type I splits from either electronically excited state and singlet–triplet intersystem crossing followed by intramolecular energy transfer is much more efficient for the γ,δ-unsaturated ketone XIII than for the β,γ-unsaturated analog III.

Similar conclusions have already been drawn by Yang and co-workers from photochemical results obtained in solution. Specifically, in pentane solution a β,γ-unsaturated ketone with allylic γ hydrogens, $CH_2{=}C(CH_3)CH_2COCH_3$, was found to be decarbonylate with a quantum efficiency of 0.33 and to form a cyclobutanol to an appreciable extent.[32] In the case of 1-hexen-5-one (XIII), only oxetane formation occurred; *cf.* reaction 8. No photodecarbonylation was reported.[33]

The cyclopropane triplet state of approximately 87 kcal/mole[34] appears too high to allow a similar energy transfer mechanism to operate to any significant extent in the corresponding cyclopropyl ketones, cyclopropyl-2-propanone (II), 1-cyclopropyl-3-butanone (IV), and bicyclo[3.1.0]hexan-3-one (XI). Accordingly, exclusive photophysical energy degradation is relatively unimportant. The isomerization of ketone II to 1-hexen-5-one, though quite inefficient ($\Phi = 0.05$), would therefore result from a mechanism other than electronic energy transfer from the keto group. This may be related to the mode of formation of traces of 2-cyclohexenone and 2-methyl-2-cyclopentenone from compound V;[1a] π^* assistance as postulated above for the ring cleavage in methyl cyclopropyl ketone (I) and bicyclo[3.1.0]hexan-2-one (V), reactions 3 and 4, seems unlikely from structural considerations. On the other hand, conversion of the photoexcited ketones to vibrationally excited ground-state molecules could account more reasonably for these low efficiency, random cyclopropane cleavages.

Acknowledgment. The authors wish to thank Dr. P. A. Leermakers and Mr. G. Vesley for synthesis of ketones II and IV and collaborative discussions in the initial phase of this work.[1c] Drs. P. Radlick and J. Vernon synthesized several compounds of interest and Mr. G. Brem gave skillful technical assistance. This research was supported by Grant AP 00109, Division of Air Pollution, Bureau of State Services, Public Health Service. L. D. H. also wishes to acknowledge financial support from a National Defense Graduate Fellowship, 1962–1965.

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The Thermal Intramolecular Rearrangement of 7-Methyl-1,3,5-cycloheptatriene in the Gas Phase. I. The Kinetics of the Unimolecular Positional Isomerization *via* a 1,5 Hydrogen Transfer

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Received February 20, 1967

Abstract: Rate constants (k_1) for the unimolecular thermal isomerization of 7-methyl-1,3,5-cycloheptatriene to 3-methyl-1,3,5-cycloheptatriene have been measured in the gas phase over the temperature range 128.7–226.0°. The reaction is first order in the pressure range studied (13 to 170 torr) and homogeneous, as shown by the insensitivity toward a 13-fold change in the surface-to-volume ratio of the reaction vessels and toward added nitric oxide. The least-squares fit of the measured rate constants to the Arrhenius equation yields (with standard errors) log k_1 (sec^{-1}) $= (12.60 \pm 0.09) - (33.25 \pm 0.19)/2.303RT$. Comparing this value with the transition-state formulation for unimolecular reactions results in -3.6 cal/deg mole for the entropy of activation. These results are in line with corresponding gas-phase kinetic data on linear 1,3-diene systems reported in the literature and they further substantiate the postulated six-center hydrogen-bridged cyclic transition state formed in this type of internal rearrangement reactions.

The internal 1,5-hydrogen-shift reaction has been postulated to account for a number of thermally induced intramolecular isomerization reactions in cyclic and acyclic cisoid 1,3-diene and in vinylcyclopropane systems.[1] Despite the fact that 1,5-hydrogen-transfer reactions have been studied for a number of accessible systems, only very few reliable kinetic parameters are available for reactions in the gas phase. The bulk of the literature data is based on pmr studies of liquid-phase reactions, carried out over narrow temperature ranges only. Arrhenius parameters derived from these data have relatively large error limits attached.

Frey, *et al.*,[2] reported the kinetic parameters for the gas-phase interconversion of the following systems: *cis*-2-methyl-1,3-pentadiene–*cis*-4-methyl-1,3-pentadi-

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(1) For a summary of the available literature data, compare D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 10, 999 (1966).

(2) (a) H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 4770 (1965); (b) R. J. Ellis and H. M. Frey, *ibid.*, *Suppl. I*, 5578 (1964); (c) H. M. Frey and B. M. Pope, *ibid.*, *Sect. A*, 1701 (1966).

ene,[2a] *cis*-1,3-hexadiene–*cis,trans*-2,4-hexadiene,[2b] and 1-methyl-2-allylcyclopropane–1,4-hexadiene.[2c] Grimme[3] studied the gas-phase kinetics of the isomerization in the bicyclo[5.1.0]oct-2-ene–1,4-cyclooctadiene system. In addition some isolated rate constants for gas-phase reactions have been reported in connection with more extensive kinetic studies in the liquid phase.[4] It has been reported that the rate constants are largely independent of the solvents used,[4–6] and only small differences in rates were obtained whether the same reaction was carried out in the liquid or gas phase.[1,4,7]

The kinetic parameters of all these concerted 1,5-hydrogen-transfer reactions are very similar. The characteristically low activation energies of about 30 kcal (precluding any simple biradical mechanism), the observed negative entropies of activation, and the strict conformational (cisoid) requirement[1,2a,b] lead to the assumption of a cyclic transition complex, similar to those proposed for the rearrangements of vinyl allyl ethers.[8] In linear 1,3-diene systems the observed negative entropy of activation of about 10 cal/deg mole[2] can be attributed primarily to a loss of the partially hindered rotation in the linear olefin when going into the stiff cyclic transition state. In cyclic conjugated diolefins considerably less internal motion should be lost in forming the transition complex. The available Arrhenius parameters based on liquid-phase studies in cyclic 1,3-dienyl systems[1,4,5,7] fail to show significant differences in the entropies of activation when compared with those of acyclic reaction systems.

Gas-phase kinetic data on the intramolecular 1,5 hydrogen transfer in cyclic 1,3-diene systems have so far not been reported. This study was undertaken to obtain accurate Arrhenius parameters for the gas-phase 1,5-hydrogen-transfer reaction in a cyclic 1,3-diene system. Substituted cycloheptatrienes lend themselves especially well to the study of this type of reaction since they have a boat conformation in the ground state,[9] holding the hydrogen to be moved in an axial position with respect to the ring. Furthermore in methylcycloheptatriene several consecutive 1,5 transfer reactions can occur,[5,10] thus demonstrating unambiguously the 1,5 mechanism involved. This paper reports the measurements of the kinetics of the thermal positional isomerization of 7-methyl-1,3,5-cycloheptatriene.

Experimental Section

(A) **Apparatus and Procedures.** The static method and reaction system used have been described in detail earlier.[11] The reactions were carried out in the gas phase in two equivalent Pyrex glass vessels of about 1000-ml volume. They had been coated with a Teflon emulsion (in *n*-pentane) prepared from commercially available Teflon spray. The excess coating material was removed by repeated washing with *n*-pentane before the reaction cells were conditioned for several days at 300° both under vacuum ($\sim 10^{-6}$ torr) and in the presence of methylcycloheptatrienes. One of the vessels was packed with glass tubing and had a 13-fold larger surface-to-volume ratio than the equivalent nonpacked reaction cell. The reaction temperature was maintained to within 0.2°.

An experiment was started by expanding 7-methylcycloheptatriene from a reservoir attached to the gas-handling system into the reaction cell. This procedure (including the pressure measurement) was completed within 3 sec. The gases are preheated upon addition to the evacuated reaction vessel. The time required to reach temperature equilibrium can be estimated to be a few seconds. This is demonstrated by the fact that after initial addition of the hydrocarbon gases no pressure changes were measurable. The detection limit was 0.05 torr.

The reaction was stopped by quenching the products in the gas-sampling system over liquid air. Depending on the initial hydrocarbon pressure used, the products condensed within 2 to 5 sec to a residual pressure below 0.1 torr.

(B) **Materials. 7-Methyl-1,3,5-cycloheptatriene** (7-MCHT) was prepared as previously described.[12] 7-Cycloheptatrienylium fluoroborate was prepared from crude cycloheptatriene, supplied by Fluka AG (Buchs, Switzerland). The salt was then allowed to react with sodium methoxide (98%), yielding 7-methoxy-1,3,5-cycloheptatriene. 7-MCHT is obtained by interaction of a methyl Grignard reagent with the 7-methoxy-1,3,5-cycloheptatriene. The main fraction was 99.9% pure as determined by gas chromatography and had bp 51° (47.5 torr), $n^{24.8}{}_{\mathrm{D}}$ 1.5020.

A mixture of the **1-, 2-, and 3-methyl-1,3,5-cycloheptatriene** (1-, 2-, 3-MCHT) was prepared by treating toluene with diazomethane in the presence of CuBr.[13,14] The percentage composition of the main fraction after distillation was: 1-MCHT (30.1), 2-MCHT (28.9), 3-MCHT (39.6), and toluene (1.3). No traces of the 7 isomer could be detected.

Starting with the above product mixture, individual isomers (for pmr analysis) have been obtained by semipreparative-scale gas chromatography.

The nitric oxide used in two experiments has been prepared from KI, KNO_2, and H_2SO_4 and was purified by passing through KOH and over P_2O_5 before fractionated distillation in a closed evacuated gas-handling system.

(C) **Analysis. Gas Chromatography.** Analysis of the product mixture was carried out by gas–liquid chromatography (glpc) with a Model 810 F & M gas chromatograph, equipped with thermal conductivity detectors. Satisfactory results were obtained with a 20-ft column, 0.25 in. in diameter, filled with Chromosorb P (mesh size 60–80) containing an 18% (by weight) coating of 3-methyl-3-nitropimellonitrile (MNPN) and 1.66% of $AgNO_3$ dissolved in 1.8% of tetraethylene glycol.[15] The following relative retention times (after the air peak) (toluene = 1.000) have been measured at 60°: benzene, 0.516; cycloheptatriene, 1.115; 7-MCHT, 1.162; 2-MCHT, 1.40; ethylbenzene, 1.54; 3-MCHT, 1.64; 1-MCHT, 1.89; *p*- and *m*-xylene, 1.95; *o*-xylene, 2.75. Except for a few per cent overlap between 3-MCHT and 1-MCHT all of the isomers were completely resolved.

Chromatograms were obtained using an automated attenuating and recording system. Microswitches attached to a special modification of a Honeywell recorder are actuated when the recorder pen reaches 95 and 5% of the full-scale deflection. The microswitches simultaneously operate an automatic attenuator (Model 50 F & M) and a time relay which shifts the chart speed for a preset time into a 60-fold faster gear. This method results in very accurately measurable deflections of the Disc Chart integrator used in the quantitative analysis of the areas under the peaks, despite fully automated attenuation.

It was reported[16] that certain column materials caused rearrangement of substituted cycloheptatrienes during their gas chromatographic analysis. No isomerization occurred with MNPN as the

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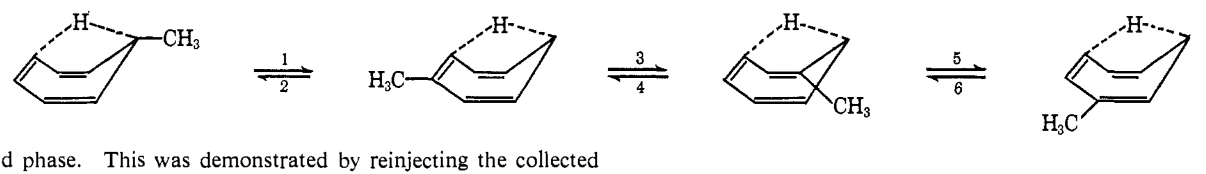
(14) G. Brauer, "Handbuch der Präparativen Organischen Chemie," Vol. II, 1962, p 888.

(15) (a) H. J. S. Winkler, private communication: (b) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1749 (1960).

(16) K. Conrow and L. L. Peasor, *J. Org. Chem.*, **30**, 4368 (1965).

Scheme I



liquid phase. This was demonstrated by reinjecting the collected eluates of several test samples with known isomer ratios.

A 20-ft column of MNPN (1 cm in diameter) was used in the semipreparative scale separation of the isomers which were to be used for identification by pmr analyses. In addition to the analyses carried out using the MNPN column, a series of reaction products was also analyzed on a 6-ft column, 0.25 in. in diameter, packed with Chromosorb W (mesh size 60–80) containing a 10% coating of benzo[7.8]quinoline. This material separates toluene quantitatively from all the methylcycloheptatriene isomers and 7-MCHT from the rest of the isomers. In addition a better separation of ethylbenzene or xylene isomers would be obtained on this column. The following relative retention times (after air) (toluene = 1.000) were measured (65°, helium flow 45 ml/min): 7-MCHT, 1.567; ethylbenzene, 2.116; *p*-xylene, 2.312; 1-, 2-, and 3-MCHT, 2.404; *m*-xylene 2.487; *o*-xylene, 3.093. Ethylbenzene and xylenes were not detectable in the product mixtures.[17] The relative amounts of toluene and 7-MCHT agreed in all the analyses within 5% with the results previously obtained using the MNPN column.

The sensitivity of the TC detector for the various MCHT isomers was checked with standard mixtures of the isomers. The response factor for the 1, 2, and 3 isomers was measured to be 1.000 ± 0.5% (std dev). For 7-MCHT the factor was 1.024 ± 0.5% with respect to the other isomers. Small amounts of toluene and benzene have been identified as side products.

Pmr Spectra. Proton magnetic resonance spectra of the individual MCHT isomers were determined on a high-resolution Varian HA 100 instrument. The spectra unambiguously verified the structural assignment of the gas chromatographic peaks. A separate communication will discuss the interesting spectra of these compounds.[18]

Infrared Spectra. A Grubb–Parson "Spectromaster" infrared spectrophotometer was used to determine the infrared spectra of the individual 1-, 2-, and 3-MCHT isomers. The results are in agreement with those reported by Müller, *et al.*[13b]

Results

The over-all reaction scheme for the intramolecular positional isomerization of methylcycloheptatrienes *via* 1,5 hydrogen transfers is given by Scheme I. Initially 7-MCHT is converted to 3-MCHT.[18] With increasing conversion the concentration of 1-MCHT and finally the 2-MCHT gradually accrued.

The reaction is apparently first order. Starting with 7-MCHT the rate expression can be formulated

$$-\frac{d(\text{7-MCHT})}{dt} = k_1(\text{7-MCHT}) - k_2(\text{3-MCHT}) \quad (1)$$

Since (3-MCHT) = $(\text{7-MCHT})_0$ − (7-MCHT) (where 0 denotes initial concentrations) and the equilibrium constant $K_{1,2} = k_1/k_2$, eq 1 may be rewritten

$$-\frac{d(\text{7-MCHT})}{dt} = k_1(\text{7-MCHT}) \times \left\{1 - 1/K_{1,2}\left[\frac{(\text{7-MCHT})_0}{(\text{7-MCHT})} - 1\right]\right\} \quad (2)$$

Integration of eq 2 yields

$$k_1 = -\frac{2.303}{(K_{1,2}+1)t}\log\left\{\frac{[(\text{7-MCHT})(K_{1,2}+1) - 1]}{[(\text{7-MCHT})_0(K_{1,2}+1) - 1]}\right\} \quad (3)$$

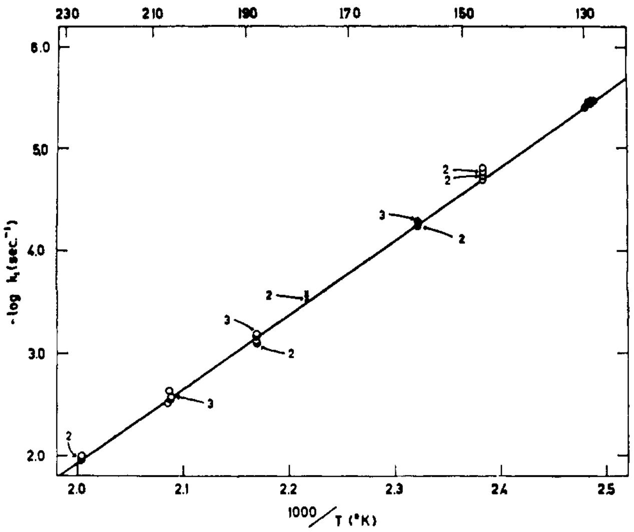


Figure 1. Arrhenius plot of the rate constant for the positional isomerization of 7-methyl-1,3,5-cycloheptatriene *via* a 1,5-hydrogen-transfer reaction: open circles, nonpacked reaction vessel; filled circles, packed reaction vessel; crosses, added NO. Figures represent numbers of overlapping points.

Depending on the conversion reached in any given experiment, variable amounts of 1-MCHT are formed besides the main product 3-MCHT (compare reaction Scheme I). The modified rate expression now reads

$$k_1 = -\frac{2.303}{Xt}\log\left\{\frac{[X(\text{7-MCHT}) - 1]}{[X(\text{MCHT})_{\text{tot}} - 1]}\right\} \quad (4)$$

where $X = (K_{1,2} + 1)$ and $(\text{MCHT})_{\text{tot}}$ = (7-MCHT) + (3-MCHT) + (1-MCHT).[19] Table I summarizes the results from 36 kinetic experiments, carried out in the temperature range 128.7 to 226.0°.

The product distribution and rate constants listed in Table I are average values of two or more independent glpc analyses. The individual rate constants were always reproducible to within ±3% (maximum deviation). While the experiments with extremely short reaction times of around 1 min were expected to have larger uncertainties attached, the rate constants from these measurements do not show any more scatter than the rest of the data. This indicates that the experimental procedures used are adequate even for very short reaction times.

The $K_{1,2}$ data used in the calculation of the rate constants were determined in separate measurements[20] and are listed (in parentheses) in the last column of Table I.

A plot of the logarithm of k_1 *vs.* $1/T$(°K) is shown in Figure 1. The least-squares fit of these data to the Arrhenius equation yields with standard errors

$$\log k_1\,(\text{sec}^{-1}) = (12.60 \pm 0.19) - (33.25 \pm 0.19)/\theta \quad (5)$$

where θ equals $2.303RT$(°K).

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[17] Ethylbenzene and xylenes are the products of the thermal intramolecular rearrangement of methylcycloheptatriene isomers in the temperature range between 300 and 400°. A separate communication will cover these studies.

[18] K. W. Egger and W. R. Moser, *J. Phys. Chem.*, in press.

[19] The very small amounts of the 2 isomer formed have not been taken into account (see Table I).

[20] K. W. Egger, publication forthcoming.

Table I. Kinetic Data for the Intramolecular Isomerization of 7-Methyl-1,3,5-cycloheptatriene *via* a 1,5-Hydrogen Transfer

Temp,[a] °C	Time, min	P_0,[b] torr	Product distribution from Gc analysis in % $(\mathrm{MCHT})_{\mathrm{tot}}$[c,g] 7-MCHT	3-MCHT	1-MCHT	2-MCHT	Tol[c]	Benz[c]	$k_1 \times 10^4$, sec^{-1} [f]
									(9.99)
128.7 (P)	476	94.1	90.5	9.3	0.2		0.3		0.0352
129.2 (P)	451	21.6	90.4	9.2	0.3		0.3		0.0378
129.2 (P)	1025	134.8	80.8	18.6	0.6		0.1		0.0350
129.6 (P)	955	39.3	81.6	17.7	0.6	0.1	0.1		0.0359
130.0 (P)	403	62.7	90.7	9.1	0.3		0.7		0.0407
									(9.12)
146.5	28	54.3	97.2	2.8	0.0		0.2		0.171
146.5	64	32.9	93.0	6.9	0.1				0.190
146.5	101	79.4	90.9	9.0	0.2		0.4		0.159
146.5	154	19.4	82.7	16.9	0.4		0.5	0.3	0.208
146.5	162	12.9	83.0	16.2	0.8		0.1	0.2	0.193
146.5	165	94.5	84.4	15.4	0.3		0.1	0.1	0.173
									(8.71)
157.7 (P)	31	31.8	90.7	9.1	0.1	0.1	0.5		0.529
157.7 (P)	45	168.4	85.5	14.2	0.3		0.6		0.584
157.7 (P)	46	13.6	86.5	13.0	0.4	0.1	0.6		0.529
157.7 (P)	67	28.2	80.5	18.7	0.7	0.1	0.6		0.546
157.7 (P)	82	15.8	75.6	23.2	0.2	0.1	0.7		0.570
									(8.52)
178.0 (P)	33	27.6	56.5	39.5	3.5	0.5	...	...	3.00
178.0[d] (P)	34	27.6	58.9	35.7	4.8	0.6	...	...	2.69
178.0[e] (P)	37	27.6	53.8	42.9	2.4	1.0	...	...	2.92
									(7.77)
187.6	6	28.4	75.4	22.0	2.1	0.4	1.6	1.9	7.98
187.6	13	86.5	55.3	39.9	4.3	0.5	1.2	...	7.96
187.8	1.5	16.7	93.1	6.4	0.6		1.0	0.4	8.03
187.8	3	20.4	88.2	10.5	0.8	0.6	1.5	0.8	7.04
187.8	4	20.4	85.5	13.0	1.0	0.3	1.1	0.2	6.58
187.8	4	88.3	85.3	13.8	0.8	0.4	1.3	1.3	6.69
187.8	3.6	38.3	85.2	13.4	1.1	0.3	0.9	0.5	7.60
									(7.25)
205.3	4.00	52.3	54.7	39.5	5.3	0.6	0.4	0.3	26.5
205.7	1.50	21.6	77.5	21.2	1.1	0.2	0.7	0.3	28.9
205.8	1.00	29.6	84.0	14.7	0.8	0.2	0.1		29.3
205.8	3.00	53.5	62.5	34.2	3.0	0.3	0.2		27.1
206.2	1.25	68.4	84.1	15.3	0.5	0.2	0.3	0.2	23.4
206.5	2.00	52.8	70.2	28.0	1.7	0.2	0.4		30.2
									(6.77)
226.0	0.75	13.0	64.7	31.9	3.1	0.2	2.9	0.3	100
226.0	1.25	23.8	47.4	46.0	6.2	0.4	1.8	0.4	107
226.0	1.88	49.0	33.4	56.5	8.2	1.9	2.9	0.5	112
226.0	2.00	99.9	32.5	54.4	12.0	1.3	1.3	0.3	108

[a] P, packed reaction vessel; no marks, unpacked reaction vessel. [b] Initial pressure of 7-MCHT. [c] Gc stands for gas chromatographic analysis, $(\mathrm{MCHT})_{\mathrm{tot}}$ for the total amount of methylcycloheptatrienes measured. Tol and benz denote toluene and benzene, respectively. [d] 261 torr of NO added. [e] 164 torr of NO added. [f] Values in parentheses give the equilibrium constant[20] $K_{1,2}$ = (3-MCHT)/(7-MCHT) used in the calculation. [g] Where no data are given, less than 0.1% of material is present in the reaction mixture.

The accuracy of the fit is reflected in the computed multiple correlation coefficient of 0.9989. In the case of an ideal fit, this value would equal 1.0000.

The over-all rate expression is confirmed by the consistent rate constants over the total temperature range, this despite up to a 12-fold variation in the pressure of the starting material at any given temperature. Within experimental error limits the same rate constants have been observed when the reactions were carried out in the packed reaction vessel. The addition of large quantities of nitric oxide to the starting material had no measurable effects upon the product distribution.

The over-all mass balance in the reaction system was measured to be within a few per cent.

Pressure changes during the reaction never exceeded 0.5 torr. This parallels the small amounts of toluene and benzene formed (Table I).[21] The foregoing evidence clearly indicates that the principal reaction is homogeneous.

Discussion

The present work establishes that the thermally induced unimolecular positional isomerization observed in the methylcycloheptatriene system proceeds *via* intramolecular 1,5-hydrogen-transfer reactions. The Arrhenius parameters obtained in this work for the isomerization of 7-MCHT are in accordance with both the gas-phase data reported for the intramolecular 1,5-hydrogen-transfer reactions in linear 1,3-diene and vinylcyclopropane systems[2] and the very similar internal rearrangements of vinyl allyl ethers.[8] The kinetic parameters for these gas-phase systems, together with those of liquid-phase data (compare ref 1 and Table II), have been rationalized with a cyclic (most likely a six-center) transition complex. There is an obvious inconsistency in the observed kinetic parameters for the thermal rearrangement of 7-substituted cycloheptatrienes in the liquid phase (compare Table II). While

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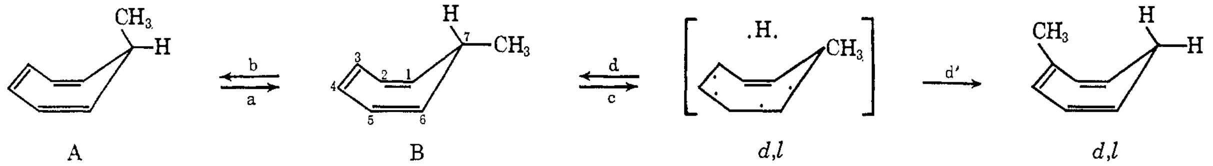
[21] The amount of toluene and benzene formed appears to be independent of the reaction vessel and of the over-all conversion. However, with increasing temperature, the amounts of toluene and benzene seem to increase.

Table II. Kinetic Parameters for Some Intramolecular 1,5-Hydrogen-Transfer Reactions[a]

Reaction	Phase[b]	Temp, °C	Analysis[b]	Arrhenius parameters		$\Delta S^{\ddagger}$,[c,d] cal/deg mole	Ref
				Log A, sec^{-1}	E_a, kcal/mole		
cis-2-Methyl-1,3-pentadiene ⟶ 4-methyl-1,3-pentadiene	Gas	200–237	Glpc	11.2	32.8	−12.4	2a
cis-1-Methyl-2-vinylcyclopropane ⟶ *cis*-1,4-hexadiene	Gas	166–220	Glpc	11.0	31.2	−13.2	2b
cis-1,3-Hexadiene ⟶ *cis,trans*-2,4-hexadiene	Gas	202–245	Glpc	10.8	32.5	−13.4	2c
7-Methyl-1,3,5-cycloheptatriene ⟶ 3-methyl-1,3,5-cycloheptatriene	Gas	129–226	Glpc	12.6	33.3	−4.9	This work
7D-1,3,5-Cycloheptatriene ⟶ 3D-1,3,5-cycloheptatriene	Liq	98–140	Pmr	11.2	31.5	−11.1	10
7-Phenyl-1,3,5-cycloheptatriene ⟶ 3-phenyl-1,3,5-cycloheptatriene	Liq	80–121	Pmr	10.8	27.6	−11.6	5
1,4-Bis(7-cycloheptatrienyl)benzene ⟶ 7,3 isomer	Liq	122–155	Pmr	12.5	30.6	−5.4	6

[a] For additional liquid-phase data compare ref 1. [b] Liq stands for liquid, glpc for gas–liquid partition chromatography, and pmr for proton magnetic resonance. [c] Compare ref 25. [d] Corrected for path degeneracy. For the first two reactions the factor is 3, for the rest it is 2.

Scheme II



the values reported by Murray and Kaplan[6] are in reasonable agreement with the results from this work, *A* factors and activation energies reported by Ter Borg, *et al.*,[5,10] are low. In view of the reported insensitivity of the reaction rates toward the media used,[1,4–7] the gas-phase data should in principle be capable of extrapolation to the liquid phase.[22] Whereas the available gas-phase data are internally consistent with the outlined concept of a cyclic intermediate most of the Arrhenius parameters reported from liquid-phase studies are not (compare ref 1 and Table II). For example, these data fail to show the expected differences in entropies of activation between linear and cyclic reaction systems. Both the activation energies and preexponential factors of most liquid-phase data are low compared to the gas-phase results (Table II). This may be attributed to the relatively large error limits attached to kinetic parameters obtained from pmr analysis[1] and over small temperature ranges.

The intramolecular and homogeneous nature of the gas-phase isomerization of 7-MCHT, studied in this work, has been demonstrated by the insensitivity of the measured reaction rates toward a 13-fold change in the surface-to-volume ratio of the reaction vessel. Furthermore the addition of nitric oxide in a 10-fold excess over the hydrocarbon pressure had no measurable effect on the reaction rates either.

The detailed reaction mechanism for the isomerization of 7-MCHT is shown in Scheme II. The 7-methyl-1,3,5-cycloheptatriene consists of an equilibrium mixture of two boat conformers[9] with the hydrogen in the 7 position either axial (B) or equatorial (A) to the ring.[24] In the ground state the conformer with the equatorial methyl group (B) is thermodynamically more stable. In conformer B there are two equivalent hydrogen-acceptor positions available (carbon atoms 3 and 4) for a 1,5 transfer. This path degeneracy results in optical isomers in the transition state and in the reaction product 3-MCHT. Consequently the observed rate constant k_{obsd} equals $2k_{d'}K_{c,d}$. Assuming $k_d = k_{d'}$ results in $k_{obsd} = 2k_c$.

The Arrhenius *A* factor of $10^{(12.6\pm0.2)}$ obtained for the positional isomerization of 7-methyl-1,3,5-cycloheptatriene is only slightly below the value of 10^{13} calculated from the transition-state theory for unimolecular reactions. The difference yields an entropy of activation of −3.6 cal/deg mole[25] (or −4.9 cal/deg mole, taking the path degeneracy into account). This result, when compared with the *A* factors of $\sim 10^{11}$ reported for 1,5-hydrogen-transfer reactions in open-chain molecules,[2] further substantiates the assumption of a cyclic transition complex for these reactions. The source of the entropy loss of 3.6 cal/deg mole in forming the bicyclic transition complex from 7-methyl-1,3,5-cycloheptatriene can be attributed primarily to losses of C–C rocking modes in the ground-state molecule and to the loss in the vibrational modes of the C–H bond ($\sim$0.5 cal/deg mole) in the 7 position. The loss of about 3 cal/deg mole in entropy due to the loss of the rocking motion of the boat conformation is not unreasonable, in view of the rigidity of the bicyclic transition complex. This only allows very limited torsional motions in the carbon ring skeleton.

In general agreement with the *A* factor obtained in this work for a cyclic 1,3-diene system, a value of $10^{13.3}$ was observed[3] for the analogous gas-phase rearrangement in a cyclic vinylcyclopropyl system.

The activation energy of 33.25 ± 0.19 kcal/mole measured for the conversion of 7-MCHT into 3-MCHT

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(22) Values for k_{liq}/k_{gas} (in brackets) have been reported for 5D-1,3-cyclooctadiene [3.2],[1,4] bicyclo[6.1.0]non-2-ene [4.5],[1,4] and 5H-perdeuterio-1,3-cyclopentadiene [3.3].[23]

(23) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

(24) (a) K. Conrow, M. E. H. Howden, and D. Davies, *J. Am. Chem. Soc.*, **85**, 1929 (1963); (b) F. A. L. Anet, *ibid.*, **86**, 458 (1964); (c) F. R. Jenson and L. A. Smith, *ibid.*, **86**, 956 (1964).

(25) $\Delta S^{\ddagger} = 2.303R[\log A - \log (kT/h) - 0.434]$ assuming a transmission coefficient of unity.

demonstrates the concerted nature of the process and is in agreement with the values generally observed for this type of reaction (compare ref 1 and Table II). The B conformation of the 7-methyl-1,3,5-cycloheptatriene favors the 1,5 hydrogen transfer. It is not surprising therefore that the activation energy observed for this cyclic 1,3-diene is similar to that previously reported for cisoid linear compounds. It can be concluded that no more than 1–2 kcal of extra strain is introduced into the bicyclic transition complex, unless some of the strain energy is compensated by a basically lower activation energy for hydrogen transfer in the 7-MCHT as compared to open-chain compounds.[2] There is, however, no evidence that would warrant this assumption.

The cyclic six-center transition complex is shown in scheme B by a static representation of a dynamic resonance system, involving three-electron and one-electron bonds, respectively.[26] The flattened carbon skeleton of the six-membered transition complex would introduce some additional strain into the molecule. Since complete flattening of the cycloheptatriene molecule requires an activation energy of about 6 kcal,[24b] 1 to 2 kcal of extra strain would appear to be reasonable. It is interesting to note that the additional double bond in the 7-MCHT which is not directly involved in the six-center transition complex has no measurable effect on the activation energy of the process.[27] The additional double bond, conjugated onto the transition complex, is not in the same plane with the transition ring and therefore has no stabilizing effect on the latter.

In general, the activation energies for 1,5 hydrogen transfer are not sensitive to changes in the substituents of the basic cisoid structure of the molecule.[1] Acyclic and cyclic systems, as well as 1,3-diene and the corresponding vinylcyclopropane systems, require closely the same activation energies, and the ring size seems to be of little influence.[1] The only exception to this general insensitivity of the reaction rates for the concerted 1,5 hydrogen transfer are the unusually low activation energies of about 23 kcal, observed for the positional isomerization in cyclopentadiene systems[7,23] (liquid phase). The thermal rearrangement in these systems appears to proceed *via* a 1,5 hydrogen transfer also.[17,23,28] The difference of nearly 10 kcal in activation energy when compared with the values for 1,5 shifts in other systems has been attributed to the unique structure and molecular orbital pattern of the ground-state cyclopentadiene.[1] Benson, *et al.*,[29] recently proposed that the pyrolysis of 1,3-cycloheptadiene involves a complex radical reaction mechanism with pseudo-unimolecular kinetics. The over-all activation energy is 41 ± 4 kcal mole^{-1}. It is conceivable that such radical reactions, initiated by the disproportionation of two diene molecules into a monoolefinic and diolefinic radical, might compete with the 1,5 hydrogen shift in some 1,3-dienes.

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(26) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 241 (1966).

(27) In agreement with this, liquid-phase studies have shown that the rate constants for 1,5 hydrogen transfer in substituted cycloheptatrienes were not significantly affected by phenyl substituents.[6]

(28) V. A. Miranov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

(29) S. W. Benson and R. Shaw, *J. Am. Chem. Soc.*, in press.

Free Radicals by Mass Spectrometry. XXXVI. Ionization Potentials of Conjugated and Nonconjugated Radicals

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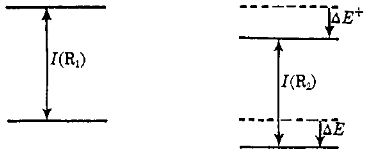
Abstract: The ionization potentials of several free radicals have been measured by electron impact: 3-cyclopentenyl, 7.54 v; acyclic pentadienyl, 7.76 v; ethylallyl, 7.65 v; 3-cyclohexenyl, 7.54 v; and 4-cyclohexenyl, 7.54 v. A comparison of allylic and corresponding nonallylic radicals shows no significant difference in ionization potential. Stabilization of the ground state of the former by π-electron delocalization is evidently paralleled by that in the cation. From appearance potentials, $\Delta H_f(\text{cyclo-C}_5\text{H}_7{}^+) = 211$ kcal/mole and $\Delta H_f(\text{cyclo-C}_5\text{H}_7) = 37$ kcal/mole can be estimated.

The effects of structural differences on the ionization potentials of free radicals has been reviewed recently[3] with respect to both the semiempirical molecular orbital method and the resonance treatment. The ionization potential, defined as the difference in energy between the ground state of the neutral radical and the lowest energy state of the cation, is a direct measure of the relative degree of stabilization in these levels, in the neutral radical by electron delocalization (ΔE) and in the cation by charge delocalization (ΔE^+).



A comparison of ionization potential differences in closely related radicals is therefore of value in interpreting the magnitude of such effects.

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(1) NATO Fellow, 1965–1966.

(2) Canada Council Fellow, 1966.

(3) A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **1**, 1 (1963).