The Thermochemical Kinetics of Retro-"Ene" Reactions of Molecules with the General Structure (Allyl)XYH in the Gas Phase. IX. The Thermal Unimolecular Decomposition of Ethyallylether in the Gas Phase*

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Abstract

The thermal decomposition of ethylallylether (EAE) has been studied in the gas phase over the temperature range of $560-648^{\circ}$ K. Propylene and acetaldehyde are the only reaction products observed. The reaction is apparently homogeneous in nature and independent of the pressure of EAE and of added foreign gases. The experimetally determined first-order rate constants, using the internal standard technique, fit the Arrhenius relationship log k(s⁻¹) = 11.84 ± 0.29 - (43.57 ± 0.77 kcal/mole)/2.303RT. Independently the same rate constants are obtained, based on the amounts of products formed. The observed activation parameters are in general agreement with expectations based on the concept of a 6-center 1,5-H-shift retro-"ene" reaction mechanism, and they agree with previous results obtained for the similar reactions involving alkylallylamines and olefins.

Introduction

Previous kinetic investigations of reaction systems of the general nature shown in eq. (1)

(1)



where X equals $-CH_2-$ [1], $-(CH_3)CH-$ [2], -CO- [3], -NH- [4-6], -N(allyl)- [7] and Y equals $-CH_2-$ [1,6], -CHR- [2,4,5,7], or -O- [8]

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showed the validity of the concerted H-shift "ene" type mechanism involving a 6-center transition state.

For allylalkylethers, which undergo the same type of a decomposition reaction into carbonyl compounds and olefins, Cookson and Wallis [9] reported a limited set of relative rate constants. Although Arrhenius parameters were not obtained, these data can be used to estimate E_a with a reasonable confidence limit at ≈ 43 kcal/mole, based on an estimated value [4-7,11] for log A of ≈ 11.2 .

Very little information is available, however, on the amount of nonsynchroneity, that is, the polar character of the reaction. Kinetic studies dealing with the effect of substituents bonded to the reacting centers and the effect of the nature of X and Y should provide interesting information regarding the amount of charge separation in the transition state. In this context the kinetics of diallylether are presently under investigation.

Experimental

Materials

Ethylallylether (EAE), obtained from Fluka Co. and fractionally redistilled, was >99.5% pure. Tetrahydrofuran (THF) of >99% purity and toluene (T) were supplied by Merck Co. and UCB, respectively. These two latter compounds were used as internal standards in the following starting mixtures (molar ratios): A--EAE/THF = 1.59; B--EAE/T = 0.666.

Apparatus and Procedures

The static reaction system and general procedure adopted for these studies has been discussed previously [4-7]. Two different static reaction systems and work-up procedures have been used for the experiments carried out with tetrahydrofuran and toluene, respectively, as internal standards. Using starting mixture A, the reactions were carried out in 1-l. Pyrex glass vessels, and the products were condensed directly into 0.5-l. bulb and analyzed by gas chromatography, injecting gaseous aliquots.

The condensed product mixture obtained from experiments carried out with toluene as the internal standard and using 2-1. Pyrex glass reaction vessels were distilled at -130° C into a light fraction containing practically exclusively propylene and a residual fraction which was analyzed by GC using liquid injections. The propylene fraction was measured volumetrically. Pressure measurements gave additional information about the extent of reaction.

In both sets of experiments noncondensable gases have not been formed. A reaction vessel packed with Pyrex glass tubing resulting in a surface-to-volume ratio 15 times that of the nonpacked glass vessel, served to investigate the effect of surface onto the reaction rate.

Analysis

Gas chromatographic (GC) analyses of the starting and product mixtures were carried out using either a Carlo Erba model G 1 Fractovap equipped with a flame ionization detector and a model CRS-208 Infotronics automatic digital integrator or an F + M model 810 TC gas chromatograph with disc integration.

Quantitative separation of the products and internal standards was achieved using columns filled with chromosorb WAW coated with 30 wt-% Carbowax 20 M. The following retention times (in minutes) and thermal conductivity response factors relative to the starting material (shown in parentheses) have been observed: propylene 2.09 (1.178), acetaldehyde 7.11 (1.561), ethylallylether $10.32 (\equiv 1.000)$, and tetrahydrofuran 18.63 (1.066). The product mixtures from starting mixture A have been analyzed using the F + M thermal conductivity setup, those from mixture B using the Carlo Erba flame-detection instrument. The reproducibility of the GC analysis of the starting and product mixtures was usually within two percent and in most cases within one percent.

Propylene and acetaldehyde have been unambiguously identified as reaction products.

Results

In the temperature range of 559-648 K, ethylallylether decomposes thermally into equimolar concentrations of propylene and acetaldehyde. No significant concentrations of any other reaction product have been observed.

$$C_2H_5OCH_2CHCH_2 \xrightarrow{1} CH_3CHO + C_3H_6$$

The equilibrium constant $K_{1,2}$ for this system has been calculated [12,13] at log $K_{1,2}$ (atm) = 6.72 + (1.0 kcal/mole)/2.303 *RT*, that is, log $K_{1,2}$ (l./mole) = 5.58 + (1.3 kcal/mole)/2.303*RT* and reaction (1) is then thermodynamically irreversible.

First-order rate constants k_1 for the depletion of the starting material EAE have been obtained using either tetrahydrofuran or toluene as internal standard. The amounts of propylene and acetaldehyde formed as well as the observed pressure change have also been used to calculate conversions of EAE attained. The relevant experimental details and results are summarized in Table I and an Arrhenius plot of the rate constants is shown in Figure 1.

Consistent values for the rate constants k_1 have been obtained despite a more than 10-fold variation in the pressure of the starting material and for conversions ranging from 3.6 to 78%. As can be seen from the data listed in Table I, conversions based on the amount of propylene or acetaldehyde formed agreed usually within about $\pm 10\%$ with those calculated, using the internal standard technique. Larger differences of up to 40% are only observed with high propylene yields and particularly at higher conversions and temperatures. The

Temp. ^e K	Time min.	Starting Material ^a		c	k, x104b			
		[Ptot]o	[EAE]	EAE	с ₃ н ₆	сн _з сно	$(\triangle p)_{tot}$	1
629.2 P	16	42	25.8	31.6	27.9	31.4		3.928
637.7 P	26	150.5	92.4	66.5	58.4	\$3.1	33	7.013
636.8 P	11	49.2	30.2	38,3	33.1	33.5	26.8	7.327
636.8	19.17	74	45.5	60.2	55.9	57.2	38.1	8.018
636.8	9.92	116.6	71.6	31.5	19.2	29.4	22.3	12.59
648.0	4.0	41	25.2	29.7	23.2	27.8		14.67
648.0	11.0	57	35	54.8	49.7	43.5	42.3	12.03
648.0	2.16	74.7	45.9	13.5	13.6	10.9		11.18
564.2	196	71.7	43.67	9.79	7.62	5.71	5.64	0.08759
564.2	95	58.1	35.69	5.78	4.51	4.72		0.1045
564.2	60	77.6	47.66	3.57	2.89	2.95		0.10108
562.7	321	83.3	51,16	14.2	13.5	15.13		0.07939
559.2	220	67.2	41.27	7.34	5.88	8.67	6.78	0.05777
589.5	76	73.0	44.8	17.4	1ő.3	17.3	13.5	0.41953
589.5	130	58.4	35.9	28.7	25.4	28.1	21.5	0.4337
589.3	60	75.5	46.0	15.9	13.7	15.2		0.4812
589.3	61	223.9	137	15.6	14.3	16.4	14.5	0.4645
589.3	30	97.1	59.2	7.83	7.62	8.53	6.4	0.4527
621.0	60	25.1	14.0 ^{c)}	59.9 ^{c)}	29.1 ^d)		36.3	2.534
621.0	10	103.2	41.3 ^{c)}	16.8 ^{c)}	13.3 ^{d)}		13.3	3.0578
620.0	45	46.1	18.4 ^{c)}	48.9 ^{c}}	36.5 ^{d)}		43	2.4891
645.6	10	43.4	17.4 ^{c)}	46.3 ^{c)}	33.3 ^{d)}		45.3	10.357
650.3	4	35.8	c)	22.4 ^{c)}	22.1 ^d)		18.5	10.542
645.2	20	34.8	13.9 ^{c)}	72.3 ^{c)}	51.2 ^{d)}		51.0	10.70
644.8	25	18.6	7.40 ^{C)}	77.8 ^{c)}	49.3 ^{d)}		48.4	10.03
644.9	25	37.4	15.0 ^{c)}	78.0 ^{c)}			65.6	10.08
645.1	20	18.4	7.36 ^{c)}	77.8 ^{c)}	42.1 ^{d)}		45.6	12.55

TABLE I. Kinetic data for the unimolecular decomposition of ethylallylether (EAE) in the gas phase.

^a [EAE]₀ and $[P_{tot}]_0$ —initial concentration of ethylallylether and total pressure; $(\Delta p)_{tot}$ total pressure change observed.

^b Rate constants based on the internal standard method.

^c Experiments using mixture B, that is, toluene, as internal standard.

^d Volumetric analysis of propylene as opposed to direct GC analyses of product mixture used in all other experiments.

* P-packed reaction vessel.

measured pressure changes are in line with expectation, considering the experimental errors involved.

The same rate constants have been obtained using two completely different experimental systems, work-up, and analysis procedures.

The homogeneity of the reaction has been tested using a packed reaction vessel with a 15-fold larger surface-to-volume ratio. The rate constants obtained from equivalent packed and nonpacked reaction vessels were found to be the same within experimental error limits. Least squares analysis of the rate constants listed in Table I yields with standard errors the Arrhenius relationship $\log k_1(s^{-1}) = 11.84 \pm 0.29 - (43.57 \pm 0.63 \text{ kcal/mole})/2.303RT.$



Figure 1. Arrhenius plot of rate constants.

Discussion

The pyrolysis of ethylallylether in particular and alkylallyl ethers in general proceeds via a H-shift "ene" reaction involving a 6-center transition state as shown in the Introduction.

The low preexponential factor of $10^{11.8}$ s⁻¹, implying an energy loss ΔS^{\pm} of 9.6 cal/K-mole when compared with transition state theory and assuming a transmission coefficient of unity is consistent with a cyclic structure of the transition state. Estimating ΔS^{\pm}_{total} for such a one-step cyclic process, using the concept and data outlined previously [4-7], a value of ΔS^{\pm}_{total} (600 K) = $\Delta S^{\pm}_{rotation}$ + $\Delta S^{\pm}_{vibration}$ + $\Delta S^{\pm}_{symmetry}$ = -15.1 + 0.8 + 1.4 = -12.9 has been calculated. This is in general agreement with the experimental data considering the combined error limits, even though the difference is larger than expected.

In Table II the results of this work are compared with those for other reactions, proceeding via the same type of mechanism outlined in eq. (1).

Practically the same rate constants have been observed in this work as were previously reported [4,6] for N-methyl,-N-allylamine, and N-cyclohexyl, N-allylamine in contrast to the much slower rates and about 7 kcal/mole higher activation energies for the similar reaction involving olefins. This observation might be interpreted with a lower energy nonsynchronous reaction path possible with heteroatoms present in one or more positions of the six reactive centers. This assumption seemed to be supported by the very large rate enhancement observed for vinyl substituents in \mathbb{R}^1 or \mathbb{R}^2 positions in diallylamine [5] and triallylamine [7].

It is then surprising however, that changing a nitrogen as the reaction center X for an oxygen atom should have essentially no effect at all on the rate of reaction.

Reactant	x	R ¹	R ²	log(A/s ⁻¹)		E _a /kcal	он ₂₉₈ о b			△ _H 1.2	Ref.
				observed	predicted	observed	(Allyl)-X	R ¹ R ² с−н	x=cR ¹ R ²		
Olefins:											
hept-l-ene	сн,	н	с,н,	11.8	11.0	50.9 ^a	69	95	58	19.7	1
pent-1-ene	ca_	н	H		11.2	49.9 ^a	69	98	57	20	14
3-4-dimethylpent-1-ene	снсн,	н	в		11.6	50.3ª	65	98	58		2
4-methylpent-l-ene	снсн,	Ħ	Ħ		11.8	51.4 ^a	68	98	58		15
4-methylhex-1-ene	CHCH,	н	CH.	12.0	11.0	50.1 ^a	68	95	58		1
4-methylpent-l-yne	сн ₂	н	н	13.1	11.7	51.9 ^a	75	98	~- 68		16
Amines:											
N-methylallylamine	NH	н	Ħ	11.4	11.2	43.4	73	98	70		6
N-cyclohexylallylamine	NH	cyclo	°6	11.4	10.9	42.2	73	~~ 95	68	-9.2	4
Ether:											
Ethylallylether	0	н	с ₂ н ₅	11.5	11.0	42.8	70	93	73	-1.3	this work

TABLE II. Activation parameters for unimolecular H-transfer "ene" decomposition of reactions of the general type (allyl)XCHR¹R² $\stackrel{1}{\longleftarrow}$ propylene + X=CHR¹R².

^a Based on experimental data using predicted A factor.

^b DH₂₉₈—homopolar bond dissociation energy at 298°K. For details see [17].

The somewhat persistently larger A factors observed for the reaction of alkylallylethers and alkylallylamines than predicted would be consistent with a polar, that is, one-step partially nonsynchronous reaction path transferring the hydrogen atom with a hydride ion character. The observed differences in A factors, however, do not warrant conclusive argumentation.

Looking at the activation parameters listed in Table II from a point of view of a homopolar concerted process and the homopolar bond dissociation energies (see Table II) involved, it becomes apparent that there is no simple relationship between the activation energies observed and the enthalpies of the bonds broken and newly formed.

Considering the substantial differences in the heats of the reaction, ranging from thermoneutrality in the case of the ether to a 20-kcal endothermicity for olefins one might expect a significant difference in the extent of bond formation and breakage, that is, relative tightness in the transition states for these reactions.

It would also be expected that with increasing endothermicity of the reaction the transition states should tend to become increasingly resemblant of the products [18], that is, looser. The estimates of the A factors and with it of the activation energies for the olefinic systems then constitute lower limit values and the difference in E_a between the allylalkyls and the allylethers might even be more pronounced.

More information is expected from the studies on diallylether presently in progress.

Bibliography

- [1] A. T. Blades and H. S. Sandhu, Int. J. Chem. Kinet., 3, 187 (1971 .
- [2] W. Tsang, Int. J. Chem. Kinet., 1, 245 (1969).
- [3] D. B. Bigley and R. W. May, J. Chem. Soc. B, 557 (1967).
- [4] K. W. Egger, J. Chem. Soc. Perkin II, 2007 (1973).
- [5] K. W. Egger and P. Vitins, Int. J. Chem. Kinet., in press.
- [6] K. W. Egger and P. Vitins, J. Chem. Soc. Trans. Faraday, submitted.
- [7] P. Vitins and K. W. Egger, Helv. Chim. Acta, 57, 17 (1974).
- [8] G. G. Smith and B. L. Yates, J. Chem. Soc., 7242 (1965).
- [9] R. C. Cookson and S. R. Wallis, J. Chem. Soc. B, 1245 (1966).
- [10] W. H. Richardson and H. E. O'Neal, in "Comprehensive Chemical Kinetics," vol. 5, C. H. Bamford and C. F. H. Tipper, Eds., 1972, p. 430.
- [11] H. E. O'Neal and S. W. Benson, J. Phys. Chem., 71, 2903 (1967).
- [12] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
- [13] S. W. Benson, F. R. Cruickshank, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
- [14] R. Walsh, unpublished data, 1973.
- [15] M. Taniewski, J. Chem. Soc., 7436 (1965).
- [16] W. Tsang, Int. J. Chem. Kinet., 2, 23 (1970).
- [17] K. W. Egger and A. T. Cocks, Helv. Chim. Acta, 56, 1516 and 1537 (1973).
- [18] G. S. Hammond, J. Amer. Chem. Soc., 77, 334 (1955).

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