Absolute Rates of the Solution-Phase Addition of Atomic Hydrogen to a Vinyl Ether and a Vinyl Ester: Effect of Oxygen Substitution on Hydrogen Atom Reactivity with Olefins

D. D. Tanner,*,† P. Kandanarachchi,†,‡ N. C. Das,§ and J. A. Franz*,‡

Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2 Canada, and Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99352

Received: August 27, 2002; In Final Form: February 12, 2003

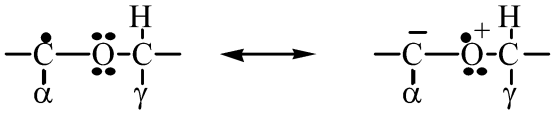
The reactions of vinyl butyl ether and vinyl butyrate with atomic hydrogen and deuterium lead to addition at the terminal position of the olefins. This observation is consistent with the reactions carried out earlier with other olefins. Both of the absolute rates of addition to vinylbutyl ether and vinyl butyrate, in acetone and hexane, were measured at several temperatures. The relative rates are consistent with only modest stabilization of the transition state of the radical adduct by the α-O substituent compared with that of hydrogen atom addition to 1-octene. The relative rates measured in acetone and hexane indicate no significant differential solvation of the ground state relative to the transition structures of the hydrogen atom addition. The kinetics reveal that the early transition states for hydrogen atom addition exhibit little selectivity (vinyl ether versus simple olefin) in either the abstraction of hydrogen α to the oxygen or by terminal addition to the olefinic ether and reflects the modest influence of the increased enthalpy of reaction associated with resonance stabilization by the oxygen substituent at the developing radical site.

Introduction

Recently, we reported a method for obtaining the absolute rate constants for the liquid-phase reaction of the addition of atomic hydrogen to an olefin.[1b] The reaction of 1-octene was reported to be very close to diffusion-controlled $k_a^{25°C} = 4.6 \times 10^9$ M^{-1} s^{-1}. The same kinetic method can be used to evaluate the stabilizing effect of a radical having a geminal oxygen substituent. The addition of hydrogen to a terminal olefin was found to be regioselective, giving addition to form only the most stable secondary or tertiary radical.[1a] It remained to be established that addition to the vinyl ether or ester also underwent regioselective addition to give a radical center on carbon containing a geminal oxygen substituent. The effect of a substituent on the enthalpy of addition should also be established.

The addition of hydrogen atoms to olefins has been extensively studied in the gas phase. Activation barriers for the addition to olefins range from 1 to 3 kcal/mol, and Arrhenius *A* factors are typically $10^{10}-10^{11}$.[2] The enthalpy of the addition of atomic hydrogen also correlates with the rate constants for addition.[3] The large rate constants, $k_a^{25°C} = 4.6 \times 10^9$ $M^{-1}s^{-1}$, reported for the solution-phase addition reactions are supported by the observation that the activation parameters ($E_a = 5.3 \pm 2.9$ kcal/mol and log $A = 14 \pm 3.5$ M^{-1} s^{-1}) are consistent with the values expected for this fast reaction. The values reported for the solution-phase reactions are within the experimental error of those reported for the vapor-phase reactions.[2] The gas-phase addition rate constants for hydrogen to olefins vary from 5×10^8 M^{-1} s^{-1} for addition to ethylene ($\Delta H_{add} = -36$ kcal/mol) to 5×10^9 $M^{-1}s^{-1}$ for addition to butadiene ($\Delta H_{add} = -44$ kcal/mol), or (very roughly) log $k_{add,H} \approx 4.5-0.12$ ΔH_{add}. For a case of intermediate exothermicity, the addition of a hydrogen atom to methyl vinyl ether ($\Delta H_{add} = -40$ kcal/mol) would be expected to exhibit a gas-phase rate constant of ca. 2×10^9 M^{-1} s^{-1}, only about a factor of 4 faster than that of ethylene or propylene. Clearly, the very high exothermicity of hydrogen addition to olefins will result in a very narrow range of addition rate constants. The thermochemistry of the addition of hydrogen atoms to olefins relevant to this work can be roughly calculated.[4−6] Past work on hydrogen atom addition to olefins shows that addition exhibits little sensitivity to adduct radical structure.

However, little work has been carried out to determine the absolute rates of reaction of the hydrogen atom in solution. The reactivity of atomic hydrogen with an olefin, which leads to a carbon-centered radical α to an oxygen substituent, will be enhanced if the transition state for addition develops a higher dipole moment than the starting material. The resonance stabilization of the product radical has been suggested to involve a polar structure.[7]

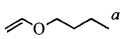
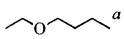
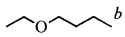
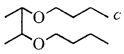


The importance of this resonance form has been substantiated by the observation that the EPR spectrum of the radical shows a γ-hydrogen hyperfine coupling constant larger than that of the α hydrogen.[8] Although such an argument may be suggestive of the polar characteristics of oxygen-substituted radicals, it does not address the question of whether the transition structure is more polar than the ground-state olefin and hydrogen atom. Indeed, theoretical calculations suggest that hydrogen atom addition to an olefin increases the dipole moment from the starting olefin to the transition state only slightly, with most of the polarization of the product radical developing after the transition state has been transited. For example, vinyl alcohol is predicted to exhibit a dipole moment of 1.2 D compared to 1.3 D for the TS of H atom addition and 1.8 D for the product

* Corresponding authors. E-mail: dennis.tanner@ualberta.ca.
† University of Alberta.
‡ Pacific Northwest National Laboratory.
§ Postdoctoral Fellow, University of Alberta, 1996.

10.1021/jp021963i CCC: $25.00 © 2003 American Chemical Society
Published on Web 04/08/2003

TABLE 1: Product Distribution from the Reaction of Atomic Hydrogen with Vinyl Butyl Ether in Acetone at −72 °C

[olefin] (mol L^{-1})	time (min)	reaction (%)	 [a] (A)	 [a] mol x 10^5 (B)	 [b] (B)	 [c] (C)
2.0	5.0	10.6	16.0	16.0	16.4	28.7
1.0	4.0	18.5	15.8	15.8	18.0	28.3
0.50	2.0	17.8	7.50	7.50	2.60	13.5
0.20	1.0	12.7	2.18	2.18	0.62	3.90

[a] Proportionation was calculated using atomic deuterium product distributions; see Table 2. [b] Product from 1,2-hydrogen addition. [c] Traces of 1,3-dibutane were also observed.

hydroxyethyl radical.[9] It is clear that whereas the radical product is more polar than the olefin the polarity is not developed in the transition state. The qualitative importance of the stability of the radical was demonstrated by Fischer, who placed oxygen, as a substituent, on a scale of substituents that show radical stabilization by resonance.[10] As indicated above, carbon-centered radicals are stabilized by 5−7 kcal/mol by oxygen substitution.

The effect of this type of resonance stabilization predicts that a large solvent effect will stabilize or destabilize the contribution of a charge-separated species. If the transition structure for hydrogen atom addition to a vinyl ether exhibits a higher dipole moment than the ground-state olefin, then the free energy of solvation of the transition state will be greater than that of the starting olefin and hydrogen atom. In the present work, the reactions were carried out in both polar (acetone) and nonpolar (hexane) solvents.

Numerous studies of the reactivity of substrates that upon reaction form carbon-centered radicals α to an oxygen atom have been described as being governed by stereoelectronic control.[11]

To probe the importance of this type of resonance stabilization, the reactivity of an olefin that formed a radical α to oxygen was compared to that of an olefin that adds hydrogen to form a secondary radical. In the present study, the α radicals formed upon the addition of a hydrogen atom in the β position to the oxygen substituent are favored by resonance stabilization over addition α to the oxygen substituent.

In principle, the rate constant for a second substrate (s^2) can be obtained by competition kinetics using a mixture of olefins (s^1 and s^2). However, in the heterogeneous gas−liquid kinetic method employed in this and previous studies, absolute rate constants (k_a) were not found to be independent of the concentration of the olefin.[1] The absolute rate constants for substrates s^1 and s^2 must be determined independently. As shown below, when the relative rate constants were determined using mixtures of substrates at $[s^1]$, $[s^2] \cong 0$, the results converged to the ratio of individually determined absolute rate constants.

The effects of the stability of the radical geminal to oxygen can likewise be investigated by comparing the rate of abstraction of hydrogen from an ether relative to the known rate constant for allylic abstraction. Thus, in this study, we present absolute and relative reactivities and solvent effects in hydrogen addition to olefins and in hydrogen abstraction by atomic hydrogen from allylic hydrocarbons or oxygen-substituted alkanes.

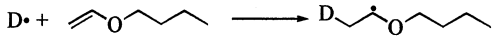
Results and Discussion

Using the procedure reported previously,[1] hydrogen atoms generated in a microwave discharge are passed over a stirred solution of the reactive substrate. The products formed in these highly chemospecific reactions are analyzed, and the solution-phase structure−reactivity relationships for the reactions of atomic hydrogen are obtained.

Regioselective Addition. When atomic hydrogen (0.25−2.5 mmol) is passed over neat vinyl butyl ether (−72 °C), the products of the reaction are ethyl butyl ether (B), *dl*- and *meso*-2,3-dibutoxy butane (C), and traces of 1,3-dibutoxybutane. See Table 1.

Some insight is obtained concerning the mechanism of the formation of these products by carrying out the reduction with deuterium atoms (−78 °C). The distributions of the products from these reactions are listed in Table 2. By comparing the mass spectra and ^{1}H and ^{2}H NMR spectra of the protiated to deuterated products of the reaction mixture, it is obvious that in each of the products, monomers or dimers, at least one deuterium is attached to a terminal position attributable to the original olefin. See Table 2.

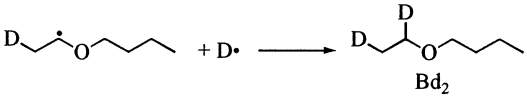
The mass spectra of the products show vinyl butyl ether (A, Ad_1, and Ad_2), ethyl butyl ether (B, Bd_2, and Bd_3), and *dl*- and *meso*-2,3-dibutoxy butane (Cd_2). All of the olefins previously studied underwent regioselective addition of atomic hydrogen to generate the most stable radical.[1a] If one assumes that the vinyl ether likewise undergoes addition to give a secondary radical (eq 1), then the formation of the products listed in Tables 1 and 2 are those formed by this primary reaction.



(1)

The ^{2}H NMR shows absorptions with intensities (I_n) at δ 1.10 (DCH_2−; I_1), 1.17, 1.20 (DCH_2−; I_2 (Cd_2)), 3.49 (−CDH−, I_3), and 4.04, 4.27 (DCH═CH−, I_4). These intensities are proportional to the concentrations of the products; see Table 1. The proportionality constant $\times c4_1$ is obtained from the equation $I_1 + I_2 = ([Bd] + [Bd_2] + 2[Cd_2])/\times c4$, and the unknown product concentrations are obtained from the following relationships: $[Ad] = \times c4 I_4$; $[Bd_2] = \times c4 I_3$; $[Bd] = [B]_{tot} - [Bd_2]$; $[Ad] + [Ad_2] = \times c4 I_4$. The $[Ad]/[Ad_2]$ ratio was estimated from GC/MS spectra by using M^+ and $M^+ + 1$ peaks after making corrections for natural abundances.

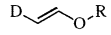
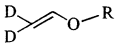
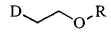
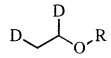
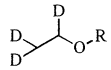
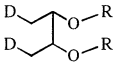
When the secondary radical encounters a deuterium atom, 1,2-dideuterio-2-butoxyethane (Bd_2) is formed (eq 2).[1b]



(2)

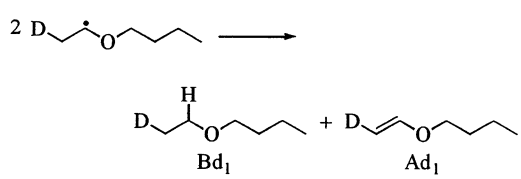
The major saturated or unsaturated products, however, contain only one deuterium atom. The incorporation of protium into

TABLE 2: Product Distribution from the Reaction of Atomic Deuterium with an Acetone Solution of Vinyl Butyl Ether[a]

temp (°C)		-63		-72		-84		-94	
time (min)		2.0	4.0	3.0	4.0	2.0	4.0	3.0	6.0
reaction (%)		11.0	33.2	14.5	18.9	17.0	27.4	13.3	26.5
		products (mol x 10^5)[b]							
	(Ad$_1$)	1.5	3.2	1.9	2.3	2.1	3.8	1.7	2.3
	(Ad$_2$)		0.50	0.30	0.40	0.40	0.60	0.30	0.64
	(Bd$_1$)	1.5	4.1	2.7	3.4	2.5	4.9	2.1	4.2
	(Bd$_2$)	2.4	5.3	2.2	3.1	2.5	4.9	1.9	4.4
	(Bd$_3$)	0.10	0.30	0.40	0.40	0.20	0.40	0.26	0.71
	(Cd$_2$)	2.9	9.1	3.9	4.8	4.6	8.8	3.4	7.1
(ρ_{MDA}/ρ_{MDO})		0.99 ± .04		1.07 ± .02		0.98 ± .04		1.04 ± .11	
(k_d/k_c)[d]		0.49 ± .04		(0.68 ± .001)[e]		0.56 ± .01		0.60 ± .04	

[a] Five milliliters of 0.20 mol L^{-1} solutions in acetone. D_2 flow rate = 6 mL/min. [b] Deuterium distribution was quantitated by ^{2}H NMR and GC/MS. [c] Monodeuterated alkanes (ρ_{MDA}) to monodeuterated olefins (ρ_{MDO}) ratio was corrected for secondary reactions. (ρ_{MDA}/ρ_{MDO} = Bd$_1$/(Ad$_1$ + Ad$_2$ + Bd$_3$)). [d] Disproportionation (k_d) to combination (k_c) ratio (k_d/k_c = (Ad$_1$ + Ad$_2$ + Bd$_1$ + Bd$_3$)/2 × Cd$_2$). [e] A value of 0.54 ± 0.05 was obtained in reactions carried out at several concentrations (1.0−0.20) of the starting material.

the saturated ether can be attributed to disproportionation (eq 3).



(3)

The observation that the ratio of monodeuterated ethyl butyl ether to monodeuterated vinyl butyl ether (ρ_{MDAE}/ρ_{MDOE}) is essentially equal to 1 (1.02 ± 0.05) is consistent with the disproportionation pathway (eq 3).

Hydrogen abstraction α to the vinyl ether can be ruled out since no secondary deutero vinyl ether nor unsaturated dimer could be detected.

Since the products of disproportionation can be identified, the disproportionation-to-combination ratio is easily determined. The value determined for the reaction carried out to low conversion (13−26% reaction) is 0.68 ± 0.001 (−72 °C). When the reaction is carried out at several temperatures, −63, −84, and −94 °C, a plot of ln k_d/k_c vs $1/T$ gives a slope of $E_{a(dis)} - E_{a(comb)}$ that is equal to 0.4 kcal/mol. (See Figure 1.)

The ratio of rate constants k_d/k_c calculated from the plot at 25 °C is 1.01 and is essentially identical to the value (k_d/k_c/H = 1.01, 1.00) reported for the *sec*-butyl radical.[12]

The rate of formation of the total products resulting from the initial addition of a hydrogen atom to a olefin in a given time, $(\Delta P/\Delta t)_{total}$, is proportional to the concentration of the reactants. In the case of a nonhomogeneous reaction, only the first molecules that react obey these kinetics. Under nonhomogeneous conditions, reaction occurs only upon the encounter of the reactants in the volume of the reaction zone (i.e., the true concentration is achieved only when the initial concentration

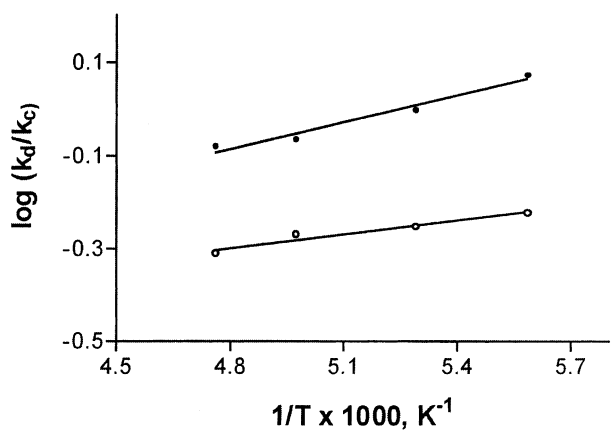


Figure 1. Plot of log(k_d/k_c) at several temperatures for reactions carried out in acetone.

of olefin, [olefin]^0, approaches zero). Under these conditions, an estimate of k_a can be obtained from eq 4.

$$\left(\frac{\Delta P}{\Delta t}\right)_{total} = k_a[\mathrm{H}\bullet][\mathrm{olefin}]^0 \quad (4)$$

Since the relative rates of the formation of combination (C) and disproportionation (D) are diffusion-controlled, the concentration of radicals formed from addition can be calculated from those products if one determines the time dependence of the products formed from their reactions:

$$\left(\frac{\Delta P}{\Delta t}\right)_{c,d} = k_{R\bullet}[\mathrm{R}\bullet]^2 \quad (5)$$

The diffusion rate constant, $k_{R\bullet}$, can be estimated using the Stokes−Einstein equation by assuming slip conditions and

TABLE 3: Absolute Rate Constants ($f^{1/2}k_a$) for the Addition of Deuterium Atoms to Vinyl Butyl Ether at −72 °C in Acetone

[olefin] mol L^{-1}	$10^4(\Delta p/\Delta t)_{tot}^{bulk}$ [a] mol L^{-1} s^{-1}	$10^4(\Delta p/\Delta t)_{c,d}$ mol L^{-1} s^{-1}	$10^7[R^-]$ [b] mol L^{-1}	$10^4(\Delta p/\Delta t)_{RD_2}$ mol L^{-1} s^{-1}	$10^8[H\bullet]$ [c] mol L^{-1}	$10^{-3}f^{1/2}k_a$ [d] M^{-1} s^{-1}
1.12	6.19	5.37	7.84	0.82	11.9	4.09
0.45	7.36	5.60	8.43	1.13	15.2	11.2
0.09	1.90	1.33	3.90	0.34	9.92	30.6
0.045	1.01	0.81	3.05	0.19	6.42	40.8
0.034	0.58	0.19	1.47	0.16	2.69	63.5
0.022	0.52				(2.35)	127

[a] Experimentally measured as the change in the concentration of vinyl butyl ether with time. [b] Calculated by using eq 5. [c] Calculated by using eq 7. [d] Calculated by using eq 9.

TABLE 4: Absolute Rate Constants ($f^{1/2}k_a$) for the Addition of Deuterium Atoms to Vinyl Butyl Ether at −72 °C in Hexane

[olefin] mol L^{-1}	$10^4(\Delta p/\Delta t)_{tot}^{bulk}$ [a] mol L^{-1} s^{-1}	$10^4(\Delta p/\Delta t)_{c,d}$ [a] mol L^{-1} s^{-1}	$10^7[R^-]$ [b] mol L^{-1}	$10^4(\Delta p/\Delta t)_{RD_2}$ [a] mol L^{-1} s^{-1}	$10^8[H\bullet]$ [c] mol L^{-1}	$10^{-3}f^{1/2}k_a$ [d] M^{-1} s^{-1}
1.00	4.90	4.50	6.86	0.40	6.10	8.03
0.50	6.34	5.85	7.82	0.49	6.60	19.2
0.17	4.77	4.33	6.73	0.44	6.80	41.3
0.067	2.40	1.57	4.05	0.16	4.10	87.4
0.033	1.23	0.91	3.09	0.06	2.86	150
0.017	0.66	0.42	2.10	0.04	2.10	185
0.0084	0.36				(1.62)[e]	261

[a] Experimentally measured as the change in the concentration of vinyl butyl ether with time. [b] Calculated by using eq 5. [c] Calculated by using eq 7. [d] Calculated by using eq 9. [e] Calculated from a plot of (H•) vs $(\Delta p/\Delta t)_{tot}^{bulk}$.

applying a spin statistic correction:[1]

$$k_{R\bullet} = \frac{(8RT)10^3}{3\eta}3 \tag{6}$$

The concentration of [R•] can then be calculated from eq 5.

The products from the reaction of hydrogen atoms with the alkyl radicals, also diffusion-controlled, (i.e., the capping reaction (eq 7)), can be determined from the products resulting from 1,2 addition:

$$\left(\frac{\Delta P}{\Delta t}\right)_{RH2} = k_{H\bullet}[R\bullet][H\bullet] \tag{7}$$

Since this radical−radical coupling will also be diffusion-controlled, an estimation of the hydrogen atom concentration can be made. Because the hydrogen atom concentration has now been determined, the addition of hydrogen to a primary olefin can likewise be determined (eq 4) if the time-dependent concentrations of the reactants and the products formed in the reaction zone, $\{(\Delta n/V)/\Delta t)\}^{RZ}$, are known. Since the volume of the reaction zone is only a fraction, f, of the bulk volume, the kinetic expressions that are listed (eqs 4, 5, and 7) are valid only at extremely low concentrations (eq 8).

$$\left(\frac{\Delta n/V}{\Delta t}\right)^{RZ} \simeq \left(\frac{\Delta n/V}{\Delta t}\right)^{bulk} \tag{8}$$

An expression (eq 9) that defines the rate constant for addition, k_a, can be derived by combining eqs 4−7:

$$k_a = f^{-1/2}\left[\frac{(\Delta P/\Delta t)_{total}(k_{diff}(\Delta P/\Delta t)_{c,d})^{1/2}}{[\text{olefin}](\Delta P/\Delta t)_{RH_2}}\right] \tag{9}$$

Absolute Rate of Addition of H• to Vinyl Butyl Ether. The experimental data (Tables 1 and 2) were used to calculate the concentrations of the reactants ([olefin], [R•], [H•]) and the rate constant for each reaction at each concentration of olefin. The apparent rate constants ($f^{1/2}k_a$) of the substrates in their reaction zone are listed in Tables 3 and 4.[13]

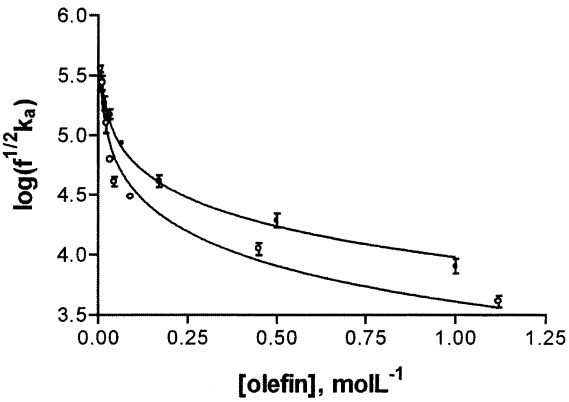


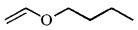
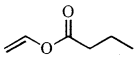
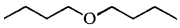
Figure 2. Variation of the apparent rate constant log($f^{1/2}$ k_a) of vinyl butyl ether with the concentration of the olefin in (○) acetone and (●) hexane.

By using the data in Tables 3 and 4, a plot of the calculated values of $f^{1/2}k_a$ versus their olefin concentrations was constructed (Figure 2).

The data were fit to an equation of the form log $f^{1/2}k_a = a[\text{olefin}]^b + c$. The function is monotonic and steeply dependent upon the concentration of the substrate. The radical concentrations and rate constants for the addition reactions are also listed in Tables 3 and 4. Since stabilization of an oxygenated substrate, by resonance, infers that the intermediate radical should exhibit polar charge-separated characteristics, carrying out the reaction in a polar solvent should stabilize the oxygenated intermediate compared to the intermediate formed from addition to the alkene. The rate constants obtained from the extrapolated values in hexane and in acetone are listed in Table 5.

The accuracy of the values of the relative rates determined by dividing the absolute rate constants for the addition of atomic hydrogen to 1-octene and vinyl butyl ether was compared to that of the values obtained by competition kinetics. The values obtained were compared at several concentrations; see Figure 3. To support the suggestion that the intermediates are solvated, the rates of the abstraction of hydrogen from two oxygenated substrates and from a dialkyl ether and the addition to vinyl butyrate were compared in both solvents. As a standard, the

TABLE 5: Absolute Rate Constants for Addition and Abstraction by Atomic Deuterium at −72 °C

substrate	solvent	k_a (M^{-1} s^{-1})[a] x 10^8	k_{abs} (M^{-1} s^{-1})[b] x 10^6
	acetone	13.8 ± 12.8	
	hexane	5.01 ± 2.1	
	acetone	4.79 ± 3.0	
	hexane	3.8 ± 1.25	
	acetone		6.96 ± 2.6
	hexane		10.3 ± 3.5

[a] Measured from the extrapolated values at zero olefin concentrations in Figure 2a and b and Figure 3. [b] Calculated from the relative rate constants in Table 7 and the absolute rate constants of addition to vinylbutyrate.

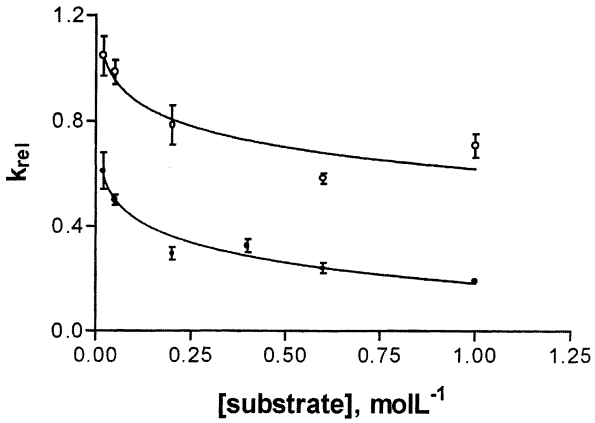


Figure 3. Variation of the relative rate for (○) vinyl butyl ether (k_e/k_o) and (●) vinyl butyrate (k_{es}/k_o) with the concentration of the substrate.

abstraction reaction of the ether was compared to the addition to the vinyl ester. If solvation was important for both of the oxygenated substrates, then it was expected that the relative rates in acetone (both substrates solvated) and hexane (both substrates nonsolvated) would show very little extra stabilization; see Table 7.

As expected, the relative rate ratios in both solvents were, within the experimental accuracy, the same.

The intermediate radical geminal to oxygen could also be formed by α abstraction from a dialkyl ether. The relative rate constant for abstraction was obtained by competition kinetics using as a competitive substrate the addition to the slowest of the olefins studied, vinyl butyrate; see Table 7. Because the absolute rate constant for allylic abstraction had previously been determined[1b] and the absolute rate of addition of atomic hydrogen to 1-octene and now vinyl butyl ether has also been determined, the relative ratios of allylic abstraction could be compared to that for abstraction of the α hydrogen from a dialkyl ether, Table 7. The products from the abstraction of hydrogen were calculated from the reactions of the mixture of the two substrates with atomic deuterium. Under these conditions, only mono-α-d and cross dimeric products resulting from the reactions of the ether (Table 7) could be detected. No correction for disproportionation or addition needed to be made for the α radical formed from the ether.

Stabilization of the radical by a geminal oxygen relative to allylic abstraction was estimated by calculating the difference

TABLE 6: Relative Rates for the Addition of Atomic Deuterium to Vinyl Butyl Ether and Vinyl Butyrate at −72 °C

solvent	[substrate mol L^{-1}][a]	(k_e/k_o)[b]	(k_{es}/k_o)[c]	(k_e/k_{es})[d]	(k_e/k_{es})[e]
acetone	1.00	0.71 ± .05	0.19	3.74 ± .05	0.56 ± .20
acetone	0.60	0.56 ± .01	0.24 ± .02	2.42 ± .03	0.67 ± .20
acetone	0.40		0.33 ± .03		0.81 ± .17
acetone	0.20	0.79 ± .07	0.30 ± .03	2.63 ± .10	1.02 ± .03
acetone	0.05	0.99 ± .05	0.50 ± .02	1.98 ± .07	1.48 ± .04
acetone	0.02	1.05 ± .07	0.61 ± .07	1.72 ± .14	1.99 ± .25
hexane	0.50	1.45 ± .13	0.74 ± .03	1.96 ± .16	1.29 ± .01
hexane	0.20	1.44 ± .27	0.76 ± .03	1.89 ± .30	1.41 ± .07
hexane	0.10	1.46 ± .20	0.79 ± .05	1.85 ± .25	1.51 ± .001
hexane	0.05	1.35 ± .21	0.72 ± .01	1.86 ± .22	1.58 ± .02
hexane	0.02	1.11 ± .16	0.83 ± .06	1.35 ± .22	1.70 ± .12
hexane	0.01	1.30 ± .12			1.74 ± .05

[a] Mixtures (1:1, M/M) of the ether or ester and 1-octene. [b] Relative rate constant of vinyl butyl ether compared to that of 1-octene. [c] Relative rate constant of vinyl butyrate compared to that of 1-octene (M/M). [d] Calculated relative rate constant between vinyl butyl ether and vinyl butyrate using (k_e/k_o) and (k_{es}/k_o). [e] Calculated relative rate constant using $f^{1/2}k_a$ values from Figures 2 and 4.

in activation energy for reactions carried out in acetone and in hexane using the data in Table 7 and the values previously determined for allylic abstraction from 1-octene.[1b]

$$\Delta\Delta E_a = E_a(\text{allyl}) - E_a(\alpha\text{-O}) = -0.76 \pm 0.9 \text{ kcal/mol}$$

$$\Delta \log A = \log A(\text{allyl}) - \log A(\alpha\text{-O}) = 1.8 \pm 2.3$$

$$E_a(\text{allyl}) = 7.64 \pm 2.9$$

$$E_a^{ab}(\alpha\text{-O}) = 8.4 \pm 3.8$$

$$\log A_{ab}(\alpha\text{-O}) = 12.2 \pm 2.3$$

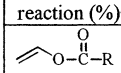
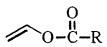
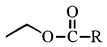
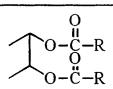
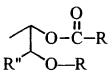
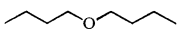
In hexane,

$$\Delta\Delta E_a = E_a(\text{allyl}) - E_a(\alpha\text{-O}) = -1.0 \pm 1.4 \text{ kcal/mol}$$

$$\Delta \log A = \log A(\text{allyl}) - \log A(\alpha\text{-O}) = 2.1 \pm 3.7$$

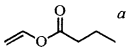
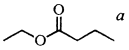
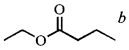
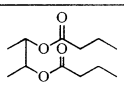
The determined activation parameters allowed the calculation of the rate constants for the abstraction of α hydrogen from an ether; see Table 5. The abstraction rate constant $k_{ab}^{\alpha-O}$ is within experimental error the same as that for allylic abstraction

TABLE 7: Product Distribution from the Reaction of Atomic Deuterium with a Mixture of Vinylbutyrate and *n*-Butyl Ether[a]

solvent		acetone	acetone	hexane	hexane	acetone	hexane
temp (°C)[b]		-72	-72	-72	-72	-94(2)	-94(2)
time (min)		10	15	10	15	15	10
reaction (%)[b]							
		49.0	69.4	70.7	88.8	56.4	61.0
R–O–R		4.7	7.67	7.1	8.7	4.2	5.0
		products (mol L^{-1} x 10^3)[c]					
	d1	13.4	16.0	12.2	6.2	19.7	24.5
	d2	1.6	1.0	0.40	0.80	1.1	1.4
	d1	26.6	33.2	34.2	42.8	24.9	35.9
	d2	15.2	25.0	18.6	30.8	16.2	17.5
	d3	3.9	6.6	3.1	8.6	1.9	0.84
		17.6	24.4	27.4	30.0	22.5	53.1
		3.0	4.3	2.8	4.4	2.6	3.3
	d1	6.4	12.0	10.0	16.8	5.0	8.1
$[(k_{be})^{ab}/(k_{es})^{add}]^d$		0.069 ± .002		0.051 ± .01		0.050 ± .01	0.054 ± .005
$[(k_{be})^{ab}/(k_o)^{add}]^e$		0.017 ± .003		0.040 ± .009		0.014 ± .005	0.041 ± .005
$[(k_{ally}/(k_{\alpha\text{-}o})_{abs}]^f$		0.74 ± 0.23		0.31 ± 0.15		0.43 ± 0.13	0.15 ± 0.08

[a] R = C_4H_9, R″ = C_3H_7. [b] Calculated from the disappearance of starting material. [c] Deuterium distribution of the products was calculated by GC/MS and ^{2}H NMR spectra. [d] Ratio of rate constants for the abstraction of hydrogen from *n*-butyl ether (k_{be}) by atomic deuterium to the rate constant of the addition of atomic deuterium to vinyl butyrate (k_{es}). [e] Calculated rate constant ratio using measured values (k_{be}/k_{es}) and (k_{es}/k_o). [f] Calculated from data in ref 3b, $(k_{all}/k_{\alpha-o})_{23°C}^{acetone(hexane)} = 3.0$ (2.1).

TABLE 8: Product Distribution from the Reaction of Atomic Deuterium with Vinyl Butyrate in Acetone at −72 °C[a]

[vinyl butyrate] mol L^{-1}	time (min)	reaction (%)	 a	 a	 b	 c
			products (mol x 10^4)			
2.0	5.0	11.9	2.54	2.54	0.94	2.95
1.0	3.0	9.18	0.89	0.89	0.73	1.04
0.50	2.0	5.36	0.23	0.23	0.34	0.27
0.10	2.0	14.2	0.11	0.11	0.23	0.13

[a] Products from disproportionation were calculated on the basis of the reactions of atomic deuterium; see Table 9. [b] Product from 1,2 radical addition. [c] Ratio (1:1) of *d,l*- to meso isomers. Traces of a dimer from radical addition to the vinyl ester was also detected.

but is substantially slower (25−50 times) than addition to 1-octene.

A similar study was carried out for the reactions of vinyl butyrate, Tables 8 and 9.

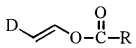
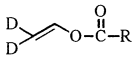
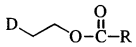
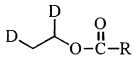
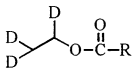
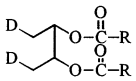
The absolute rates were calculated for reactions carried out in acetone and hexane; see Tables 10 and 11.

The mechanism for addition, disproportionation, and combination is the same as that for all of the other terminal olefins. The absolute rate constant (see Figure 4 and Table 5) is within experimental error the same as was found for the ether. The relative rates for addition, as expected, are measurably slower than those for the ether for reactions carried out in both acetone and hexane; see Table 6. Arrhenius plots for the data constructed from the competing relative rates between the ether or ester and 1-octene, in both solvents, are consistent with the absolute rate constants (i.e. the ether is marginally faster than the olefin, and the ester is slower than the ether and the olefin; see Figure 5).

Experimental Section

Materials. 1-Octene (98%), butyl ether (99+%), chloroheptane (99%), butyl ethyl ether (99%), and ethyl butyrate (99%, Aldrich) were checked for purity by GC and used as received. Butyl vinyl ether (98%) and vinyl butyrate (Eastman) were fractionally distilled before use. Acetone (99.5%) and hexane (99%, Aldrich) were distilled before use.

TABLE 9. Product Distribution of the Reaction of Atomic Deuterium with an Acetone Solution of Vinyl Butyrate[a]

temp (°C)[b]	-63		-72		-84	-94	
time (min)	3.0	5.0	4.0	6.0	3.0	3.0	6.0
reaction (%)	27.3	29.8	31.3	40.8	16.3	10.5	20.8
	Products (mol x 10^5)[b]						
 (Kd)	4.7	5.1	5.4	7.0	3.0	2.4	4.1
 (Kd_2)	0.10	0.20	0.20	0.30			0.30
 (Ld)	5.8	6.7	6.6	9.6	3.9	2.4	4.9
 (Ld_2)	2.8	3.4	3.3	4.7	1.7	1.4	2.8
 (Ld_3)	0.12	0.30	0.20	0.40	0.07	0.10	0.20
 (Md_2)	6.7	7.2	7.5	9.7	3.5	2.0	4.2
$(\rho_{MDA}/\rho_{MDO})^c$	1.00 ± .20		1.19 ± .05		1.27	1.02 ± .06	
$(k_d/k_c)^d$	0.83 ± .02		0.86 ± .03		0.99	1.18 ± .05	

[a] 0.20 mold M^{-3} solutions in acetone. D_2 flow rate 6 mL/min; R = C_3H_7. [b] Deuterium distributions were calculated by ^2H NMR and GC/MS spectra. [c] Monodeuterated alkanes (ρ_{MDA}) to monodeuterated olefins (ρ_{MDO}) ratio, which was corrected for secondary reactions. (ρ_{MDA}/ρ_{MDO} = Ld/(Kd + Kd_2 + Ld_3)). [d] Disproportionation (k_d) to radical combination (k_c) ratio (k_d/k_c = (Kd + Kd_2 + Ld + Ld_3)/2Md_2).

TABLE 10: Absolute Rate Constants ($f^{1/2}k_a$) for the Addition of Deuterium Atoms to Vinyl Butyrate at −72 °C in Acetone

[olefin] mol L^{-1}	$10^4(\Delta p/\Delta t)_{tot}^{bulk}$ [a] mol L^{-1} s^{-1}	$10^4(\Delta p/\Delta t)_{c,d}$ [a] mol L^{-1} s^{-1}	$10^7[R^-]$ [b] mol L^{-1}	$10^4(\Delta p/\Delta t)_{RD_2}$ [a] mol L^{-1} s^{-1}	$10^8[H^\bullet]$ [c] mol L^{-1}	$10^{-3}f^{1/2}k_a$ [d] M^{-1} s^{-1}
1.12	6.58	5.89	8.21	0.69	9.62	6.11
0.22	2.75	2.46	5.31	0.29	6.25	20.0
0.09	0.89	0.81	3.04	0.08	3.56	27.8
0.056	0.92	0.82	3.06	0.10	3.70	44.4
0.033	0.44	0.39	2.11	0.05	2.71	49.2
0.022	0.40	0.33	1.94	0.07	2.67	67.2
0.011	0.18				(2.26)[e]	72.4
0.0056	0.12				(2.14)[e]	100.1

[a] Experimentally measured as the change in the concentration of vinyl butyrate with time. [b] Calculated by using eq 5. [c] Calculated by using eq 7. [d] Calculated by using eq 9. [e] Calculated from a plot of ($H^\bullet$) vs $(\Delta p/\Delta t)_{tot}^{bulk}$.

TABLE 11: Absolute Rate Constants ($f^{1/2}k_a$) for the Addition of Deuterium Atoms to Vinyl Butyrate at −72 °C in Hexane

[olefin] mol L^{-1}	$10^4(\Delta p/\Delta t)_{tot}^{bulk}$ [a] mol L^{-1} s^{-1}	$10^4(\Delta p/\Delta t)_{c,d}$ mol L^{-1} s^{-1}	$10^7[R^-]$ [b] mol L^{-1}	$10^4(\Delta p/\Delta t)_{RD_2}$ mol L^{-1} s^{-1}	$10^8[H^\bullet]$ [c] mol L^{-1}	$10^{-3}f^{1/2}k_a$ [d] M^{-1} s^{-1}
1.00	5.54	4.98	7.22	0.56	8.11	6.84
0.50	4.68	4.20	6.63	0.48	7.57	12.32
0.17	3.91	3.37	5.94	0.42	7.39	30.96
0.067	2.40	1.97	4.54	0.29	6.68	52.78
0.033	1.17	0.92	3.10	0.12	4.05	88.09
0.017	0.52				(2.26)[e]	109.3
0.0084	0.21				(1.00)[e]	150.0

[a] Experimentally measured as the change in the concentration of vinyl butyrate with time. [b] Calculated by using eq 5. [c] Calculated by using eq 7. [d] Calculated by using eq 9. [e] Calculated from a plot of ($H^\bullet$) vs $(\Delta p/\Delta t)_{tot}^{bulk}$.

Identification and Characterization of the Reaction Products. The products from the reactions of hydrogen atoms were identified by comparing their GC retention times and GC/IR and GC/MS spectra with those of authentic samples. The dimeric products were isolated from the reaction mixture by reduced-pressure distillation, and the dimers were separated by preparative gas chromatography. The products from the reactions of deuterium atoms were identified by their GC/MS spectra and ^2H NMR spectroscopy.

The ^1H, ^2H, and ^{13}C NMR spectra were obtained using either a Bruker AM-400 (400 MHz) or a Bruker AM-300 (300 MHz) NMR spectrometer. The ^1H NMR spectra are referenced to TMS as an internal standard at 0.00 ppm unless otherwise noted. The ^{13}C spectra were studied by APT (attached proton test) to determine the number of protons attached to each carbon. GC/IR spectra were obtained using an HP 5965A IRD GC/FTIR interfaced to an HP 5890 gas chromatograph fitted with a DB-5 (30 m × 0.25 mm) glass capillary column. GC/MS data were

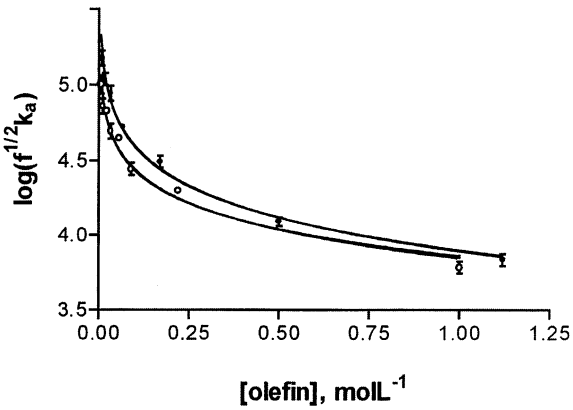


Figure 4. Variation of the apparent rate constant $\log(f^{1/2}\ k_a)$ with the concentration of vinyl butyrate in (○) acetone and (●) hexane at −72 °C.

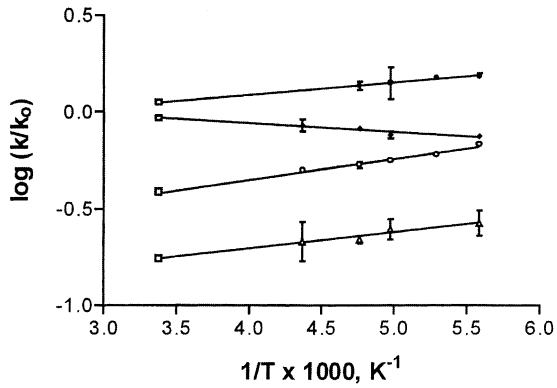


Figure 5. Arrhenius plot for the relative rate of vinyl butyl ether in (○) acetone and (●) hexane and for vinyl butyrate in (◆) hexane and (□) acetone. (△) Extrapolated values at 23 °C.

obtained by using a VG-70E EI+ spectrometer fitted with a Varian Vista 6000 gas chromatograph having a glass capillary column (DB-5 30 m × 0.25 mm, J & W Scientific).

***dl* and *meso*-2,3-Dibutoxybutane.** These were separated from the product mixture resulting from the addition of atomic hydrogen to *n*-butyl vinyl ether by column chromatography (silica gel column, eluted with 10% methylene chloride in hexane). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 0.90 (t, 6H), 1.00 (d, 3H), 1.10 (d, 3H), 1.40 (m, 4H), 1.5 (m, 4H), 3.00 (t, 4H), 3.50 (m, 2H). ^{13}C NMR (300 MHz, CD_3COCD_3): δ 14.1, 14.5, 16.3, 29.5, 33.1, 69.4, 77.7, 79.2. The APT spectrum was consistent with the above structure. IR (vapor phase) ν: 2942, 2882, 1466, 1381, 1114 cm^{-1}. Anal. Calcd for $C_{12}H_{26}O_2$: C, 71.29; H, 12.90. Found: C, 71.01; H, 13.07; m/z^+ 202.

2-Butoxy-3-methyl-nonane. This compound was separated from the product mixture resulting from the addition of atomic hydrogen to a mixture of 1-octene and *n*-butyl vinyl ether by preparative GC on a packed column (15% Apiezon on 60/80 chromosorb W: 10 ft × 0.25 in). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 0.88 (m, 6H), 1.00 (d, 3H), 1.10 (d, 3H), 1.30 (m, 14H), 2.80 (m, 1H), 3.20 (m, 2H), 3.50 (m, 1H). ^{13}C NMR (300 MHz, CD_3COCD_3): δ 14.2, 15.4, 15.6, 16.5, 20.1, 23.3, 28.0, 30.4, 32.6, 38.9, 33.2, 33.7, 68.8, 79.2, 79.4. The APT spectrum was consistent with the above structure. IR (vapor phase) ν: 2937, 2877, 1464, 1381, 1106 cm^{-1}. Anal. Calcd for $C_{14}H_{30}O$: C, 78.50; H, 14.02. Found: C, 78.30; H, 13.60; m/z^+ 214.

***dl* and *meso*-2,3-Dibutenoxybutane.** These were separated from the product mixture resulting from the addition of atomic hydrogen to vinylbutyrate by column chromatography on silica gel. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 0.90 (t, 6H), 1.20 (t, 6H), 1.60 (m, 4H), 2.40 (m, 4H), 4.95 (m, 2H). ^{13}C NMR (300 MHz, CD_3COCD_3): δ 13.8, 15.2, 16.2, 19.0, 36.6, 71.5, 71.6, 172.8. The APT spectrum was consistent with the above structure. IR (vapor phase) ν: 2981, 2889, 1753, 1458, 1379, 1253, 1174, 1095 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.62; H, 9.56. Found: C, 62.60; H, 9.71; m/z^+ 230.

2-Butenoxy-3-methyl-nonane. This compound was separated from the reaction mixture by preparative GC on a packed column (15% Apiezon L on 60/80 chromosorb W: 10 ft × 0.25 in). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 0.90 (m, 6H), 1.10 (m, 6H), 1.30 (m, 8H), 1.60 (m, 4H), 2.30 (t, 2H), 2.80 (m, 1H), 4.80 (m, 1H). ^{13}C NMR (300 MHz, CD_3COCD_3): δ 13.8, 14.3, 15.0, 16.3, 17.3, 19.2, 23.2, 27.7, 30.6, 33.3, 38.3, 73.7, 74.1, 175.0. The APT spectrum was consistent with the above structure. IR (vapor phase) ν: 2938, 1749, 1462, 1377, 1255, 1184, 1096, 947 cm^{-1}. Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.68; H, 12.28. Found: C, 73.45; H, 12.15; m/z^+ 228.

Reactions with Hydrogen (Deuterium) Atoms. The apparatus for the microwave discharge was as described previously.[1a] A solution of the substrate (10 mL, 1 M) in acetone or hexane with an added standard (1-chloroheptane) was placed in the "U"-shaped reactor, and hydrogen or deuterium atoms generated by the H_2/He or D_2/He plasma (H_2/D_2 flow rate 5 mL/min, pressure 3−4 Torr) were swept over the stirred solution from −42 to −94 °C for 10−60 min. The reaction mixtures were analyzed by GC, GC/MS, GC/IR, and ^{2}H and ^{13}C NMR spectroscopy.

Determination of Absolute Rates. Solutions of substrates (vinyl butyl ether or vinyl butyrate) and the internal standard (1-chloroheptane) were subjected to D_2/He or H_2/He plasma as described above, and the disappearance of the starting material and appearance of the products were measured for a given time. The rate constant $f^{1/2}k_a$ was calculated using eqs 3−7. The concentrations and viscosities of solutions were corrected for temperature. Some cross dimers with the solvents and substrates were observed at low substrate concentrations. These were taken into account when the appearance of products was calculated.

Determination of the Relative Rates. A 1:1 mixture of vinyl ethers or esters and 1-octene was prepared in acetone or hexane in the presence of an unreactive internal standard (1-chloroheptane) and allowed to react with hydrogen or deuterium atoms. The relative rates were calculated by the GC analysis of initial and final reaction mixtures according to eqs 10 and 11.

The relative rate of disappearance of the vinyl ether was determined by competition kinetics from mixtures of 1-octene and vinyl butyl ether using the relationship given in eqs 10 and 11; see Table 2:

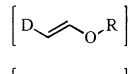
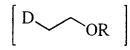
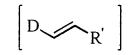
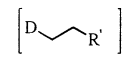
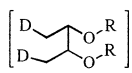
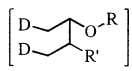
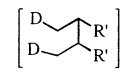
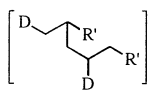
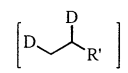
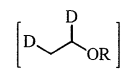
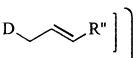
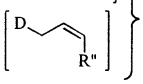
$$k^{e}_{add} = k^{o}_{add}\left\{\frac{\log(C^{e}_{t}/C^{e}_{o})}{\log(C^{e}_{t}/C^{e}_{o})}\right\} \qquad (10)$$

The concentrations of the ether or octene that had undergone reaction were corrected for reformation by disproportionation and for disappearance by radical addition. The area ratios (A) were calibrated using an unreactive internal standard (S).

$$k^{e}_{add} = k^{o}_{add}\left\{\frac{\log[((A^{e} - A^{(Ad)} + A^{(D)})/A^{s})_{t}/(A^{e}/A^{s}_{d})_{o}]}{\log[((A^{o} - A^{(Ad)} + A^{(I)})/A^{s})_{t}/(A^{e}/A_{s})_{t}]}\right\} \qquad (11)$$

where superscript o is 1-octene, superscript e is vinyl ether; subscript t is the reaction time, and subscript o is the initial area or concentration. The superscript capital letters in eq 11 refer to the compounds in Table 12.

TABLE 12: Product Distribution from the Reaction of Atomic Deuterium with a Mixture of 1-Octene and Vinyl Butyl Ether in Acetone Solutions[a]

temp (°C)[b]		-44		-63(2)	-72		-84(2)	-94(2)
time (min)		2.0	2.5	3.0	2.0	3.0	3.5	4.0
reaction (%)								
		7.90	4.58	15.7	9.3	13.1	23.8	23.8
		12.2	9.03	27.6	18.8	21.7	36.6	33.0
		products (mol dm^{-3} x 10^3)						
	(Ad)	1.2	1.2	5.6	6.4	6.4	12.4	9.4
	(Bd)	2.6	2.0	8.4	7.3	8.4	15.4	14.2
	(Ed)	1.6	1.6	4.8	6.8	10.2	12.8	8.2
	(Fd)	1.8	4.0	9.4	16.7	14.6	19.6	15.6
	(Cd2)	1.8	1.6	3.8	4.0	4.2	6.8	6.6
	(Gd2)	2.6	2.2	16.2	7.6	6.6	10.6	9.2
	(Hd2)	0.80	1.6	4.6	3.6	4.2	5.4	4.0
	(Id2)	<0.20	<0.20	0.4	<0.20	<0.20	0.40	0.20
	(Fd2)	6.0	7.4	18.2	10.6	11.2	19.6	16.4
	(Bd2)	3.0	2.2	4.6	3.5	4.0	8.6	6.8
	(Jd)	1.6	2.2	6.4	5.8	5.4	7.8	7.8
	(Jd)	0.40	0.60	1.2	1.2	1.0	1.6	1.4
$(\rho_{MDA}/\rho_{MDO})^c$		1.04 ± .04		1.03	1.09 ± 0.10		1.03 ± 0.10	1.12 ± 0.10
k_e/k_o [d]		0.50 ± .002		0.53 ± 02	0.56 ± .01		0.60 ± .01	0.68 ± .010
k_d/k_c [e]		0.99 ± .10		1.14 ± .17	1.28 ± 0.05		1.45 ± .38	1.46 ± .15

[a] R = C_4H_7, R′ = C_6H_{13}, R″ = C_5H_{11}. [b] Numbers in parentheses indicate the average values of two independent reactions carried out for the same times. [c] ρ_{MDO} = monodeuterated octene and vinyl butyl ether, ρ_{MDA} = monodeuterated octane and ethyl butyl ether. [d] Rates corrected for the addition and disproportionation products. [e] k_d/k_c is the disproportionation/combination ratio.

Reactions of Vinyl Butyl Ether with Atomic Deuterium. The ^{2}H spectra of the reaction mixture showed absorptions at δ 0.75, 0.83, 0.86, and 1.09 (DCH_2−), 3.12 (−DCH−O−), and 3.66, 3.88 (DCH═CH−O−), indicating that the products are formed from the deuterium atom addition to the terminal position of the double bond.

Reactions of Vinyl Butyrate with Atomic Deuterium. The ^{2}H spectra of the reaction mixture showed absorptions at δ 1.19, 1.24 (DCH_2−), 4.00, 4.10 (−DCH−O−), and 4.50, 4.60, 4.80, 4.90 (DCH═CH−O−), indicating that the products are formed from the deuterium atom addition to the terminal position of the double bond.

Acknowledgment. This work was supported in part by the Office of Science, Office of Basic Energy Science, U.S. Department of Energy under Contract DE-AC06-76 RLO 1830.

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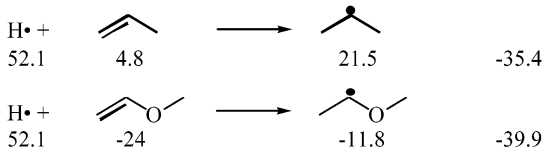

The α-O substituted radicals are estimated from the parent hydrocarbons using a bond dissociation energy of 92−93 kcal/mol. The value of 92−93 kcal/mol is in good agreement with limited available experimental values.[5] This value of 93 kcal/mol for a secondary C−H bond with α-O substitution is in agreement with high-level ab initio isodesmic calculations (*Gaussian 98*, G2MP2 level of theory) of the enthalpy of reaction, 5.4 kcal/mol, for the reaction $CH_3CH_2CH_2CH_3$ (−28.9) + $CH_3OCH{\bullet}CH_3$ (−9.05) → $CH_3CH_2CH{\bullet}CH_3$ (19.7) + $CH_3CH_2OCH_3$ (−52.3) from the experimental bond dissociation of secondary alkyl radical, 98.4 kcal/mol. Values in parentheses are G2MP2 enthalpies of formation at 298 K. The C−H bond dissociation energy of methanol is 98 kcal/mol, compared to 105 kcal/mol for methane. Thus, oxygen substitution of an alkane carbon reduces the bond dissociation energy by 5−7 kcal/mol.[6]

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(9) (a) The potential surface for the addition of a hydrogen atom to vinyl alcohol was examined using the Gaussian 98 set of programs (ref 10b). Geometries were calculated at the all-electron MP2/6-31G(d, p) level of theory, ground and transition states were verified by vibrational calculations, and electronic properties were calculated at the QCISD(T)/6-311G((d, p)//MP2=FU/6-31G(d, p) level of theory. The hydrogen atom adduct (hydroxyethyl radical) exhibited a dipole moment of 1.8 D, the transition state exhibited a dipole moment of 1.3 D, and vinyl alcohol exhibited a dipole moment of 1.2 D. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

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(13) A small error is introduced (∼6%) in the overall reaction rate constant from the values of 1,2-dideutero olefin since disproportionation from the monodeutero radical may also transfer a deuterium to yield the 1,2-dideutero product and undeuterated olefin. This process causes a maximum error in the value of ∼6% in $(p/t)_{RH2}$, which is moderated by a deuterium isotope effect of 1.2−2; see eq 9 and data from Tables 3 and 4. This error may account for the small deviation (within experimental error) in the 1:1 ratio of monodeutero olefin to alkane. An estimate of the error (∼6%) could be made by using the values in eq 9. The reproducibility of each value determined from two or more reactions at several olefin concentrations at varying percentages of reaction yielded only k_a, which differed by ∼6%.