Thermochemical Kinetics of Nitrogen Compounds. Part III.* The Unimolecular Thermal Decomposition of *N*-Allylcyclohexylamine in the Gas Phase

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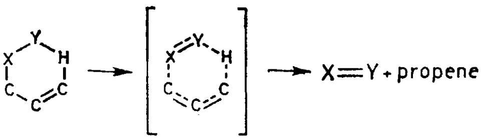
The thermal. unimolecular gas-phase decomposition of *N*-allylcyclohexylamine to cyclohexylimine and propene has been studied in the temperature range 562—652 K. The rate constants for the homogeneous depletion of the starting material. using the internal standard technique fit the Arrhenius relationship $\log k/\mathrm{s}^{-1} = 11{\cdot}44 \pm 0{\cdot}21 - (42{\cdot}18 \pm 0{\cdot}57\ \mathrm{kcal\ mol}^{-1})/2{\cdot}303RT$) and were independent of the initial pressure in the range 15—150 Torr.† When toluene or ethylbenzene were added as diluent and potential radical traps. rate constants calculated on the basis of the products formed and the pressure changes observed were consistent with the internal standard results. The homogeneiety of the reaction was demonstrated by the concurring rate constants obtained in a packed reaction vessel with a 15-fold larger surface:volume ratio. The observed activation parameters are consistent with a concerted mechanism involving a cyclic six-centre-transition state and they are in good agreement with those reported for the analogous decompositions of allyl ethyl ether. but-3-en-1-ol, and but-3-enoic acid.

THERMOCHEMICAL kinetic and thermodynamic gas-phase data on organic nitrogen compounds are very limited.[1-7] For amines and related compounds only a few kinetic studies of thermal decompositions have been reported.[5] The pyrolysis of benzylamines and alkyl-substituted hydrazines have been studied at very low pressure by Golden *et al.*[6] Parry and Robinson recently reported the gas-phase pyrolysis of cyclopropylamine.[7] By flushing allylamines in a stream of nitrogen down a Vycor pyrolysis tube filled with Pyrex helices at temperatures of *ca.* 500 °C, Hartz[8] observed both apparent free radical and concerted decomposition paths. The effect of surface on the pyrolysis mechanism has not been investigated.

This paper reports the thermal decomposition of *N*-allylcyclohexylamine as part of an overall effort to obtain more quantitative information about the nature and effect of polar character in concerted reactions in the gas phase. The kinetics of the thermal decomposition of a number of substituted allylamines and related compounds which should all follow the general reaction scheme indicated in equation (1) (involving a six-centre transition state) are under investigation.



(1)

EXPERIMENTAL

Materials.—*N*-Allylcyclohexylamine (ACA) and *p*-ethyltoluene (PET) (used as as internal standard), supplied by Aldrich, were further purified by distillation. Both samples contained <1% of isomeric impurities, which did not affect the kinetic analysis of the system. Ethylbenzene (EB) (used as diluent) of >99·5% purity was obtained from Fluka. Two mixtures with ACA : PET mole ratios of 0·9428 (mixture I) and 1·1285 (mixture II) were used. To mixture I, ethylbenzene was added as a diluent to give an EB : PET molar ratio of 3·55. The mixtures were stored in the cold under dry nitrogen.

Apparatus and Procedure.—The conventional static reaction system used for the kinetic studies was essentially as described previously.[9] A cylindrical Pyrex reaction vessel (2053 ml) was normally employed. For testing heterogeneity an equivalent vessel packed with thin-walled Pyrex tubing giving a surface : volume ratio 14 times that of the unpacked vessel was used. Experiments carried out at a 'low' temperature of 545 K in a Teflon-coated stainless steel reactor resulted in the same products but gave rate constants up to five times greater than those extrapolated from the results obtained using the glass vessel in the temperature range 562—652 K. Due to the obvious surface effect, these results have been disregarded.

The procedure was as described previously.[10] Mixture I or II was injected into the reaction vessel and the initial pressure was measured. In some experiments, toluene as diluent was injected immediately after the addition of the starting mixture. Prior to quenching the reaction the pressure was measured and subsequently the dead space was evacuated. Amounts of non-condensible material at the liquid nitrogen temperature were negligible. The material collected was warmed to −60 °C and propene was transferred to a gas burette by means of an automated Toepler pump. This fraction as well as the product retained at −60 °C were removed from the system and analysed by g.l.c.

Analyses.—G.l.c. analyses of liquid portions of the starting and product mixtures were carried out using a Carlo Erba model G 1 Fractovap instrument equipped

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† Throughout this paper 1 Torr = (101·325/760) kN m^{-2} and 1 cal = 4·184 J.

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with a flame ionization detector (f.i.d.). A column (3 m × 2 mm) containing Chromosorb WAW 80—100 coated with 10% silicones oil DC 550 and operated at 100 °C gave quantitative separation of the products whereby the following retention times (in minutes) were observed: toluene 2·7, EB 3·7, PET 5·9, major reaction product (see text) 8·5, ACA 9·9.

An Infotronics model CRS-208 automatic digital integrator was used to measure the peak areas. The composition of the starting mixtures were checked daily and were found to be constant over a period of several weeks. The following ratios were observed: ACA : PET = 0·8008 ± 0·010 (mixture I) and 0·9579 ± 0·011 (mixture II) and EB : PET = 3·37 ± 0·15. Compared with the molar ratios of the starting mixtures relative response factors with respect to PET of 0·8496 (mixture I) and 0·8488 (mixture II) for ACA and 0·9493 for EB are obtained, in agreement with expectation. The g.l.c. analyses of the product mixtures, carried out at least in duplicate, always agreed within 1% and were generally within 0·3%.

One of the primary products, identified as cyclohexylimine, underwent partial decomposition (O_2,H_2O, polymerization) upon storage. To check the reliability of the g.l.c. analyses the product mixtures of six experiments were additionally analysed using an F and M model 810 gas chromatograph equipped with thermal conductivity detectors (t.c.), a ' Disc ' integrator and a column (4 m × 0·25 in) packed with Chromosorb P 60—80, coated with 10% silicone oil DC 710. Operation at 155 °C gave an apparent baseline separation of the compounds. However, in contrast to the results obtained using the Carlo Erba f.i.d. equipment the major product, cyclohexylimine (or its hydrolysis product cyclohexanone), was not observed, despite the fact that in both analyses silicone oil columns were used.

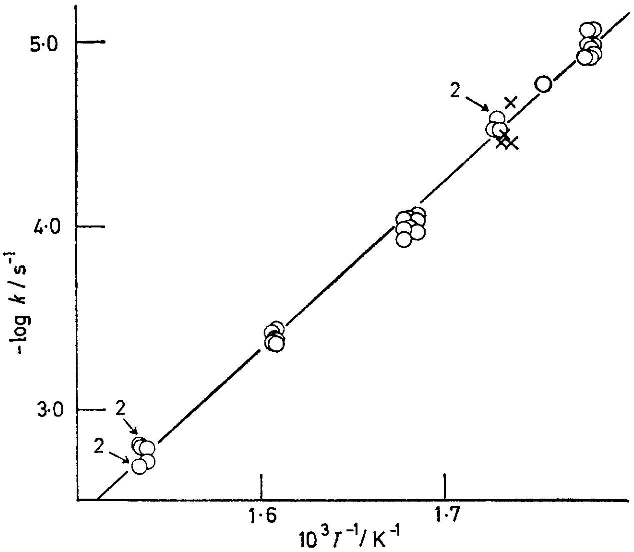
In general, primary or secondary amines in contrast with tertiary amines showed a tendency to undergo partial decomposition or to be irreversibly retained using the F and M equipment. This is attributed to surface effects in connection with larger dead spaces. Nevertheless the rate constants calculated from the analysis using these two systems (based on the internal standard), agreed on average within 2·15%, with a maximum difference of 3·7%, despite the largely different response factors operative in the t.c. and f.i.d. detection of the materials.

N.m.r. analyses were used to help identify cyclohexylimine as a primary product. The n.m.r. spectrum of the collected product from g.l.c. analysis is consistent with the presence of either cyclohexylimine or cyclohexanone apart from the fact that the =NH proton (which is expected to show up as a broad signal at τ 1—2) could not be unambiguously identified.

Identification of Products.—The major gaseous product has been identified by n.m.r. and g.l.c. analyses (silica gel column) to consist of >95% propene. The formation of cyclohexylimine as a primary product is established by (*a*) hydrolysis of the product to cyclohexanone, which has been identified unambigously; (*b*) pyrolysis of the starting material in presence of methylamine or propylamine to yield *N*-methyl- or -propyl-cyclohexylimine; and (*c*) the n.m.r. spectrum of the product.

RESULTS

The thermal decomposition of ACA in the gas phase at 562—652 K yields propene and cyclohexylimine as the only major observable products. First-order rate constants (k_1) for the depletion of starting material have been obtained using the internal standard technique. The relevant experimental details and results are summarized in Table 1 and an Arrhenius plot of the rate constants is shown in the Figure. Consistent values for k_1 have been obtained despite variation in the initial pressure between 15 and 150 Torr and conversions ranging from 4·7 to 75·6%. Either ethylbenzene or toluene have been added as diluent and as hydrogen donors (RH) in case of radical-initiated decomposition. No variation in rate constants with initial ratios of RH : ACA varying from 5 to 90 could be observed, indicating the absence of an appreciable radical decomposition path. This is further substantiated by the same relative concentrations of EB and PET obtained in the product and the starting mixture (Table 1).



Arrhenius plot for the thermal decomposition of *N*-allylcyclohexylamine in the gas phase. ○ and × indicate runs carried out in the non-packed and packed vessels respectively. Numerals indicate overlapping points

Conversions based on pressure changes were on average *ca.* 15% and at a maximum 40% lower than those based on the internal standard. Considering the experimental errors involved in measuring relatively small pressure changes and the fact that one of the products, cyclohexylimine is somewhat unstable under the conditions used, the agreement with the internal standard results can be considered satisfactory.

The amount of products formed can also, in principle, be used to calculate the degree of conversion and the rate constants. Conversions based on propene recovered ranged between *ca.* ±25% of the conversions calculated from the internal standard and were on average about 9% lower. These differences can be attributed to shortcomings in the experimental procedures, particularly the problems related to quantitative separation and collection of the relatively small amounts of propene formed (10^{-5}—5×10^{-4} mol) in the presence of an up to 100-fold excess of starting materials and other compounds. Conversions based on cyclohexylamine (CI) formed have also been incorporated into Table 1. These values have also been derived from the internal standard method, *i.e.* the CI : PET ratio observed in the g.l.c. analyses corrected for the differences in relative response factors estimated at 1·5 and 1 respectively. For the lowest temperatures and conversions excellent agreement was obtained with the values from the depletion of ACA.

With increasing temperature and extent of reaction the conversions calculated from the amounts of CI formed are consistently too low indicating a progressive loss of cyclohexylimine. At the highest temperatures and conversions only *ca.* 25% of the CI formed is accounted for in the g.l.c. analysis. The partial loss of CI with increasing concentration and temperature is not surprising considering the readiness of imines to undergo oligomerization in the liquid phase. Small amounts of higher molecular weight materials have been observed in the g.l.c. and n.m.r. analyses.

TABLE 1

Thermal, unimolecular decomposition of ACA in the gas phase to form propene and cyclohexylimine (CI)

	Starting material					Products		Conversions (%) based on				$10^4k/\mathrm{s}^{-1}$ based on g.l.c.
T/K	t/min	Mixture [a]	p_0/Torr [b]	10^3(ACA)/M	$\frac{\mathrm{RH}}{\mathrm{ACA}}$ [c,d]	$\frac{\mathrm{EB}}{\mathrm{PET}}$	$\frac{\mathrm{ACA}}{\mathrm{PET}}$	G.l.c.	Δp	C_3H_6 formed	CI formed	
563·1	65	I	20	0·2005	50·8 T	3·46	0·726	4·66			4·7	0·1225
562·4	90	II	145·7	1·566	14·6 T		0·881	5·48			4·3	0·1044
562	120	II	56·4	0·6066	4·44		0·855	8·29		6·13	6·2	0·1202
561·6	120	II	58·7	0·6318	18·7 T		0·864	7·31			6·0	0·1054
561·5	180	II	19·3	0·2077	67·6 T		0·851	8·78		8·90	10·6	0·08507
562·4	150	II	38·9	0·4181	27·4 T		0·892	7·43			7·3	0·08577
561·9	240	II	32·6	0·3507	48·9 T		0·799	14·3			10·5	0·1075
561·6	342	II	33·4	0·3596	29·7 T		0·759	21·3			11·7	0·1166
570·0	112	II	18·6	0·1972	62·3 T		0·853	10·8		6·36	10·6	0·1698
578·5	35	II	34·8	0·3636	32·5 T		0·916	5·34			6·1	0·2614
575·9 [f]	60	II	37·4	0·2562	39·5 T		0·886	7·31		8·09	6·9	0·2110
578·3	71	II	12·7	0·1327	86·6 T		0·856	10·2			10·6	0·2595
579·5 [f]	75	II	13·0	0·1206	89·9 T		0·834	12·8			10·7	0·3034
575·9 [f]	97	II	(54·2)	0·1856	9·89T		0·778	19·5			7·4	0·3725
577·8 [f]	130	II	(54·2)	0·1480	12·6 T		0·729	24·6			10·2	0·3623
577·1	135	II	48·5	0·3315	31·4 T		0·742	23·3			10·1	0·3269
578	180	II	28·5	0·298	38·2 T		0·686	28·2			16·8	0·3074
594·1	10	I	140·8	1·338	4·83	3·46	0·719	5·54			3·7	0·9504
595·0	20	I	23·4	0·222	28·4 T	3·46	0·672	11·7		14·6	6·3	1·039
596·2	38	I	42·8	0·4053	45·5 T	3·48	0·576	24·4	16·4	17·5	6·6	1·225
596·2	60	I	51·0	0·483	4·83	3·42	0·518	31·9	28·6	27·7	9·7	1·068
596·2	64	I	144·4	1·367	21·8 T	3·47	0·535	29·7	26·3	22·6	10·7	0·9179
593·8	91	I	48	0·4564	4·83	3·39	0·414	45·7		36·5	15·7	1·118
594·9	120	I	74·2	0·7041	4·83	3·26	0·407	48·8	44·8	39·2	23·6	0·9296
593·6	150	I	48·3	0·4594	23·0 T	3·42	0·350	54·0	54·3			0·8644
621·8	3·25	II	14·8	0·1439	4·44		0·867	8·28			5·6	4·432
621·8	5·0	II	(41·0)	0·1594	12·6 T		0·832	12·0			7·3	4·261
622·5	11·0	II	37·3	0·3622	4·44		0·705	25·4	21·9	24·2	10·2	4·446
622·0	20·5	II	(144·2)	0·1844	40·4 T		0·573	39·5		40·2	17·5	4·080
622·5	30	II	78	0·7574	16·5 T		0·474	49·9	55·2		15·5	3·841
622·0	41	II	131·8	1·2808	15·5 T		0·379	59·9	55·4		15·5	3·713
651·6	3	I	55·6	0·4817	4·83	3·34	0·554	30·8	27·3	27·7	11·6	20·47 (20·76)
650·4	4·16	I	43·1	0·3741	4·83	3·12	0·490	38·9	32·5	38·5	12·8	19·68 (19·27) [e]
650·4	5	I	158·1	1·3723	4·83	3·41	0·489	38·9	22·1	30·5	14·4	16·44 (16·00) [e]
651·6	5	I	84·5	0·7321	4·83	3·10	0·432	46·1	27·6	37·9	19·5	20·62 (20·78)
651·6	7	I	84·7	0·7338	4·83	3·31	0·417	47·9	40·0	41·0	13·9	15·53 (14·97) [e]
651·6	9·6	I	131·5	1·1393	4·83	3·45	0·316	60·5	41·7	60·0	16·6	16·03
651·6	15·083	I	31·7	0·2456	4·83	3·41	0·195	75·6	65·5	75·7	27·8	15·59 (15·92) [e]

[a] I and II refer to mixtures I and II (see text). [b] Initial pressure of the reaction mixture without the pressure of toluene, added as a diluent in most experiments. [c] RH refers to the amount of aromatic compound (toluene, ethylbenzene, or *p*-ethyltoluene) present in the system. [d] T indicates the addition of a variable excess of toluene. [e] These data are based on g.l.c. analyses using different procedures and instrumentation. For details see Experimental section. [f] Experiments carried out in the packed reaction vessel.

Least squares analysis of the rate constants listed in Table 1, disregarding those obtained for the packed vessel, yields the Arrhenius relationship (2). The errors are standard deviations. Rate constants obtained for the

$$\log (k/\mathrm{s}^{-1}) = 11\cdot44 \pm 0\cdot21 - (42\cdot18 \pm 0\cdot57\ \mathrm{kcal\ mol^{-1}})/(2\cdot303RT) \quad (2)$$

packed vessel are in general agreement with those for the empty vessel ranging between ±30% of the calculated values.

DISCUSSION

The first-order kinetics and the essentially homogeneous and concerted nature of the process are apparent from the experimental data. Consideration of the primary products cyclohexylimine and propene and the reaction parameters observed leaves little doubt that the reaction proceeds *via* the six-centre reaction path indicated in equation (1). The pre-exponential factor of $10^{11 \cdot 45}$ s^{-1} implying an entropy loss of 9·6 cal K^{-1} mol^{-1} is consistant with a six-centre cyclic transition state. Based on the method outlined by O'Neal and Benson[11] a log A factor of 11·5 can be estimated, in good agreement with experiment.

The Arrhenius parameters are summarized in Table 2. The close agreement of the parameters observed for the chemically quite different reactants listed in Table 2, the excellent agreement between observed and predicted A factors, and the low activation energies when compared with the dissociation energies of the bonds involved[1] strongly support the concept of a concerted process and a six-centre cyclic transition state being involved in all these reactions.

Consideration of the activation energies of the reaction systems in Table 2 from the point of view of the bond dissociation energies involved (listed in the last three columns of Table 2) reveals no simple relationship. In all these reactions an allyl–X bond and a H–Y bond are broken and a X=Y π-bond and a C=C–H bond in propene (108 kcal mol^{-1}) are formed. The heats of the reaction range from −5 to +14 kcal mol^{-1}. In this context the absence of a significant effect on the activation energy from the very stable π-bond formed in CO_2 in the case of the butenoic acid reaction is particularly noteworthy. Work presently in progress on the pyrolysis of a variety of allylamines should provide essential information concerning the substituent effect involved in these reactions.

TABLE 2

Thermal decomposition of molecules of the type allyl XYH *via* a six-centre transition state to form propene [equation (1)]

			$\log(A/s^{-1})$				Bond dissociation energy/kcal mol^{-1} [c]			
Reactant	X	Y	Obs. [b]	Calc.	E_a/kcal mol^{-1}	Ref.	Allyl–X	H–Y	X=Y [d]	ΔH_r/kcal mol^{-1} [g]
But-3-en-1-ols	CH_2	O	11·65	11·7	41·0	12, 13	72·4	103·6	72·8	13·5
	CHMe	O	11·9	11·7	40·9	12, 13	71·5	103·6	75·8	9·9
	CMe_2	O	12·1	11·9	40·7	12, 13	68·3	103·6	77·8	7·3
Enoic acids	C=O	OH	11·3	11·1	40·6	12, 14	68	110·4	100	−5·1
Allyl ether	O	C_2H_4	(11·7) [a]	11·7	44·7	15	70·3	93·3	75·8	−0·6
Allylamine	NH	C_6H_{10}	11·5	11·6	42·2	This work	72·7	95	(68) [e]	(9·2) [f]

[a] Estimated value. [b] Obs. and calc. stand for observed and calculated[11,12] A factors respectively. [c] Data have been taken from ref. 1. [d] The π-bond strength X=Y is defined as the heat of the reaction to form the ·X–Y· biradical. [e] ΔH_f^0(cyclohexylamine) taken as − 25·2 kcal mol^{-1}. [f] Based on ΔH_f^0(allylcyclohexylamine) − 6·1 kcal mol^{-1} (calculated using the group additivity concept[4]) and on an estimated value of − 1·73 for cyclohexylimine. [g] Heat of the decomposition reaction.

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