

of the N-alkylation processes will be discussed elsewhere.^{5e} It suffices to point out here that most of the various reaction paths in the catalyzed epoxidation of diene II have been observed with other alkenes such as norbornene and cyclohexene, indicating that this diene is not special with regard to its reaction with the high-valent iron intermediate.

The present results demonstrate that the high-valent iron intermediate can remove an electron from these two alkenes. However, the conclusions we reach with regard to other alkenes must include effect of ionization potentials. The gas-phase ionization potentials of I¹⁹ and II²⁰ are 7.8 and 8.1 eV, respectively, compared to 9.0 eV for norbornene²¹ and 9.1 eV for cyclohexene.²¹ It seems unlikely that alkenes bearing very electronegative substituents would be epoxidized through radical cations. Therefore, a change in mechanism might occur at some higher ionization

potential. We believe that the exo/endo ratios in epoxidation^{5c} of norbornene are consistent with a radical cation intermediate even though the ionization potential is somewhat higher than are those of I and II.

Since alkenes I and II are known to undergo radical cation chain rearrangements, it is possible that the rearrangement represents a minor pathway unrelated to epoxidation. However, the observation of simultaneous alkene isomerization, epoxidation, production of rearranged oxidation products, and formation of N-alkylhemin, the last three reactions also occurring with other alkenes, encourages us to conclude that all of these processes are related, very probably through radical cation. Thus, all of our results to date are consistent with an electron transfer from alkene to the "oxene" followed by one of the processes discussed above. With most alkenes the dominant process is formation of epoxide.

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Kinetics and Mechanism of Hydration of Alkylketenes

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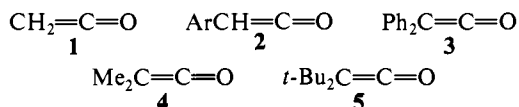
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Abstract: The hydration reactivities of CH₂=C=O (**1**), *t*-Bu₂C=C=O (**5**), Et₂C=C=O (**7**), (CH₂)₄C=C=O (**8**), (C₆H₅)₂C=C=O (**9**), and *t*-BuCH=C=O (**10**) in H₂O or H₂O/CH₃CN mixtures have been examined, including acid and base catalysis and solvent and structural isotope effects. These results provide the first systematic comparison of structural effects on the hydration of aliphatic ketenes, as well as the first measurements of base-induced hydration and pH-rate profiles for this process. The significant steric and electronic effects of the substituents observed lead to the interpretation that the acid-catalyzed reaction involves rate-limiting proton transfer to C_β perpendicular to the ketene plane, while the H₂O- and OH⁻-induced reactions involve nucleophilic attack in the ketene plane. These results resolve the many conflicting previous reports and interpretations regarding ketene hydration.

Ketenes have long been the topic of chemical study, the results of which have been frequently reviewed.^{1,2} There has been intense recent interest in ketene addition reactions, including both cycloadditions³ and other additions,^{2c,4} and prevalent views that both of these processes proceed through cyclic as opposed to open transition states have been challenged.^{2c,3e} This report deals with the prototypical but controversial hydration of ketenes.

The mechanism of ketene hydration has been the object of several experimental studies, including the reactions of ketene (**1**)^{5a}

and arylketenes (**2**)^{5b} in H₂O, diphenylketene (**3**) and dimethylketene (**4**) in ether containing up to 0.351 M H₂O,^{6a,b} di-*tert*-butylketene (**5**)⁷ in 50% acetonitrile/H₂O, and ketene (**1**) in the gas phase.^{6c} Theoretical studies of ketene hydration have also been presented.⁸



Several rather different mechanisms for the hydration of ketenes have been presented and reviewed.^{2c} For the uncatalyzed reaction these include rate-limiting H₂O attack on C_α of the ketene followed by rearrangement to a carboxylic acid (eq 1),^{5a} reaction of **3** with water trimer and **4** with water dimer via cyclic transition states (eq 2),^{6a,b} and in theoretical studies attack of water monomer or dimer on the C=C or C=O double bonds of the ketene via cyclic transition states.⁸ Additions to the C=C bond were depicted with

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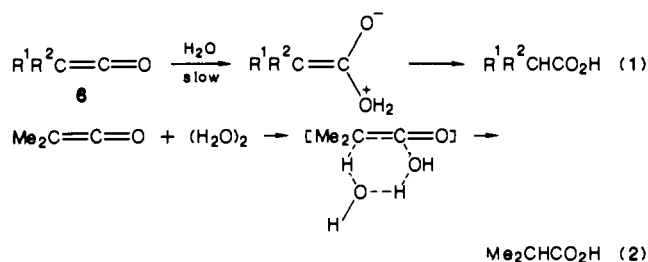
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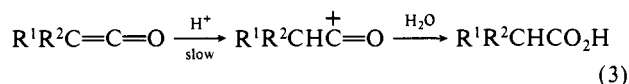
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attack perpendicular to the plane of the ketene,^{8,9} whereas addition to the C=O bond was shown in the plane of the ketene.^{8a}



For acid-catalyzed hydration rate-limiting proton transfer to C_β followed by reaction with water (eq 3) has been proposed to occur for strong acids,^{6,7} although for some weak carboxylic acid catalysts addition was proposed to occur via cyclic transition states.⁶ Base catalysis of ketene hydration has not previously been reported, and the rates of reaction of arylketenes were independent of pH in the range of 4 to 10.8.⁵

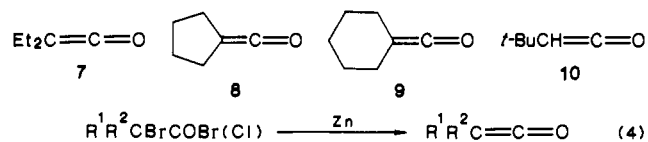


We have reviewed these previous studies of ketene hydration as well as mechanistic studies of other nucleophilic additions to ketenes in detail elsewhere,^{2c} but it is clear that no comprehensive and consistent interpretation of ketene hydration is available, in contrast to the related processes of alkene¹⁰ and carbonyl group hydration.¹¹ One reason for the diversity in the interpretations of ketene reactivity is the wide variation in ketene structures and particularly reaction conditions utilized in the different studies, so that systematic comparisons of the effect of changes of structure and reaction conditions on reactivity are not possible. The high reactivity of some ketenes with H₂O and their propensity for dimerization have been major contributing factors for the paucity of good kinetic data on the hydration of ketenes under conditions comparable to the abundant studies of alkenes¹⁰ and carbonyl compounds.¹¹

The current report deals with kinetic studies of some simple alkylketenes in solvents with high concentrations of H₂O that may be readily compared to wholly aqueous media. Base-induced ketene hydration has been measured for the first time, and the first pH-rate profiles for ketenes have been constructed.

Results

Diethylketene (7), tetramethyleneketene (8), pentamethyleneketene (9), and *tert*-butylketene (10) were obtained as solutions in tetrahydrofuran (THF) by zinc debromination of the corresponding α-bromoacyl halides (eq 4) as reported,^{4a,b} C-H₂=C=O (1) was obtained by pyrolysis of the dimer, and *t*-Bu₂C=C=O (5) was prepared from the acid chloride.^{4a}



The ketene solutions were stored in a Teflon sealed container at -78 °C, and samples were withdrawn with a syringe when needed for kinetic experiments. The kinetic behavior was the same regardless of the age of the sample. However, the gradual appearance of a UV absorption near 340 nm due to the formation

Table I. Hydration Reactivity of Ketenes in H₂O/CH₃CN (μ = 0.0)

[H ₂ O]		k _{obsd} (s ⁻¹)				
vol %	M	1 (CH ₂ =C=O) 25.0 °C	7 (Et ₂ C=C=O) 5.5 °C ^a	7 (Et ₂ C=C=O) 25.0 °C ^b	10 (<i>t</i> -BuCH=C=O) 5.5 °C ^c	10 (<i>t</i> -BuCH=C=O) 25.0 °C ^d
10	5.56	0.270				
15	8.33	0.789				
20	11.1	1.42	0.0200	0.0492	0.0368	0.0873
30	16.7					0.196
40	22.2		0.0615	0.196	0.152	0.381
50	27.8		0.107	0.357	0.263	
60	33.3		0.202	0.606		
70	38.9		0.390	1.26		

^alog k_{obsd} = 0.0462[H₂O] - 2.23 (r = 0.999). ^blog k_{obsd} = 0.0496[H₂O] - 1.836 (r = 0.999). ^clog k_{obsd} = 0.0515[H₂O] - 1.99 (r = 0.998). ^dlog k_{obsd} = 0.0596[H₂O] - 1.73 (r = 0.998).

Table II. Hydration Reactivity of CH₂=C=O (1) in 10% (v/v) H₂O/CH₃CN at 5.5 °C as a Function of [HCl] and [NaOH]

[HCl] × 10 ³	k _{obsd} (s ⁻¹)	[NaOH] × 10 ³	k _{obsd} (s ⁻¹)
1.72 ^a	0.508	0.0 ^a	0.169
1.10 ^a	0.393	1.00	0.200
0.854 ^a	0.342	2.00	0.238
0.637 ^a	0.289		

^aμ = 0.05 (NaCl).

of the ketene dimer could be observed, but a study of the effect of hydration on this absorption showed it did not interfere with the hydration kinetics. The ketenes were too reactive for rate studies in 100% H₂O, so H₂O/CH₃CN mixtures were used. The pH values of buffer and base solutions were corrected for the mixed solvents as described in the Experimental Section.

The kinetics of the ketene hydrations were followed by observing the decrease in absorption at 210 (for 1) or 221 nm, and in some cases these results were confirmed by rate constants measured at 380 nm. However, study at the latter wavelength was less convenient because of the lower extinction coefficients and hence lower absorbance changes observable.

The reactivity of CH₂=C=O (1) toward H₂O is quite high but could be measured in 10–20% H₂O in CH₃CN at 25 °C (Table I). Comparison of these data to those previously measured^{5a} by conductivity for 1 in 33–100% H₂O shows a much stronger dependence of the rate on H₂O concentration in the 10–20% range than above 33%. Comparative values of k_{H₂O} are 13.5 s⁻¹ in 33% H₂O^{5a} and 1.42 s⁻¹ in 20% H₂O.

The influence of HCl and NaOH on the reactivity of 1 could be measured only in 10% H₂O/CH₃CN at 5.5 °C (Table II). Reactions catalyzed by HCl gave a good correlation k_{obsd} = 199[H⁺] + 0.168 (r = 0.998) with k_{obsd} in units of s⁻¹ and [H⁺] in molar units. Because of the low solubility of NaOH in this medium, reactions could be observed only at two base concentrations, and at lower ionic strengths than for the neutral and HCl-catalyzed reactions. However, significant OH⁻-induced reaction was detected (Table II).

Previously⁷ the reactivity of *t*-Bu₂C=C=O (5) in 100% water could not be measured because of low substrate solubility, but now using a 10-cm cell this is possible in neutral H₂O and acid buffers and we measure k_{obsd} = (3.24 s⁻¹ M⁻¹)[HO₂CH] + (41.7 s⁻¹ M⁻¹)[H⁺] + (1.57 × 10⁻⁴ s⁻¹), and k_{obsd} = (0.869 s⁻¹ M⁻¹)[HOAc] + (452 s⁻¹ M⁻¹)[H⁺] + (1.57 × 10⁻⁴ s⁻¹) (25.0 °C, μ = 0.1, NaCl). These values of k_{H⁺} and k_{HA} are 94 to 360 times larger than the previously reported⁷ values in 50% H₂O/CH₃CN, and k_{H₂O} is 157 times greater than the previous⁷ upper limit of 10⁻⁶ s⁻¹ estimated for 50% H₂O/CH₃CN, where no uncatalyzed reaction was detected.

The reactivity of Et₂C=C=O (7) in H₂O/CH₃CN could be monitored as a function of solvent composition from 20 to 70% H₂O at both 5.5 and 25 °C, as reported in Table I. At higher water concentrations the rates were too fast to measure by our techniques, but excellent empirical correlations between the water concentration and the rates were observed: log k_{obsd} = 0.0496-

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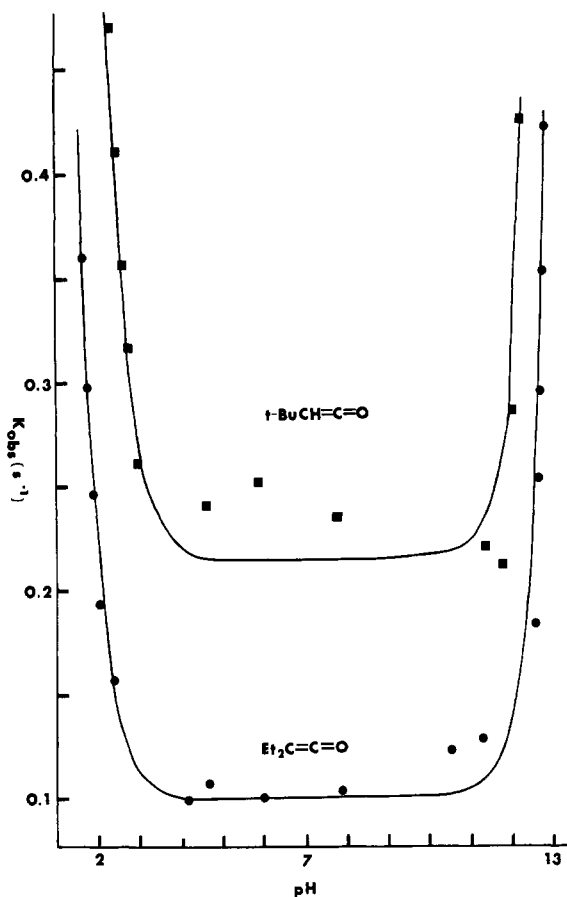
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Table III. Hydration Reactivity of Et₂C=C=O (7) in 50% (v/v) H₂O/CH₃CN,^a 5.5 °C, as a Function of pH^a

[HCl] or [NaOH] × 10 ³ or buffer	pH	k _{obsd} (s ⁻¹)
19.9	1.70 ^b	0.360
16.2	1.79 ^b	0.298
12.3	1.91 ^b	0.247
8.22	2.08 ^b	0.194
4.19	2.38 ^b	0.157
ClCH ₂ CO ₂ H ^{d,e}	4.11 ^c	0.0994
HCO ₂ H ^{d,f}	4.67 ^c	0.107
HOAc ^{d,g}	5.97 ^c	0.100
H ₂ PO ₄ ^{-d,h}	7.82 ^c	0.103
HCO ₃ ^{-d,i}	10.50 ^c	0.122
HCO ₃ ^{-d,j}	11.27 ^c	0.128
3.68	12.56 ^k	0.183
4.60	12.66 ^k	0.252
5.20	12.72 ^k	0.295
5.93	12.77 ^k	0.352
6.67	12.82 ^k	0.422

^a μ = 0.05 (NaCl). ^b pH = -log [HCl]. ^c pH = pH_{meas} + 0.18. ^d Molar concentrations of acid and conjugate base. ^e 0.0204, 0.0200. ^f 0.0229, 0.0200. ^g 0.0204, 0.0200. ^h 0.0125, 0.0149. ⁱ 0.0361, 0.0045. ^j 0.0123, 0.0125. ^k pH = 15.0 + log [NaOH].

**Figure 1.** pH-rate profiles for hydration of Et₂C=C=O (7, circles) and *t*-BuCH=C=O (10, squares) at 5.5 °C in 50% CH₃CN/H₂O.

[H₂O] - 1.836 (25 °C, *r* = 0.999) and log *k*_{obsd} = 0.0462[H₂O] - 2.23 (5.5 °C, *r* = 0.999), with [H₂O] in molar units. These correlations give values of *k*_{H₂O} for pure water of 8.26 and 2.16 s⁻¹ at 25 and 5.5 °C, respectively.

The effect of pH on the reactivity of 7 in 50% H₂O/CH₃CN was measured at 5.5 °C with use of HCl, NaOH, and a variety of buffer solutions. The data are reported in Table III and shown graphically in Figure 1. The data were fitted to the expression *k*_{obsd} = 13.0[H⁺] + 4.0[OH⁻] + 0.100 where *k*_{obsd} is in units of s⁻¹ and the acid and base concentrations are in molar units. The curve generated by this expression is included in Figure 1.

Table IV. Isotope effects and Comparative Hydration Reactivity of CH₂=C=O (1), Et₂C=C=O (7), Pentamethyleneketene (9), and *t*-BuCH=C=O (10), μ = 0.05 (NaCl)

substrate	<i>T</i> (°C) ^b	% H ₂ O(D ₂ O)	<i>k</i> _{H⁺(D⁺)} ^a (M ⁻¹ s ⁻¹)	<i>k</i> (H ₂ O) (s ⁻¹)	<i>k</i> _{H⁺}/<i>k</i>_{D⁺}}	<i>k</i> _{H₂O}/<i>k</i>_{D₂O}}
1	5.5	10% H ₂ O ^f	199 ^d	0.169	1.82	1.86
		10% D ₂ O ^f	109 ^d	0.0911		
7	5.5	20% H ₂ O	5.66	0.0179		
		50% H ₂ O	13.0	0.0943	2.99	1.45
	9.0	50% D ₂ O	4.35 ^c	0.0649		
		50% H ₂ O	17.3	0.119	2.60	1.70
9	25	50% H ₂ O	6.65	0.0702		
		50% D ₂ O		0.201		1.59
	5.5	20% H ₂ O	30.1	0.0508		
		10% H ₂ O ^f	18.4 ^d	0.0212		
10	5.3	50% H ₂ O	60.1 ^e	0.216		
		20% H ₂ O	21.4	0.0915		
	5.5	20% H ₂ O	29.0	0.0354		
		50% H ₂ O	67.8	0.218		
8.8	50% H ₂ O	95.3	0.279	3.60	2.58	
	50% D ₂ O	26.5	0.108 ^d			
25.0	20% H ₂ O	135	0.0780			
	50% H ₂ O	79.6	0.238			

^a Obtained from plots of *k*_{obsd} vs. [HCl]([DCI]) for five acid concentrations, *r* = 0.993 to 0.999 except as noted. ^b ±0.1 °C. ^c *r* = 0.986. ^d Four acid concentrations. ^e *r* = 0.987. ^f μ = 0.005.

Table V. Hydration Reactivity of *t*-BuCH=C=O (10) in 50% (v/v) H₂O/CH₃CN at 5.5 °C as a Function of pH (μ = 0.05, NaCl)

[HCl] ^a or [NaOH] × 10 ³ or buffer	pH	<i>k</i> _{obsd} (s ⁻¹)
4.06	2.39 ^b	0.470
3.22	2.49 ^b	0.411
2.46	2.61 ^b	0.357
1.67	2.78 ^b	0.317
1.09	2.96 ^b	0.262
HCO ₂ H	4.62 ^c	0.240
HOAc	5.91 ^c	0.252
H ₂ PO ₄ ⁻	7.74 ^c	0.235
HCO ₃ ⁻	11.38 ^c	0.220
0.620	11.79 ^d	0.212
1.24	12.09 ^d	0.285
1.55	12.19 ^d	0.426

^a *k*_{obsd} = 67.8[HCl] + 0.193 (*r* = 0.997). ^b pH = -log [HCl]. ^c pH = pH_{meas} + 0.18. ^d pH = 15.0 + log [NaOH].

Pentamethyleneketene (9) was more reactive than 7 and so rates of the neutral and acid-catalyzed reactions of this substrate were measured only in 10 and 20% H₂O at 5.5 °C, as reported in Table IV. Comparative rate data for 7 in 20% H₂O, as well as solvent isotope effect measurements for 7 and 9, are also included in Table IV.

Tetramethyleneketene (8) was quite reactive in 10% H₂O and we were unable to obtain reliable rate constants for this substrate, which is estimated to be at least 5 times as reactive as 9.

The reactivity of *t*-BuCH=C=O (10) in neutral H₂O/CH₃CN was intermediate between that of 7 and 9, and this ketene showed little tendency to dimerize in solution, and so considerable kinetic data could be obtained for this substrate, as recorded in Tables I, IV, and V. The correlation of log *k*_{obsd} with [H₂O] (Table I) gives extrapolated rates for 10 in pure H₂O of 37.9 s⁻¹ (25.0 °C) and 7.38 s⁻¹ (5.5 °C).

The effect of pH on the rate of 10 in 50% H₂O/CH₃CN at 5.5 °C in HCl, NaOH, and buffer solutions is given in Table V and shown graphically in Figure 1, where the calculated line fits the expression *k*_{obsd} = 67.8[HCl] + 8.0[OH⁻] + 0.216. Additional rates for 10 for comparison to the other substrates, and solvent isotope effects, are given in Table IV.

The stoichiometries of the hydrations of 7 and 10 were confirmed by titration of the acid produced, which agreed with the amount of ketene capturable by aniline by ±4%.

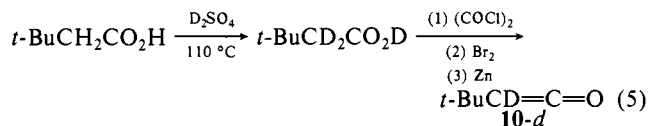
For measurement of the structural isotope effect, *t*-BuCD=C=O (10-*d*) was prepared by the route of eq 5, and mass spectral

Table VI. Rates of Acid-Catalyzed Hydrolysis of Vinyl Ethers in H₂O at 25 °C^a

substrate	k_{H^+} (M ⁻¹ s ⁻¹)	k_{D^+} (M ⁻¹ s ⁻¹)	k_{H^+}/k_{D^+}
11	0.0394	0.0208	1.89
12	0.0715	0.0341	2.10
13	0.0491	0.0226	2.17

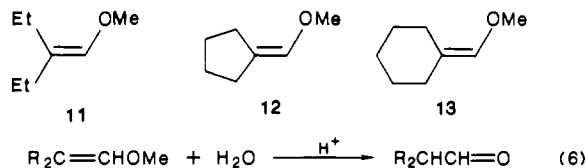
^a $\mu = 0.1$ (NaCl), duplicate runs ($\pm 5\%$) at five acidities each for each substrate spaced between 0.0197 and 0.0998 M HCl or 0.0195 and 0.106 M DCl.

examination of the derived anilide revealed 95% deuterium incorporation in the ketene.



Measured values of k_{H^+} and k_{H_2O} for **10** and **10-d** are given in Table IV and lead to rate ratios $k(t\text{-BuCH}=\text{C}=\text{O})/k(t\text{-BuCD}=\text{C}=\text{O})$ of 0.77 ± 0.05 for k_{H^+} and 0.91 ± 0.02 for k_{H_2O} . For determination of the corresponding structural isotope effect for k_{OH^-} , rates of **10** and **10-d** were measured on the same day by using a series of 50% H₂O/CH₃CN solutions at 5.3 °C, $\mu = 0.05$ (NaCl), with added NaOH to give the following rate ratios ([NaOH] (M) in parentheses): 0.87 ± 0.02 (0.0), 0.87 ± 0.07 (0.0026), 0.66 ± 0.01 (0.0034), and 0.73 ± 0.08 (0.0035). Rates at higher base concentration were too fast to measure.

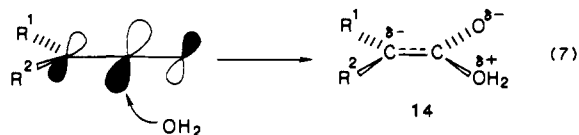
For comparative purposes the reactivity of the vinyl ethers **11–13** according to eq 6 were also examined by observing the disappearance of the alkene absorption at 207 nm for each as a function of acid concentration. Measure rate constants in HCl and DCl, and the derived isotope effects are listed in Table VI. No uncatalyzed reactions were detectable.



The reactions of **11–13** were also carried out at higher substrate concentration than in the kinetic runs in order to observe the UV spectra of the product aldehydes, and the expected absorptions appeared near 284 nm, $\epsilon = 25$.

Discussion

As considered in detail below, we believe our results as well as those reported previously⁵⁻⁷ for neutral ketene hydration in solution are best interpreted in terms of nucleophilic attack on the ketene in the plane of the molecule on the lowest unoccupied molecular orbital (LUMO), which has a large coefficient at C_α.¹² This process (eq 7) involves a rather polar transition state, **14**, with more negative charge on oxygen than carbon.



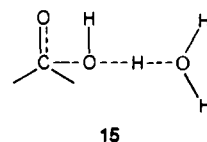
The steric and electronic effects of the substituents R¹, R² on the reactivity of the ketenes studied here as well as others which have been reported previously are consistent with this mechanistic scheme. Thus the hydration reactivities of arylketenes (**2**) were correlated by σ_p^n constants for the aryl substituents, with $\rho = 1.2$,^{5b} consistent with a transition state such as **14** with modest development of negative charge on C_β. Ketene itself (**1**)^{5a} had a rate constant for hydration at 25 °C of 44 s⁻¹, which is 86 times less

than the least reactive of the aryl ketenes, *p*-MeC₆H₄C=C=O.^{5b}

The extrapolated values of k_{H_2O} in pure water at 25 °C of Et₂C=C=O (**7**) and *t*-BuCH=C=O (**10**) are 8.26 and 37.9 s⁻¹, respectively, less than the value for CH₂=C=O by factors of only 5.3 and 1.2, while from the data in Table III, (CH₂)₅C=C=O (**9**) is about 5 times as reactive as **7**. However, k_{H_2O} for *t*-Bu₂C=C=O (**5**) is 1.57×10^{-4} s⁻¹, which is 5×10^4 and 2.4×10^5 times less reactive than **7** and **10**, respectively. This large rate depression only occurs when there are bulky substituents on both sides in the plane of the ketene, and it provides strong evidence for the mechanism of eq 7 involving rate-limiting nucleophilic attack in the ketene plane.

The solvent isotope effects $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$ for **7** at different temperatures range from 1.45 to 1.70, and that for **10** is 2.58, all in 50% water/CH₃CN (Table III), as compared to reported values of 1.8 to 2 for ArCH=C=O and of 1.9 for CH₂=C=O in wholly aqueous media.⁵ These values are generally similar and are consistent with a uniformity of mechanism throughout the series.

Isotope effects which have been reported for the uncatalyzed reaction of water to other carbonyl groups including ketones, esters, and carboxylic anhydrides range from 2.2 to 4.0.¹³ These isotope effects are commonly interpreted in terms of transition states involving two molecules of water as depicted in **15** in which one water molecule acts as a general base. If this interpretation is correct the solvent isotope effects of 1.45 to 2.58 observed now may indicate this mechanism is applicable to ketenes as well. Previously reaction of Me₂C=C=O (**4**) in moist ether was reported by Lillford and Satchell^{6a} to be second order in H₂O, and a transition state analogous to **15** was considered, although a cyclic form was favored (eq 2).



Thus all the rate data for the uncatalyzed hydration of ketenes reported here and previously available⁵⁻⁷ appear to be quite consistent with nucleophilic attack of water in the plane of the ketene at C_α giving **14** (eq 7). In particular, the high reactivity of arylketenes and the correlation with σ^{5b} demonstrate the polar character of the transition state, and the large rate retardation experienced by *t*-Bu₂C=C=O shows the addition occurs in the ketene plane. The alternative proposal^{6a,b,8} of a process involving a relatively nonpolar transition state with significant bond formation at C_β such as that shown in eq 2 accounts neither for the polar effects nor for the large rate retarding effect of two bulky groups, for as noted below the steric inhibition to attack at C_β is not nearly so large.

A variant of the concerted process in which the transition state is highly unsymmetrical so that considerable polar character may develop is little different from the mechanism of eq 7 with concomitant solvation at C_β, with the exception that in the former process addition occurs from perpendicular to the plane of the ketene and the observed steric effects are inexplicable.

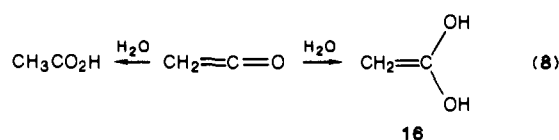
Theoretical studies of ketene hydration have included MINDO/3 calculations of the transition-state structure for the addition of monomeric H₂O across the C=C bond of CH₂=C=O,^{8b} and STO-3G geometries have been calculated for the reaction of H₂O monomer, dimer, and trimer with the C=C and C=O bonds of CH₂=C=O.^{8a} The former process would give a carboxylic acid directly, whereas the latter would give the enediol **16** initially (eq 8). So far there does not appear to be any experimental evidence

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(13) (a) Gandour, R. D.; Coyne, M.; Stella, V. J.; Schowen, R. L. *J. Org. Chem.* **1980**, *45*, 1733–1737. (b) Menger, F. M.; Venkatasubban, K. S. *Ibid.* **1976**, *41*, 1868–1870. (c) Venkatasubban, K. S.; Davis, K. R.; Hogg, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 6125–6128. (d) Bell, R. P.; Critchlow, J. E. *Proc. R. Soc. London, Ser. A* **1971**, *325*, 35–55. (e) Rossall, B.; Robertson, R. E. *Can. J. Chem.* **1975**, *53*, 869–877. (f) Allen, J. M.; Venkatasubban, K. S. *J. Org. Chem.* **1985**, *50*, 5108–5110. (g) Neuvonen, H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1141–1145.

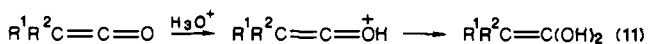
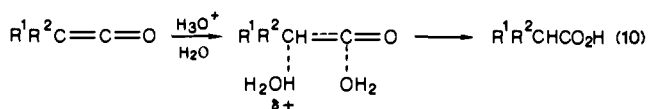
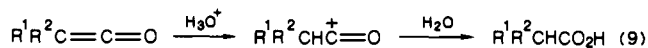
(14) Knittel, P.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 3408–3414.

for the formation of an enediol as an intermediate in ketene hydration, and furthermore this process would not account for the observed polar effects on the reaction. Formation of an enediol after the initial addition, for example, by a transformation of **14**, cannot, however, be excluded.



Formation of the enediol **16** would be another example of carbonyl group hydration, which has been a topic of continuing interest.¹¹ Analysis of available results favored a cyclic transition state involving three water molecules for gas-phase formaldehyde hydration, but in solution a choice between open and cyclic transition states could not be made.^{11e} For the hydration of ketenes the structural effects indicate that a transition-state **14** with considerable polar character is involved, whereas transition states leading to **16** would not appear to be subject to any significant polar interactions with the substituents.

Acid catalysis of the hydration reaction occurs with proton transfer to carbon leading to a carboxylic acid, and this process could occur in a stepwise process with the intermediacy of an acylium ion as shown in eq 9, or it may involve direct formation of the carboxylic acid through a concerted addition (eq 10). Proton transfer to oxygen leading to a diol as shown in eq 11 is also conceivable, but as discussed below the evidence does not support this alternative.



Whether or not an acylium ion could exist as a discrete intermediate in this ketene hydration depends on its lifetime in this rather nucleophilic medium, so that the process of eq 9 could be "enforced", with the nucleophilic role played by a preassociated water molecule, as in eq 10.

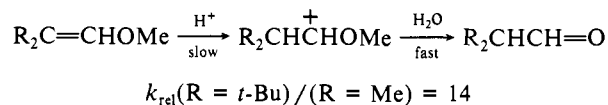
There are several strong arguments against the intervention of oxygen protonation as the rate-limiting step. These include the fact that carbon protonation of ketenes to give acylium ions is thermodynamically favored in the gas phase,¹⁵ and this is observed to occur on oxygen only with very strong proton donors.^{15a} Acylium ions are also favored over the corresponding O-protonated ions in solution.^{15g} Diphenylketene in ether does not show acid catalysis of hydration, although such catalysis does occur for dimethylketene.^{6a,b} This is consistent with the known much greater barrier to proton transfer to an alkenyl carbon bearing a phenyl as opposed to an alkyl substituent.¹⁴ No such barrier is expected for oxygen protonation.

The observation of an isotope effect $k(t\text{-BuCH}=\text{C}=\text{O})/k(t\text{-BuCD}=\text{C}=\text{O})$ of 0.76 for the acid-catalyzed process is consistent with rehybridization of C_β in the transition state and also argues against rate-limiting oxygen protonation.

Values of $k_{\text{H}^+}/k_{\text{H}_2\text{O}}$ are 1.2×10^3 for $\text{CH}_2=\text{C}=\text{O}$ (5.5 °C, 10% H_2O), 140 for $\text{Et}_2\text{C}=\text{C}=\text{O}$ (5.5 °C, 50% H_2O), 280 for $t\text{-BuCH}=\text{C}=\text{O}$ (5.3 °C, 50% H_2O), and 2.8×10^6 for $t\text{-Bu}_2\text{C}=\text{C}=\text{O}$ (25 °C, 100% H_2O). The very high ratio for $t\text{-Bu}_2\text{C}=\text{C}=\text{O}$

$\text{C}=\text{O}$ illustrates the fundamental difference between the H^+ and H_2O reactions, and the large steric barrier to H_2O attack in the plane for $t\text{-Bu}_2\text{C}=\text{C}=\text{O}$.

There is a modest steric barrier to k_{H^+} in $t\text{-Bu}_2\text{C}=\text{C}=\text{O}$, as values for k_{H^+} of 60 and 320 s^{-1} may be estimated¹⁶ for $\text{Et}_2\text{C}=\text{C}=\text{O}$ and $t\text{-BuCH}=\text{C}=\text{O}$, respectively, in 50% H_2O at 25 °C, as compared to the measured value of $3.6 \text{ M}^{-1} \text{ s}^{-1}$ for $t\text{-Bu}_2\text{C}=\text{C}=\text{O}$ (**5**).⁷ This is in contrast to the estimated^{14,17} relative reactivities of the corresponding methyl vinyl ethers $t\text{-Bu}_2\text{C}=\text{CHOMe}$, (*Z*)- $t\text{-BuCH}=\text{CHOMe}$, and $\text{Me}_2\text{C}=\text{CHOMe}$ of 14, 16, and 1.0, respectively.



We have argued before¹⁷ that the high reactivity of the di-*tert*-butylvinyl ether arises from strong steric interactions between the *cis*-*t*-Bu and OMe groups in $t\text{-Bu}_2\text{C}=\text{CHOMe}$ which are relieved upon protonation.¹⁷ As compared to the mono-*tert*-butyl analogue (*Z*)- $t\text{-BuCH}=\text{CHOMe}$, the second *tert*-butyl is butressing the first and increasing the ground-state strain. The OMe group is not present in the ketene **5** so this accelerating influence is absent.

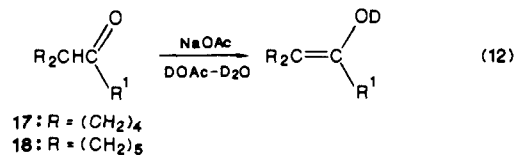
Retardation of the protonation rate of $t\text{-Bu}_2\text{C}=\text{C}=\text{O}$ evidently arises from steric interference in the transition state of the bulky groups with the proton donor and the solvent and also from increased steric interaction between the *tert*-butyl groups as the carbon changes from sp^2 to sp^3 hybridization.

The solvent isotope effects $k_{\text{H}^+}/k_{\text{D}^+}$ for the ketenes vary from 1.82 to 3.60, within the range observed for ketene-limiting proton transfer to vinyl ethers and other alkenes,^{10,14,17} and so support the mechanism of eq 9.

In the case of $t\text{-Bu}_2\text{C}=\text{C}=\text{O}$ (**5**) general acid catalysis of the hydration is observed, confirming the occurrence of rate-limiting proton transfer. The uncatalyzed reactivities of **7** and **10** are too great to permit a reliable test for the occurrence of general acid catalysis in these substrates, although the greater reactivity of **10** in the acidic buffers from that expected in the pH-rate profile (Figure 1) could indicate a contribution from this effect.

The vinyl ethers **11–13** were included in the study as models of the protonation of the ketenes **7–10**. Unfortunately the observed trends in the k_{H^+} values for **11–13** cannot be compared in detail to those of the ketenes as the rapid H_2O reaction of **9** precluded extensive studies of its acid-catalyzed reaction, and no rates at all could be obtained for **8**. It may be noted that the ratio of k_{H^+} for **9/7** of 3.8 is larger than that of 1.2 for **13/11**, but further interpretation of this difference does not appear warranted.

The rate ratio for hydration $k(\mathbf{12})/k(\mathbf{13})$ of 1.5 for the exocyclic vinyl ethers may be compared to the rate ratio $k(\mathbf{17})/k(\mathbf{16})$ of 0.28 for deuterium exchange of the corresponding ketones with NaOAc in aqueous HOAc.¹⁹ These rate ratios are consistent, as the vinyl ether hydration involves rate-limiting protonation as in eq 9, with a change in hybridization from sp^2 to sp^3 , whereas the proton abstraction in the ketone exchange involves the opposite hybridization change (eq 12).



The base-induced hydrolyses of $\text{CH}_2=\text{C}=\text{O}$ (**1**), $\text{Et}_2\text{C}=\text{C}=\text{O}$ (**7**), and $t\text{-BuCH}=\text{C}=\text{O}$ (**10**) are the first examples of this process

(15) (a) Vogt, J.; Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3478–3483. (b) Armitage, M. A.; Higgins, M. J.; Lewars, E. G.; March, R. E. *Ibid.* **1980**, *102*, 5064–5068. (c) Beach, D. D.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. L. *Ibid.* **1984**, *106*, 536–539. (d) Nobes, R. H.; Bouma, W. J.; Radom, L. *Ibid.* **1983**, *105*, 309–314. (e) Ausloos, P.; Lias, S. G. *Chem. Phys. Lett.* **1977**, *51*, 53–56. (f) Debrou, G. B.; Fulford, J. E.; Lewars, E. G.; March, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 345–352. (g) Olah, G. A.; Dunne, K.; Mo, Y. K.; Szilagyi, P. *J. Am. Chem. Soc.* **1972**, *94*, 4200–4205.

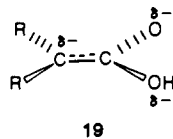
(16) Assuming $k(25 \text{ °C})/k(5.5 \text{ °C}) = 4.7$ measured for $t\text{-BuCH}=\text{C}=\text{O}$ in 20% H_2O applies in 50% H_2O as well.

(17) Chlang, Y.; Kresge, A. J.; Tidwell, T. T.; Walsh, P. A. *Can. J. Chem.* **1980**, *58*, 2203–2206.

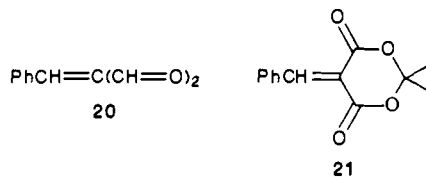
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reported for ketenes. The pH must be rather high before this reaction can compete with the water reaction, and this explains why previous efforts⁵ to detect hydroxide catalysis of ketene reactions failed, as the water reaction dominated in the pH range studied.⁵ The transition state **19** for OH⁻-induced hydration involves attack in the plane of the ketene, similar to the H₂O reaction.



The relative reactivity of Et₂C=C=O (**7**) toward H₂O and OH⁻ may instructively be compared to that of PhCOCF₃,^{11a} 3-ClC₆H₄CH=O,^{11b} and formaldehyde,^{11c} which give ratios of $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$ (M⁻¹s⁻¹)/k_{H₂O}(s⁻¹) of 1.6 × 10⁵, 1.2 × 10⁷, and 5.0 × 10⁵, respectively. For **7**, $k_{\text{H}_2\text{O}} = 0.10 \text{ s}^{-1}$ at 5.5 °C in 50% H₂O/CH₃CN (Table II), and a value of 4.0 M⁻¹ s⁻¹ for k_{OH^-} is obtained from the fit of the corrected (see Experimental Section) pH values in the pH-rate profile (Figure 1), whereas use of the stoichiometric concentrations of NaOH gives $k_{\text{OH}^-} = 79 \text{ M}^{-1} \text{ s}^{-1}$. The resulting $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$ ratios are 40 and 790, respectively, and would be doubled if corrected to 100% H₂O. Other rather low values of $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$ of 3.3 × 10³ and 1.3 × 10³ have been found for **20** and **21**, respectively.^{20c} The origin of these variations of selectivity with structure is a challenge for further study.



The structural isotope effects $k(t\text{-BuCH=C=O})/k(t\text{-BuCD=C=O})$ appear to be consistent with these interpretations. Thus as already noted a k_{H^+} process of rate-limiting proton transfer to carbon according to eq 9 or 10 involves rehybridization of the isotopically labeled carbon from sp² to sp³, which is the reverse of the frequently studied process involving ionization to give a carbocation, for which values of $k(\text{H})/k(\text{D})$ between 1.1 and 1.25 are often observed.²¹ The ketene value is 0.77 ± 0.05, or the inverse of 1.30, and this is consistent with the pathway envisaged. Interestingly a rate ratio $k(\text{PhCH=C=N-}i\text{-Pr})/k(\text{PhCD=C=N-}i\text{-Pr})$ of 1.22 for acid-catalyzed hydrolysis was reported, and a mechanism analogous to that of eq 9 was proposed,^{20c} but no explanation was advanced for the seemingly anomalous isotope effect.

The isotope effects $k(t\text{-BuCH=C=O})/k(t\text{-BuCD=C=O})$ for $k_{\text{H}_2\text{O}}$ and k_{OH^-} are 0.91 ± 0.01 and 0.73 ± 0.08 (for [NaOH] = 0.0035 M), respectively. Both of these are distinctly less than 1.0, and within the sizable experimental uncertainty the value for k_{OH^-} is less than that for $k_{\text{H}_2\text{O}}$. The transition states **14** and **19** envisaged for the H₂O- and OH⁻-induced reactions, respectively, presumably involve more negative charge buildup on carbon in the latter case, and evidently the isotope effect arises from a stiffening of the C-H vibration frequencies in the transition state due to this increased charge, as the hybridization of the carbon does not change. No previous examples of structural H/D isotope effects due to increased charge without rehybridization at sp²

carbon are known to us, and additional study of such isotope effects appears warranted.

In general support of our mechanistic interpretations for ketenes, it may be noted that similar proposals have been made for other heterocumulenes, including isocyanates,^{20a,b} ketenimines,^{20c} and diazomethane.^{20d} One exception is the neutral hydrolysis of PhCH=C=N-*i*-Pr for which a general acid catalysis mechanism with protonation at C_β was proposed primarily on the basis of the large solvent isotope effect $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 4.8$, and the absence of an OH⁻-catalyzed route.^{20c} However, it may be noted that these reactions were only followed up to pH 12, and if the $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$ rate ratio is similar to that of **7** it may not have been detected.

In conclusion we have made the first measurements of ketene hydration across the pH range in highly aqueous solutions and have observed the acid, neutral, and OH⁻ reactions of CH₂=C=O, Et₂C=C=O, and *t*-BuCH=C=O. These reactions show major effects of substituents that are both steric and electronic in nature, and the results indicate the acid-catalyzed reaction involves rate-limiting proton transfer to C_β (eq 3) while the H₂O and OH⁻ reactions involve rate-limiting nucleophilic attack in the plane of the ketene via transition states **14** and **19**, respectively. The evidence does not favor previous proposals of additions through cyclic transition states or proton transfer to oxygen. Ketenes show a rather low $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$ rate ratio and β-structural isotope effects $k(\text{H})/k(\text{D})$ of less than 1.0 for hydration.

Experimental Section

The carboxylic acid precursors to **7-10** were obtained from Aldrich and converted to the dibromides as reported previously.^{4a,b} Ketenes were prepared as before^{4a,b} and were always kept under an Ar atmosphere. Ketene (**1**) was prepared by pyrolysis of the dimer.²²

In a typical procedure for ketene generation Et₂CBrCOBr (2.46 g, 9.53 mmol) and Zn (0.62 g, 9.5 mmol, activated with HCl) were stirred in 80 mL of THF at 0 °C for 1.5 h under Ar and then the product ketene was codistilled with the THF (25 °C, 20 Torr) and the yellow-green distillate was stored at low temperature in a sealed bottle. The ketene concentration was measured when needed by adding aniline to an aliquot at -78 °C and weighing the product anilide. A ketene concentration 5% higher was determined when a sample of the ketene solution was titrated with 0.02 N NaOH. The ketene solution displayed λ_{max} 378 nm, and based on the measured concentration **7** had ε = 13.3 (cm M)⁻¹. A similar analysis of the concentration of **10** was carried out, with λ_{max} 360 nm (THF), ε = 13.2.

Solutions for measuring the reactivity of **7-10** in H₂O/CH₃CN (Table I) were prepared by diluting samples of 10, 20, 25, 30, and 35 mL of distilled H₂O to 50 mL with CH₃CN, with addition of the last portion of CH₃CN after the bulk of the solution had reached thermal equilibrium. For the pH-rate profile 0.1 M NaOH, HCl, and NaCl solutions in appropriate ratios were diluted to the mark with CH₃CN to give the high and low pH solvents, and the concentrations of H⁺ and OH⁻ were determined by titration. Buffer solutions were prepared by reacting solutions of ClCH₂CO₂H, HCO₂H, CH₃CO₂H, NaH₂PO₄, and NaHC₂O₃ with NaOH solution to give the buffer ratios indicated and then adding 0.1 M NaCl solution and CH₃CN. The solutions in Table IV were prepared by similar methods.

Kinetics for **7-10** were carried out by injecting 10 μL of approximately 0.1 M ketene solution in THF into the reaction solvent in 1.2 mL of solvent thermostated in the UV cell, shaking and monitoring the decrease in absorption at 221 nm with a Cary 210 spectrophotometer. For the fastest runs (Table I) a Hewlett-Packard 8451 diode array spectrophotometer with magnetic stirring of the sample cells was used. All rate constants were measured at least in duplicate with maximum deviations of ±5%.

The vinyl ethers **11-13** are known: **11** was prepared by the reaction of 3-pentanone with MeOCHPh₃,^{23a} and **12** and **13** were prepared from cyclopentanone and cyclohexanone by a reaction sequence^{23b} using Me₃SiCH₂OMe conducted at Toronto Research Chemicals. Authentic samples of the dimers of **7**,^{24a} **8**,^{24b} and **9**^{24b} were prepared by the reported methods.²⁴

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(21) (a) Shiner, V. J., Jr. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand: New York, 1970; Vol. 2. (b) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980. (c) Yamataka, H.; Tamura, S.; Hanafusa, T.; Ando, T. *J. Am. Chem. Soc.* **1985**, *107*, 5429-5434.

It has been found by Jordan that the effective pH of HCl in aqueous acetonitrile may be approximated by $-\log [\text{HCl}]$.^{25a} For the buffer and NaOH solutions in 50% CH₃CN, corrections derived by McGall and McClelland^{25b} at 25 °C and $\mu = 0.25$ were found to also be valid at $\mu = 0.05$ and were applied to our measured pH values. For buffers, $\text{pH} = \text{pH}_{\text{meas}} + 0.18$, where the factor 0.18 accounts for the difference in the

(25) (a) Jordan, F. *J. Phys. Chem.* 1973, 77, 2681-2683. (b) McGall, G.; McClelland, R. A., University of Toronto, unpublished results privately communicated.

medium from pure H₂O, and for NaOH, $\text{pH} = 15.0 + \log [\text{NaOH}]$, where 15.0 is the $\text{p}K_w$ determined for H₂O in this medium.

Acknowledgment. Financial support was provided by the Natural Sciences and Engineering Research Council of Canada. We thank Professor A. J. Kresge for the use of the HP 8451 spectrophotometer, L. Baigre for the preparation of **10**, and Dr. Glenn McGall and Professor R. A. McClelland for their unpublished procedure for correction of pH values in mixed solvents.

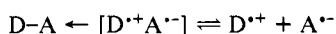
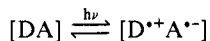
Simultaneous Capture of Two Distinct Radical Ion Intermediates Generated from the EDA Complexes of Three-Membered Compounds with TCNE by Photoexcitation and in the Dark¹

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Abstract: Irradiation of the electron donor-acceptor (EDA) complexes of 2,2-diaryl-1-methylenecyclopropanes, 1,1,2,2-tetraarylcyclopropanes, 2,3-diaryloxiranes, or 2,3-diarylaziridines with tetracyanoethylene (TCNE) under aerated conditions involved oxygenation and/or the [3 + 2] cycloaddition with TCNE. The same oxygenation took place in the dark when the EDA complexes of 2,2-diaryl-1-methylenecyclopropanes or 1,1,2,2-tetraarylcyclopropanes with TCNE were simply stirred in oxygen-saturated solvents. Oxygenation occurred much more efficiently as the solvent polarity and the electron-donative nature of donor substrates increased. 1,2,4,5-Tetramethoxybenzene (TMB) used as a quencher efficiently suppressed oxygenation but not the [3 + 2] cycloaddition at all. Oxygenation occurs through the solvent-separated radical cations diffused from the photogenerated geminate radical ion pairs, whereas the cage coupling of the radical ion pairs involves the [3 + 2] cycloaddition with TCNE.

The electron-transfer reactions which proceed through EDA complexes have been recognized as important processes not only in photochemical but also in thermal reactions. In fact, many organic photochemical and thermal reactions initiated by electron donor-acceptor interactions have appeared in literature.² Despite that, simple isomerization of donor substrates or donor-acceptor adduct (D-A) formation reactions usually occur,³ and experimental identifications of resulting radical ion intermediates are often ambiguous, mainly because such reactions may occur via complex multiple processes, all of which do not necessarily participate in the product formation step. Recent time-resolved spectroscopic studies by Hilinski and co-workers spectroscopically demonstrated those and clearly gained insight into an initial step of the photoexcitation of EDA complexes and roles of successively generated radical ion intermediates.⁴



Interestingly, the irreversible donor-acceptor adduct formation pathway was found to occur competitively with reversible diffusion

between the solvent-separated radical cations $\text{D}^{+\bullet}$ and the radical ion pairs $[\text{D}^{+\bullet}\text{A}^{\bullet-}]$. Experimental verification of such processes is thus obviously difficult as long as chemical capture of $\text{D}^{+\bullet}$ cannot be simultaneously performed. It may be, however, possible if the photoexcitation of EDA complexes is investigated under conditions in which the D-A formation competitively occurs with chemical capture of $\text{D}^{+\bullet}$, such as oxygenation. For this purpose, we thought that strained three-membered compounds such as 2,2-diaryl-1-methylenecyclopropanes (**1**), 1,1,2,2-tetraarylcyclopropanes (**6**), 2,3-diaryloxiranes (**12**), and 2,3-diarylaziridines (**16**) seemed to be suitable as donor substrates since these donors make the EDA complexes with TCNE as shown in Table I, and their electron-transfer oxygenations⁵⁻⁸ under photosensitized conditions and their

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(7) Oxygenation of oxiranes: (a) Schaap, A. P.; Siddiqui, S.; Balakrishnan, P.; Lopez, L. *Isr. J. Chem.* 1983, 23, 415. (b) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* 1983, 105, 663. (c) Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *J. Am. Chem. Soc.* 1983, 105, 5149. (d) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Rahman, A. F. M. M.; Oliver, J. P. *J. Am. Chem. Soc.* 1984, 106, 6087. (e) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* 1984, 25, 167. (f) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Sandison, M. *Tetrahedron* 1985, 41, 2229. (g) Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Chem. Commun.* 1982, 1223. (h) Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Perkin Trans. 1* 1984, 15. (i) Kirschenheuter, G. P.; Griffin, G. W. *J. Chem. Soc., Chem. Commun.* 1983, 596.