

THE SOLUTION PHASE CHEMISTRY OF ATOMIC HYDROGEN. REACTIONS WITH ORGANIC SUBSTRATES.

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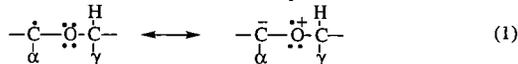
ABSTRACT

The solution-phase reaction of microwave-generated hydrogen atoms with terminal olefins is regioselective. Since addition is to the terminal end of the olefin, the reaction yields a secondary radical which undergoes either reaction with atomic hydrogen, disproportionation, combination, or addition to another olefin. At higher temperatures (23 °C) the olefin undergoes competitive allylic abstraction. The absolute rate constants for the addition of atomic hydrogen to mono- and trisubstituted olefins were determined and the data was used to extract the activation parameters for addition. Using competition kinetics the absolute rate constants for allylic abstraction were also determined. The stabilization of the carbon centered radical by an oxygen substituent was determined by the regioselective addition of a hydrogen atom to the terminal carbon of a vinyl ether or acetate. The same secondary radical can be formed by abstraction of an α -hydrogen from a dialkyl ether. The stereoelectronic enhancement or lack thereof of the rate constants for the reaction responsible for the formation of the radical intermediates will be discussed. The resonance effects due to oxygen were also investigated for addition to the five and six-membered rings of dihydrofuran and dihydropyran and for abstraction of the α -hydrogen from the saturated heterocycles.

I. INTRODUCTION

Recently, we reported a method for obtaining the absolute rate constants for the nonhomogeneous (gas-liquid) reaction of the addition of atomic hydrogen to an olefin.^{3b} The reaction of 1-octene was reported to be very close to diffusion controlled ($k_a^{25^\circ\text{C}} = 4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The same kinetic method can be used to evaluate the stabilizing effect of a carbon centered radical having a geminal oxygen substituent. The addition of hydrogen to a terminal olefin was found to be regioselective, (i.e., only addition to give the most stable secondary, or tertiary radical)^{3a} The same regioselectivity was found for addition to the vinyl ether, a vinyl ester also underwent regioselective addition to give a radical center on carbon containing a geminal oxygen substituent.

The high reactivity and selectivity for a hydrogen atom on carbon α - to an oxygen substituent has been attributed to the resonance stabilization of the radical, eq. 1.⁴



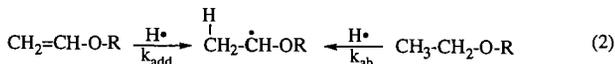
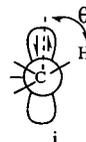
The importance of this resonance form has been substantiated by the observation that the EPR spectra of the radical shows a γ -hydrogen hyperfine coupling constant larger than that of the α -hydrogen (i.e., hyperconjugation).^{5,6}

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. The reactions were carried out in both polar (acetone) and nonpolar (hexane) solvents.

Another approach to the question of reactivity and stability of the carbon radical α to an oxygen atom has been popularly termed stereoelectronic control.⁷

II. RESULTS & DISCUSSION

In order to probe the importance of this type of resonance stabilization the reactivity of an olefin which formed a radical α - to oxygen was looked at as a function of the dihedral angle formed between the reactive hydrogen and the doubly occupied orbitals on the oxygen lone pair, i . The secondary radical formed from addition to a vinyl ether can also be formed by abstraction of hydrogen from the α -position of the saturated ether, see eq. 2.



Using the same kinetic method developed for the reactions of atomic hydrogen with one octene,^{3a-c} after correcting the addition results for abstraction, disproportionation, combination, and addition of the α -radical to another molecule of vinyl ether the algorithm for the absolute rate constant for addition, eq. 3 was used to determine the value of k_a . The results of the addition and abstraction reactions for several ethers are listed in Table 1. An example of the entries used in the algorithm (eq. 3) for one of the determinations (-72 °C, acetone) is given in Table 2. A similar table was constructed for the other solvent.

$$k_a = f^{-1/2} \left[\frac{(\Delta P/\Delta t)_{\text{total}} (k_{\text{diff}}(\Delta P/\Delta t)_{\text{C,D}})^{1/2}}{[\text{olefin}][\Delta P/\Delta t]_{\text{RH}_2}} \right] \quad (3)$$

A plot of $\log (f^{1/2} k_a)$ vs the olefin concentration was used to calculate the value of k_a in both acetone (O) and hexane (●). When [olefin] is equal zero, $f = 1$, and the absolute rate constant for addition was determined, see Fig. 1.

[Fig. 1]

When the reactions were carried out at several temperatures an Arrhenius plot was used to calculate the activation parameters and the absolute rate constants of k_a for the reactions of ether in both solvents, see Fig. 2.

[Fig. 2]

The abstraction rate constant for the abstraction of the α -hydrogen from dibutyl ether was determined from the competition kinetics between the abstraction reaction and addition of $H\cdot$ to 1-octene. Since the value of k_a for 1-octene is known,^{3b} the value for k_{ab} from the ether could be calculated. The competition kinetics was carried out to diminished olefin concentration. Using the experimentally determined activation parameters for the addition and abstraction reactions listed in Table 1 and using the calculated and experimental ΔH_f of the reactants intermediates and products the free energy profile, Fig. 3 was constructed.

Stereoelectronic control for radical reactions has been proposed to have its maximum effect when the dihedral angle, θ , is 30° .^{7b} Model compounds claimed to have this geometry are cyclic ethers, tetrahydrofuran and tetrahydropyran. When $H\cdot$ was allowed to react with tetrahydrofuran or tetrahydropyran, at several temperatures (see Table 1) the abstraction reactions which form the radical at the 2-positions showed rate constants which were slower than the open chain ether. The rate constants determining for the formation of the radical by regioselective addition were the approximately same for the 6-membered ring, and only 5 x faster for the formation of the radical at the 2-position of furan, see Table 1.

The effect of multiple oxygen substitution α - to a radical center was investigated using as models, diethyl acetal and triethyl orthoformate. The relative rate of abstraction by $D\cdot$ of the tertiary hydrogen compared to the secondary hydrogen of the acetal, $CH_3CH(OCH_2CH_3)_2$ was estimated from the 2H -NMR of the reaction mixtures at several temperatures. A plot of the relative rates of deuterium incorporation vs. $1/T$ gave a value of $(k_{3^\circ}/k_{2^\circ}/H = 0.91 \pm 0.12)^{25^\circ C}$, while abstraction of the tertiary radical from the orthoformate, $(C_2H_5-O)_3C-H$ could not be detected although there was considerable $D\cdot$ incorporation from secondary H abstraction.

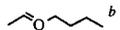
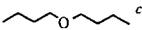
III. CONCLUSIONS

The absolute rate constants for the carbon centered radicals geminally substituted with oxygen can be compared to the value obtained from both addition to 1-octene or allylic abstraction from the terminal olefin.³ Both the addition and abstraction rate constants are within experimental error the same for the olefin and the vinyl ether. Only in the case of 2,3-dihydrofuran is the rate constant for addition more than one power of 10 faster, while abstraction from furan is slower than the open chain ether.

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Table 1. The Absolute Rate Constants for Addition and Abstraction Reactions by Atomic Hydrogen

Substrate	Solvent	($k_{\text{rel}}^{25^\circ\text{C}}$) ^a	$k^{25^\circ\text{C}} \times 10^9$ ($\text{M}^{-1}\text{s}^{-1}$)	$\Delta\Delta E_a$ (Kcal/mol)	ΔE_a (Kcal/mol)	log A
	Acetone	0.38±0.06	1.59	-0.49±0.05	4.8±2.9	13.2±4.2
	Hexane	1.14±0.40	4.79	-0.28±0.05	5.0±2.9	13.8±3.6
	Acetone	0.03±0.02	0.13	0.63±0.5	5.9±3.4	12.9±4.1
	Hexane	0.04±0.08	0.16	-0.1±1.0	5.2±3.9	12.5±4.9
	Acetone	0.20±0.10	0.84	-0.45±0.8	4.8±3.7	12.9±4.4
	Acetone	0.06±0.05	0.25	1.93±1.2	7.2±4.1	14.0±4.9
	Acetone	0.55±0.15	2.31	0.66±0.4	5.96±3.3	14.0±3.9
	Acetone	0.005±0.003	0.02	0.06±0.5	5.4±3.4	11.7±4.1

^a1-Octene was used as reference ($k_{\text{rel}} = k/k_{1\text{-octene}}$). ^bAddition reactions. ^cAbstraction reactions by atomic deuterium.

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

[olefin]	$10^4(\Delta p/\Delta t)_{\text{tot}}^{\text{bulk}}$ ^a	$10^4(\Delta p/\Delta t)_{\text{c,d}}$ ^b	$10^7[R^*]$	$10^4(\Delta p/\Delta t)_{\text{RD}_2}$ ^c	$10^8[\text{H}^*]^c$	$10^{-3}f^{1/2}k_a^d$
mol L ⁻¹	mol L ⁻¹ s ⁻¹	mol L ⁻¹ s ⁻¹	mol L ⁻¹	mol L ⁻¹ s ⁻¹	mol L ⁻¹	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	11.20
0.09	1.90	1.33	3.90	0.34	9.92	30.57
0.045	1.01	0.81	3.05	0.19	6.42	40.83
0.034	0.58	0.19	1.47	0.16	2.69	63.47
0.022	0.52	-	-	-	(2.35)	126.7

^aExperimentally measured as the change in the concentration of vinyl butyl ether with time. ^bThe rate of the formation of combination and disproportionation products (see ref. 3b). ^cThe rate of the formation of radical-deuterium atom combination products (see ref. 3b). ^dCalculated by using eq. 3.

Table 3. Experimental and G2MP2 Enthalpies, 298K

Species	$\Delta H_{\text{f},298}$ Kcal/mol, calcd, G2MP2	$\Delta H_{\text{f},298}$ Kcal/mol, exptl	G2MP2 Enthalpy, 298K, hartrees
H	-	52.1 ^a	-0.497639
C(3P)	-	171.3 ^a	-37.781527
O(3P)	-	59.6 ^a	-74.976317
	-	-53.3 ^a	-
	-	-29.9 ^a	-
	-43.85	-44.0 ^a	-232.004551
	-18.28	-21.47 (Benson ^b)	-230.802457
CH ₃ OCH=CH ₂	-24.67	-24 ±2 ^a	-192.758133
CH ₃ OCH ₂ CH ₃	-52.3	-51.7 ^a	-193.963445
CH ₃ OC•HCH ₃	-9.05	-11.8 (bde 93)	-193.313900
	-0.9	-4.0, -2.9 (92.1 ^c or 93.2 ^d bde)	-231.355426
	-7.65	-12.4 (est., assumes 93 bde) ^e	-270.582035 -270.150798 ^f

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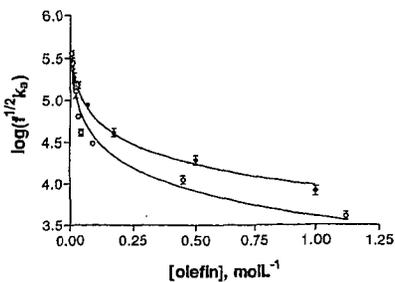


Fig. 1. The variation of the apparent rate constant $\log(f^{1/2}k_a)$ of vinyl butyl ether with the concentration of the olefin in (O) acetone and (●) hexane.

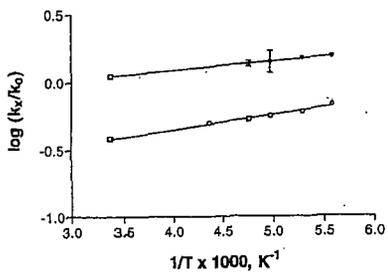


Fig. 2. An Arrhenius plot for the relative rates of addition to vinyl butyl ether in; (O) acetone, and (●) hexane.

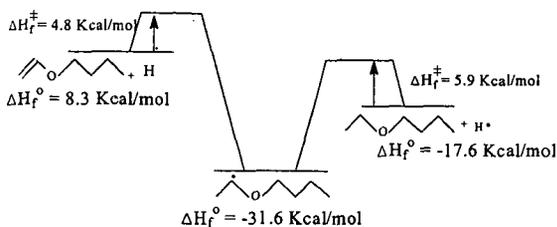


Fig 3. The free energy profile for the formation of methyl butoxy methyl free radical