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3. Thermochemical Kinetics of Nitrogen Compounds

Part 4

The Gas Phase Unimolecular Thermal Decomposition of Triallylamine¹⁾by Peter Vitins²⁾ and Kurt W. Egger

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(3. IX. 73)

Summary. The gas phase thermal decomposition of triallylamine was studied in the temperature range 531 to 620 K. The major products observed in the reaction were propylene and 3-picoline. The first order rate constants for depletion of triallylamine, obtained using the internal standard technique, are found to be independent of pressure and conversion, and fit the *Arrhenius* relationship

$$\log(k/s^{-1}) = 11.74 \pm 0.07 - (38.27 \pm 0.19)/\theta \quad \text{where } \theta = 2.303 RT \text{ kcal/mol}$$

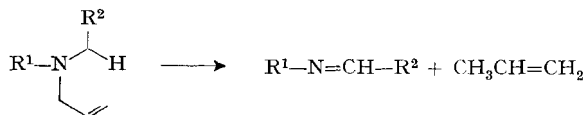
The reaction appears to be homogeneous, as a 15-fold change in the surface-to-volume ratio of the vessel left the rate constants unchanged. The *Arrhenius* parameters are consistent with a molecular elimination reaction involving a six-center transition state, yielding propylene and N-allyl-prop-2-enalimine. It is proposed that the latter product undergoes a 1,5-hydrogen transfer, followed by a ring closure reaction to yield dihydropicoline, which in turn reacts forming 3-picoline *via* a self-initiated decomposition reaction.

A. Introduction. – The thermal chemistry of organic nitrogen compounds has received only scant attention [1]. While the pyrolysis of alkylamines in general proceeds *via* radical chain mechanisms, recent investigations have shown that certain allylamines undergo interesting molecular elimination and rearrangement reactions. Parry & Robinson [2] demonstrated that the thermolysis of cyclopropylamine initially yields N-propylidene amine which is formed either by a concerted process or *via* a biradical intermediate. Maccoll & Nagra [3] and Egger [4] found that the thermal decomposition of N-*t*-butylacetamide and cyclohexylallylamine, respectively, undergo molecular rearrangement reactions *via* a six-center transition state, in analogous fashion to the reactions of oxygenated compounds such as allylethers, allylcarbinols and 'enoic' acids [5]. The thermal decomposition of allylamines also provides a simple, clean method of producing imines in the gas phase.

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The pyrolysis of allylamines is of particular interest as it lends itself to the investigation of substituent effects and the nature of non-synchronicity in six-center transition



states. This study forms a part of a general attempt to gain information about these processes.

B. Experimental. – *Materials:* Triallylamine (TAA) (*Fluka*) was purified further by distillation, and was used with > 99% purity. 1,2,4-Trimethylbenzene (TMB), used as an internal standard, and cyclohexene (CH), used as a diluent (both *Fluka*) were distilled prior to use. The work was carried out using two mixtures of TAA, TMB and CH in ratios of 1:0.83:8.37 and 1:0.85:5.93, respectively. The mixtures were stored under nitrogen.

Apparatus and Procedure. A conventional static system was used and the experimental procedure was essentially identical to that described earlier [4]. The experiments were carried out using a Pyrex reaction vessel of 2148 ml, except for those experiments in which the extent of heterogeneous decomposition was investigated. In this case, an identical vessel of 15-fold larger surface-to-volume ratio packed with Pyrex tubing was used.

The starting mixture was injected into the reaction vessel, and the initial pressure measured. In some experiments the overall pressure change was determined. The products non-condensable at -196° were either pumped away or transferred to a gas burette by an automatic *Toepler* pump. A light fraction was then distilled at -130° .

Analysis. The gas chromatographic analysis of the experiments was carried out using a *Carlo Erba* model G1 Fractovap instrument equipped with a flame ionization detector and an *Infotronics* Model CRS-208 automatic digital integrator. A 3m glass column packed with Chromosorb 103 was used at an operating temperature of 250° and with a flow rate of $23 \text{ cm}^3/\text{min}$. Good base line separation was obtained.

The following retention times were observed: cyclohexene, 5.3 min; TAA, 4.4 min; 3-picoline, 12.9 min; and TMB, 17.8 min. The relative response factors agreed with those expected for flame ionization detection. The GLC. analyses which were usually carried out in duplicate in 75% of the experiments agreed to within 1% or better. As an additional control on the data, six analyses were also carried out using a Model 810 F and M gas chromatograph equipped with thermal conductivity detectors, a "disc" integrator, and a 4 m, 0.6 cm column packed with 20% Carbowax 20M on Chromosorb W. The two methods agreed within 1% the largest scatter being 10%.

Conversions based on 3-picoline, were calculated using relative response factors of TAA and 3-picoline of 1.5 and 1.0 respectively determined using mixtures of the two compounds in a known ratio.

Product Identification. Propylene, which constituted all of the material distilled at -130° , was identified by NMR. and GLC. using a silicagel column. 3-Picoline, which was the other major product, was identified by separate experiments in which TAA was pyrolyzed to 100% conversion, followed by distillation of the more volatile materials at -90° . The product was distilled at 0° and identified by GLC. and NMR. The following absorptions (in τ) were observed: CH_3 7.67, 31.5; H-2 1.45, 7.3; H-4 2.51, 8; H-5 2.85, 9.5; H-6 1.45, 7.3. The spin-spin coupling constants were $J_{4,5} = 7.5 \text{ Hz}$ and $J_{5,6} = 5.0 \text{ Hz}$.

C. Results. – The thermal decomposition of TAA was studied in the gas phase in the temperature range 531 to 620 K. The principal products of the reaction are propylene and 3-picoline. Small amounts of hydrogen were observed and there were indications that materials of higher molecular weights were also formed.

First order rate constants (k_1) for the depletion of the substrate, obtained using the internal standard technique, remained invariant over an approximately tenfold

Table 1. Kinetic Data for the thermal unimolecular Decomposition of Triallylamine (TAA) in the Gas Phase

Temp. [°K]	Pressure [Torr]		Time [min]	Conversion [%]		3-Picoline [%]	Mix ^{a)}	$k \times 10^6$ [s ⁻¹]	Hydrogen [%]
	Total	TAA		GLC.	C ₃ H ₆				
531.0	104.2	10.21	8	4.9			B	10.78	
531.9	111.4	10.9	10	6.0			B	10.36	1.5
535.4	135.0	13.2	20	14.0		5.1	B	12.58	1.9
536.7	100.3	9.8	30	23.1	20.3	10.0	B	14.56	
534.6	130.4	12.8	60	36.0		15.0	B	12.41	9.3
536.3	36.3	17.4	75	40.8	35.5		A	10.78	
536.6	139.0	13.3	100	59.2		25.4	B	14.94	2.1
535.9	139.7	13.7	120	61.9		28.6	B	13.40	2.3
532.5	155.3	15.2	150	63.5		38.2	B	11.19	
556.0	112.2	14.3	5	13.4		4.5	C	47.88	
556.5	69.1	8.9	5	13.6		3.1	C	48.73	
557.0	132.2	17.0	10	26.7		10.0	C	51.67	
556.6	32.4	4.2	15	34.8			C	47.57	
557.5	56.5	7.3	17	37.8			C	49.74	
555.6	51.7	6.7	20	41.3	41.3		C	44.35	1.6
556.5	65.6	36.4	20	44.3		16.3	D	48.72	
558.9	118.6	15.3	30	65.6		24.6	C	59.36	
557.5	61.4	7.9	45	76.0	74.8	36.2	C	52.89	3.6
584.8	55.6	7.2	2	28.3		6.2	C	277.7	
585.3	22.6	2.9	3.5	46.7			C	299.7	
583.6	26.8	3.5	4	43.8			C	240.3	
578.1	68.1	8.8	4	37.4			C	194.9	
580.5	66.9	8.6	6	54.8	52.6	17.1	C	220.4	4.8
586.3 ^{d)}	58.1	5.7	3	38.5		10.4	B	269.9	
585.2 ^{d)}	134.9	13.2	5.5	57.4	45.5	19.7	B	258.6	
576.1	149.5	19.2	7	49.4		21.8	C	162.2	
583.0	51.2	6.6	7.1	61.4	59.0	33.7	C	223.4	
584.6	177.5	22.8	8	71.6		34.3	C	262.5	
617.5	64.5	8.3	2	86.3		37.4	C	1654	
617.8	96.3	12.4	2	86.6		46.5	C	1673	
623.0	121.4	13.5	2	91.7		55.6	E	2079	
614.4	38.5	5.0	2.5	86.6			C	1329	
626.0	61.4	7.9	3	98.5	90.6		C	2324	
617.8	59.6	7.7	3.1	95.3	95.8	50.1	C	1648	
617.0	92.7	11.9	3.1	93.9	81.5	48.1	C	1502	

a) A-TAA: 1,2,4-TMB = 1:0.915; B-TAA: 1,2,4-TMB: C₆H₁₀ = 1:0.83:8:37; C-TAA: 1,2,4-TMB: C₆H₁₀ = 1:0.85:5.93; D-TAA: 1,2,4-TMB = 1:0.70; E-TAA: 1,2,4-TMB: C₆H₁₂ = 1:0.78:7.17. b) Expressed as the percentage of the initial TAA. c) Based on GLC results.

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

change in substrate pressure and for conversions varying between 4 and 98%. Diluent gas also had no effect.

Apart from the most reliable internal standard technique for obtaining the net conversion, these can also be calculated from pressure changes and product yields. The data in Table 1 show that conversions calculated on the basis of propylene are up to 12% lower and those based on pressure changes up to 14% lower when compared with those obtained using the internal standard technique. This finding is attributed to secondary reactions of the shortlived imine product which ultimately lead to polymerization. The conversions based on 3-picoline show interesting behavior as they are low and vary depending on the net (internal standard) conversion, being as little as 23% of the expected 3-picoline in experiments of low conversion and reaching 52% in the higher ones.

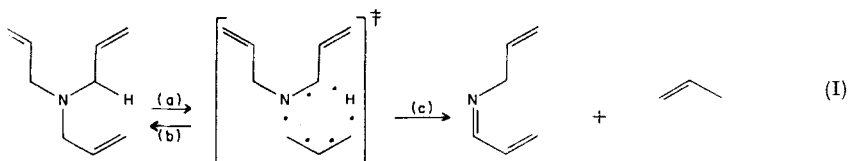
A least mean square analysis of an *Arrhenius* plot of the first order rate constants (based on the internal standard) listed in Table 1 yields the following relationship:

$$\log (k_1/\text{s}^{-1}) = (11.74 \pm 0.08) - (38.27 \pm 0.19)/\theta$$

The errors quoted are standard deviations.

Heterogeneous decomposition of TAA is seen to be unimportant, as the results obtained using a packed vessel of 15-fold greater surface-to-volume ratio agree with the results using the unpacked vessel.

D. Discussion. – The gas phase thermal decomposition of TAA follows first order kinetics and appears to be free of heterogeneous reaction paths. In analogous fashion to the pyrolysis of N-allylcyclohexylamine [4] the reaction proceeds *via* the molecular



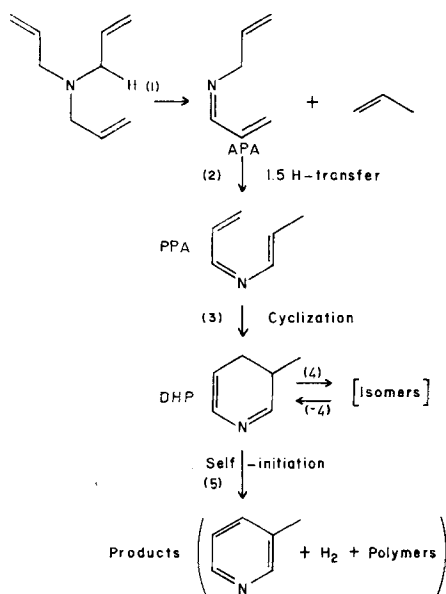
elimination of propylene as shown in Equation (I), followed by a series of fast intramolecular rearrangements leading ultimately to picoline.

The reaction manifests a low preexponential factor ($\log A/\text{s}^{-1} \approx 11.74$) which on the basis of transition state theory (using a transmission coefficient of unity) corresponds to a net entropy change of $8.1 \text{ cal K}^{-1} \text{ mol}^{-1}$. This is consistent with a concerted process and the formation of a cyclic 6-center transition state (equation I) [6]. Using the method of *O'Neal & Benson* [7] [17] an A-factor of $10^{11.5}$ can be calculated in good agreement with the experimental value of $10^{11.74} \text{ s}^{-1}$.

In analogy with the thermolysis of N-allylcyclohexylamine [4], recently investigated in this laboratory, TAA is expected to yield N-allyl-prop-2-en-aldimine (APA) besides propylene as a primary product. From inspection of molecular models it is readily seen that APA must be formed in the *cis* configuration.

Liquid phase studies have shown [8] that for N-allylaldimines only one of the two geometrical isomers (assigned the *trans* structure) is always observed. Neither thermal nor acid catalyzed *trans-cis* isomerization could be induced. Accepting the *trans*-

Scheme for Thermal Decomposition of TAA



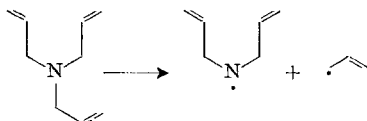
isomer to be thermodynamically significantly more stable with respect to the *cis* when compared with the parent olefin, it must then be concluded that at our reaction conditions *cis-trans* isomerization must be a very facile process. Three basically different mechanisms for the *trans-cis* isomerization of imines can be visualized [9]: a) Torsional motion *via* a homolytic splitting of the π -electrons, b) Surface assisted heterolytic or partially heterolytic polarization splitting of the π -electrons and c) a 'lateral shift' of the nitrogen substituent in the molecular plane. Assuming that the A-factor is the same as for but-2-ene isomerization [16], and using a value of 65.8 kcal mol⁻¹ for the C=N π -bond energy [10], the rate constant for the homolytic mechanism (a) is estimated to be $\log k_{cis-trans} = 14-53.2/\theta$. Hence, for *cis-trans* isomerization to be a facile process, mechanism (c) must be operative in gas phase.

It is then to be expected that equilibrium between *cis*- and *trans*-N-allylpropenaldimines (APA) is established fast. Apart from *cis-trans* isomerization, *cis*-APA formed as primary product can undergo a facile 1,5-hydrogen transfer reaction to yield the conjugated trienyl product N-propenyl-prop-2-enaliminine (PPA). Considering that the activation parameters for analogous reactions of alkenes and oxygenated compounds *via* six-center transition states are usually similar [5] [6], it is reasonable to assume that similar to the rearrangement reaction in *cis*-1,3-hexadienes [12], the half-life of APA for this reaction at mid-temperature is 1.2 seconds. In turn PPA in analogy with 1,3,5-heptatrienes, is expected to react further (half-life of about 0.2 seconds [13]) by concerted ring closure to yield the 2,3-dihydronicotinic acid (DHP) which reacts further *via* a series of 1,5-hydrogen shifts to yield six isomers. Due to the lack of thermochemical data on imines, it is not possible to estimate the relative stabilities of these isomers and 3,4-DHP will be used for purposes of discussion.

The formation of 3-picoline as a major product and of hydrogen are now readily explained as arising from the decomposition of DHP. It has been established [14] that the analogous 1,3-cyclohexadiene decomposes to yield benzene, cyclohexene and hydrogen *via* a self-initiated radical chain at conditions similar to those used here. For conditions of very low pressure, a molecular mechanism has been found [18]. Self-initiation results in the formation of the cyclic allyl and dienyl radicals, and the latter forms the aromatic molecule through a facile loss of a hydrogen atom. Since no tetrahydro-3-picoline is observed amongst the products, it appears that the former radical preferentially undergoes addition reactions rather than hydrogen abstraction, ultimately leading to the formation of high boiling materials. The fact that considerably less hydrogen is formed than 3-picoline suggests that the major mode of reaction of the hydrogen atoms is addition, which is in line with estimates of the relative rates of addition to abstraction of $k_{\text{add}}/k_{\text{abstr}} \simeq 45$ [15].

The data in Table 1 reveal that the yield of 3-picoline is comparatively larger with experiments carried out to higher conversion than those of low conversion. This result suggests that at low concentration of dihydropicoline some other modes of depletion apart from self-initiation are more important, *e.g.* a *Diels-Alder* addition to a double bond. At higher conversions, the amount of picoline equals up to one half the amount of starting material consumed as would be expected on the basis of the outlined overall reaction scheme.

The pyrolysis of TAA to propylene and picoline could conceivably occur *via* a radical route. In such a process, the initiation step would involve rupture of the C–N bond (63.8 kcal/mol) [1] as follows:



Characteristic of radical chain reactions, products due to chain termination should have been observed namely, hexa-1,5-diene and 4-phenyl-but-1-ene (due to the toluene diluent). Due to the absence of such products and the expected sensitivity of the rate constants to pressure and radical trap diluents, a predominant radical route appears unlikely.

Furthermore, the formation of 3-picoline as the only major product apart from propylene cannot be explained by such a radical process.

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4. Alkylierung der 3-Acyl-thio- und -dithio-carbazinester-Gruppierung —CO—NH—NH—CS—YR

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(24. X. 73)

Summary. 3-Benzoyl-thiocarbazic acid O-methyl ester **7a** and 3-benzoyl-dithiocarbazic acid methyl ester **7b** are methylated, in presence of alkali, at the SH group of **1a**, the ene-thiol tautomer of **1**, to give the 3-benzoyl-isothiocarbazic acid O, S-dimethyl ester **8a** and the 3-benzoyl-isodithiocarbazic acid dimethyl ester **8b** resp., which clearly differ from the N-methylated compounds **11a** and **12a** or **11b** and **12b** prepared from the two N-methyl benzohydrazides **9** and **10** resp. (melting points, thin-layer chromatography and NMR. spectra).

The previously reported [1] ring closure of 3-(ω -chloroalkanoyl)-thiocarbazic acid O-alkyl esters and -dithiocarbazic acid alkyl esters can be interpreted as an intramolecular auto-alkylation of —CO—NH—NH—CS—YR : the 3-(chloroacetyl)-compounds **2** are *S*-alkylated (ene-thiol form) to the six-membered thiadiazinones **4**, but the 3-(3-chloropropionyl)-compounds **3** are *N*-alkylated to the pyrazolidinones **6**, the five-membered ring being preferred in the latter case to the seven-membered ring **5** which would be formed by S-alkylation. Hence the position of alkylating attack depends on the size of the ring to be formed.

As a consequence, starting from 3-(4-chlorobutyryl) compounds **13**, an alternative between the two N-alkylation products **14** (five-membered ring) and **15** (six-membered ring) would be expected. On the contrary however, a combination of 1,3,4-thiadiazole ring closure and chlorine elimination predominates, giving the 5-(3-hydroxypropyl)-1,3,4-thiadiazoles **16**. This reaction may proceed *via* the butyrolactone intermediates **18** and could therefore be interpreted as *O*-alkylation followed by rearrangement.

Bei den kürzlich beschriebenen Ringschlüssen [1] von 3-Chloracetyl-thiocarbazinsäure-O-alkylestern **2** und von 3-(3-Chlorpropionyl)-thiocarbazinsäure-O-alkyl- und -dithiocarbazinsäure-alkylestern **3** (Y = O, S) mit Alkali handelt es sich um intra-