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75. The Gas-Phase Thermal Decomposition of 5-Ethyl-1-pyrroline

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(13. 1. 72)

Summary. The gas-phase thermal decomposition of 5-ethyl-1-pyrroline has been studied in the temperature range 721–786 K. The decomposition appears to proceed by two pathways, one a radical route yielding pyrrole, ethylene and ethane as major products, and the other a molecular hydrogen elimination to form initially 2-ethyl-3*H*-pyrrole which rapidly rearranges to other ethylpyrroles *via* a series of 1, 5-hydrogen shifts. Approximate rate constants for the unimolecular hydrogen elimination have been calculated and fit the *Arrhenius* relationship:

$$\log(k/s^{-1}) = 12.5 \pm 0.4 - (55.5 \pm 1.4 \text{ kcal mol}^{-1})/\Theta \text{ where } \Theta = 2.303 RT.$$

Approximate calculations based on the radical pathway yield a value of $\sim 14 \text{ kcal mol}^{-1}$ for the stabilization energy in the 1-pyrrolin-5-yl radical, in good agreement with that reported earlier for the substituted 2-aza-allyl radical.

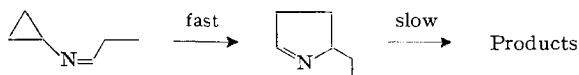
Introduction. – Kinetic parameters for thermal 1,4-hydrogen elimination reactions have been reported for cyclopentene [1] [2], 1-methylcyclopentene [3], 3-pyrroline [4], 2,5-dihydrofuran [5], and 2,5-dihydrothiophene [6]. In all these reactions, the eliminating hydrogens involved in the orbital symmetry allowed process [7] are in essentially identical environments, and it is of interest to examine the effects of enforced asymmetry on the activation parameters. In 5-ethyl-1-pyrroline, the presence of nitrogen in a terminal position of the double bond, together with the 5-ethyl substituent, render the hydrogen atoms in the 3- and 5-positions non-equivalent.

Experimental. – a) *Preparation of Materials.* N-propylidene-cyclopropylamine was prepared from cyclopropylamine by Dr. A. F. M. Iqbal of MRSA, using a novel catalytic disproportionation reaction [8]. This compound has been shown to pyrolyze cleanly to 5-ethyl-1-pyrroline [9], with a half life of 0.1 to 2 seconds in the temperature range of the studies reported in this paper. 5-Ethyl-1-pyrroline could, therefore, be generated practically instantaneously *in situ*.

b) *Apparatus and Procedure.* The conventional static reaction system used in these studies was essentially the same as that described previously [10]. The reaction vessel was a pyrex cylinder of 1 l volume. For runs to test the homogeneity of the reaction, a similar vessel packed with thin-walled glass tubes giving a surface to volume ratio 14 times that of the unpacked vessel was used.

N-propylidene-cyclopropylamine was normally introduced into the reaction vessel in the gas phase from a storage bulb. For runs with propylene as a radical scavenger, the propylene was added from a storage bulb immediately following the addition of reactant. For runs with added toluene, the toluene was injected into the reaction volume *via* a silicone rubber septum. The reaction vessel was isolated from the injection volume by means of a Teflon valve, and the material remaining in the dead space was condensed out. A kinetic run was quenched by condensing the contents of the reaction vessel into a trap cooled in liquid nitrogen, the non-condensable gases being continuously transferred into a gas-burette by means of an automatic *Toepler* pump. The contents of the trap were warmed to -70°C and the evolved gases were transferred to the burette. The material remaining in the trap was transferred to a small volume sampling vial and stored under nitrogen at 0°C . The contents of the vial were analyzed by gas-chromatography using liquid injections. An *F + M* model 810 gas chromatograph fitted with TC. detectors was employed. An 18 ft \times 0.25 in column packed with 20% Carbowax 20M on 60–80 Chromosorb W operated at 150°C with a helium flow rate of 100 ml min^{-1} gave a good separation of the components of the mixture, although some problems with peak-tailing were encountered. Peak areas were measured with a 'Disc' integrator, and calibration factors were assumed to be inversely proportional to molecular weight, an assumption previously shown to be valid. Pressures in the reaction system were measured with a *Pace* pressure transducer.

Results. – In the temperature range 721–786 K, 5-ethyl-1-pyrroline decomposes to give as main products hydrogen, ethane, ethylene, and material condensable at -70°C which gives five major gas-chromatographic peaks.



Hydrogen was identified as the major component of the evolved gases, non condensable at -196°C , by its gas-chromatographic behaviour. A small amount of methane was also found in this fraction. Ethane and ethylene, in approximately equal amounts, were identified together with smaller quantities of butane and butene as the components of the gaseous fraction transferred at -70°C by comparison of retention times with those of authentic samples on a BMEA column operated at 0°C .

Three components of the mixture condensable at -70°C were identified as pyrrole (typically 30–55%), 2-ethylpyrrole (20–35%) and 2-ethyl-2*H*-pyrrole (2–12%) by NMR. and mass spectroscopy. Due to tailing of the remaining two peaks, positive identification of the components was not possible. However, NMR. and mass spectral evidence indicated the presence of at least three compounds, two of which were isomers of ethylpyrrole. The third component appeared to have a molecular weight of 81 and was presumed to be a methylpyrrole. In addition to these products, several minor peaks of shorter retention time were observed on the chromatograms.

The amount of hydrogen produced generally agreed within 20% with the amount of substituted pyrroles, based on the GC. analysis. A similar agreement between the amount of C_2 and C_4 compounds and pyrrole was also observed.

Agreement between total conversions based on pressure changes and on GC-analysis were normally better than 20%. However, total rate constants based on GC.-determined conversions showed a large scatter within a given temperature range. The values were not systematically dependent on the amount of conversion or initial pressures in the range 9–60 Torr. With very large initial pressures (> 150 Torr), however, systematically higher rates were observed.

By assuming that decomposition occurred by two parallel first order pathways, one to yield pyrrole and the other to yield the substituted pyrroles, it was possible to split the overall rate constants into two components. For initial pressures less than 60 Torr, the component related to pyrrole showed a high random scatter (up to $\pm 50\%$), but that related to the substituted pyrroles showed a much smaller scatter ($\pm 12\%$).

The effect of added propylene or toluene on these rate constants was small, although a tendency for slightly lower rate constants for the substituted pyrrole path was apparent.

The rate constants, k_1 , for the substituted pyrrole path, together with relevant experimental data, are presented in Table 1.

Table 1. *The Thermal 1,4-Hydrogen Elimination from 5-Ethyl-1-pyrroline*

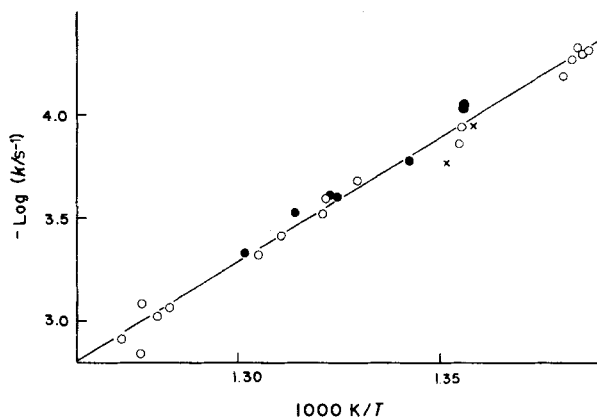
Temp [K]	Time [min]	Pressure [Torr]	$k_1 \times 10^4 / s^{-1}$
721.2	240	19.6	0.483
722.0	30	16.8	0.503
722.6	60	19.3	0.450
723.3	120	16.6	0.534
724.5	45	20.1	0.643
736.5 ^{a)}	5	12.2	1.24
737.5 ^{b)}	3	33.2	0.875
737.6 ^{b)}	45	14.6	0.902
737.9	45	14.4	1.14
738.1	5	16.6	1.37
740.0 ^{a)}	31	19.0	1.69
745.0 ^{b)}	60	29.9	1.65
752.1	60	36.1	2.08
754.9 ^{c)}	2	60.0	2.47
755.7	2	35.0	3.09
755.8 ^{c)}	2	20.0	2.41
756.6	5	41.5	2.51
757.0	10	18.7	3.01
761.1 ^{b)}	6	14.4	2.98
763.0	6	17.3	3.85
766.3	3	17.2	4.77
768.2 ^{b)}	3	19.0	4.63
779.5	4	9.0	8.51
781.3	10	35.0	9.42
783.7	7	31.4	8.19
783.9	3	26.0	14.2
786.6	5	17.2	12.2

a) Packed reaction vessel, not included in least-squares analysis.

b) Added toluene.

c) Added propylene.

The figure shows the *Arrhenius* plot based on these data. Least-squares analysis of all the data yields the *Arrhenius* relationship:



Arrhenius plot for the elimination of hydrogen from 5-ethyl-1-pyrroline

Filled circles denote runs with radical scavengers and crosses denote packed vessel runs

$$\log k_1/s^{-1} = 12.5 \pm 0.4 - (55.5 \pm 1.4 \text{ kcal mol}^{-1})/\Theta,$$

where $\Theta = 2.303 RT$.

Least-squares analysis omitting the runs with added radical scavengers gives the same A-factor and a slightly lower activation energy (55.3 kcal mol⁻¹).

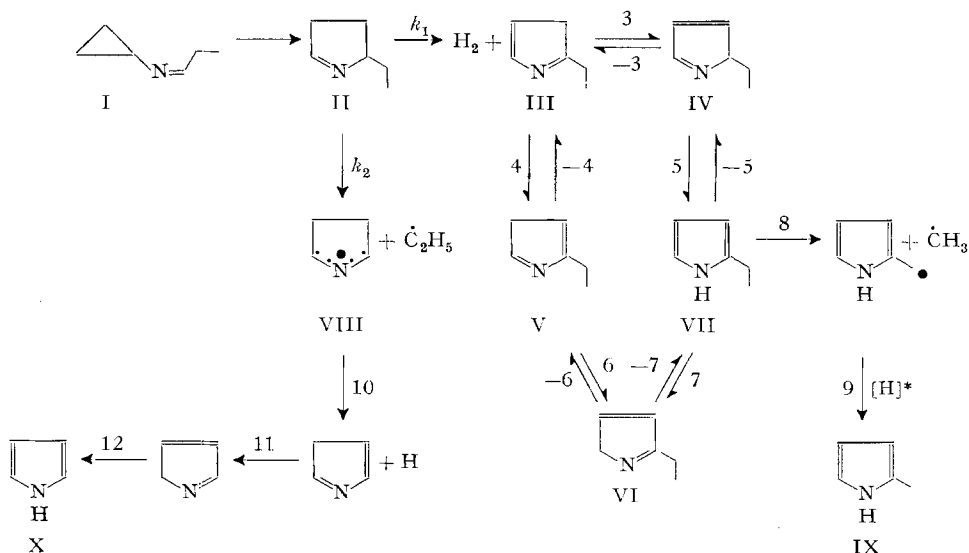
In the packed vessel, these rate constants were increased between 16 and 30%. A larger increase (~100%) was observed for the rate constants related to pyrrole formation.

Discussion. - The formation of ethylpyrroles is most conveniently accounted for by a molecular hydrogen elimination followed by intramolecular isomerization *via* 1,5-hydrogen shifts. This isomerization would be expected to be rapid at the temperatures of this study [10].

It is most unlikely that pyrrole itself is formed by a molecular elimination of ethane, and a radical reaction initiated by the loss of the ethyl group from 5-ethyl-1-pyrroline would appear to be the most likely route to this product.

The probable overall reaction scheme for the decomposition of 5-ethyl-1-pyrroline is shown below (p. 684).

The small effect of added radical scavengers and the good agreement (considering the small amounts involved) between the amounts of hydrogen + light hydrocarbons and pyrrole + substituted pyrroles indicates, surprisingly that, the atoms and radicals formed do not undergo abstraction or addition reactions to any great extent under the conditions of the study. Ethane, ethylene and butane can be accounted for by elimination and termination reactions of ethyl radicals, but considerations of the likely pathways, in the radical reaction path, reveals a deficit in the amount of hydrogen observed, and it would appear that most of the hydrogen atoms are removed from the system by a process which does not significantly involve the molecular components of the reaction mixture. Wall reactions may account for this discrepancy.



* Either reaction with H-atoms or *via* H-abstraction.

The apparatus used was not suited for the low pressure and low conversion studies necessary to gain further insight into the radical pathway. This reaction is obviously complex and even a simple analysis reveals the possible occurrence of 30 steps.

From the above evidence, it would appear that the rate of formation of pyrrole is governed mainly by the rate constant for the initial bond-fission, k_2 , although a 6% heterogeneous component also appears to be involved. Assuming a reasonable A-factor of $\sim 10^{15.5} \text{ s}^{-1}$ for the bond-breaking and using a mean value for k_2 at the middle temperatures of the study, an approximate activation energy of 66 kcal mol⁻¹ for this step is calculated. This yields a stabilization energy for the 1-pyrrolyl radical (VIII) of about 14 kcal mol⁻¹, in good agreement with the reported value for the substituted 2-aza-allyl radical [9].

In the proposed molecular route, 2-ethylpyrrole (VII) normally accounting for between 50 and 70% of the substituted pyrrole products, appears to decrease slightly with extent of reaction while 2-ethyl-2*H*-pyrrole (IV) appears to increase. From the outlined scheme, it therefore appears that the formation of 2-ethylpyrrole is faster *via* route III → V → VI → VII than by route III → IV → VII.

It is surprising that as 2-ethylpyrrole appears to be almost instantaneously formed, it never exceeds 70% of the total ethylpyrrole isomers. It would be predicted that, due to aromatic character, the 2-ethylpyrrole would be the most stable isomer by over 20 kcal mol⁻¹ [6]. Depletion *via* reaction 8 obviously complicates the overall scheme and it is possible that the other substituted pyrroles also undergo radical reactions yielding pyrrole or methylpyrrole (IX).

Because of the obvious mechanistic complexities, quantitative deductions based on the outlined scheme may only be regarded as approximate. However, assuming that k_1 is an adequate measure of the 1,4-hydrogen elimination process, it is of

interest to compare the *Arrhenius* parameters with those obtained from other 5-membered ring systems. The values are summarized in Table 2.

Table 2. *Activation Parameters for the Molecular Hydrogen Elimination Reactions of 5-Membered Cyclic Compounds*

Compound	$\log(A/s^{-1})$	E_a [kcal mol ⁻¹]	Ref.
Cyclopentene	13.0	58.8	[1]
	13.3	59.9	[2]
1-Methylcyclopentene	13.4	60.0	[3]
3-Pyrroline	12.3	44.6	[4]
5-Ethyl-1-pyrroline	12.5	55.5	This paper
2,5-Dihydrofuran	12.7	48.5	[5]
2,5-Dihydrothiophene	13.2	54.8	[6]
1-Methyl-3-phospholene	12.1	> 50.0	[11]

The observed trend in activation energies for the compounds previously studied has been qualitatively rationalized by assuming that the energy differences are dependent on the conjugation energy released in the transition state and the 1,4 H–H bond distances [6]. The results for 5-ethyl-1-pyrroline are also in agreement with this. The H–H distances would not be expected to be greatly different to those in cyclopentene, and the conjugation energy in the transition state would be expected to be a little higher. Thus, a slightly lower energy than that for cyclopentene would be predicted. In all the other five-membered heterocyclic compounds studied to date, a quasi-aromatic transition state is possible, leading to a more pronounced conjugative stabilization.

The A-factor for 5-ethylpyrroline is also reasonable compared with that for cyclopentene, as a lowering by at least $10^{0.3}$ would be expected from path degeneracy considerations.

It would appear, therefore, that the approximate rate constants calculated for the molecular hydrogen elimination from 5-ethyl-1-pyrroline are compatible with the 'allowed' 1,4-elimination process proposed and that non-equivalence of the eliminating hydrogen atoms has little effect on the energetics of the reaction.

We thank Dr. *A. F. M. Iqbal* for the sample of N-propylidene-cyclopropylamine.

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