Theoretical Study of the Reactivity of Ketene with Free Radicals

Kuangsen Sung*,† and Thomas T. Tidwell*

Department of Chemistry, University of Toronto Toronto, Ontario, Canada M5S 3H6

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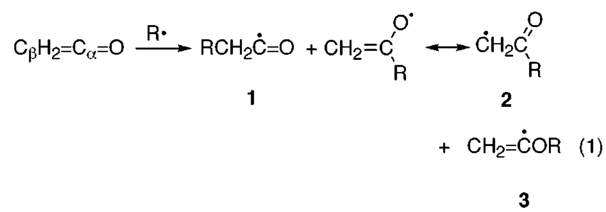
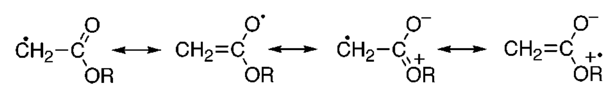
The structures and energies for the addition of free radicals R• (R = H, CH_3, OH, F, SiH_3, Cl) to $CH_2{=}C{=}O$ to give the radicals $RCH_2\dot{C}{=}O$, $\dot{C}H_2(C{=}O)R$, $CH_2{=}\dot{C}OR$ have been calculated by ab initio and B3LYP-DFT methods, and the latter method gives good agreement with available experimental energies. Product radicals $\dot{C}H_2C({=}O)R$ for groups R which possess electron lone pairs are stabilized and have predominant spin density on carbon, and this is attributed to conjugation of the carbonyl group in the product with substituents OH, F, and Cl at the α-position. Additions of H and SiH_3 have lower barriers to form the more stable product $RCH_2\dot{C}{=}O$, which for the latter is favored due to hyperconjugative stabilization by the β-SiH_3. For CH_3 attack at both carbons is competitive, while for OH, F, and Cl, the barriers are low for attack at either carbon, although attack at C_α gives much more stable products. Initial complexes between ketene and the CH_3, OH, SiH_3, and Cl radicals are detected, and for Cl using B3LYP this species has the structure of a π-complex with the C=C double bond that is stabilized by 16.2 kcal/mol relative to the reactants and forms $\dot{C}H_2C({=}O)Cl$ with a barrier of 2.8 kcal/mol. For F no barriers for addition to either carbon were found, but for B3LYP there is a barrier of 27.6 kcal/mol for conversion of $FCH_2\dot{C}{=}O$ to $\dot{C}H_2C$-(=O)F, which is more stable by 19.1 kcal/mol. The corresponding rearrangement of $ClCH_2\dot{C}{=}O$ has a barrier of 4.6 kcal/mol, and the predicted preference for initial attack at C_β to give the less stable product agrees with experiment.

The study of free radical chemistry long lay in the domain of interest of mechanistic and industrial chemists, but in recent years it has become apparent that free radical reactions are of great value in synthesis, particularly because they proceed under mild conditions and with proper care can be highly selective.[1] This has led to a dramatic increase in the utilization of free-radicals in preparative organic chemistry, and this has been fueled in significant part by the fundamental understanding of free radical reactivity that has been built up by patient study since the discovery of organic free radicals by Gomberg a century ago. Interestingly, the free-radical chemistry of ketenes has remained a *terra incognita*, despite early indications that ketenes are susceptible to radical reactions. Because of the promise of this field and our interests in ketene chemistry,[2] we have undertaken a study of such reactions using both theoretical and experimental methods.

The ionic reactivity of ketene is known to involve preferential nucleophilic attack at the in-plane LUMO at C_α (the carbonyl carbon), preferential electrophilic attack at the HOMO perpendicular to the molecular plane at C_β (the terminal olefinic carbon), and at the oxygen.[2] Attack of radicals on ketene at C_β, C_α, and oxygen would lead to acyl radicals **1**, enolic radicals **2**, and vinyl radicals **3**, respectively (eq 1).



Acyl radicals **1** have proven to be of great value in synthesis and are attracting increasing mechanistic and synthetic study.[3,4] There have also been recent studies of enolic radicals related to **2**,[5] which have been generated both by hydrogen atom abstraction from esters[5a] and by radical addition to acrylate esters $CH_2{=}CHCO_2R^1$.[5b] The stabilization of such enolic radicals derived from esters has been visualized by the resonance structures **4**,[5a] including the polar forms **4c** and **4d**.



4a **4b** **4c** **4d**

Vinyl radicals are formed by free radical additions to alkynes,[6] and the addition of radicals to alkynyl ethers

† Current address: Department and Graduate School of Chemistry, National Cheng Kung University, Tainan, Taiwan, R.O.C. E-mail: kssung@mail.ncku.edu.tw.

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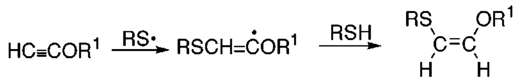
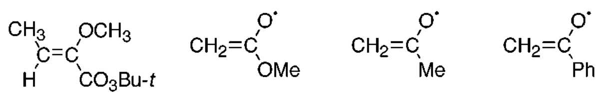
gives alkoxyvinyl radicals **5** (eq 2), analogous to the products of radical addition to ketenyl oxygen.[6c] For thiol addition to alkynyl ethers there is evidence that the *Z*-product is favored,[6c] and radicals of the type **5** generated by decomposition of peresters **6** form products by hydrogen abstraction with retention of configuration.[6d] This result, as well as ESR evidence,[6a,h] indicates that many vinyl radicals are bent σ-type radicals. Recent theoretical studies[6j,k] indicate that vinyl radicals bearing σ-type substituents (Me, SH, Cl, OH, F) are bent, whereas those with π-type substituents ($CH{=}CH_2$, CHO, CN, C_6H_5) are linear.



(2)

5

There have been increasingly detailed experimental and theoretical studies of the effect of substituents on the stabilities of methyl radicals.[7] Interestingly, the radical stabilization energies of the different types of enolic radicals **7a**−**c** have been estimated to be very similar (10, 11, and 12 kcal/mol, respectively).[7a]



6 **7a** **7b** **7c**

Reactivity in radical addition to alkenes has been a subject of great recent theoretical and experimental interest,[8] and the question of the respective influence of product stability and of polar transition state factors has attracted particular attention.[8] Recent studies of the addition of substituted alkyl radicals to substituted alkenes have shown that in the transition states there are angles of 106 to 110° between the incoming radical and the alkene C−C bond.[8d,e] There is a general correlation between the calculated structures of the transition states, and the overall calculated enthalpies of the reactions,[8d,e] and for some radicals the variations in the calculated barriers with changes in the substituents depend only upon the reaction enthalpy changes, while for other radicals there are polar influences on the barriers that do not affect the enthalpies of reaction.

In a comparative study of different theoretical methods for the calculation of the geometries and energetics of free radical additions to ethylene Hartree−Fock (HF), Møller−Plesset (MP), CASSCF, and density functional theory (DFT) methods were examined.[8b] It was found that the calculated geometries do not differ dramatically between the different methods, but that the MP methods give better agreement with the experimental energetics of the reaction compared to UHF, while the best agreement is found with Becke's three-parameter hybrid functional (B3LYP). Similarly in a comparative study of Hartree−Fock, perturbation, and DFT methods for study of hydrogen abstraction reactions from halomethanes by methyl radicals, the B3LYP method gave the best agreement with experiment.[8f] The B3LYP method was found to be the best DFT technique for calculating the barriers for H addition to $CH_2{=}CH_2$, and using B3LYP/6-31G-(2d,2p)(0 K) these were computed accurately.[8g] The latter method was also used in a recent study of the structures of vinyl radicals.[6j] In the current study the geometries and energetics are calculated using Gaussian 94[9a] with the HF, MP2, QCISD(T),[9b] and B3LYP[9c] methods. To avoid complications resulting from spin-contamination due to spin states of higher than doublet multiplicity, spin-projected energies[9d] were calculated at the HF and MP2 levels.

There have been only scattered references to experimental studies of reactions of free radicals with ketenes.[10] The reaction of $Ph_2C{=}C{=}O$ with $^3O_2$ was proposed to give

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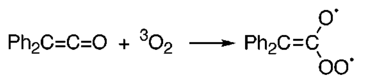
a diradical **8** (eq 3),[10a] and peroxy radicals were proposed to react similarly.[10c] The attack of hydrogen atoms on ketenes occurs at least partially on C_β and results in decarbonylation.[10d−h] In a benzene matrix, hydrogen atom addition to C_α of $CH_2{=}C{=}O$ was observed.[10h] Hydrogen atom addition to t-$Bu_2C{=}C{=}O$ occurs at both C_α and C_β (eq 4), and addition of C_6F_5 and CF_3 radicals to t-$Bu_2C{=}C{=}O$ was observed at C_α.[10g]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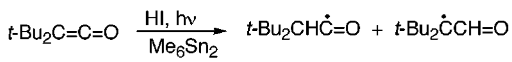
8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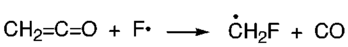
The addition of EtO• to $Me_2C{=}C{=}O$ was proposed to occur on C_α,[10i] while attack of HO• on ketenes was proposed to occur at both C_α and C_β,[10j−l] and carbon radicals (in mass spectrometric processes)[10m,n] were proposed to attack at C_β. Addition to C_β (eq 5) as well as hydrogen atom abstraction and displacement were proposed[10o] to occur for F•, and there was also evidence for the formation of products resulting from attack at C_α. Rate constants for Cl• addition analogous to eq 5 were reported.[10o−q] In previous work in our laboratory the reaction of the bisketene $(Me_3SiC{=}C{=}O)_2$ with oxygen was tentatively suggested to involve an initial biradical related to **8**.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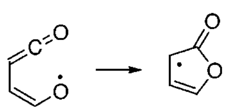
The calculated cyclization of a ketenyl radical at the UHF/6-31G*//UHF/3-21G level (eq 6)[10r] gave E_{act} of 9.6 kcal/mol, and ΔE of 20.9 kcal/mol. Related processes have been observed experimentally.[10s,t]


(6)

Thus it appears that the free radical reactivity of ketenes is a promising area for investigation, particularly as many of the putative intermediates are involved in other free radical processes, but have not been the subject of systematic theoretical study. We plan such a theoretical and experimental study of ketene reactions with free radicals and in this work have examined by theoretical methods the pathways for reaction of representative radicals with $CH_2{=}C{=}O$.

Results

The structures and energies have been calculated using Gaussian 94[9a] for the energy minimum and transition structures resulting from addition of radicals R• (R = H, CH_3, OH, F, SiH_3, Cl) at the HF/6-31G*//HF/6-31G*, MP2/6-31G*//MP2/6-31G*, and QCISD(T)/6-31G*//MP2/6-31G* levels, and using the Becke hybrid functional B3LYP/6-31G*.[9c] Calculated zero point vibrational energies were scaled by the reported factor of 0.8929.[8e] To avoid complications[6j,k] resulting from spin-contamination due to spin states of higher than doublet multiplicity, spin-projected energies were calculated at the HF and MP2 levels. In all cases the $<s^2>$ parameter for the reported results was 0.75, indicating doublet multiplicity with no errors resulting from spin contamination.

The adducts found include the acyl radicals **1** from attack at C_β, enolic radicals **2** from attack at C_α, and vinyl radicals **3** (eq 1). In all cases a search was made for other geometries of these radicals, and no other energy minimum structures were found. Prereaction complexes between ketene and the radicals were also observed in a few examples. For attack at C_α, different transition structures were found for attack perpendicular to and in the ketene plane for H, CH_3, and SiH_3, while for OH, F, and Cl, only structures for perpendicular attack were found. The energy changes in these processes, including scaled ZPVE corrections, are given in Table 1, and the calculated energies, zero point vibrational energies, B3LYP calculated entropies and free energies, selected bond distances, and bond angles are given in Tables 2−5 (Supporting Information). Calculated spin densities, atomic charges, and SOMO energies are given in Tables 6−8, and comparisons to experimental data and previous calculations are in Tables 9 and 10 (Supporting Information).

Other recent theoretical studies concerned with radical processes have included calculations of the structures and energies of certain of the species considered in this study, including $CH_3\dot{C}{=}O$,[11a−e] $CH_2{=}C(\dot{O})H$,[11f−h] $CH_2{=}C(\dot{O})OH$,[11i] and $CH_2F\dot{C}{=}O$.[11b] The geometries obtained in this study (Table 10) are in reasonable agreement with these previous results.

As discussed above, the B3LYP method was found to give the most satisfactory results in other theoretical studies of the energetics of free radical reactions.[6j,8b,f,g] Comparison of the results obtained here by the different methods (Table 1) shows that for a particular radical the prediction for the most stable product and the lowest barrier is the same for the MP2, QCISD(T) and B3LYP methods, with a single exception for CH_3, where the values are very similar at all levels. As noted below there is good quantitative agreement between the B3LYP calculations and the available experimental data. The QCISD(T) results are in qualitative and in most cases quantitative agreement with the B3LYP energy comparisons, and this lends confidence in the reliability of the results. The discussion below is based on the latter level, unless noted.

For addition of free radicals to $CH_2{=}CH_2$, the experimental values of E_{act} for H,[7g] CH_3,[7g] and $SiEt_3$[6a] are reported as 2.8, 7.7, and 1.4 kcal/mol, as compared to the B3LYP calculated values for addition to CH_2 of ketene (Table 1) of 0.5, 9.3, and 3.3 (for SiH_3) kcal/mol, respectively. For OH,[8i] F,[8j] and Cl,[8k] no barriers are found for addition to $CH_2{=}CH_2$ either experimentally or theoretically, and this parallels our calculations for attack at C_β of $CH_2{=}C{=}O$. Experimental values for radical additions to alkenes show a rather modest dependence on the alkene structure.[6a,7g] For example, values of E_{act} for CH_3

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Table 1. Comparative Energies (kcal/mol) with Scaled ZPVE for Radical Additions to $CH_2{=}C{=}O$

R	level[a]	$RCH_2\dot{C}{=}O$			$\dot{C}H_2C({=}O)R$				$CH_2{=}\dot{C}OR$	
		ΔE_{cplx}[b]	ΔE_{ts}[b]	ΔE^o	ΔE_{ts}[b,c]	ΔE_{ts}[b,d]	ΔE_{ts}[b,e]	ΔE^o	ΔE_{ts}[b]	ΔE^o
H	HF//HF		4.3	−42.2		5.5	10.4	−53.4	19.7	−13.4
	MP2//MP2		8.2	−35.3		13.8	17.6	−26.0	28.8	5.5
	QCISD(T)//MP2		5.5	−44.1		9.4	10.2	−36.2	21.5	−7.5
	B3LYP		0.5	−44.2	2.6	5.4	6.6	−39.5	13.4	−9.3
CH_3	HF//HF	−0.1[d]	10.0	−24.3		11.6	15.7	−39.3	27.3	9.5
	MP2//MP2	−0.7[e]	12.9	−31.2		15.1	14.4	−28.8	31.6	14.9
	QCISD(T)//MP2	*f*	13.7	−30.9		15.4	13.0	−29.2	30.1	13.1
	B3LYP	−0.2[e]	9.3	−29.7		11.9	8.5	−31.4	22.5	10.0
OH	HF/HF		7.1	−14.7		7.9		−46.2		
	MP2//MP2	−1.2[d]	2.6	−32.6		2.4		−55.6		
	QCISD(T)//MP2	*f*	1.1	−29.1		0.5		−50.4		
	B3LYP	−4.9[d]		−32.6		3.8		−54.7		
F	HF//HF	−0.4[d]	3.0	−26.0		1.8		−54.8		
	MP2//MP2			−47.4	−12.3			−66.3		
	QCISD(T)//MP2			−46.7	−16.0			−61.1		
	B3LYP			−50.1	−22.5			−69.2		
SiH_3	HF//HF	−0.1[d]	6.8	−26.6		9.1	12.6	−10.5	18.6	−25.8
	MP2//MP2	−0.6[d]	6.6	−26.1		13.8	10.6	6.2	19.3	−10.7
	QCISD(T)//MP2	*f*	7.3	−27.4		12.1	7.9	3.3	16.7	−14.2
	B3LYP	−0.3[d]	3.3	−20.6		9.2	6.3	−4.2	11.2	−12.9
Cl	HF//HF	−1.1[d]	0.2	−10.4		0.6		−28.0		
	MP2//MP2	−8.3[d]		−19.6	−9.1	−6.5		−24.2		
	QCISD(T)//MP2	*f*		−19.2	−7.0	−4.5		−24.3		
	B3LYP	−16.2[d]		−20.5	−15.9	−13.4		−28.6		

[a] HF//HF: PUHF/6-31G*//UHF/6-31G*; MP2//MP2: PUMP2/6-31G*//UMP2/6-31G*; QCISD(T)//MP2: QCISD(T)/6-31+G**//UMP2/6-31G*; B3LYP: B3LYP/6-31G*//B3LYP/6-31G*. [b] Energy difference from reactants. [c] Transition structures for interconversion of $RCH_2\dot{C}{=}O$ and $CH_2{=}C(O\bullet)R$. [d] Perpendicular approach. [e] In-plane approach. [f] Not done.

addition to 20 alkenes $CH_2{=}CXY$ ranged from 6.7 to 3.6 kcal/mol.[8h] Thus the B3LYP-calculated values of E_{act} appear to be in the range expected and should be a reliable guide to radical reactions to ketenes.

Calculations for hydrogen atom addition to $CH_2{=}C{=}O$ located four different transition structures, and these led to three different radicals (Figure 1A). The lowest energy barrier at the B3LYP level of 0.5 kcal/mol was for attack at C_β perpendicular to the ketene plane, leading to $CH_3\dot{C}{=}O$, which is 44.2 kcal/mol lower in energy than the reactants. Two different structures for attack at C_α were found, with respective B3LYP barriers of 5.4 and 6.6 kcal/mol for perpendicular and in-plane attack, respectively. These each led to the same enolic radical $\dot{C}H_2C({=}O)H$, 39.5 kcal/mol below the reactants, and 4.7 kcal/mol less stable than is $CH_3\dot{C}{=}O$. A fourth transition structure, for attack at the oxygen LUMO in the ketene plane, has the highest barrier, of 13.4 kcal/mol, and forms $CH_2\dot{C}OH$, which is 9.3 kcal/mol below the reactants.

The acyl and vinyl radicals from H atom attack at C_β and O, respectively (Figure 1A), are bent σ-type radicals in accord with previous experimental and theoretical studies,[4,6] while the enolic radical from attack at C_α is planar. The B3LYP transition structure for interconversion of these radicals resembles recently reported[12a,b] MP2 structures, and as found by Donaldson et al.,[12a] the migrating hydrogen is out of the CCO plane (Figure 1A). Reported[12b] data indicating that this hydrogen is in the CCO plane appear to be a typographical error. An intrinsic reaction coordinate (IRC) calculation indicates that the migrating hydrogen is that indicated in Figure 1Ae.

These results are in good agreement with experimental studies in which H atom attack on C_β of ketene was observed,[12c] with $E_{act} = 2.6$ kcal/mol, compared to our calculated value of 0.5 kcal/mol. It was concluded[12c] either that addition of H to C_α of ketene did not occur, or that it was necessarily followed by isomerization to $CH_3\dot{C}{=}O$. This agrees with our finding of a 4.9 kcal/mol higher barrier for attack at C_α. The radical $\dot{C}H_2C({=}O)H$ is also formed by reaction of vinyl radicals with oxygen atoms[12a] and gives $CH_3\bullet$ and CO by a process involving hydrogen migration to form $CH_3\dot{C}{=}O$. This process also occurs upon photoexcitation of $\dot{C}H_2C({=}O)H$, together with elimination of H and formation of $CH_2{=}C{=}O$.[12b] The B3LYP barrier for this migration is 42.1 kcal/mol, as compared to reported MP2 values of 40[12a] and 41[12b] kcal/mol.

The most recent experimental values for $\Delta H_f°(0\ K)$ are −0.9 kcal/mol $CH_3\dot{C}{=}O$ and 4.0 kcal/mol for $\dot{C}H_2C({=}O)H$,[12d−f] giving an energy difference of 4.9 kcal/mol for the two radicals, compared to our calculated value of 4.7 kcal/mol. For comparison, our calculations at the MP2 and QCISD(T) levels give differences of 9.3 and 7.9 kcal/mol, respectively, in agreement with other recent reports.[12a,b] Thus the B3LYP calculations are in good

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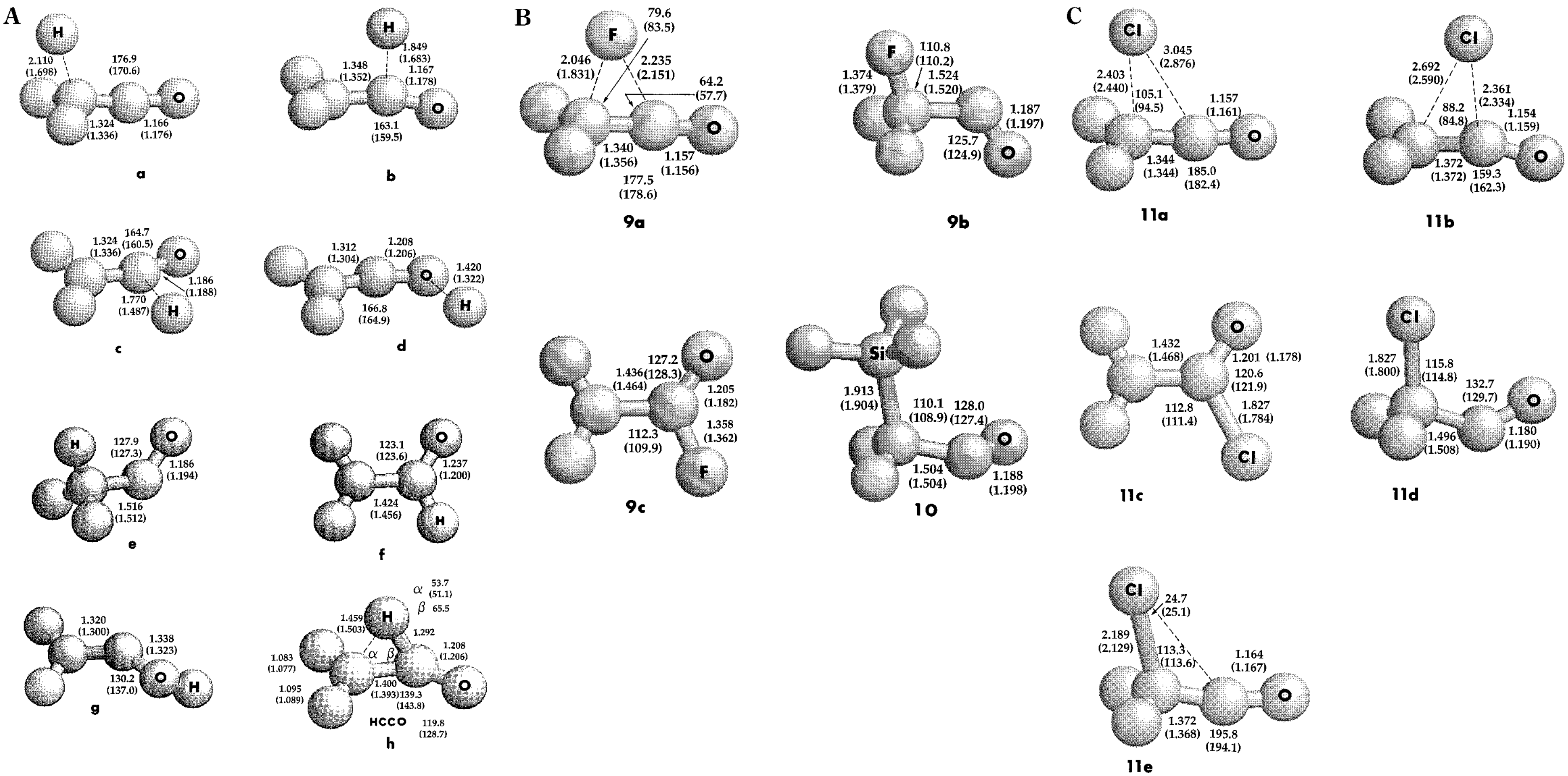

Figure 1. Calculated structures for radical additions to $CH_2{=}C{=}O$ with B3LYP bond distances (Å) and angles (deg), and comparative MP2/6-31G* data in parentheses. (A) Transition structures for H addition: (a) attack at C_β, (b) perpendicular attack at C_α, (c) in-plane attack at C_α, (d) attack on oxygen, (e−g) products of H addition, (h) transition structure for H rearrangement. (B) Transition structure for F migration and acyl radicals from F and SiH_3. (C) Complex with Cl (**11a**) and TS **11b** for rearrangement to enolic radical **11c**; acyl radical **11d**, and TS for rearrangement **11e**.

agreement with the experimental results, not only in predicting the preferred position of attack and the magnitude of the barrier, but the relative energies of the products. In Table 9 (Supporting Information) further literature[11b,f,12] values of $\Delta\Delta H_f°$ between acyl radicals **1** and enolic radicals **2** are compared to our B3LYP $\Delta\Delta E$, and ($\Delta\Delta E - \Delta\Delta H_f°$) values (kcal/mol) are 0.2 (H), 2.2 (CH_3), 3.0 (OH), −0.1 (F), and 0.1 (Cl). The agreement is well within the uncertainty of the literature data. No data for silyl radical adducts appears to be available.

For attack by CH_3, the situation is similar to that for H, but at the MP2 level two initial complexes are found, with CH_3 either perpendicular to or in the ketene plane, and these are stabilized by 0.6 and 0.7 kcal/mol, respectively, relative to the reactants. These structures are evidently similar to the gas phase complexes observed experimentally between electrophilic species such as HCl with alkenes[13a] and ketenes,[13b,c] the ketene complex with acetylene,[13d] and solution phase complexes observed between Cl atoms and benzene.[13e−h] The Br_2 complex with $CH_2{=}CH_2$ has been studied theoretically and experimentally, and upon photolysis is proposed to give $BrCH_2CH_2^•$.[13i] At the B3LYP level the stabilization of the in-plane complex decreases to 0.2 kcal/mol, and the perpendicular complex is no longer an energy minimum. There is a slight preference at the B3LYP level for attack at C_α in the ketene plane, with a barrier of 8.5 kcal/mol, as opposed to 9.3 kcal/mol for attack at C_β.

For the electrophilic OH radical, attack occurs only on the HOMO perpendicular to the ketene plane and adds to C_β with no barrier, while attack at C_α proceeds by initial formation of a complex stabilized by 4.9 kcal/mol at the B3LYP level. Product formation for attack at C_β and C_α is exothermic by 32.6 and 54.5 kcal/mol, respectively, with a barrier of 8.7 kcal/mol for formation of the coplanar enolic π radical structure from the complex.

For F at the B3LYP level there are no barriers for attack, and the product radicals from attack at C_α and C_β are stabilized by 69.2 and 50.1 kcal/mol, respectively. At this level no energy minimum complex is observed but there is a bridged TS **9a** for interconversion of these radicals (Figure 1B), which at the B3LYP level is 22.5 kcal/mol more stable than the reactants, but 27.6 and 46.7 kcal/mol above $FCH_2\dot{C}{=}O$ (**9b**) and $\dot{C}H_2C({=}O)F$ (**9c**), respectively. The energy profile for these reactions is given in Figure 2.

For the reaction of SiH_3, at the B3LYP level both perpendicular and coplanar initial complexes are slightly stabilized by 0.25 and 0.19 kcal/mol, respectively, and there are four transition structures, with a preference for attack at C_β leading to an acyl radical **10** (Figure 1B), which is 16.4 kcal/mol more stable than the enolic radical from attack at C_α.

For the reaction of Cl, an initial perpendicular complex **11a** is formed (Figure 1C), which at the B3LYP level is

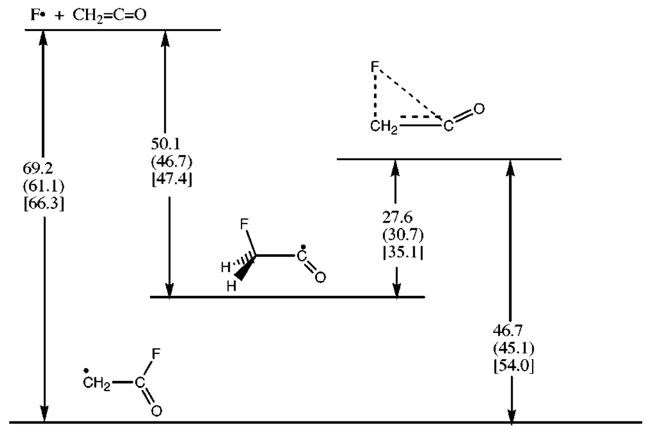

Figure 2. B3LYP energy profile for F addition to $CH_2{=}C{=}O$, with QCISD(T) and MP2 comparative energies, parentheses and brackets, respectively.

stabilized by 16.2 kcal/mol relative to the reactants and is converted through a TS **11b** 2.8 kcal/mol above the complex to the enolic radical **11c** that is 28.6 kcal/mol more stable than the reactants. This complex may be compared to that calculated[13j,k] for Cl and $CH_2{=}CH_2$ which at the (UMP2/DZP) level[13k] was stabilized by 7.3 kcal/mol with C−Cl bond lengths of 2.584 Å, with $ClCH_2CH_2^•$ 13.3 kcal/mol more stable. These calculations and others[8k] agree with the conclusions reached by Russell[13h] in his pioneering studies of complexes of Cl• with benzene, in which he deduced that while such complexes with alkenes may be rapidly formed, they collapse to σ-bonded radicals.

The reaction of Cl with $CH_2{=}C{=}O$ also proceeds with no barrier to the acyl radical $ClCH_2\dot{C}{=}O$ **11d**, and this can rearrange through a TS **11e** 4.5 kcal/mol above the acyl radical to the enolic radical, which is 8.2 kcal/mol more stable. The energy profile for these processes is given in Figure 3. Although the complex **11a** and the TSs **11b** and **11e** have somewhat similar energies, their stuctures (Figure 1C) are distinctly different.

These acyl and vinyl radicals have bent σ-radical type structures while the enolic radicals are planar π-type radicals. Linear acyl and vinyl structures were checked and are not energy minima. For the acyl radicals with OH and Cl substituents the C−R bond lies in the CCO plane anti to the half-filled σ-orbital on the acyl carbon. For $FCH_2\dot{C}{=}O$ (**9a**) the C−F bond is, however, anti to the C=O bond, as shown in Figure 1B, in agreement with another theoretical study.[11b] This conformation avoids repulsive interactions between the fluorine and the lone pairs on the carbonyl oxygen. The acyl radical **10** from SiH_3 (Figure 1B) addition to ketene has the C−R bond in a conformation nearly coplanar with the p orbital on the carbonyl carbon, permitting hyperconjugatively stabilizing electron donation to the carbonyl group.

Comparison of the geometries of the enolic radicals **12**−**14** formed by addition of CH_3, H, and SiH_3 to $CH_2{=}C{=}O$ indicates the former two have substantial $C_1{-}C_2$ single bond character, and C−O double bond character, as shown. This is in accord with previous calculations[7c] on the structure of the radical **13**, but a significant radical stabilization energy (RSE) of 7.7 kcal/mol for the CHO group in this radical was also found.[7d] There is considerable evidence for the stabilization of enolic radicals by delocalization; for example, the RSE values of CN and

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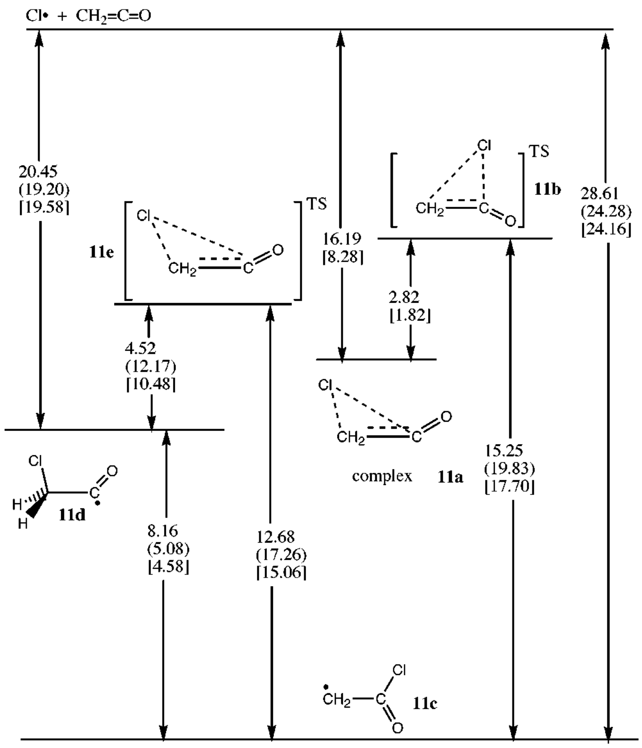
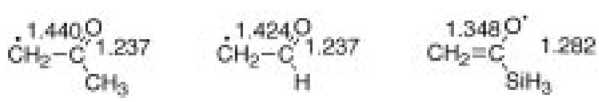


Figure 3. B3LYP energy profile for Cl addition to $CH_2{=}C{=}O$, with QCISD(T) and MP2 comparative energies, parentheses and brackets, respectively.

CH_3CO are similar (−12 and −11 kcal/mol, respectively) for $RCH_2^•$, but for fluorenyl radicals the values (−5.7 and −2.5 kcal/mol, respectively) are interpreted[7a] as indicating a significant steric barrier to conjugation for CH_3CO in the fluorenyl system.



12 **13** **14**

The preference for alkoxy radical character in the silyl-substituted radical as shown in **14** is analogous to the greater than 10^3 preference for enol formation by $CH_3COSiMe_3$ compared to acetone.[14a] This latter behavior has been attributed to Coulombic repulsion of an electron deficient carbonyl carbon by the positive silicon.[14b] For the acyl radicals resulting from attack at C_β the B3LYP spin densities (Table 6) (Supporting Information) are all concentrated on C_α, with similar values (0.58 to 0.62), while in the transition states these values are 0.12 to 0.26, and there is a large spin density (0.75 to 0.88) on the attacking radical.

The enolic radicals from attack at C_α have a large spin density at C_β (0.86 to 0.97). The exception to this behavior is the adduct from SiH_3, which has spin density of −0.01 at C_β, and instead has a high spin density of 0.74 on oxygen. This is consistent with the structural evidence that enolic radicals from attacking groups more electrophilic than SiH_3 have predominant C−O double bond character as shown in **12**, with the spin localized on C_β, while for the product from SiH_3 the predominant resonance structure is **14**. For all but the SiH_3 case these are π radicals, with the spin density concentrated on the planar C_β, as shown experimentally and theoretically.[5,10g,h,11g,i] For the SiH_3-substituted radical **14** this was probed using MP2/6-31G*//MP2/6-31G* calculations, and the SOMO was concentrated on oxygen in the molecular plane, indicating a σ radical structure. We hope to test this prediction by experimental studies.

Radical attack on the oxygen of ketenes gives vinyl radicals with spin density on C_α of 0.88−0.95, and 0.39−0.56 in the transition states. Radicals more electrophilic than carbon do not give attack on the carbonyl oxygen.

Calculated values of entropies at the B3LYP level for these reactions (Table 3b, Supporting Information) show that as expected these bimolecular reactions have appreciable values of $\Delta S^\ddagger$ and ΔS, which range from −20.8 to −23.3 for attack of H, and −27.5 to −37.3 for the other radicals. As a result the values of $\Delta G^\ddagger$ are more positive than the corresponding values of ΔE_{ts}, by factors of 6.3−7.0 and 9.0−11.0 kcal/mol for H, F, Cl and CH_3, OH, and SiH_3, respectively, while ΔG values are more positive than ΔE by values ranging from 9.1 to 16.3 kcal/mol. For the prediction of the regiochemistry of attack at C_α or C_β, the greatest difference in the use of ΔE_{ts} as apposed to $\Delta G^\ddagger$ is 1.2 kcal/mol.

Discussion

An important question in the reaction of free radicals with ketenes involves the regiochemistry of the reaction. Radical reactions with alkenes have been described by the Frontier Molecular Orbital (FMO) model, which considers the interactions of the SOMO (singly occupied molecular orbital) of the radical with the LUMO (lowest unoccupied molecular orbital) of the substrate for nucleophilic radicals, and with the HOMO (highest occupied molecular orbital) for electrophilic radicals.[8] The correlation of activation energies with heats of reaction in radical addition has also been considered.[8]

The position of radical attack on ketenes may be expected to be affected by interaction of the radicals with the ketene orbitals. For ketene the HOMO is perpendicular to the plane of the molecule with large coefficients at C_β and O, and the LUMO is in the ketene plane, with large coefficients at C_α and on oxygen. The properties of the radicals may be characterized by their group electronegativities,[15] first ionization energies, electron affinities, and calculated SOMO energies (Table 8, Supporting Information). The experimental first ionization energies and the SOMO energies give rather good agreement (Table 8 and Figure 4, Supporting Information), and there is a modest correlation of the SOMO energies with the group electronegativities χ_{BE} by the relationship $E_{SOMO} = -3.19\,\chi_{BE} - 3.79$ ($r = 0.83$) (Figure 5, Supporting Information). However attempted correlation of ΔE values with the group electronegativities or electron affinities of the radicals (Figures 6−9, Supporting Information) gave a fair correlation coefficient in the former case, and poor ones in the latter three.

For three radicals (H, CH_3, and SiH_3) attack at C_α occurs from both the perpendicular and in-plane directions, corresponding to electrophilic and nucleophilic attack, respectively, while for OH, F, and Cl only

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perpendicular (electrophilic) attack was found. For SiH_3 and H the acyl radicals from attack at C_β are the most stable and also have the lowest barriers for formation. For CH_3 in-plane attack at C_α forming an enolic radical has the lowest barrier and leads to the most stable radical by a small margin. For OH, F, and Cl the enolic radicals from attack at C_α are significantly more stable, but for OH and Cl, form with 8.7 and 2.8 kcal/mol barriers from the initial complexes. For these three highly electrophilic radicals, addition to C_β, which has a higher HOMO coefficient, is predicted to occur without barriers even though the product radicals are less stable.

For the nucleophilic SiH_3 attack preferentially occurs on the HOMO at C_β, leading to the most stable product, while for attack on C_α in-plane approach to the LUMO is favored. The attack of H is also predicted to give the most stable product by attack at C_β, while for the CH_3 radical attack at C_α is 1.7 kcal/mol more favorable at the B3LYP level. For attack at C_α there is a small preference by H for perpendicular approach, while CH_3 favors in-plane approach to the HOMO.

The enolic radicals with OH, F, and Cl groups capable of *n*-π conjugation with the carbonyl as in **4c** are significantly stabilized, whereas SiH_3 favors attack at C_β, forming an acyl radical **10** which can be stabilized by $\sigma-\pi$ conjugation involving the Si−C bond.[6a,h,16]

Experimentally[10o] F was observed to react with ketene at C_β resulting in the formation of $\dot{C}H_2F$ (eq 5), and there was also evidence for the formation of products from attack at C_α.[10o] Reaction of OH may occur at both C_α and C_β,[10j−l] but as reported[10k] the primary adducts are highly activated and will undergo rapid isomerization and fragmentation to form the observed products. The products from attack of F and OH at C_α are calculated to be more stable by 29.1 and 22.1 kcal/mol, respectively, but the reaction with fluorine atoms is calculated at the B3LYP level to have no barrier for attack at either position, while reaction with OH is calculated to have no barrier for attack at C_β and a 3.8 kcal/mol barrier from the reactants for attack at C_α, and so selectivity in these processes to give the most favorable attack, at C_α, is not expected. The reaction of Cl• with ketene has been observed to occur preferentially on C_β,[10o−q] with a rate constant that is close to diffusion controlled[10q] in agreement with the results obtained here.

The question of halogen-bridged radical transition states or intermediates has been a subject of intense interest,[13e−j,17] and 1,2-chlorine migrations in free radicals are well-known. For $CH_2{=}CH_2$ and $Cl^\bullet$, as noted above,[13k] there is a symmetrical minimum energy complex, which is converted with a small barrier to $ClCH_2CH_2^\bullet$, which is 13 kcal/mol more stable than the reactants. The σ-bonded radical $FCH_2CH_2^\bullet$ is calculated to be much more stable than the bridged structure compared to the chloro analogue,[13j] and ESR spectra of fluoro radicals provided no evidence of bridging.[18a,b] Reported cases of 1,2-fluorine migration in radicals involve high energy processes[18c,d] and evidently have high barriers. This agrees with the high barrier we find for the TS **9a** between the acyl radical **9b** and enolic radical **9c** and suggests these latter species may be experimentally observable.

In summary these studies predict that reactions of radicals with ketenes should involve a diverse chemistry, and the calculations are in essential agreement with available experimental data. Specifically these calculations successfully account for the available data on the relative energies of acyl and enolic radicals and also predict the observed regiochemistry of radical additions to ketenes, including those cases where the most stable radical is not formed preferentially. The formation of radical/ketene complexes and the occurrence of radical rearrangements in ketene adducts are predicted and are subject to experimental examination.

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Supporting Information Available: Calculated energies, geometries, spin densities, SOMO energies, atomic charges, comparative data for free radical addition to ketenes, and Figures 4−9 (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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