Reversibility in the Gas-Phase Decomposition of Cyclopentene. The Entropy of Cyclopentadiene

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Summary The entropy of cyclopentadiene has been determined from the unexpectedly reversible decomposition of cyclopentene.

THE gas phase decomposition of cyclopentene to cyclopentadiene and hydrogen has commonly been regarded as a good example of a simple first order unimolecular reaction, which proceeds to completion.[1] These conclusions, however, have been based upon studies[2,3] which used pressure changes as the means to follow the reaction. Using analytical techniques, we have obtained evidence of greater product complexity than hitherto suspected and, moreover, that the reaction does not proceed to completion. In fact the equilibrium position at the usual pyrolysis temperatures is such that, in the presence of excess hydrogen, comparable concentrations of cyclopentene and cyclopentadiene are generated and the equilibrium constant can be measured quite readily (Table).

The most important side products are ethylene, propylene and cyclopentane, although small quantities of methane are also observed. Other products never exceed 1% of the total of cyclopentene and cyclopentadiene. Kinetic data indicate that these products result from the hydrogenation of cyclopentene (probably by a reaction path involving hydrogen atoms).

The stationary state ratio, $\frac{[\text{cyclopentadiene}]\,[H_2]}{[\text{cyclopentene}]}$,

has been approached from both sides at several different initial pressures of hydrogen. At constant hydrogen pressure the same value is obtained from either side, but the values vary slightly with large changes in hydrogen pressure.

TABLE

Initial pressure (torr)				Product ratios[a]: [product]/[cyclopentene]				Final pressure (torr)	
cyclo-pentene	cyclo-pentadiene	H_2	Time min.	C_2H_4[b]	C_3H_6	cyclo-pentane	cyclo pentadiene	H_2	$\frac{[\text{Cyclopentadiene}]\,[H_2]}{[\text{cyclopentene}]}$ (torr)
1·1		702	90	0·89	0·71	0·132	0·555	702	390
	1·0	701	90	0·41	0·36	0·061	0·584	700	409
1·0		27·2	210	1·16	0·75	$\sim 10^{-3}$	11·06	28·1	311
	1·0	26·5	210	0·43	0·19	$\sim 10^{-3}$	13·26	26·4	350
10·5		427	90	0·40	0·33	0·053	0·924	429	396
	9·0	431	90	0·36	0·24	0·036	1·006	425	427

[a] Product ratios determined by gas chromatography, using a combination column, ββ′-oxydiprionitrile and silicone oil.
[b] This includes in some cases a small quantity of CH_4 which was not resolved from C_2H_4 on the chromatograms.

This variation can be attributed to the perturbations of the ratio from the true equilibrium value caused by the side reactions, which tend to remove cyclopentene preferentially. These perturbations are largest at high hydrogen pressures. We have applied a correction for the rate of the side reactions and the resulting values for the equilibrium constant show very little scatter. The value obtained is:

$$K\ (501{\cdot}2^{\circ}) = 0{\cdot}424 \pm 0{\cdot}059 \text{ atm.}$$

where the error includes the uncertainty from all sources. From this figure, the Gibbs free energy change for the reaction, $\Delta G^{\circ}\ (774{\cdot}4^{\circ}\ \text{K}) = 1{\cdot}32 \pm 0{\cdot}20$ kcal. mole^{-1}. Taken in conjunction with the enthalpy of reaction[4] and with the proper temperature corrections† this leads to

$$\Delta S^{\circ}\ (298{\cdot}2\ ^{\circ}\text{K}) = 26{\cdot}6 \pm 1{\cdot}0 \text{ cal. }^{\circ}\text{K}^{-1}\text{ mole}^{-1}.$$

(Standard state 1 atm.)

Hence from the known standard entropies of cyclopentene[5] and hydrogen,[6] $S^{\circ}_{298\cdot2}(\text{cyclo-}C_5H_6\ g) = 64{\cdot}6 \pm 1{\cdot}0$ cal.°K^{-1} mole^{-1}.

The entropy of cyclopentadiene has not previously been determined but its value is closely similar to that for pyrrole,[7] a fact which is consistent with the general rule that compounds of similar mass and structure tend to have similar standard entropy values.[8]

A knowledge of the entropies of cyclic compounds is an important factor in the critical assessment of kinetic data for processes where cyclic transition states are proposed. Cyclopentadiene itself has recently been invoked as a model compound whose tight structure must provide a limit to the structure of the transition state for thermal 1,5-hydrogen shift processes.[9] The entropy value obtained in this work implies *A* factors for these reactions $\geqslant 10^{10\cdot4}$ sec.$^{-1}$, which is more consistent with observed *A* factors than an earlier estimate.[9]

Our attention has been called to a spectroscopic determination:[10]

$$S^{\circ}_{298\cdot2}\ (\text{cyclo-}C_5H_6\ g) = 65{\cdot}6 \text{ cal. }^{\circ}\text{K}^{-1}\text{ mole}^{-1}.$$

R. W. thanks the S.R.C. for the provision of an equipment grant.

(*Received, April 28th,* 1969; *Com.* 596.)

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† In order to correct ΔH° and ΔS° for temperature variations, reliable values of C°_p for H_2, cyclopentene and cyclopentadiene are required. There are no literature values for C°_p (cyclopentadiene) and so these had to be estimated by making corrections to C° (pyrrole) (ref. 7) according to well established procedures (ref. 8, p. 39).

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[4] $\Delta H^{\circ}\ (355\ ^{\circ}\text{K}) = 23{\cdot}95 \pm 0{\cdot}05$ kcal. mole^{-1}, obtained from vapour phase heat of hydrogenation studies of Kistiakowsky and co-workers; *J. Amer. Chem. Soc.*, 1936, **58**, 146; *ibid.*, 1937, **59**, 831.

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