



ment. The effect of heteroatoms in one of the 6 reactive centers as well as the observed substituent effects suggest the occurrence of a non-synchronous process, *i.e.* significant charge separation in the transition state structure (as indicated in equation 1).

It was then of immediate interest to investigate the effect of R<sup>3</sup>-substituents in order to obtain more information about the polar character of the reaction. It is to be expected [8] that phenyl substituents would have about the same effect, both hetero- or homopolarly as vinyl substituents, and since N-vinyl-N-allylamines would react *via* a different intramolecular route, shown in equation (2), N-allyl-N-methylaniline appeared to be the most reasonable choice for this investigation.



**Experimental.** – *Materials:* N-Methyl-N-allylaniline (MAA), obtained from *Aldrich Chemicals Corp.* was purified by vacuum distillation at 30° and used with 99.4% purity. The sole impurity, N-methylaniline did not affect the rate or course of the reaction. 1,2,4-Trimethylbenzene (TMB), used as an internal standard, was purchased from *Fluka Chemical Corporation*, Switzerland. After distillation it was 99% pure with the other trimethylbenzene isomers as only detectable impurities. Toluene used as a diluent and obtained from *UCB Belgium* was 99.7% pure by gas chromatography. Three mixtures of MAA/TMB of 1.329, 1.037 and 1.461 respectively were used. Two additional mixtures were made up with toluene as a diluent with ratios of MAA:TMB: toluene of 1:0.684:9.1 and 1:0.581:2.308. All ratios are molecular.

*Apparatus and Procedure:* The principal features of the static reaction system have been described earlier [1–4]. A Pyrex reaction vessel of 2148 ml volume was used except for experiments carried out in an equivalent vessel packed with Pyrex tubing affording a 15-fold greater surface to volume ratio. The starting mixture was injected into a heated deadspace above the reaction vessel from where it expanded rapidly into the reaction cell. Pressure measurements were carried out with a PACE pressure transducer. In about half the experiments, the diluent was injected separately immediately following the starting mixture while in the others, the components were mixed before injection. The method of injection had no effect on the results.

An experiment was stopped by fast condensation of the contents of the reaction vessel into a trap cooled to 77 K. Non-condensable gases were continuously moved to a gas burette with an automatic *Töpler* pump. The collected product mixture was then distilled at 223 K into a volatile 'light' fraction, which was measured volumetrically prior to the analysis by gas chromatography, and into a 'heavy' fraction retained at 223 K. This latter fraction was analyzed directly by gas chromatography.

*Analysis:* The gas chromatographic analysis of the experiments was carried out using a *Carlo Erba* Model G 1 Fractovap instrument equipped with a flame ionization detector and an *Infotronics* Model CRS-208 automatic digital integrator. A 2.3 m, 3 mm diameter glass column, packed with Chromosorb 103 operated with a flow rate of 23.3 ml/min was used for the gas chromatographic analysis of the 'heavy' product and starting mixtures (at 270°) and the 'light' product fraction (at 194°).

Observed *retention times* at 270°: hexane 1.9, toluene 3.7, 1,2,4-trimethylbenzene 7.4, 4-phenylbut-1-ene 8.6, N-methylaniline 12.3, and N-methyl-N-allylaniline 18.0, at 194°: ethane 1.1, propylene 1.4, but-1-ene 1.8, but-2-ene and buta-1,3-diene 2.0, hexa-1,5-diene 4.2, and toluene 13.8.

The analyses of the 'heavy' product mixtures (containing an added excess of hexane or toluene as diluents to remove the sample quantitatively from the reaction system) usually agreed to within 1%. In contrast, the analyses of the undiluted starting mixtures showed an unusual scatter of about 2%, which is attributed primarily to the problems of reproducibility in injecting small amounts of relatively viscous sample mixtures.

Relative response factors of methylaniline and MAA of 1.0 and 1.35 respectively have been determined. These data are used in the calculation of conversions based on the amount of methylaniline formed.

In addition to the analysis using the *Carlo Erba* FID-instrument and a Chromosorb 103 column, the reaction products ethane, propylene, but-1-ene and buta-1,3-diene have also been identified using a silicagel column and a *F+M* 810 gas chromatograph equipped with TC-detectors.

*Proton Magnetic Resonance* analysis served to identify methylaniline (MA) as major 'heavy' reaction product.

**Results.** – The kinetics of the gas phase thermal decomposition of N-allyl-N-methylaniline was studied in the temperature range 575 to 665K. Methylaniline was the major nitrogen containing product always accounting for more than 36% and in 6 out of 43 experiments for more than 86% of the MAA consumed. Another unidentified N-containing product with the same GLC retention time as aniline was observed amounting to an average of about 25% of the methylaniline formed. Propylene and methane were the major light products besides ethane, but-1-ene and but-2-enes. The variety of products, the formation of sizeable amounts of the apparent recombination and crosscombination products of methyl, allyl and benzyl radicals, such as ethane, but-1-ene, 4-phenylbut-1-ene, and hexa-1,5-diene<sup>5)</sup> are inconsistent with a molecular decomposition path, which would exclusively yield propylene and N-phenylmethyleimine (PhMI). In the presence of added methylamine, the primary product of the molecular reaction, PhMI, would add to form  $C_6H_5NHCH_2NHCH_3$ . Such a product could not be detected either by GLC or <sup>1</sup>H-NMR. analyses.

Unlike the pyrolyses of the N-cyclohexyl-N-allylamine [3], triallylamine [2] and diallylamine [1], which are shown to involve a concerted retro-'ene' reaction mechanism, MAA obviously decomposes *via* a radical path. Further evidence for a radical chain mechanism is provided by the effect of added gases such as toluene. A considerably faster depletion of the starting material has been observed in the absence of radical trapping diluents. Furthermore, closer agreement has been observed between conversions based on the formation of methylaniline and aniline as compared to those obtained from the depletion of MAA for experiments of lower overall conversions. It appears that both methylaniline and MAA are partially consumed in secondary radical processes.

In the presence of toluene as a diluent, up to 5% 4-phenyl-but-1-ene were observed in product mixtures of experiments carried to high conversions. For low conversions the yield was generally less than 0.2%.

In *Table 1* the product distribution of a few experiments carried to relatively large conversions are listed. For one half-life only about one half to two thirds of the molecules decomposed are accounted for in nitrogen containing products. For lower conversions, nitrogen-massbalances are acceptable within experimental error limits.

In terms of the C<sub>3</sub>-fragment of the starting material, the massbalance is much less satisfactory. Only about 30% are accounted for in products, the major loss occurring in heavier materials that escaped analyses. Better hydrocarbon massbalances are observed with low overall conversions but the variety of products leading to

<sup>5)</sup> Bibenzyl has also been observed but escaped reproducible and reliable analyses.

Table 1. *Products observed in the Thermal Decomposition of MAA<sup>a)</sup>*

Temp. K	Time min	Starting Material		Conversions in Percent of [MAA] <sub>0</sub> <sup>b)</sup>									
		[MAA] <sub>0</sub> Torr	[T/MAA] <sub>0</sub>	GCA <sup>c)</sup>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub> <sub>a, b)</sub>	1-B	2-B	HD	PhB	MA	A
665.1	3	22.3	4.0	58.6	3.1	0.57	4.32	0.46	1.06	1.35	5.0	27.4	11.1
624.7	20	15.47	7.6	53.5	4.5	0.97	8.81	0.57	1.65	1.23	4.7	19.7	7.7
627.2	21	12.99	13.1	59.0	3.9	0.84	7.88	0.42	1.23	0.59	4.3	20.7	9.3
626.4	15	12.41	2.31	49.0	1.6	0.82	8.00	0.67	1.55	0.69	3.1	24.8	12.5
586.2	86	29.8	4.75	19.9	–	0.33	3.7	0.12	0.29	0.23	3.0	20.0	7.9

a) Abbreviations: N-methyl-N-allylaniline MAA, N-methylaniline MA, aniline A, 4-phenylbenzene PhB, hexa-1,5-diene HD, toluene T, but-1-ene 1-B, but-2-ene 2-B, gas chromatographic analyses GCA. [<sub>0</sub>] denotes initial concentrations.

b) Based on the internal standard method and volumetric analyses as well as GCA.

c) Depletion of the starting material.

d) Bibenzyl which is also present in the product mixture, escaped reliable analyses.

relatively small individual concentrations reduced the accuracy of the data significantly.

The relevant experimental information for the kinetic treatment of the data are summarized in *Table 2*.

 Table 2. *Kinetic Data for the Thermal Decomposition of N-Methyl-N-allylaniline in the Gas Phase<sup>a)</sup>*

Temp. K	Time min	Starting Material		Conversion in % [MAA] <sub>0</sub>			k × 10 <sup>-4</sup> s <sup>-1</sup> <sub>b, c)</sub>
		[MAA] <sub>0</sub> Torr	[T/MAA] <sub>0</sub> <sup>e)</sup>	GCA <sup>b, c)</sup>	MA <sup>b)</sup> d)	Ab <sup>b)</sup> d)	
574.7	25	16.1	5.60	4.7	–	–	0.3182
575.3	97	17.8	6.23	18.3	16.2	3.2	0.3474
575.5	17	21.4	3.65	–	–	–	0.2966
576.5	10	–	–	3.2	–	–	0.3626
577.3	15	–	–	3.3	–	–	0.2871
579.4	122	11.2	6.23	21.3	11.3	8.0	0.3264
579.5	101	9.5	6.22	–	9.4	–	0.1957
586.2	86	29.8	4.75	19.9	21.1	7.9	0.4302
588.5	21	18.8	5.27	4.1	4.3	0.24	0.3333
588.6	15	17.5	8.19	2.2	–	–	0.2484
588.8	11	18.8	5.31	5.5	–	–	0.8561
589.7	36	19.2	6.61	12.1	8.0	3.8	0.5993
597.7 P	25	43.6	7.03	9.4	9.4	1.0	0.6545
598.1 P	23	25.9	6.13	12.7	6.2	0.5	0.9807
598.3 P	30	16.7	5.23	11.5	12.2	1.5	1.4744
598.4 P	20	15.9	5.64	10.1	–	–	0.8918
601.0	20	24.2	5.97	12.0	8.1	1.7	1.0681
601.7	15	22.0	5.65	9.1	8.4	1.7	1.0651
601.5	10	22.7	6.77	6.3	3.2	1.1	1.0701
601.3	39	18.8 <sup>e)</sup>	4.79	29.2	15.0	3.9	1.4757
602.1	8	38.2	neat	11.4	–	–	2.5294
602.0	41	11.1 <sup>f)</sup>	5.66	28.7	17.7	5.4	1.3767
602.1	10	15.3 <sup>f)</sup>	4.36	8.7	5.4	1.6	1.2939

Temp. K	Time min	Starting Material		Conversion in % [MAA] <sub>0</sub>			k × 10 <sup>-4</sup> s <sup>-1</sup> b, c)
		[MAA] <sub>0</sub> Torr	[T/MAA] <sub>0</sub> <sup>e)</sup>	GCA <sup>b, c)</sup>	MA <sup>b) d)</sup>	A <sup>b) d)</sup>	
602.1	10	7.6 <sup>f)</sup>	9.16	6.2	5.0	0.9	1.0746
603.0	15	17.4	10.45	14.1	6.9	1.7	1.6933
603.6	20	19.6	neat	20.6	7.8	1.0	1.9184
627.7	6	20.9 <sup>f)</sup>	4.32	24.2	12.6	3.3	7.7059
626.0	10	23.3 <sup>f)</sup>	4.86	34.9	18.8	4.7	7.1508
625.7	7	24.9 <sup>f)</sup>	5.13	26.1	13.4	3.8	7.1967
627.2	4	15.0	9.50	18.0	7.5	1.4	8.2465
626.3	10	23.2	7.94	36.5	16.3	3.4	7.5609
626.4	8	18.3	3.57	30.3	11.9	2.4	7.5254
627.6	3.5	23.7	6.52	10.2	7.7	2.1	5.1125
627.4	3.333	16.3	6.18	13.4	6.9	1.3	7.1745
627.1	2.7	14.8	7.32	11.6	3.4	1.0	7.5908
624.7	20	15.5	7.60	53.5	19.7	7.7	6.384
625.9	7.5	15.7	7.98	32.8	21.6	9.7	8.829
627.2	21	13.0	9.24	59.0	21.7	9.3	7.0725
626.4	15	12.4	2.31	49.0	26.8	9.0	7.487
633.9 P	7	29.3	5.21	31.6	19.1	2.7	12.168
643.0	2.667	20.9	4.32 <sup>e)</sup>	29.1	16.4	4.2	21.511
643.0	4	23.9	9.08 <sup>e)</sup>	40.7	22.3	6.0	21.757
644.6	3	15.0	8.97	29.4	13.9	2.6	19.317
644.5	4.33	9.7	23.10	38.6	–	–	18.760
644.0	3	7.4	26.25	26.8	–	–	17.337
643.0	7	31.4	8.23 <sup>f)</sup>	57.6	37.6	9.3	20.434
643.5	6	37.4	3.98 <sup>f)</sup>	52.2	31.1	7.6	20.497
643.0	3	59.8	4.60 <sup>f)</sup>	34.4	20.6	4.7	21.511
654.6	4	13.2	5.21	48.1	21.2	8.1	27.35
665.7	3	15.8	12.32	60.9	–	–	52.158
665.3	2.5	6.2	–	54.0	30.5	6.2	51.794
664.6 P	3.5	37.3	5.34	69.7	33.0	7.8	56.81
665.1	3	22.3	7.93	58.6	27.4	11.1	48.88
665.7	3	15.8	12.52	60.9	32.1	5.4	52.158

a) Abbreviations: N-methyl-N-allyl-aniline MAA, toluene (diluent) T, N-methylaniline MA, aniline A, [ ]<sub>0</sub> denotes initial concentrations, P: reactions carried out in the packed reaction vessel.

b) Based on the internal standard method using gaschromatographic analysis.

c) For the depletion of the starting material.

d) For the formation of products.

e) Instead of toluene, propylamine has been used as diluent.

First order rate constants for the depletion of MAA have been calculated using 1,2,4-trimethylbenzene as an internal standard. Conversions based on the nitrogen products methylaniline and aniline formed, have also been incorporated in *Table 2*. They are on average about one-third lower than those based on the depletion of MAA, with reasonably good agreement for low conversions and temperatures. At temperatures of 625K and higher, *agreement in rate constants* within about  $\pm 10\%$  was observed despite a more than 5-fold variation in conversion, a 6-fold variation in the initial pressure of the starting material, [MAA]<sub>0</sub>, and for diluent pressures ranging between 2.3[MAA]<sub>0</sub> and 27[MAA]<sub>0</sub>.

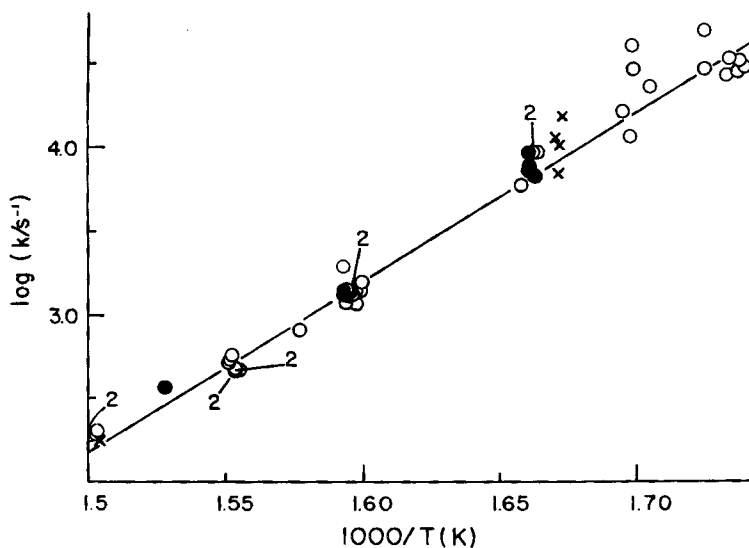
Furthermore, experiments carried out in presence of toluene or propylamine as diluents, resulted in about the same values for the rate constants. In the absence of, or with relatively small amounts of diluents, substantially faster rates have been observed due to the secondary reaction of MAA (two of these experiments are included in *Table 2*). The scatter of the rate constants particularly at the lower temperatures can then in part be attributed to the complexities of the radical chain mechanism and an inefficient quenching of the initial radicals formed by toluene and propylamine.

The much more pronounced scatter of the data at lower temperatures might also be taken as indication of a heterogeneous component involving the overall reaction. However, the reaction appears to be essentially homogeneous in nature. Experiments carried out in a packed reaction vessel with a 15-fold larger surface to volume ratio gave rate constants consistent with those obtained from the unpacked reaction vessel.

A least mean square analysis of the kinetic data listed in *Table 1*, disregarding the two values obtained in the absence of any diluent, yields the *Arrhenius* relationship  $\log(k/s^{-1}) = 13.27 \pm 0.38 - (47.15 \pm 1.05 \text{ kcal mol}^{-1})/2.303 RT$ . Practically the same results were obtained when the data from the packed reaction vessel were omitted.

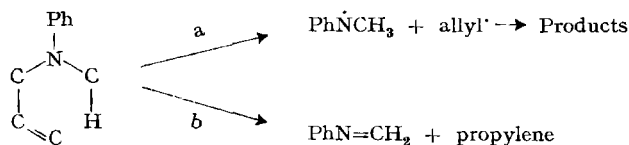
Disregarding the widely scattered results obtained at temperatures below 600K yields the preferred relationship  $\log(k/s^{-1}) = 13.75 \pm 0.43 - (48.50 \pm 1.23 \text{ kcal mol}^{-1})/2.303 RT$ .

*Fig.* shows an *Arrhenius* plot of the data.



*Fig.* Arrhenius plot of the unimolecular rate constants for the thermal decomposition of *N*-methyl-*N*-allylaniline in the gas phase. Numbers indicate overlapping points. × stands for experiments using the packed reaction vessel, o using toluene and ● using propylamine as a diluent.

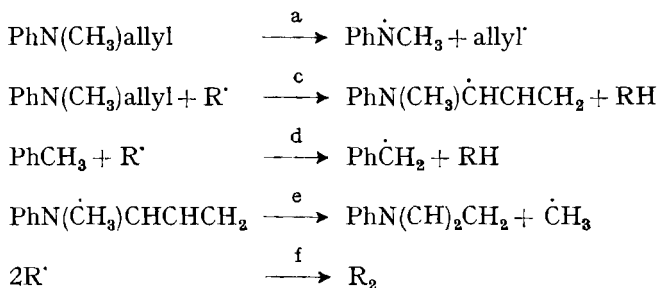
**Discussion.** – In principle the two reaction mechanisms, schematically represented below with a and b, must be anticipated for the thermal decomposition of MAA:



In contrast to N-alkyl-N-allyl-amines [1], diallylamine [2], triallylamines [1] which react exclusively *via* the molecular route (b), a radical chain mechanism of the type (a) has been established for MAA. Overall first order kinetics are obeyed within the experimental error limits quoted. The observed reaction products and activation parameters imply that the starting material is also involved in secondary reactions, thereby leading to a more complex radical scheme.

The presence of significant quantities of methane, ethane and butenes demonstrates the importance of the methyl radical in the chain process.

Based on the experimental results with toluene as added hydrogen donor, the following generalized radical chain mechanism can be derived:



R stands for allyl, benzyl and methyl radicals in propagation and termination,  $\text{Ph}\dot{\text{N}}\text{CH}_3$  and  $\text{PhN}(\text{CH}_3)\dot{\text{C}}\text{HCHCH}_2$  intervene in propagation only.

The rate constant for the initiation *reaction*,  $k_a$ , which would be equivalent to the total overall first order rate constant  $k_{\text{tot}}$  in case of  $k_d \gg k_c$ , can be estimated based on the data given in references [8] [9] at  $\log(k_a/\text{s}^{-1}) = 14.4 \pm 0.4 - (51.3 \pm 1.5)/2.303 RT$ . The ratio  $k_d/k_c$ , *i.e.* the abstraction of a hydrogen from toluene or from MAA may be estimated in analogy with hydrocarbons [10] at about 0.5 for a mean temperature of 620K. With an average 6-fold excess of toluene over MAA the ratio of the rates  $R_d/R_c$  would be expected to favor abstraction from toluene by a factor of about 3, *i.e.* every fourth radical would be expected to abstract hydrogen from the starting material.

Based on the available literature data [11], propylamine can be expected to be about as efficient a hydrogen donor as toluene which appears to be corroborated by the experimental findings.

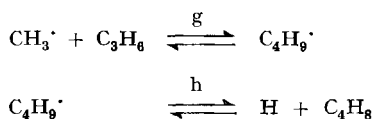
The prediction that MAA should compete with toluene or propylamine as hydrogen donor is evidenced by the experimental fact that methane is a significant reaction product from the beginning. The disproportionation of the intermediate  $\text{MAA} \cdot$

radical can be estimated<sup>6)</sup> at  $\log (k_e/s^{-1}) \approx 16 - (18.5 \text{ kcal mol}^{-1})/2.303 RT$ , *i.e.* a very fast process.

In view of the relatively large experimental error limits reasonable agreement between the observed overall activation parameters for the first order depletion of MAA with those expected for the unimolecular bond breakage ( $k_a$ ) can be noted. It is evident, however, that the experimental values both for  $\log A$  and  $E_a$  are low compared with prediction which is perfectly in line with the added complexities of the mechanism due to secondary reactions involving the starting material MAA. Based on the predicted value of  $14.4 \pm 0.4$  for  $\log A_a$  and the observed overall rate constant  $k_{tot}$  at the mid-temperature of this study, an activation energy of  $50.5 \pm 1.2 \text{ kcal mol}^{-1}$  is calculated for the bond breaking process. This is in very good agreement with an expected [8] value for  $E_a$  of 51.3 (assuming  $E_{-a} \approx 0$ ).

From the ratio of the observed  $\text{CH}_3\cdot$  and allyl termination products, (Table 1) and accepting that methyl radicals terminate about five times faster than allyl radicals, the relative concentrations of these two radicals in the system is calculated to  $[\text{allyl}\cdot]/[\text{CH}_3\cdot] \approx 12.5$ . This is in line with the experimental data.

The fact that both but-1-ene and but-2-ene in approximately thermodynamic equilibrium concentrations are observed in the product mixture raises the question whether butenes are indeed exclusively formed *via* recombination or whether addition to propylene is also taking place.



$k_g$  is estimated at  $10^{8.1-8.8/\theta}$ ,  $k_{-g}$  at  $10^{15.1-30.6/\theta}$  and  $k_h$  at  $10^{14-40/\theta}$  resulting in  $k_{-g}/k_h$  of  $\approx 10^{4.5}$  at 600 K. The abstraction rate of methyl radicals can be estimated at  $k_a \approx 10^{9-7.4/\theta}$  leading to  $k_a/k_g$  of  $\approx 2.5$  at 600 K. It can then be concluded that methyl radicals either abstract or recombine and that but-1-ene is a recombination product. This is substantiated by the absence of hydrogen as a measurable reaction product. The origin of but-2-ene however is not understood as it could not have been formed *via* thermal isomerization at the reaction conditions used. The observed preexponential factor of  $10^{13.75 \pm 0.43}$  also rules out a significant contribution to the overall conversion from the molecular path (b), for which  $\log A$  can be estimated at 11.8. Assuming that experimentally we would have noticed a 20% contribution from the molecular process, this would put a lower limit on the activation energy of the 6-center concerted retro-'ene' decomposition path (b) of  $\sim 44.8 \text{ kcal mol}^{-1}$ . Compared

<sup>6)</sup> Based on a (alkyl)<sub>2</sub>N—CH<sub>3</sub> bond strength of 76.4 kcal mol<sup>-1</sup> [8], a C=N π-bond strength of 54.1<sup>7)</sup> kcal mol<sup>-1</sup> and an activation energy of 8 kcal mol<sup>-1</sup> for the backreaction -e, the activation energy for splitting a methyl radical off the intermediate MAA'-radical is 76.4 - 12.6 (radical stabilization) - 54.1 + 8.1 = 18.8 kcal mol<sup>-1</sup>.

<sup>7)</sup> The C=N π-bond strength is calculated following the concept outlined in reference [8]. Using a value of 20.0 kcal mol<sup>-1</sup> for the enthalpy of hydrogenation [12] the C=N π-bond strength is determined as 65.8 kcal mol<sup>-1</sup> and using the enthalpies of formation of amines and imines (obtained using group additivities) a value of 67.4 kcal mol<sup>-1</sup> is calculated. An average value of 66.6 kcal mol<sup>-1</sup> is used here. For the case of a phenylsubstituted C=N π-bond, a stabilization energy of 12.5 kcal mol<sup>-1</sup> [8] must be taken into account yielding a value of 54.1 kcal mol<sup>-1</sup>.



with the activation energies observed for N-methyl-N-allyl-amine (43.5 kcal mol<sup>-1</sup>) [13] and N-cyclohexyl-N-allyl-amine (42.2) [3], this implies that the phenyl group bonded to the nitrogen atom has no measurable effect on the 6-center transition state structure involved in these reactions, and shown in equation (1).

This is a most remarkable finding which ties in with the large effect observed for vinyl substituents in R<sup>1</sup> or R<sup>2</sup> position [1] [2] in view of the suggested non-synchronicity, *i.e.* polar character of the transition state. The hydrogen would then be transferred with a pronounced hydride ion character. It has been well established [14] for the reaction alkylhalides → olefin + HX, that phenyl substituents bonded to a reactive center emerging with a partial negative charge in the transition state, exercise only a small polarizability stabilization (1.5 kcal mol<sup>-1</sup>) compared to the effect on partial positive charges (13 kcal mol<sup>-1</sup>).

In case of a homopolar concerted retro-'ene' reaction of the type (b) phenyl substituents in R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> positions would be expected to have about the same effect. To a first approximation, a lowering of the activation energy due to the stabilization energy gained from delocalization, would be anticipated. If this were the case a predominant decomposition of MAA *via* the concerted route (b) would have been observed.

#### REFERENCES

- [1] K. W. Egger & P. Vitins, Internat. J. chem. Kin., 6, in print (1974).
- [2] P. Vitins & K. W. Egger, Helv. 57, 17 (1974).
- [3] K. W. Egger, J. chem. Soc., Perkin II, 1973, 0000.
- [4] K. W. Egger & P. Vitins, J. Amer. Chem. Soc., submitted.
- [5] W. H. Richardson & H. E. O'Neal, in 'Comprehensive Chem. Kinetics', p. 419, C. H. Bamford & C. F. H. Tipper, editors, Elsevier Publ. Corp., Amsterdam (1972).
- [6] D. B. Bigley & R. W. May, J. chem. Soc. (B) 1967 557.  
G. G. Smith & S. E. Blau, J. Physic. Chemistry 68, 1231 (1964).
- [7] G. G. Smith & B. C. Yates, J. chem. Soc. 1965 7242.
- [8] K. W. Egger & A. T. Cocks, Helv. 56, 1516, 1537 (1973).
- [9] H. M. Frey & R. Walsh, Chem. Rev. 69, 107 (1969).  
S. W. Benson & H. E. O'Neal, 'Kinetic Data on Gas Phase Unimolecular Reactions', NSRDS-NBS 21, National Bureau of Standards 1970, Washington.  
S. W. Benson, 'Thermochemical Kinetics', John Wiley, New York 1968.  
G. L. Esteban, J. A. Kerr, & A. F. T. Trotman-Dickenson, J. chem. Soc. 1963 3873.
- [10] D. A. Leathard & J. H. Purnell, Proc. Roy. Soc. A 305, 517 (1968).
- [11] A. F. Trotman-Dickenson & G. S. Milne, 'Tables of Bimolecular Gas Reactions', NSRDS-NBS 9, U.S. National Bureau of Standards 1967.  
E. Ratajczak & A. F. Trotman-Dickenson, 'Supplementary Tables of Bimolecular Gas Reactions', Office of Scientific and Technical Information, Department of Education and Science, London 1970.  
J. A. Kerr & E. Ratajczak, 'Second Supplementary Tables of Bimolecular Reactions', University of Birmingham 1971.
- [12] A. F. Bedford, P. B. Edmondson & C. I. Mortimer, J. chem. Soc. 1962, 2927.
- [13] P. Vitins & K. W. Egger, J. chem. Soc. Faraday II, 1974.
- [14] K. W. Egger & A. T. Cocks, in 'The Chemistry of C-X Bonds', part 2 p. 676, S. Patai, ed., Wiley Corp., New York 1973.