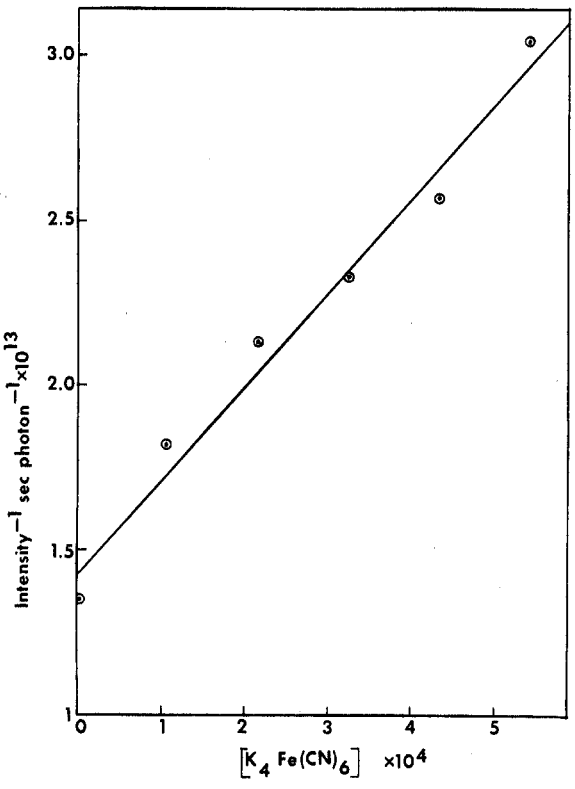

Figure 7.—Plot of concentration of $K_4Fe(CN)_6$ *vs.* reciprocal of initial intensity: initial concentration of hydroxide, 8.2×10^{-2} ml^{-1}; of luminol, 4.99×10^{-4} ml^{-1}; of $K_3Fe(CN)_6$, 5.06×10^{-4} ml^{-1}.

mechanism in which the nonluminescent reaction is the oxidative dimerization of luminol is ruled out because the reaction would not be first order in luminol.

A key feature of the reaction is competition of oxygen and ferricyanide for the semidione. Systems which provide a direct source of hydroperoxy radical for reaction with the semidione will enhance light production. Thus hydrogen peroxide increases the intensity and quantum yield. A solution 4.62×10^{-5} *M* in luminol, 5.14×10^{-4} *M* in $K_3Fe(CN)_6$, and 0.08 *M* in hydroxide has a quantum yield of 3.8×10^{-7}. A similar solution 8×10^{-3} *M* in hydrogen peroxide has a quantum yield of 3.25×10^{-6}. In the presence of oxygen, the semidione is consumed by further oxidation with ferricyanide.

This competition between reaction with oxygen and further oxidation is probably a general feature of all chemiluminescent reactions of luminol in which a one-electron oxidant is employed. The fact that chemiluminescence occurs at all is due to the stability of the semidione to further oxidation. In this connection, note that electron-donating substituents on the aromatic ring enhance luminescence. Such substituents would be expected to increase the stability of the semidione.[12]

Registry No.—Potassium ferricyanide, 13746-66-2; **1**, 521-31-3.

(12) E. H. White and M. M. Bursey, *J. Org. Chem.*, **31**, 1912 (1966). A referee has pointed out that electron-donating substituents also increase the fluorescence quantum yield of the phthalates.

Pyrolysis Studies. XIX.[1] Substituent Effect of 1-Aryl-3-buten-1-ols

GRANT GILL SMITH[2a] AND KENT J. VOORHEES[2b]

Department of Chemistry, Utah State University, Logan, Utah 84321

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The unimolecular homogeneous thermolysis of nine 1-aryl-3-buten-1-ols has been studied in a seasoned, constant-volume, stainless steel reactor. Arrhenius parameters have been evaluated in the temperature range of 610–644°K. The small ρ value (-0.26) from a Hammett $\rho\sigma$ plot indicates a minor substituent effect for the *meta* and *para* isomers with apparently little or no charge development at the 1 position in the proposed concerted six-membered ring transition state. An *o*-methoxy substituent showed a marked proximity effect with an activation energy 4–7 kcal/mol lower and an entropy of activation of 6–9 eu, more negative than the other compounds studied.

β-Hydroxy olefins have been reported to pyrolyze to olefins and carbonyl compounds by a unimolecular homogeneous reaction, likely through a six-membered-ring transition state.[3,4] The influence of 3- and 4-phenyl and 1-alkyl substituents on the ease of thermolysis of 3-buten-1-ol has been reported by Smith and Yates.[5]

They found that π contribution increased the rate of pyrolysis at the 3 position more than at the 4 position and that the rate of pyrolysis followed the sequence tertiary > secondary > primary for alkyl substitution at the carbinol position. They presented a qualitative picture consisting of a positive charge forming at the 3 position and a slight negative charge developing at the 4 position in the transition state.

No direct study of π contribution has been reported at the carbinol position; only competitive[6,7] type reactions have been studied.

The gas-phase thermolysis of 1-aryl-3-buten-ols reported in this study, when compared with the result reported by Smith and Yates,[5] further substantiates the nature of this reaction and gives additional insight concerning the transition state.

Results

1-Aryl-3-buten-1-ols were pyrolyzed in a deactivated stainless steel reactor[8] over a temperature range of

(1) Part XVIII: K. K. Lum and G. G. Smith, *Int. J. Chem. Kinetics*, **1**, 401 (1969).

(2) (a) To whom all communications should be sent; (b) National Defense Education Act Predoctoral Fellow, 1968–1970.

(3) R. T. Arnold and G. Smolinsky, *J. Org. Chem.*, **25**, 129 (1960).

(4) G. G. Smith and R. Taylor, *Chem. Ind.* (London), **35**, 949 (1961).

(5) G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965).

(6) A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *J. Amer. Chem. Soc.*, **89**, 3462 (1967).

(7) K. J. Voorhees, G. G. Smith, R. T. Arnold, D. G. Mikolasek, and R. R. Covington, *Tetrahedron Lett.*, 205 (1969).

(8) G. G. Smith and J. A. Kirby, *Analyst* (London), **94**, 242 (1969).

TABLE I

RATE CONSTANTS, TEMPERATURES, AND $1/T$ FOR THERMOLYSIS OF 1-ARYL-3-BUTEN-1-OLS

Compound	No. of runs	10^2k, sec^{-1}	Temp, °K	$1/T \times 10^3$
1-Phenyl-3-buten-1-ol	6	3.26	644.8	1.551
	3	1.82	630.9	1.558
	3	1.21	622.9	1.605
	4	0.877	615.4	1.625
	3	0.622	610.4	1.638
1-*p*-Methylphenyl-3-buten-1-ol	3	2.10	632.6	1.581
	3	1.53	625.5	1.599
	3	1.14	618.3	1.617
	3	0.738	609.7	1.640
1-*p*-Chlorophenyl-3-buten-1-ol	5	2.92	641.7	1.558
	3	1.84	632.0	1.582
	3	1.35	625.5	1.599
	3	0.943	618.0	1.618
	3	0.696	610.8	1.637
1-*p*-Methoxyphenyl-3-buten-1-ol	3	2.45	633.9	1.578
	5	1.48	623.5	1.604
	3	1.08	614.9	1.626
	3	0.737	607.6	1.646
1-*m*-Methoxyphenyl-3-buten-1-ol	3	2.00	631.9	1.583
	4	1.28	621.7	1.608
	3	0.787	612.9	1.632
	3	0.665	608.6	1.643
1-*m*-Methylphenyl-3-buten-1-ol	3	2.00	633.7	1.578
	3	1.26	622.5	1.606
	3	0.767	613.2	1.631
	3	0.629	608.1	1.645
1-*o*-Methylphenyl-3-buten-1-ol	3	2.29	632.2	1.582
	3	1.49	622.2	1.607
	3	1.16	615.5	1.625
1-*o*-Chlorophenyl-3-buten-1-ol	3	2.07	631.3	1.584
	3	1.20	621.7	1.609
	3	0.755	609.7	1.636
1-*o*-Methoxyphenyl-3-buten-1-ol	6	1.79	634.4	1.577
	6	1.10	622.5	1.607
	10	0.704	611.2	1.636

608–645°K, and the products, propene and substituted benzaldehydes, were identified. Table I lists the first-order rate constants which were obtained over 95% of the pyrolysis and the temperature of pyrolysis for these compounds. The stoichiometry was established by the ratio of P_0/P_∞ (1:1.99).

Reproducibility of the first-order rate constants was ±2%, and introduction of cyclohexene had no effect on the rate (3.24×10^{-2} compared with 3.18×10^{-2} with cyclohexene for 1-phenyl-3-buten-1-ol), thus demonstrating the absence of a radical chain reaction and the unimolecularity of the reaction. Variation of the sample size (0.10–0.25 ml) and initial pressure (80–200 mm) was made (for each compound) with no effect on the reproducibility.

An Arrhenius plot of each compound gave a straight line which is illustrated for 1-phenyl-3-buten-1-ol in Figure 1. The quality of the data is shown by the correlation coefficient of the linear regression of each Arrhenius plot (Table II).

Figure 2 is a Hammett $\rho\sigma$ plot resulting in a ρ of a −0.26 calculated using a linear repression analysis.

Discussion

As stated, the results from this study on the thermolysis of 1-aryl-3-buten-1-ols further substantiate the unimolecularity and homogeneity of this reaction and also supports a six-membered-ring transition state.[3-5,9] Furthermore, they demonstrate that a 1-phenyl substituent has twice the effect on the ease of thermolysis

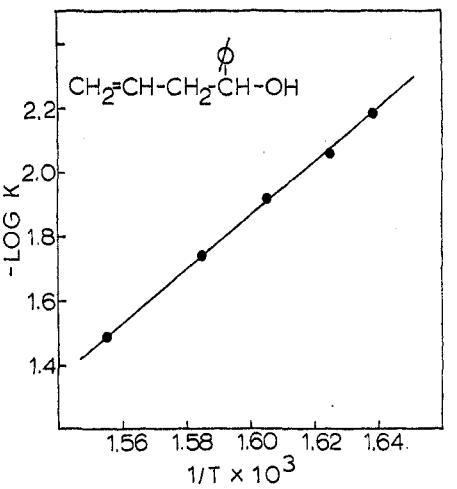


Figure 1.—Arrhenius plot of 1-phenyl-3-buten-1-ol thermolysis.

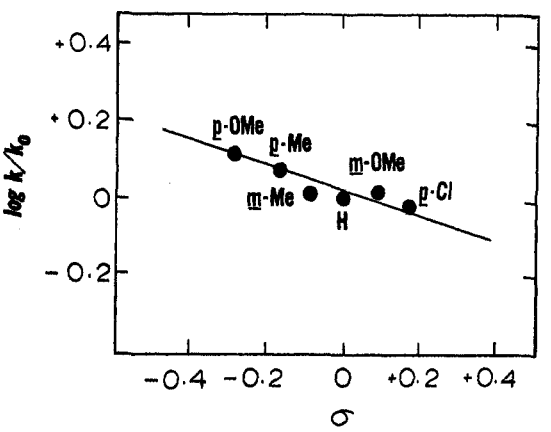


Figure 2.—Hammett plot of 1-aryl-3-buten-1-ols, ρ = −0.26.

TABLE II

ARRHENIUS PARAMETERS FOR 1-ARYL-3-BUTEN-1-OLS

Compound	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu, at 619 °K	Log A	Correlation coefficient
1-Phenyl-3-buten-1-ol	36.2	−10.5	10.8	−0.999
1-*p*-Methylphenyl-3-buten-1-ol	34.9	−12.3	10.4	−0.999
1-*p*-Chlorophenyl-3-buten-1-ol	36.1	−10.8	10.7	−0.999
1-*p*-Methoxyphenyl-3-buten-1-ol	35.6	−10.9	10.7	−0.987
1-*m*-Methoxyphenyl-3-buten-1-ol	36.9	−9.3	11.0	−0.998
1-*m*-Methylphenyl-3-buten-1-ol	34.9	−12.5	10.4	−0.998
1-*o*-Methylphenyl-3-buten-1-ol	36.5	−9.8	11.0	−0.999
1-*o*-Chlorophenyl-3-buten-1-ol	38.4	−6.8	11.6	−0.998
1-*o*-Methoxyphenyl-3-buten-1-ol	31.4[a]	−18.4	9.1	−0.999

[a] Special care was taken to ensure that the reactor surfaces were completely deactivated.

(9) (a) R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **82**, 4919 (1960); (b) R. T. Arnold and G. Metzger, *J. Org. Chem.*, **26**, 5185 (1961); (c) R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **81**, 6443 (1959).

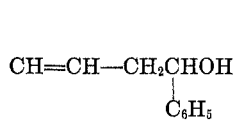
at 619°K as does a 3-phenyl substituent and 83 times the influence that was reported for a 4-phenyl substituent. This substituent also showed 7.5 times the influence of a methyl group at the carbinol position. Rate constants and relative rates are shown in Table III.

TABLE III
RATE CONSTANTS AND RELATIVE RATES FOR THE THERMOLYSIS OF β-HYDROXY OLEFINS

β-Hydroxy olefins	$10^2 k$ (sec^{-1}), at 619 °K	Rel rate
3-Buten-1-ol	0.053	4.4
4-Penten-2-ol	0.131	10.9
2-Methyl-4-penten-2-ol	0.280	23.3
1-Phenyl-3-buten-1-ol	1.0	83.0
3-Phenyl-3-buten-1-ol	0.5	41.5
4-Phenyl-3-buten-1-ol	0.012	1.0

At least two factors may contribute to the rate enhancement: (a) crowding in the ground state at the carbinol position which may cause steric acceleration; and (b) electronic stabilization of the transition state. Neither of these factors alone offers a completely satisfactory explanation.

Crowding in the ground state by a phenyl substituent would not be expected to be as large as by two methyl groups at the same position (E_s for phenyl is −0.90 and E_s for methyl is 0); yet 1-phenyl-3-buten-1-ol (1) pyrolyzes *four* times more readily than 2-methyl-4-penten-2-ol (2) which has two methyl groups attached at the carbinol position. The comparative rate constants for



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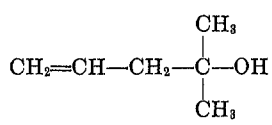

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thermolysis of 1-phenyl *vs.* a 1-methyl and 1,1-dimethyl substituents are shown in Table III.

The greater effect of phenyl over alkyl substituents at the carbinol position suggests that a charge develops at the carbinol carbon in the transition state. The extent of this charge, however, must be modest as the ρ value in the $\rho\sigma$ plot was small (−0.26), and the correlation was significantly better with σ than σ^+. A plot of Brown's and Okamoto's[10] σ^+ against log k/k_0 gave a slightly curved line with considerably more scattering than was observed for the regular Hammett plot. Steric effects are reported to be minor in the gas phase.[11] The acceleration in rate is more likely caused by a weakening of the C–C bond at the carbinol carbon by the attached phenyl substituent through a slight stabilization of the transition state. The most significant observation, however, is that gas-phase thermolysis of β-hydroxy olefins proceeds *via* a highly concerted electrocyclic process resulting in only minor substituent effect activity.

Energy of activation values reported in Table II range between 34.9 and 38.4 kcal/mol excepting that for 1-*o*-methoxyphenyl-3-buten-1-ol which is reported as 31.4 kcal/mol. The $\Delta S^{\ddagger}$ for this compound is also considerably more negative, (−18.4 eu). Since these values are significantly lower than the others, they were carefully reinvestigated several times, particularly to determine if the reactor surface was activated. (E_a values are lower for reactions showing heterogeneous reactivity.) After taking extensive deactivation and standardization precautions,[12] no change in the values of E_a and $\Delta S^{\ddagger}$ was detected.

The explanation for these marked differences is, of course, caused by a proximity effect peculiar to the alkyoxy group which is not found with either an *o*-chloro or *o*-methyl substituent. The entropy difference (degrees of freedom) between the ground state and activation complex is significantly more negative for the *o*-methoxy derivative than for other *ortho* derivatives or the *p*-methoxy compound. Perhaps the methoxy group is less free to rotate in the transition state than in the ground state, although the reason for this is not clearly understood. It is possible that an *o*-methoxy group raises the entropy of the ground state and also raises the ground-state energy. But it is more logical, however, that the *o*-methoxy group lowers the energy of the transition state, probably through a direct field effect between the *o*-methoxy group and the reacting group. A better understanding of this interesting proximity effect awaits future study.

Generally speaking, the results from this study seem to indicate that the thermolysis of β-hydroxy olefins proceeds through a highly concerted electrocyclic process with modest substituent effects. Since, however, a 1-aryl group has the most significant effect, the bond cleavage most important in controlling the activation energy is between C_1 and C_2 carbon atoms. In highly concerted electrocyclic reactions conjugation is known to be especially important.[13] The results for the 1-, 3-, and 4-phenyl-3-buten-1-ol study bear this out. When 3-buten-1-ol is substituted at the 4 position with a phenyl group, conjugation is lost during the reaction, and, therefore, a phenyl group at this position slows down the rate of thermolysis while it increases the rate at the other two positions as expected, based on the importance of conjugation to highly concerted electrocyclic reactions. The partial charge developing at the 1 position is stabilized by the developing C=O group as well as by the ring which helps to explain the small value (0.26).

Experimental Section

Synthesis of 1-Aryl-3-buten-1-ols.—All of the 1-aryl-3-buten-1-ols were prepared by the same procedure, beginning with the appropriate substituted benzaldehyde and allylmagnesium bromide. The synthesis of 1-phenyl-3-buten-1-ol is given as a typical case. Information concerning the synthesis of the other 1-aryl-3-buten-1-ols can be found in Table IV.

1-Phenyl-3-buten-1-ol.—Allyl bromide (40 g) dissolved in 50 ml of ether was added dropwise to magnesium ribbons (8.25 g) suspended in a 10 *M* (250 ml) excess of ether. Two hours later the reaction has subsided, and the mixture was cooled to −10°, and 32 g of benzaldehyde in 50 ml of ether was added dropwise. After addition of the benzaldehyde, stirring was continued for 1 hr at which time a saturated solution of ammonium chloride was added to hydrolyze the complex. The ether layer was separated from the aqueous layer and dried using magnesium sulfate. The aqueous layer was extracted with three 100-ml portions of ether. These portions were dried and combined with the first portion. The resulting solutions were filtered and the

(10) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).
(11) G. G. Smith, K. K. Lum, J. A. Kirby, and J. Pospisil, *J. Org. Chem.*, **34**, 2090 (1969).
(12) R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, **84**, 4817 (1962).
(13) A. Maccoll, and P. J. Thomas, *Progr. React. Kinet.*, **4**, 119 (1967).

TABLE IV
PHYSICAL CONSTANTS AND YIELDS OF 1-ARYL-3-BUTEN-1-OLS

Compound	Index of refraction, $n^{25}D$	Bp (mm), °C	Yield, %	Calcd, % C	Calcd, % H	Formula	Found,[a] % C	Found,[a] % H	Found,[a] % Cl
1-Phenyl-3-buten-1-ol (a)	1.5314[b]	71 (0.75)	41	81.04	8.10	$C_{10}H_{12}O$	81.16	7.92	
1-*p*-Methoxyphenyl-3-buten-1-ol (b)	1.5365	102–103 (0.35)	18	74.13	7.92	$C_{11}H_{14}O_2$	73.53	7.78	
1-*p*-Chlorophenyl-3-buten-1-ol (c)	1.5511	98.5–99 (0.30)	60	65.76	6.07	$C_{10}H_{11}OCl$	65.39	5.91	19.88[d]
1-*o*-Methylphenyl-3-buten-1-ol (d)	1.5313	74 (0.50)	19	81.44	8.70	$C_{11}H_{14}O$	81.24	8.70	
1-*p*-Methylphenyl-3-buten-1-ol (e)	1.5280	74–75 (0.42)	26	81.44	8.70	$C_{11}H_{14}O$	81.80	8.80	
1-*m*-Methylphenyl-3-buten-1-ol (f)	1.5272	79–80 (0.80)	31	81.44	8.70	$C_{11}H_{14}O$	81.88	8.57	
1-*m*-Methoxyphenyl-3-buten-1-ol (g)	1.5372	96–97 (0.30)	18	74.13	7.92	$C_{11}H_{14}O_2$	73.53	7.95	
1-*o*-Chlorophenyl-3-buten-1-ol[c] (h)		83 (0.38)	16	65.76	6.07	$C_{10}H_{11}OCl$	65.43	6.0	19.91[d]
1-*o*-Methoxyphenyl-3-buten-1-ol[c] (i)		96 (0.32)	20	74.13	7.92	$C_{11}H_{14}O_2$	74.52	8.06	

[a] The analytical work was done by M. H. W. Laboratories, Garden City, Mich. [b] Lit.[14] $n^{25}D$ 1.5305. [c] Solids at room temperature. [d] Calcd 19.42%.

excess ether removed by evaporation under vacuum. Distillation yielded 18.4 g of product: bp 71° (0.75 mm); yield 41%; $n^{25}D$ 1.5314 (lit. $n^{25}D$ 1.5305[14]); nmr δ 7.1, 5.1–6.0, 4.6, 2.3, 2.2; ir OH at 3400–3800 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.0; H, 8.1. Found: C, 81.16; H, 7.92.

Method of Pyrolysis.—The kinetics of pyrolysis were done using a carefully deactivated stainless steel static reactor[8] fitted with a null point gauge and an exterior pressure measuring system. A small sample (0.15–0.25 ml) of alcohol was injected, the reactor sealed, and the pressure followed with time. A pressure at time ∞ (reaction complete) was determined, and a plot of ln $(P_\infty - P_t)$ *vs.* time, where P_t is pressure at time t, was used to determine first-order rate constants. The furnace temperature was monitored to ±0.1° using an iron–constantan thermocouple which had previously been standardized against a Bureau of Standards calibrated platinum resistance thermometer.

Product Analysis.—The pyrolysis products from three or four 0.3-ml injections were collected in a Dry Ice–isopropyl alcohol trap attached directly to the exhaust value in the reaction vessel. To ensure that all products were retained in the trap, the trap was sealed and left in the Dry Ice–isopropyl alcohol slurry before removing from the vacuum line. Since the products from the pyrolysis of 1-aryl-3-buten-1-ols are propene and substituted benzaldehydes, a method was designed to separate the gas by distillation. The propene was distilled into a cold (−72°) mass spectrometer gas cell and analyzed from this directly by mass spectroscopy. The aldehydes were dissolved in deuteriochloroform containing an internal tetramethylsilane standard for nmr analysis.

The products, the stoichiometry, and excellent kinetic data conclusively demonstrated that the pyrolysis in a seasoned reactor of these β-hydroxy olefins followed first-order kinetics to greater than 99% of the reaction in the temperature range studied.

(14) M. Gaudeman, *Bull. Soc. Chim. Fr.*, **5**, 974 (1962).

Registry No.—Table IV—a, 936-58-3; b, 24165-60-4; c, 14506-33-3; d, 24165-62-6; e, 24165-63-7; f, 24165-64-8; g, 24165-65-9; h, 24165-66-0; i, 24165-67-1.

Acknowledgment.—We wish to thank the National Science Foundation, Grant GP 9251, the National Defense Education Act, and the Utah State University Research Council for generous support of this work. We are also indebted to Mr. George Eddington of Electrodynamic Laboratory at Utah State University for the maintenance of the kinetic equipment. Grateful acknowledgment is given to the National Bureau of Standards for the calibration of a platinum resistance thermometer and to the local chapter of Sigma Xi for a small research award to one of us (K. J. V.).

Redox Behavior of α-Tocopherol and Model Compounds. II. Ring Opening of 8a-Hydroxy-2,2,5,7,8-pentamethyl-6-chromanone

M. F. MARCUS AND M. D. HAWLEY

Department of Chemistry, Kansas State University, Manhattan, Kansas 66502

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Double-potential-step chronoamperometry has been used in the study of the kinetics and the mechanisms of the ring opening of 8a-hydroxy-2,2,5,7,8-pentamethyl-6-chromanone, a model of the hemiketal intermediate in the oxidation of α-tocopherol to α-tocopherylquinone. Working curves for the determination of the rate constants were obtained by a digital simulation technique. The system was observed to be both general acid and general base catalyzed. The mechanism proposed for general acid catalysis involves proton transfer from the acid to the oxygen in the 1 position followed by removal of a proton from the hydroxy group in the 8a position by the solvent, water. In the case of general base catalysis, the reaction proceeds by removal of the proton from the hydroxy group by the base and transfer of a proton from the solvent to the oxygen in the 1 position.

The widespread occurrence of chromanols and quinones in nature has led to extensive studies into their possible roles in biological processes.[1-3] The observance of the ready ease with which these compounds enter into redox reactions has led to several proposals relating oxidation–reduction processes to biological activities. Although elucidation of these biological processes must be provided ultimately by studies *in vivo*, the results of chemical studies *in vitro* can provide considerable information regarding intermediates, products, and rates of chemical processes.

(1) G. E. W. Wolstenholme and C. N. O'Connor, Ed., "Quinones in Electron Transport," Little, Brown and Co., Boston, Mass., 1960.

(2) R. A. Morton, Ed., "Biochemistry of Quinones," Academic Press, Inc., New York, N. Y., 1965.

(3) "International Symposium on Recent Advances in Research on Vitamins K and Quinones (Vitamins K, Ubiquinones or Coenzymes Q, Plastoquinones) in Honor of Professor Henrik Dam," in *Vitamins Hormones*, **24**, 291 (1966).