Very Low Pressure Pyrolysis of 1,3-Cyclohexadiene. An Orbital Symmetry Nonallowed Reaction

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Abstract: Very low pressure pyrolysis (VLPP) of 1,3-cyclohexadiene yields only benzene and hydrogen unimolecularly between 670 and 800°. RRKM calculations indicate that the data are compatible with the Arrhenius expression log (k/sec^{-1}) = 13.4 − (59 ± 1)/θ. These parameters are very close to those to be expected from a mechanism wherein 1,3-cyclohexadiene is converted to 1,4-cyclohexadiene *via* a biradical intermediate. Concerted, orbital symmetry forbidden pathways cannot, however, be rejected as possibilities.

Benson and Shaw[2] studied the pyrolyses of 1,4- and 1,3-cyclohexadiene (CH) to benzene and hydrogen (cyclohexene is produced as well in the case of 1,3) and found that at several Torr of pressure the pyrolysis of the 1,4 isomer is a unimolecular process, while the elimination of hydrogen from 1,3-cyclohexadiene occurs through a chain reaction. This finding agrees with the prediction of the Woodward–Hoffmann[3] rules that only the 1,4 thermal elimination is an orbital-symmetry allowed reaction. The tendency for a chain process in the 1,3 pyrolysis is also supported by the fact that both of the radicals formed in the initiation reaction are stabilized in the case of 1,3 and not in the case of the 1,4 isomer.[2a] This chain reaction prevents measurement of any competing unimolecular elimination of H_2 from the 1,3 isomer, and thus prevents comparison of the rate of the allowed with the nonallowed reaction. In order to eliminate this chain reaction, it is necessary to work at low pressures where the rate of the higher order chain processes will be much slower than the unimolecular path. An appropriate technique for such a study is very low pressure pyrolysis (VLPP), where unimolecular reactions are studied[4-6] at pressures of about 10^{-3} Torr.

Experimental Section

The reaction was carried out in a triple-aperture quartz reactor in which each aperture was calibrated (measurement of the geometrical size of the hole) independently, and thus the system effectively consists of three different reactors. The apparatus and nature of the experiment have been fully described previously.[6,7]

1,3-Cyclohexadiene (Matheson Coleman and Bell) was thoroughly degassed and was distilled bulb-to-bulb. Benzene (Matheson Coleman and Bell spectro quality) was treated similarly. Hydrogen (Matheson, prepurified) was used directly and found to be >99.5% pure mass spectrometrically.

Flow rates were measured by observing the pressure drop per unit time from a calibrated volume, through the flow-setting capillaries. 1,3-CH was monitored at its mass spectral parent peak of 80 amu, and benzene was monitored at its 78 amu parent peak after correction for the contribution of 1,3-CH to mass 78. This correction was calculated from the 80 amu signal intensity and the ratio of the intensity of the mass 78 to mass 80 signals for pure 1,3-CH. As an internal standard, we used fluorobenzene which was admitted to the mass spectrometer directly through a bypass. The flow of fluorobenzene was ≤20% of the flow of 1,3-CH and was monitored at its parent peak of 96 amu.

Results

All the experiments include the measurements of both the disappearance of 1,3-CH and the formation of benzene. The percentages of the decomposition of 1,3-CH calculated from the two measurements usually agreed to within better than 10%. As an example, the results of one experiment are given in Table I. A complete mass-balance experiment in which the amount of

Table I. Comparison of Percentage Decomposition of 1,3-Cyclohexadiene (CH) from 1,3-Cyclohexadiene Disappearance and from Benzene Appearance[a]

Temp, °C	% CH disappearance	% benzene formation
755	13.5	15.5
761	18.2	19.7
766	18.5	20.5
775	25.2	26.7
784	27.2	29.5
789	31.2	31.0
794	34.0	34.0
798	38.7	36.1
804	39.4	39.4
809	42.3	42.3
815	45.5	45.9
820	48.3	47.5
828	50.5	52.1
832	54.8	54.2
837	55.8	56.9
842	58.4	59.1
850	62.1	62.7
854	63.6	64.2
860	65.6	67.1
864	66.6	68.2
869	70.3	69.8
874	71.5	71.7
879	73.5	72.8
887	75.6	75.8
891	74.5	76.7
897	78.2	78.9
902	79.4	80.1
906	80.0	83.5
911	81.5	85.2

[a] 1920-collision reactor, flow = 1.08 × 10^{16} molecules sec^{-1}.

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(2) (a) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 985 (1967); (b) *J. Amer. Chem. Soc.*, **89**, 5351 (1967).

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) P. C. Beadle, D. M. Golden, K. D. King, and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 2943 (1972).

(5) P. C. Beadle, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, 4, 265 (1972).

(6) S. W. Benson and G. N. Spokes, *J. Amer. Chem. Soc.*, **89**, 2525 (1967); D. M. Golden, G. N. Spokes, and S. W. Benson, *Angew. Chem.*, in press.

(7) K. D. King, D. M. Golden, G. N. Spokes, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 411 (1971).

Table II. Mass Balance of the Decomposition of 1,3-Cyclohexadiene[a]

Temp, °C	% 1,3-cyclohexadiene decomp	% benzene formation	% H_2 formation
634	13	12	10
640–642	15	14	12
651–654	22	23	19
661–663	24	25	21
673–675	28.5	30.5	30
685–688	35	36	36
706–708	50	53	56
723.5–727.5	61.5	60.5	69
746–757.5	74	75	77

[a] 280-collision reactor, flow = 1.62 × 10^{15} molecules sec^{-1}.

Table III. Rate Constants for 1,3-Cyclohexadiene Pyrolysis[a]

22,400-collision reactor		1920-collision reactor		280-collision reactor	
Temp, °C	k_{uni}, sec^{-1}	Temp, °C	k_{uni}, sec^{-1}	Temp, °C	k_{uni}, sec^{-1}
670	0.21	772	1.8	824	12.5
676	0.25	776	2.3	828	13.5
680	0.29	780	2.55	833	14.5
684	0.33	784	2.95	837	16.0
690	0.39	791	3.45	841	17.5
696	0.44	795	3.95	844	18.5
701	0.51	800	4.55	846	19.5
706	0.56	805	5.1	849	21.5
711	0.68	810	5.6	852	23.0
716	0.73	813	6.2	855	25.0
721	0.83	816	6.5	859	26.5
724	0.90	820	7.0	862	28.0
727	1.00	822	7.4	866	30.0
733	1.15	828	8.1	870	31.0
737	1.22	833	9.0	874	33.0
743	1.33	837	10.0	879	36.0
746	1.5	841	10.5	883	38.5
750	1.68	845	11.5	887	42.0
753	1.8	850	13.0	891	46.0
757	1.95	853	14.0	894	49.5
761	2.1	857	15.0	897	53.0
766	2.3	860	16.5	902	56.5
772	2.7	865	17.5	906	60.0
777	3.05	870	19.5	911	65.0
782	3.3	875	22.0	916	69.5
790	4.0	880	23.5	921	74.5
795	4.5	883	24.0	925	82.0
798	4.9	887	25.5	930	87.0
804	5.4	892	26.0	936	94.0
		897	28.5	940	97.0
		902	30.5	943	104.0
		906	32.5	948	109.0
				952	115.0
				956	120.0

[a] Flow = 1–2 × 10^{15} molecules sec^{-1}.

hydrogen (*m*/*e* 2) was monitored was also performed, and the results, given in Table II, show that the amounts of H_2 and benzene formed are equal to the amount of 1,3-CH reacted. No cyclohexene was found, in contrast to the high-pressure studies,[2b] where the ratios of the products were benzene : cyclohexene : hydrogen, ~6 : 4 : 1. An upper limit for cyclohexene present (calculated from the sensitivity of the instrument) would be 0.5% of the amount of 1,3-CH decomposed.

The rate constant of the unimolecular reaction, k_{uni}, was obtained from the equation

$$k_{uni} = k_{ea}f/(1 - f) \quad (1)$$

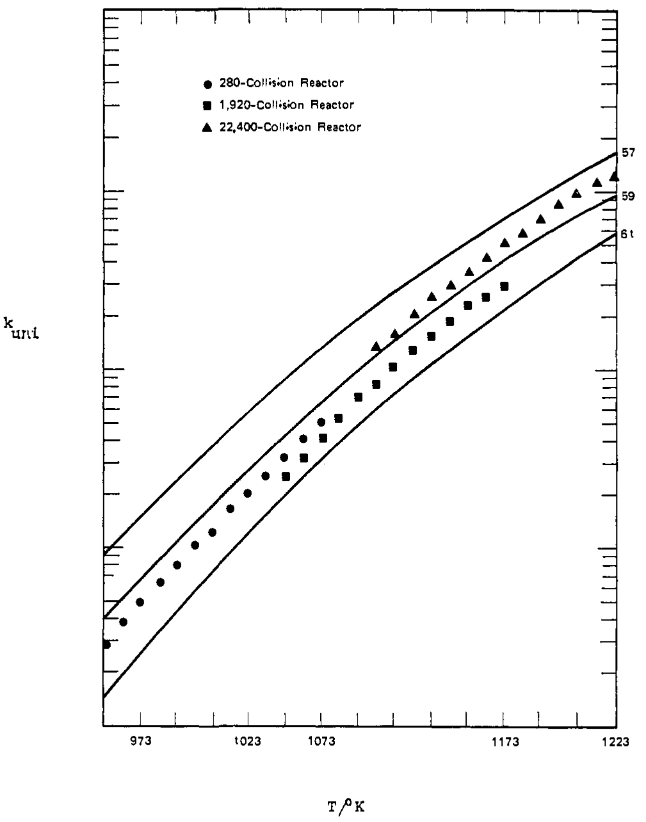

Figure 1. The rate constants k_{uni} of the pyrolysis of 1,3-cyclohexadiene.

where k_{ea} is the unimolecular escape rate constant for the reactant and f is the fraction of decomposition. Table III gives the unimolecular rate constant for the pyrolysis of 1,3-CH as measured from its disappearance for the three different reactors. Each result is an average of 3 to 4 different experiments and the spread of the results is about ±30%. This spread was caused both by the inherent error of the method (the measurement of the ion signals, the measurement of the temperature, and the magnification of uncertainty in the expression $f(1 - f)$ as f differs from 0.5) and by the variation in aperture area each time the movable plates were repositioned (a problem which is being overcome by a new reactor design).

The results are plotted in Figure 1. This figure shows a continuous behavior of the rate constant *vs.* temperature for each reactor separately, but a slightly discontinuous behavior for the different reactors. This discontinuity is due to the error in the calibration in k_{ea}, which is independent for each reactor, and to the fact that in some of the experiments the movable plates were not well seated.

The measurements shown in Table III were carried out at flows of 1–2 × 10^{15} molecules sec^{-1}. Measurements of flow dependence show that these rate constants are flow independent as can be seen from the data in Table IV.

This flow independence was found for the entire range of possible flows (10^{14}–2 × 10^{16} molecules sec^{-1}) when employing either the 280- or the 1920-collision reactor. With the 22,400-collision reactor, this flow independence was observed only for flows up to 1–2 × 10^{15} molecules sec^{-1}. At higher flows the rate constant starts to increase with increasing flow. This is a result

Table IV. Flow Dependence of k_{uni}

	(a) 1920-Collision Reactor, 817 ± 3°C							
	Flow, molecules sec^{-1} × 10^{-14}							
	3.1	5.9	8.2	11.3	19.1	34.7	81.5	
k_{uni}, sec^{-1}	6.5	6.7	5.6	6.5	8.0	7.1	5.4	
	(b) 280-Collision Reactor, 906 ± 2°C							
	Flow, molecules sec^{-1} × 10^{-14}							
	3.0	6.0	11.3	21.3	42	82	180	213
k_{uni}, sec^{-1}	59	54	60	68	70	53	49	66

of the fact that for the largest collision reactor at these higher flows, the frequency of gas–gas collisions is close to, or higher than, the frequency of gas–wall collisions, and thus an increase of the flow leads to an increase in the total collision frequency. Since these reactions are in the "fall-off" region, this gives rise to an increase in the rate constant. This type of flow dependence can be used to calculate the efficiency of gas–gas collisions.

Discussion

Unimolecular Reaction. The fact that the measured rate constant is independent of the gas flow shows that the reaction does not contain a bimolecular component. The contribution of the chain reaction, observed in static higher pressure systems,[2b] can be computed by comparing the measured rate with the rate calculated from the rate constants measured at the high pressures for the chain reaction. The rate of disappearance of 1,3-CH, assuming a chain length of unity, is given by $\mathrm{d(CH)}/\mathrm{d}t = 10^{6-31/\theta} \cdot (1{,}3\text{-CH}) \approx 10^{-16}$ mol l.$^{-1}$ sec^{-1} at 1100°K, while the measured rate is of the order of 10^{-7} mol l.$^{-1}$ sec^{-1}. Another experimental difference between the high-pressure pyrolysis (40 Torr) and the pyrolysis under VLPP conditions (10^{-3} Torr) is that in the high-pressure experiments, the amount of H_2 formed was only about 10% of the amount of 1,3-CH which was reacted and cyclohexene was also formed in amounts close to (60–70%) benzene, while in our experiments, no cyclohexene was formed and the rates of H_2 and benzene formation were equal to each other and to the rate of 1,3-CH disappearance.

Temperature Dependence. The results of the dependence of k_{uni} on temperature were fitted to RRKM theory. In order to determine the value of the high-pressure activation energy (E_∞) from the k_{uni} of VLPP data, A_∞ must be known. A_∞ would be expected to be $10^{13.5\pm0.5}$ for cis-hydrogen elimination in accordance with similar four-center elimination reactions.[8] An A factor of $10^{13.4}$ at 600°K was obtained using the vibrational normal modes of 1,3-cyclohexadiene measured by Dilauro, *et al.*,[9] by making the assignments by comparison with the assignments of cyclohexene[10] and 1,4-cyclohexadiene[11] and by modifying some of these in order to obtain the vibrational frequencies of the activated complex. These frequencies were used to calculate the RRKM theoretical curves, given in Figure 1, for activation energies of 57–61 kcal mol^{-1}. (The results depend only on the A factor and not on the exact model of the transition state.) From the comparison of the experimental results and the RRKM curves, it can be concluded that the activation energy for the unimolecular pyrolysis, corresponding to the A factor chosen, is 59 ± 1 kcal mol^{-1}. In order to check the effect of the chosen A factor, we also calculated the RRKM curves for $\log A_{600} = 14.34$. It was found that this change of log A by one unit requires a change in the activation energy of 2 kcal mol^{-1} (61 ± 1 kcal mol^{-1}). Since it does not seem reasonable that the estimate of the A factor is wrong by more than a factor of 10 (regardless of the mechanism, see below), it can be concluded that the activation energy is 59 ± 3 kcal mol^{-1}, where the error limits are twice the most probable uncertainty.

The Mechanism of the Unimolecular Pyrolysis. There are three possible mechanisms by which the elimination of H_2 from 1,3-cyclohexadiene can occur: (1) a concerted 1,2-H_2 elimination, (2) a radical reaction in which the first and rate-determining step is a C–H bond rupture

$$C_6H_8 \longrightarrow \dot{C}_6H_7 + H \tag{2a}$$

$$\dot{C}_6H_7 \longrightarrow C_6H_6 + H \tag{2b}$$

$$H + H \xrightarrow{\text{wall}} H_2 \tag{2c}$$

and (3) isomerization of 1,3-CH to 1,4-CH, by either 1,3-H migration (nonallowed) or *via* a biradical, followed by the faster known reaction, a concerted 1,4 elimination of H_2 from 1,4-CH.

There are several indications that mechanism 2 does not contribute considerably to the VLPP of 1,3-CH. The first is from the comparison of an estimated rate constant for reaction 2a with the experimental rate constant. The estimated A factor for reaction 2a at 1000°K is $\sim 10^{15.3}$ ($\Delta S^{\ddagger} \sim 7.4$ cal mol^{-1} deg^{-1}: 2.8 from symmetry considerations and ~4.6 from loosening of the H–C–H and C–C–H bends). The activation energy can be estimated from the known secondary C–H bond strength (95 kcal mol^{-1})[12] and the stabilization energy of the cyclohexadienyl radical, which can be expected to be the same as that for the pentadienyl radical (18 ± 3 kcal mol^{-1});[13] thus, $\Delta E = 95 - 18 = 77$ kcal mol^{-1} and $\log k_\infty = 15.3 - 77/\theta$ ($\theta = 2.303RT$ kcal mol^{-1}). At 1000°K $\log k_\infty = 4 \times 10^{-2}$ sec^{-1}. RRK estimates[14] (using $s = C_v/R$) give $k/k_\infty = 0.3$; thus, $k \simeq 1.2 \times 10^{-2}$ sec^{-1} compared with the observed value of $k = 1.0$ sec^{-1}.

Another indication of the absence of the radical pathway comes from experiments on the pyrolysis of 1,3-CH and equimolar amounts of perdeuteriobenzene (C_6D_6) at temperatures corresponding to 65–70% decomposition. If H atoms were produced, we would expect them to add to the benzene and replace D atoms to yield C_6D_5H, and some HD should also be observed. In fact, the ratios C_6D_5H/C_6D_6 and HD/H_2 were less than 1–0.5%. Unfortunately, this test is not as sensitive as one would like, since a competing process, namely H-atom recombination at the reactor surfaces,

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(8) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **21**, 63 (1970).

(9) C. Dilauro, N. Neto, and S. Califano, *J. Mol. Struct.*, **3**, 219 (1969).

(10) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 70, 4227 (1948).

(11) H. D. Stidham, *Spectrochim. Acta*, **21**, 23 (1965).

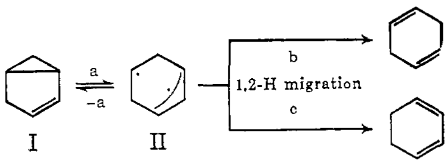
(12) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); S. W. Benson, *Chem. Educ.*, 42, 502 (1965).

(13) (a) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 241 (1966); (b) H. M. Frey and A. Krantz, *J. Chem. Soc. A*, 1159 (1969); (c) K. W. Egger and M. Jola, *Int. J. Chem. Kinet.*, 2, 265 (1970).

(14) G. Emanuel, *Int. J. Chem. Kinet.*, 4, 591 (1972).

is very rapid[15] and the maximum expected yields of C_6D_5H or HD are approximately 10%.

The rate of the isomerization of 1,3-CH to 1,4-CH (mechanism 3) can be estimated from the data on the kinetics of the thermal isomerization of bicyclo[3.1.0]-hex-2-ene[16] to 1,3- and 1,4-cyclohexadienes, which is consistent with the assumption of a biradical mechanism.[17,18]



Internal ring-closing activation energies seem to be lower than those of 1,2-H migration, and, therefore, O'Neal and Benson[18a] assume that $k_{-a} \gg k_b \approx k_c$, and hence, $k = K_a(k_b + k_c) \simeq 2K_ak_c$. Ellis and Frey found $\log (k/\text{sec}^{-1}) = 14.5 - 50.2/\theta$, and hence, $E_c = 50.2 - \Delta H_a$. ΔH_a can be calculated from known thermodynamic data.[19-21] $\Delta H_a = 34.9$ and, therefore, $E_c = 15.3$ kcal mol^{-1}. This value agrees well with the 16.2 kcal mol^{-1} found for the activation energy for 1,2-H migration in bicyclo[2.1.0]pentane[18b] and with the 16.5 ± 1 kcal observed[8] for 1,2-H migration in vinylcyclopropane pyrolysis.[19b] The assumption that the isomerization of 1,3-CH to 1,4-CH takes place *via* a similar mechanism (a 1,2-H migration to the biradical II, which then goes to 1,4-CH) should give a lower limit to the rate constant since a concerted nonallowed 1,3 process could conceivably be faster, Since $k_c \approx k_b$, the rate constant for this isomerization would be about $0.5k_{-c}$. The activation energy, E_{-c}, can be calculated from the enthalpy of the reaction to the biradical, ΔH_c and E_c; $E_{-c} = \Delta H_{-c} + E_c$. ΔH_{-c} is calculated from the estimated heat of formation of II, 72.5 kcal mol^{-1}, and the measured heat of formation of 1,3-CH, 26.0 kcal mol^{-1}.[21] $\Delta H_{-c} = 46.5$ and $E_{-c} = 61.8$. The *A* factor would be expected to be close enough to $10^{13.4}$ such that the same RRKM calculation used previously applies here. This estimate may easily be in error by ±2–3 kcal mol^{-1}, and since the difference from the experimental result is 3 ± 3 kcal mol^{-1}, this mechanism could easily be operative.

(Note that this calculation is independent of the thermochemical values for the biradical. Since the isomerizations of the bicyclic compound and the 1,3-cyclohexadiene are assumed to go through the same transition state, we can deduce

$$E^{\ddagger}{}_{\text{act}(1,2)} = E^{\ddagger}{}_{\text{bicyclic}} + \Delta(\Delta H_f{}^{\circ})[1,3 \rightarrow \text{bicyclic}]$$

$$\Delta S^{\ddagger}{}_{\text{act}(1,2)} = \Delta S^{\ddagger}{}_{\text{bicyclic}} + \Delta S^{\circ}[1,3 \rightarrow \text{bicyclic}] + R \ln n$$

where $n = {}^1/_4$ represents the correction for the two equal paths for bicyclic pyrolysis as well as the correction for return of biradical to 1,3 in the 1,3 pyrolysis.)

Comparison with Allowed Reactions. Since no definite conclusion can be drawn concerning the mechanism of the unimolecular decomposition of 1,3-CH, both possibilities (mechanisms 1 and 3) have to be discussed. If the dominant reaction is mechanism 1, *i.e.*, the concerted cis elimination of H_2, comparison of the measured activation energy with the activation energy of the allowed pyrolysis of the 1,4 isomer shows a difference of 15 ± 3 kcal mol^{-1} as the extra barrier height, perhaps due to nonallowed nature of the reaction. This difference of 15 kcal mol^{-1} agrees favorably with other values of the extra barrier heights comparing orbital-symmetry allowed and nonallowed isomerization of ≥ 15 kcal mol^{-1}.[22,23] While there is no reason to believe that the increases in the activation energies have to be the same for all nonallowed reactions, this similarity is quite striking.

If the dominant reaction is the isomerization of 1,3-CH, we can compare the activation energy for the biradical formation (or 1,3-H migration) with the 1,5-H migration through coupled double bonds (an allowed reaction) where the activation energy[24] is about 25 kcal mol^{-1}. If this is the case, the cost of following the orbital symmetry nonallowed path is about 35 kcal mol^{-1}, much more than has been previously found for other reactions.

The agreement with parameters predicted on the basis of the biradical intermediate strongly suggests that the biradical mechanism is operative. If the real mechanism is the biradical isomerization to the 1,4 isomer, this sets an upper limit to the rate constant for the concerted 1,2 elimination and thus a lower limit to the activation energy of this process. Hence the cost of following the nonallowed, 1,2-concerted elimination reaction is ≥ 15 kcal mol^{-1}.

(When the experimental work and writing of this manuscript were complete, a communication by Orchard and Thrush[25] appeared which disclosed the measurement of very similar Arrhenius parameters and which reached essentially the same conclusions. We only differ by not ruling out the possible 1,2-concerted elimination processes. This paper may be

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(15) H. Wise and B. J. Wood, *Advan. At. Mol. Phys.*, **3**, 321 (1967).

(16) S. W. Benson, ""“Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters," Wiley, New York, N. Y., 1968.

(17) R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 553 (1966).

(18) (a) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, 2, 423 (1970). (b) Additional evidence for a biradical intermediate can be found from the results of W. Doering and W. Roth, *Angew. Chem., Int. Ed., Engl.*, **3**, 115 (1963), who found that 6,6-dideuteriobicyclo-[3.1.0]hex-2-ene isomerizes to 4,4-dideuteriobicyclo[3.1.0]hex-2-ene faster than isomerization to the cyclohexadienes. (c) Further evidence for a biradical mechanism has recently been put forth by R. S. Cooke and U. H. Andrews (to be published), who found from an examination of the deuterium distribution in the cyclohexadienes, d_{-1} formed in the pyrolysis of 3-deuteriobicyclo[3.1.0]hex-2-ene a statistical distribution as expected from the biradical mechanism and, contrary to expectations, from concerted mechanisms.

(19) (a) Group additivity gives as the heat of formation of I, 37.6 kcal mol^{-1}, and the heat of formation of II can be calculated from cyclohexene ($\Delta H_f{}^{\circ} = -0.8$) by adding the bond dissociation energy of two C–H bonds ($2 \times 95 = 190$) and deducting the heat of formation of two hydrogen atoms (104.2)[16] and the allylic resonance energy (12.5)[20] to give 72.5 kcal mol^{-1}. There is some uncertainty about the strain energy, since there is a difference of 3 kcal mol^{-1} between the strain energies in cyclohexene and cyclohexadiene.[18] (b) The production of 1,3- and 1,4-pentadienes *via* a biradical mechanism requires 1,2-H migration and in the 3,5-diyl pentene-1 biradical.

(20) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(21) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(22) J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **94**, 4262 (1972).

(23) (a) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968); (b) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(24) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

(25) S. W. Orchard and B. A. Thrush, *J. Chem. Soc., Chem. Commun.*, 14 (1973).

viewed as one more example of VLPP results agreeing with known high-pressure Arrhenius parameters *via* an estimated A factor and RRKM theory.)

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Thermodynamics of Molecular Association by Gas–Liquid Chromatography. IV. Haloalkane Acceptors with Di-*n*-octylmethylamine and Tri-*n*-hexylamine

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Abstract: Equilibrium constants, enthalpies, and entropies of complex formation between ten haloalkane acceptors and the electron donors di-*n*-octylmethylamine and tri-*n*-hexylamine have been determined by gas–liquid chromatography in the temperature range 30 to 60°. The results are discussed in terms of the possible contributing forces of stabilization for complex formation and are compared with those previously obtained with the electron donors di-*n*-octyl ether and di-*n*-octyl thioether.

This paper represents a further contribution to the quantitative study of molecular association in binary nonelectrolyte solutions by means of gas–liquid chromatography (glc). Previously we reported a glc study of the complexes formed between a variety of haloalkane acceptors and the donors di-*n*-octyl ether and di-*n*-octyl thioether.[1] While the initial purpose of this work was to carry out a systematic study of the hydrogen-bonding propensities of the haloalkane systems, the trends observed in the measured equilibrium constants indicated that there was an additional interaction present in many of the systems. This trend was most marked in those systems involving the thioether with bromo-substituted methanes. On the basis of indirect evidence for the existence of stable complexes between halomethanes and n-donors, it was postulated that this additional contribution to the equilibrium constants might be due to a charge-transfer interaction ($n \rightarrow \sigma^*$ type) involving Cl and Br as acceptors with the O and S donors.

It has been well established that tertiary amines form relatively strong H-bonded complexes with haloforms, N being a stronger electron donor than O or S. Direct spectroscopic evidence also exists for the presence of charge-transfer complexes of the $n \rightarrow \sigma^*$ type in solutions of tertiary amines with halomethanes.[2] In fact, it has been postulated that the reaction of chloroform with amines occurs through this mechanism.[3] Thus, a glc study of solutions of haloalkanes in tertiary amines might be expected to yield further evidence of the ability of these types of systems to undergo molecular association *via* two different mechanisms. Accordingly, in the present study we have extended our investigation to those systems involving di-*n*-octylmethylamine and tri-*n*-hexylamine as the electron donors together with the same series of haloalkanes previously used as electron acceptors.[1] The choice of two tertiary amines of differing hydrocarbon chain structure was made with a view to evaluating the effect of electron donor accessibility on the thermodynamic association parameters.

As in the previous study, the method of evaluating the thermodynamic association constants is that devised recently by Martire and Riedl.[4] The validity of this approach and the assumptions made in deriving the expressions used have very recently been critically evaluated in this laboratory.[5] A comparison has been made for some of the systems studied here, between the results obtained using the Martire–Riedl approach[4] and those obtained by using the more general method of Cadogan and Purnell.[6] The conclusion reached from this comparative study was that the former method yields results identical with those obtained from utilization of the Purnell method provided certain explicit conditions are met.[5] These conditions are, in general, fulfilled for the systems involved in the present and previous[1] studies. Thus the Martire–Riedl approach remains our method of choice for these systems since it has the advantage of much greater speed at comparable precision.

The method of extracting the thermodynamic association parameters from glc measurement of specific retention volumes has already been described in detail in previous papers.[1,4]

Experimental Section

Liquid Phases. The electron donors di-*n*-octylmethylamine (DOMA) and tri-*n*-hexylamine (THA) were obtained from Eastman Chemical Co. Both amines required further purification; this was done by fractional distillation at reduced pressure on a Nester-Faust spinning band column. The major fraction collected of the di-*n*-octylmethylamine had a bp of 114° at 0.8 mm while that

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[1] J. P. Sheridan, D. E. Martire, and Y. B. Tewari, *J. Amer. Chem. Soc.*, **94**, 3294 (1972).

[2] D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962).

[3] E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 134 (1965).

[4] D. E. Martire and P. Riedl, *J. Phys. Chem.*, **72**, 3478 (1968).

[5] Paper V in this series: H.-L. Liao, D. E. Martire, and J. P. Sheridan, *Anal. Chem.*, in press.

[6] D. F. Cadogan and J. H. Purnell, *J. Chem. Soc. A*, 2133 (1968); D. F. Cadogan and J. H. Purnell, *J. Phys. Chem.*, **73**, 3849 (1969).