6-Oxocyclohexa-2,4-dienylideneketene: A Highly Reactive α-Oxoketene

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Abstract: The title ketene **2** has been generated by laser flash photolysis and observed in solution for the first time, using time-resolved infrared spectroscopy. The kinetics of the reactivity of **2** with H_2O, MeOH, and Et_2NH with relative reactivities of 1.0, 2.0, and 73 have been measured. These are the first direct measurements of the reactivities of a ketene with these different nucleophiles under the same conditions. Ab initio molecular orbital calculations indicate the hydration occurs by in-plane attack of the H_2O molecule on the ketenyl carbonyl through a pseudopericyclic transition state with assistance by coordination to the keto-carbonyl.

α-Oxoketenes have been the subject of continuing chemical study because of their interesting structural features, high reactivity, and synthetic utility.[1] Photolysis of 2-phenyl-3,1-benzoxan-4-one (**1**) at 77 K gave an IR band at 2118 cm^{-1} attributed to the title ketene **2** (*Chemical Abstracts* name 2,4-cyclohexadien-1-one, 6-carbonyl [21083-33-0]), which was trapped by MeOH to give methyl salicylate (eq 1).[2a] Photolysis of **3** was also reported to give **2**, as evidenced by capture with water, phenol, or benzoic acid,[2b] and matrix photolysis of the peroxide **4** was suggested to give **2**, as identified by comparison with the UV spectrum observed from photolysis of **1** or **3**.[2c] This latter transformation was suggested to involve the intermediacy of lactone **5**.[2c] Photolysis of **4** at 8 K gave rise to IR bands at 2139 and 1650 cm^{-1} assigned to **2**,[2d] and an IR absorption at 1904 cm^{-1} was assigned to **5**.[2d] The photoelectron spectrum of **2** generated by pyrolysis of salicylic acid has also been reported.[2e] The formation of some polycyclic analogues of **2** from diazoketones has also been suggested.[2f]
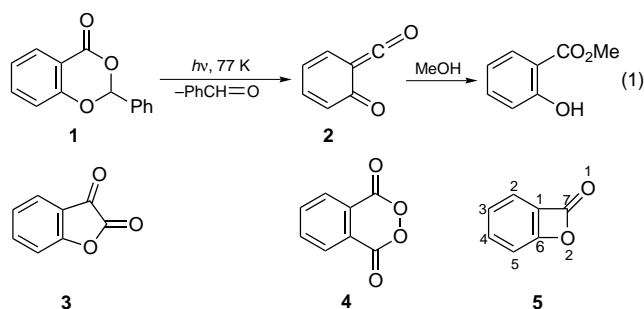
The 1,4-isomer **6** of **2** and its 2,6-dimethyl analogue have been suggested to be intermediates in the base induced hydrolysis of aryl 4-hydroxybenzoates **7** (eq 2).[3a,b] Formation of **6**, identified by its IR bands at 2110 and 1635 cm^{-1} at 10 K in an Ar matrix, was also reported from CO addition to the corresponding carbene.[3c] It was also proposed[3a] by analogy to calculations on the exomethylene analogue of **6**[3d] that nucleophilic attack on such ketenes would be favored to occur from a perpendicular direction at the ketenyl carbonyl carbon. This is contrary to the accepted mechanism of nucleophilic addition to other ketenes.[1a]
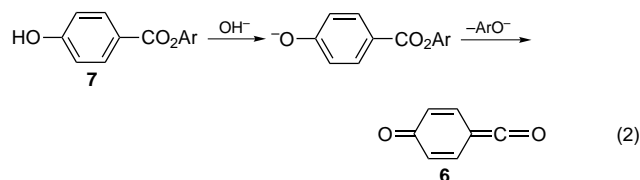
α-Oxoketenes are characterized by their high reactivity,[1] including unusual rearrangements,[1i,j] concerted additions involv-

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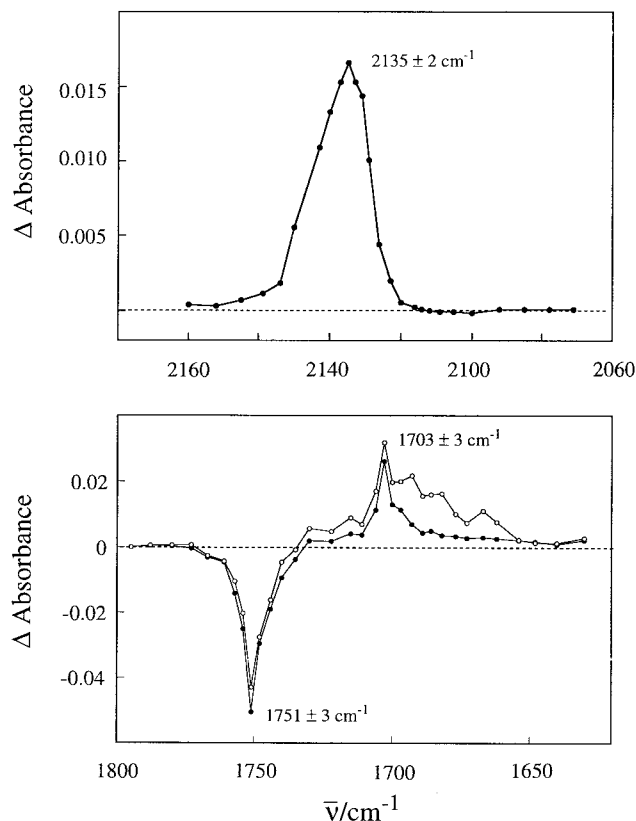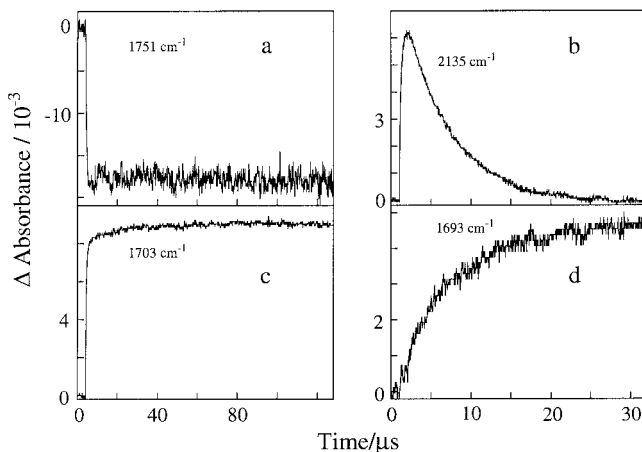
Figure 1. IR spectra observed upon 308 nm LFP of **1** in CH$_3$CN. Top: Ketenyl absorption of **2** at 2135 cm^{-1}. Bottom: Spectra observed 1 μs (filled circles) and 25 μs (open circles) after the laser pulse indicating instantaneous bleaching of the lactone band of **1** at 1751 cm^{-1}, instantaneous formation of benzaldehyde absorption at 1703 cm^{-1}, and growth of absorptions in the 1680–1700 cm^{-1} region corresponding to salicylic acid.

ing the α-oxo and ketenyl groups,[1f,k] and their ability to promote DNA cleavage.[1h] The latter reaction has been shown to involve amide formation by nucleophilic attack of the NH$_2$ group of guanine residues with a highly electrophilic α-oxoketene.[1h] The ketene **2** also possesses a restricted geometry and upon conversion to salicylic acid derivatives (eq 1) gains in aromatic stabilization, and might be expected to have enhanced reactivity. There have, however, been no quantitative studies on the structure and reactivity of this interesting intermediate, and no studies of the relative stabilities of **2** and the ring-closed form **5**. Reported herein are the first generation and observation of **2** in solution at room temperature, quantitative reactivity studies of this species with nucleophiles, and theoretical studies of its structure and reaction mechanism with H$_2$O.

Results

Laser flash photolysis of **1**[4] in CH$_3$CN with 308 nm light and time-resolved infrared detection (TRIR)[5] resulted in the irreversible disappearance of the IR band of **1** at 1751 cm^{-1} and the instantaneous formation of new IR bands at 2135 and 1703 cm^{-1}, identified as due to the ketene absorption of **2**, and the benzaldehyde carbonyl, respectively (Figure 1). The band

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Figure 2. Kinetic traces obtained upon 308 nm LFP of **1** in CH$_3$CN. (a) Irreversible disappearance of absorption of **1** at 1751 cm^{-1}. (b) Exponential decay of absorption of **2** at 2135 cm^{-1}. (c) Generation of the benzaldehyde absorption at 1703 cm^{-1}. (d) Exponential growth of absorption of salicylic acid (**10**) formed from **2** and H$_2$O, monitored at 1693 cm^{-1}.
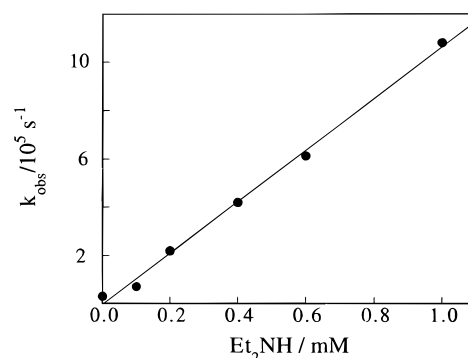
Figure 3. Quenching plot of **2** in CH$_3$CN by Et$_2$NH.

at 2135 cm^{-1} disappeared with first-order kinetics (Figure 2), even in CH$_3$CN freshly distilled from CaH$_2$, and this reaction was shown to involve hydration by adventitious H$_2$O by the observation of the concurrent growth of the IR absorption of salicylic acid at 1693 cm^{-1}, and by the observation of a linear dependence on [H$_2$O] of the rate of reaction of **2**, which indicated a [H$_2$O] of 0.0026 M in the distilled CH$_3$CN. No IR band near 1900 cm^{-1} attributable to the lactone **5** was observed. The observed rate constants for first-order disappearance of **2** in CH$_3$CN gave linear plots as a function of the concentration of H$_2$O, MeOH, and Et$_2$NH (Figure 3), and these gave rate constants at 22 °C, $k_2 = (1.5 \pm 0.3) \times 10^7$, $(3.0 \pm 0.6) \times 10^7$, and $(1.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, respectively.

The reaction of photogenerated **2** with MeOH has been shown to give methyl salicylate (eq 1)[2a] and the formation of salicylic acid upon hydration has also been reported previously.[2b] The assignment of the salicylic acid IR absorption in CH$_3$CN was confirmed by measurement of an absorption of an authentic sample at 1684 cm^{-1}. The reaction of α-oxoketenes with amines to form amides is also well-known.[1b,k] No dimeric products from **2** have been found by us or others,[2] and the observed first-order kinetics for the disappearance of **2** in the presence of nucleophiles show that dimerization is not significant under these conditions.

Ab initio molecular orbital calculations of the structure and energy of **2** and **5**, an initial complex **8** of **2** with H$_2$O, a transition state **9** for hydration of **2**, and two conformations **10a** and **10b** of salicylic acid (the reaction product of **2**) were carried

Table 1. Calculated Energies and ZPVE (hartrees) and Relative Energies (kcal/mol) of Ketene **2** and Related Structures

level[a]	2	5	8	9	10a	10b	12
HF/6-31G*	−417.0923	−417.0864	−493.1112	−493.1004	−493.1835	−493.1892	−493.1520
ZPVE (×0.9)[b]	0.0882	0.0895	0.1108	0.1127	0.1169	0.1172	0.1150
E_{rel}[c]	0.0	4.5 (5.8)[d]	−3.9[e]	4.0[e]	−45.5[e]	−48.9[e]	−26.9[e]
MP2//HF	−418.3060	−418.3098	−494.5121	−494.5191	−494.5872	−494.5924	−494.5581
E_{rel}[c]	0.0	−1.6 (−0.3)[d]	−5.2[e]	−8.4[e]	−48.5[e]	−51.5[e]	−31.4[e]
MP3//HF	−418.3184	−418.3213					
E_{rel}[c]	0.0	−1.0 (0.3)[d]					
MP4 (SDQ)//HF	−418.3402	−418.3384					
E_{rel}[c]	0.0	1.9 (3.2)[d]					
QCISD//HF	−418.3414	−418.3408					
E_{rel}[c]	0.0	1.2 (2.5)[d]					
MP2//MP2	−418.3137	−418.3153	−494.5213		−494.5931	−494.5983	
E_{rel}[c]	0.0	−0.2 (1.1)[d]	−6.8[e]		−46.5[e]	−49.8[e]	
MP3//MP2	−418.3202	−418.3236					
E_{rel}[c]	0.0	−1.3 (0.0)[d]					
MP4(SDQ)//MP2	−418.3453	−418.3427					
E_{rel}[c]	0.0	2.4 (3.7)[d]					
QCISD//MP2	−418.3463	−418.3452					
E_{rel}[c]	0.0	1.5 (2.8)[d]					

[a] HF/6-31G*//HF/6-31G*; MP2/6-31G*//HF/6-31G*; MP3/6-31G*//HF/6-31G*; MP4(SDQ)/6-31G*//HF/6-31G*; QCISD/6-31G*//HF/6-31G*; MP2/6-31G*//MP2/6-31G*; MP3/6-31G*//MP2/6-31G*; MP4(SDQ)/6-31G*//MP2/6-31G*; QCISD/6-31G*//MP2/6-31G*. [b] Zero-point vibrational energy for HF/6-31G* geometry. [c] Including 0.9 ZPVE (HF/6-31G*). [d] Including the $T\Delta S$ term at 300 K. [e] Energy relative to **2** + H_2O. H_2O energy (ZPVE): HF//HF −76.0107 (ZPVE 0.0207); MP2//HF −76.1960; MP2//MP2 −76.1968.

out with Gaussian 92 and 94,[6] and the resulting energies and geometries obtained are given in Tables 1 and 2 respectively, in the Supporting Information. The geometries for **2**, **5**, **8**, and **10** were optimized at both the HF/6-31G* and MP2/6-31G* levels, but the transition structure **9** could only be located at HF/6-31G*, and at the MP2 level no barrier for conversion of the complex **8** to form **10a** could be located. The structure and energy of the enol **12** from H_2O addition to the ketenyl group was also calculated at the HF/6-31G*//HF/6-31G* and MP2/6-31G*//HF/6-31G* levels. The relative energies reported (Table 1) include scaled HF/6-31G* ZPVE corrections, and for **2** and **5**, energies including $T\Delta S$ terms at 300 K were also obtained.

The HF/6-31G* calculated frequency of the ketene band in **2** is 2383.4 cm^{-1}, which when scaled by the factor of 0.895 used in a previous study of ketene IR[6c] gives a predicted value of 2133.1 cm^{-1}, in good agreement with our observed value of 2135 cm^{-1} in CH_3CN. Our calculated value of 2003.4 cm^{-1} for benzaldehyde requires a scaling factor of 0.85 to reproduce the experimental value of 1703 cm^{-1}. For the ketone band of **2** we calculate a value of 1919.6 cm^{-1}, with an intensity relative to the ketenyl band of 0.25, and scaling of the frequency by 0.85 leads to a predicted value of 1631.7 cm^{-1}. In our measured spectrum (Figure 1) there is no observable band below 1650 cm^{-1}. However, 1630 cm^{-1} is the spectral limit of the diode used in the experiment and the region below this frequency has not been explored. Absorption at 1650 cm^{-1} in Ar at 8 K was attributed to the ketone band of **2**,[2d] while a band at 1635 cm^{-1} was observed for the isomer **6**.[3c] For the lactone **5** the significant HF/6-31G* calculated infrared frequencies with intensities and assignments (parentheses) are 1620.8 (70.8, C−H

stretch), 1813.6 (198.1, C=C stretch), and 2163.4 cm^{-1} (733.3, C=O stretch). Application of the scaling factors of 0.895 and 0.85 used above to the calculated C=O band leads to values of 1936 and 1839 cm^{-1}, on either side of the assigned[2d] value of 1904 cm^{-1}. No bands attributable to **5** were detected in our study.

Discussion

The formation of **2** and its hydration to salicylic acid (**10**) are clearly demonstrated by the instantaneous appearance of the ketene band of **2** at 2135 cm^{-1} and of benzaldehyde at 1703 cm^{-1} upon photolysis, and the subsequent first-order disappearance of **2** as a function of H_2O concentration, with formation of the IR band of **10** at 1693 cm^{-1}.

The kinetics of the hydration of **2** are first order in [H_2O], and infrared studies of H_2O in CH_3CN indicate there is extensive hydrogen bonding between the two, and that at mole fractions below 0.04 no water dimers are present.[7a] Calculations at the HF/6-31G**//HF/6-31G** level[7b] indicate that the favored geometry of the CH_3CN- - -H_2O complex involves a linear arrangement of the C≡N- - -H−O bonds, with an interaction energy of 4.3 kcal/mol, so the oxygen is free for nucleophilic attack.
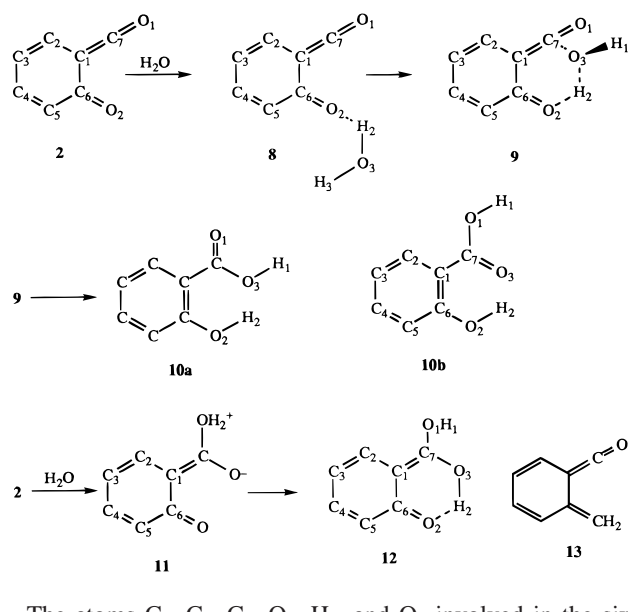
The calculations favor a reaction pathway for hydration of **2** analogous to that proposed for formylketene[1f] in which there is initial formation of a hydrogen bonded complex **8**. At the HF/6-31G*//HF/6-31G* level there is a barrier of 7.9 kcal/mol for conversion of **8** to a cyclic transition structure **9**, which then forms salicylic acid (**10**) (Scheme 1). The initial hydrogen bonded complex **8** is calculated to be 6.8 kcal/mol below the reactants at the MP2//MP2 level. However, at the MP2/6-31G*//HF/6-31G* level the energy of **9** is less than that of the complex **8** by 3.2 kcal/mol and there is no barrier to the formation of **10a**. At the MP2/6-31G*//MP2/6-31G* level no transition structure corresponding to **9** could be located, and there is no barrier for conversion of the complex **8** to **10a**, which is more stable than **8** by 39.7 kcal/mol. Studies of other pseudopericyclic reactions such as the hydration of formylketene[1f] show similar results.

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Scheme 1

The atoms C_7, C_1, C_6, O_2, H_2, and O_3 involved in the six-membered ring for H_2O transfer in **9** at the HF/6-31G* level are in an almost coplanar arrangement, with dihedral angles (Table 2, Supporting Information) $H_2O_3C_7C_1$ of 10.8°, $O_3C_7C_1C_6$ of −9.3°, $C_7C_1C_6O_2$ of 1.5°, $O_3H_2O_2C_6$ of −0.4°, and $C_7O_3H_2O_2$ of −7.9°. This type of process involving in plane attack orthogonal to the π-system has been described by Birney and Wagenseller[1f] as a pseudopericyclic reaction, and does not contain a cyclic array of overlapping orbitals.

There is no enthalpic barrier to the addition of H_2O to **2**, and the transition state **9** is 8.4 kcal/mol below the reactants (**2** + H_2O) at the MP2/6-31G*//HF/6-31G* level. However, experimentally the unfavorable entropy of attaining this rather ordered transition state evidently gives rise to the experimentally observed free energy barrier. These results are rather similar to those[1f] found at the MP2/6-31G*+ZPE//MP2/6-31G* level for the addition of H_2O to formylketene (**14**), in which there is initial formation of a hydrogen bonded complex **15** 5.9 kcal/mol below the reactants, and this complex has a barrier of 3.1 kcal/mol for forming the transition state **16**, which is 2.8 kcal/mol below the reactants, and then forms the product **17**, which is 26.0 kcal/mol below the reactants (eq 3). At the highest level of theory utilized (MP4(SDQ)/6-31G*+ZPE//MP2/6-31G*) the complex **15** was 5.4 kcal/mol below the reactants, and this complex had a barrier of 6.4 kcal/mol to form **16**, and **17** is 26.3 kcal/mol below the reactants.
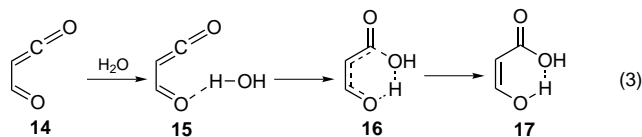
There is no barrier for H_2O addition to **2** at the MP2/6-31G*//MP2/6-31G* level and salicylic acid **10a** is 46.5 kcal/mol more stable than the reactants, as compared to 2.8 and 26.3 kcal/mol greater stabilities for the structures **16** and **17** relative to **14** + H_2O. The greater propensity for hydration of **2** compared to **14**, by 20.2 kcal/mol relative to the products, is expected because of the gain in aromatic stabilization. The hydration of **2** to the enediol **12** is calculated to be exothermic by 31.4 kcal/mol at the MP2/6-31G*//HF/6-31G* level, but this is 17.1 kcal/mol less than for direct formation of **10a**, and this difference again reflects the aromatic stabilization of **10a**.

The rate constant for the hydration of acetylketene (**18**) in H_2O has been determined[1c] as 1.5×10^6 s^{-1}, and the extrapolated rate constant for **2** in 55.5 M H_2O based on the rate constant determined here of 1.5×10^7 M^{-1} s^{-1} is 8.3×10^8 s^{-1}, or 550 times greater than that for **18**. Normally the hydration reactivity of ketenes in H_2O/CH_3CN is strongly accelerated as the fraction of H_2O in the medium increases, and this has been attributed to the increase in solvent polarity with increasing water content[8a−c] in addition to the mass law effect. Thus the reactivity of **2** in pure H_2O may be even closer to the diffusion controlled limit. However, for the ketene t-BuC(CO$_2$-Et)=C=O the increase in rate with increasing [H_2O] in H_2O/CH_3CN mixtures was strongly attenuated, and this may arise from a less polar transition state when addition to an acylketene by a cyclic transition state is involved.[8a] However, **2** is still indicated to be much more reactive than **18**, as expected for the gain in aromatic stabilization.
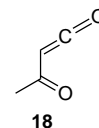
Solvent isotope effects have been taken to indicate that hydration of many ketenes occurs with the participation of a second molecule of H_2O acting as a general base.[8a−c] A recent study of the hydrolysis of bis(2,4-dinitrophenyl) carbonate with a wide range of H_2O/CH_3CN mixtures has been interpreted similarly,[8d] and in this latter study a close parallel between the effect of the mole fraction of H_2O in CH_3CN on the reaction rate and upon the solvent polarity parameter E_T was noted, and interpreted as showing similar solute−solvent interaction mechanisms in the two systems, namely H-bonding and dipolar interactions.

An alternative pathway for hydration of **2** is by attack of H_2O on the ketene from the side opposite the keto group, leading to a zwitterionic transition structure **11** and then to salicylic acid enol **12** (Scheme 1). An analogus pathway has been proposed for the hydration of 6-methylenecyclohexa-2,4-dienylideneketene (**13**), and the in-plane attack opposite the methylene group was confirmed by the rate depressing effect of substituents *ortho* to the ketenyl group.[9] However, the calculations of the interaction of **2** with H_2O give **8** as the only detectable complex, and as discussed above this leads to **10a** with no barrier at the MP2/6-31G*//MP2−6-31G* level. An optimized geometry for **12** was found at the HF/6-31G* level, but the HF/6-31G* and MP2/6-31G* energies for this structure are 18.6 and 17.1 kcal/mol, respectively, above those for **10a**. No transition structure **11** was located for H_2O attack on the ketene opposite the keto carbonyl, and this pathway suffers not only from the lack of aromaticity in **12**, but also from oxygen−oxygen repulsion and a lack of H-bonding in **11**.

It has also been proposed[3a] that nucleophilic addition to the ketene **6** would occur perpendicular to the ketene plane, largely on the basis of MO calculations[3d] that the LUMO lies in this perpendicular plane. However, these calculations used the low-level CNDO/2 method for the analogous structure **13**, and do not appear to be reliable for analyzing the hydration mechanisms of either **2** or **6**.

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The rate constant for addition of MeOH exceeds that for hydration by a factor of 2. There is also infrared data supporting the formation of H bonds between MeOH and CH_3CN,[10a] and the calculated structure of this complex[10b] resembles that for H_2O and CH_3CN. Thus the MeOH pathway for reaction with **2** evidently is similar to that for H_2O.

Studies of amines in CH_3CN by ^{1}H NMR[11a] and IR[11b] indicate that hydrogen bonding interactions of the type R_2NH- - -$NCCH_3$ are present. In this complex the amine lone electron pair is available for nucleophilic attack, and by analogy to the H_2O reaction (Scheme 1) a transition state **19** for addition of Et_2NH to **2** leading directly to the salicylamide appears reasonable. This resembles the calculated transition state **20** recently reported by Birney et al.[1k] for the addition of NH_3 to formylketene (**14**).
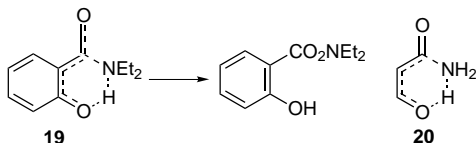
The rate constant for addition of Et_2NH to **2** exceeds those for H_2O and MeOH by factors of 73 and 37, respectively, and for comparison competition studies[12a] of the reactivity of a dienylketene in CH_3CN lead to a rate ratio $k(n\text{-BuNH}_2)/k(n\text{-BuOH})$ of 50, while measured rates[12b] for $Ph_2C=C=O$ in H_2O give the rate ratio $k(n\text{-BuNH}_2)/k(H_2O) = 7.1 \times 10^4$. For reactions of both H_2O and $n\text{-BuNH}_2$ in H_2O the solvent is expected to be strongly hydrogen bonded to the nucleophile, and it has been suggested that a desolvation step may affect the observed reactivities.[13] The rate constant of 1.1×10^9 M^{-1} s^{-1} for the reaction of Et_2NH with **2** is near the diffusion controlled limit, and the rather small difference between Et_2NH, MeOH, and H_2O rate constants for reaction with **2** may be attributed to low selectivity because of the high reactivity of this substrate.

There is calculated to be no enthalpic barrier for addition of NH_3 to formylketene (**14**) to give **20**,[1k] whereas there is a 6.3 kcal/mol calculated enthalpic barrier for conversion to the H_2O/ **14** complex **15** to **17** (eq 3).[1f] This calculated greater reactivity of **14** with NH_3 relative to H_2O is consistent with the observed greater reactivity of **2** with Et_2NH compared to H_2O. In a competition experiment the relative reactivity of acetylketene (**18**) with $n\text{-PrNH}_2$ and $n\text{-BuOH}$ was found to be 2.3/1.[1k] Thus the amine was more reactive, as predicted by the calculation, but a possible cause of the rather low selectivity was proposed to be hydrogen bonding of the amine which diminished its reactivity.[1k] For the addition of NH_3 to **14** a $\Delta G^{\ddagger}$ value of 7.3 kcal/mol may be derived,[1k] indicating that the unfavorable entropy leads to a net free energy barrier for the reaction.

Calculations at different levels of theory (Table 1) consistently predict that the acylketene **2** and the ring-closed benzodioxetane **5** are close in energy, but particularly when the free energy is considered **2** is more stable by 2.8 kcal/mol at the highest level considered. This difference is much less than the 17.5 kcal/mol higher energy calculated for the ring-closed structure **21** from formylketene,[14] and the greater relative stability of **5** may be attributed to aromatic stabilization, partially offset by ring strain. Previously the photochemical interconversion of **2** and **5** in an argon matrix at 8 K was reported,[2d] with identification of **5** by its IR band at 1904 cm^{-1}. At low temperatures the entropy factor disfavoring **5** is reduced, and this species may also be stabilized by the matrix. Thus the calculations offer confirmatory evidence for the possible observation of **5**.
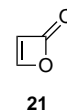
In summary the reactive acylketene **2** has been observed in solution for the first time, and calculations and kinetic studies favor a pseudopericyclic process for the hydration of this species. By analogy the reactions with CH_3OH and Et_2NH follow similar pathways. The calculated energy of the lactone **5** is close to that of **2**, and provides supporting evidence for the reported[2d] matrix observation of **5**.

Experimental Section

The precursor **1** was prepared as described.[4] Laser flash photolyses of **1** with time-resolved IR detection were carried out with a 308 nm Lumonics Excimer-500 laser and a Mutek MPS-1000 diode laser as a monitoring source. Details of this system and the methods for kinetic measurements are provided elsewhere.[5b]

Supporting Information Available: Quenching data and rate versus concentration plots for **2** and calculated energy and geometry for **2** and related structures (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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