JOC Article

A Comparison of Acetyl- and Methoxycarbonylnitrenes by Computational Methods and a Laser Flash Photolysis Study of Benzoylnitrene

Jin Liu, Sarah Mandel, Christopher M. Hadad,* and Matthew S. Platz*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

hadad.1@osu.edu; platz.1@osu.edu

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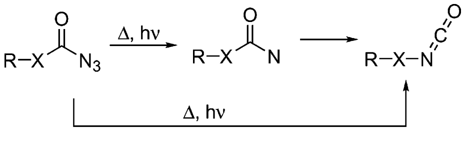
Density functional theory (DFT), CCSD(T), and CBS-QB3 calculations were performed to understand the chemical and reactivity differences between acetylnitrene ($CH_3C(=O)N$) and methoxycarbonylnitrene ($CH_3OC(=O)N$) and related compounds. CBS-QB3 theory alone correctly predicts that acetylnitrene has a singlet ground state. We agree with previous studies that there is a substantial N−O interaction in singlet acetylnitrene and find a corresponding but weaker interaction in methoxycarbonylnitrene. Methoxycarbonylnitrene has a triplet ground state because the oxygen atom stabilizes the triplet state of the carbonyl nitrene more than the corresponding singlet state. The oxygen atom also stabilizes the transition state of the Curtius rearrangement and accelerates the isomerization of methoxycarbonylnitrene relative to acetylnitrene. Acetyl azide is calculated to decompose by concerted migration of the methyl group along with nitrogen extrusion; the free energy of activation for this concerted process is only 27 kcal/mol, and a free nitrene is not produced upon pyrolysis of acetyl azide. Methoxycarbonyl azide, on the other hand, does have a preference for stepwise Curtius rearrangement via the free nitrene. The bimolecular reactions of acetylnitrene and methoxycarbonylnitrene with propane, ethylene, and methanol were calculated and found to have enthalpic barriers that are near zero and free energy barriers that are controlled by entropy. These predictions were tested by laser flash photolysis studies of benzoyl azide. The absolute bimolecular reaction rate constants of benzoylnitrene were measured with the following substrates: acetonitrile ($k = 3.4 \times 10^5$ M^{-1} s^{-1}), methanol (6.5×10^6 M^{-1} s^{-1}), water (4.0×10^6 M^{-1} s^{-1}), cyclohexane (1.8×10^5 M^{-1} s^{-1}), and several representative alkenes. The activation energy for the reaction of benzoylnitrene with 1-hexene is -0.06 ± 0.001 kcal/mol. The activation energy for the decay of benzoylnitrene in pentane is -3.20 ± 0.02 kcal/mol. The latter results indicate that the rates of reactions of benzoylnitrene are controlled by entropic factors in a manner reminiscent of singlet carbene processes.

Introduction

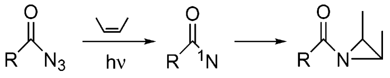
Carbonyl-substituted azides are readily synthesized and have been studied by physical and organic chemists for several decades.[1] Upon activation with heat or light, both acyl and alkoxycarbonyl azides extrude molecular nitrogen and form carbonyl nitrenes. These nitrenes can undergo intramolecular rearrangement (Curtius rearrangement) to form isocyanates.[2]



RX = alkyl or aryl or RX = O-alkyl or O-aryl

There is evidence that migration of RX can proceed in concert with nitrogen extrusion in some cases, without the intervention of a free nitrene. There is also evidence that the stepwise or concerted nature of the process varies with the mode of azide decomposition.[3]

Carbonyl-substituted nitrenes are efficiently intercepted with a variety of reagents, and *cis* and *trans* substituted alkene traps are particularly diagnostic trapping agents. Extending the Skell−Woodworth rules from carbenes[4] to nitrenes allows deduction of the multiplicity of the reactive intermediate that is captured. Product studies with acylnitrenes and *cis* alkenes revealed retention of configuration in the aziridine product.[5]



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* To whom correspondence should be addressed. Fax: (614) 292-1685 (C.M.H.); (614) 292-1685 (M.S.P.).

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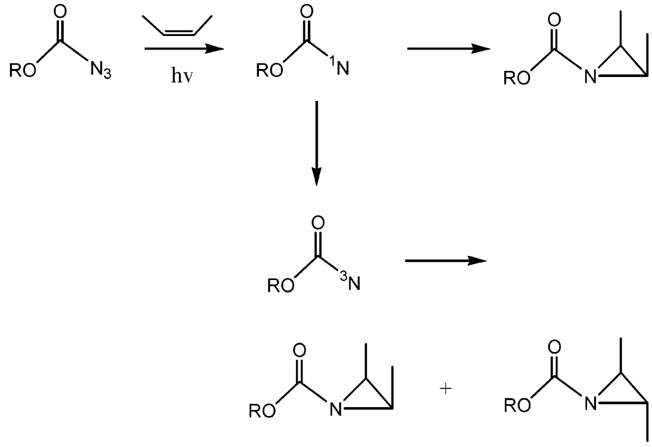
10.1021/jo048433y CCC: $27.50

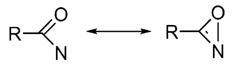
This result is consistent with trapping of the *singlet* state of the acylnitrene. Different results are obtained with alkoxycarbonyl azides, which form mixtures of aziridines upon photolysis, in the presence of alkenes.[6]



This result is consistent with the interception of both the singlet and triplet states of an alkoxycarbonylnitrene.

The conclusions deduced from chemical trapping studies are also consistent with matrix spectroscopic experiments. The triplet ESR spectra of alkoxycarbonylnitrenes are observed upon low-temperature photolysis of alkoxycarbonyl azides,[7,8] confirming that alkoxycarbonylnitrenes have triplet ground states. However, triplet acylnitrenes have never been detected by ESR spectroscopy when acyl azides are irradiated at cryogenic temperatures. Photolysis of benzoyl azide and related azides fails to produce ESR spectra characteristic of a benzoylnitrene. Taken together, the chemical trapping studies and matrix spectroscopic studies indicate that acylnitrenes have singlet ground states.

Imidogen (NH),[9] alkyl[7,10] and arylnitrenes[7,11] have triplet ground-state multiplicities. Recent density functional theory (DFT) and high level ab initio calculations, however, indicate that other acylnitrenes have closed-shell singlet ground states because of a bonding interaction between the oxygen and nitrogen atoms of the intermediate.[12,13]



The position of the carbonyl vibration of singlet benzoylnitrene, observed by matrix and time-resolved infrared (TRIR) spectroscopy, is consistent with the prediction of DFT calculations.[13] A recent report by Pritchina, Gritsan, and Bally have examined the chemical preferences of formylnitrene ($HC(=O)N$) and hydroxycarbonylnitrene ($HOC(=O)N$).[13b]

TABLE 1. Singlet−Triplet Energy Gap [ΔH (298 K) (kcal/mol)] of Species 1, 2, and 3 by DFT, CCSD(T), and CBS-QB3 Methods[a]

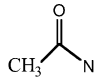
level of theory	**1**	**2**	**3**
B3LYP/6-311+G**//B3LYP/6-31G*	4.9	13.9	3.7
CCSD(T)/6-311+G**//B3LYP/6-31G*	1.9	12.2	4.4
CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G*	1.6	12.0	3.6
CBS-QB3	−4.0	5.7	1.3

[a] A negative sign denotes a singlet ground state.

To better understand the differences between acetylnitrene ($CH_3C(=O)N$) and methoxycarbonylnitrene ($CH_3OC(=O)N$), we have performed calculations to predict their ground state multiplicities and reactivity at consistent levels of theory and have attempted to directly compare alkylcarbonylnitrenes and alkoxycarbonylnitrenes with the use of isodesmic equations. Herein, we are pleased to report our results. Some of these predictions are tested by Laser Flash Photolysis studies of benzoylnitrene.

Results

Computational Chemistry. A. Singlet−Triplet Energy Splittings. The singlet−triplet energy splitting of nitrenes **1** and **2** and carbene **3** were computed using B3LYP, CCSD(T), and CBS-QB3 methodologies. In particular, the CBS-QB3 method relies on a B3LYP geometry, a CCSD(T) energy as an estimate for electron correlation, and an extrapolation to the infinite basis set limit. As such, it is the most accurate method utilized in this study. The results are given in Table 1.



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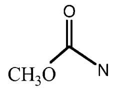

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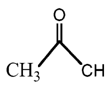

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B3LYP and CCSD(T) methods predict that compounds **1**−**3** will all have triplet ground states, as opposed to CBS-QB3 theory, which indicates that whereas **2** and **3** have triplet ground-state multiplicities, acetylnitrene **1** is predicted to have a singlet ground state. This conclusion is in agreement with G2 calculations by Faustov et al.[12c] B3LYP predicts the triplet nitrenes to be too stable, relative to CBS-QB3, by approximately 8−9 kcal/mol. In the case of the carbene, the discrepancy is only 2.4 kcal/

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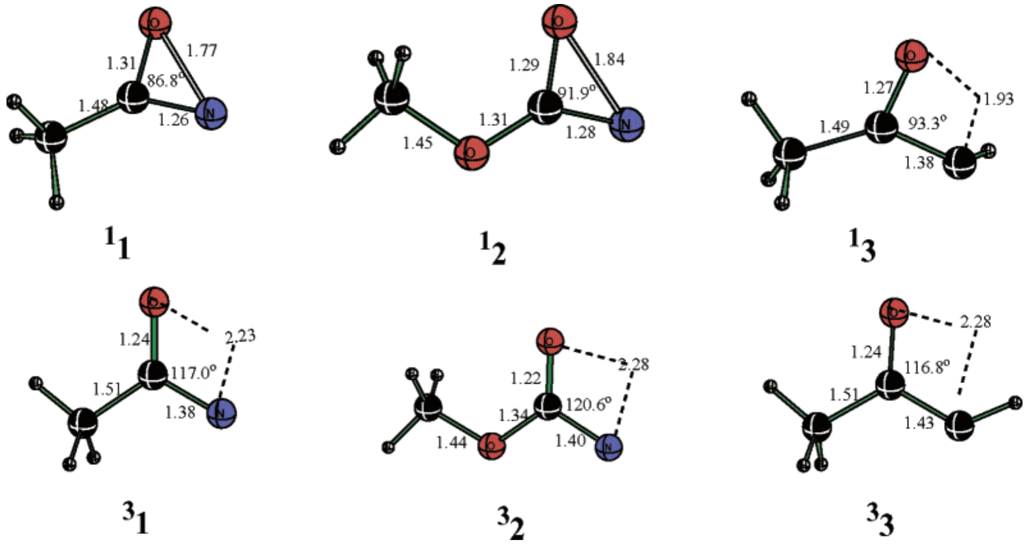
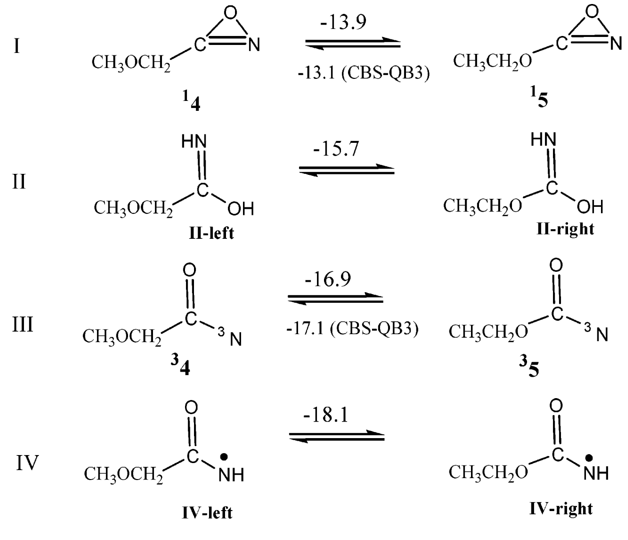


FIGURE 1. Geometries of **1**–**3** in their singlet and triplet states. Distances are shown in Å, and angles are in degrees.

mol. Scott et al. came to similar conclusions in their studies of carbonyl carbenes.[23]

The geometries of **1**–**3** in their singlet and triplet states are shown in Figure 1. The bond distance between the oxygen and nitrogen atoms in the singlet state is about 0.46 Å shorter than that in the triplet state for acetylnitrene, and the O–C–N bond angle in the singlet state is also smaller than that in the triplet state. Therefore, as noted in earlier studies,[13] a bonding interaction between the oxygen and nitrogen atoms provides an explanation for the singlet ground state of acetylnitrene **1**. Methoxycarbonylnitrene **2** and carbene **3** have weaker bonding interactions between oxygen and nitrogen or between oxygen and carbon in their singlet states, as demonstrated by the longer bond distances and larger bond angles (Figure 1). Our results are reminiscent of the results obtained by Pritchina et al.[13] in which B3LYP/6-31G* and CCSD methods, coupled with a complete basis set extrapolation, predicted that H(C=O)N has a triplet ground state, but CCSD(T) with a complete basis set extrapolation predicted that this same species has a singlet ground state.

To better understand why the ground-state multiplicities of **1** and **2** differ, several isodesmic reactions were calculated with DFT methods. To verify the accuracy of DFT methods in this case, CBS-QB3 methods were also applied to the isodesmic reactions I and III. Compared to the CBS-QB3 method, the B3LYP results differ by less than 1 kcal/mol and indicate that DFT is a reliable method for this purpose. Upon consideration of reaction I, it can be seen that singlet methoxycarbonylnitrene **5** is 13.1 kcal/mol more stable than acylnitrene **4** in the singlet state. On comparing the triplet state, methoxycarbonylnitrene ^{3}**5** is even more stable, relative to ^{3}**4**, by 17.1 kcal/mol (reaction III) than the singlet state analogues. The difference in the singlet–triplet energy splitting of **1** and **2** is explained by isodesmic equations II and IV. Conjugation of oxygen with a C(=NH)OH group is stabilizing by 15.7 kcal/mol (reaction II) as in the carbonylnitrene singlet state, but conjugation of oxygen to a C(=O)NH$^{\bullet}$ radical (reaction IV), as in the



ΔH (kcal/mol)
B3LYP/6-311+G**//B3LYP/6-31G*

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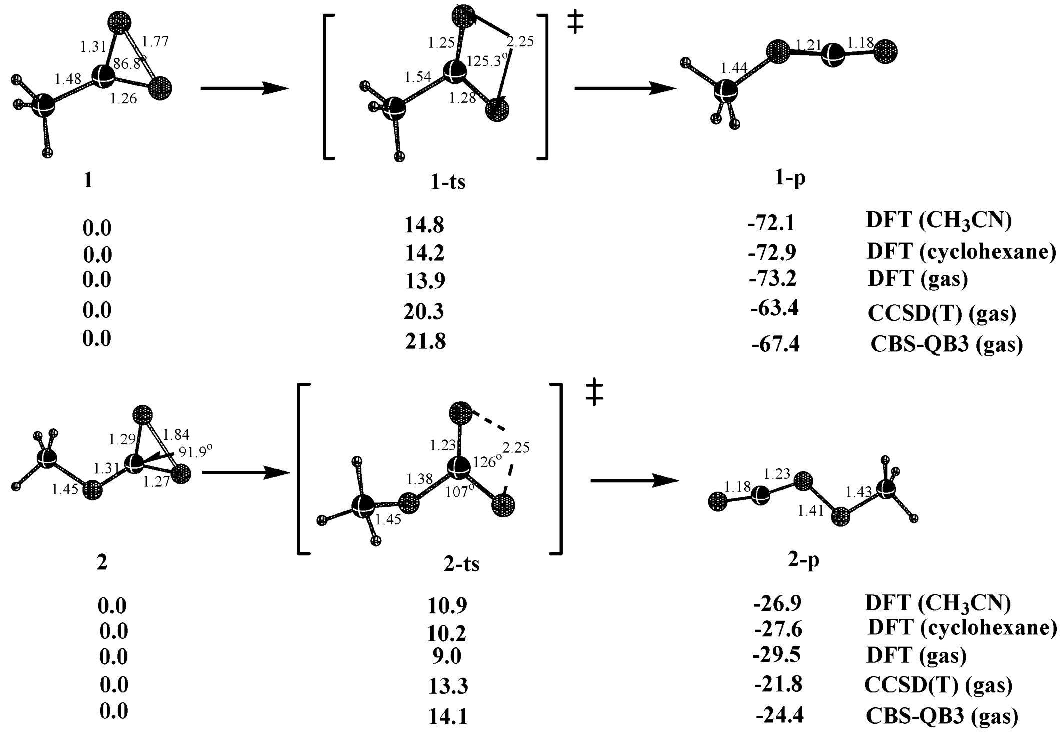
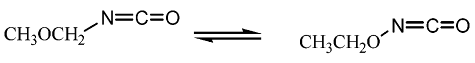


FIGURE 2. Energy surface [ΔG (298 K) (kcal/mol)] for Curtius rearrangement of **1** (top) and **2** (bottom) at the B3LYP/6-311+G**//B3LYP/6-31G* level in acetonitrile and cyclohexane and in the gas phase, as well as CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* and CBS-QB3 levels. Distances are shown in Å, and angles are in degrees.

triplet nitrene, is even more stabilizing (by 18.1 kcal/mol). Thus the methoxycarbonylnitrene has a triplet ground state, and the acetylnitrene does not.

B. Curtius Rearrangement. The reaction surfaces for Curtius rearrangement of nitrenes **1** and **2**, as computed by DFT and CBS-QB3, are shown in Figure 2, and these results are in agreement with previous calculations[12c] on the activation barrier for rearrangement of **1**. The Curtius rearrangement of **1** is substantially more exoergic than that of **2** because a relatively weak N−O bond is formed in the isocyanate product, but surprisingly, rearrangement of **1** has a larger free energy of activation. A substantial solvent effect is not predicted by the polarizable continuum model (PCM) calculations using either polar solvent acetonitrile or the nonpolar solvent cyclohexane for the Curtius rearrangements.

The relative free energies of the two reactions can be understood upon consideration of the following isodesmic equations.



$$CH_3OCH_2{-}N{=}C{=}O \rightleftharpoons CH_3CH_2O{-}N{=}C{=}O$$

6 **7**

$\Delta G = 36.8$ kcal/mol

$$CH_3OCH_2{-}NH_2 \rightleftharpoons CH_3CH_2O{-}NH_2$$

6' **7'**

$\Delta G = 27.8$ kcal/mol

A C−O bond is simply much stronger than an N−O bond, which makes the product of the Curtius rearrangement of **1** much more stable than that of **2**.

To understand the difference in the respective activation barriers, the isodesmic reactions shown in Figure 3 were calculated for the configurational isomers: ethoxycarbonylnitrene **5** and methoxymethylacylnitrene **4**. The transition state for Curtius rearrangement of **5** is 20−30 kcal/mol more stable relative to the transition state for Curtius rearrangement of its isomeric methoxymethylacylnitrene **4**. The oxygen atom present in **5** is responsible for an interaction that stabilizes the transition state for the Curtius rearrangement. This interaction is not present in the transition state of the isomeric acylnitrene **4**. The extra oxygen atom stabilizes the transition state of Curtius rearrangement more than it stabilizes nitrene **5**, and thus methoxycarbonylnitrene should rearrange faster than acetylnitrene. Thus we predict that Curtius rearrangement of singlet acetylnitrene **1** will be much slower than that of singlet methoxycarbonylnitrene **2,** despite the greater exoergicity of the former process. Furthermore, Curtius rearrangement of **1** should not be competitive with bimolecular reactions of this nitrene at ambient temperature. This is in good agreement with the reports of Lwowski and co-workers.[3,5]

We also considered a concerted pathway for Curtius rearrangement from the precursor azides for isocyanate formation (Figure 4). CBS-QB3 calculations find two stable conformations of acetyl azide in a manner reminiscent of diazo carbonyl compounds.[24] To the best of our knowledge, experimental studies of the conformational isomerism of methoxycarbonyl azide or acetyl azide have not been reported; however, experimental and computational studies of fluorocarbonyl azide ($F(C{=}O)N_3$) have

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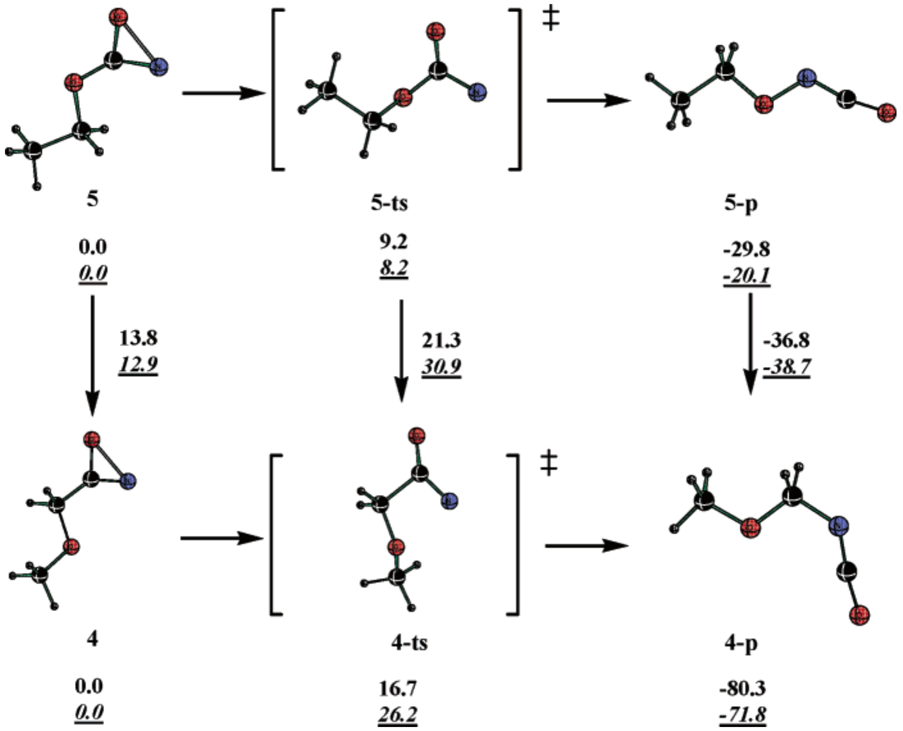


FIGURE 3. Energy surface [ΔG (298K) (kcal/mol)] and isodesmic reactions for Curtius rearrangement of **5** and an isomeric analogue **4** at the B3LYP/6-311+G**//B3LYP/6-31G* (top) and CBS-QB3 (bottom) levels of theory. Distances are shown in Å, and angles are in degrees.

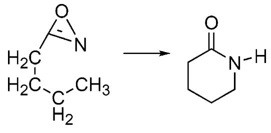
been reported[25] and the conformer with syn relationship between the carbonyl and the azide group is favored as we predict for acetyl azide. In the gas phase for acetyl azide, the less stable form ($\Delta G = 4.5$ kcal/mol at the CBS-QB3 level) positions the azide group anti to the carbonyl group. The energy difference is slightly reduced in cyclohexane (4.1 kcal/mol) and in acetonitrile (3.2 kcal/mol). CBS-QB3 theory predicts that this conformer will extrude nitrogen ($\Delta G^{\neq}$ ~32 kcal/mol) to form acetylnitrene, which can subsequently isomerize to methylisocyanate in the absence of trapping agents.

The lower energy conformer (by 4.5 kcal/mol) of acetyl azide has a syn relationship between the carbonyl and the azide groups. CBS-QB3 theory predicts that acetyl azide will decompose by concerted migration of the methyl group along with nitrogen extrusion and that the free energy of activation for this concerted process is only 27 kcal/mol. Thus we predict that a free nitrene is not produced upon pyrolysis of acetyl azide. This explains the failure of Lwowski and co-workers to intercept pivaloylnitrene upon pyrolysis of pivaloyl azide.[3] In this Curtin–Hammett situation, the relative barriers between concerted and stepwise Curtius rearrangement may, of course, be very sensitive to substituents on the carbonyl group. Indeed, for methoxycarbonyl azide (Figure 4b), the stepwise process to generate the free nitrene is favored over the concerted Curtius rearrangement. This is in good agreement with experimental studies of alkoxycarbonyl azides,[7,8] which do form trappable alkoxycarbonylnitrenes upon thermolysis. Essentially the alkoxy group stabilizes the alkoxycarbonylnitrene and destabilizes the alkoxyisocyanate. These effects are felt by the transition states that lead to these products. Thus, formation of the alkoxycarbonylnitrene is formed in the pyrolysis of the alkoxycarbonyl azide.

This computational result is well-precedented as Kaplan, Meloy, and Mitchell[26] have experimentally demonstrated similar behavior in carbonyl-substituted diazo compounds. Pyrolysis of syn diazo carbonyls leads to Wolff rearrangement in concert with loss of nitrogen, but heating compounds with anti-disposed carbonyl and diazo groups produces the trappable carbene.

The barriers predicted for loss of nitrogen are consistent with the activation energies to thermal decompostion of a number of azides.[27] The barriers to decomposition of phenylacetyl azide and benzoyl azide in toluene are 21.5 and 27.1 kcal/mol, respectively.

C. Intramolecular C–H Insertion. The potential energy surfaces for the intramolecular C–H insertion reactions of **8** and **9** were calculated using DFT methods. The insertion reaction of **9** is about 1.8 kcal/mol more exoergic than that of **8** and has a smaller free energy of activation barrier by about 0.7 kcal/mol (see Supporting



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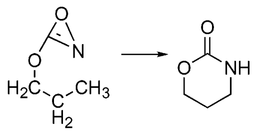

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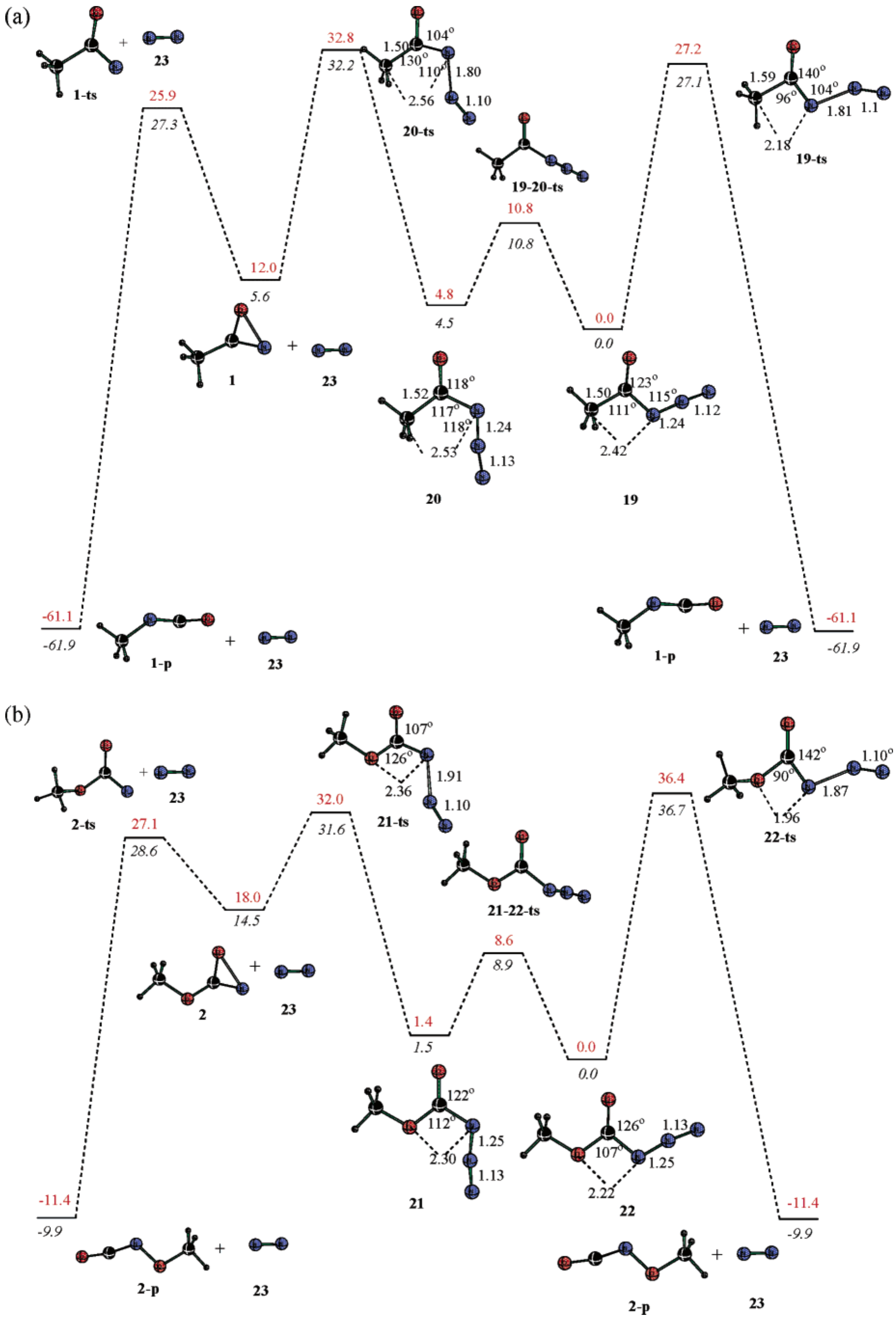

FIGURE 4. Energy surface [Δ*G* (298 K) (kcal/mol)] for stepwise and concerted Curtius rearrangement of (a) acetyl azide and (b) methoxycarbonyl azide at the B3LYP/6-311+G**//B3LYP/6-31G* (red, top) and CBS-QB3 (black, bottom) levels of theory. Distances are shown in Å, and angles are in degrees.

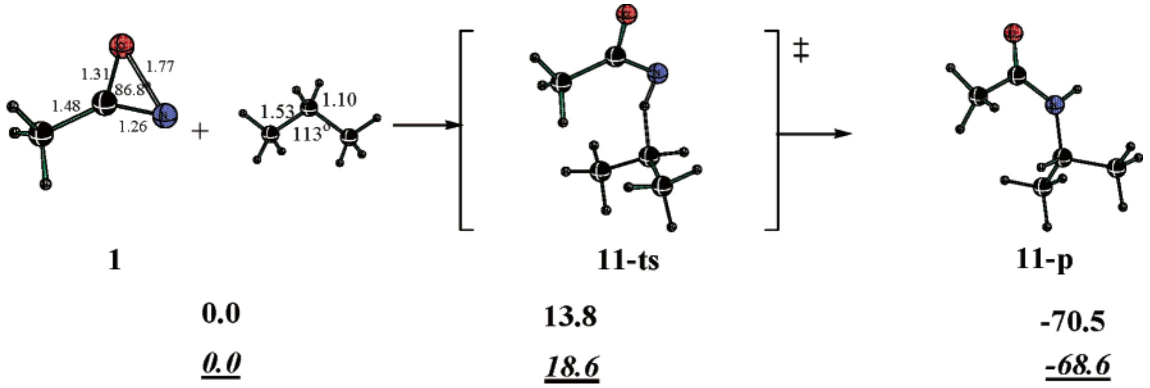

FIGURE 5. Energy surface [Δ*G* (298 K) (kcal/mol)] for the reaction of singlet **1** with propane at the B3LYP/6-311+G**//B3LYP/6-31G* (top) and *CBS-QB3* (bottom) levels of theory. Distances are shown in Å, and angles are in degrees.

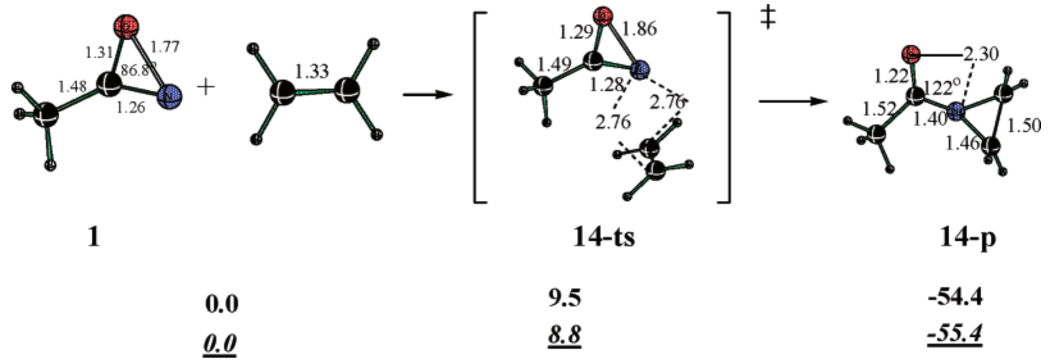

FIGURE 6. Energy surface [Δ*G* (298 K) (kcal/mol)] for the reaction of singlet **1** with ethylene at the B3LYP/6-311+G**//B3LYP/6-31G* (top) and *CBS-QB3* (bottom) levels of theory. Distances are shown in Å, and angles are in degrees.

Information). In each case, the free energy of activation is positive but the enthalpy of activation is slightly negative. The barriers of these reactions are entirely entropic as found previously for the reaction of dichlorocarbene with alkenes.[28, 29]

D. Bimolecular Reactions. Energy surfaces for the reactions of singlets **1** and **2** with propane, ethylene, and methanol were calculated by both DFT and CBS-QB3 methods. The results are given in Figures 5−7. Both methods predict that all of these reactions with singlet acetylnitrene (**1**) and methoxycarbonylnitrene (**2**) are extremely exoergic. The reactions of **1** with propane are the most exoergic, −68.6 kcal/mol. The alkene cycloaddition reactions are exoergic by about −55 kcal/mol, and the O−H insertion reactions are the least exoergic, with a change of free energy of approximately −40 kcal/mol. Compound **2** reacts more exoergically than **1** in all three reactions. The changes in activation enthalpies are given in Figures 5−7, as well as the changes in free energies.

Indeed, transition-state structures could be located for the propane and ethylene reactions with acetylnitrene (**1**) wherein the target reactant approaches anti to the carbonyl oxygen of the nitrene. A transition state for attack syn to the carbonyl oxygen could be located, but it does not lead to an insertion product (see Supporting Information).[13b] Instead, the syn transition state leads to the Curtius rearrangement as verified by an IRC calculation. In essence, syn attack corresponds to a concerted Curtius rearrangement with the small effect of solvation by an associated propane or ethylene molecule. However, for methoxycarbonylnitrene (**2**), transition states for true insertion into the C−H bond of propane and into the C═C bond of ethylene could not be located (see Supporting Information). Instead, the reactions of **2** with propane and ethylene are barrierless processes and proceed directly to products. Once again, approach of the substrate to the nitrene occurs anti to the carbonyl oxygen.

Two unique transition states for **1** and for **2** could be located for reactions with methanol. These transition states, once again, differ by the orientation of the substrate relative to the carbonyl oxygen of the nitrene, and in general, anti attack is preferred (see Figure 7 and Supporting Information). The O−H insertion barrier for methoxycarbonylnitrene (**2**) is lower than that of compound **1** by ~5 kcal/mol. Activation enthalpies are close to zero and are even negative in certain cases. This is reminiscent of the experimental findings of Moss and Turro[28] and the theoretical work of Houk and Rondan[29] that demonstrated that the free energy barriers to bimolecular reactions of halocarbenes are dominated by unfavorable entropic changes. In each case calculated

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(29) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

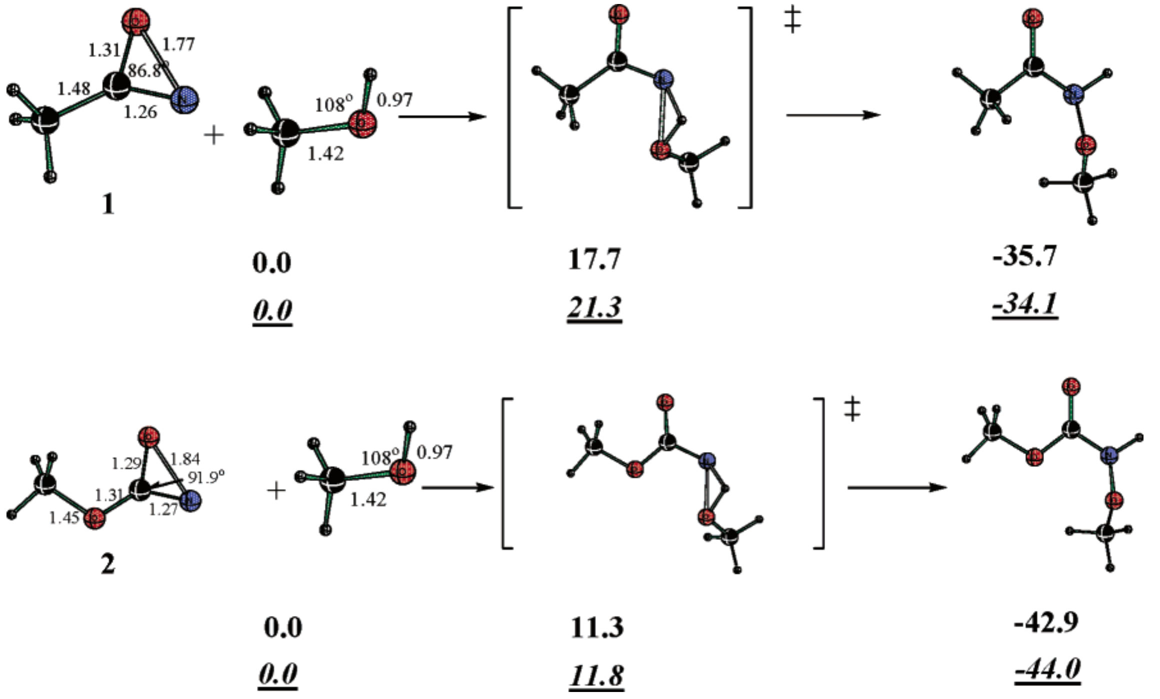
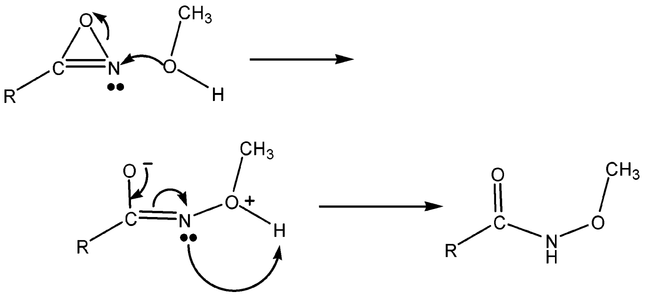


FIGURE 7. Energy surface [ΔG (298K) (kcal/mol)] for the reaction of singlet **1** and **2** with methanol at the B3LYP/6-311+G**//B3LYP/6-31G* (top) and CBS-QB3 (bottom) levels of theory. Distances are shown in Å, and angles are in degrees.

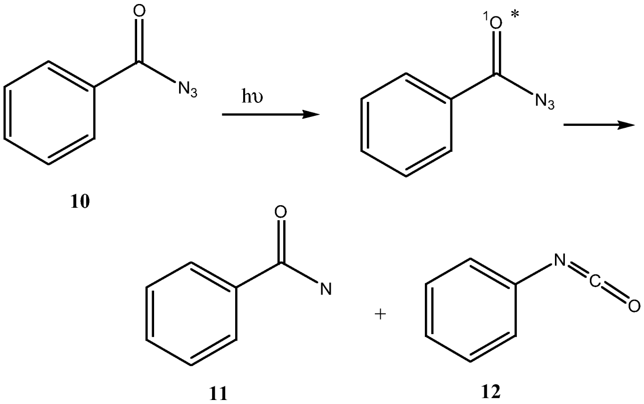
here, the bimolecular reactions look like nucleophilic attack on nitrogen.



The calculations predict that bimolecular reactions of singlet acetylnitrene and methoxycarbonylnitrene will be faster than the Curtius rearrangements of these species, particularly at low temperatures where the unfavorable $T\Delta S$ component of the free energy barrier is small.

Laser Flash Photolysis Studies. To test the predictions of computational chemistry, laser flash photolysis (LFP) studies were performed. Benzoyl azide was studied because it has previously received considerable attention, is easier to handle than acetyl azide, and should have a superior UV−vis chromophore to facilitate LFP studies.[13] Chemical trapping studies are consistent with the intermediacy of benzoylnitrene, and the bulk of the studies are consistent with an intermediate with a singlet ground state.[30−33] This conclusion is supported by the failure to detect a triplet ESR spectrum upon photolysis of benzoyl azide in a matrix at low temperature[5,7] and the excellent agreement of the IR spectrum of benzoylnitrene in an argon matrix with that predicted by theory for the singlet ground state.[13]

Laser flash photolysis (LFP, XeCl excimer laser, 308 nm, 17 ns) of benzoyl azide **10** in $CF_2ClCFCl_2$ (Freon-113) solvent produces the transient spectrum of benzoylnitrene in its singlet ground state (Figure 8). The transient spectrum observed is in good agreement with the spectrum of this species obtained in an argon matrix and with the predictions of CASSCF/CASPT2 procedures.[13]



10

11

12

We find that the lifetime of benzoylnitrene (**11**) in deoxygenated Freon-113 is approximately 2 μs. The lifetime of **11** in acetonitrile is 330 ns as measured by time-resolved IR (TRIR) spectroscopy using relatively concentrated samples.[13a]

Benzoylnitrene (**11**) reacts with pyridine to form an ylide (Supporting Information). The spectrum of the ylide formed by reaction of **11** with *p*-cyanopyridine is particularly intense (Figure 9, λ_{max} = 380−390 nm), and ylide

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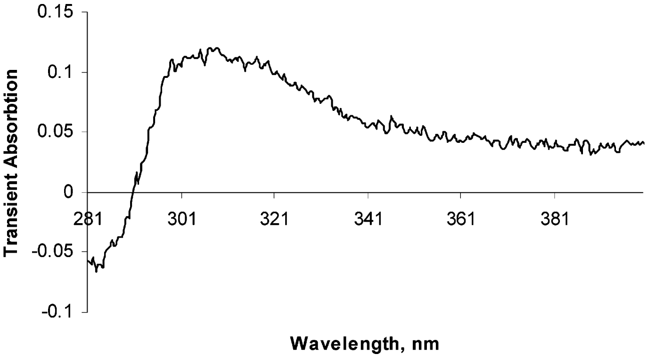


FIGURE 8. Transient spectrum of benzoylnitrene (**11**) produced by 308 nm LFP of benzoyl azide in $CF_2ClCFCl_2$ at ambient temperature. The spectrum was recorded 10 ns after the laser pulse over a window of 20 ns.

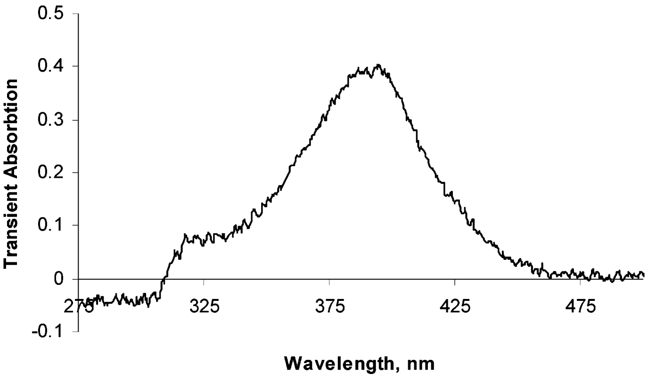
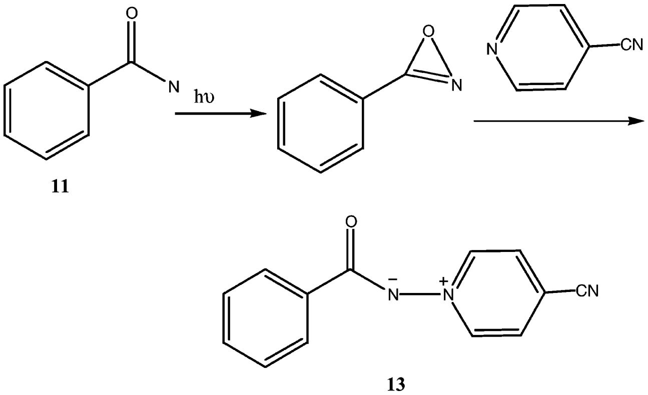


FIGURE 9. Transient spectrum of ylide **13** produced by 308 nm LFP of benzoyl azide in $CF_2ClCFCl_2$ containing 0.1 M *p*-cyanopyridine. The spectrum was recorded over a 20 ns window, 100 ns after the laser pulse.

13 is indefinitely stable in solution. The ylide structure was confirmed by X-ray crystallography (Supporting Information).



The lifetime of **11** is reduced in the presence of quenchers. A plot of $1/\tau$ versus [acetonitrile] is linear (Figure 10) with slope equal to the absolute rate constant of reaction of benzoylnitrene (**11**) with acetonitrile. Absolute reaction rate constants of benzoylnitrene obtained in this manner are collected in Table 2.

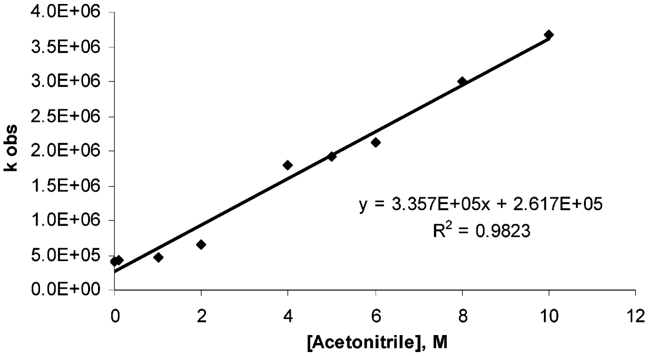


FIGURE 10. Plot of the observed rate constant for the disappearance of benzoylnitrene (**11**) as a function of [acetonitrile] in $CF_2ClCFCl_2$.

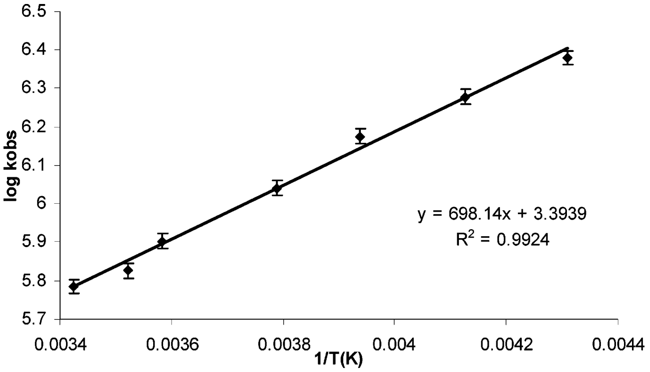


FIGURE 11. Plot of the log k_{obs} for the decay of benzoylnitrene (**11**) in pentane versus $1/T$ (in K).

TABLE 2. Absolute Rate Constants for Reaction of Benzoylnitrene (11) with Various Quenchers at Ambient Temperature

substrate	solvent	k (M^{-1} s^{-1})
CH_3CN	$CF_2ClCFCl_2$	$(3.4 \pm 0.6) \times 10^5$
CH_3OH	$CF_2ClCFCl_2$	$(6.5 \pm 0.4) \times 10^6$
CF_3CH_2OH	$CF_2ClCFCl_2$	$(1.7 \pm 0.1) \times 10^8$
H_2O	CH_3CN	$(4.0 \pm 0.2) \times 10^6$
cyclohexane	$CF_2ClCFCl_2$	$(1.8 \pm 0.2) \times 10^5$
$CH_3CH_2CH_2CH_2NH_2$	CH_3CN	$(6.6 \pm 0.4) \times 10^8$
1-methylcyclohexene	$CF_2ClCFCl_2$	$(4.2 \pm 0.2) \times 10^7$
2,3-dimethylbutene	$CF_2ClCFCl_2$	$(2.2 \pm 0.1) \times 10^7$
1-hexene	$CF_2ClCFCl_2$	$(1.1 \pm 0.04) \times 10^7$
trans-1,2-dichloroethylene	$CF_2ClCFCl_2$	$(4.2 \pm 0.5) \times 10^6$
DABCO	CH_3CN	$(3.7 \pm 0.1) \times 10^8$
p-cyanopyridine	CH_3CN	$(2.3 \pm 0.03) \times 10^8$

The lifetime of benzoylnitrene in pentane decreases as the temperature decreases. An Arrhenius treatment of the temperature dependence of the pseudo-first-order decay of benzoylnitrene is shown in Figure 11. The apparent activation energy for the disappearance of benzoylnitrene is −3.2 kcal/mol.

Benzoyl azide was photolyzed in pentane at 223 and 298 K, the extremes of the Arrhenius plot of Figure 11. The products of photolysis were analyzed by GC−MS at each temperature, and C−H insertion products were the only products detected at both temperatures (see Supporting Information). It is clear that C−H insertion is the major reaction channel at 223 and 298 K but is not necessarily the only process that consumes benzoylnitrene in pentane. Thus, the negative activation energy of −3.20 ± 0.02 kcal/mol is an effective activation energy only and cannot be associated with an elementary process.

To obtain the activation energy of an elementary process, a more rapid quencher of benzoylnitrene was

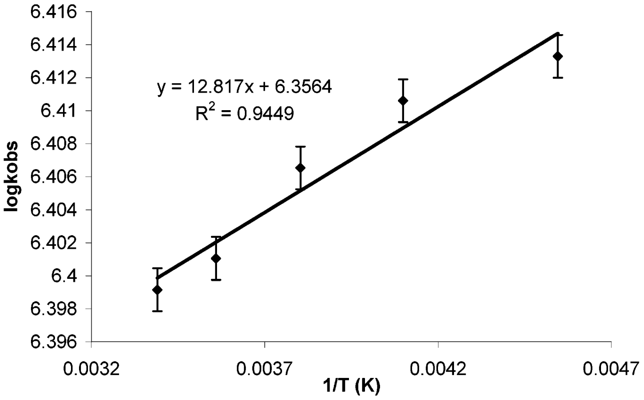


FIGURE 12. Plot of the log of the absolute rate constant for reaction of benzoylnitrene (**11**) with 1-hexene in $CF_2ClCFCl_2$ versus 1/*T* (in K).

studied. The absolute rate constant for reaction of benzoylnitrene with 1-hexene in $CFCl_2CFCl_2$ at a given temperature was determined by measuring the observed rate of decay of benzoylnitrene as a function of alkene concentration. This process was repeated at several temperatures. An Arrhenius treatment of the data is given in Figure 12. The activation energy for the reaction of singlet benzoylnitrene with 1-hexene is −0.06 ± 0.001 kcal/mol.

On the basis of previously reported[30−33] product studies, we expected that the kinetics of benzoylnitrene with alkenes and alkanes correspond to typical addition and insertion chemistry. This is consistent with GC−MS analysis of the products formed in photolysis of benzoyl azide in pentane containing 1-hexene (see Supporting Information). The laser flash photolysis results indicate that the enthalpy of activation for C−H insertion is slightly negative and that for addition is essentially zero. The latter result is in excellent agreement with the value predicted by theory for the reaction of acetylnitrene with ethylene. This demonstrates that the addition of benzoylnitrene to 1-hexene is dominated by entropic factors in a manner reminiscent of the addition of singlet carbenes to olefins.

Conclusions

CBS-QB3 calculations correctly predict that methoxycarbonylnitrene has a triplet ground state, whereas acetylnitrene has a singlet ground state. B3LYP/6-311+G**//B3LYP/6-31G*, CCSD(T)/6-311+G**//B3LYP/6-31G*, and CCSD(T)/aug-cc-pDVZ//B3LYP/6-31G* calculations incorrectly predict that acetylnitrene has a triplet ground state. Isodesmic reactions reveal that the oxygen atom stabilizes both the singlet and triplet states of the carbonyl nitrenes but stabilizes the triplet more than the singlet state. Thus, methoxycarbonylnitrene has a triplet ground state. Our calculations are consistent with that of earlier studies[12,13] that indicated a significant bonding interactions in the singlet state of acetylnitrene. We find a comparable (but slightly weaker) interaction in the singlet state of methoxycarbonylnitrene.

The Curtius rearrangement of singlet acetylnitrene is much more exoergic than that of methoxycarbonylnitrene. Nevertheless, the Curtius rearrangement of the methoxycarbonylnitrene is predicted to be faster than that of acetylnitrene because the oxygen atom stabilizes the transition state of the Curtius rearrangement of methoxycarbonylnitrene.

Bimolecular reactions of singlet acetylnitrene and methoxycarbonylnitrene with propane, ethylene, and methanol have enthalpic barriers that are close to zero and free energy barriers that are completely entropic in nature, as found previously for halocarbene singlet states.[20,21] Bimolecular reactions of the singlet states of acetylnitrene and methoxycarbonylnitrene will be much faster than the Curtius rearrangement, particularly at low temperatures.

These predictions were tested by laser flash photolysis (LFP) studies of benzoylnitrene. Absolute rate constants of the reaction of benzoylnitrene with several substrates were determined at ambient temperature. The pseudo-first-order rate constant of decay of benzoylnitrene in pentane increases as the temperature decreases. The apparent activation energy is −3.20 ± 0.02 kcal/mol. The activation energy for the reaction of benzoylnitrene with 1-hexene is essentially zero. The LFP data demonstrate that entropic factors control the bimolecular reactivity of benzoylnitrene as predicted by theory.

Experimental Methods

Synthesis of Benzoyl Azide. Benzoyl azide was synthesized by the method of Barret et al.[33] Briefly, benzoyl chloride (7.0 g, 0.05 mol) was dissolved in 12.5 mL of acetone. To this mixture was slowly added a solution of NaN_3 (3.7 g, 0.057 mol) in 10 mL of water at 0 °C. When addition of the NaN_3 solution was complete, the reaction was allowed to mix at 0 °C for 30 min. Two layers formed and the top layer was removed and dried with anhydrous magnesium sulfate. The dried solution had the solvent removed in vacuo to yield a white solid. Mp: 24−25 °C. IR (NaCl, neat): 2135, 1693, 1600 cm^{-1}. ^{13}C NMR ($CDCl_3$): 128.66, 129.47, 131.00, 135.01, 172.00 ppm. UV max: 240 nm.

Materials. All quenchers were purchased at 99.5% purity and used as received with the exception of pyridine, which was distilled from KOH before using.

Laser Flash Photolysis of Benzoyl Azide. Apparatus. A Nd:YAG laser (17 ns, 10 mJ, 266 nm) and a Lambda Physics LPX (XeCl, 30 ns, 50 mJ, 308 nm) were used as the excitation light sources.

Laser flash photolysis experiments with benzoyl azide were performed using either a 266 or 308 nm pump and were probed at 320 nm. The Ohio State University ns spectrometer has been described elsewhere.[35] Briefly, all samples were dissolved in spectroscopic grade solvent to an absorption of 1 at either 266 or 308 nm and placed in a 3-mL quartz cuvette. Samples were not purged before use. Transient UV spectra were obtained using a CCD camera as described elsewhere.[35] For variable temperature experiments, the temperature was controlled by passing a thermostabilized nitrogen gas stream and kept within 1 K of the reported temperature. In the Arrhenius plots, at least three kinetic traces were obtained.

Isolation of *p*-Cyanopyridine Benzoylnitrene Ylide. Benzoyl azide (0.043 g, 0.29 mM) and *p*-cyanopyridine (0.037 g, 0.355 mM) were dissolved in 3 mL of dichloromethane. The reaction was irradiated with 365 nm light for 2 h. The solvent was then removed under reduced pressure to yield a yellow oil. This oil was then purified on a silica gel column and eluted with acetone and hexanes. The product was isolated in the

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[34] Barret, E. W.; Porter, C. W. *J. Am. Chem. Soc.* **1941**, *63*, 3434.

[35] Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 2833.

third fraction and identified by X-ray crystallography (Supporting Information).

Product Studies of Benzoyl Azide at 285 and 240 K. A 0.29 M solution of benzoyl azide in pentane in the presence or absence of 3.7 M 1-hexene was placed in a quartz cuvette and irradiated with 254 nm mercury lamps in a Rayonet photoreactor until no more starting material was present. The sample was then analyzed by GC−MS to determine products and ratios. Samples irradiated at 240 K were kept in a dry ice/acetonitrile bath maintained at 240 K during photolysis.

Computational Methods

Density functional theory (DFT)[14] and ab initio methods[15] have been applied in this study. The geometries were completely optimized at the B3LYP/6-31G* level. Analytical vibrational frequencies were calculated at the same level for each stationary point to verify a minimum energy structure and to provide zero-point vibrational energy corrections, which were scaled by a factor of 0.9806.[16] Each transition state was verified to connect to the respective reactant and product by careful optimization (opt = calcfc or calcall) after displacement (typically 10%) along the reaction path for the normal coordinate of the imaginary vibrational frequency. In some cases, intrinsic reaction coordinate (IRC)[17] calculations were also performed. The zero-point vibrational energies as well as thermal and entropic contributions to the free energies were obtained from the B3LYP/6-31G* frequency calculations; the thermal and entropic corrections used the unscaled vibrational frequencies. Single-point energy calculations of all stationary points were performed at the B3LYP/6-311+G** level using the corresponding B3LYP/6-31G* geometries. Six Cartesian d functions were used for these calculations.

In some cases, CCSD(T)[18] singlet-point energies were evaluated using the B3LYP/6-31G* geometries, with the 6-311+G** (6d) basis set as well as Dunning's correlation consistent basis set, aug-cc-pVDZ.[19] For further comparison, Complete Basis Set (CBS) methods[20] have also been applied to increase the accuracy of the results. The energies provided are CBS-QB3 enthalpies and free energies at 298.15 K. All stationary points, including transition states, were re-characterized at the CBS-QB3 level, complete with full geometry optimization at the required level. To study the influence of solvent, polarizable continuum model (PCM)[21] calculations were used for the Curtius rearrangement with acetonitrile and cyclohexane as solvents. Population analyses were performed at the B3LYP/6-311+G**//B3LYP/6-31G* level using the natural population analysis (NPA)[36] method of Weinhold and co-workers.

All DFT, CCSD(T), and CBS-QB3 calculations were performed with Gaussian 98[22] at the Ohio Supercomputer Center.

Acknowledgment. Support of this work by the National Science Foundation and the Ohio Supercomputer Center is gratefully acknowledged.

Supporting Information Available: Tables of energies, Cartesian coordinates, vibrational frequencies, and selected figures of computational and experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Reed, A. E.; Weinhold, F.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899.