The Thermal Intramolecular Rearrangement of Methyl-1,3,5-cycloheptatrienes in the Gas Phase. III. Kinetic Data for the Unimolecular Skeletal Rearrangement into Benzene Derivatives and the Equilibrium between 1,3,5-Cycloheptatriene and Bicyclo[4.1.0]hepta-2,4-diene

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Abstract: Over-all rate constants ($k_{\text{over-all}}$) for the rearrangement of methyl-1,3,5-cycloheptatriene (MCHT) isomers into xylenes, ethylbenzene, and styrene have been measured in the gas phase over the temperature range from 295.5 to 414°. The reaction is truly homogeneous and first order in the pressure range studied. The computed least-squares analysis yields $\log k_{\text{over-all}} = (13.97 \pm 0.08) - (51.66 \pm 0.22)/\Theta$, where Θ equals $4.575 \times 10^{-3}T$ (°K). The rate constants were independent of the isomer ratio of the initial MCHT mixtures owing to the very fast positional isomerization (*via* 1,5 hydrogen transfer) at these temperatures. Neglecting the coupling from the internal hydrogen transfer, rate constants ($k_{x\text{-MCHT}}$) for the conversion of the individual *x*-MCHT isomers have been calculated based on the observed product distribution assuming the formation of methylbicyclo[4.1.0]hepta-2,4-diene (MBHD) intermediates. These rate constants are internally consistent for all four isomers and over the total temperature range studied. The isomerization of methylbicyclohepta-2,4-dienes (k_c) *via* biradical intermediates control the over-all rate of the skeletal rearrangement of MCHT isomers. $k_{x\text{-MCHT}}$ then equals k_cK_{ab}, with $K_{ab} = k_a/k_b = (x\text{-MBHD})/(x\text{-MCHT})$. For the four MCHT isomers the equilibrium constants K_{ab} (for 600°K) are estimated to be between $10^{-4.2}$ and $10^{-5.4}$. The activation parameters for k_c derived from these data are similar to those generally observed for cyclopropane bond rupture. These results demonstrate the presence of small amounts of the bicyclic (norcaradiene) species in equilibrium with the corresponding cycloheptatriene isomer.

Klump and Chessick[1] reported the kinetics of the thermal rearrangement of 1,3,5-cycloheptatriene into toluene. Based on the observed low activation energy (51.1 ± 0.8 kcal/mole), the authors precluded any simple biradical mechanism, and it was suggested that the reaction might proceed *via* a bicyclo[4.1.0]-hepta-2,4-diene (norcaradiene) intermediate.

The question of the existence of bicycloheptadiene isomers in equilibrium with cycloheptatriene has received considerable attention.[2] So far no evidence has been offered that would demonstrate the presence of equilibrium quantities of norcaradiene in cycloheptatriene. Thermodynamic considerations lead to the conclusion[1,3] that the concentrations of the bicyclo[4.1.-0]hepta-2,4-diene would have to be very small. Attempts to identify norcaradiene in cycloheptatriene samples using pmr and other analytical techniques failed.[2a] A careful study of the product distribution and the kinetics of the gas-phase skeletal rearrangement of substituted cycloheptatrienes into benzene derivatives should be capable of demonstrating the presence of the corresponding bicycloheptadiene isomers. The gas-phase kinetics[4] and thermodynamics[5] of the related thermally induced intramolecular positional isomerization of methyl-1,3,5-cycloheptatrienes have been reported previously.

This paper presents the results from the thermal intramolecular rearrangements of these same isomers into benzene derivatives, taking place at measurable rates between 300 and 400°. The equilibrium between the positional isomers of methyl-1,3,5-cycloheptatriene (MCHT) (proceeding *via* 1,5-hydrogen-transfer reactions) is long established at these temperatures before any conversion into benzene derivatives can be observed. The study of the skeletal rearrangement of MCHT isomers then yields, in addition to the kinetic data reported in this paper, equilibrium constants for the positional isomerization. These latter data have been incorporated into a previous publication.[5]

Experimental Section

A. **Apparatus and Procedure.** The apparatus, static method, and general procedures used in this study have been described in detail earlier.[4-6] The reaction temperature was maintained to within 0.2°. An automated Toepler pump served to transfer noncondensable gases (hydrogen) into calibrated volumes and into sampling bulbs for analyses.

B. **Materials. 7-Methyl-1,3,5-cycloheptatriene** (7-MCHT) was prepared as previously described[5,7] and was 99.9% pure as determined by gas chromatography (bp 51° (47.5 torr), $n^{24.8}\text{D}$ 1.5020). A mixture of the 1-, 2-, and 3-methyl-1,3,5-cycloheptatriene (subsequently denoted mixture I) was obtained by allowing toluene to react with diazomethane in the presence of CuBr.[5,8] Mixtures with

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(1) K. N. Klump and J. P. Chessick, *J. Am. Chem. Soc.*, **85**, 130 (1963).

(2) (a) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, 77, 4941 (1955); 78, 180 (1956); (b) G. Maier, *Chem. Ber.*, **98**, 2438, 2446 (1965); (c) J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, 43, 2196 (1960); (d) J. Gripenberg, *Acta Chem. Scand.*, 10, (1956); (e) F. R. Jensen, and L. A. Smith, *J. Am. Chem. Soc.*, **86**, 956 (1964); (f) E. Ciganek, *ibid.*, **87**, 1149 (1965); (g) E. Ciganek, *ibid.*, **89**, 1454, 1458 (1967).

(3) (a) D. M. Golden, H. E. O'Neal, and S. W. Benson, *J. Phys. Chem.*, in press; (b) compare Table IV.

(4) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 3688 (1967).

(5) K. W. Egger, *ibid.*, **90**, 1 (1968).

(6) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964); (b) K. W. Egger, *ibid.*, **89**, 504 (1967).

(7) (a) H. J. Dauben, Jr., L. R. Honnen, and K. H. Harman, *J. Org. Chem.*, **25**, 1442 (1960); (b) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

(8) (a) E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Letters*, 1501 (1963); (b) E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, *Ann.*, 63 (1964); (c) E. Müller and H. Fricke, *ibid.*, 38 (1963).

largely different isomer ratios have been obtained by heating evacuated, liquid samples of 7-MCHT or mixture I in sealed ampoules. The products were distilled and analyzed. The compositions of these initial isomer mixtures have been reported previously,[5] and the same notation has been used in this study.

C. Analyses. Analysis of the product mixtures was carried out by gas–liquid partition chromatography (glpc) with a Model 810 F & M gas chromatograph, equipped with thermal conductivity detectors. Complete separation of all cyclic C_8H_{10} isomers, styrene, and toluene could not be achieved using a single column material. Satisfactory data were obtained by combining the results from two independent analyses using different coatings on Chromosorb P (60–80 mesh).

A first column (20 ft × 0.25 in.) contained a coating of 18% (by weight) 3-methyl-3-nitropimellonitrile[9] (MNPN) and 1.66% $AgNO_3$ dissolved in 1.8% tetraethyleneglycol. It separated all the MCHT isomers, styrene, and *o*-xylene quantitatively. *m*- and *p*-xylenes however, were obscured by 1-MCHT and ethylbenzene eluted together with the 3-MCHT. The following relative retention times (toluene = 47 min = 1.000) have been measured at 78° and a helium flow of 140 ml/min: 7-MCHT, 1.12; 2-MCHT, 1.33; ethylbenzene, 1.44; 3-MCHT, 1.53; 1-MCHT, 1.73; *m*- and *p*-xylene, 1.81; *o*-xylene, 2.48; styrene, 3.46.

A second column (30 ft × 0.25 in.) which contained Chromosorb P coated with Bentone 34 (10%) and silicone gum rubber GE SE-52 (10%) was operated at 78° with a helium flow of 140 ml/min. It separated the 7-, 2-, and 3-MCHT and styrene quantitatively. The relative amount of *p*-xylene was obtained after correcting for the small overlap with the ethylbenzene peak. Ethylbenzene was obscured by 1-MCHT, and *o*- and *m*-xylenes were not suitably separated for quantitative purposes. The following relative retention times (toluene = 66.1 min = 1.000) have been observed: 7-MCHT, 1.16; 2-MCHT, 1.49; 3-MCHT, 1.69; 1-MCHT, 1.85; ethylbenzene, 1.89; *p*-xylene, 2.06; *o*-xylene, 2.53; *m*-xylene, 2.60; styrene, 4.66.

Chromatograms were obtained, using an automated attenuating and recording system. By reinjecting collected eluates, the reaction products have been shown to be stable during the gas chromatographic analysis with the exception of styrene, which is partly polymerized in the detector cell.

The reproducibility of the glpc analyses depends primarily on the relative concentration of a given component in the product mixture. For the majority of the product mixtures, two or three independent analyses have been carried out. Based on the complete set of experimental data, the following standard deviations (in ± per cent of the average value) have been calculated: 7-MCHT, 1.7; 2-MCHT, 0.5; 3-MCHT, 1.0; ethylbenzene, 2.5; 1-MCHT, 0.4; *p*-xylene, 1.2; *m*-xylene, 1.4; *o*-xylene, 1.4; and styrene, 4.7. Even for over-all conversions as low as 5%, the analyses were always reproducible to within ±4% (standard deviation). The only exception was styrene, which showed in 3 out of 35 experiments deviations exceeding 10%. This is still a very satisfactory result, considering that styrene concentrations as low as 0.5% (of the total of the reaction products) have been measured.

The sensitivity of the TC detector has been checked with standard mixtures of the individual products. The following response factors were obtained: *p*-xylene, 0.982; 1-, 2-, and 3-MCHT, 0.986; ethylbenzene, 0.988; 7-MCHT, 1.000; *o*-xylene, 1.005; and styrene, 1.012.

The collected styrene eluate from the glpc analysis has been identified by ir and pmr. The assignment of the proper structure to the individual MCHT isomers has been reported earlier.[5,10] The xylene isomers have been identified by comparing the pmr spectra and glpc retention times with those of pure samples of the isomers.

The *over-all mass balance* for the reaction system has been checked for several of the experiments. The amount of products recovered agreed within a few per cent with that of the initial hydrocarbon mixture.

In three experiments, with purposely high conversions, the amount of hydrogen produced was measured volumetrically and agreed within 10% with the molar concentration of styrene observed in the product mixture. In addition the measured small pressure increases during the reaction are in line with the quantities of styrene and hydrogen produced.

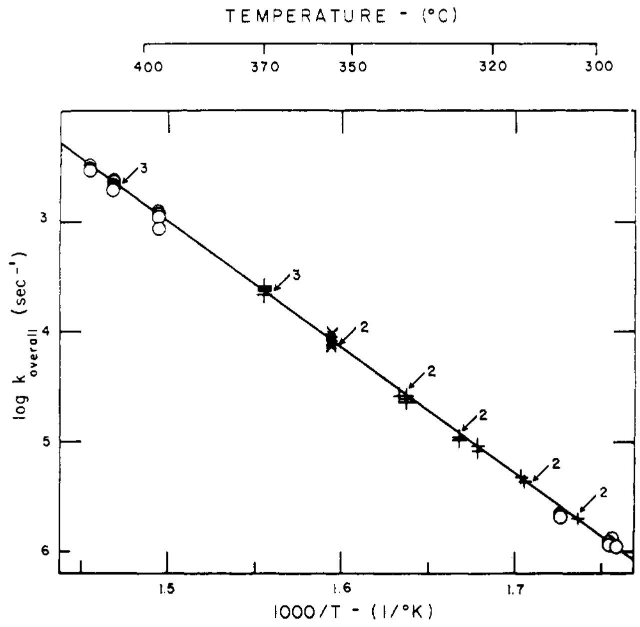

Figure 1. Arrhenius plot of the over-all rate constant for the conversion of methyl-1,3,5-cycloheptatriene isomers into benzene derivatives. The reaction vessels used are indicated by × (non-packed Pyrex), + (packed Pyrex), or ○ (quartz). Numbers represent coinciding points.

Results

The results of 50 kinetic experiments carried out in the temperature range between 295.5 and 414.0° are summarized in Table I. The reaction products consisted of ethylbenzene, xylenes, and styrene. Small amounts of toluene and of lower boiling hydrocarbons (C_6 and lower) were also found. The formation of toluene and benzene did not appear to be a function of any of the known reaction parameters.

The over-all rearrangement reaction of MCHT isomers into benzene derivatives follows first-order kinetics and apparently proceeds *via* an intramolecular skeletal rearrangement reaction. The over-all rate constant can be expressed as[11]

$$k_{\text{over-all}} = -\frac{2.303}{t}\log\left[\frac{(\text{MCHT})_f}{(\text{MCHT})_f + (\text{products})}\right]$$

The observed product distributions (glpc) are listed in Table I, and Figure 1 shows a plot of log $k_{\text{over-all}}$ *vs.* $1/T$ (°K). The results from the computed least-squares analyses are shown in Table II. It is seen that the first-order kinetics are obeyed despite a large variation in experimental conditions. These include (a) conversions ranging from 4 to 70%, (b) up to a 17-fold variation in pressure at any given temperature, and (c) drastic changes in the composition of the starting material.

It has previously been shown that the positional isomerization of the methyl-1,3,5-cycloheptatriene isomers (*via* 1,5-hydrogen-transfer reactions) is very fast at the temperatures used in this study. For all practical purposes the starting materials can therefore be considered to consist of thermally equilibrated mixtures of the MCHT isomers, regardless of the actual composition of the initial isomer mixture. The isomer ratios

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[9] (a) H. J. S. Winkler, private communication, Nov 1966; (b) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, 82, 1749 (1960).

[10] K. W. Egger and W. R. Moser, *J. Phys. Chem.*, 71, 3699 (1967).

[11] $(\text{MCHT})_f$ represents the final and $(\text{MCHT})_0$ the initial concentrations of the (MCHT) isomers.

Table I. Kinetic Data for the Intramolecular Rearrangement of Methylcycloheptatrienes into Benzene Derivatives

Temp,[a] °C	Starting[b] material (MCHT) vessel	Pressure, torr	Time, min	Product distribution (glpc)[c] in % of $(C_9H_{12} + C_9H_{10})_{tot}$										EB/S[c]
				1	2	3	7	EB	O	M	P	S	T[d]	
295.5 q	III	115.5	960	46.0	19.5	24.5	3.6	1.1	2.4	1.6	0.8	0.5	0.0	1.7
296.3 q	IV	26.7	1025	45.5	19.0	24.4	3.1	1.1	2.9	1.8	0.9	1.3	0.6	0.9
296.9 q	IV	88.3	1851	43.2	18.2	23.0	3.4	2.0	4.3	3.2	1.5	2.0	0.6	1.0
297.0 q	IV	68.2	1440	44.4	18.8	23.8	3.5	1.3	3.5	2.6	1.1	1.0	0.2	1.2
302.6	II	109.4	1440	41.7	17.7	22.5	3.1	2.5	6.4	4.1	2.2	1.2	0.2	2.1
	II	49.2	3780	30.8	13.2	16.6	2.3	6.1	14.1	9.0	4.7	3.2	1.0	1.8
306.3 q	IV	50.3	435	46.1	19.7	25.1	3.7	0.6	2.3	1.2	0.8	0.4	0.5	1.3
q	IV	60.7	960	42.6	17.6	23.3	2.8	2.0	5.5	3.0	1.7	1.5	0.0	1.2
313.0	II	89.3	456	43.0	18.7	23.8	3.7	1.7	4.4	3.2	1.6	1.0	0.1	1.7
313.2	II	50.5	1440	33.6	14.3	17.9	2.7	4.3	12.3	8.1	4.1	2.8	0.1	1.5
313.9	II	21.2	963	37.0	16.0	20.3	2.9	3.9	8.9	5.7	3.1	2.2	0.0	1.5
322.6	7	17.8	120	45.1	19.8	24.9	4.4	0.8	2.3	1.4	0.7	0.6	1.2	1.2
	II	123.5	251	41.9	18.3	23.3	3.5	2.0	4.9	3.2	1.8	1.3	0.0	1.4
324.8	II	51.7	180	42.8	18.7	24.1	3.6	1.2	4.3	2.8	1.5	1.0	1.0	1.1
	II	72.4	360	37.3	16.8	21.4	3.2	3.6	7.8	5.2	2.8	1.9	0.0	1.8
	II	115.6	1023	27.5	10.4	12.5	2.1	8.9	18.3	10.2	6.0	4.1	0.6	2.1
337.3	7	160.6	60	41.9	19.6	23.5	5.3	1.5	2.9	2.1	1.2	0.5	0.9	2.6
	7	78.1	105	40.0	18.1	22.8	4.5	2.2	5.5	3.8	1.9	1.3	...	1.6
	I	103.6	257	31.9	14.6	18.1	2.9	5.5	11.4	8.7	4.1	2.9	0.6	1.8
	I	62.7	375	28.9	13.0	15.2	2.3	8.0	15.4	8.6	5.4	3.3	1.2	...
339.0	I	73.0	156	36.2	17.7	21.4	3.0	3.4	8.2	5.5	2.9	1.9	0.0	1.7
354.4 n	I	31.5	26	40.9	19.2	23.7	3.9	1.8	4.3	3.1	1.6	1.6	1.3	1.0
n	I	79.3	50	36.8	17.4	21.7	3.1	3.2	7.8	5.9	2.3	1.7	2.2	1.7
n	I	46.7	63	33.9	15.9	18.5	2.3	5.5	11.3	6.4	3.3	2.9	0.0	1.9
n	7	57.9	106	28.2	12.9	15.9	2.6	6.7	14.9	10.5	4.8	3.5	0.9	1.9
n	I	92.6	143	25.1	11.7	14.5	2.3	7.8	17.4	11.4	6.0	3.8	0.8	2.0
n	I	95.3	237	15.6	7.6	9.2	1.4	11.2	24.3	17.2	8.4	5.2	0.8	2.0
n	I	27.7	273	12.7	6.2	7.7	0.9	10.6	28.7	17.5	9.2	6.4	1.7	1.6
369.1	I	20.4	91	14.5	6.8	8.5	1.3	18.5	21.7	15.7	8.1	4.6	1.1	3.9
369.9	II	63.5	10	41.5	18.4	24.4	1.9	1.9	5.5	3.6	1.8	1.0	0.0	1.6
	II	89.6	15	37.9	17.8	22.4	3.8	3.2	7.1	5.3	2.7	1.2	1.2	2.0
	II	122.9	30	30.7	14.4	18.2	3.1	5.9	12.0	8.8	4.4	2.6	1.1	2.3
	7	54.3	30	29.6	14.1	17.5	4.7	5.6	12.5	8.9	4.5	2.7	0.6	2.0
	II	46.2	45	25.6	11.6	14.6	2.4	7.7	16.8	11.5	6.2	3.7	0.6	2.0
395.9 q	IV	33.3	1.5	42.4	20.6	25.3	4.3	1.1	2.8	1.9	1.0	0.6	0.7	2.0
q	IV	34.0	2.0	39.7	19.5	24.1	4.1	1.9	4.2	3.4	1.8	1.0	0.4	1.9
q	IV	19.8	2.5	38.6	18.8	23.0	3.8	3.0	5.4	4.2	2.1	1.2	0.3	2.3
q	IV	32.4	3.5	36.2	17.6	21.5	3.7	3.8	7.1	5.5	2.8	1.9	0.4	1.9
407.8 q	IV	15.2	1.0	39.8	19.5	23.9	4.2	2.1	4.4	3.5	1.7	0.9	0.0	2.3
q	IV	20.0	1.0	40.3	19.6	24.1	4.3	2.3	4.5	3.2	1.8	0.9	0.0	2.4
q	IV	27.5	1.5	37.6	18.3	22.7	3.9	3.0	6.3	4.5	2.4	1.2	0.9	2.2
q	IV	8.1	2.0	35.4	17.3	21.0	3.8	4.1	7.9	5.7	3.1	1.7	0.8	2.3
q	IV	13.7	3.0	31.7	15.8	19.0	3.1	5.3	10.8	7.9	4.0	2.5	0.7	2.1
q	III	129.5	5.0	23.2	11.6	15.0	3.3	8.0	16.4	12.5	6.4	3.6	1.0	2.2
q	I	138.6	7.0	19.8	10.4	12.3	2.1	9.8	19.5	14.4	7.7	4.0	0.8	2.3
414.0	IV	23.0	0.83	38.8	18.9	23.2	4.1	2.6	5.5	3.8	1.9	1.2	0.1	2.1
	IV	37.0	1.0	37.2	18.0	23.0	4.4	2.6	6.3	4.7	2.4	1.3	0.2	1.8
	IV	18.0	2.0	32.0	15.6	19.3	3.5	5.1	10.8	7.4	4.0	2.4	0.2	2.0
	IV	62.0	3.0	26.8	12.9	16.2	2.8	7.1	14.8	10.9	5.6	2.9	0.4	2.4

[a] q stands for quartz vessel, n for nonpacked, and no marks for the packed Pyrex glass vessel. [b] 7 stands for 7-MCHT; I, II, III, and IV denote the corresponding isomer mixtures. For the composition of the mixtures compare the Experimental Section B. [c] glpc stands for gas–liquid partition chromatography; 1, 2, 3, and 7 for the corresponding MCHT[b] isomers. The benzene derivatives are marked as shown in parentheses: toluene (T), ethylbenzene (EB), *o*-xylene (O), *m*-xylene (M), *p*-xylene (P), styrene (S). [d] Corrected for the amount of toluene present in the starting material.

observed in the product mixtures served to calculate equilibrium constants for the positional isomerization. These data have been incorporated into a previous communication.[5]

Within the experimental error the same rate constants have been obtained when the reactions were carried out in a packed (13-fold larger surface to volume ratio) or a quartz reaction cell. The following attempt to derive individual rate constants (k_{MCHT}) for the conversions of the four MCHT isomers is based on the assumption that methylbicyclo[4.1.0]hepta-2,4-dienes are formed as intermediates. This assumption was prompted by the

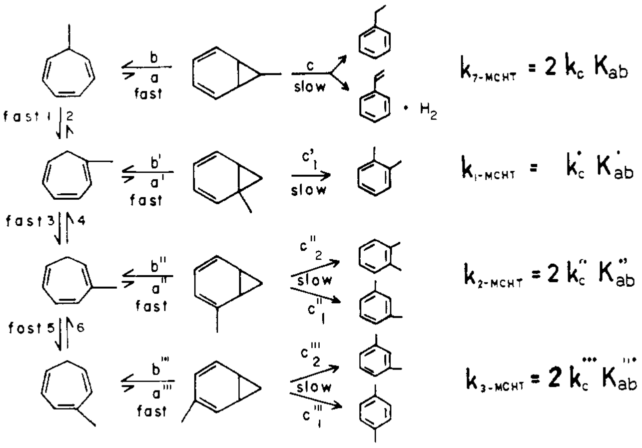
Table II. Arrhenius Parameters Computed from Least-Squares Fits of the Observed Rate Constants

Rate constant	MC[a]	E_a[b]	Log A[b]
$k_{1\text{-MCHT}}$	0.9989	51.8 ± 0.3	13.9 ± 0.1
$k_{2\text{-MCHT}}$	0.9953	51.9 ± 0.5	14.1 ± 0.2
$k_{3\text{-MCHT}}$	0.9989	51.9 ± 0.2	14.1 ± 0.1
$k_{7\text{-MCHT}}$	0.9930	49.8 ± 0.7	13.7 ± 0.3
$k_{\text{over-all}}$	0.9992	51.7 ± 0.2	14.0 ± 0.1

[a] MC stands for multiple correlation coefficient, which would equal 1.0000 in case of an ideal fit. [b] Deviations are listed as standard errors.

following observations. (a) An open biradical mechanism is excluded on the basis of the observed activation energies.[1,12] (b) The observed product distributions (Table I) are consistent with the reaction scheme (Scheme I) involving norcaradiene-type intermediates. In this scheme, the simultaneous unimolecular skeletal rearrangements of the individual MCHT isomers into benzene derivatives are coupled with the fast intramolecular 1,5 hydrogen transfer. The mathematical solutions for the individual rate constants $k_{x\text{-MCHT}}$ are complicated. If, however, all of the isomers are depleted at approximately equal rates, as would be expected, the system could then be treated as a set of four independent unimolecular rearrangement reactions, with $k_{x\text{-MCHT}} = k_c K_{ab}$. The rate-controlling rearrangement (c) of the bicycloheptadiene intermediates can be expected to be of the same order of magnitude for all four isomers, with $k_{c_1}'' = k_{c_2}''$ and $k_{c_1}''' = k_{c_2}'''$.[13] The equilibrium constants K_{ab} are also expected to be similar,[3] with $K_{ab}'' = K_{ab}'''$.

Scheme I



It is then justified (at least for low conversions) to neglect in a first approximation the coupling of the individual rate constants, k_{MCHT}, due to the positional isomerization of the MCHT isomers. Based on Scheme I and the above approximation, values for k_{MCHT} can be calculated from the observed product distributions. The validity of this simplified reaction scheme is checked for each of the isomers by observing the required stoichiometric relationship $(\text{MCHT})_0 = (\text{MCHT})_f +$ products.[11] Any deviation from this relationship reflects differences in the values of k_{MCHT} for the individual isomers. The measured average standard deviations from the demanded stoichiometry are summarized for conversion intervals of 15%, in Table III. The deviations were independent of the reaction temperatures used. It is seen that the stoichiometric relationship is well obeyed for 2- and 3-MCHT, but in the case of 1-MCHT this holds for low conversions only. In contrast, 7-MCHT depletes about three times faster than the other isomers at the net expense of 1-MCHT.

Table III. Average Deviation from the Stoichiometric Relationship $(\text{MCHT})_0 = (\text{MCHT})_f + \text{Pr}_{\text{tot}}$[a]

Conversion[b]	Average deviation in % of $(\text{MCHT})_0$[c] (7-MCHT)	(3-MCHT)	(2-MCHT)	(1-MCHT)
0–15	+35 ± 10	0 ± 2	0 ± 1	− 5 ± 1
15–30	+45 ± 10	0 ± 2	+1 ± 1	−10 ± 5
30–45	+70 ± 10	−1 ± 2	+2 ± 1	−15 ± 5
45–60	+100 ± 10	−1 ± 3	+3 ± 2	−20 ± 5
>60	>+140	−3 ± 3	+5 ± 3	<−43

[a] Subscripts 0 and f denote initial and final concentrations, respectively. Pr_{tot} stands for the total of the reaction products from a given isomer (compare text). All available experimental data have been considered. [b] Refers to the conversions reached for the inindividual isomers. [c] Calculated from $100\,[(x\text{-MCHT})_f + (\text{Pr}_{\text{tot}}{}^{+}) - 1]/[(x\text{-MCHT})_0]$.

The relative deviations from the demanded stoichiometric relationship are much lower for the 1-MCHT than for the 7 isomer because of the large amounts of 1-MCHT (43–49%) initially present as compared to 7-methyl-1,3,5-cycloheptatriene (4–4.5%). These data demonstrate, that the simplified kinetic treatment of the over-all reaction system should yield reliable data for $k_{1\text{-MCHT}}$, $k_{2\text{-MCHT}}$, and $k_{3\text{-MCHT}}$. Larger error limits have to be expected for $k_{7\text{-MCHT}}$.

The rate expressions used to calculate the individual rate constants (neglecting the back-reactions) are given below.[14]

$$k_{2\text{-MCHT}} = -\frac{2.303}{t}\log\left[\frac{(2\text{-MCHT})_f}{(2\text{-MCHT})_f + 2(\text{M}) - 2(\text{P})}\right]$$

$$k_{3\text{-MCHT}} = -\frac{2.303}{t}\log\left[\frac{(3\text{-MCHT})}{(3\text{-MCHT})_f + 2(\text{P})}\right]$$

$$k_{1\text{-MCHT}} = -\frac{2.303}{t}\log \times$$

$$\left[\frac{2(1\text{-MCHT})_f}{(1\text{-MCHT})_f + (1\text{-MCHT})_0 + (\text{O}) + (\text{P}) - (\text{M})}\right]$$

$$k_{7\text{-MCHT}} = -\frac{2.303}{t}\log \times$$

$$\left[\frac{2(7\text{-MCHT})_f}{(7\text{-MCHT})_f + (7\text{-MCHT})_0 + (\text{EB}) + (\text{S})}\right]$$

The calculations of $k_{7\text{-MCHT}}$ and $k_{1\text{-MCHT}}$ take the deviations from the demanded stoichiometric relationship into account. Instead of using the initial concen-

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(12) Such a mechanism would imply a resonance stabilization energy of ~36 kcal/mole in the open-chain biradical intermediate. This is an unreasonably high value considering the stabilization energies of 12.6 [K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964)] and 15.4 kcal/mole [K. W. Egger and S. W. Benson, *ibid.*, **88**, 241 (1966)] in the methallyl and pentadienyl radicals, respectively. Studies on the magnitude of the resonance energy in a linear triallylic radical (which are in progress in our laboratories) further substantiate this conclusion.

(13) S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, **16**, 397 (1965).

(14) *m*-, *p*-, and *o*-xylenes are represented by M, P, and O, respectively; ethylbenzene and styrene with EB and S.

Table IV. Kinetic Data for the Conversion of MCHT Isomers into Benzene Derivatives

	$k_{x\text{-MCHT}}$		$K_{ab}(300°K)^d$		k_c		
Reaction[a]	E_{obsd}, kcal	Log A_{obsd}, sec^{-1}	ΔH_{ab},[e] kcal	ΔS_{ab},[e,f] eu	E_c, kcal	E_{cor},[g] kcal	Log A_c, sec^{-1}
1-MCHT → *o*-xylene	51.8	13.9	11.9	−4.9	39.9	62.9	15.0
2-MCHT → *o*- + *m*-xylene	51.9	14.1	10.2	−2.2	41.7	64.7	14.3[i]
3-MCHT → *m*- + *p*-xylene	51.9	14.1	10.6	−2.5	41.3	64.3	14.4[i]
7-MCHT → EB + S	49.8	13.7	10.4	−2.5	39.4	62.4	14.0[i]
Bicyclo[3.1.0]hexane							
→ cyclohexene[b]	57.4	13.3			57.4	63.6	13.3
→ methylcylopentene[b]	61.2	13.9			61.2	67.4[h]	13.9
CHT − toluene[c]	51.1	13.6	10.5	−2.5	40.6	63.6	13.9[i]

[a] CHT stands for 1,3,5-cycloheptatriene, MBHD for methylbicyclo[4.1.0]hepta-2,4-diene, EB for ethylbenzene, and S for styrene. [b] Reference 15a. [c] Reference 1. [d] The differences in heat capacities between the MCHT and MBHD isomer pairs are very small and $K_{ab}(630°K) \approx K_{ab}(300°K)$. [e] Based on the concept of additivity of increment properties using the data given in ref 3a. The ring correction for the MBHD isomers is taken as the sum of the ring corrections for cyclopropane and 1,3-cyclohexadiene. The over-all uncertainties in those data are estimated at ±1 kcal and ±2 cal/mole, respectively. [f] The entropy correction for the 1,3-cyclohexadiene ring is estimated at 26.0 ± 1 eu. [g] Corrected for 23 kcal of resonance energy in biradical intermediate: S. W. Benson and R. Shaw, *Trans Faraday Soc.*, **63**, 991 (1967). [h] Corrected for strain energy in cyclopentane. [i] The path degeneracy has been taken into account.

trations of these isomers, corrected "average initial" concentrations (defined below) have been used.

$$\overline{(\mathrm{MCHT})_0} = \tfrac{1}{2}[(\mathrm{MCHT})_0 + (\mathrm{MCHT})_f + \text{products}]$$

The depletion of 1-MCHT to form eventually 7-MCHT (*via* the 1,5 hydrogen transfer) never exceeded 30% of the total conversion of the 1 isomer.

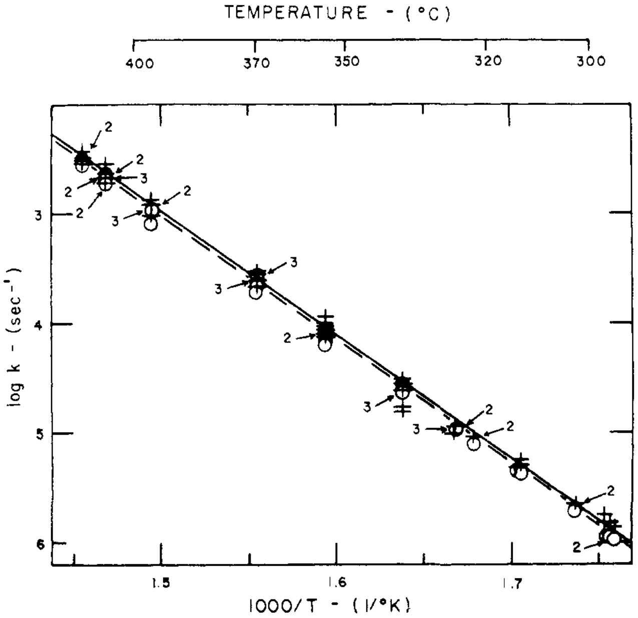

Figure 2. Arrhenius plots of the rate constants for the conversion of 2-MCHT (+, ———) into *m*- and *o*-xylenes, and of 3-MCHT (O, - - - -) into *m*- and *p*-xylenes. Numbers indicate overlapping points.

Figures 2 and 3 show the Arrhenius plots of the rate constants $k_{x\text{-MCHT}}$. It is seen that the first-order kinetics are obeyed for all four individual rate constants, and the data for $k_{2\text{-MCHT}}$ and $k_{3\text{-MCHT}}$ practically coincide. The computed least-squares analyses of these same data are summarized in Table IV together with the multiple correlation coefficients, which would equal 1.000 in case of an ideal fit.

Discussion

The skeletal intramolecular rearrangement of the MCHT isomers into xylenes, ethylbenzene, and styrene is a truly homogeneous and unimolecular process in the pressure range studied. The activation parameters observed for the over-all conversion are in perfect agreement with literature data for the similar gas-phase isomerization of 1,3,5-cycloheptatriene.[1]

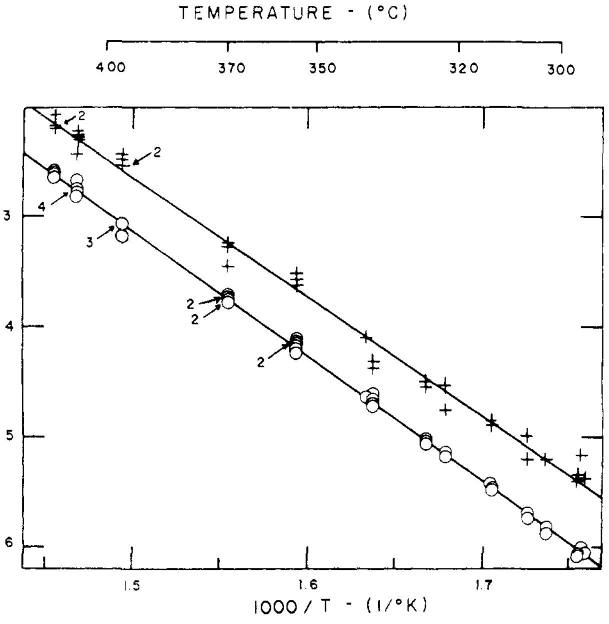

Figure 3. Arrhenius plots of the rate constants for the conversion of 1-MCHT (O) into *o*-xylene, and of 7-MCHT (+) into ethylbenzene + styrene. Numbers indicate overlapping points.

The product distribution and the measured activation energy are consistent with a mechanism involving methylbicyclo[4.1.0]hepta-2,4-diene (MBHD) intermediates (Scheme I). The validity of the proposed reaction scheme is demonstrated with similar activation parameters calculated for the conversions of the individual MCHT isomers, despite large variations in pressure and composition of the initial isomer mixture and with conversions ranging between 5 and 70% for each of the four methylcycloheptatriene isomers involved. The consistency of the calculated rate constants $k_{\mathrm{MCHT}} = k_c K_{ab}$ and the general accord of the observed stoichiometry with the demanded relationship, $\overline{(\mathrm{MCHT})_0} = (\mathrm{MCHT})_f +$ products, justify the use of the approximated simplified kinetic treatment of the detailed reaction mechanism (Scheme I, assuming independent rearrangements of the individual isomers).

The larger uncertainties in the data for $k_{7\text{-MCHT}}$ (calculated for conversions up to 60%) are reflected in a significantly larger scatter. Nevertheless, consistent rate constants are obtained, despite the very large variations in experimental conditions (compare Table I). The amount of styrene formed is clearly a function of the over-all conversion reached in the system, and styrene appears to be indeed a primary reaction product of 7-methyl-1,3,5-cycloheptadiene. Both ethylbenzene and styrene were found to be stable under the reaction conditions used. As would be expected from Scheme I, the ratio of ethylbenzene to styrene (EB/S) is within experimental error limits constant for a given reaction temperature and appears to increase with increasing temperatures. The size of the error limits for the relatively small amounts of products preclude, however, conclusive comments on the temperature dependence of the observed EB/S ratios.

Either of two external cyclopropane bonds in the bicyclic isomers can be broken yielding biradical intermediates. Only in the case of the 7-MCHT are these intermediates the same. In the case of the 1-methylbicyclo[4.1.0]hepta-2,4-diene (derived from 1-MCHT), one of the biradical intermediates would have to split off methylene in order to form a stable product (toluene). From the data listed in Table I it can be concluded that toluene is not a primary reaction product of 1-MCHT, and the observed rate constant $k_{1\text{-MCHT}}$ then equals $k_c'K_{ab}'$.

The path degeneracy introduces a factor of 2 into the rate constants for the other three isomers (compare Scheme I), and, consequently, $k_{2\text{-MCHT}} = 2k_c''K_{ab}''$; $k_{3\text{-MCHT}} = 2k_c'''K_{ab}'''$ and $k_{7\text{-MCHT}} = 2k_cK_{ab}$. The Arrhenius parameters for the $k_{x\text{-MCHT}}$ data (listed in Table II) can be checked by comparing the activation energies and preexponential factors for k_c with those generally observed for the pyrolysis of cyclopropane derivatives.[13]

In order to obtain data for k_c, the equilibrium constants (K_{ab}) between the methylcycloheptatriene and bicycloheptadiene isomers have been estimated. These data are summarized in Table IV. The calculated kinetic parameters (k_c) for the rearrangement of the methylbicyclo[4.1.0]hepta-2,4-diene isomers are similar to those reported for other bicyclic compounds[15] and for substituted cyclopropanes[13] (Table IV). The observed preexponential factors (A_c) are in good agreement with those for the isomerization of fused and nonfused cyclopropane rings.[13] The calculated activation energies (E_c) (when corrected for the resonance energy generated in the biradical intermediate)[15b] agree with the data of Frey and Smith[15a] for the similar rearrangement of bicyclo[3.1.0]hexane. Within experimental error limits they also fall in the range of 62 to 65 kcal/mole, generally observed for structural isomerization of cyclopropane derivatives.[13] This agreement again substantiates the validity of the proposed detailed reaction mechanism, outlined in Scheme I.

The interconversion of the MBHD and MCHT isomers is assumed to proceed *via* a cyclic (electron delocalized), six-center transition state similar to the one proposed for the 1,5 hydrogen transfer in bicyclo[*x*.1.0]-2-ene ("homodiene") systems.[16] In analogy to these systems, k_b is estimated to $10^{13}10^{-(34\pm5)/\theta}$. This value is in line with the observed activation energies (~44 kcal) for the thermal rearrangements of comparable bicyclic compounds[17] which would involve a four-center transition state.[18] The value calculated for k_b, when compared with an estimate[13,19] of $10^{15}10^{-41/\theta}$ for k_c and with the estimated equilibrium constants $K_{ab} = k_a/k_b$ (compare Table IV) shows that the isomerization of the bicyclo[4.1.0]hepta-2,4-dienes into benzene derivatives (proceeding *via* 1,3 biradicals) is indeed the rate-controlling process.

Both ethylbenzene and styrene appear to be primary reaction products of 7-MCHT. The unexpected, apparently homogeneous formation of styrene, might involve an intramolecular hydrogen transfer to the cyclohexadienyl radical site in the biradical intermediate, prior to a molecular elimination of hydrogen.

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(16) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 999 (1966).

(17) (a) G. R. Branton, H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, **62**, 659 (1966); (b) G. R. Branton, H. M. Frey, and R. F. Skinner, *ibid.*, **62**, 1546 (1966).

(18) An additional double bond was shown to lower the activation energy of the process by about 6 kcal/mole: M. R. Willcott and E. Goerland, *Tetrahedron Letters*, 6341 (1966).

(19) The activation energies observed for structural isomerization of cyclopropane derivatives were shown[13] to fall in the range 62–65 kcal. Correcting for 23-kcal resonance energy [S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 991 (1967)] in the biradical intermediate, this yields $E_c \approx 64-23 = 41$ kcal/mole.