

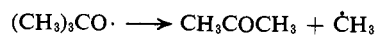
Examination of the rate constants listed in Table II indicates that only steric factors have any significant effect on the rates of the bimolecular self-reactions of iminyl radicals. Neither potential polar effects (*e.g.*, $(\text{CF}_3)_2\text{C}=\dot{\text{N}}$) nor the presence of aromatic rings (*i.e.*, $\text{Ph}_2\text{C}=\dot{\text{N}}$) reduces the rate significantly below the diffusion-controlled limit. The latter observation may relate to the structure of these radicals which precludes substantial delocalization of the unpaired electron into the π system of the aromatic rings. It is also of interest in connection with reports¹⁶ that iminyl radicals can be detected when certain alkaryl- and diaryloxime thionocarbamates, $\text{RR}'\text{C}=\text{NOC}(\text{S})\text{NMe}_2$, are heated to temperatures where they rearrange to the corresponding thioxime carbamates, $\text{RR}'\text{C}=\text{NSC}(\text{O})\text{NMe}_2$. The rates of radical generation in these experiments (so far as they can be ascertained) appear to be quite sufficient to account for the ready detection of the iminyl radicals even though they couple at close to the diffusion-controlled limit (see Table II).

As is usually the case,¹⁹ only steric factors have a dramatic effect on the rates of the bimolecular self-reactions of iminyl radicals. The 6.4-kcal/mol activation energy for the dimerization of $(t\text{-Bu})_2\text{C}=\dot{\text{N}}$ causes the rate to be seven orders of magnitude slower than diffusion controlled at -35° . It indicates that the steric retardation is due principally to enthalpy rather than to entropy effects.

Reaction mechanisms involving the β scission of intermediate iminyl radicals have sometimes been suggested previously.^{31,32} It is interesting to compare the

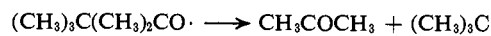
(32) See, *e.g.*, G. L. Pratt and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, **260**, 317 (1961); *Trans. Faraday Soc.*, **58**, 692 (1962); J. Kalvoda, *Helv. Chim. Acta*, **51**, 267 (1968); T. P. Forshaw and A. E. Tipping, *Chem. Commun.*, 816 (1969); M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **34**, 2848 (1969); L. J. Winters, J. F. Fischer, and E. R. Ryan, *Tetrahedron Lett.*, 129 (1971).

rate constant for β scission of $(t\text{-Bu})_2\text{C}=\dot{\text{N}}$ with that for β scission of some structurally related alkoxy radicals, since the two types of radical are isoelectronic. Thus, for *tert*-butoxy³³



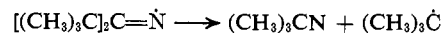
$$\log(k/\text{sec}^{-1}) = 12.4 - 13.9/\theta; \tau_{1/2} = 3.4 \times 10^{-2} \text{ sec at } 0^\circ$$

for *tert*-butyldimethylmethoxy³⁴



$$\log(k/\text{sec}^{-1}) = 14.8 - 7.5/\theta; \tau_{1/2} = 1.1 \times 10^{-9} \text{ sec at } 0^\circ$$

and for di-*tert*-butyliminyl



$$\log(k/\text{sec}^{-1}) = 14.4 - 17.1/\theta; \tau_{1/2} = 1.4 \times 10^{-1} \text{ sec at } 0^\circ$$

The loss of *tert*-butyl from the iminyl occurs at a rate comparable to the loss of methyl from *tert*-butoxy, but is much slower than the loss of *tert*-butyl from *tert*-butyldimethylmethoxy. These rate differences are related to the differences in the exothermicities of the β scission. Thus, from the heats of formation of methyliminyl (34.4 kcal/mol)³⁵ and acetonitrile (19 kcal)³⁶ and of ethoxy (-4.9 kcal)³⁵ and acetaldehyde (-39.7 kcal)³⁶ the heats of the reactions $\text{CH}_3\text{CH}=\dot{\text{N}} \rightarrow \text{CH}_3\text{C}\equiv\text{N} + \text{H}\cdot$ and $\text{CH}_3\text{CH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{CH}=\text{O} + \text{H}\cdot$ are estimated to be endothermic by 36.7 and 17.3 kcal/mol, respectively.

(33) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **89**, 4891 (1967).

(34) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 630 (1974).

(35) H. E. O'Neal and S. W. Benson, "Free Radicals," Vol. 2, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 17.

(36) Estimated from data given in ref 37.

(37) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

A Complete Kinetic Analysis of the A-Se2 Mechanism of Acid-Catalyzed Addition of Methanol to an Olefinic Double Bond

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Abstract: In 80% methanol-water 1,1-bis(*p*-dimethylaminophenyl)ethylene (**1**) undergoes slow, general acid catalyzed protonation at the double bond to form a carbonium ion (**2**) which is rapidly converted to the methyl ether (**3**) upon reaction with methanol or methoxide ion. This system is unique in that **1**, **2**, and **3** coexist at detectable concentration in acidic solution; it thus provides the first example of an A-Se2 addition to an olefinic double bond in which a complete kinetic and equilibrium analysis of the component steps has been accomplished. Rate constants for protonation of **1** by lyonium ion and for deprotonation of **2** by the solvent are $23 M^{-1} \text{ sec}^{-1}$ and $4.8 \times 10^{-2} \text{ sec}^{-1}$, respectively. These are rather low even for carbon bases and acids. Rate constants for nucleophilic attack on the cation **2** by methoxide ion and methanol are $4.9 \times 10^4 M^{-1} \text{ sec}^{-1}$ and 2.5 sec^{-1} , respectively, ratio $\sim 2 \times 10^4$. This ratio is considerably lower than expected on the basis of Ritchie's N_+ value.

The mechanism of hydration (or alcoholation) of olefins² has been the subject of some controversy

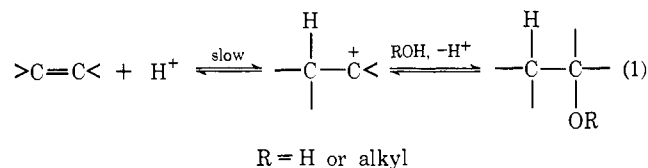
(1) Alfred P. Sloan Fellow, 1971-1973.

(2) P. B. D. De La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966, p 25.

since the hypothesis of Taft³ that the acid-catalyzed hydration of simple olefins involves rapid, reversible

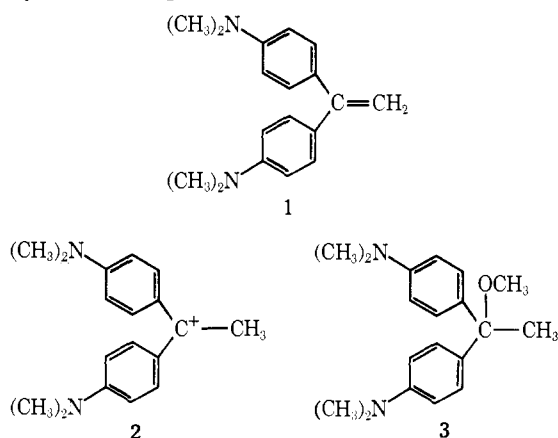
(3) (a) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 5372 (1952); (b) R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).

formation of a π complex which undergoes rate-limiting conversion to a carbonium ion, followed by fast addition of water. This mechanism has now been ruled out for a number of ethylenic compounds,² including styrenes⁴ and simple alkenes,⁵ by the observation of *general* acid catalysis. These results established addition of the proton to the double bond as the rate-determining step, followed by rapid attack of water on the carbonium ion, eq 1 (A-SE2 mechanism). A similar



mechanism is expected for alcohol addition (R = alkyl).

In this paper we show that addition of methanol to 1,1-bis(*p*-dimethylaminophenyl)ethylene (**1**) indeed proceeds by the A-SE2 mechanism. More significantly, this system is unique in that the three species **1**, **2**, and **3**



coexist in acidic solution at measurable concentrations, allowing the determination of the four rate constants of their interconversion.

This work was originally prompted by a desire to measure rates of protonation at a vinylic carbon and deprotonation of a methyl carbonium ion (first step in eq 1). It has been known for a long time that addition of small amounts of HCl to a methanolic solution of **1** produces rapidly the deep blue carbonium ion **2**.⁶ A recent study of the prototropic equilibria of **1** in methanol⁷ indicated that such a kinetic investigation would be quite feasible, in spite of competing protonation on the dimethylamino groups of **1**.⁷ We discovered, however, that acidic solutions of **1** are characterized by two separate kinetic processes instead of only one expected on the basis of the equilibrium study.⁷ We will show that this second process must be due to the formation of **3**.

Though it is the two dimethylaminophenyl groups which, by resonance interaction, are responsible for the high stability of the ion **2** and thus made this study feasible, their own basicity introduces a significant complication into our study, leading to the complex inter-

(4) W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964).

(5) A. J. Kresge, Y. Chiang, P. H. Fitzgerald, R. S. McDonald, and G. H. Schmid, *J. Amer. Chem. Soc.*, **93**, 4907 (1971).

(6) P. Pfeiffer and R. Wizinger, *Justus Liebigs Ann. Chem.*, **461**, 132 (1928).

(7) C. F. Bernasconi, T. Iijima, W. Koch, M. Wakae, and H. Zollinger, *Helv. Chim. Acta*, **56**, 2667 (1973).

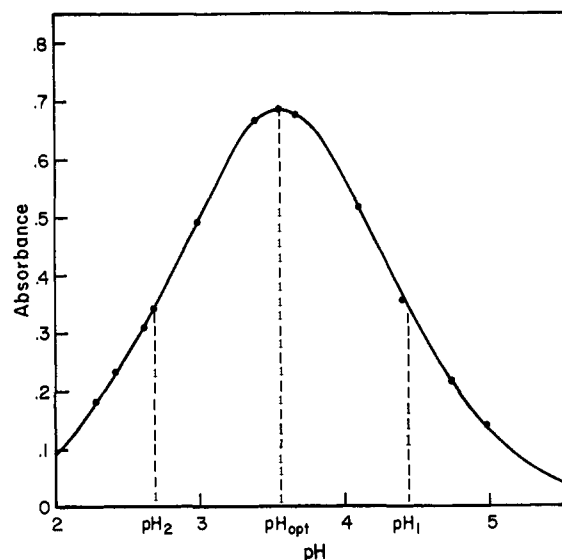


Figure 1. pK determinations. Plot of absorbance vs. pH, $[1]_0 = 2.51 \times 10^{-4} M$, $\lambda = 605 \text{ nm}$. $\text{pH}_{\text{opt}} = 3.56$, $\text{pH}_1 = 4.44$, $\text{pH}_2 = 2.69$.

play of acid-base equilibria of Scheme I. It will be shown that except for **8** all species in Scheme I play a kinetic role under appropriate conditions.

Results

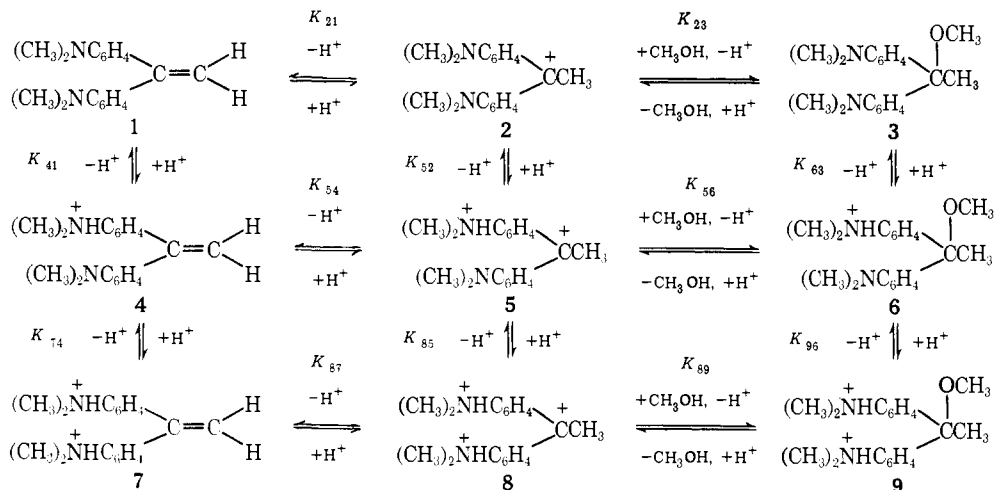
Because of the anticipated general acid-base catalysis we chose an 80% (v/v) methanol-water mixture in order to facilitate pH measurements and choice of buffer. Electronic spectra of **1** showed qualitatively the same pH dependence as in pure methanol;⁷ notably the absorption at 605 nm (λ_{max} of **2**) passes through a maximum at pH 3.56 as shown in Figure 1, indicating that below pH 3.56 the concentration of **2** decreases in favor of some doubly protonated species (**7** and **9**).

Rate of Formation of Carbonium Ion 2 from Olefin 1. The rate was measured spectrophotometrically at 605 nm at various pH values by mixing a neutral solution of **1** with HCl or with a chloroacetic-chloroacetate buffer. All reactions reported here and throughout this paper were run under pseudo-first-order conditions. The reciprocal relaxation times for equilibrium approach, $1/\tau_1$, are summarized in Table I. In the buffer experi-

Table I. Determination of $1/\tau_1$ at 25°^a

pH	$[H^+]^b, M$	$10^3(1/\tau_1) \text{ (pH), sec}^{-1}$		$10^3(1/\tau_1) \text{ (buffer)}^c, M^{-1} \text{ sec}^{-1}$
		Obsd	Calcd (eq 7)	
A. Formation of 2 from 1, Monitored at 605 nm^d				
2.53	2.95×10^{-8}	1.3 ^e	1.5	<i>e</i>
2.93	1.17×10^{-8}	2.5 ^e	2.9	<i>e</i>
3.29	5.13×10^{-4}	3.8 ^e	4.4	<i>e</i>
3.78	1.66×10^{-4}	5.5 ^f	5.2	9.1 ^g
4.09	8.12×10^{-5}	6.0 ^f	4.8	12 ^g
B. Equilibration of 1 and 3, Monitored at 289 nm^h				
5.32	4.78×10^{-6}	0.78 ⁱ	0.82	4.2 ⁱ
5.52	3.02×10^{-6}	0.50 ⁱ	0.55	4.0 ⁱ
5.71	1.95×10^{-6}	0.35 ⁱ	0.36	3.8 ⁱ
5.92	1.20×10^{-6}	0.25 ⁱ	0.23	3.0 ⁱ
6.21	6.16×10^{-7}	0.14 ⁱ	0.12	2.4 ⁱ

^a $\mu = 0.1 M$, maintained by adding KCl. ^b $[H^+] = 10^{-\text{pH}}$. ^c Slope of plot of τ_1^{-1} vs. $[\text{buffer}]_{\text{tot}}$. ^d $[1]_0 = 2 \times 10^{-4} M$. ^e HCl solutions, no buffer added. ^f Intercept of plot of τ_1^{-1} vs. $[\text{buffer}]_{\text{tot}}$. ^g Buffer was chloroacetic acid-chloroacetate ($\text{pK}_a = 4.4$ in 80% methanol). ^h $[1]_0 = 2-3 \times 10^{-5} M$. ⁱ Buffer was acetic acid-acetate ($\text{pK}_a = 6.2$ in 80% methanol).



ments the rate increased linearly with buffer concentration, indicating general acid-base catalysis; the values of $1/\tau_1(\text{pH})$ in the table are extrapolated to zero buffer concentration. The table includes the slopes, $1/\tau_1$ (buffer), of the buffer plots.

Temperature Jump Experiments. Discovery of Ether 3 Formation. When the equilibrated solutions resulting from the above experiments were subjected to a temperature jump, we discovered a much faster relaxation process (τ_2) in the 0.3-sec range, nearly independent of pH and buffer concentration, with a large amplitude at 605 nm. The results are reported in Table II. We

equilibrium reaction between (2 + 5) and (3 + 6 + 9).⁸

Derivation of $(1/\tau_1)(\text{pH})$ and $1/\tau_2$. In deriving expressions for $(1/\tau_1)(\text{pH})$ and $1/\tau_2$, we can safely assume that all vertical proton transfer equilibria in Scheme I are rapidly established. Furthermore, the large separation between $(1/\tau_1)(\text{pH})$ and $1/\tau_2$ ($\tau_1(\text{pH})/\tau_2 \geq 500$) indicates that some horizontal step(s) is (are) much faster than the others. We will make the assumption that the equilibration (3 + 6 + 9) \rightleftharpoons (2 + 5) is much faster than the equilibration (1 + 4 + 7) \rightleftharpoons (2 + 5). This assumption is consistent with the fact that the rapid $1/\tau_2$ process cannot be observed when mixing 1 with acid since ether formation occurs after the rate-determining step. With this assumption, $(1/\tau_1)(\text{pH})$ and $1/\tau_2$ are derived following known principles¹² and are given by eq 2 and 3.¹³

Table II. Determination of $1/\tau_2$ at 25°

pH	$10^3[\text{H}^+],^b$ M	[HA], M	[A ⁻], M	$10^4 \times$ [1] ₀ , M	$1/\tau_2, \text{sec}^{-1}$
A. Temperature-Jump Experiments ^c					
3.78	0.01 ^d	0.0025 ^d	2	2.92	
3.78	0.02 ^d	0.005 ^d	2	3.30	
3.78	0.05 ^d	0.0125 ^d	2	3.29	
3.78	0.10 ^d	0.025 ^d	2	3.48	
3.90	0.008 ^d	0.002 ^d	0.5	3.09	
3.90	0.008 ^d	0.002 ^d	5	3.23	
3.90	0.008 ^d	0.002 ^d	50	3.51	
3.42	<i>e</i>		2	3.47	
2.97	<i>e</i>		2	3.72	
B. Neutralization of Carbonium Ion Containing Solutions, Stopped-Flow Experiments ^c					
6.07	0.001 ^f	0.0005 ^f	1	2.47 ± 0.02 ^g	
6.15	0.0105 ^f	0.0095 ^f	1	2.53 ± 0.04 ^g	
6.32	0.0008 ^f	0.0007 ^f	1	2.48 ± 0.03 ^g	
C. Addition of HCl to Carbonium Ion Containing Solutions, Stopped-Flow Experiments ^c					
2.44	3.63	<i>e</i>	0.5	2.66 ± 0.02 ^g	
2.16	6.92	<i>e</i>	0.5	2.75 ± 0.01 ^g	
1.86	13.8	<i>e</i>	0.5	2.84 ± 0.03 ^g	
1.57	26.9	<i>e</i>	0.5	3.11 ± 0.04 ^g	
1.41	38.9	<i>e</i>	0.5	3.38 ± 0.01 ^g	
1.28	52.5	<i>e</i>	0.5	3.66 ± 0.01 ^g	

^a $\mu = 0.1 M$, maintained by adding KCl. ^b $[\text{H}^+] = 10^{-\text{pH}}$. ^c Relaxation monitored at 605 nm. ^d HA = chloroacetic acid, A⁻ = chloroacetate. ^e HCl. ^f HA = acetic acid, A⁻ = acetate. ^g Average of three runs.

will show that these and further kinetic data on τ_1 and τ_2 , as well as an equilibrium and a product study, are consistent with the assumption that τ_2 arises from the

$$\frac{1}{\tau_1}(\text{pH}) = \frac{k_{12} + k_{45} \frac{[\text{H}^+]}{K_{41}} + k_{78} \frac{[\text{H}^+]^2}{K_{41}K_{74}}}{D_1} [\text{H}^+] + \frac{k_{21} + k_{54} \frac{[\text{H}^+]}{K_{52}} + k_{87} \frac{[\text{H}^+]^2}{K_{52}K_{85}}}{D_2 + \frac{K_{23}}{[\text{H}^+]} D_3} \quad (2)$$

(8) Since our solvent contains 35% water on a molar basis, we must consider the possibility that water reacts with 2 to form an alcohol competitively with the ether. For two cations which have a reactivity comparable to 2 (*vide infra*), phenyl- and *p*-methoxyphenyltropylium ions, the rate ratios for combination with methanol in methanol compared to combination with water in water are 71 and 48, respectively,^{9,10} while the much less reactive *p*-nitro(Malachite Green) cation gave a ratio of only 3.2.¹¹ If the relative nucleophilicity toward 2 in our mixed solvent is as small as 3.2, then the ether will be favored over the alcohol by a factor of 6 to 1; with larger reactivity ratios the preference will be greater. In any event, it seems likely that the ether is the dominant component.

(9) C. D. Ritchie and P. O. I. Virtanen, *J. Amer. Chem. Soc.*, **94**, 4963 (1972).

(10) C. D. Ritchie and H. Fleischauer, *J. Amer. Chem. Soc.*, **94**, 3481 (1972).

(11) (a) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, **89**, 2063 (1967); (b) C. D. Ritchie and P. O. I. Virtanen, *ibid.*, **94**, 4966 (1972).

(12) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 893.

(13) (a) All equilibrium constants in Scheme I are defined as acid dissociation constants; e.g., $K_{21} = [\text{H}^+][1]/[2]$. The rate constants refer to reaction in the direction indicated by the subscripts; thus, k_{21} refers to the reaction $2 \rightarrow 1 + \text{H}^+$ and $K_{21} = k_{21}/k_{12}$. (b) Note that protonation of 1, 4, and 7 can occur by either MeOH_2^+ or H_3O^+ ; hence $k_{12} = k_{12}^{\text{MeOH}_2^+} K/(1 + K) + k_{12}^{\text{H}_3\text{O}^+}/(1 + K)$ with $K = [\text{MeOH}_2^+]/[\text{H}_3\text{O}^+]$.

$$\frac{1}{\tau_2} = \frac{k_{23} + k_{56} \frac{[H^+]}{K_{52}} + k_{89} \frac{[H^+]^2}{K_{52}K_{85}}}{D_2} + \frac{k_{32} + k_{65} \frac{[H^+]}{K_{63}} + k_{98} \frac{[H^+]^2}{K_{63}K_{96}}}{D_3} [H^+] \quad (3)$$

$$D_1 = 1 + \frac{[H^+]}{K_{41}} + \frac{[H^+]^2}{K_{41}K_{74}} \quad (4)$$

$$D_2 = 1 + \frac{[H^+]}{K_{52}} + \frac{[H^+]^2}{K_{52}K_{85}} \quad (5)$$

$$D_3 = 1 + \frac{[H^+]}{K_{63}} + \frac{[H^+]^2}{K_{63}K_{96}} \quad (6)$$

Since species **5** and **8** are not observed in detectable concentrations (see also ref 7) over the pH range used, we assume that the reactions $4 \rightleftharpoons 5$ and $7 \rightleftharpoons 8$ do not contribute greatly to $1/\tau_1$; for the same reason $D_2 \approx 1$. With these assumptions eq 2 simplifies to eq 7.

$$\frac{1}{\tau_1} (\text{pH}) = \frac{k_{12}[H^+]}{D_1} + \frac{k_{21}}{1 + (K_{23}/[H^+])D_3} \quad (7)$$

Similar simplifications apply to $1/\tau_2$, but because it was observable down to lower pH than $1/\tau_1$ (*vide infra*), the contribution of the reaction $5 \rightleftharpoons 6$ cannot be neglected. Thus we obtain eq 8.

$$\frac{1}{\tau_2} = k_{23} + k_{56} \frac{[H^+]}{K_{52}} + \frac{k_{32} + k_{65}([H^+]/K_{63})}{D_3} [H^+] \quad (8)$$

Ionization Constants of Ammonium Ions (4, 6, 7, 9). A knowledge of these ionization constants is a prerequisite to a kinetic analysis. We can derive expressions for two apparent ionization constants, one for dissociation of mono- and one for diprotonated species. For monoprotated species, we have

$$K_{1a} = \frac{(2 + 4 + 6) \xrightleftharpoons{K_{1a}} (1 + 3) + H^+}{([1] + [3])[H^+]} = \frac{K_{21} + K_{23}}{1 + \frac{K_{21}}{K_{41}} + \frac{K_{23}}{K_{63}}} \quad (9)$$

We now assume $K_{21} \gg K_{41}$ and $K_{41} = K_{63}$ which leads to $K_{1a} = K_{41}$. The first assumption is valid in methanol⁷ and shown below to be valid in our solvent as well; the second is an approximation, to be refined later.

In a similar manner one can derive the expression for ionization of diprotonated species.

$$(5 + 7 + 9) \xrightleftharpoons{K_{2a}} (2 + 4 + 6) + H^+$$

Again a complex equation results, but with the additional assumptions $K_{54} \gg K_{74}$ and $K_{74} = K_{96}$ (to be refined later), we obtain $K_{2a} = K_{74}$.

K_{1a} and K_{2a} were evaluated from the pH dependence of the absorbance at 605 nm in Figure 1. At pH_{opt} the concentration of **2** and along with it the concentrations of **4** and **6** are at their maximum, at pH_1 and pH_2 at one-half their maximum. It can be shown¹⁴ that eq 10 and 11 are satisfied. Solving the two simultaneous

$$[H^+]_1 + [H^+]_2 = K_{2a} + 4[H^+]_{\text{opt}} \quad (10)$$

$$[H^+]_{\text{opt}} = \sqrt{K_{1a}K_{2a}} \quad (11)$$

(14) M. Dixon and E. C. Webb, "Enzymes," Academic Press, New York, N. Y., 1964, p 118.

equations affords $K_{1a} = K_{41} = 7.8 \times 10^{-5} M$ and $K_{2a} = K_{74} = 9.8 \times 10^{-4} M$.

By a procedure described in the Experimental Section we obtain the refined values $K_{63} = 4.2 \times 10^{-5}$ and $K_{96} = 5.4 \times 10^{-4}$, both only about 45% lower than their first approximations.¹⁵

Determination of K_{21} and K_{23} . From our values for K_{1a} and K_{2a} and from inspection of Figure 1, it is clear that at $\text{pH} \geq 5.7$ only **1** and **3** are significantly present in a fully equilibrated solution; the ratio $[3]/[1] = K_{13} = K_{23}/K_{21}$ can be estimated from the absorbance at 289 nm (λ_{max} of **1**, $\epsilon = 29,000$ ¹⁶). Though **3** could not be obtained as a pure substance, the uv spectrum of bis(*p*-dimethylaminophenyl)methane provides a good model for **3** from which ϵ_{289} was estimated to be 4000 (for details see Experimental Section, "Refinement of K_{63} and K_{96} "). Since this number is small compared to ϵ_{289} of **1**, its uncertainty has little influence on the accuracy of the calculated ratio $[3]/[1]$. We obtained $K_{13} = K_{23}/K_{21} = 0.13$ in a number of solutions of pH 5.7 to 6.5.

By combining the values for K_{41} , K_{74} , K_{63} , K_{96} and K_{13} , K_{21} can be calculated from the spectral data in Figure 1 according to eq 12, where $[1]_0$ is the stoichio-

$$K_{21} = \frac{([1]_0 - [2])[H^+]}{(D_1 + K_{13}D_3)[2]} \quad (12)$$

metric concentration of **1** and $[2] = \text{absorbance}/\epsilon_{605}$ ($\epsilon_{605} = 150,000$). The constancy of K_{21} for 11 values of $[H^+]$ in the range of pH 2.29 to 4.99 is excellent; the maximum deviation from the average $K_{21} = 2.1 \times 10^{-3} M$ is $\pm 10\%$; the value of 2.1×10^{-3} is now seen to be much larger than K_{41} as was required in assuming $K_{1a} = K_{41}$.

Combining with K_{13} we also obtain $K_{23} = K_{13}K_{21} = 2.7 \times 10^{-4} M$.

Additional Kinetic Studies on $1/\tau_1$ and Fit of Data with Eq 7. In order to ensure the reliability of our analysis, additional data on $1/\tau_1$ covering a wider pH range were obtained as follows. Neutralization of carbonium ion containing solutions (pH ~ 3 to 3.5) in a pH 5.3 to 6.2 buffer rapidly converts all **2**, **6**, and **9** into **3** (plus some **6**) and all **4** and **7** into **1** (plus some **4**), but produces a non-equilibrium mixture with respect to the equilibrium between **1** and **3**. This mixture then slowly equilibrates with a rate governed by $1/\tau_1$, which was monitored at 289 nm. As the process is general acid-base catalyzed, it was again necessary to use buffer plots and take the intercept at zero buffer concentration as $(1/\tau_1)(\text{pH})$. The results are in Table IB.

A k_{12} (which automatically fixes $k_{21} = k_{12}K_{21}$) was now chosen which gave the best fit between the observed $(1/\tau_1)(\text{pH})$ and eq 7; this value is $k_{12} = 23 M^{-1} \text{sec}^{-1}$ which also provides $k_{21} = 4.8 \times 10^{-2} \text{sec}^{-1}$. The fourth column in Table I shows the fit to be quite satisfactory in view of the difficulty in obtaining highly accurate intercepts in the buffer plots and some approximation and experimental uncertainties in the equilibrium constants.

Initial Rates. An alternative approach to obtaining k_{12} and k_{21} is to measure the initial rate of conversion of

(15) In principle we should now use the refined K_{63} and K_{96} to refine K_{41} and K_{74} , *e.g.*, via eq 9. However, because $K_{23} \ll K_{21}$ (*vide infra*), K_{41} is not sensitive to small changes in K_{63} (eq 9). Similarly K_{74} is not sensitive to small changes in K_{96} .

(16) Determined in a *non*-equilibrated solution of **1** ($t \ll \tau_1$).

of **2** by either ion. However, nucleophilic attack by HO^- can be neglected because MeO^- is known to be a much stronger nucleophile toward similar cations;^{11b, 22} it is also more abundant.²⁰ As for deprotonation, if the data for methanol attack *vs.* deprotonation by the solvent are any indication ($k_{23}/k_{21} = 48$), nucleophilic attack by MeO^- may also be expected to be faster than deprotonation by lyate ion. This is supported by an extrapolation of the Eigen plot (Figure 2) which suggests $k_{21}^{\text{RO}^-} \ll 4.9 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ (slope). Thus it appears that $k_{23}^{\text{MeO}^-}$ is the main contributor to the slope.

Pmr Evidence for Ether. Pmr spectra of the reaction mixture²³ were obtained as follows. An acidified solution of **1** in 100 ml of methanol was allowed to equilibrate and then made alkaline; the methanol was evaporated. The pmr spectrum of the residue, dissolved in CDCl_3 , showed, in addition to the resonances of **1**, three new singlets which are attributable to the ether **3**: a singlet due to the alkyl methyl group at δ 1.78, in the region expected for a methyl group on a benzhydryl carbon.²⁴ A new singlet for the dimethyl groups on nitrogen occurs at δ 2.91, just upfield from the alkene dimethylamino resonances at δ 2.96. The third new singlet appears at δ 3.12 and is due to the methoxy methyl group of **3**. In addition to the singlets, the aromatic region, which exhibits an A_2B_2 spectrum centered at δ 6.95 in the alkene, is considerably more complicated owing to the overlap by the A_2B_2 pattern of the ether. From the ratio of the area of the alkene vinyl resonance at δ 5.20 to the area of the methyl singlet at δ 1.78, it is possible to estimate that the mixture consists of 76% **1** and 24% **3**.

On standing for several days in CDCl_3 solution, the resonances attributed to the ether slowly decrease and eventually disappear, while those due to the alkene slowly increase in intensity. At the same time a singlet appears at δ 3.43; this singlet is due to the methyl group of methanol as was verified by comparison with the spectrum of methanol in CDCl_3 . These results provide compelling evidence that the ether is in fact an important component of the reaction scheme.

Discussion

All our results are summarized in Table V.

Rate of Proton Transfer to and from Carbon. No previous measurements have been reported on the kinetics of the equilibrium protonation of diarylethylenes in protic solvents, but our data can be compared with other proton transfer reactions to and from carbon.²⁵ It is generally known that such proton transfers are usually much slower than similar reactions involving oxygen and nitrogen acids and bases.^{17, 25} The main factors believed to be responsible for the slow rates are (1) the lack or weakness of hydrogen bonding between carbon site and (hydroxylic) solvent and (2) configurational and mesomeric changes involved in the conversion between acid and base form.

(22) C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972).

(23) We thank Professor J. F. Bunnett for suggesting this experiment.

(24) The methyl groups of 1,1-diphenylethanol absorbs at δ 1.85 in CCl_4 solution: A. Jung, *Bull. Soc. Chim. Fr.*, 269 (1966).

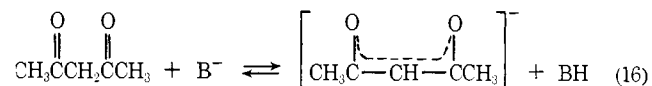
(25) For recent reviews see (a) R. P. Bell, "The Proton in Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1973; (b) C. D. Ritchie in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 246.

Table V. Summary of Results^a

Equil constant	K^b	$\text{p}K^b$	Rate constant, $\text{M}^{-1} \text{ sec}^{-1}$ ^c
K_{21}	2.1×10^{-3}	2.68	k_{12} , ^c 23
K_{41}	7.8×10^{-5}	4.11	k_{21} , $4.8 \times 10^{-2} \text{ sec}^{-1}$ k_{21}^{ROH} , ^d 1.56×10^{-3} $k_{12}^{\text{Cl-AcOH}}$, ^e 9.32×10^{-2}
K_{74}	9.8×10^{-5}	3.01	$k_{21}^{\text{Cl-AcO}^-}$, ^e 4.70
K_{23}	2.7×10^{-4}	3.55	k_{12}^{AcOH} , ^e 5.83×10^{-3}
K_{63}	4.2×10^{-5}	4.28	$k_{21}^{\text{AcO}^-}$, ^e 19.1
K_{96}	5.4×10^{-4}	4.17	k_{23} , 2.5 sec^{-1}
$K_a^{\text{Cl-AcOH}}$ ^e	4.1×10^{-6} ^f	4.39	$k_{23}^{\text{MeO}^-}$, ^h $\leq 4.9 \times 10^4$ k_{32} , 9.3×10^3
K_a^{AcOH} ^e	6.4×10^{-7} ^f	6.20	k_{36}/K_{32} , 20.3
$K_a^{\text{ROH}_2^+}$	30.8 ^g	-1.49	

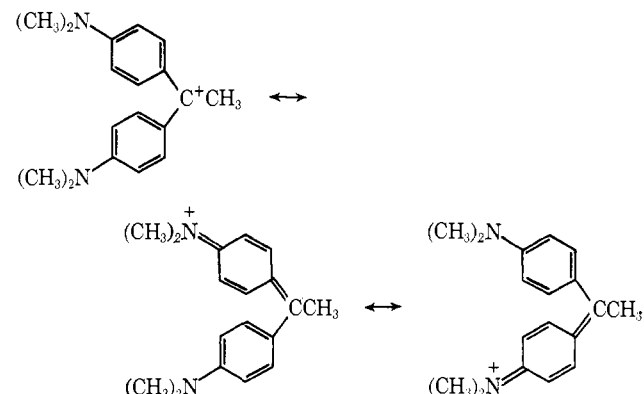
^a All values for 80% (v/v) methanol-water at 25°, $\mu = 0.1 \text{ M}$.
^b All equilibrium constants are apparent constants, not corrected for activity coefficients or medium effects on the pH; $[\text{H}^+] = [\text{MeOH}_2^+] + [\text{H}_3\text{O}^+]$ defined as $10^{-\text{pH}}$ with pH measured on pH meter. ^c For definition see ref 13b. ^d $k_{21}^{\text{ROH}} = k_{21}/([\text{MeOH}] + [\text{H}_2\text{O}]) = k_{21}/30.8$, value used in Eigen plot, Figure 2. ^e Cl-AcOH = chloroacetic acid, AcOH = acetic acid. ^f From pH of half-neutralized solution. ^g $K^{\text{ROH}_2^+} = [\text{MeOH}] + [\text{H}_2\text{O}]$. ^h Reaction $2 + \text{MeO}^- \rightarrow 3$; value is upper limit because of possible contribution of reaction $2 + \text{RO}^- \rightarrow 1$ with R = H or Me; see text. ⁱ Excerpt where noted.

Besides their low rates, proton transfers to and from carbon are also usually characterized by Eigen plots¹⁷ which show a much more gradual change in the slope (α or β) with changing $\Delta\text{p}K$ than "normal" acids and bases. A thoroughly investigated example is the equilibrium deprotonation of acetylacetone²⁶ (eq 16).



Though we have only few data, our plot looks qualitatively the same as the one for acetylacetone, except that for any given $\Delta\text{p}K$ our rate constants are considerably lower. For example, for a hypothetical acid with $\text{p}K_a^{\text{HB}} = \text{p}K_{21}$ ($\Delta\text{p}K = 0$) our plot suggests that the rate constant (in either direction) should be $\sim 1 \text{ M}^{-1} \text{ sec}^{-1}$, while in the acetylacetone case it is $\sim 2000 \text{ M}^{-1} \text{ sec}^{-1}$ when $\Delta\text{p}K = 0$ (for OH acids; for NH acids it is $\sim 400 \text{ M}^{-1} \text{ sec}^{-1}$).

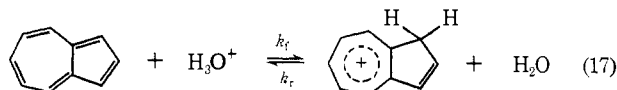
Since it is not expected that the solvent 80% methanol-20% water would have a drastic effect on the proton transfer rates,^{25b} a possible interpretation of our very low rates is that they reflect a greater electronic reorganization between **1** and **2** than is the case between



(26) M.-L. Ahrens, M. Eigen, W. Kruse, and G. Maass, *Ber. Bunsenges. Phys. Chem.*, **74**, 380 (1970).

acetylacetone and its anion. In view of the extensive delocalization of the positive charge in **2**, this is not too surprising.

A reaction our system compares well with is the protonation of azulene by H_3O^+ in aqueous solution: $k_f = 1.28 \text{ M}^{-1} \text{ sec}^{-1}$ (not statistically corrected), $k_r =$



135 sec^{-1} , $K_a^{AZ} = k_r/k_f = 105 \text{ M}$ ($\text{p}K_a^{AZ} = -2.02$) at 7° .²⁷ On an Eigen plot the point for k_f would be at $\Delta\text{p}K \approx 0.3$. We see from Figure 2 that the rate constant for protonation of **1** (k_{12}^{HB}) by an acid for which we have $\Delta\text{p}K = 0.3$ would be about $0.5 \text{ M}^{-1} \text{ sec}^{-1}$, very close to k_f for azulene. This could suggest that electronic reorganization in converting the base into the acid form is comparable for **1** and azulene.

Reactivity of Cation toward MeOH and MeO⁻. Comparison with Ritchie's Data. The rate of combination of **2** with methanol ($k_{23} = 2.5 \text{ sec}^{-1}$) is close to the rate of the analogous reaction of the *p*-methoxyphenyltropylium ion ($k = 13 \text{ sec}^{-1}$)⁹ for which the equilibrium constant for ether formation ($\text{p}K_R = 4.06$)⁹ is comparable to our $\text{p}K_{23} = 3.55$. On the other hand, our $k_{23}^{\text{MeO}^-} \leq 4.9 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ is much lower than the corresponding constant ($6.8 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$)⁹ for the same tropylium ion. Thus our ratio $k_{23}^{\text{MeO}^-}/k_{23} \leq 2 \times 10^4 \text{ M}^{-1}$ is ≥ 260 -fold lower than $k^{\text{MeO}^-}/k^{\text{MeOH}}$ = 5.24×10^6 for the *p*-methoxyphenyltropylium ion.

This discrepancy is noteworthy because $k^{\text{MeO}^-}/k^{\text{MeOH}}$ ratios have been found to be remarkably constant ($\sim 5 \times 10^6$), *i.e.*, independent of the cation, for a number of cations spanning quite a range of reactivity. This and similar findings with other nucleophiles led Ritchie²² to propose the simple relation of eq 18 for

$$\log(k^n/k^{\text{H}_2\text{O}}) = N_+ \quad (18)$$

nucleophilic attack on cations; k^n is the rate constant for a given nucleophile in a given solvent, $k^{\text{H}_2\text{O}}$ the rate constant of the same cation with water in water, and N_+ is a parameter characteristic of the nucleophile and independent of the action.

Our data do not correlate well with eq 18. Though we refrain from speculating about the possible reasons at this time, we note that recently some other cations have also been found to correlate poorly with eq 18. Thus Bunton and Huang²⁸ report $k^{\text{OH}^-}/k^{\text{H}_2\text{O}} = 680 \text{ M}^{-1}$ for the reaction of tri-*p*-anisylmethyl cation, while according to Ritchie²² this ratio should be $3 \times 10^4 \text{ M}^{-1}$; Bunting and Meathrel²⁹ find $k^{\text{OH}^-}/k^{\text{H}_2\text{O}} = 2.5 \times 10^5 \text{ M}^{-1}$ for 10-methylacridinium and 10-methyl-9-phenylacridinium ion, $7.9 \times 10^6 \text{ M}^{-1}$ for 2-methyl-4-nitroisoquinolinium ion.

Experimental Section

Material. 1,1-Bis(*p*-dimethylaminophenyl)ethylene (**1**) was prepared according to Pfeiffer and Wizinger;⁶ it was recrystallized numerous times from slightly alkaline ethanol, mp $122\text{--}123^\circ$ (lit.⁶

(27) B. C. Challis and F. A. Long, *J. Amer. Chem. Soc.*, **87**, 1196 (1965).

(28) C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, **94**, 3536 (1972).

(29) J. W. Bunting and W. G. Meathrel, *Can. J. Chem.*, **51**, 1965 (1973).

mp 123°); nmr (CDCl_3) δ 2.96 (s, 12 H, $(\text{CH}_3)_2\text{N}$), 5.20 (s, 2 H, $=\text{CH}_2$), 6.5–7.4 (A_2B_2 m, 8 H, $-\text{C}_6\text{H}_4-$). Anhydrous reagent grade methanol was distilled from magnesium methoxide. Ordinary distilled water was further purified by distillation in a Corning all-glass still. Chloroacetic acid (MCB), mp $62\text{--}64^\circ$, was recrystallized once from hexane and dried *in vacuo* over P_2O_5 . Reagent grade glacial acetic acid (B + A) was used without further purification, as was reagent sodium chloride. Standard HCl and NaOH solutions were prepared from Titrisol (Merck) ampoules; 80% methanol was prepared by mixing 80 parts of methanol with 20 parts of water.

Isolation of Ether-Alkene Mixture. **1** (27 mg, 0.1 mmol) was dissolved in a 100-ml volumetric flask; then 0.20 ml of a 1.0 M solution of HCl in water was added and the flask filled to the mark with methanol. The final concentrations were $[\text{1}] = 10^{-3} \text{ M}$ and $[\text{HCl}] = 2 \times 10^{-3} \text{ M}$; the solution was allowed to stand at room temperature for 45 min, then treated with 0.20 ml of 2.0 M NaOH, and transferred to a round bottom flask; the methanol was evaporated at 0° *in vacuo*. The residue was dissolved in CCl_4 (25 ml), dried with Na_2SO_4 , and then filtered; the CCl_4 was evaporated at 0° *in vacuo*. The crystalline residue was dissolved in 0.5 ml of CDCl_3 and the nmr spectrum recorded, as described in the Results section.

Refinement of K_{63} and K_{96} . Rather than assuming $K_{63} = K_{41}$ and $K_{96} = K_{74}$, we now only assume that $K_{96}/K_{63} = K_{74}/K_{41}$.³⁰ This allows the calculation of K_{63} and K_{96} from eq 19. The ratio

$$\frac{[\text{3}] + [\text{6}] + [\text{9}]}{[\text{1}] + [\text{4}] + [\text{7}]} = \frac{[\text{3}]}{[\text{1}]} \left(\frac{1 + \frac{[\text{H}^+]}{K_{63}} + \frac{[\text{H}^+]^2}{K_{63}K_{96}}}{1 + \frac{[\text{H}^+]}{K_{41}} + \frac{[\text{H}^+]^2}{K_{41}K_{74}}} \right) \quad (19)$$

on the left-hand side of eq 19 was determined at pH 3.33 as follows. After a solution of **1** was allowed to equilibrate at pH 3.33, we calculated from the absorbance at 605 nm ($\epsilon_{605} = 150,000$)⁷ that 1.7% of the initial **1** was in the form of **2**. The solution was then neutralized to pH 6.09. This rapidly converted all of **2**, **6**, and **9** present into **3**, and all of **4** and **7** into **1**. From the absorbance at 289 nm (λ_{max} of **1**) recorded immediately after neutralization, *i.e.*, before slow equilibration between **1** and **3** takes place, the relative concentrations of **1** and **3** were determined. For ϵ_{289} of **3** we used ϵ_{289} of bis(*p*-dimethylaminophenyl)methane. This compound shares with **3** the principal chromophore and is of similar molecular weight; it is expected to have an absorption spectrum very similar to that of **3**. Its spectrum in ethanol³² shows λ_{min} 285 nm (ϵ 3400) and λ_{max} 301 nm (ϵ 4700^{32a} or ϵ 4200^{32b}) and λ_{max} 262 nm (ϵ 33,000). The very flat region near 289 nm suggests ϵ 4000 is a good estimate for ϵ_{289} of **3**.³³ The relative concentrations were 76.5% **1** and 23.5% **3**. Since only 1.7% of **2** had been present at pH 3.33, the remaining 21.8% (23.5 – 1.7) must have been present as **3**, **6**, and **9**. Thus the ratio on the left-hand side of eq 19 at pH 3.33 is $21.8/76.5 = 0.285$, while for the equilibrium ratio $[\text{3}]/[\text{1}]$ we have $K_{23}/K_{21} = 0.13$.

pH Measurements. The apparent pH's of all solutions were measured on a Corning Model 110 Digital pH meter using a Beckmann glass electrode, No. 39000, and a Calomel reference electrode, No. 39400.

Ultraviolet and Visible Spectra. Spectra were recorded on a Cary 14 recording spectrophotometer. For determination of equilibrium constants, absorbance values were measured on a Gilford Model 2000 uv-visible spectrophotometer equipped with a jacketed cell holder and thermostated at $25.0 \pm 0.1^\circ$.

Rate Measurements. Temperature-jump determinations were performed on a Messanlagen GmbH, temperature-jump transient spectrometer. Temperature jumps of 2° were found to give satisfactory results and excellent reproducibility. Stopped-flow

(30) This is probably a good assumption. The pK difference between K_{41} and K_{74} is 1.1 as is the difference between the pK's of bis(dimethylaminophenyl)methane, a model for **3**, in 70% ethanol-water.³¹

(31) P. H. Grantham, E. K. Weisburger, and J. H. Weisburger, *J. Org. Chem.*, **26**, 1008 (1961).

(32) (a) A. Mangini and R. Passerini, *J. Chem. Soc.*, 4954 (1956); (b) V. V. Perekalin, M. V. Savost'yanova, and R. I. Morozova, *Zh. Obshch. Khim.*, **22**, 821 (1952).

(33) A second maximum in the spectrum of mixtures of **1** and **3** occurs between 260 and 270 nm, the exact position depending on the relative amounts of **1** and **3**. This is in agreement with the expected spectrum of **3**, by analogy with our model compound.

measurements of $1/\tau_2$ were carried out on a Durrum stopped-flow spectrophotometer. Determinations of $1/\tau_1$ and initial rate measurements were carried out on a Gilford Model 2000 spectrophotometer. All relaxation times reported in Tables I, II, and IV represent averages of three (in a few cases two) determinations.

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The Kinetics of Carbonium Ion Formation from Anhydroretinol

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Abstract: The initial stages of the reaction between anhydroretinol and anhydrous hydrogen chloride in 1,2-dichloroethane were studied using stopped-flow spectrophotometry. The results are explained in terms of a five-step mechanism, involving two carbonium ions, with the anhydroretinylic cation forming much more rapidly than the more stable retinylic cation. Evidence is presented indicating that the former cation may be a precursor of the latter.

Highly conjugated polyenes when treated with acid generally give rise to absorption maxima in the visible region. These absorptions have been attributed to charge transfer or to carbonium ion formation. Wasserman¹ showed by conductance measurements that, in the case of protonic acids, carbonium ions are present, and presumably are responsible for the color observed.

The carbonium ions from *all-trans*-retinol and related compounds have been of particular interest because their spectral properties are similar to those of visual pigments, and they may be meaningful as models of visual pigments. Blatz and Pippert² showed the retinylic cation (Figure 1,II) to be the only cation observed on protonating *all-trans*-retinyl acetate or retinol; their results also demonstrated that λ_{\max} of the cation is only a weak function of solvent and independent of the nature and concentration of the protonic acid. Protonation of anhydroretinol (I) gave rise to a longer wavelength absorption, which was assigned to the anhydroretinylic cation (III) by Blatz on the basis of protonation at the C₁₅ position.³ (Protonation at the other most likely point of attack, C₄, would give rise to the retinylic cation.) Symmetry considerations also favored the assignment of the longer wavelength absorption to the anhydroretinylic cation. Baumgartner⁴ observed both cations to form when anhydroretinol is protonated by HCl in 1,2-dichloroethane. It could not be determined which of the cations formed first.

A kinetic study of the rate of formation of carbonium ions from anhydroretinol was undertaken, in order to establish the mechanism of the reaction, to ascertain the relative rates of formation of the cations, to indicate the relative ease of protonation at the C₄ and C₁₅ positions of anhydroretinol, and to give some indication as to the relative stabilities of the two cations.

The reaction was studied at 10.0, 21.2, and 30.0°, using HCl as protonating agent in 1,2-dichloroethane solvent. Only the initial (up to several minutes) portion of the reaction was studied in detail, since it has been shown by Sorenson,⁵ Deno,⁶ and Blatz⁷ that cyclization and polymerization of such carbonium ions take place at longer times. In all of the studies, a very large excess of HCl was used in order to achieve first-order kinetics. The concentration of HCl was varied to obtain the HCl dependency.

Results and Discussion

Typical action spectra taken on the Cary 14R at -30° are shown in Figure 2. During the time period of these observations (0.5-4 min), it appears that the first-formed anhydroretinylic cation (~620 nm) is decreasing slightly with time, while the retinylic cation (~580 nm) is increasing.

Typical reaction profiles from the stopped-flow data are shown in Figure 3, which also illustrates the effect of temperature. The data are plotted as absorbance vs. log time for convenience. Allowing for some overlap in the spectra of the two cations, there appear to be four regions in time corresponding to four rate processes. These are labeled ϕ_1 , ϕ_2 , ϕ_d , and ϕ_3 , with overlap in rates occurring between ϕ_2 and ϕ_d . ϕ_2 and ϕ_3 were assigned to the formation of anhydroretinylic and retinylic cations, respectively, ϕ_1 to the formation of a precursor which absorbs rather broadly over the 580-620-nm region, and ϕ_d to a process involving the disappearance of the anhydroretinylic cation. The ϕ_2 , ϕ_d , and ϕ_3 assignments were made after comparing the stopped-flow data with the Cary 14 action spectra. The time scale of the action spectra suggests a correspondence with processes occurring in the ϕ_d - ϕ_3 region of the stopped-flow data. The ϕ_1 assignment, that of a reaction leading to a precursor to the carbonium ions,

(1) A. Wasserman, *J. Chem. Soc.*, 245 (1954).

(2) P. E. Blatz and D. L. Pippert, *J. Amer. Chem. Soc.*, **90**, 1296 (1968).

(3) The numbering system is that used in the carotenoid literature.

(4) N. R. Baumgartner, Ph.D. Dissertation, University of Wyoming, 1969.

(5) T. S. Sorenson, *Can. J. Chem.*, **43**, 2744 (1965).

(6) N. C. Deno, C. U. Pittman, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 2153 (1965).

(7) P. E. Blatz and D. L. Pippert, *Tetrahedron Lett.*, 1117 (1966).