THE DIELS-ALDER REACTION BETWEEN STYRENE AND METHYL SORBATE-II* KINETICS

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Abstract—Absolute rate constants, activation enthalpies and activation entropies were determined for the formation of the four possible isomeric Diels–Alder adducts from methyl sorbate and styrene in toluene solution between 140 and 200°. The differences between the activation parameters are small. The degree of significance of these differences was evaluated by statistical methods. An interpretation of the differences between the rates of formation of the four adducts is given in terms of steric and electronic effects.

INTRODUCTION

IN A thorough investigation of the kinetics of the Diels-Alder reaction, the influence of change of structure in diene or dienophile, the effects of substituents, solvents and catalysts have been studied in detail,¹ but the simultaneous formation of different isomeric adducts in one reaction has not been followed kinetically.



FIG. 1 The structure of the four isomeric adducts from the Diels-Alder reaction between styrene and methyl sorbate.

It has been shown that four isomeric adducts (Fig. 1) are formed from the Diels-Alder reaction between styrene and methyl sorbate and that the reaction is kinetically

* Ref. 2 is considered to be Part I.

controlled.² It seemed interesting to study this reaction kinetically to evaluate the importance of enthalpy and entropy factors for the isomer distribution. The differences between these factors are very small, therefore the degree of significance of these differences was computed by statistical methods.

Calculation of the kinetic results. Because of a great number of parallel reactions of different types the reaction mixture is too complicated to be described with the aid of an integrated rate equation. Assuming that a Diels-Alder reaction is first order both in diene and dienophile,³ the following differentiated form can be used to calculate the rate constants of adduct formation:

$$\frac{d [adduct_i]}{dt} = k_i [diene] [dienophile]$$
(1)

This formula is correct because the adducts are not subject to secondary reactions. The individual rate constants have been calculated according to a method analogous to Benson.⁴

Toluene was used as an internal standard in the analyses.

Concentrations of a compound were expressed as:

(concentration
$$X$$
) = $\frac{(\text{peak area } X)}{(\text{peak area toluene})}$. (correction factors)

Estimation of correction factors

1. Detector response to the components of interest have been measured relative to toluene as internal standard.

2. Correction factors for the methyl sorbate (trans, trans) content were determined on Column II.

3. The specific volume of the initial reaction mixture depends on the reaction temperature. Correction factors were calculated assuming the mixture to be ideal. The densities of toluene at reaction temperature are known.⁵ For styrene the correction factors for ethylbenzene are used.⁵ For methyl sorbate the densities were estimated using a value of 0.001 for the thermal expansion coefficient.

4. The errors introduced by changes of specific volume of the reaction mixture as a consequence of the formation of products of higher density will be smaller than 1% and are neglected.

5. The influence of the applied reaction pressure (10 kg/cm^2) on the specific volume is neglected.

Corrected absolute rate constants have been calculated after introduction of the correction factors. Activation enthalpy (ΔH^{\ddagger}) and activation entropy (ΔS^{\ddagger}) have been calculated using Eyring's equation:

$$\log(k/T) = \log(k_{\rm B}/h) + \frac{\Delta S^{*}}{2 \cdot 303R} - \frac{\Delta H^{*}}{2 \cdot 303RT}$$
(2)

where $\mathbf{k} = \text{reaction constant}$

 k_{B} = Boltzmann's constant

R = gas constant

h =Planck's constant

T = absolute temperature.

Statistical procedures

The kinetic study of this process can be regarded, according to Eyring's equation as a mathematical problem to determine the position of four planes in the threedimensional space of log (k/T), t and 1/T, each corresponding to the rate constants of one isomeric Diels-Alder adduct.

There are some special features of this system. The kinetic Eq. (2) requires that all planes should run parallel to the time axis, so each plane is completely determined by two characteristic constants (the energy parameters ΔH^{\ddagger} and ΔS^{\ddagger}).

It is to be noted that experimentally the four planes are connected :

1. Physically because concentrations are determined from the same samples and from the same gaschromatograms,

2. Chemically by the monomer concentrations through Eq (1).

Most of the experimental uncertainties therefore are in the same direction and of the same magnitude for all four $\log (k/T)$ values simultaneously and, consequently, the position of the planes relative to each other can be determined much more accurately than their absolute position in space. These systematic errors and correction factors were estimated and corrected for only as far as it is meaningful to fix the absolute positions of the planes in space.

The energy parameters ΔH^{\ddagger} and ΔS^{\ddagger} are far out extrapolations from a limited temperature range to the extremities of the 1/T-axis. Their expected scatter would be larger by one or more orders of magnitude compared to those of log (k/T). The four planes run nearly parallel and very close to each other. Differences in ΔH^{\ddagger} and ΔS^{\ddagger} that are valuable for a discussion of the reaction mechanism, therefore, are very small and tend to get drowned in the scatter.

In view of these difficulties a large number of determinations is necessary in combination with statistical procedures. Samples of the reaction mixture were taken at several time intervals. Duplicate analyses were made of all samples. A third analysis was made of all samples of which duplicates show a deviation larger than 10%. Mean concentration values were used to calculate individual reaction rate constants. The mean reaction rate constants were calculated using the method of least squares. Values deviating more than three standard deviations were discarded. Mean k-values, the expected standard deviations and the number of individual rate constants used for the calculations are given in Table 1.

The calculations of ΔH^{\ddagger} , ΔS^{\ddagger} and the estimated standard deviations of the activation parameters were carried out on an X-8 computer using a least squares program.*

Lines of best fit for $\log (k/T)$ against 1/T were calculated assigning equal statistical weight to the values of Table 1, they are shown in Fig. 2.

The estimated standard deviations of log (k/T) from the lines of best fit (σ_2) are given in Table 3, ΔH^{\ddagger} and ΔS^{\ddagger} are given in Table 2. Next, different values of ΔH^{\ddagger} and ΔS^{\ddagger} were assumed, lines of log (k/T) against 1/T, and the standard deviation of log (k/T) recalculated. The variations of ΔH^{\ddagger} and ΔS^{\ddagger} are thus based on the estimated standard deviation of log (k/T) and are therefore proportional to it, they are also given in Table 2.

* The authors are indebted to Drs. C. Kort for assistance. Details of the program could be supplied on request.

r °C		•			æ			U			0	
	Rate constant	Estim. st. dev.	r	Rate constant	Estim. st. dev.	E	Rate constant	Estim. st. dev.	u	Rate constant	Estim. st. dev.	2
140	16-73	0.062	1	7-20	0-055	2	3-77	0-076	-	6.46	0-062	1
150	34:60	0-055	7	14-40	0-102	*	11-1	0-088	٢	12.91	0-075	- 00
170	1069	0-053	9	54-20	0-114	¢	27-91	0-046	9	45·54	0-031	9
180	193-4	0-131	9	102-6	0-126	9	49-87	0-138	9	17-17	0-159	9
190	302-3	0-027	5	170-7	0-028	ŝ	91-32	0-017	ŝ	144.6	0-044	9
200	573-9	0-213	7	330-5	0-226	7	188-4	0-229	٢	268-4	0-224	-

* The mean values of the absolute rate constants at any one temperature were calculated using the least squares method. The number of individually measured k's were also tabulated (n). The scatter is given as the estimated standard deviations. Numbers given in this table were used for the statistical evaluation.

H	E FORMATION O	F FOUR ISOMEI	RIC DIELS-ALDE	R ADDUCTS FRO	M STYRENE AN	D METHYL SORBAT	TE IN TOLUENE SC	NUTION
	React	tion enthalpy	(kcal/mol)		H	Reaction entropy	(cal/mol degree)	
	τHτ	* ‡H∆	Estimated st. dev.	Corrected estimated st. dev.†	ΔS ¹	₹;s	Estimated st. dev.	Corrected estimated st. dev.†
A	21-5	21:48	0-42	0:42	- 33-5	- 33-54	0-95	0-95
æ	23-7	23-71	0-30	0-35	- 29-9	- 29-88	0-67	0-77
υ	23-9	23-91	0-52	0-52	- 30-7	- 30-70	0-12	0-12
۵	23-0	22-95	0-34	0-34	- 31.9	31-93	0.76	0-77

Table 2. Activation parameters ΔH^4 (red $_{\rm s}/{
m mol}^{-1}$) and ΔS^4 (cal $_{\rm sm}$ mol $^{-1}$ degree $^{-1}$) with estimated standard deviations for

These values were used for the statistical calculations and for the construction of Fig. 2.
 The correction factor is taken from Table 3.

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FIG. 2 Mean reaction rate constants $[\log (k/T)]$ against reciprocal temperatures and calculated lines of best fit.

There is a possibility that the estimated standard deviations calculated from the best fit method (σ_2) will, by chance, be smaller than should be expected from the accuracy of the experiments. The estimated standard deviations in log (k/T) were therefore also directly calculated from the values of Table 1 (σ_1) and are given in Table 3. Whenever σ_1 is larger than σ_2 the estimated standard deviations of ΔH^{\ddagger} and ΔS^{\ddagger} were corrected by a factor σ_1/σ_2 . Because of the relatively large number of determinations only a small if any correction is to be expected (see Tables 2 and 3).

	N	σ1	σ2	σ_1/σ_2
A	38	0-0181	0-0244	0-742
В	39	0-0201	0-0174	1.155
С	38	0-0197	0-0303	0-650
D	40	0-0197	0-0195	1-010

TABLE 3. ESTIMATED STANDARD DEVIATIONS OF $\log (k/T)$ and factors for the correction of standard deviations of energy parameters

N = number of individual rate constants used for calculations.

 σ_1 = estimated standard deviation calculated directly from the scatter of individual log (k/T).

 σ_2 = estimated standard deviation calculated from best fit by the method of least squares.

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	Probability	0-19	0- 5 0	0-0027	0.11	0-054	0-0030
∇S [‡]	Dev./st. dev.	1-32	1-05	3-00	1-58	1-88	2-97
	St. dev.	1-22	0-78	1·22	0-78	1-09	96-0
	Dev.	1-1-1	0.82	3-66	1:23	205	2.84
	Probability	0-0069	0-75	0-0006	0-12	0.12	0-00028
tHt	Dev./st. dev.	2-74	0-32	4-5	1-55	1-55	3-64
	St. dev.	0.54	0-63	0-55	0-62	0-49	0-67
	Dev.	1-48	0-20	2:44	0-96	0.76	2-43
		A = D	$\mathbf{B} = \mathbf{C}$	A = B	$\mathbf{C} = \mathbf{D}$	$\mathbf{B} = \mathbf{D}$	$\mathbf{A} = \mathbf{C}$
		cis isomers	trans isomers	"ortho" isomers	"meta" isomers		

The activation parameters with their estimated standard deviations are also shown in Fig. 3.



FIG. 3 Activation parameters with estimated standard deviations, indicated with lines, for the formation of four isomeric Diels-Alder adducts of styrene and methyl sorbate in toluene solution.

The statistical significance of the difference of the activation parameters is expressed as the probability of the two values being identical. The ratio of the deviation to the standard deviation of the difference is calculated from the data of Table 2 with Eq (3).

$$\left| \text{dev/st dev.} \right|_{\mathbf{A},\mathbf{B}} = \left| \mathbf{A} - \mathbf{B} \right| / (\sigma_{\mathbf{A}}^{2} + \sigma_{\mathbf{B}}^{2})^{\frac{1}{2}} \dots$$
(3)

From this ratio the probability of occurrence can be found, which are given in Table 4.

DISCUSSION

In more-center reactions, as for instance the Diels-Alder reactions, the activation entropy has a large negative value. This reflects the loss of rotational and translational degrees of freedom in the transition state.¹

The differences in activation entropy for the four isomeric adducts A, B, C and D (Fig. 1) will mostly arise from differences in restriction of rotation in the transition states. It is understandable that the entropy of activation for adduct A (carbomethoxy and phenyl group next and *cis* to each other) has the largest negative value. Because a Me group is smaller than a carbomethoxy group rotation will be somewhat less restricted in the transition states leading to adduct D (Me and Ph groups next and *cis* to each other). In the transition states leading to adducts B and C (Ph group *trans* to carbomethoxy and Me group) rotation is still less restricted.

In spite of the unfavourable entropy of activation A is still the main product of the reaction in our temperature range because of the low enthalpy of activation. The enthalpy gain may arise from the interaction of the π -orbitals of the Ph and the carbomethoxy groups. This is in agreement with the so-called "rule of maximum accumulation of unsaturation"⁶ for the Diels-Alder reaction.

In the transition state leading to D (also a *cis*-isomer) less interaction between the Ph and the carbomethoxy group is possible because of their larger distance. The activation enthalpy of D thus is larger than that of A. In the transition states leading

to B and C (*trans*-isomers) conditions for interaction between Ph and carbomethoxy group are still more unfavourable. This results in a larger activation enthalpy for both B and C than for D. The difference between the activation enthalpies of B and C is much less than one standard deviation and is therefore not significant (Fig. 3, Table 4). The statistical analysis of the data shows that the difference between the rates of formation of B and C is probably determined by the difference between the activation entropies.

Diels-Alder reactions are often considered to be very selective or even specific.⁷ In the reaction under investigation, however, all four possible adducts are formed and the main product does never account for more than 50% of the total reaction mixture in our temperature range.

Small differences in activation entropy and enthalpy determine the relative rates of formation of the four adducts. It is conceivable therefore that small differences in bulk or electronic properties of the substituents in diene and/or dienophile may alter the relative amounts of the adducts.

EXPERIMENTAL

The reaction was carried out in a thermostated, stirred stainless steel* 100 ml autoclave under a N_2 press of 10 kg/cm² at 140, 150, 170, 180, 190 and 200°. The autoclave was constructed in such a way that samples could be taken during the reaction. The reaction was carried out using toluene (PA) as a solvent; the initial concentrations of both reactants amounted to 15 wt %. Commercially available pure styrene was distilled under reduced press (b.p. 38.40/18 mm) with addition of some sulphur.

Methyl sorbate (trans,trans-2,4-hexadienoic methyl ester) was prepared from commercially available sorbic acid by the diazomethane method and distilled under reduced press (b.p. 64-5-66-5/17 mm). Analysis was done by GLC.

GLC analysis. The reaction product from styrene and methyl sorbate contains in addition to four adducts a number of dimers of methyl sorbate. On column I (see below) the adducts and dimers could be analyzed conveniently. A complication is the isomerization of methyl sorbate (*trans, trans*) to its *cis, trans* and *trans, cis* isomers which occurs during the reaction (at 200° even the *cis, cis* isomer appears). All samples were therefore analyzed on column II (see below) in order to determine the actual percentage of the *trans, trans* isomer.

Gaschromatographic conditions. Chromatograph: F & M, model 810–15; Detector: Hydrogen Flame ionization; Recorder: Honeywell, -0.05 mV, +100 to 1; 1 second; equipped with a Disc integrator; Carrier gas: He at 100 ml/min. measured at exit at atmospheric pressure.

Column 1. 8·20 m × 0·435 cm i.d. coiled stainless steel tube filled with Apiezon L and Diethyleneglycol succinate (DEGS) coated on Anakrom AS (50/60 Mesh) (0·10:0·16:99·74); column efficiency was about 3100 theoretical plates; temp cycle: post-injection at 8 min 107° (toluene, methyl sorbate, styrene) —linear program 15°/min—hold at limit of 142° (addition products, methylsorbate dimers etc); Analysis time was about 40 min including recycle; Sample size 0·20 µl.

Column 11. 2 m × 0.455 cm i.d. coiled copper tube filled with carbowax 20 M coated on Diatoport P (45/60 Mesh) (5:95); column efficiency was about 1000 theoretical plates; temp 117°. Analysis time was about 10 min, addition products were kept on the column during analysis and flushed out during the night; sample size 1 μ l.

¹ J. Sauer, H. Wiest and A. Mielert, *Chem. Ber.* 97, 3183 (1964); J. Sauer, D. Lang and H. Wiest. *Ibid.* 97, 3208 (1964) and Refs cited here.

² O. Korver, T. L. Kwa and C. Boelhouwer, Tetrahedron 22, 3305 (1966).

• Working in the stainless steel vessel is necessary. Glass vessels cause isomerization of the double bond in the cyclohexene derivatives formed. cf. Ref. 2, p. 3310.

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