The Thermochemical Kinetics of the Retro-' ene ' Reactions of Molecules with the General Structure (Allyl)XYH in the Gas Phase. Part IX.† Unimolecular Thermal Decomposition of Allylmethylamine

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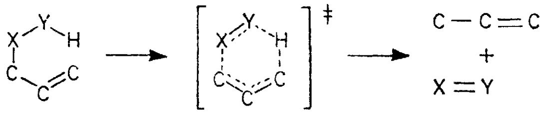
The gas-phase unimolecular thermal decomposition of *N*-allyl-*N*-methylamine (AMA) was investigated in the temperature range 602—694 K. The principal products are propene and methyleneamine. First-order rate constants, calculated using the internal standard method, fit the Arrhenius relationship (i). The reaction appears

$$\log (k_1/\mathrm{s}^{-1}) = (11{\cdot}37 \pm 0{\cdot}56) - (43{\cdot}38 \pm 1{\cdot}62\ \mathrm{kcal\ mol}^{-1})/2{\cdot}3RT\ § \qquad \text{(i)}$$

to be homogeneous as a 15-fold change in surface : volume ratio of the reaction vessel yields no significant change in the rate constants. The decomposition of AMA follows a retro-' ene ' mechanism *via* a 6-centre transition state. The Arrhenius parameters for AMA decomposition are compared with those observed for other alkylallylamines. The significance of these observations in an evaluation of the extent of charge separation, *i.e.* non-synchronism, in the transition state is discussed.

EARLIER studies of the thermal decomposition of *N*-substituted allylamines [1-3] have shown that reaction proceeds *via* a retro-' ene ' type mechanism analogous to the reactions of butenols,[4,5] butenoic acids,[5,6] ethers,[5,7] and certain olefins such as hepta-1,6-diene,[8] involving a six-centre transition state (Scheme 1). In the course of previous work from this laboratory [1-3,9] it became evident that the activation energies for *N*-alkylallylamine decomposition are strongly sensitive towards substitution at X and Y. Systematic kinetic studies on these systems should therefore yield interesting information concerning the extent of charge separation, *i.e.* non-synchronism, in the transition state.



SCHEME 1 X = CH_2, CO, or O; Y = O or CH_2

EXPERIMENTAL

Materials.—*Allylmethylamine* (AMA) was obtained from Fluka and purified by g.l.c. Toluene (T) (99·7%), used as an internal standard, was purchased from UCB and recrystallized benzene (B) (99·9%), also used as an internal standard, was obtained from Merck. Hexylamine and n-butylamine, which were used as traps for methyleneamine, were obtained from Fluka.

The following mixtures of starting material and internal standards were used (molar ratios): AMA/T = 0·7950, AMA/B = 0·8242, AMA/B = 1·1997.

Apparatus and Procedure.—The static high vacuum reaction system and procedure used have been described previously.[10] The experiments were carried out in 2148 and 1000 ml vessels. The latter vessel was packed with Pyrex tubing with fire-polished ends resulting in a 15-fold greater surface : volume ratio. Liquid portions of the starting mixtures were injected into a heated dead-space, whence they were immediately expanded into the reaction vessel. The reactions were quenched by rapidly condensing the contents of the vessel into a trap at 77 K. This was followed by the distillation of products of low molecular weight (propene and NH_3) at 173 K. The distillate was then passed through a trap containing phosphorous pentaoxide for the removal of ammonia and then moved to a calibrated gas burette *via* an automatic Toepler pump for propene measurement. The fraction of higher molecular weight was then distilled into a vial at room temperature.

Analysis.—G.l.c. analysis was carried out using an instrument equipped with a flame ionization detector coupled to an automatic digital integrator. A 2·2 m × 2 mm glass column packed with Chromosorb 103 was used throughout at 80° and with a flow rate of 23 ml min^{-1}. Base line separation was achieved and the following retention times (in min) were observed: AMA, 3·5; butylamine, 4·4; benzene, 5·8; toluene, 9·6; hexylamine, 12·0. Separation of *N*-butylmethyleneamine from butylamine and *N*-hexylmethyleneamine from hexylamine proved to be too difficult for quantitative purposes, as expected and verified using the corresponding *N*-methylalkylamines. The column used had been shown to separate amines largely on the basis of size regardless of degree of unsaturation.

With the exception of eight experiments, analyses were carried out in duplicate and found to be reproducible to within 1% or better. In five experiments reproducibility was within *ca.* 4%.

RESULTS

In the temperature range 602—694 K, thermal decomposition of allylmethylamine yields propene as the principal observed product. When the reaction was carried out in

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† Part VIII, K. W. Egger and P. Vitins, *Helv. Chim. Acta*, 1974, **57**, 214.

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

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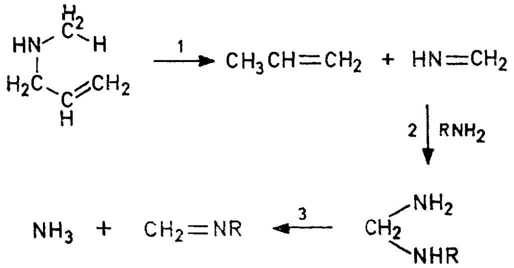
the presence of primary alkylamines, a further product was found and assigned as *N*-alkylmethyleneamine on the basis of g.l.c. retention times. Owing to the virtual inseparability from the diluent amine, more conclusive identification proved too difficult. The *N*-alkylmethyleneamine is formed in the reaction of the amine diluent with methyleneamine,[11] which by analogy with cyclohexyl-,[1] triallyl-,[2] and diallyl-amine[3] is an expected product in the concerted decomposition of *N*-alkyl-*N*-allylamines.



SCHEME 2 Thermal decomposition of AMA

TABLE 1

Kinetic data for the unimolecular decomposition of AMA in the gas phase

T/K [d]	(AMA)$_0$/ Torr	Diluent [a] AMA	t/min	Conversion (%) G.l.c.	Conversion (%) C_3H_6	10^5k_1/ s^{-1} [c]
602·7	21·5		80	18·6	16·8	4·289
602·9	16·5	1·89	60	11·3	13·7	3·325
601·9	16·7		45	7·7	9·5	2·956
601·9	11·4	1·95	40	8·2		3·578
601·5	11·4	1·81	85	20·7		4·550
602·0	9·1	5·18 [b]	120	29·0		4·760
602·8	15·2	2·22	80	17·4		3·991
625·8 P	39·3	4·27	30	21·2		13·25
623·7 P	68·6	4·23	10	12·0		21·25
627·3	19·9	1·12	25	13·2	20·9	9·443
627·4	18·0	2·76	90	58·6	71·6	16·33
626·4	13·3	2·70	65	41·4	48·2	13·73
626·1	40·3	2·30	35	24·2	30·5	13·18
626·8	11·5	3·89	45	44·5		21·84
626·3	71·1	2·06	100	64·0		17·04
626·4	26·3	1·97	65	48·9	55·3	17·23
645·4	17·7	3·72	20	43·3	40·5	45·76
645·8	9·7	4·93	25	49·5	60·6	45·57
645·3	17·7	3·97 [b]	67			43·74
646·4	27·5	2·90	10	21·8		40·94
640·2	20·4	3·06	10		18·8	
646·2	12·4	2·81	15	34·4		46·83
665·3	34·0	1·85 [b]	4	21·0		98·31
668·7	35·5	2·78	7	49·5	52·4	162·6
669·0	25·7	3·23	4	39·6	31·4	210·2
670·4	19·6	2·35	5	38·2	38·1	160·7
669·6	36·5	1·73	6	42·2	40·3	152·4
671·4	28·4	1·77	13·33	72·1		159·8
671·0	19·8	2·32	8	50·0		144·5
670·8	11·2	2·24	5	40·9	43·1	175·1
670·8	25·4	1·67	5	45·6	40·6	203·8
691·9	14·8	2·87	3	57·3		473·2
693·0	9·2	7·17	5	75·1		463·2
692·3	21·5	3·58 [b]	5	73·7		444·6
691·7	19·2	2·71	4	64·0		425·5
694·0	14·8	3·08	3	59·4		501·3
692·7	18·3	3·18	8	86·3		414·1

[a] Diluent hexylamine unless indicated otherwise. [b] Diluent n-butylamine. [c] First-order rate constants based on the internal standard method. [d] P Indicates experiments carried out using a ' packed ' reaction vessel.

As seen from the data presented in Table 1, conversions based on the propene yields agree reasonably well with those using the internal standard technique.* Unfortunately, the difficulty in quantitative analysis of the methyleneamine adduct precluded the determination of the complete mass balance.

On the basis of known thermodynamic data[12] and the incremental additivity method,[13] the equilibrium constant is given by log (K/atm) = 7·8—9·8/2·3RT. Hence, the reaction is essentially thermodynamically irreversible.

Kinetic experiments were carried out using toluene or benzene as internal standard and butyl- or hexyl-amine as a diluent and trap for methyleneamine. The first-order rate constants, listed in Table 1, were independent of pressure and conversion. Least-mean-square analysis of the data in Arrhenius form yields the relationship (1) where the

$$\log (k/\mathrm{s}^{-1}) = (11{\cdot}37 \pm 0{\cdot}56) - (43{\cdot}38 \pm 1{\cdot}62\ \mathrm{kcal\ mol}^{-1})/2{\cdot}3RT \quad (1)$$

errors quoted are standard deviations. The slightly larger than usual errors are attributed to the experimental work-up. The thermal decomposition of AMA appears to be homogeneous as the rate constants obtained using a packed reaction vessel of 15-fold greater surface : volume ratio, agree with those obtained using the unpacked vessel.

It is interesting to note that in two experiments without amine as a diluent, reasonable agreement of the data with experiments employing diluent was obtained. However, methyleneamine could not be identified and presumably polymerized upon condensation from the reaction vessel, as indicated by the presence of some nitrogen-containing high molecular weight material.

DISCUSSION

The pyrolysis of AMA appears to be a homogeneous reaction as indicated by the similarity in rate constants obtained in packed and unpacked vessels. The predominant formation of propene and methyleneamine, and absence of further products, apart from some nitrogen-containing polymer, attributed to imine polymerization, suggests a straight-forward, concerted retro-' ene ' decomposition mechanism. The low pre-exponential factor of $10^{11.37}$ s^{-1} is consistent with the predicted value of $10^{11.2}$ s^{-1} using the method of O'Neal and Benson.[14] Furthermore, the Arrhenius parameters are similar to those obtained for the thermal retro-' ene ' reactions of *N*-allyl-*N*-cyclohexylamine (CAA),[1] triallylamine (TAA),[2] diallylamine (DAA),[3] hepta-1,6-diene,[8] and allyl ethyl ether.[15] The reaction can be visualized as proceeding *via* a six-centre transition state as described earlier.[3]

A comparison of the Arrhenius parameters for AMA

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* While some propene yields seem high, this might be attributed to incomplete removal of ammonia by P_2O_5.

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pyrolysis with those of other allylamines are presented in Table 2. Inspection of the listed A factors reveals good agreement between the observed and predicted values, with the observed values being consistently higher by 0·1—0·2 units in log A and *ca.* 9 kcal mol^{-1} in E_a. Recognizing that there is a loss of three rotors in the transition state and taking the corresponding path degeneracy into account, an average net loss in entropy of *ca.* 4·1 cal mol^{-1} K^{-1} per rotor is calculated, except in the case of CAA where the value is 3·3 cal mol^{-1} K^{-1} per rotor. As reactions with loose six-centre transition states typically exhibit entropy losses of 3·5—4 cal mol^{-1} K^{-1} per rotor, these results indicate a moderately tight transition state for the allylamine retro-' ene ' decomposition.

TABLE 2

Arrhenius parameters for the thermal decomposition of various N-alkyl-N-allylamines

Reactant	log(A/s^{-1}) Obs.	Calc.	E_a/kcal mol^{-1}	Ref.
N-Allyl-N-methylamine	11·4	11·2	43·4	This work
N-Allyl-N-cyclohexylamine	11·4	10·9	42·2	1
Diallylamine	11·4	11·3	38·0	3
Triallylamine	11·7	11·6	38·3	2
N-Allyl-N-methylaniline	13·8 [a]	11·2 [b]	48·5 [a] 42·9 [b]	9
NN-Diallylaniline		11·1	38·2 [c]	19

[a] For decomposition *via* a radical process. [b] For a hypothetical concerted process. [c] Obtained using the predicted A factor and unpublished data.

The activation energies for the concerted alkylallylamine decomposition listed in Table 2, demonstrate a marked effect of substitution on the reaction with differences of 5·4 and 5·1 kcal mol^{-1} for di- and tri-allylamine, respectively, relative to AMA. This difference is clearly outside the range of experimental error (typically *ca.* 0·5 kcal mol^{-1}). The drop in activation energy of 1·2 kcal mol^{-1} exhibited by CAA is probably due to steric constraint.

The effect of substituents at the Y position (Scheme 1) on the activation energies is indicative of polar character in the transition state, since the vinyl group is known to induce a polarizability stabilization on a cation of the order of 13 kcal mol^{-1}.[16,17] Further evidence for this effect is provided by the observation [9] that N-allyl-N-methylaniline (NAMA) is thermolysed *via* a radical mechanism rather than in a concerted fashion. Considering that the phenyl group, as with vinyl, is considerably less effective in stabilizing negative than positive sites,[18] phenyl substitution at nitrogen (*e.g.* NAMA) would be expected to show little effect on the activation energy of the concerted process. On the other hand, as the phenyl group reduces the C–N bond strength by 12·5 kcal mol^{-1},[16] the radical process becomes competitive. Indeed, if we assume competition would be observed for $k_{\text{concerted}} = 0{\cdot}1k_{\text{radical}}$ at the mid-temperature, using the predicted A factor of $10^{11\cdot2}$ s^{-1} for the concerted process, the minimum expected activation energy for the concerted mechanism is calculated to be 42·9 kcal mol^{-1}. This value is essentially the same as that for AMA decomposition.

In view of the fact that the mechanism of the reaction changes from molecular to radical going from DAA to NAMA, it would be of interest to examine the effect of simultaneous substitution at X and Y by substituents which stabilize equally readily on a homo- and heteropolar basis. Exploratory experiments in this laboratory [19] on the decomposition of NN'-diallylaniline show that the reaction is molecular with an activation energy equal to that of DAA and TAA, again pointing to a fair degree of polarization in the transition state.

As anticipated, a comparison of the substituent effects found for the allylamine retro-' ene ' reaction and the well known polar HX elimination reactions reveals considerably greater polarization of the transition state in the latter as indicated by the polarizability stabilizing effect of the vinyl group of 5·1 and 8·0 kcal mol^{-1} respectively. Inasmuch as polar character of a transition state can be identified with non-synchronism, the above conclusions imply that bond breaking and formation is a non-synchronous process in the transition state of allylamine decomposition reactions.

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[18] K. W. Egger and A. T. Cocks in ' The Chemistry of the Carbon–Halogen Bond,' ed. S. Patai, Wiley, New York, 1973, p. 677.

[19] P. Vitins and K. W. Egger, unpublished results.