Mechanisms of Thermolytic Fragmentation of Allyl Ethers. I

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Abstract: The relative reactivities in the gas-phase thermolysis of eight allyl alkyl ethers possessing α hydrogen on the alkyl moiety are separated at most by a rate factor of 4 and are very similar in all other respects, falling largely within a narrow activation energy range of less than 1 kcal/mol. Such insensitivity of rate to extensive variation in substitution can be construed as indicative of a cyclic, concerted transition state. The small effects of substitution on the activation parameters of reaction can be readily explained in terms of a pericyclic, retro-ene structure of the transition state in the general reaction. Thermolysis of the analogous benzyl propargyl ether shows a very similar reaction pattern. However, thermolysis of *tert*-butyl allyl ether, where an α hydrogen on the alkyl moiety is not present, results in a reaction with distinctively different activation parameters. The fragmentation reaction products here, which were simple and unique with the other alkyl allyl ethers, are more numerous and complex, the predominant component representing methyl migration in a six-centered transition state. The reaction of the substrates in the liquid phase is little different from the gas phase; the small decreases in activation entropy are not unexpected for a concerted process. The striking increase in the activation entropy of the liquid-phase decomposition of *tert*-butyl allyl ether, on the contrary, is interpreted as a manifestation of the free-radical character of this reaction. The total absence of a substituent effect on the rates of thermolysis in a series of para (polar) substituted benzyl allyl ethers, in contradiction to an earlier report by Cookson and Wallis, is found to be consonant with the proposed structure of the concerted transition state.

The uncatalyzed thermal decomposition of ethers has not received much attention in the past. Reviews of thermolytic mechanisms by Steacie[1] and by DePuy and King[2] reflect the general scarcity of information on this general reaction up to 1960. The succeeding decade has witnessed a greatly accelerated pace of work in this area as indicated by the large amount of data cited in both published[3,4] and unpublished[5] reviews.

Numerous contributions by Stavely and Hinshelwood,[6-8] Magram and Taylor,[9] Lossing and Ingold,[10,11] Elkobaisi and Hickenbottom,[12,13] and Freidlin, Balandin, and Nazarova[14] have established the free-radical character of the thermal cleavages taking place in dialkyl, diaryl, and alkyl aryl ethers. Even cyclic ethers like dioxane, dioxalane, and tetrahydrofuran react in this fashion.[15-22] Finally, preliminary reports[11,23,24] on the thermolysis of divinyl ether also suggest the operation of a free-radical mechanism. The sole exception to this pattern of free-radical cleavage in the thermolysis of saturated and aromatic ethers appears to be in the case where one of the substituent groups on the ether oxygen is *tert*-butyl. Daly and Wentrup[25,26] have claimed that at least in the case of the ethyl *tert*-butyl the reaction occurs *via* a four-centered activated complex, representing a unique (for ether thermolysis) unimolecular elimination of ethanol and formation of isobutylene as the only other reaction product.

Unsaturated ethers, on the other hand, with the exception of divinyl ether mentioned above, undergo unimolecular thermolytic fragmentations and rearrangements with simple stoichiometry. The Claisen rearrangement is one of the best known examples of this type of reaction taking place in aryl allyl ethers. The literature of this widely studied case has been most recently reviewed by Rhoads.[27] The reaction is characterized by a six-centered transition state leading cleanly to an *o*-allylphenol product in the liquid-phase reaction. The reaction has not been studied extensively in the gas phase. Schmiegel, Litt, and Cowan[28] have determined the activation parameters to be normal under these circumstances but an unusual cleavage to phenol seems to be the favored reaction course. This, however, is due only to a deviation in the final product forming step and not to any change in the rate controlling sigmatropic rearrangement.[29] The analogous reaction of vinyl allyl ethers, possessing the skeleton

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essential for the six-centered transition state to occur, is also very facile. It has been carefully studied by a number of investigators[30–37] with both substituted and unsubstituted reactants.

Another generalization which emerges from study of the literature is that vinyl alkyl ethers, allyl propargyl, and 1-alkynyl alkyl ethers, undergo a very similar course of thermally induced fragmentation reaction. The activated complex can be described by a six-centered structure with the transferring H as one of the centers. Some suggestions to the effect that the reaction has a free-radical intermediate in the case of the vinyl alkyl ether substrates[23,38–44] have been advanced. Moreover, more detailed studies of the reaction of 1-alkynyl alkyl ethers have urged[45–54] a two-step reaction mechanism in these instances. The first step, which is rate controlling, yields a ketene and an ethylene; the second step finds the ketene adding to another molecule of ether forming a cyclobutenone ether.

Prior work on the thermolysis of allyl alkyl ethers has been largely semiquantitative in character. Malzahn[46] investigated a number of these examples but obtained no rate data. Cookson and Wallis[47,48] determined the relative rates of a group of substituted cases. They reported no absolute rate data for this class of reactions. Molera and Ariza,[45] however, have determined the rates of thermolysis of ethyl allyl and diallyl ethers. In all cases, however, where the stoichiometry was examined it appears that reaction takes place cleanly, forming an olefin and a carbonyl containing product in molar ratios, without significant indications of competing side reactions, in a unimolecular process.

The activation parameters in thermolysis of the several classes of ethers for which such information has been reported show marked differences corresponding to differences in mechanism of cleavage. In dialkyl or diaryl ethers the activation energies are of the order of 60 kcal/mol with preexponential terms of about 10^{15}, and activation entropies of small, positive magnitudes. Such values are customarily regarded as indicative of free radical cleavage mechanisms. The cyclic ethers which also decompose *via* free-radical pathways are characterized by slightly lower (on the average) values of 50–60 kcal and lower preexponential terms (*ca.* 10^{13}). However, the activation parameter values are not considered to be a sufficiently unique identification of the free radical cleavage mechanism. Even in the case of *tert*-butyl ethyl ether,[26] where a cyclic transition state seems to be preferred to the usual two-step radical intermediate process, the activation energy is only slightly less than 60 kcal and the preexponential term is close to 10^{15}.

Nonetheless, some generalizations regarding activation energy magnitudes are often invoked. For example, the six-center transition states of vinyl alkyl and allyl alkyl ethers require significantly lower activation energies (*ca.* 40 kcal/mol) and preexponential terms (*ca.* 10^{10}–10^{12}). The large negative activation entropies of these reactions are taken as evidence of the highly organized, cyclic structure of this transition state (see Table I). The 1-alkynyl alkyl ethers, however, have been discussed[45–54] as exceptions in the class of unsaturated ether thermolysis reactions. A facilitated two step radical cleavage mechanism has been proposed to account for their extremely low activation

Table I. Activation Parameters for Unimolecular Ether Thermolyses in the Gas Phase

Substrate ether[a]	Log A	$\Delta E^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
	Claisen Reaction			
Phenyl allyl (L)	11.20	33.1	−8.1	55
		33.2		28
2,6-Dimethylphenyl allyl (L)	10.77	30.3	−10.1	56
	Vinyl Allyl Ethers			
Vinyl allyl	11.70	30.6	−7.7	30
Isopropenyl allyl	11.73	29.3	−7.7	31
Vinyl 2-methallyl	11.15	29.1	−10.2	32
Vinyl 1-methallyl	11.32	27.9	−9.5	34
in decane soln (L)	10.78	25.7	−11.9	34
in benzene soln (L)	10.91	25.3	−11.3	34
Allyl-3-allyloxy-2-butenoate (L)	10.43	26.3	−11.3	33
Crotyl-3-crotyloxy-2-butenoate (L)	11.72	28.0	−5.4	33
	Vinyl Alkyl Ethers			
Vinyl ethyl	11.60	44.4	−9.1	23
	11.43	43.8	−10.2	38
Vinyl isopropyl	12.58	43.6	−4.8	40
	12.12	42.6	−6.5	57
Vinyl *n*-butyl	11.15	42.4	−11.1	58
		40	−11.0	41–43
Vinyl *sec*-butyl		45.7	−4.0	41–43
Vinyl *tert*-butyl	10.86	36.2	−12.0	57
	Allyl Alkyl Ethers			
Ethyl allyl	12.89	48.5	−0.6	45
Diallyl	11.95	42.3	−5.0	45

[a] (L) denotes reaction in liquid phase.

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energies (25–30 kcal) along with the low A (preexponential) factors (10^{10}–10^{12}). However, the low activation energies cannot be the only basis for a two-step mechanism here since analogous reactions such as the Claisen and related vinyl allyl ether rearrangements,[55–57] which are accepted as purely concerted, sigmatropic processes, possess activation parameters which are comparable to those of the 1-alkynyl alkyl ether thermolysis.

The results of quantitative studies to be reported from these laboratories on the thermolysis of unsaturated ether substrates were gathered with the aim of developing kinetic criteria which would be applied to correlate the mechanistic patterns of such gas-phase reactions with structural and theoretical (orbital) factors controlling reactivity. This report will be concerned with the rate effect of substituents on the allyl alkyl ether skeleton. Subsequent articles will deal with kinetic isotope effects[58a] and thermodynamic factors in appraising the driving forces of this general type of reaction.

Experimental Section

Apparatus. (A) Gas-Phase Thermolysis. The instrumentation and techniques used to obtain the kinetic data in this study have been described[58b] previously in detail. The gas-phase system is a flow reactor in which an incoming sample is diluted with a large volume of helium, which serves as carrier for the pulse, thus precluding intermolecular reactions. It contains a gold, tubular reactor with a sufficient length to diameter ratio to ensure that the results can be analyzed using static reactor equations. The gold tube also serves to present a noncatalytic surface, thereby eliminating any possible wall effects. The tube is coiled on a cylindrical core heated with cartridge heaters, and temperature controlled to within 0.2° by proportional controllers.

The sample flows through the reactor, through a thermal conductivity cell detector, and into an open-ended valve and coil arrangement. While the sample is in the coil (timed by the appearance of the sample at the detector), the valve is turned, and a second gas flow backflushes the coil and transfers the sample to an analytical gas chromatograph.

Samples can be directly injected into the reactor flow stream, or prepurified in a gas chromatograph and then transferred to the reactor stream using a built-in selector valve for sampling. A bypass valve is also available to bypass the reactor coil for system checking or for nonreaction condition analyses.

By variation of both the reactor flow rate (time parameter) and the temperature, a wide range of conditions can be obtained, allowing for study of the reaction over temperature ranges wider than 100°, thereby resulting in extremely precise activation parameters.

(B) Liquid-Phase Thermolysis. The reaction samples were heated in an aluminum block thermostat regulated by a proportionating temperature controller. The reaction vessels were fashioned from 8-mm o.d. Pyrex tubing with >2-mm wall thickness and standing *ca.* 10 cm when sealed. In a typical rate experiment, a series of tubes were filled with reactant solution to approximately 1/3 their (ultimate) free volume, sealed under an inert atmosphere, and placed in the thermostat. A tube, after heating for a specified interval, was cooled to room temperature within 1 min after withdrawal, opened, and analyzed by glc methods. The data obtained in this way were treated in the same manner as in the gas-phase thermolysis.

Kinetic and Analytical Results. The thermolysis of each of the ethers was carried out in the apparatus described, and the data were fitted by linear regression techniques to the general Arrhenius equation.

In each thermolysis the only products obtained were those expected from the assumption of a unimolecular elimination through a six-centered transition complex (except for *tert*-butyl allyl ether), namely, the appropriate carbonyl compound and olefin (see Table II). Identification of the reaction products was realized by observation of the retention times as compared with those of standard samples, and noting that the product patterns of the liquid and gaseous reactions were identical. The liquid reaction product identification was achieved by peak enhancement, and in some cases by mass spectrometry. The detailed data obtained for the gas phase thermolysis of each of the ethers in these experiments are given in Tables III–XIII.[59]

Table II. Reactions of Alkyl Allyl Ethers Studied

Substrate	Temp range, °C	Reaction product: Carbonyl	Reaction product: Olefin
1	452–537	Formaldehyde	Propene
2	452–519	Acetaldehyde	Propene
3	437–519	Acetone	Propene
4	422–505	Benzaldehyde	Propene
5	441–503	Benzaldehyde	Isobutene
6	462–513	Mesitylaldehyde	Propene
7	445–516	Formaldehyde	1-Phenyl-1-propene
8	424–486	Formaldehyde	1-Mesityl-1-propene
9	399–482	Propenealdehyde	Propene
10	402–490	Benzaldehyde	Allene
11	519–577	Acetone[a]	1-Butene[a]

[a] Predominant products; a minor proportion of the product (less than ~25%) considered to be a complex mixture of highly volatile unsaturated compounds which were not fully identified.

Synthesis of Substrates. Methyl Allyl Ether (1). This compound was prepared by the method reported by Bailey and Nicholas[60] in which 0.5 mol of allyl bromide was added to 0.55 mol of sodium methoxide in methanol, in small portions with vigorous stirring. The precipitated salt was removed by filtration, and the filtrate was distilled to give the ether.

Ethyl Allyl Ether (2). This compound was obtained pure from Borden Chemical Co. and distilled prior to using.

Isopropyl Allyl Ether (3). According to the method used by Skrabal,[61] 1 mol of allyl bromide was refluxed, with stirring, with mol of 2-propanol and 2 mol of sodium hydroxide in water. After 3 hr, the mixture was washed, dried, and distilled. Prior to distillation, however, it was required to warm the mixture with sodium methoxide to remove the excess allyl bromide which would otherwise cause polymerization. Thus, some methyl allyl ether was also in the products, but was removed by distillation.

Benzyl Allyl Ether (4). The general method of preparation was the Williamson synthesis, described below, and was used for several of the other ethers as mentioned below.

A solution of benzyl alcohol (32.4 g, 0.3 mol, Fisher) in 50 ml of dry glyme (ethylene glycol dimethyl ether) was added dropwise over a period of 45 min to a stirred suspension of sodium hydride (7.4 g, 0.31 mol, as a 57% dispersion in oil) in 350 ml of glyme. The reaction was exothermic and evolved hydrogen. After refluxing for 1 hr, the mixture was cooled to 30° and 36.3 g (0.3 mol) of allyl bromide in 50 ml of glyme was added dropwise over a period of 45 min. The reaction was exothermic and a white precipitate (NaBr) was formed. The mixture was then refluxed for 2 hr, cooled to 20°, and filtered to remove the NaBr. Ethyl ether was added, followed by extraction with water, drying ($MgSO_4$), and removal of solvent on the rotary evaporator. Distillation through a Vigreux column gave 35.5 g (80%): bp 45° (1 mm) [lit.[48] bp 208°]; nmr (CCl_4) δ 3.88 (d with allylic fine splitting, 2,

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(59) Listings of the kinetic data derived from gas phase thermolysis measurements with substrates 1–11 comprising Tables III–XIII will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-5234. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

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J = 5 Hz, (OCH$_2$C), 4.40 (s, 2, PhCH$_2$), 7.22 (s, 5, aromatic); ir (neat) 1650 (C=C), 1090 (C—O—C), 920 and 985 (CH=CH$_2$), 735 and 695 (monosubst benzene), C-H stretch 2850 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) parent peak – 148 (2), 107 (15), 105 (12), 92 (58), 91 (100), 79 (17), 77 (12), 65 (12), 41 (10), 39 (10).

Benzyl 2-Methylallyl Ether (5). This compound was synthesized from benzyl alcohol and 2-methylallyl chloride (Eastman) in 60% yield by the Williamson method: bp 53° (0.5 mm); nmr (CCl$_4$) δ 1.68 (s split, 3, CH$_3$C=C), 3.80 (broad s, 2, OCH$_2$C), 4.37 (s, 2, PhCH$_2$O), 4.88 (complex m, 2, C=CH$_2$), 7.22 (s, 5, aromatic); ir (neat) 1650 (C=C), 1095 (C—O—C), 900 (C=CH$_2$), 732 and 692 cm^{-1} (monosubst benzene); mass spectrum (70 eV) m/e (rel intensity) parent peak – 162 (0.1), 118 (8), 107 (44), 105 (9), 92 (25), 91 (100), 79 (8), 65 (11), 56 (12), 55 (6), 41 (7), 39 (10).

2,4,6-Trimethylbenzyl Allyl Ether (6). Chloroisodurene (2,4,6-trimethylbenzyl chloride) was synthesized by the chloromethylation of mesitylene with HCl and formaldehyde according to the method Fuson and Rabjohn.[62]

Chloroisodurene (25 g, 0.15 mol) was added dropwise to a solution of silver nitrate (35 g, 0.2 mol) in an excess of allyl alcohol (60 ml). The reaction was exothermic and AgCl precipitated immediately. The mixture was stirred for 2 hr and, after the addition of saturated NaCl solution to react with the excess AgNO$_3$, was filtered, extracted with ether, dried (K$_2$CO$_3$), concentrated, and distilled to give 17.6 g (90%): bp 80° (0.2 mm); nmr (CCl$_4$) δ 2.27 (m, 9, Ar(CH$_3$)$_3$), 3.90 (d with allylic fine splitting, 2, OCH$_2$C), 4.42 (s, 2, ArCH$_2$), 5.35 (complex m, 2, C=CH$_2$), 5.92 (complex m, 1 CH=C), 6.75 (broad s, 2, aromatic); ir (neat) 1080 (C—O—C), 985 and 920 (CH=CH$_2$), 850 cm^{-1} (isolated aromatic hydrogen); mass spectrum (70 eV) m/e (rel intensity) parent peak – 190 (11), 147 (8), 134 (21), 133 (77), 132 (100), 119 (25), 117 (24), 105 (19), 91 (24), 77 (13), 45 (20), 41 (19).

4-Methoxybenzyl Allyl Ether. This compound was synthesized from 4-methoxybenzyl alcohol (Aldrich) and allyl bromide in 87% yield: bp 80° (0.4 mm) [lit.[48] bp 86° (0.5 mm)]; nmr (CCl$_4$) δ 3.50 (s, 3, CH$_3$O), 3.87 (d with allylic fine splitting, 2, J = 5 Hz, OCH$_2$C), 4.33 (s, 2, PhCH$_2$), 5.15 (complex m, 2, C=CH$_2$), 5.88 (complex m, 1, CH=C), 6.73 (dt, 2, J = 9 and 2 Hz, aromatic), 7.17 (dt, 2, J = 9 and 2 Hz, aromatic); ir (neat) 1640 (C=C), 1240 (ArOCH$_3$), 1270 (C—O—C), 985 and 920 (CH=CH$_2$), 820 cm^{-1} (1,4 disubst benzene); mass spectrum (70 eV) m/e (rel intensity) parent peak – 178 (18), 136 (28), 135 (17), 122 (22), 121 (100), 109 (13), 94 (10), 78 (18), 77 (19), 69 (13), 52 (12), 41 (27), 39 (24).

4-Chlorobenzyl Allyl Ether. This compound was synthesized from 4-chlorobenzyl alcohol (Aldrich) and allyl bromide in 88% yield: bp 62° (0.4 mm) [lit.[48] bp 78° (0.4 mm)]; nmr (CCl$_4$) δ 3.92 (d with allylic fine splitting, 2, J=5 Hz, (OCH$_2$C), 4.37 (s, 2, ArCH$_2$), 5.18 (complex m, 2, C=CH$_2$) 5.88 (complex m, 1, CH=C), 7.22 (s, 4, aromatic); ir (neat) 1650 (C=C), 1080 (C—O—C), 985 and 920 (CH=CH$_2$), 804 cm^{-1} (1,4 disubst benzene); mass spectrum (70 eV) m/e (rel intensity) 182 (5), 141 (19), 140 (19), 139 (16), 127 (34), 126 (18), 125 (100), 113 (11), 91 (22), 80 (19), 77 (29), 75 (10), 63 (13), 51 (12), 50 (11), 41 (29), 39 (25).

4-Methylbenzyl Allyl Ether. This compound was synthesized from 4-methylbenzyl alcohol (Aldrich) and allyl bromide in 84% yield: bp 64° (0.5 mm); nmr (CCl$_4$) 2.28 (s, 3, ArCH$_3$), 3.88 (d with allylic fine splitting, 2, J = 5 Hz, OCH$_2$C), 4.38 (s, 2, ArCH$_2$), 5.17 (complex m, 2, C=CH$_2$), 5.90 (complex m, 1, CH=C), 7.12 (s, 4, aromatic); ir (neat) 1650 (C=C), 1085 (C—O—C), 985 and 920 (CH=CH$_2$), 800 cm^{-1} (1,4, disubst benzene); mass spectrum (70 eV) m/e (rel intensity) parent peak – 162 (8), 120 (21), 119 (22), 106 (47), 105 (100), 103 (8), 93 (19), 91 (30), 78 (9), 78 (8), 77 (24), 65 (10), 51 (10), 41 (21), 39 (22).

Methyl 1-Phenylallyl Ether (7). This compound was synthesized from methyl iodide and α-phenylallyl alcohol (1-phenyl-2-propen-1-ol) in 50% yield by the Williamson method: bp 34° (0.02 mm); nmr (CCl$_4$) δ 3.23 (s, 3, OCH$_3$), 4.52 (d with allylic fine splitting, 1, PhCH), 5.17 (complex m, 2, C=CH$_2$), 5.92 (complex m, 1, CH=C), 7.25 (s, 5, aromatic); ir (neat) 1640 (C=C), 1080 (C—O—C), 980 and 920 (CH=CH$_2$), 755 and 695 cm^{-1} (monosubst benzene).

Methyl 1-(2,4,6-Trimethylphenyl)allyl Ether (8). Bromomesitylene was prepared according to the method of Smith[63] and was converted to mesitylmagnesium bromide by reaction with magnesium in ether[64] (initiated with 1 g of ethyl bromide). A solution of acrolein (Aldrich, freshly distilled) in ether was added to the Grignard reagent. Work-up and distillation gave 1-(2,4,6-trimethylphenyl)-2-propen-1-ol (**8a**) in 80% yield: bp 95° (1.5 mm); nmr (CCl$_4$) δ 2.25 (m, 9, Ar(CH$_3$)$_3$), 4.01 (broad s, 1, OH), 5.07 (complex m, 2, C=CH$_2$), 5.55 (complex m, 1, ArCH), 6.08 (complex m, 1, CH=C), 6.75 (s, 2, aromatic); ir (neat) 3400 (OH), 1650 (C=C), 985 and 920 (CH=CH$_2$), 850 cm^{-1} (isolated aromatic hydrogen).

The ether (**8**) was synthesized from alcohol (**8a**) and methyl iodide in 85% yield by the Williamson method: bp 75° (0.2 mm); nmr (CCl$_4$) δ 2.26 (m, 9, Ar(CH$_3$)$_3$), 3.17 (s, 3, OCH$_3$), 5.00 (complex m, 3, ArCH, and C=CH$_2$), 6.07 (complex m, 1, CH=C), 6.75 (broad s, 2, aromatic); ir (neat) 1650 (C=C), 1080 (C—O—C), 990 and 920 (CH=CH$_2$), 848 cm^{-1} (isolated aromatic hydrogen); mass spectrum (70 eV) m/e (rel intensity) parent peak – 190 (70), 175 (46), 163 (51), 159 (39), 158 (75), 157 (15), 145 (21), 144 (30), 143 (100), 132 (25), 129 (22), 128 (27), 119 (12), 112 (16), 88 (16).

Diallyl Ether (9). This compound was prepared by the reaction of allyl bromide and 50% aqueous potassium hydroxide at 100° according to a procedure described by Biltz and Beck.[65a] The product utilized in the kinetic measurements boiled at 94° at atmospheric pressure. Its purity and constitution were established by glc and nmr standards.

Benzyl Propargyl Ether (10). This compound was synthesized from benzyl alcohol and propargyl bromide (Aldrich) in 50% yield by the Williamson method: bp 43° (0.4 mm); nmr (CCl$_4$) δ 2.33 (t, 1, J = 2.5 Hz, C≡CH), 4.01 (d, 2, J = 2.5 Hz, OCH$_2$—C≡C), 450 (s, 2, PhCH$_2$O), 7.25 (s, 5, aromatic); ir (neat) 3300 C—C≡), 2120 (HC≡C), 1070 (C—O—C), 734 and 694 cm^{-1} (monosubst benzene); mass spectrum (70 eV) m/e (rel intensity) parent peak – 146 (13), 145 (10), 117 (18), 116 (42), 115 (20), 107 (26), 105 (41), 92 (62), 91 (100), 79 (61), 78 (17), 77 (59), 65 (30), 63 (15), 51 (43), 50 (20), 40 (12), 39 (73), 38 (21).

***tert*-Butyl Allyl Ether (11).** This ether was prepared by the method of Talley, Hunter, and Yanovsky,[65b] in which 3.5 mol of sieve-dried *tert*-butyl alcohol was added to 700 ml of dry xylene in a stirred reaction flask. Gradually, 3.5 mol of sodium was added while heating at 80°, and then the mixture was heated to 100° for 6 hr. After the mixture stood overnight, the solid cake was broken up, and the mixture was heated again while stirring at 110–115° for 8 hr. Then 100 ml more of *tert*-butyl alcohol was added and the mixture heated overnight and cooled to room temperature. Allyl bromide was added (3.5 mol) dropwise with stirring over a 20-min period and the mixture heated on a steam bath for 24 hr.

It was then cooled, washed with water, dried, and distilled at atmospheric pressure. The properties of the distilled product were nearly identical with those described in the literature.[65b]

Results and Discussion

(A) Substituent Effects. Substitution at R$_1$ and R$_3$. With the exception of the *tert*-butyl allyl ether (**11**), the activation parameters for the thermolyses of all the allyl ethers studied are remarkably similar. The data in Table XIV confirm that the range of $\Delta E^{\ddagger}$ values for the entire series (exclusive of **11**) is only 3.7 kcal/mol, with seven of the ten substrates falling within a maximum spread of only 0.7 kcal/mol. Moreover, at the normal temperatures of measurement (400–500°) the maximum range of relative rate values encompasses only a factor of <4 for the most usual substituents, a factor of only 11 results when including the most unsaturated ones (case **9**) and ignoring the statistical factor due to multiple unsaturation. Even the factor of 11 is considerably diminished when the entropy term is corrected for multiple unsaturation. This pattern

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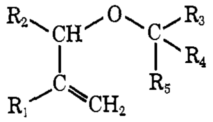
[62] R. C. Fuson and N. Rabjohn, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 557.

[63] L. I. Smith, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 95.

[64] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, p 29.

[65] (a) H. Biltz and A. Beck, *J. Prakt. Chem.*, [2] **118**, 221 (1927); (b) E. A. Talley, A. S. Hunter, and E. Yanovsky, *J. Amer. Chem. Soc.*, 73, 3528 (1951).

Table XIV. Activation Parameters in the Thermolysis of Various Allyl Alkyl Ethers in the Gas Phase



	R_1	R_2	R_3	R_4	R_5	$\Delta E^{\ddagger}$, kcal/mol	Log A	$-\Delta S^{\ddagger}$, eu	Relative rate at 500°	Relative rate at 450°	Relative rate at 400°
Methyl allyl (**1**)	H	H	H	H	H	41.6 ±0.6	11.09 ±0.02	11.6 ±0.7	1.0	1.0	1.0
Ethyl allyl (**2**)	H	H	CH_3	H	H	41.6 ±0.6	11.26 ±0.17	10.8 ±0.8	1.5	1.5	1.5
Isopropyl allyl (**3**)	H	H	CH_3	CH_3	H	41.3 ±0.3	11.34 ±0.09	10.5 ±0.4	2.1	2.2	2.2
Benzyl allyl (**4**)	H	H	C_6H_5	H	H	41.2 ±0.1	11.53 ±0.03	9.5 ±0.1	3.6	3.6	3.7
Benzyl 2-methylallyl (**5**)	CH_3	H	C_6H_5	H	H	40.9 ±0.3	11.43 ±0.09	10.1 ±0.4	3.4	3.5	3.6
2,4,6-Trimethylbenzyl allyl (**6**)	H	H	Mes[a]	H	H	44.6 ±1.0	11.96 ±0.28	7.6 ±1.3	1.0	0.9	0.8
Methyl 1-phenylallyl (**7**)	H	C_6H_5	H	H	H	43.5 ±0.2	12.21 ±0.06	6.5 ±0.3	3.8	3.5	3.1
Methyl 1-mesitylallyl (**8**)	H	Mes[a]	H	H	H	43.4 ±0.3	12.16 ±0.06	6.6 ±0.4	3.6	3.3	3.0
Diallyl (**9**)	H	H	Vinyl	H	H	40.9 ±0.03	11.91 (11.61)[c] ±0.10	7.8 (9.2)[c] ±0.5	10.2 (5.1)[c]	10.6 (5.3)[c]	11.0 (5.5)[c]
Benzyl propargyl (**10**)	*b*	H	C_6H_5	H	H	40.9 ±0.1	11.92 ±0.04	7.7 ±0.2	10.5	10.9	11.3
tert-Butyl allyl (**11**)	H	H	CH_3	CH_3	CH_3	54.6 ±1.2	13.53 ±0.33	0.6 ±1.6	0.06	0.03	0.02

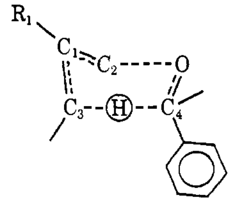
[a] Abbreviation for (2,4,6-trimethylphenyl). [b] $\equiv$C—H rather than $=CH_2$ at terminal position. [c] Values corrected for the statistical factor of 2.

of extreme insensitivity of rate to variation in the substituents R_1 through R_4 (Table XIV) constitutes a clear indication of the cyclic concerted transition state of bond making and breaking. It appears to be the most identifying characteristic of this class of thermolysis reactions in contrast to others in which charged intermediates are developed or free-radical species are formed in the transition state.

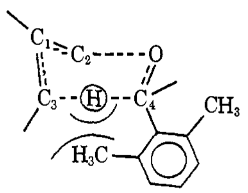
Comparing the results for ethers **1**–**4** (see Table XIV), in which the α substituent on the carbon bearing the transferring hydrogen is altered while the allyl moiety is unchanged, the activation energy ($\Delta E^{\ddagger}$) is unaffected by substituent variation, but the entropy ($\Delta S^{\ddagger}$) term suffers a slight increase (*ca.* 2 eu) in going from methyl (**1**) to benzyl (**4**). That is to say, the small rate factor (*ca.* 4) which separates the extremes of this series is entirely attributable to small entropy variations. Again, the magnitude of variation is exceedingly minor by contrast with $\Delta E^{\ddagger}$ decreases of at least 5–10 kcal mol[66a] (and accompanying rate increases) which are to be expected if the substituents involved were able to conjugate with radicals or partial charges developed in the activated complex of the reaction. The entropy increases experienced in the series (**1**–**4**) are most probably caused by progressively greater internal rotation barriers in the ground state.[66b]

Substituting mesityl (in **6**) for phenyl (in **4**) produces an almost 3.5 kcal increase in $\Delta E^{\ddagger}$ and a 2 eu increase in $\Delta S^{\ddagger}$. Clearly, the data considered above do not disclose any degree of conjugation of the phenyl with the incipient carbonyl in the transition state. Thus, considering the total range of $\Delta E^{\ddagger}$ and $\Delta S^{\ddagger}$ values in the reaction series, this relatively prodigious effect of the mesityl substitution cannot be correlated with inhibition of transition-state resonance by its *o*-methyl groups. Some understanding of the origin of the mesityl group's influence can be attained by consulting Scheme I. Here it is presumed that the essential retro-ene reaction pattern, characteristic of all members of the reaction series, has a pericyclic transition state,[67a] *i.e.*, a sigmatropic fragmentation.[67b] This specificity of the steric influence here can be perceived by comparison with the result of introducing a methyl group at the R_1 position (substrate **5**). The near identity of rates

Scheme I. Pericyclic Transition States



4, $R_3 = C_6H_5$
5, $R_3 = C_6H_5$; $R_1 = CH_3$
no interference at C_4



6, R_3 = Mes; R_1 = H
O-methyl interference illustrated at C_4

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(66) (a) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); (b) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968.

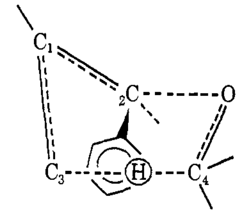
(67) (a) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, 10, 761 (1971); (b) R. B. Woodward and R. Hoffman, *ibid.*, **8**, 781 (1969).

and activation parameters in **4** and **5** confirms that the R_1 methyl is geometrically and electronically incapable of influencing the structure of the pericyclic transition state.

(B) Substitution at R_2. A phenyl or mesityl group at the allylic position of a retro-ene substrate would certainly be expected to produce dramatic changes in the activation parameters if the reaction involved a charged or radical transition state. The total absence of such influences in the rate data, listed in Table XIV and displayed in Figure 1, establish beyond cavil that the R_2 substituent cannot be conjugated with the incipient double bond at the allylic position of the activated complex. The entries in the table for substrates **1**, **7**, and **8** attest to this conclusion. Apparently, the aromatic rings in **7** and **8** have measurably increased the activation energy in **1**, where, in fact, conjugation effects would have anticipated a very considerable decrease in $\Delta E^{\ddagger}$ (by some 5 kcal/mol). Moreover, if phenyl had experienced this conjugation, mesityl would most assuredly have resisted it through steric inhibition of resonance and created a great disparity in their $\Delta E^{\ddagger}$ values. Instead, a highly unusual effect is realized where both $\Delta E^{\ddagger}$ and $\Delta S^{\ddagger}$ terms are *identical* for phenyl and mesityl.

To explain these results appropriately, the pericyclic transition state must reveal how phenyl, independently of the degree of ortho steric or polar substitution, can increase $\Delta E^{\ddagger}$ by 2 kcal and $\Delta S^{\ddagger}$ by 5 eu. One possible explanation is that the incipient double bond must be developing in the activated complex in the cis configuration in which resonance stabilization is inhibited. Presumably there are considerations arising from $\pi-\pi$ interactions which enforce a preference for the conformation[68a] of the transition state depicted in Scheme II. The importance of conformational preference as a factor in reactions with symmetrical transition states has been frequently discussed.[68b]

Scheme II. Pericyclic Transition State



7, $R_2 = C_6H_5$
8, $R_2 = \text{Mes}$

These considerations allow for a large proportion of the product olefins initially formed (propenylbenzene and propenylmesitylene) being in the cis configuration in which resonance is sterically hindered. However, a product containing greater than 90% of *trans*-propenylbenzene is realized. The possible occurrence of cis–trans isomerization under the conditions of the fragmentation reaction giving rise to the (postulated) *cis*-propenylbenzene was considered. An estimate of $\Delta G^{\ddagger}_{480°} = 53$ kcal/mol (the activation energy for this isomerization) was deduced by determining the rate of isomerization at 550° (0.10 min^{-1}), and assuming a value of $\log A = 13.2$ which is characteristic[69] of such reactions. This estimate is also reasonable on the basis of the known activation energies for cis–trans isomerization of 2-butene (63 kcal/mol)[69c] and stilbene (43 kcal/mol).[69] Consequently, the $\Delta G^{\ddagger}_{480°} = 48$ kcal/mol for the fragmentation of **7** is only about 5 kcal lower than is required to activate (ground state) *cis*-propenylbenzene for isomerization to trans.

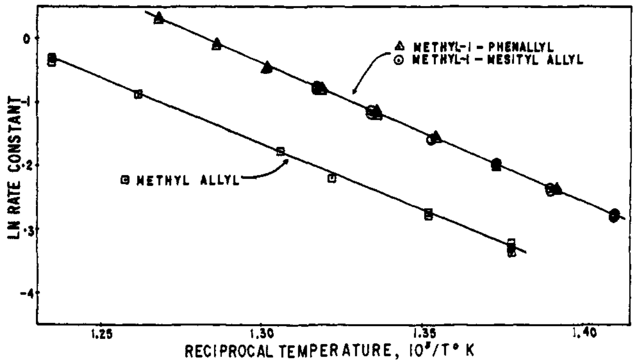


Figure 1. Allyl alkyl ether kinetics. The influence of the R_2 substituent.

Thus, immediately following upon the transition state some nine-tenths of the developing *cis*-propenylbenzene may be transformed to the trans isomer over a nearby (*ca.* 5 kcal higher) barrier even before it could reach the ground state. This provides an alternative route for the isomerization and also accounts for the observed isomeric content of the propenylbenzene product approaching that of the equilibrium composition. In highly exothermic unimolecular reactions such as we have in the fragmentation of allylic ethers, it is not unusual[69d] to encounter isomerization of "hot" molecules in what appears to be a non-Arrhenius rate dependence.

(C) Origins of Effects in Diallyl and Benzyl Propargyl Ethers. Substrates **9** and **10** are cases in point. The fact is that these cases have identical activation parameters ($\Delta E^{\ddagger}$ and $\Delta S^{\ddagger}$) within experimental uncertainy, though they differ considerably in the nature of their respective centers of (excess) unsaturation. At the same time, also, both closely resemble in their rate parameters the remaining members of the reaction series considered in Table XIV. Clearly, the factors responsible for the small rate difference which distinguishes **9** and **10** from (say) **4** are almost completely correlated with a measurable increase in activation entropy. In the case of **9**, apparently, this entropy increase may be traceable to an increased probability of forming the transition state in a substrate possessing

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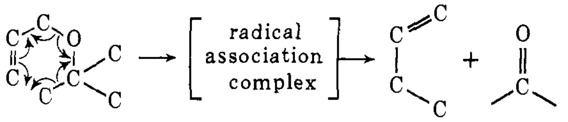
(68) (a) A referee has asked the reasonable question, "Since α-methyl groups cause steric difficulties in the pericyclic transition state of 6 in Scheme I, why do we fail to see a similar effect created by *O*-methyl groups in phenyl substitution at R_2 in Scheme II?" The answer must be viewed in models of these activated complexes which allow a suitable degree of extension of the $C_2 \cdots O$ bond. If this is (say) about twice the normal bond distance, the mesityl ring can be accommodated without extraordinary compressive strain, particularly when it is not conjugated with the double bond developing between C_1 and C_2. On the other hand, the $C_3 \cdots H$ bond in Scheme I is close to a normal C–H bond distance. Thus, ortho substitution on aryl at C_3 could not fail to exert strain and deform the required linear relationship of the H-transfer bond between C_4 and C_3. (b) See discussion by H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 655; W. von E. Doering and W. R. Rosh, *Angew. Chem., Int. Ed. Engl.*, 2, 115 (1963).

(69) (a) G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, 56, 638 (1934); (b) F. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938); (c) see p 74 of ref 66b; (d) see, for example, M. C. Flowers, H. M. Frey, and H. Höpf, *J. Chem. Soc., Chem. Commun.*, 1284 (1972).

two equivalent ground-state conformations which can be activated. In the case of **10**, the $\Delta S^{\ddagger}$ increase, when compared to the allylic analog **4**, is undoubtedly attributable to the increased rigidity of the substrate originating in the triple bond moiety. Though the propargyl structure must be bent to accommodate the pericyclic transition state geometry, this is easily realized in a low energy bending vibrational mode[70] that is ordinarily active in the Raman.

(D) Nature of the Fragmentation Reaction in *tert*-Butyl Allyl Ethers. As mentioned earlier,[25,26] the most common thermolytic reaction of *tert*-butyl ethers (*t*-Bu-OR) is a high-activation demand (*ca.* 60 kcal), four-center process resulting in isobutylene and an alcohol fragment (ROH). The fragmentation process which is now found to occur in preference to this is analogous to the six-centered fragmentation course preferred by all the other allyl ethers (considered in Table XIV). The principal difference, of course, lies in the fact that a methyl group is being transferred in the rate-determining step of the process taking place in **11**.

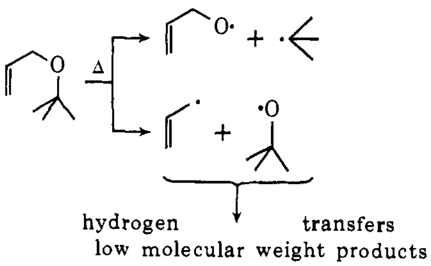
It is therefore not surprising that a much greater (*ca.* 14 kcal) activation energy requirement characterizes the fragmentation process in **11** compared to other alkyl allyl ether fragmentations. This increase in $\Delta E^{\ddagger}$, in fact, places the fragmentation reaction of **11** in the same class energetically as the free-radical cleavages of dialkyl and aryl alkyl ethers. Some evidence for free-radical formation in this reaction are indeed to be observed, the most prominent of which is the comparatively large increase in entropy. The entropy change ($\Delta S^{\ddagger}$) of the fundamental fragmentation reaction occurring in **11** may actually be higher (more positive) than experimentally measured. The difficulty in attaining a more accurate assessment of $\Delta S^{\ddagger}$ is due to the complication of considerable side reactions leading to a good proportion (*ca.* 25%) of unidentified, volatile products. The predominant products (>75%) could be identified as acetone and 1-butene consistent with the six-centered transition state (eq 1). However, the activated complex depicted by **11a** cannot be regarded as a concerted process. Rather, the radicals generated in the bond-breaking steps (consistent with the observed activation parameters) can remain in some form of association long enough to recombine to products before they can separate for participation in other product forming reactions.



(1)

11a

Conceivably, too, a part of the product arises from the normal[25,26] four-centered concerted thermolysis course of *tert*-butyl alkyl ethers resulting here in isobutylene and allyl alcohol. The side-reaction products, for the most part, were smaller than 1-butene (as indicated by glc analysis) but included some 4,4-dimethyl-1-pentene. The latter could arise from the recombination of *tert*-butyl and allyl radicals formed from an initial radical cleavage of the substrate. It is conceivable, too, that the reaction course shown by eq 2 could also be responsible for the multiplicity of low molecular weight products.



(2)

(E) Reaction in the Liquid Phase. All substrates were reacted in chlorobenzene which was taken as representative of a nonpolar solvent. Two of the substrates were also reacted in *N*-methylacetamide to determine whether this highly polar solvent would produce any significantly different results. Finally, one substrate was also reacted in a polar solvent of high complexing ability such as acetonitrile. The relevant data and activation parameters determine in each case are compared in Table XV. The results obtained in the liquid phase are not as precise as those gathered by the more sophisticated method applied in the gas phase thermolysis studies. Thus, in chlorobenzene solvent allyl methyl (**1**), ethyl (**2**), and isopropyl (**3**) ethers have activation energies which are, within the experimental error, very close to the average of all ($\Delta E^{\ddagger} = 39.0 \pm 0.8$ kcal/mol). This is slightly lower (by only about 1.5 kcal) than the average gas-phase value. The activation entropies of all three processes are similarly close ($\Delta S^{\ddagger} = -15 \pm 1.5$) and only about 5 eu smaller (more negative) than the corresponding gas-phase average. However, they are sufficiently precise to establish that the nature and mechanism of the liquid-phase thermolysis of allyl alkyl ethers is essentially identical with that of the gas phase. No difficulties were experienced that could be traced to instability of the solvents used at the elevated reaction temperatures.

This clear-cut conclusion can also be inferred from the plots of Figure 2. Therein it can be seen that the liquid phase rate points fall on lines which represent (more or less) a low temperature linear extrapolation of the Arrhenius lines drawn through the higher temperature gas-phase runs. In fact, the differences between the gas-phase and liquid-phase rates reside primarily in the activation entropy term. These can be reconciled, therefore, with the factor of solvent reorganization in going from ground to transition state. The magnitude of entropy differences involved are sufficiently small to preclude any consideration of charge development in the transition state. This is also borne out by the similarity of entropy effects between the highly polar solvent NMA and the nonpolar chlorobenzene. The slight element of dissimilarity which can be perceived by comparison with the reaction in acetonitrile (in the case of **3**) can be readily accounted as a specific solvent effect. It is conceivable that acetonitrile, even at the elevated temperatures of reaction, forms a weak interaction complex with substrate which persists in the transition state. This results in a very slight increase in both $\Delta E^{\ddagger}$ and in $\Delta S^{\ddagger}$ compared with the gas-phase parameters; certainly this is not enough to suggest that any significant change has occurred in the cyclic concerted reaction

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[70] A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Amer. Chem. Soc.*, **93**, 6967 (1971); H. G. Viehe, "Chemistry of Acetylenes," Marcel Dekker, New York, N. Y., 1969, Chapter 1.

Table XV. Arrhenius Parameters for Allyl Ether Solution Kinetics

Solvent	A, sec^{-1}	Log A	$\Delta E^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Correlation coeff	Rate at 450° relative to	
						Gas phase	**1**[a]
			Methyl Allyl Ether				
Chlorobenzene	2.67×10^{10}	10.43	40.4	−14.2	0.998	0.5	1.0
		±0.24	±0.7	±1.1			
NMA[b]	4.27×10^{9}	9.63	3.80	−17.8	0.995	0.4	0.8
		±0.82	±2.2	±3.7			
Gas phase		11.09	41.6	−11.6			
			Ethyl Allyl Ether				
Chlorobenzene	1.10×10^{10}	10.04	38.7	−15.8			
		±0.25	±0.6	±1.2	0.999	0.5	1.3
Gas phase		11.26	41.6	−10.8			
			Isopropyl Allyl Ether				
Chlorobenzene	1.29×10^{10}	10.11	37.8	−15.5	0.998	0.7	2.9
		±0.44	±1.1	±2.0			
Acetonitrile	4.56×10^{11}	11.66	42.1	−8.4	0.999	1.2	5.2
		±2.1	±0.5	±0.9			
NMA[b]	3.24×10^{10}	10.51	38.7	−13.7	0.999	0.9	3.9
		±0.5	±0.1	±0.2			
Gas phase		11.34	41.3	−10.5			
			tert-Butyl Allyl Ether				
Chlorobenzene	5.70×10^{16}	16.76	54.8	+15.0	0.978	1500	94.6
		±2.6	±6.8	±12			
Gas phase		13.53	54.6	−0.6			

[a] Methyl allyl ether in chlorobenzene. [b] *N*-methylacetamide.

Table XVI. Para-Substituent Rate Effects in the Gas-Phase Thermolysis of Benzyl Allyl Ethers at 473.3°

Para substituent	$k_{\rm rel}$
$-OCH_3$	0.98
$-CH_3$	0.95
-H	1.00
-Cl	0.98

mechanism as a consequence of solvent involvement in the instance of the common alkyl allyl ether substrates, **1**→**9**. The *tert*-butyl allyl ether (**11**) represents a striking contrast. While its liquid phase activation energy, $\Delta E^{\ddagger}$, is nearly identical with the gas-phase value, it is the fastest thermolysis reaction in the liquid phase, though it is the slowest in the gas-phase series. The ratio of rates of the liquid to gas phase reactions of this substrate is of the order of 1500. This dramatic change is entirely attributable to the pre-exponential term, corresponding to a large increase in $\Delta S^{\ddagger}$ in the liquid-phase reaction. Product analysis by means of a gas chromatograph coupled to a mass spectrometer indicates little or no increase in the proportion of the side products consisting of lower molecular weight hydrocarbons and 4,4-dimethyl-1-pentene, besides the normal products, acetone and 1-butene.

In the normal six-center cyclic transition state, a measurable activation entropy decrease attends the change from gas- to liquid-phase conditions. This was correlated with some solvent reorganization even in the absence of polar or radical character in the activated complex. In other words, since bond making and bond breaking occur in concert, the external solvent cage has little influence on this process and *vice versa*. However, in the reaction of **11**, where the evidence would indicate formation of a radical pair in the gas phase transition state, the imposition of a solvent cage[71] in the liquid-phase reaction introduces a constraint which greatly increases the frequency factor (as observed in Table XV).

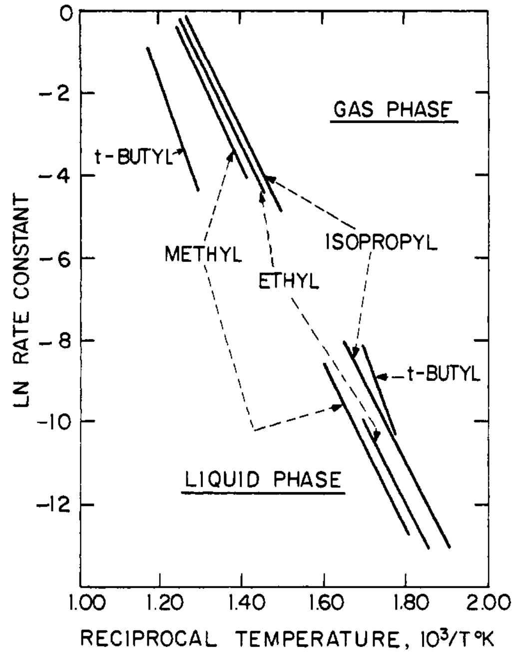

Figure 2. Comparison of liquid and gas phase thermolysis kinetics of alkyl allyl ethers.

(F) The Question of Substituent Effects in Para-Substituted Benzyl Allyl Ethers. In previous sections of these discussions it has been determined that substituents of the six-membered cyclic, transition-state structure exert no polar substituent effect on rate. Whatever effects of substitution have been observed can be

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(71) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, 30, 120 (1934).

correlated with steric considerations alone. In striking contrast to these observations is the report of Cookson and Wallis[47] who have previously studied a series of para-substituted benzyl allyl ethers. These authors noted a trend of decreasing rate in the series p-OCH$_3$ > p-H ≅ p-Cl > p-NO$_2$, suggesting a reaction mechanism characterized by a negative Hammett ρ constant of significant magnitude.

Because of the implied contradictions, and because the apparatus used by Cookson and Wallis[47] was better suited for preparative work rather than kinetics, it was considered necessary to reinvestigate this question. The data obtained in this study are presented in Table XVI. Clearly, no significant rate differences are to be observed amongst the various para-substituted benzyl allyl ethers on gas-phase thermolysis. To all intents and purposes the Hammett p of this reaction is zero, providing full support for the conclusion reached earlier that no direct polar substituent effects are exercised in the pericyclic transition state of this retro-ene reaction.

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The Kinetic Deuterium Isotope Criterion Applied to the Thermolysis of Alkyl Allyl Ethers. II

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Abstract: Measurements of $k_{\mathrm{H}}/k_{\mathrm{D}}$ as a function of the temperature of thermolysis of three different unsaturated ethers, the benzyl allyl, benzyl propargyl, and isopropyl allyl, have been carried out. The maximum theoretical isotope effect has been realized in each instance; no evidence has been found for proton tunneling. In accordance with previous application of this criterion of transition-state structure in H-transfer reactions, these results suggest fully symmetrical bond making and breaking in the activated complex of each of these typical retro-ene fragmentation processes. Earlier proposals of a completely planar transition state which have been advanced for related thermolysis reactions are also ruled out.

In a previous article,[1] studies of the thermolysis of alkyl allyl ethers were discussed in which the data gathered on product analysis, substituent effects on rate, and activation parameters were applied to elucidate the nature of this intramolecular H-transfer process. The results clearly indicated that the general reaction had a highly concerted transition state of bond making and breaking with no evidence of free radical or charge development.

The studies to be reported here were addressed to the question of whether the concerted transition state was symmetrical or otherwise. An attractive way of describing the symmetrical transition state is in terms of the bond order between hydrogen and the atoms between which it is being transferred.[2] In the instance of the thermolysis of alkyl allyl ethers, where hydrogen is transferred from carbon to carbon in a six-centered structure, the symmetrical transition state is simply that in which the bond order between hydrogen and each carbon is $^1/_2$. In this linear arrangement $(\mathrm{C}\cdots\mathrm{H}\cdots\mathrm{C})$ of maximum energy content on the reaction path, the real hydrogen vibrations to carbon are immobilized and all the C–H stretching vibrational energy is lost.

This picture of the symmetrical transition state is the basis of the simplified theoretical treatments[2-6] often referred to as the three-center model of the kinetic deuterium isotope effect, which predict that under such circumstances $k_{\mathrm{H}}/k_{\mathrm{D}}$ will exhibit a maximum value determined entirely by the zero-point differences of the respective C–H and C–D bonds. This analysis also anticipates that in a transition state which can be classified as either product-like or reactant-like the values of $k_{\mathrm{H}}/k_{\mathrm{D}}$ will be considerably below the maximum.

Despite the expression[7-10] of numerous theoretical reservations concerning the validity of this simplified treatment of the kinetic deuterium isotope effect, it has recently been shown[11] to provide a useful criterion for the characterization of the symmetrical transition state. Thus, in cases where independent evidence can be obtained supporting the symmetrical structure of the transition state, it has been shown that $k_{\mathrm{H}}/k_{\mathrm{D}} = (A_{\mathrm{H}}/A_{\mathrm{D}}) \exp(\Delta E°/RT)$ applies, where $A_{\mathrm{H}}/A_{\mathrm{D}} \cong 1.0$, and $\Delta E° =$ the zero-point energy differences of the critical bond to hydrogen and deuterium. On the other hand, any significant departure from symmetry in this linear array of the three-center model involves a very large increase in the vibrational energy of the bond to hydrogen in the transition state. Thus, contrary to the predictions of the simplified treatment of the kinetic deuterium isotope effect, in which reactant-like and

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