J. Am. Chem. Soc. **1980**, *102*, 5835–5838

quantum yield in our system. Figure 7 presents the results of this determination. We obtain for ϕ_{cl} the approximate value 0.10. Though this value contains the cumulative errors of two relative measurements, its mere largeness indicates that the chemical step studied here is really the one directly responsible for light generation. It should be pointed out that here ϕ_{cl} is defined as the ratio of the number of photons produced to the number of luminol molecules consumed.

Some Reflections on the Luminol–O_2 System. Upon comparison of the luminol–O_2 system studied by Baxendale[5] and Würzberg et al.[14] with the present system, the following striking similarities are observed.

(a) The integrated light intensity vs. pH displays approximately the same apparent pK_a value.

(b) The light obtained remains constant in both systems between pH 10 and 11.

(c) The rise time for chemiluminescence decreases monotonously with increasing pH.

These observations strongly suggest that in both cases the same crucial intermediate (namely, the peroxide adduct) is operative. In the O_2 system, the formation of the peroxide adduct should be the result of a dismutation of the peroxy radicals. If so, formation of the peroxide could be paralleled by the production of azaquinone and O_2. Indeed, Baxendale and Würzberg et al. observe an increase in absorbance between 500 and 600 nm, a spectral region where azaquinone has a sizable extinction coefficient.[16] The lower quantum yield found in the luminol–O_2 system is most probably due to competing reactions in the dismutation step of the peroxy radicals.

Relating the Present Work to Existing Theories. Finally, relating the present reaction scheme with modern theories on chemiluminescence as proposed by White et al.,[20] McCapra et al.,[21] and Schuster et al.[22] is appropriate. First it will be noticed that the kinetic findings in this work in no way contradict or confirm the presence of an electron transfer in the final excitation step. At present we are not able to assess the nature of the decomposition step. Reaction schemes[20,21] where expulsion of nitrogen is followed by further steps are not inconsistent with our results. Since only one kinetic step can be measured in the decay of the peroxide, it transpires that, if further steps exist, they should be very rapid indeed ($k > 10^6\ s^{-1}$). Further work will be done to determine the activation parameters of this reaction.

Acknowledgments. The Swedish Work Environment Fund and The Swedish Natural Science Research Council are acknowledged for financial support. The authors are grateful to Dr. Frank McCapra for stimulating discussions and valuable comments. Drs. T. E. Eriksen, P. Forslind, P. Sand, and L. Sjöberg are acknowledged for helpful comments during the course of this work.

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Mechanistic Change in Acid-Catalyzed Hydrolysis of Silyl Vinyl Ethers[1]

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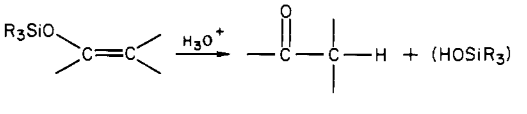
Abstract: *tert*-Butyldimethylsilyl vinyl ethers $t\text{-BuMe}_2\text{SiOCR}{=}\text{CH}_2$ hydrolyze in 50% CH_3CN–H_2O with general and specific acid catalysis and a linear dependence of log k_{H^+} on $\sigma_p^+(R)$, indicating that the reaction occurs with rate-determining proton transfer to carbon (the $A_{SE}2$ mechanism). By contrast the rates of trimethylsilyl vinyl ethers $\text{Me}_3\text{SiOCR}{=}\text{CH}_2$ are not correlated by $\sigma_p^+(R)$ but still depend on proton and general acid concentrations. Nucleophilic attack on silicon is implicated in the rate-determining step of the latter compounds, and the possibilities for the details of this process are considered.

Trialkylsilyl vinyl ethers have become of pervasive importance in synthetic organic chemistry,[2] but studies of their reaction mechanisms have been conspicuously neglected. Hydrolysis of the silyl vinyl ethers to carbonyl compounds (eq 1) is an important transformation of these materials, and we have now studied the kinetics of the acid catalysis of the process.



(1)

Results

Silyl vinyl ethers of representative structural types were prepared by known procedures[3,4] for rate studies. The solubilities of these substrates in water were low so 50% by volume H_2O–acetonitrile solutions were utilized for the kinetic measurements. Rates were measured by monitoring the change of the alkene or carbonyl chromophore by UV spectroscopy.

For the least reactive compound studied, $t\text{-BuMe}_2\text{SiOCH}{=}\text{CH}_2$, the rate could be conveniently monitored by using HCl catalyst, and a linear dependence of rate on HCl concentration in the range 0.03–0.12 M was observed. For all other substrates acetate or formate buffers were used as catalysts. The rate law $k_{obsd} = k_{H^+}[H^+] + k_{HA}[HA]$ where HA is the buffer acid was

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Table I. Summary of Acid-Catalyzed Hydrolysis Rates of Silyl Vinyl Ethers $R'Me_2SiOR$ in 50% H_2O–Acetonitrile at 25 °C[a]

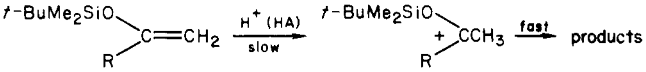
R	R′	k_{H^+}, M^{-1} s^{-1}	k_{HA}, M^{-1} s^{-1} × 10^2 [b]
$CH{=}CH_2$ (1)	Me	50.4	8.92
$CPh{=}CH_2$ (2)	Me	5.51	1.35
$CMe{=}CH_2$ (3)	Me	23.0	4.82[c]
C(c-Pr)$=CH_2$ (4)	Me	58.0	19.3[d]
$CH{=}CH_2$ (5)	*t*-Bu	0.0635[e]	
$CPh{=}CH_2$ (6)	*t*-Bu	0.919	0.392
$CMe{=}CH_2$ (7)	*t*-Bu	21.6	5.11
C(c-Pr)$=CH_2$ (8)	*t*-Bu	132	115
p-$MeOC_6H_4C{=}CH_2$ (9)	Me	19.2	11.7
p-$MeC_6H_4C{=}CH_2$ (10)	Me	8.47	2.68
p-$ClC_6H_4C{=}CH_2$ (11)	Me	4.48	0.839
m-$O_2NC_6H_4C{=}CH_2$ (12)	Me	1.84	1.08
p-$O_2NC_6H_4C{=}CH_2$ (13)	Me	2.25	1.15
1-cyclohexenyl[f] (14)	Me	22.7	0.892
(*Z*)-CMe=CHPh (15)	Me	2.50	0.393
(*E*)-CMe=CHPh (16)	Me	6.54	1.09
(*Z*)-CH=CHPh (17)	Me	2.80	0.624
(*E*)-CH=CHPh (18)	Me	6.71	5.08
C_6H_5 (19)	Me	7.97	1.62

[a] Measured by UV observation of the decrease of the alkene absorption using acetate or formate buffers except as noted. Ionic strength kept at $\mu = 0.05$ with NaCl. [b] HA is HCO_2H except as noted. [c] Also observed in acetate buffer, $k_{HOAc} = 5.47 \times 10^{-3}$ M^{-1} s^{-1}. [d] Catalysis by HOAc. [e] Catalysis by 0.03–0.12 M HCl. [f] For methyl cyclohexenyl ether in 50% H_2O-CH_3CN (measured at 234 nm) k_{H^+} is 2.99 M^{-1} s^{-1}, k_{HCO_2H} is 7.98×10^{-3} M^{-1} s^{-1}; k_{H^+} in H_2O at 25 °C is 42.3 M^{-1} s^{-1} (ref 6b).

observed in each case. At pH below 4.5 and buffer anion A^- concentration below 0.04 M no rate terms dependent on $[A^-]$, $[OH^-]$, or $[H_2O]$ could be detected. At higher pH there was basic catalysis of the reaction, and the details of this process will be the subject of further study. The rates of the acid-catalyzed reactions are summarized in Table I. For comparative purposes rates of methyl cyclohexenyl ether and trimethylsilyl phenyl ether were also measured in this solvent system and are included in Table I.

Discussion

In Figure 1 a reasonable correlation (slope = −7.32, $r = 0.992$) of log k_{H^+} for *tert*-butyldimethylsilyl vinyl ethers *t*-$BuMe_2SiOCR{=}CH_2$ (R = H, Ph, Me, c-Pr) with $\sigma_p^+(R)$ is compared to the correlation (slope = −8.27, $r = 0.994$) for the corresponding methyl vinyl ethers derived[5] from reported[6] rates in H_2O solutions. We have previously demonstrated[5] linear correlations of log k_{H^+} with $\sigma_p^+(R)$ for alkenes, including methyl vinyl ethers,[6] that react by the $A_{dE}2$ mechanism of rate-limiting proton transfer to the double bond. The same mechanism (eq 2) is therefore established for the *tert*-butyldimethylsilyl vinyl ethers by the observed specific and buffer acid catalysis and the correlation with $\sigma_p^+(R)$.



(2)

The apparent rate difference between the silyl and methyl ethers in Figure 1 is largely due to a solvent effect, in that the former rates were measured for 50% H_2O–acetonitrile solutions, whereas the latter were obtained[6] in H_2O. For methyl cyclohexenyl ether (footnote *f*, Table I) k_{H^+} is 14 times larger in water, and assuming that this factor holds for the ethers in Figure 1 the methyl ethers are 2.5 times as reactive on average as their *tert*-butyldimethylsilyl counterparts. Application of this factor to the equation log $k_{H^+} = -10.5\sum\sigma_p^+(R) - 8.92$ derived for all alkenes[5] leads to a $\sigma_p^+(R)$ value of −0.74 for *t*-$BuMe_2SiO$, in reasonable agreement with the value of −0.60 derived for Me_3SiO from a correlation of carbonyl stretching frequencies of substituted acetophenones.[7]

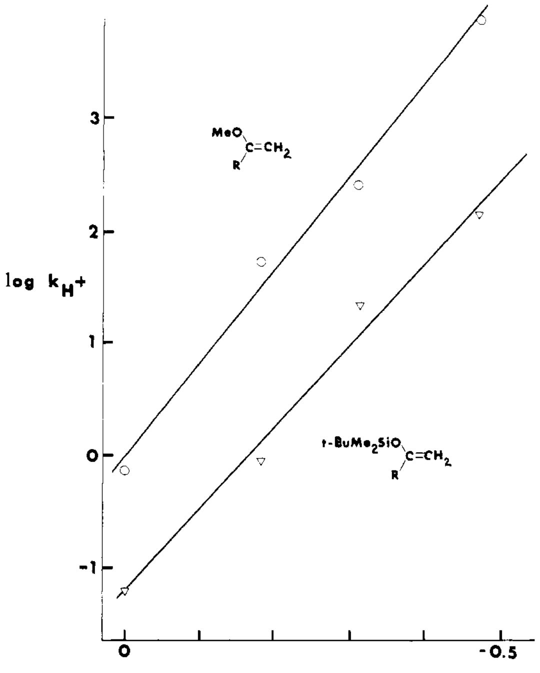


Figure 1. Correlation of the acid-catalyzed hydrolysis rates of vinyl ethers $R'OCR{=}CH_2$ with $\sigma_p^+(R)$.

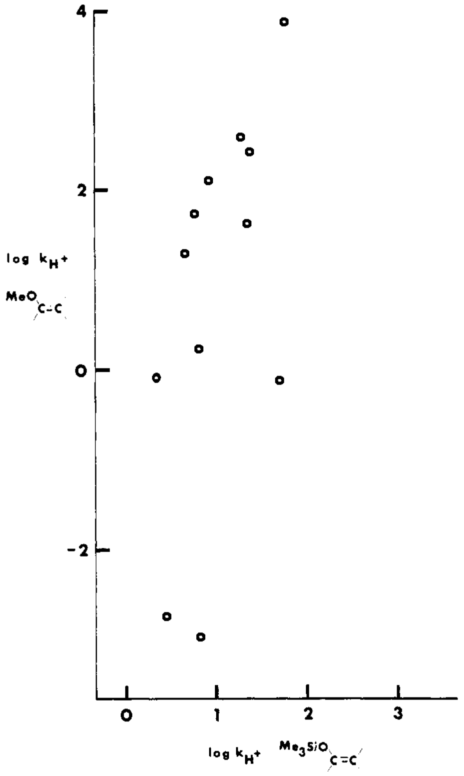


Figure 2. Comparison of rates of acid-catalyzed hydrolysis of vinyl ethers.

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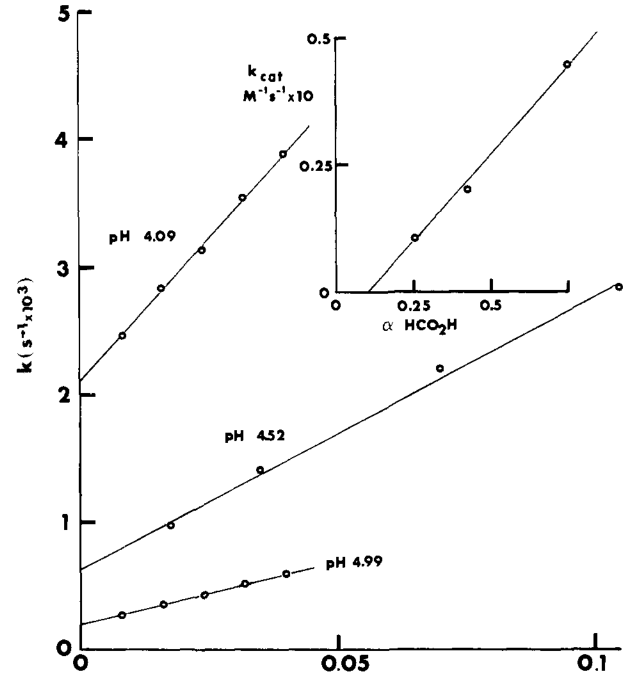


Figure 3. Dependence of k_{obsd} for $Me_3SiOCMe{=}CH_2$ as a function of total concentration of HCO_2H and HCO_2Na. Inset: dependence of k_{cat} $(=(k_{obsd} - k_0)/[\text{formate}])$ on mole fraction HCO_2H.

By contrast the results for the trimethylsilyl vinyl ethers are not consistent with the operation of rate-determining proton transfer alone (eq 2) as a major reaction path throughout the entire series. This may be illustrated by comparison of the rates with those of the corresponding methyl vinyl ethers (in H_2O),[6] as shown graphically in Figure 2. The latter compounds react exclusively by the Ad_E2 mechanism in acid, and cover a range of reactivity of almost 10^7 for the substrates considered. By contrast the corresponding trimethylsilyl compounds show a range in reactivity of only 13 and no correlation with the methyl vinyl ether reactivities, thus strongly implicating a change in mechanism for the trimethylsilyl ethers as compared to the *tert*-butyldimethylsilyl ethers which react according to eq 2.

The competing mechanism that intervenes when the trimethylsilyl group is substituted for the more crowded *tert*-butyldimethylsilyl group surely involves nucleophilic attack on silicon. Indeed prevention of such nucleophilic attack is the rationale for the synthetic application of the *tert*-butyldimethylsilyl group.[2]

The details of this reaction cannot, however, be specified with certainty. Specifically there are two types of mechanism that combine the kinetic dependence on $[H^+]$ and [HA] with nucleophilic attack on silicon. One of these involves rate-limiting proton transfer with simultaneous water attack in the rate-determining step (eq 3), and this could apply to both the specific- (H^+) and general- (HA) acid-catalyzed routes. In a second type of mechanism there is a preequilibrium protonation (eq 4) followed by either rate-limiting general-base-catalyzed nucleophilic attack (eq 5) for the overall general-acid-catalyzed route or simple rate-determining hydration (eq 6) for the specific-acid-catalyzed process. The kinetic expression for either of the mechanisms involving participation of the buffer (eq 3 or eq 4 and 5) is rate $= k[ROSiMe_3][HA][H_2O]$, so they cannot be differentiated on the basis of these kinetic measurements.

$$H_2O + H^+(HA) + ROSiMe_3 \xrightarrow{\text{slow}} ROH + HOSiMe_3 \tag{3}$$

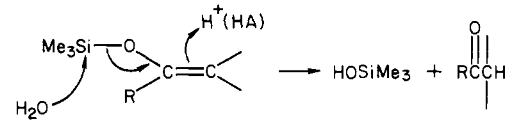
$$ROSiMe_3 + H^+ \overset{k_{eq}}{\rightleftharpoons} RO^+HSiMe_3 \tag{4}$$

$$RO^+HSiMe_3 + H_2O + A^- \xrightarrow{\text{slow}} ROH + HOSiMe_3 + HA \tag{5}$$

$$RO^+HSiMe_3 + H_2O \xrightarrow{\text{slow}} ROH + HOSiMe_3 \tag{6}$$

A similar dilemma arises in other systems, for example, the acid hydration of formaldehyde, for which the kinetic expression rate $= k[CH_2O][HA]$ is observed.[8] In this case detailed consideration of the interrelation of cleavage rates of formaldehyde hemiacetals with Brønsted coefficients for the general acids led to the conclusion that a concerted process analogous to eq 3 was involved.[8] It does not appear that this approach is applicable to the silyl ether system. Nevertheless some limitations as to the probable path followed can be made.

Two reasonable variants for a rate-limiting transition state combining nucleophilic solvent participation as well as proton transfer by H_3O^+ or HA (eq 3) are shown in eq 7 and 8. Neither of these involves significant charge development on C_α and are thus consistent with a lack of rate dependence on R. Of the two eq 8, involving oxygen protonation, is rendered more likely by the fact that $PhOSiMe_3$ has comparable reactivity to the vinyl trimethylsilyl ethers. The fact that vinyl and phenyl groups have similar properties as remote substituents (as measured by σ or σ^+ values) leads to the expectation that the rate of hydration of the phenyl ether by the mechanism of eq 8 would be comparable to the same reaction of vinyl ethers. However, if the path of eq 7 involving carbon protonation were followed, no similarity in rate would be anticipated as the loss of resonance energy that would occur on carbon protonation of the aryl ether would surely render this path less favorable than carbon protonation of the vinyl ether. It is conceivable that $PhOSiMe_3$ could react by a mechanism analogous to eq 8 and the vinyl ethers react at a comparable rate by the reaction of eq 7 but this would be an unusual coincidence.



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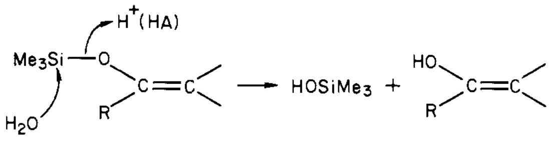

(8)

Studies by Åkerman[9] of HCl-catalyzed hydrolysis of aryl silyl ethers $ArOSiR_3$ in 51.4% by weight $EtOH-H_2O$ at 25 °C revealed a correlation of the rate constants with the σ values of the aryl substituents with $\rho = 0.53$, consistent with a substituent effect on oxygen basicity. It is improbable that ring protonation would give such a correlation. Åkerman[9] also observed a rate ratio for acid-catalyzed hydrolysis $k_{H^+}(Me_3SiOPh)/k_{H^+}(t\text{-}BuMe_2SiOPh)$ of 10^5, indicating that nucleophilic participation is also significant in the rate-limiting step for Me_3SiOPh, and supporting the analogy between the phenyl and vinyl ethers.

In summary for $t\text{-}BuMe_2SiOCR{=}CH_2$ (R = H, Ph, Me, c-Pr) the Ad_E2 mechanism (eq 2) is clearly indicated. For the trimethylsilyl vinyl ethers (and $PhOSiMe_3$) the predominant reaction involves nucleophilic participation, but this could involve either synchronous proton transfer and water attack (eq 3) or an equilibrium protonation (eq 4) and general-base-assisted H_2O attack (eq 5), with or without unassisted H_2O attack (eq 6). If the route of eq 3 occurs, proton transfer to oxygen (eq 8) appears most likely.

It is to be hoped that continuing studies into the role of solvent and nucleophilic and base catalysis of these reactions will permit a choice between the different possibilities to be made.

Experimental Section

Trialkylsilyl ethers were prepared by several of the known procedures for preparation of such compounds: (A) reaction of a ketone or aldehyde with $Me_3SiCl-Et_3N-DMF$;[3a,b] (B) reaction of a ketone or aldehyde with lithium diisopropylamide in THF followed by Me_3SiCl or *t*-

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$BuMe_2SiCl$;[3a,b,e] (C) treatment of a ketone or aldehyde in THF with KH followed by Me_3SiCl or *t*-$BuMe_2SiCl$;[4c,d,f] (D) treatment of THF with *n*-BuLi to generate acetaldehyde enolate followed by *t*-$BuMe_2SiCl$.[3c] The silyl ethers were purified by gas chromatography and their identities and purities confirmed by NMR examination. The *E*/*Z* isomeric pairs **15**/**16** and **17**/**18** were separated by VPC by using a 6 mm × 3 m TCEP on Chromosorb P column. Differentiations of **15**/**16**[3b] and **17**/**18**[4b,c] were confirmed by comparison with their published NMR spectra. With the exception of **12** and **13**, trimethylsilyl ethers corresponding to each of the structural types **1**–**19** have been reported in the literature. Correct elemental analyses (C, H) and spectral data were obtained for **12** and **13**. Methods of preparation (A–D above), wavelengths (nm) for kinetics studies, and previous literature references were as follows: **1** (A) 215;[3c,d] **2** (A) 243;[4a] **3** (A) 228;[4e] **4** (B) 230;[3e] **5** (D) 215;[3c] **6** (C) 262;[4f] **7** (C) 228; **8** (C) 225; **9** (A) 280;[4a] **10** (A) 225;[4a] **11** (A) 223;[4a] **12** (A) 225; **13** (A) 265; **14** (A) 228;[3f] **15** (A) 261;[3b] **16** (A) 256;[3b] **17** (A) 257;[4b,c] **18** (A) 257;[4b,c] **19** (A) 272.[9]

Kinetics were measured by observing the change of the alkene or carbonyl absorption in the UV by using Cary 14 or 118 spectrophotometers. Buffer solutions were prepared by mixing aliquots of aqueous HA, NaOH, and NaCl solutions to a total of 50 mL (ionic strength $\mu = 0.10$) and diluting to 100 mL with spectral-grade acetonitrile (Matheson Coleman and Bell). Proton concentrations of the buffer solutions were measured with Beckman Zeromatic or Corning 130 pH meters. Acid concentrations of the HCl solutions were measured by titration. For the kinetic runs 3 mL of catalyst solution was equilibrated in 1-cm cells in the thermostated cell compartments and the alkene was added either neat or dissolved in acetonitrile to give solutions approximately 2×10^{-3} M in alkene. The solutions were shaken and the change of the UV absorption was monitored with time.

Data for $Me_3SiOCMe{=}CH_2$ illustrating the formate buffer catalysis at different buffer ratios and the dependence of k_{cat} (the catalytic constant for the buffer-catalyzed reaction) on the mole fraction HCO_2H of the total buffer species present are shown in Figure 3.

Acknowledgment is made to the Natural Science and Engineering Research Council of Canada and the Undergraduate Research Fund of Scarborough College for support of this work.

Hydration of the Flavylium Ion

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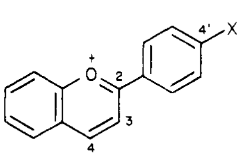
Abstract: A spectral and kinetic investigation has been carried out of the transformations undergone in aqueous solution by the parent flavylium ion and its 4′-methyl and 4′-methoxy derivatives. Evidence is reported for the existence at some time under some condition of seven species, the flavylium ion (F^+), two pseudobases, a 2-hydroxy adduct (B2) and a 4-hydroxy adduct (B4), the *cis*-2-hydroxychalcone and its ionized form (cC and cC^-), and the *trans*-2-hydroxychalcone and its ionized form (tC and tC^-). At pH 6.5–8.5, F^+ is relatively rapidly hydrated producing a mixture of B4, B2, and cC. The latter two are in equilibrium, their equilibration proceeding far more rapidly than F^+ is hydrated. B4 is a kinetic product of the hydration only; over a short period of time it rearranges via F^+ to the equilibrium mixture of B2 and cC. In base solution the behavior is similar, but the B2 ⇌ cC equilibrium is displaced toward the chalcone since it ionizes. Thus, at pH 12, F^+ reacts very rapidly with OH^- producing a mixture of B4 and cC^-, the latter coming from B2 initially formed. This is followed by the rearrangement of B4, the kinetic product, to cC^-. In acid solutions, pH 2–6, an acid–base type of equilibrium is relatively rapidly established between the cationic F^+ and the neutral species B2 and cC. In all of these solutions, with the exception of strong acids, a slow further reaction occurs resulting eventually in complete transformation to tC or, in base, tC^-. The upper limit on the relative amount of *cis*-chalcone or pseudobase present in equilibrium with the *trans*-chalcone after complete reaction is 0.02%. For a scheme $B4 \rightleftarrows F^+ \rightleftarrows B2 \rightleftarrows cC\ (\rightleftarrows cC^-) \rightarrow tC\ (\rightleftarrows tC^-)$, rate constants and equilibrium constants for each reaction stage have been obtained by a kinetic and spectral analysis.

The anthocyanin pigments responsible for a variety of plant and flower colors have been known for some time to be derivatives of polyhydroxyflavylium ions.[1-3] Also well established[4,5] is the fact that these colored cations are stable only in relatively acidic solutions, undergoing various structural transformations when placed in less acidic, neutral, or basic media, often with quite dramatic color changes or color disappearance. This chemistry has now been examined for a number of these cations,[4,5] including various anthocyanins, anthocyanidins, and synthetic flavylium salts.[6] There appears, however, not to have been a detailed investigation of the parent ion. We report here such a study, for three ions (F^+), the parent and two 4′-substituted derivatives.



F^+, X = H, Me, MeO

Results

Spectra of Flavylium Ions, pH 1–7, and pK_a Determination. Our general experimental approach was to prepare a stock solution in 0.1 M HCl of the perchlorate salt of each flavylium ion and to adjust this to the desired pH by mixing with appropriate buffers. The flavylium ions appear to be almost indefinitely stable in these stock solutions, in that there is little change over a period of days or even weeks in the absorption spectra of the solutions. One such spectrum showing the characteristic visible absorption peak of the flavylium ion is drawn in Figure 1.

Adjustment of the pH of the stock solution to 7 results in rapid decolorization, a spectrum taken as quickly as possible showing several overlapping peaks below 300 nm, but having little residual absorbance in the visible region. One example of such a spectrum can be seen in the curve labeled neutral-initial in Figure 1.

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0002-7863/80/1502-5838$01.00/0