The Volume Change of Activation in the Claisen and Curtius Rearrangements

BY K. R. BROWER

The volume change of activation, ΔV^*, for the Curtius rearrangement of benzazide is $+ 2$ ml. in alcohol–water and $+ 5$ ml. in ligroin. The predominance of bond-breaking in the transition state suggests that an intermediate azene is formed. The ΔV^* for the Claisen rearrangement of allyl vinyl ether and allyl p-cresyl ether in non-polar solvents is -18 ml. and for allyl m-methoxyphenyl ether and allyl p-cresyl ether in alcohol–water is -15 ml. The transition state is not highly polarized, and the ΔV^* is appropriate to the formation of a ring.

Introduction

For several reactions involving intermolecular rearrangements it has been shown that asymmetric migrating groups retain their configurations.[1] One may infer that the migrating group is bonded during the entire process or at least is not free for any time comparable to h/kT. It would be interesting to know for each particular case whether the transition state shows a predominance of bond-making or bond-breaking, and it seems possible that the question might be answered by measurement of the volume change of activation. The volume change reflects not only the motion of the reactant along the reaction coördinate but also the variation of the volume of electrostricted solvent due to change in the electrical polarization of the reactant,[2a] and it would be necessary to separate these factors by variation of the solvent as described in a previous paper.[2b]

For the present study the Claisen and Curtius rearrangements were selected because their rate controlling steps are not preceded by combination of the starting material with an acid or basic catalyst. Such catalysis would introduce an additional volume change the estimation of which would pose a considerable although perhaps not insuperable difficulty.[3] The Claisen and Curtius rearrangements have the further advantage that the starting materials are neutral and relatively stable, and the reactions are kinetically well behaved. Both reactions have been very extensively investigated, and reviews of the literature are available.[4]

Results and Discussion

The rates of rearrangement of allyl p-cresyl ether, allyl m-methoxyphenyl ether, allyl vinyl ether and benzazide in solvents differing in polarity were measured at various pressures to 1400 atm. The volume changes of activation listed in Table I were calculated from the equation

$$RT(\delta \ln k/\delta P)_T = - \Delta V^*$$

in which k is the reaction rate constant and ΔV^* is the change of molar volume resulting from the transformation of one mole of reactant into activated complex. The value of the derivative at zero pressure was estimated from a graph of $\ln k$ vs. P. Experimental error in the measurement of ΔV^* is approximately ± 1 ml. Owing to differences in reactivity depending on substrate and solvent, it was necessary to use a range of about $50°$ for the various Claisen rearrangements. The measurement of ΔV^* for allyl p-cresyl ether in 65% ethanol–35% water was carried out at two temperatures $20°$ apart in order to test the legitimacy of comparing volume changes measured at different temperatures. The two values of ΔV^* agreed within the limit of experimental error in concordance with the result of a previous test of this kind.[5] The use of two temperatures also made it possible to calculate ΔE^* (27 ± 1 kcal./mole) and ΔS^* (-20 e.u.). The same rearrangement is reported to have ΔE^* 31.2 and ΔS^* $- 12.6$ in Carbitol[6] and ΔE^* 34.0 and ΔS^* -7 in diphenyl ether.[7]

The rearrangement of benzazide involves the production of two neutral molecules from one, and it is perhaps not surprising that ΔV^* is positive. The decomposition of aromatic diazonium salts which also has N_2 as the leaving group has ΔV^*, $+ 10$ ml./mole.[8] The somewhat smaller values found for benzazide might indicate that the leaving group is effectively smaller due to the absence of ionic solvation. If bond formation were significantly involved in the transition state ΔV^* probably would have been negative since the compression accompanying bond-formation normally ranges from 10 ml. upwards whereas the expansion due to bond-breaking is rarely as large as 10 ml.

The small difference in ΔV^* for the benzazide decomposition in the two solvents indicates that the transition state is not highly polarized. Reactions which are known to involve strongly polar transition states such as the S_N2 reactions of halides with amines have very different volume changes of activation in polar and non-polar solvents.[2,9] It also has been reported recently that the effect of solvent ionizing power on the reaction rate is small.[10] Since the structure of azides is commonly

(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. 9–10; Jack Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, Chap. 14–15; G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, Chap. 12–13; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, Chap. 14–15.

(2) (a) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London, 1957; (b) K. R. Brower, J. Am. Chem. Soc., 81, 3504 (1959).

(3) J. Koskikallio and E. Whalley, Trans. Faraday Soc., 55, 798, 809 (1959).

(4) The Claisen rearrangement is reviewed by D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. 1, and the Curtius rearrangements by P. A. S. Smith in Vol. III, Chap. 9. See also ref. 1.

(5) K. R. Brower, J. Am. Chem. Soc., 80, 2105 (1958).

(6) W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, ibid., 80, 3271 (1958).
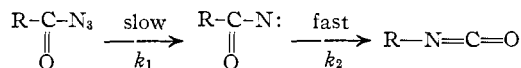
(7) H. L. Goering and R. R. Jacobson, ibid., 80, 3277 (1958).

(8) K. R. Brower, ibid., 82, 4535 (1960).

(9) A. P. Harris and K. E. Weale, J. Chem. Soc., 146 (1961).

(10) S. Smith, A. Fainberg and S. Winstein, J. Am. Chem. Soc., 83, 618 (1961).

represented as a resonance hybrid involving polarized contributing forms it is possible that the slight variation of ΔV^* with solvent polarity is due to differences in solvation of the starting material. The apparent molar volumes of 0.1 M benzazide in 50% alcohol–water and petroleum ether are 127.6 ml. and 123.5 ml., respectively. The difference of 4 ml. is nearly equal to the difference in ΔV^*.

A mechanistic picture of the Curtius rearrangement which is consistent with the present findings is

$$\underset{O}{\overset{R\text{-}C\text{-}N_3}{\|}} \xrightarrow[k_1]{\text{slow}} \underset{O}{\overset{R\text{-}C\text{-}N:}{\|}} \xrightarrow[k_2]{\text{fast}} R\!\!-\!\!N\!\!=\!\!C\!\!=\!\!O$$

It has been argued that the bond-breaking and migration steps must be nearly simultaneous or the azene intermediate would be trapped by addition of a nucleophile such as water.[11] The condition of "near" simultaneity could be satisfied, however, without k_2 being as great as 10^{12} sec.$^{-1}$ and therefore without involvement of a component due to bond-formation in the measured ΔV^*. It is interesting to note recent evidence of the intermediacy of an azene in the decomposition of an aryl azide.[12]

For the Claisen rearrangements the substantially negative ΔV^* suggests a highly compressed transition state. The slight increase which accompanies the change of solvent from hydrocarbon to alcohol–water mixture indicates that the transition state is only slightly more polar than the starting material. The increase of 3-4 ml. found here contrasts sharply with the 20 ml. increase noted elsewhere.[2] The effect of substituents on the rate of rearrangement has been studied extensively,[6,7] and it is reported that m- and p-electron donating groups accelerate the reaction. It should be emphasized that the substituent effects are slight; for example, the p-nitro group reduces the rate by a factor of two, and the p-amino group increases the rate somewhat less than tenfold. The reported effect of solvent on reaction rate[7] is that an increase of polarity causes acceleration of about the same low magnitude as that noted here. A further striking demonstration of the low polarity of the transition state is that allyl vinyl ether rearranges in the vapor phase[13] at 200° with rate constant, 3.8×10^{-3} sec.$^{-1}$, and by means of the reported activation energy, it can be calculated that at the temperature used here the reaction in the vapor phase is only one-sixth as fast as in the condensed phase.

The compression of 14–18 ml. in the transition states of the Claisen rearrangements is evidently a property of the reactant molecules themselves since it is not sensitive to solvent polarity. A compression of this magnitude is appropriate to the formation of a new ring; for example, the molar volume of cyclohexane is 17 ml. less than that of 1-hexene. The entropies of activation[6,7] also indicate that bond-formation is important in the activation process. Below is a set of structures which may account for the role of bond-formation.

(11) C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **72**, 4284 (1950).

(12) P. A. S. Smith, Abstracts of Papers Presented at the St. Louis Meeting of the American Chemical Society, March 21-30, 1961, p. 42-O.

(13) F. W. Schuler and G. W. Murphy, *J. Am. Chem. Soc.*, **72**, 3155 (1950).
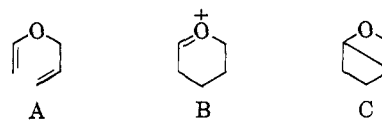
The transition state for the rearrangement of allyl vinyl ether is illustrated for the sake of simplicity and because the kinetic evidence indicates similarity of mechanism for the aryl and vinyl ethers. Hybridization of A and B gives a structure which is closely analogous to one recently proposed for a Diels–Alder reaction.[14] Structure C, which is admittedly improbable, is included because it is the only reasonable cyclic structure other than a biradical which is unpolarized. Evidence against the involvement of a biradical intermediate in the Diels–Alder reaction is given in the preceding reference. The insensitivity of ΔV^* to solvent polarity could be explained by the participation of structure C. On the other hand, participation of structure B, which is polarized in the sense opposite to that of the starting material, might result in a change of sign of polarization without appreciable change of magnitude.

According to a recent study of the steric course of the Claisen rearrangement of cis- and trans-α,γ-dimethallyl phenyl and vinyl ethers only the more stable trans-product is formed.[15] If the transition state has a well-developed six-membered ring as proposed above, then the two methyl groups may occupy equatorial positions when the aryl or vinyl group attacks from the side which leads to a trans-product.

It has been reported[16,17] that cis-γ-substituted allyl phenyl ethers rearrange about half as fast as the trans-isomers. One pair of authors interprets this result as evidence in favor of a certain conformation of the allyl group in the transition state, whereas the other draws the conclusion that bond-formation from γ-carbon to the ring is insignificant in the transition state. Both, however, consider only structures in which the π-orbital of the allyl group is more or less parallel to that of the benzene ring. Burgstahler[15] summarizes the evidence in

TABLE I

Compound	Solvent	ΔV^* (ml.)
Benzazide	EtOH–H$_2$O	+ 2
Benzazide	Ligroin	+ 5
p-Cresyl allyl ether	Benzene	−18
p-Cresyl allyl ether	Cyclohexane	−18
p-Cresyl allyl ether	EtOH–H$_2$O	−15^a
p-Cresyl allyl ether	EtOH–H$_2$O	−14^b
m-Methoxyphenyl allyl ether	EtOH–H$_2$O	−15
Vinyl allyl ether	Neat	−18

^{a} At 167.5°. ^{b} At 147.0°.

favor of the $S_N i'$ attack of the ring or vinyl group on the γ-carbon which would require the orbitals to be inclined to one another as shown below. In the latter case there is no reason to expect a great difference in reactivity between the two geometrical isomers.

(14) R. P. Lutz and J. D. Roberts, *ibid.*, **83**, 2199 (1961).

(15) A. W. Burgstahler, *ibid.*, **82**, 4681 (1960).

(16) W. N. White and B. E. Norcross, *ibid.*, **83**, 1968 (1961).

(17) L. D. Huestis and L. J. Andrews, *ibid.*, **83**, 1963 (1961).

TABLE II

SUMMARY OF KINETIC DATA

Benzazide in ligroin, 63.9°

P (atm.)	68	340	610	880	1220	1360
k (hr.⁻¹)	0.051	0.049	0.048	0.045	0.041	0.041

Benzazide in 50% alcohol–50% water, 50.3°

P (atm.)	68	1440
k (hr.⁻¹)	0.208	0.194

p-Cresyl allyl ether in benzene, 186.4°

P (atm.)	68	680	1440
k (hr.⁻¹)	0.062	0.091	0.113

p-Cresyl allyl ether in 65% alcohol–35% water, 167.5°

P (atm.)	68	750	1440
k (hr.⁻¹)	0.136	0.181	0.240

p-Cresyl allyl ether in 65% alcohol–35% water, 147.0°

P (atm.)	68	750	1440
k (hr.⁻¹)	0.0267	0.0346	0.0443

p-Cresyl allyl ether in cyclohexane, 176.4°

P (atm.)	68	750	1440
k (hr.⁻¹)	0.0249	0.0337	0.0430

m-Methoxyphenyl allyl ether in 65% alcohol–35% water, 155.9°

P (atm.)	68	405	750	1440
k (hr.⁻¹)	0.125	0.148	0.178	0.214

Vinyl allyl ether, neat, 130.4°

P (atm.)	68	405	750	1080	1470
k (hr.⁻¹)	0.307	0.394	0.446	0.510	0.525

Experimental

Benzazide was prepared by the method of Barrett and Porter.[18]

(18) E. W. Barrett and C. W. Porter, *J. Am. Chem. Soc.*, **63**, 3434 (1941).
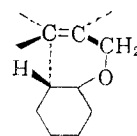
Allyl *p*-cresyl ether was prepared by the method of Kincaid and Tarbell.[19]

Allyl *m*-methoxyphenyl ether was prepared by the method of Mauthner.[20]

Allyl vinyl ether was prepared by the method of Watanabe and Conlon.[21]

Rearrangement of Benzazide.—A 2 ml. sample of 0.1 *M* solution was allowed to react in an inverted glass bell, and the volume of nitrogen was measured by the method developed for the decomposition of diazonium salts.[8]

Rearrangement of Allyl Aryl Ethers.—A 6 ml. sample of 0.333 *M* solution reacted for approximately one half-life and then was added to 15 ml. of 10% potassium hydroxide solution. The mixture was steam-distilled until approximately 20 ml. of distillate containing unreacted ether was collected. The residue then was acidified and another 20 ml. of distillate containing rearranged phenol was collected. Each distillate was diluted to 50 ml. with ethanol and a portion of each was again diluted tenfold with ethanol. The maximum optical densities of the *p*-cresyl ether at 277 mμ, its phenolic product at 281 mμ, the *m*-methoxyphenyl ether at 273 mμ and its phenolic product at 279 mμ were measured, and the concentrations were calculated from the optical densities of known solutions.

Rearrangement of Allyl Vinyl Ether.—Samples of the pure liquid reacted for approximately one half-life and were injected into a gas chromatograph. The concentrations of ether and rearranged aldehyde were calculated from the areas under the recorder trace.

High Pressure Apparatus and Thermostat Bath.—The equipment has been described in a previous paper.[5]

(19) J. P. Kincaid and D. S. Tarbell, *ibid.*, **61**, 3085 (1939).
(20) F. Mauthner, *J. prakt. Chem.*, **102**, 41 (1921).
(21) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

The Influence of Solvent and Metal Ion on the Rate of Reaction of Alkali Metal Borohydrides with Acetone[1]

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In water, ethanol and isopropyl alcohol the rate of reaction of sodium borohydride with acetone exhibits second-order kinetics, first order in each of the two reactants. The rate constants at 0° are (10^{-4} l. mole⁻¹ sec.⁻¹) 93 in water, 97 in ethanol and 15.1 in isopropyl alcohol. The addition of lithium chloride in water has no effect upon the rate, whereas in isopropyl alcohol the rate constant increases by a factor of three, to 50.3. Moreover, the rate constant increases with increasing concentrations of lithium halide. These results indicate that in water the reaction involves the dissociated borohydride ion, whereas in isopropyl alcohol the reacting species must be the ion pair, $M^+ BH_4^-$. In aprotic solvents, such as acetonitrile, pyridine, dimethylformamide and diglyme, no detectable reaction of sodium borohydride with acetone was observed at 0°. Consequently, the ability of the solvent to ionize must be involved in the mechanism of the reaction between the borohydride and the ketone.

In an earlier study we examined a number of solvents for sodium borohydride and their utility as reaction media for the reduction of ketones by the reagent.[3] We observed that methyl alcohol

(1) Addition Compounds of the Alkali Metal Hydrides. XII.
(2) Post-doctorate research assistant on Contract DA-33-008-ORD-992, supported by the Office of Ordnance Research, U. S. Army.
(3) H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

reacted very rapidly with the borohydride, ethyl alcohol somewhat slower, whereas the reaction of isopropyl and *t*-butyl alcohols was almost negligible, so that these solvents could be considered as suitable media for kinetic studies.[4] Diglyme[5] and triglyme[5] were also excellent solvents for

(4) H. C. Brown, O. H. Wheeler and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).