

## KINETICS OF THE ACID-CATALYSED SOLVOLYSIS OF SIX-MEMBERED CYCLOSILAZOXANES CONTAINING TWO SILAZANE BONDS

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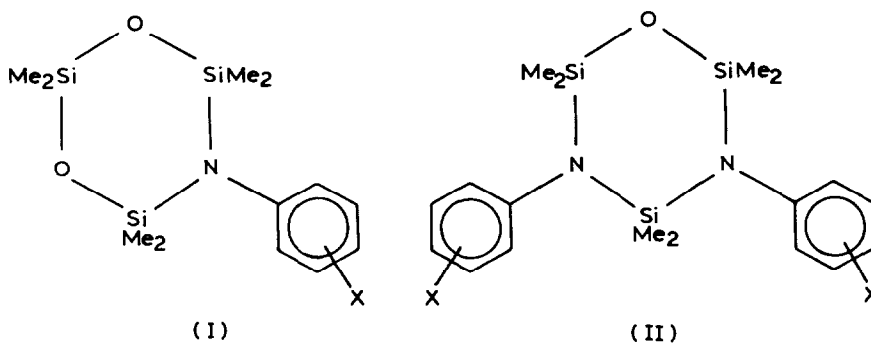
(Received February 17th, 1986)

### Summary

The solvolysis of *N,N'*-diphenyl-1,1,3,3,5,5-hexamethyl-1,3,5-trisila-2,4-diaza-6-oxacyclohexane (II) in methanol/water in the presence of an acetate buffer is a two-step, pseudo-first-order, process. Both steps are subject to general acid catalysis and their catalytic rate constants have been determined spectrophotometrically. The ring cleavage is faster than that of analogous cyclosilazoxanes containing a single silazane bond (I), but the catalytic mode, substituent effects, and the solvent isotope effect indicate a close mechanistic similarity for the solvolysis of I and II.

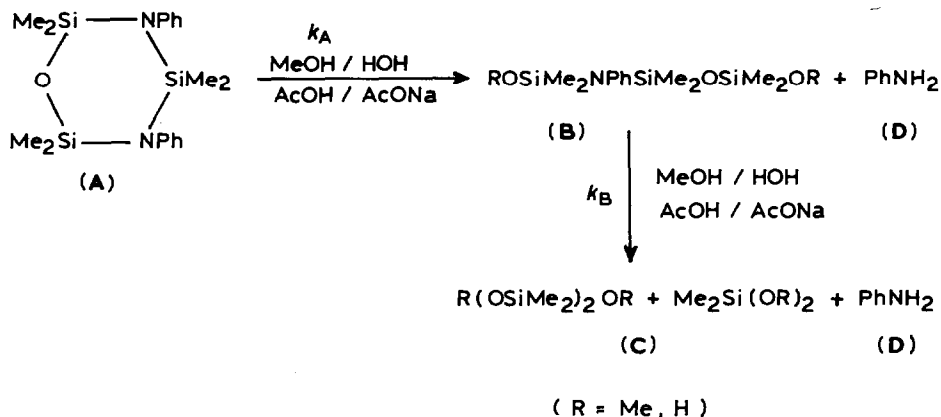
### Introduction

Studies on the heterolysis of the silicon–nitrogen bond in cyclic silazoxanes I [1] have now been extended to reactions of compound II in order to determine the effect of introducing a second silazane linkage into the ring system. The same solvolysis medium (aqueous methanol and acetate buffer) and the same reaction conditions (fixed concentration of water and constant ionic strength) used for I [1] were employed. The progress of the reaction was monitored spectrophotometrically in the UV region, as before.



## Results and discussion

Analysis by linked GLC-mass spectrometry at various reaction times showed that in the acidic aqueous-methanolic medium only the silicon–nitrogen bonds were broken, leaving the siloxane grouping unaffected, as was found for the reactions of compounds I. The kinetics are, however, more complicated in the present case because the intermediate linear product reacts further with methanol/water at a rate comparable to that of the ring cleavage (Scheme 1).



SCHEME 1

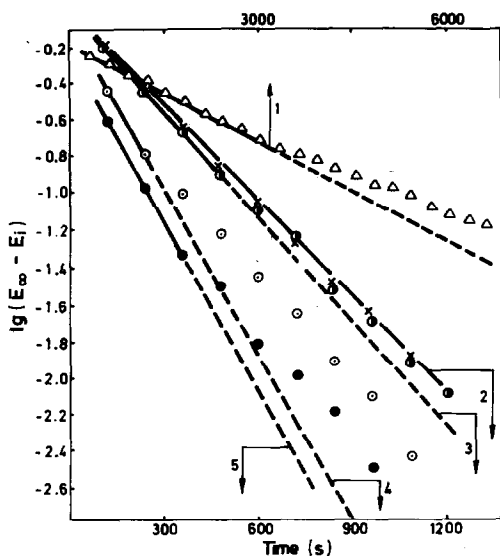


Fig. 1. First order plots for the solvolysis of *N,N'*-diphenylcyclosilazoxane (II, X = H) in aqueous methanol,  $[\text{H}_2\text{O}]$  0.56 M;  $I = 0.02$ ;  $T$  25°C;  $[\text{AcOH}]/[\text{AcONa}] = 10$ . Concentrations (M): 1,  $[\text{AcOH}]$  0.0,  $c_0$   $2.1 \times 10^{-4}$ ; 2,  $[\text{AcOH}]$  0.01,  $c_0$   $2.5 \times 10^{-4}$ ; 3,  $[\text{AcOH}]$  0.04,  $c_0$   $3.5 \times 10^{-4}$ ; 4,  $[\text{AcOH}]$  0.06,  $c_0$   $2.7 \times 10^{-4}$ ; 5,  $[\text{AcOH}]$  0.07,  $c_0$   $3.0 \times 10^{-4}$ ;  $c_0$  = initial concentration of silazoxane.

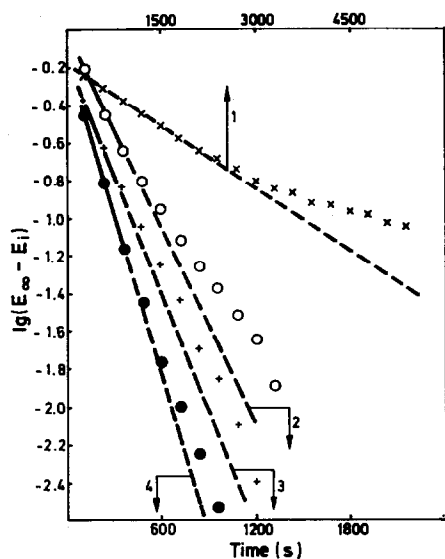


Fig. 2. First order plots for the solvolysis of  $N,N'$ -diarylcyclosilazoxanes (II) in aqueous methanol,  $[\text{H}_2\text{O}]$  0.56  $M$ ;  $I = 0.02$ ;  $T$  25°C,  $[\text{AcOH}]/[\text{AcONa}] = 10$ . X, concentrations ( $M$ ): 1,  $m\text{-Br}$ ,  $[\text{AcOH}]$  0.04,  $c_0$   $1.2 \times 10^{-4}$ ; 2,  $m\text{-CH}_3\text{O}$ ,  $[\text{AcOH}]$  0.05,  $c_0$   $2.0 \times 10^{-4}$ ; 3,  $m\text{-CH}_3$ ,  $[\text{AcOH}]$  0.05,  $c_0$   $2.0 \times 10^{-4}$ ;  $p\text{-CH}_3$ ,  $[\text{AcOH}]$  0.06,  $c_0$   $2.5 \times 10^{-4}$ ;  $c_0$  = initial concentration of silazoxane.

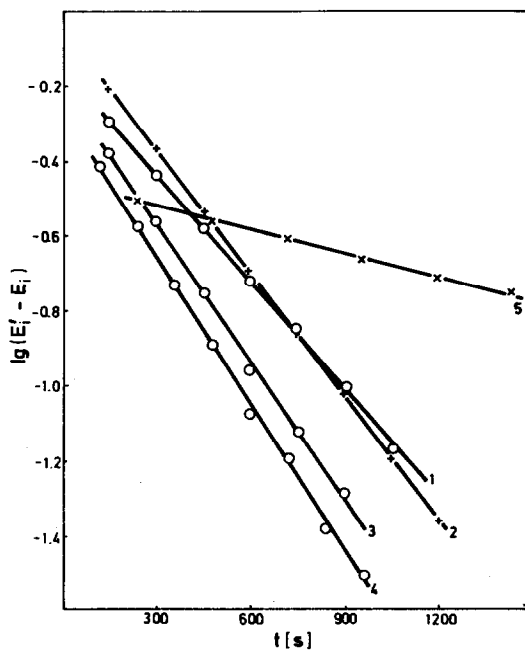


Fig. 3. First order plots for the solvolysis of the intermediate **B** in aqueous methanol,  $[\text{H}_2\text{O}]$  0.56  $M$ ;  $I = 0.02$ ;  $T$  25°C;  $[\text{AcOH}]/[\text{AcONa}] = 10$ . Concentrations ( $M$ ): 1;  $[\text{AcOH}]$  0.025,  $c_0$   $3.0 \times 10^{-4}$ ; 2,  $[\text{AcOH}]$  0.05,  $c_0$   $2.8 \times 10^{-4}$ ; 3,  $[\text{AcOH}]$  0.1,  $c_0$   $2.8 \times 10^{-4}$ ; 4,  $[\text{AcOH}]$  0.16,  $c_0$   $3.6 \times 10^{-4}$ ; 5,  $[\text{AcOH}]$  0.0,  $c_0$   $4.8 \times 10^{-4}$ ;  $c_0$  = initial concentration of **B**.

As shown in Fig. 1, most of the first-order plots of  $\log(E_\infty - E_i)$  vs. time deviate at some point from linearity in the direction suggestive of a decrease in the rate constant ( $k_B < k_A$ ); straight lines of lower slopes can be drawn through the experimental points obtained at higher conversions. The same is true for solvolyses of siloxanes II substituted in the benzene ring (Fig. 2). Similar behaviour has been observed before for reactions of some cyclosilazanes with nucleophiles [2,3].

The intermediate product (**B**), 1-methoxy-2-phenyl-1,1,3,3-tetramethyl-3-(methoxydimethyl)siloxydisilazane was prepared independently and its reaction with aqueous methanol found to give good first-order plots up to over 90% conversion (Fig. 3).

Thus  $k_B$  for the reaction of II ( $X = H$ ) could be derived from the slopes of the straight lines in Fig. 3. It should be noted, however, that the initial slopes in Figs. 1 and 2 do not represent the pseudo-first-order rate constant  $k_A$  but an apparent constant  $k'_A$ . The constant  $k_A$  can be calculated from the expression

$$\frac{E_i}{[A]_0} = \epsilon_A e^{-k_A t} + (\epsilon_B + \epsilon_D) \frac{k_A}{k_B - k_A} e^{-k_A t} - (\epsilon_B - \epsilon_D) \frac{k_A}{k_B - k_A} e^{-k_B t} - \epsilon_D \frac{2k_B}{k_B - k_A} e^{-k_A t} + 2\epsilon_D \quad (1)$$

$E_i$  = absorption at time  $t$ ,

$[A]_0$  = initial concentration of cyclosilazoxane II,

$\epsilon_A, \epsilon_B, \epsilon_D$  = molar extinction coefficients of cyclosilazoxane II, intermediate (**B**) and aniline, respectively.

Equation 1 is based (see Experimental section) on the assumption of consecutive first-order reactions



where C represents a non-absorbing product.

The apparent rate constants  $k'_A$  of the cleavage of cyclosilazoxanes II were used in determining the catalytic mode, the substituent effects and solvent isotope effect. The detailed values of the partial catalytic constants and activation parameters for the reaction of II ( $X = H$ ) were based on the calculated values of the real rate constants  $k_A$ . Owing to the scarcity of experimental points in the case of faster reactions run at higher temperatures, the possible errors in some of the  $k_A$  values and activation parameters are rather large but this does not affect the validity of the subsequent discussion.

The catalytic mode was found to be the same as that established for the acidic solvolysis of cyclosilazoxanes I, viz. general acid catalysis, and the values of the catalytic constants  $k_0$ ,  $k_{AcOH}$  and  $k'_{ROH_2^+}$  were calculated in the same manner [1] from the slopes of the straight line plots of the experimental pseudo-first-order rate constants  $k_A$  vs.  $[AcOH]$  at constant buffer ratio and vs.  $[AcOH/AcONa]$  at constant concentration of acetic acid. The rate of solvolysis of the linear intermediate (**B**) was found to depend in the same way on the concentration of the

TABLE 1

SOLVOLYSIS OF CYCLOSILAZOXANES I AND II (X = H) AND THE INTERMEDIATE (B) IN METHANOL/WATER/ACETATE BUFFER

	$k_0$ ( $\times 10^{-4}$ ) ( $s^{-1}$ ) <i>T</i> 298 K	$k_{AcOH}$ ( $\times 10^{-2}$ ) ( $dm^3 mol^{-1} s^{-1}$ ) <i>T</i> 298 K	$k_{ROH_2}^{\ddagger}$ ( $\times 10^{-4}$ ) ( $s^{-1}$ ) <i>T</i> 298 K	$\Delta H^{\ddagger}$ ( $kcal mol^{-1}$ )	$\Delta S^{\ddagger}$ (e.u.)
I [1]	1.07	1.07	1.92	$6.0 \pm 1.4$ ( $25.8 \pm 6 kJ mol^{-1}$ )	$-46.5 \pm 4.4$ ( $-0.195 \pm 0.02 kJ mol^{-1} deg^{-1}$ )
II	2.95	$6.9 \pm 0.1$ $9.4 \pm 0.1^a$ $10.5 \pm 0.1^b$	$6.5 \pm 0.2$	$3.8 \pm 1.4$ ( $15.8 \pm 6 kJ mol^{-1}$ )	$-51 \pm 5$ ( $-0.21 \pm 0.02 kJ mol^{-1} deg^{-1}$ )
B	1.76	$0.41 \pm 0.04$	$2.57 \pm 0.1$		

<sup>a</sup> *T* 308 K. <sup>b</sup> *T* 318 K.

catalytic system. The values of the partial catalytic rate constants of the solvolysis of cyclosilazoxane II (X = H) and the intermediate as well as the activation data are listed in Table 1 together with, for comparison, those for cyclosilazoxane I (X = H) [1].

It is seen from Table 1 that the rates of the reaction of II are higher than those of I; in particular the contribution of catalysis by undissociated acid molecules to the overall rate is larger for II. Part of the increase in rate could be expected on statistical grounds. However, the overall electronic effect of the presence of a second NPh group in place of an oxygen adjacent to the bond being cleaved must also be significant. Finally, the larger ring strain in silazoxanes containing two nitrogens as compared with those with a single silazane linkage (cf. [4] and [5]) can be expected to provide an additional driving force for the ring cleavage. On the other hand, the comparatively low rate of reaction catalyzed by undissociated acid, as represented by  $k_{AcOH}$ , in the solvolysis of the intermediate B may result from the large delocalization of the nitrogen electrons by (*p-d*) $\pi$  interaction with silicon promoted by the inductive effect of the terminal methoxyl group.

Substituents in the benzene ring affect the rates of solvolysis of compounds II in a similar way as they do in those for the reactions of cyclosilazoxanes I [1]. The relative catalytic rate constants  $k_{AcOH}^X/k_{AcOH}^H$  at 25°C are for X = *p*-CH<sub>3</sub>, 2.18; *m*-CH<sub>3</sub>, 1.39; *m*-CH<sub>3</sub>O, 0.48 and *m*-Br, 0.13; thus electron-donating substituents accelerate the reaction.

All these results indicate a close similarity of mechanisms in the solvolytic cleavage of the silicon–nitrogen bond in the two series I and II of six-membered silazoxane rings. Therefore, the previously suggested nucleophilic attack on silicon by a solvent molecule synchronous with proton transfer from the catalysing acid to nitrogen [1] should also be valid in the present case.

The value of the kinetic solvent isotope effect was found to be even closer to unity ( $k_{AcOH}/k_{AcOD} = 0.96$ ) in the solvolysis of II (X = H) than in that of I (X = H) (0.87) [1]. In order to get a closer insight into the structure of the transition state supplementary measurements of the kinetic isotope effect for two substituted compounds of series I, X = *p*-CH<sub>3</sub> and X = *m*-Cl were made, and values of  $k_H/k_D = 1.35$  and 0.67, respectively, were obtained. The large enhancement of the

TABLE 2

PROPERTIES AND ANALYSES OF *N,N'*-DIARYL-1,1,3,3,5,5-HEXAMETHYL-1,3,5-TRISILA-2,4-DIAZA-6-OXACYCLOHEXANES (Me<sub>2</sub>Si)<sub>3</sub>O(NC<sub>6</sub>H<sub>4</sub>X)<sub>2</sub>

X	Yield (%)	M.p. (°C)	Analysis (Found (calcd.)) (%)						MW Found <sup>a</sup> (calcd.)	Chemical shifts, δ(ppm) in <sup>1</sup> H NMR spectra (solvent CCl <sub>4</sub> , internal standard CH <sub>2</sub> Cl <sub>2</sub> )			λ <sup>b</sup> (nm)
			C	H	N	Si	Br	NSi(CH <sub>3</sub> ) <sub>2</sub> N		NSi(CH <sub>3</sub> ) <sub>2</sub> O	X	C <sub>6</sub> H <sub>4</sub>	
H	15	110	57.48 (58.01)	7.74 (7.57)	7.37 (7.52)	23.10 (22.61)	—	385 (372.7)	0.0s (6H)	0.163s (12H)	7.17m (10H)	253	
<i>p</i> -CH <sub>3</sub>	15	126	59.54 (59.94)	8.15 (8.05)	6.47 (6.99)	21.21 (21.03)	—	366 (400.75)	0.015s (6H)	0.15s (12H)	2.35s (6H)	253	
<i>m</i> -CH <sub>3</sub>	10	135	59.64 (59.94)	7.87 (8.05)	7.00 (6.99)	21.08 (21.03)	—	— (400.75)	—0.05s (6H)	0.12s (12H)	2.33s (6H)	250	
<i>m</i> -CH <sub>3</sub> O	15	76–78	55.55 (55.51)	7.41 (7.45)	6.58 (6.47)	19.25 (19.47)	—	420 (432.74)	0.025s (6H)	0.18s (12H)	3.80s (6H)	250	
<i>m</i> -Br	12	136	41.05 (40.75)	5.18 (4.94)	5.23 (5.28)	15.85 (15.86)	29.9 (30.1)	— (530.5)	0.01s (6H)	0.18s (12H)	7.0 m (8H)	256	

<sup>a</sup> Osmometric (Hewlett-Packard 302B). <sup>b</sup> Wavelength, at which UV absorptions were recorded in kinetic runs.

isotope effect by the electron donating *p*-methyl group, can in terms of the relation between the bond-order and the primary isotope effect [6], be taken to indicate a rather reagent-like structure of the transition state, which is equivalent to a small extent of proton transfer from the catalyzing acid to the reagent. This unusual result can be only accounted for the very low basicity of nitrogen in the cyclosilazoxane molecules. In this connection it is interesting to note that general acid catalysis, suggestive of slow proton transfer, was found in the methanolysis of trimethylsilylbenzamides [7], whereas the similar reaction of trialkylsilylanilines is subject to specific proton catalysis [8]; obviously, the basicity of nitrogen is much smaller in the benzamides than in the anilines.

## Experimental

All *N,N'*-diarylcyclosilazoxanes (II) were prepared by the method used for the parent compound *N,N'*-diphenyl-1,1,3,3,5,5-hexamethyl-1,3,5-trisila-2,4-diaza-6-oxacyclohexane [9]. They were purified by repeated crystallization from ethyl acetate or acetonitrile immediately before the rate studies, and were dried on a vacuum line and stored in vacuo. The yields, melting points, elemental analyses and spectroscopic data are listed in Table 2. For comments on the low yields see [9].

### *1-Methoxy-2-phenyl-1,1,3,3-tetramethyl-3-(methoxydimethyl)siloxydisilazane*

To a solution of *N,N'*-diphenyl-1,1,3,3,5,5-hexamethyl-1,3,5-trisila-2,4-diaza-6-oxacyclohexane (II, X = H) (0.01 mol) in dry dioxane (30 ml) was added anhydrous methanol (0.02 mol = 0.85 ml). The reaction was monitored by GLC and allowed to proceed for 34 h until the ratio of the peak areas of the product and unreacted substrate remained constant. Small amounts of the final products of methanolysis, dimethoxydimethylsilane and 1,3-dimethoxytetramethylidisiloxane were formed, as determined by GLC. After evaporation of the solvent and the low boiling compounds under reduced pressure, the unchanged II was filtered off and the main product obtained from the solution by preparative GLC (Found: C, 49.10; H, 8.40; N, 3.85. C<sub>14</sub>H<sub>29</sub>NO<sub>3</sub>Si<sub>3</sub> calcd.: C, 48.93; H, 8.51; N, 4.08%; Mol. wt. calcd. and molecular ion peak: 343). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub> as solvent and int. standard, δ, ppm): 0.049 s (12H), 0.101 s (6H), 3.423 s (3H), 3.472 s (3H), 7.163 s (5H).

### *Kinetic measurements*

The method described for the solvolysis of compounds I was used [1]. The change in UV absorption (*E*) in vapour-tight thermostatted cells was recorded at the wavelengths λ, shown in Table 2. A Specord UV-VIS spectrophotometer was used throughout.

The apparent pseudo-first-order rate constants *k'<sub>A</sub>* for the first stage of solvolysis were determined by use of the equation  $2.303 \log (E_{\infty} - E_t) = -k'_A t + c$ , where *E<sub>t</sub>* is the absorption at time *t* and *E<sub>∞</sub>* that after 24 h. The real pseudo-first-order rate constants *k<sub>A</sub>* were calculated from eq. 1 by numerical methods, using a program in language FORTRAN 1900, designed for computers ICL 1900 and Odra 1300. Computing was carried out on an Odra 1305, controlled by a George 3 operating system.

The observed rate constants *k<sub>B</sub>* of solvolysis of the linear intermediate **B** were calculated by the Guggenheim method and least-squares regression analysis. The

TABLE 3

EFFECT OF ACETATE BUFFER CONCENTRATION ON THE RATE CONSTANTS  $k'_A$ ,  $k_A$  AND  $k_B$  OF BOTH STEPS OF SOLVOLYSIS OF  $(\text{Me}_2\text{Si})_3\text{O}(\text{NPh})_2$  (II, X = H) IN AQUEOUS METHANOL,  $[\text{H}_2\text{O}]$  0.56 M,  $I = 0.02$ ,  $T$  25°C. ( $\lambda$  for B 250 nm)

[AcOH] (M)	0.01	0.025	0.05	0.06	0.07	0.1	0.05	0.05	0.05	0.05	
[AcONa] (M)	0.001	0.0025	0.005	0.006	0.007	0.01	0.02	0.01	0.004	0.0025	
$10^3 k'_A$ ( $\text{s}^{-1}$ )	2.86	3.10	4.05	4.47	4.56		1.61	2.25	4.0	6.0	
$10^3 k_A$ ( $\text{s}^{-1}$ )	8.26	8.45	11.23	11.62	11.81		4.07	4.96	9.3	13.8	
$10^3 k_B$ ( $\text{s}^{-1}$ )	2.48	2.54	2.63				2.82	1.59	2.25	4.1	6.0

TABLE 4

EFFECT OF ACETATE BUFFER CONCENTRATION ON THE RATE CONSTANTS,  $10^3 k'_A$  ( $\text{s}^{-1}$ ) OF SOLVOLYSIS OF  $(\text{Me}_2\text{Si})_3\text{O}(\text{NC}_6\text{H}_4\text{X})_2$ , II, IN AQUEOUS METHANOL,  $[\text{H}_2\text{O}]$  0.56 M,  $I = 0.02$ ,  $T$  25°C,  $[\text{AcOH}]/[\text{AcONa}] = 10$ , (for  $\lambda$ , see Table 2)

[AcOH] (M)	0.01	0.025	0.04	0.05	0.06	0.07	0.09	0.11	0.15
X = <i>p</i> -Me	3.25	3.90	4.70	5.42	6.10				
<i>m</i> -Me	3.44	3.78	4.14	4.32	4.65	4.82			
<i>m</i> -MeO	3.34	3.63	3.79	3.90	3.99				
<i>m</i> -Br	0.51			0.62		0.64	0.66	0.74	0.92

uncertainties in  $k'_A$  and  $k_B$  were  $\pm 5\%$  to  $\pm 10\%$ , and all data are averages of at least 3 determinations. Values of  $k'_A$ ,  $k_A$  and  $k_B$  for some of the runs are given in Tables 3 and 4.

The partial catalytic constants were calculated by least-squares using the equation  $k = k_0 + k_{\text{AcOH}} + k_{\text{ROH}_2}^+ [\text{AcOH}]/[\text{AcONa}]$ , ( $k = k_A$ ,  $k'_A$  or  $k_B$ ). All the uncertainties are expressed as standard deviations. The activation parameters were obtained by using the Eyring equation. Details of the chromatographic and spectroscopic analyses are given in ref. 1.

Equation 1 is derived for the system (2) in the following way. The differential equations for the changes in concentrations of A, B and D with time,  $d[A]/dt = k_A[A]$  (3);  $d[B]/dt = k'_A[A] - k_B[B]$  (4);  $d[D]/dt = k_A[A] + k_B[B]$  (5) yield on integration:

$$[A] = [A]_0 e^{-k_A t} \quad (6)$$

$$[B] = [A]_0 \frac{k_B}{k_B - k_A} (e^{-k_A t} - e^{-k_B t}) \quad (7)$$

$$[D] = [A]_0 \left[ \frac{k_A e^{-k_B t} - (2k_B - k_A) e^{-k_A t}}{k_B - k_A} + 2 \right] \quad (8)$$

Equation 1 is directly obtained by applying the law of additivity of absorptions  $E_i = \epsilon_A[A] + \epsilon_B[B] + \epsilon_D[D]$  (9) and substituting [A], [B] and [D] from (6) to (8) into (9).



## Acknowledgements

This work was supported by funds available under research project MR. I-12.

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