rm H}/k_{\rm D} = [(C_2H_2/C_2H_6)/(C_2D_2/C_2D_6)] = 1.39 \pm 0.26$

The above relationships are strictly valid for pseudo-firstorder kinetics. However, the error introduced, when the radical-radical reaction rate constants are rather similar, is small compared with the measurement errors.¹²

The indicated uncertainties include only the random errors in the experimental determinations of the product yields and are evaluated from the propagation of errors.

The primary source of ethylene, in both the protonated and perdeuterated systems, is the self-disproportionation of vinyl radicals, a process which will produce an identical amount of acetylene (2b). Results shown in Tables 1 and 2, however, show the yield of acetylene is greater than that of ethylene, as had been observed previously.³ But, acetylene is not an adequate measure of the disproportionation channel since its mode of formation involves more than the single pathway³ of reaction (2b). In addition to direct photolysis, formation routes include the vinyl-methyl disproportionation as well as dissociation of photolytically produced excited vinyl radicals.³ Therefore, the isotope effect for vinyl radical disproportionation is best shown by the ratio of the yields for ethylene, that is $k_{\rm H}/k_{\rm D} = 1.20$. This value agrees well with previous determinations of the deuterium isotope effect, at room temperature and in the gas phase, for ethyl radicals (1.4)^{4a} as well as cyclopentyl and cyclohexyl radicals (1.24).7

The combination reaction of vinyl radicals to form 1,3butadiene and that of methyl radicals to form ethane are not expected to be sensitive to isotopic modifications since the C-H(D) bonds in the respective radicals are but spectators and secondary to C-C bond formation.

In contrast with the combination processes, a primary isotope effect might be expected to be observed in the several disproportionation reactions between the radical species where the C-H(D) bond is actively involved in the reaction coordinate. The disproportionation reaction of C_2H_3 radicals to yield C_2H_2 and C_2H_4 is highly exothermic (299 kJ/mol⁸) and is not expected to have a significant reaction barrier. The isotope effect, therefore, will not simply reflect the differences in zero-point energy of a C-H vs a C-D bond and hence the energy required for simple bond-breaking as in an abstraction reaction. The alternative process,

$$C_2H_3 + C_2H_3 \rightarrow (^1A_1)H_2C = C + C_2H_4$$
 (5)

is less exothermic than reaction 2b by 192.5 kJ/mol and is unlikely to be a significant contributor to the vinyl radical loss mechanism. Theoretical background for interpretation of a weak primary isotope effect for highly exothermic processes has been described earlier.^{7,9,10} The theoretical constructs are frequently limited to consideration of both the reduced mass and active vibrational normal modes of the transition state, which, in the case of highly exothermic disproportionation processes, is considered to be "loose and reactant-like". However, the attribution of the primary kinetic isotope effect to the ratio of imaginary vibrational frequencies in the transition state may not describe the kinetic effect completely.⁹ An obvious omission is the effect of tunnelling, but here the effect of the barrier width needs elucidation. The active C-H(D) bond in the disproportionation reaction is quite weak, on the order of 145 kJ/mol,⁸ and the relatively small isotope effect observed is not unexpected.¹⁰

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(11) Certain commercial instruments and materials are identified in this paper to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the instrumentation or materials identified are necessarily the best available for this purpose.

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