Kinetics and Mechanism of the Pyrolysis of 1,3-Cyclohexadiene. A Thermal Source of Cyclohexadienyl Radicals and Hydrogen Atoms. The Addition of Hydrogen Atoms to Benzene and Toluene[1a]

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Abstract: The pyrolysis of 1,3-cyclohexadiene (1,3-CH) has been studied in a static system between 10 and 90 torr and 362 and 421°. The products were benzene, cyclohexene, hydrogen, and traces (less than 5%) of C_{12} hydrocarbons. At 391° and 40 torr initial pressure, the initial rate of reaction is $10^{-6.8}$ mole l.$^{-1}$ sec^{-1}. The order is between one-half and three-halves and is close to five-fourths. The activation energy, obtained at constant (~40 torr) initial pressure, is 40 ± 5 kcal mole^{-1}. The rate is unaffected by added CF_4 and is halved by increasing the surface-to-volume ratio 20 times. The observed products were accounted for by a chain mechanism involving hydrogen atoms, cyclohexadienyl radicals, and cyclohexenyl-3 radicals. The order, initial rate, and activation energy for the pyrolysis of 1,3-CH, calculated from the mechanism, were in reasonable agreement with experiment. From the pyrolysis of 1,3-CH alone, and in the presence of hexadeuteriobenzene and toluene, we have concluded that at 391°, $k_{-4}:k_{16}:k_5:k_6 = 1:1.5:3:12$ (see the corresponding eq −4, 16, 5, and 6 in the text). We have estimated that the lower limit for E_{11} is 4 kcal mole^{-1} and that the lower limit for E_{20} is 53 kcal mole^{-1} (see eq 11 and 20 in the text).

Suart[2] has recently studied the thermochemistry and kinetics of the decomposition of the cyclohexadienyl radical. In spite of a careful and detailed analysis of the system, the complexities were such that the error limits were large. It was hoped that the present study would provide additional information.

The pyrolysis of 1,4-CH has recently[3] been shown to be a homogeneous elimination of hydrogen to give benzene with $k = 10^{12.36-43.8/\theta}$ sec^{-1}, where θ is 2.3 RT kcal mole^{-1}. In view of the theoretical prediction of Hoffmann[4] that it would be more difficult to eliminate hydrogen thermally from 1,3-CH than 1,4-CH, it was of interest to study the pyrolysis of 1,3-CH. While the present work was being completed, a very brief preliminary communication was published by Ellis and Frey.[3a]

Experimental Section

Materials. 1,3-CH (Aldrich Chemical Co., Milwaukee) contained several per cent cyclohexene and benzene. It was purified to better than 99.9% by preparative gas chromatography (F and M Model 775, carbowax column) and bulb-to-bulb distillation. Cyclohexene (Aldrich Chemical Co.) was reagent grade. Other materials have been described previously.[3b]

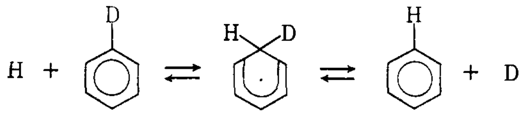
Apparatus. Hydrogen was estimated with a gas buret. Hydrocarbons were analyzed by gas chromatography. Typical analyses were confirmed mass spectrometrically. The details of the system and technique have been described previously.[3b]

Results and Discussion

Chain Pyrolysis of 1,3-CH. The products of pyrolysis of 1,3-CH were benzene, cyclohexene, hydrogen, and traces (less than 5% of the products) of C_{12} hydrocarbons. The mass balances confirmed that the yields of C_{12} and higher hydrocarbons were small. The dimers were not individually identified, but they had mass spectrometric cracking patterns and gas chromatographic retention times consistent with C_{12} hydrocarbons.

The apparent first-order k (Table I) increased with increasing pressure, showing that the order of the reaction was greater than 1. In the initial stages, the three-halves-order rate constant is approximately equal to the ratio (first-order rate constant/(initial pressure)$^{1/2}$. Similarly, the five-fourths-order rate constant is approximately (first-order rate constant)/(initial pressure)$^{1/4}$. An accurate assessment of the order is not possible, but the over-all rate is clearly between first and three-halves order, and is close to five-fourths order. The temperature coefficient was determined by plotting the apparent first-order rate constant at constant pressure (~40 torr), giving an activation energy of 40 ± 5 kcal mole^{-1}. The rate was unaffected by added CF_4 and was halved by increasing the surface-to-volume ratio 20 times. (See Figure 1.)

The results show features of a radical-chain reaction. The inhibiting effect of surface indicates that surface termination makes a small contribution to the total termination. The hydrogen:benzene:cyclohexene ratios are independent of initial pressure or temperature. The hydrogen yield is one-fifth that of benzene, so the unimolecular decomposition of 1,3-CH to give equal amounts of hydrogen and benzene cannot be the predominant mode of decomposition. Hydrogen atoms and cyclohexadienyl radicals were shown to be involved because addition of hexadeuteriobenzene gave HD.



$$D + RH \longrightarrow HD + R$$

Similarly, addition of toluene gave methane.

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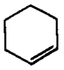
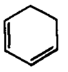
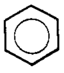
[1] This work has been supported in part by Grant No. AP 00353-02 from the Air Pollution Division of the Public Health Service. (b) Post-Doctorate Research Associate.

[2] R. D. Suart, Thesis, University of British Columbia, Vancouver, B. C., Canada, 1966.

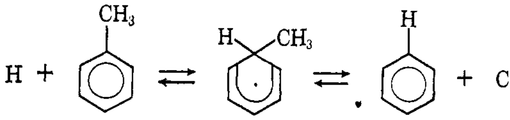
[3] (a) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 553 (1966); (b) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, 63, 985 (1967).

[4] R. Hoffmann, *Trans. N. Y. Acad. Sci.*, 475 (1966).

Table I. Pyrolysis of 1,3-Cyclohexadiene[a]

Temp, °C	Initial pressure, torr	Length of run, 10^3 sec	Pressure, torr  a		 b	H_2	b/a	H_2/a	a + b (x), torr	Total C_6 (y), torr	10^5k, sec^{-1}	$10^5k/P_i^{1/2}$, sec^{-1} $torr^{-1/2}$	$10^5k/P_i^{1/4}$, sec^{-1} $torr^{-1/4}$
362	20	5.4	1.04	17.8	1.58	...	1.52	...	2.62	19.4	2.7	0.60	1.3
362	20	5.4	0.86	18.5	1.26	0.26	1.47	0.30	2.12	20.6	2.1	0.47	1.0
362	44	3.6	2.40	41.8	3.16	0.52	1.32	0.21	5.56	47.4	3.5	0.53	1.4
362	44	3.6	2.30	40.2	3.07	0.43	1.33	0.19	5.37	45.6	3.5	0.53	1.4
362	76	3.6	4.23	64.0	6.30	1.43	1.49	0.34	10.53	74.5	4.2	0.48	1.4
391	10	1.8	0.70	9.70	0.95	...	1.36	...	1.65	11.4	8.4	2.7	4.8
391	10	3.6	1.23	8.27	1.59	...	1.29	...	2.82	11.1	8.2	2.6	4.6
391	20	1.8	1.34	17.8	1.75	...	1.31	...	3.09	20.9	8.9	2.0	4.2
391	40	1.8	3.60	28.0	5.30	0.78	1.47	0.22	8.90	36.9	15.3	2.4	6.0
391	80	1.8	5.8	56.3	8.7	1.35	1.50	0.23	14.5	70.8	12.7	1.4	4.2
391	80	1.8	7.7	52.0	11.4	1.51	1.48	0.20	19.1	71.1	17.5	2.0	6.0
391	80	1.8	6.1	60.0	9.1	1.13	1.49	0.19	15.2	75.2	12.5	1.4	4.2
421	40	0.9	5.9	21.5	8.0	1.35	1.35	0.23	13.9	35.4	55	8.7	2.2
421	40	0.9	5.4	24.0	7.4	1.25	1.37	0.23	12.8	36.8	48	7.6	1.9
421	80	0.9	13.5	49.0	19.0	3.02	1.41	0.22	32.5	81.5	57	6.4	1.9
421	80	0.9	12.1	42.7	17.2	2.65	1.42	0.22	29.3	72.0	58	6.5	1.9
391[b]	20	1.8	1.12	17.9	1.74	...	1.55	...	...	20.8	8.2	2.6	4.6
391[c]	40	1.8	2.46	26.4	4.30	...	1.74	...	...	33.2	...	...	...
391[d]	40	1.8	2.40	15.8	6.70	...	2.8	...	...	22.9	...	...	...
391[e]	40	1.8	1.63	32.6	2.30	0.44	1.41	0.27	3.93	36.5	6.4	1.0	2.5
391[e]	40	1.8	1.64	34.0	2.36	0.39	1.44	0.24	4.00	38.0	6.1	1.0	2.5

[a] k calculated from $k = (1/t) \ln 1/[1 - (x/y)]$ sec^{-1}. [b] 450 torr of CF_4 added initially. [c] 40 torr of NO added initially. [d] 141 torr of NO added initially. [e] Surface to-volume ratio increased 20 times.

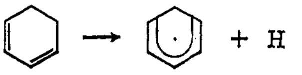


$$CH_3 + RH \longrightarrow CH_4 + R$$

These exchange reactions are discussed quantitatively in a later section.

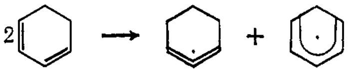
In spite of some scatter in the results, the initial rate of the over-all reaction in the middle of the temperature and pressure ranges is reasonably accurately measured. The rates of only a few of the possible elementary reactions have been measured, so in order to calculate an over-all rate some estimates must be made.

The observed rate of pyrolysis of 1,3-CH at 40 torr and 391° is $10^{-6.8}$ mole l.$^{-1}$ sec^{-1}. The upper limit of initiation rate, assuming a chain length of one, is then $10^{-6.8}$ mole l.$^{-1}$ sec^{-1}. Ellis and Frey[3a] have suggested that the initiation is



(1)

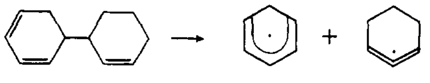
From the transition state theory quantity (ekT/h) sec^{-1}, the heats of formation of the cyclohexadienyl radical,[2] 1,3-CH,[5] and the hydrogen atom,[6] and assuming E_{-1} is zero, $k_1 = 10^{13.6-71/\theta}$ sec^{-1} and $R_1 = k_1[\text{CH}] = 10^{-13.1}$ mole l.$^{-1}$ sec^{-1}. An alternative initiation is



(2)

From the heat of formation of cyclohexenyl-3 radical,[6] ΔH_2 = 22 kcal mole^{-1}. There is evidence that E_{-2} is greater than zero. Benson, Cruickshank, and Shaw[7] have shown that the hydrogen abstraction by nitric oxide from 1,3-CH, which is also 22 kcal mole^{-1} endothermic, has an activation energy of 9 kcal mole^{-1} in excess of its endothermicity. We therefore estimate E_2 = 31 kcal mole^{-1}

Consider the reaction



(3)

We have estimated that ΔS_3 is 44 cal mole^{-1} deg^{-1}. If A_3 is $10^{13.5}$ sec^{-1}, then A_{-3} is 10^6 mole^{-1} l. sec^{-1}.

Suart[2] has shown that the ratio of rate constants for combination and disproportionationof two cyclohexadienyl radicals is about 2, and his results indicate that the absolute rate constants are of the order of 10^6 l. mole^{-1} sec^{-1}. Thus it is reasonable that $A_{-3} \sim A_{-2}$. Now $\ln A_2/A_{-2} = \Delta S_2/R$, where ΔS_2 is the over-all entropy change in reaction 2. There are no published values for the entropies of the radicals, but the over-all entropy change must be small as the changes in translational and rotational entropies are negligible; that is, $A_2 \sim A_{-2} \sim 10^6$ mole^{-1} l. sec^{-1}. Then $k_2 = 10^{6-31/\theta}$ mole^{-1} l. sec^{-1} and $R_2 = k_2[\text{CH}]^2 = 10^{-10.3}$ mole l.$^{-1}$ sec^{-1}, so that initiation 2 is $10^{2.8}$ faster than reaction 1. Even allowing for some uncertainty in the estimates of rate constants, it seems certain that initiation is predominantly by reaction 2.

The products may be explained by the propagation steps shown in eq 4–8. From the small yields of C_{12} and higher hydrocarbons, we can neglect reaction 8 and subsequent steps, so that the bulk of the cyclohexadienyl-3 radicals form cyclohexene, and then $R_6 = R_7$. The results show that $R_{H_2}/R_{\text{cyclohexene}}$ does not vary significantly with initial pressure of 1,3-CH or temperature, so $R_{H_2}/R_{\text{cyclohexene}} = 0.25 = R_5/R_7 = R_5/R_6 = k_5/k_6$.

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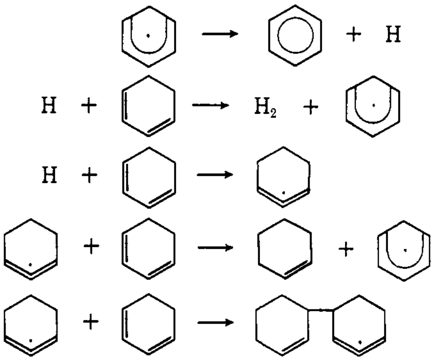
(5) J. D. Cox, *Tetrahedron*, 1175 (1963).

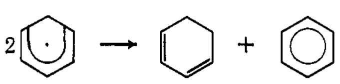
(6) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(7) S. W. Benson, F. R. Cruickshank, and R. Shaw, to be published.



(4)
(5)
(6)
(7)
(8)

To know which radicals are most likely to terminate, it is necessary to calculate their steady-state concentrations. From the propagations, $[C_6H_9]/[H] = k_6/k_7$ and $[C_6H_9]/[C_6H_7] = k_4k_6/\{(k_5 + k_6)k_7[CH]\}$. The present experiments give $k_6/(k_5 + k_6) = 0.8$. From Yang's value,[8] $k_{-4} = 10^{9.5-3.9/\theta}$ mole^{-1} l. sec^{-1}, and from our study of exchange reactions (see later) $k_6 = 10^{10.6-4/\theta}$ mole^{-1} l. sec^{-1}. Yang's value[8] for A_{-4}, together with a calculated entropy change $\Delta S_4 = 25$ cal mole^{-1} deg^{-1}, leads to $A_{-4} = 10^{13}$, and $E_4 = 31$ kcal mole^{-1} is consistent with Suart's measurement[2] so that $k_4/k_9^{1/2} = 10^{19.5-31/\theta}$ mole$^{1/2}$ l.$^{-1/2}$ sec$^{-1/2}$. Reaction 7 has not previously been studied, but by comparison with hydrogen abstraction[9,10] by ethyl and isopropyl from 1,3-CH, we estimate $k_7 = 10^{8.5-10/\theta}$ mole^{-1} l. sec^{-1}.



(9)

Substituting for k_6 and k_7, $[C_6H_9]/[H] = 10^4$. The hydrogen atom concentration is, therefore, too small to be important in termination. In the second expression at 40 torr of 1,3-CH, $[C_6H_9]/[C_6H_7] = 10^{0.4}$. Termination by two C_6H_9 radicals gives second-order kinetics over-all which is not observed. Similarly, termination by two C_6H_7 radicals can be discounted because this gives first-order kinetics. On the other hand, cross termination (eq 10) gives three-halves order, which is close to that obtained experimentally. This termination is also favored by a statistical factor of 2 and by a high exothermicity of 57 kcal mole^{-1}. This exothermicity is similar to that for the disproportionation of normal alkyl radicals, so k_{10} may be as high as 10^9 mole^{-1} l. sec^{-1}.

(10)

It follows from the mechanism that the calculated initial rate of pyrolysis of 1,3-CH is $(1.25k_2k_4k_7/k_{10})^{1/2}\cdot[CH]^{3/2} = 10^{9.3-36/\theta}[CH]^{3/2} = 10^{-7.2}$ mole l.$^{-1}$ sec^{-1} at 360° and 40 torr of 1,3-CH. The calculated order, activation energy, and initial rate are in reasonable agreement with experiment.

Because of the complexity of the pyrolysis, we feel that the most progress in understanding it will be made by an independent study of the various possible elementary reactions, rather than further study of the pyrolysis itself.

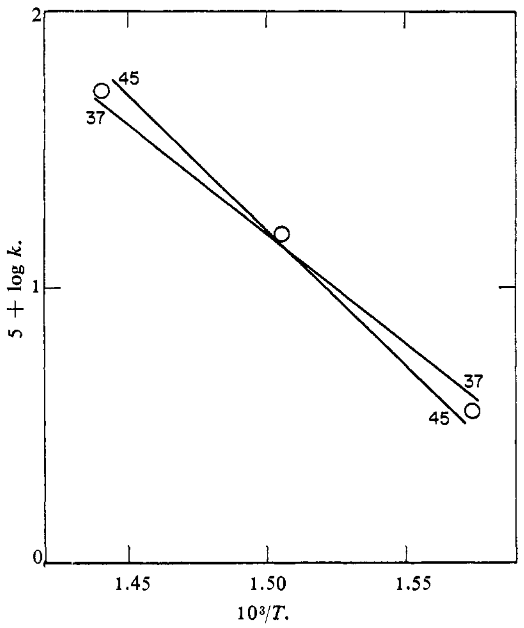
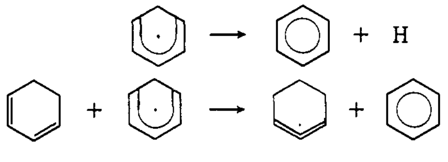


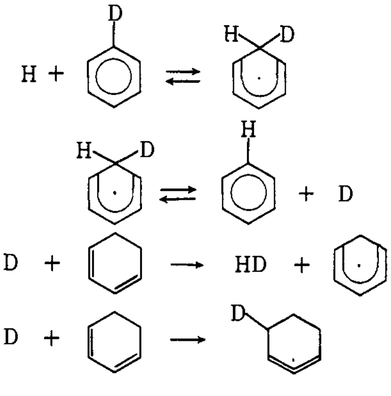
Figure 1.

Hydrogen Abstraction by 1,3-Cyclohexadiene. An interesting result from the pyrolysis of 1,3-CH is that reaction 4 is faster than reaction 11; that is, $k_{11}[CH] < k_4$, *i.e.*, $k_{11} < 10^{3+13-34/\theta} = 10^{4.7}$ mole^{-1} l. sec^{-1} at 40 torr and 391°. If $A_{11} = 10^6$ mole^{-1} l. sec^{-1}, then $E_{11} > 4$ kcal mole^{-1} although the reaction is 20 kcal mole^{-1} exothermic. This seems a reasonable result. A value of $A_{11} = 10^7$ mole^{-1} l. sec^{-1} would require $E_{11} > 7$ kcal mole^{-1}.



(4)
(11)

Addition of Hydrogen Atoms to Benzene and Toluene. When hexadeuteriobenzene was added initially to 1,3-CH, mass spectrometric analysis of the hydrogen showed the presence of HD (Table II). This may be explained by



(12)
(13)
(14)
(15)

From symmetry and thermochemistry we have estimated that $K_{12}K_{13} = 6$ and $k_{12}/k_{-13} = 6$, so $k_{13}/k_{-12} = 1$. It was shown earlier that $k_5/k_6 = 0.25$, and, if $k_{14}/k_{15} = k_5/k_6$, then $k_5/k_{12} = R_{H_2}[C_6D_6]/10R_{HD}[CH]$. Using the initial pressures of reactants as a measure of their concentrations, the results show that $k_5/k_{12} \sim 3$.

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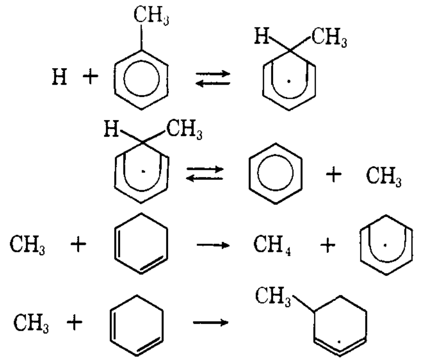
(8) K. Yang, *J. Am. Chem. Soc.*, **84**, 719 (1962).
(9) A. C. R. Brown and D. G. L. James, *Can. J. Chem.*, **43**, 660 (1965).
(10) D. G. L. James and R. G. Suart, *J. Phys. Chem.*, **69**, 2362 (1965).

Table II. Pyrolysis of 1,3-CH with Added C_6D_6 or $PhCH_3$ at 391°

Initial pressures, torr			Length of run,	Relative yields				
1,3-CH	C_6D_6	$PhCH_3$	10^3 sec	H_2	HD	CH_4	k_5/k_{12}	k_5/k_{16}
10	40		5	100	11.1		3.6	
40	40		1.8	100	3.4		2.7	
20		10	1.8	100		11		2

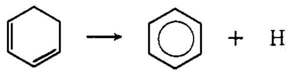
When toluene is added initially to 1,3-CH, methane is produced. This may be explained[11] by eq 16–19.



(16)
(17)
(18)
(19)

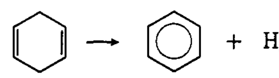
From thermochemistry at 391°, $K_{16}K_{17} = 10^{4.5}$, and, as k_{16}/k_{-17} is unlikely to be greater than $10^{2.5}$, then $k_{17}/k_{-16} = 10^2$. That is the error in assuming $R_{16} = R_{17}$ is about 1% and may be neglected. No value has been reported for k_{18}/k_{19}, but from the results of Gresser, Rajbenbach, and Szwarc,[12] and also James and Suart[9,10] k_{18}/k_{19} can be estimated to be equal to 1. Then, $k_5/k_{16} = R_{H_2}[PhCH_3]/2R_{CH_4}[CH] \sim 2$. Thus, at 391°, $k_{12}:k_{16}:k_5:k_6 = 1:1.5:3:12$.

Unimolecular Elimination of Hydrogen from 1,3-CH. From the constancy of the ratio $R_{H_2}/R_{\text{cyclohexene}}$ over the temperature range, it may be deduced that the unimolecular elimination of hydrogen from 1,3-CH contributes less than 10% to the yield of hydrogen; that is, $R_{20} < 10^{-8}$ mole l.$^{-1}$ sec^{-1} at 391° and 40 torr, and $k_{20} < 10^{-5}$ sec^{-1}. From the measured[3] rate of reaction 21, k_{21}/k_{20}



(20)

$> 10^3$, so, if $A_{21} \sim A_{20}$, $E_{20} - E_{21} > 9$ kcal mole^{-1}, and, as $E_{21} = 44$ kcal mole^{-1}, then $E_{20} > 53$ kcal mole^{-1}.



(21)

The marked difference in the rates of thermal unimolecular elimination of hydrogen from 1,3-CH and 1,4-CH is in line with the theoretical predictions of Hoffmann.[4]

Acknowledgment. We thank Dr. R. D. Suart for communication of his results prior to publication, Miss J. S. Whittick and Mr. F. M. Church for mass spectrometric analyses, and Miss E. A. Lawler and Mr. L. J. Salas for preparative gas chromatographic purifications.

(11) M. Szwarc, *J. Chem. Phys.*, 17, 128 (1948).

(12) J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 3005 (1961).

The Kinetics of Competitive-Consecutive Second-Order Reactions Involving Difunctional Unsymmetrical Molecules. The Kinetics of the Alkaline Hydrolysis of Diethyl Malate

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Contribution from the Chemistry Department, University of Maryland, College Park, Maryland.

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Abstract: A kinetic process of a four-step competitive-consecutive second-order reaction involving an unsymmetrical difunctional molecule can be written as $A + B \rightarrow C + M$, $A + B \rightarrow E + M$, $A + C \rightarrow P + M$, and $A + E \rightarrow P + M$, having the rate constants k_1, k_2, k_3, and k_4, respectively. The rate equations have been solved in terms of the variable λ where $\lambda = \int_0^t A\,dt$. The solution is of the form $A/B_0 = G_1e^{-(k_1 + k_2)\lambda} + G_2e^{-k_3\lambda} + G_3e^{-k_4\lambda} + (A_0/B_0) - 2$, where the G's are constants involving various combinations of k_1, k_2, k_3, and k_4. A least-squares solution can be used which allows the calculation of the k's. The procedure was used to determine the k's for the alkaline hydrolysis of diethyl malate, an unsymmetrical diester containing a hydroxyl group, in dioxane–water mixtures of varying composition at several temperatures. A mechanism involving the inductive effect of the hydroxy substituent is postulated for the reaction, and each of the k's is assigned to a particular step in the reaction. The various thermodynamic activation values have been calculated.

During the past few years, there have appeared from our laboratory a series of papers concerned with the kinetics of competitive-consecutive second-order reactions involving multifunctional symmetrical compounds.[2] Our investigations have been extended to kinetic studies of difunctional and trifunctional unsym-

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(1) Abstracted from a thesis submitted by F. A. Kundell to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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