chromatography; $\epsilon < 100$ in the region 220–300 mμ; intense carbonyl absorption at 5.78 μ; n^{24}_D 1.4341.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.51; H, 10.79.

The last elution peak shown by each of the above product mixtures in gas chromatography (Fig. 1) corresponded in retention time to that of authentic 2-methoxyisophorone. A mixture of the pair of methoxyisophorones obtained in the present reactions was warmed on a steam-bath for 30 minutes with concentrated hydrochloric acid. This treatment converted the lower-boiling methoxyisophorone component into 3,4,5-trimethylphenol, m.p. 108.5° (lit.[3] m.p. 108.5°), but left 2-methoxyisophorone largely unchanged. A sample of 2-methoxyisophorone recovered from the hydrochloric acid treatment gave a single elution peak in gas chromatography, and gave a 2,4-dinitrophenylhydrazone derivative, m.p. 190–191.5° dec. after recrystallization from ethanol. The structure of this product was confirmed by hydrolysis[11] to 2-hydroxyisophorone, m.p. 91–93° (lit.[11] m.p. 92–93°).

From the product mixture of run C, a sample of **6-methoxy isophorone** was obtained by distillation, b.p. 101–103° (12.5 mm.), n^{25}_D 1.4735, λ_{max} 236 mμ (ethanol). Gas chromatography revealed the presence of a few mole % of 2-methoxyisophorone as the only impurity.

Anal. Calcd. for $CH_3OC_9H_{13}O$: C, 71.39; H, 9.59; OCH_3, 18.45. Found: C, 71.55; H, 9.88; OCH_3, 18.94.

The 2,4-dinitrophenylhydrazone derivative of 6-methoxyisophorone was recrystallized from ethanol; m.p. 129.5–130.5°.

Anal. Calcd. for $C_{16}H_{20}N_4O_5$: C, 55.16; H, 5.78; N, 16.08. Found: C, 55.08; H, 6.08; N, 16.17.

In control experiments, known mixtures of the methoxyisophorone products and of the methyl trimethylcyclopentenecarboxylate products of the above reactions were treated with methanolic potassium hydroxide for 3 hours at room temperature. Products recovered from the alkaline solutions were examined by means of gas chromatography, and in neither mixture was any change in composition found to have resulted from the treatment with alkali.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

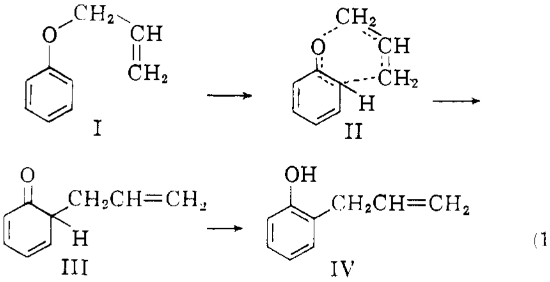
Organic Reactions under High Pressure. VI. Some Claisen and Cope Rearrangements[1]

BY CHEVES WALLING AND MICHAEL NAIMAN[2]

RECEIVED JANUARY 27, 1962

Measurements are reported on the effect of pressures up to 6000 kg./cm.² on the rates of rearrangements of allyl phenyl ether (I) at 160° and ethyl (1-ethylpropenyl)-allylcyanoacetate (VIII) at 119°, each in several solvents. Both reactions are pressure-accelerated, ΔV^*'s being generally −6 to −7 cc./mole between 1000–6000 kg./cm.² and essentially solvent independent. Extrapolations to atmospheric pressure are less certain, but indicate ΔV^*'s of −10 to −15 cc./mole, again with no obvious solvent dependence. These results are interpreted as consistent with rather tightly bonded cyclic transition states in which new bond formation has proceeded farther than bond breaking, rather than with transition states which are essentially ion-pairs, or in which homolytic bond cleavage has been extensive.

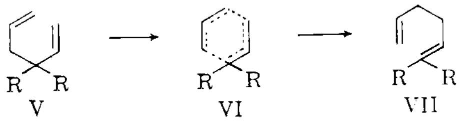
Although there is a general agreement[3] that the mechanism of the Claisen rearrangement is represented by a sequence such as



(1)

the detailed structure of the transition state II remains ill-defined. Several recent studies have attempted to establish more precisely the degree of bond breaking and bond forming, amount of ionic character and exact geometry which is involved through investigation of the effects of solvents,[4,5] and substituents[4–6] on reaction rates, and of the stereochemical course[7,8] and geometric requirements[9,10] of the rearrangement.

A similar situation arises in connection with the Cope rearrangement of 1,4-dienes, usually activated by cyano, carbethoxy or similar substituents on carbon 3.[11] Here the reaction has been shown to be intramolecular[12] and to possess a large negative entropy of activation,[13] so that it may be considered a close analog of the Claisen rearrangement, occurring in an all-carbon chain system.[11]



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It seemed to us that a study of the effect of high pressures of the rates of some typical Claisen and Cope rearrangements would provide further information on the nature of the transition states involved, and our results are described here. Since our work was completed, Brower[14] has reported a study on the effect of pressure on three Claisen rearrangements leading to conclusions which are in qualitative agreement with our own.

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(1) Taken from the Ph.D. Dissertation of Michael Naiman, 1961. Support of this research by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

(2) Columbia University Fellow, 1959-1960.

(3) For recent reviews, *cf.* (a) D. J. Cram and M. S. Newman "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 295–303; (b) E. S. Gould "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, pp. 644–649.

(4) W. N. White, D. G. Wynn, R. Schlitt, C. Girard and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

(5) H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958).

(6) W. N. White and W. K. Fife, *ibid.*, **83**, 3846 (1961); W. N. White, C. D. Slater and W. K. Fife, *J. Org. Chem.*, **27**, 627 (1961).

(7) E. N. Marvel and J. L. Stephenson, *ibid.*, **25**, 676 (1960).

(8) A. W. Burgstahler, *J. Am. Chem. Soc.*, **82**, 4681 (1960).

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(10) W. N. White and B. E. Norcross, *ibid.*, **83**, 1968, 3265 (1961).

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(12) D. E. White and A. C. Cope, *ibid.*, **65**, 1999 (1943).

(13) E. G. Foster, A. C. Cope and F. Daniels, *ibid.*, **69**, 1893 (1947).

(14) K. R. Brower, *ibid.*, **83**, 4370 (1961).

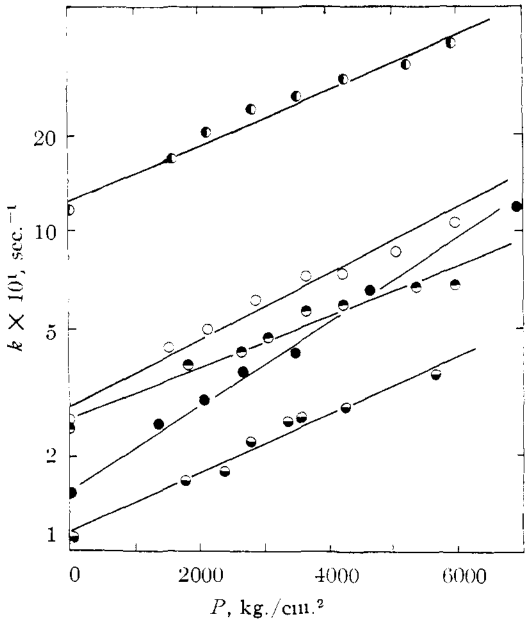


Fig. 1.—Effect of pressure on the rearrangement of allyl phenyl ether: ◐, ethylene glycol; ○, *n*-octanol; ◓, butyl Cellosolve; ●, no solvent; ◒, decalin.

Results.—The Claisen rearrangement of allyl phenyl ether to *o*-allylphenol was investigated at 160° alone and in four solvents over a pressure range of 1 to approximately 6000 kg./cm.^{2}. Semilogarithmic plots of first-order rate constants *vs.* pressure are shown in Fig. 1, and typical original data are presented under experimental details below.

From simple transition-state theory, the effect of pressure on a reaction rate is given by the relation

$$\mathrm{d} \ln k/\mathrm{d}P = -\Delta V^*/RT \qquad (3)$$

where ΔV^* represents the difference in volume between reactants and transition state. The quantity ΔV^* may be evaluated from the slope of the curves passing through the sets of data plotted in Fig. 1. The determination, however, is complicated, not only by the experimental scatter of points, but by the fact that ΔV^* is not pressure independent. Four methods were used to estimate ΔV^*s, and results are summarized in Table I: (A) using all experimental points; (B) ignoring the atmospheric pressure point; (C) using only the data from three lowest pressure experiments; and (D) employing the extrapolation technique of Benson and Berson.[15] The lines in Fig. 1 are those used in calculation A. Inspection of Fig. 1 shows that all curves are reasonably linear between 1000 and 6000 kg./cm.^{2}, so that ΔV^*s in column B should represent true values in that range. The estimation of ΔV^*'s at atmospheric pressure is more equivocal. The actual values are probably somewhat larger than those listed in column C, but application of the Benson–Berson extrapolation (column D) often gave such a scatter of points that it seemed unreasonable to assign any experimental errors, and values have been rounded off to the nearest cc./mole.[16] There also seems to be a small quantitative discrepancy between our data and those of Brower,[14] gathered over a lower pressure range of 1–1500 kg./cm.^{2}. In the range where the two sets overlap, his results show a somewhat larger percentage increase in rate with pressure than do ours. However, since he employed allyl *p*-cresyl ether in a different set of solvents, the significance of the discrepancy is hard to assess. Our experiments on the Cope rearrangement involved the rearrangement of ethyl (1-ethylpropenyl)-allylcyanoacetate (VIII) to ethyl (1-ethyl-2-methyl-4-pentenylidene)-cyanoacetate (IX) in four solvents at 119°. Results of runs at 1–6000 kg./cm.^{2} are shown in Fig. 2, and calculations of activation volumes are listed in Table II, the four columns having the same significance as in Table I. Again, plots in the higher pressure region are quite linear, giving values of ΔV^* listed in column B, while the extra-polation to atmospheric pressure is perhaps even more uncertain than in the Claisen rearrangement.

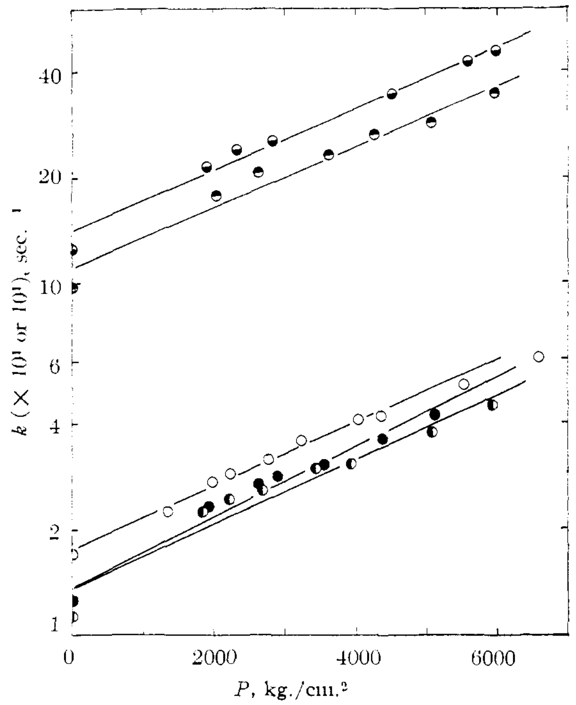
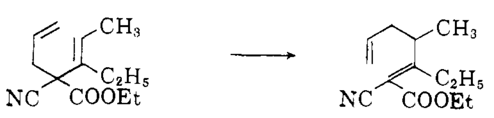


Fig. 2.—Effect of pressure on the Cope rearrangement of VIII: ◒, butyl Cellosolve; ◓, decalin (k's × 10^7); ○, propylene glycol; ●, 1,4-dibromobutane; ●, 1-octanol (k's × 10^6).



VIII IX (4)

Discussion

The data presented in the previous section were obtained as part of a general survey of the effect of pressure on a variety of organic reactions before we had appreciated fully the problem of the

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[15] S. Benson and J. Berson, *J. Am. Chem. Soc.*, **84**, 152 (1962), who kindly made their manuscript available to us prior to publication.

[16] We intend to discuss this whole problem of the compressibility of transition states and the variation of $\Delta V^{\neq}$ with pressure in another paper, using more appropriate data.

TABLE I

VOLUMES OF ACTIVATION FOR THE REARRANGEMENT OF ALLYL PHENYL ETHER AT 160°

Solvent	(Molarity)[b]	*k*(atm.), sec.$^{-1}$ × 10^6	ΔV^*, cc./mole A	B	C	D
None	(7.2)	1.53	−10.6 ± 0.2	−10.3 ± 0.2	−12.1 ± 1.2	−18
n-Octanol	(0.73)	2.59	− 8.3 ± .4	− 7.3 ± .3	−11.5 ± .6	−16
Decalin	(2.05)	1.12	− 7.7 ± .4	− 7.2 ± .5	− 9.2 ± .5	−14
Ethylene glycol	(0.11)	10.5	− 7.0 ± .4	− 6.2 ± .4	− 9.5 ± .5	−15
Butyl Cellosolve[a]	(0.61)	2.41	− 6.5 ± .4	− 5.5 ± .4	− 8.1 ± .9	−13

[a] Monobutyl ether of ethylene glycol. [b] At room temperature.

TABLE II

VOLUMES OF ACTIVATION IN THE COPE REARRANGEMENT OF VIII AT 119°, INITIAL CONCENTRATION 119%

Solvent	*k*(atm.), sec.$^{-1}$ × 10^5	ΔV^*, cc./mole A	B	C	D
1,4-Dibromobutane	1.25	−7.5 ± 0.4	−6.0 ± 0.2	− 9.9 ± 0.4	−14
n-Octanol	1.13	−7.0 ± .5	−5.3 ± .2	−11.6 ± .5	−17
Butyl Cellosolve	1.27	−6.7 ± .3	−6.0 ± .1	− 9.3 ± .2	−14
Decalin	0.97	−6.7 ± .4	−5.3 ± .2	− 9.0 ± .4	−14
Propylene glycol	1.69	−6.3 ± .2	−5.8 ± .1	− 8.0 ± .2	..

dependence of ΔV^*'s on pressure and the difficulties of extrapolation from the pressures conveniently available in our apparatus to atmospheric pressure. Nevertheless, we feel that the results are adequate to draw significant conclusions as to transition state structures.

For both types of rearrangement (ignoring the fine points of molecular geometry on which our pressure measurements throw no light) three limiting types of process leading to different variants of the transition states II and VI in eq. 1 and 2 may be considered; e.g. for II: (1) heterolytic scission of O–allyl bond leading to an ion pair; (2) homolytic scission of the O-alkyl bond, giving two essentially unbonded fragments within a solvent cage; (3) new bond formation preceding significant bond breaking to yield an extensively bonded cyclic transition state.

Scheme 1 was first proposed by Cram,[3a] and is perhaps the most difficult to discuss in the light of our observations. Numerous studies, principally by Hammann,[17] have shown that ionization processes are accompanied by negative values of ΔV^*, since the volume increase due to bond-breaking is more than compensated by electrostriction of solvent around the ions produced. While this is consistent with our results (particularly since the magnitude of the resultant of two conflicting effects is difficult to predict quantitatively), one might also anticipate a marked variation in ΔV^* with solvent which is not observed.

Rather qualitatively, this prediction arises from a consideration of the forces leading to electrostriction in solvents. If the free energy of solvation of a mole of univalent ions is considered to be given by Born's formula

$$\Delta F^0 = \frac{Ne^2}{2r_i}\left(1 - \frac{1}{\epsilon}\right) \qquad (5)$$

since

$$\Delta \bar{V}^0 = \partial \Delta F^0/\partial P \qquad (6)$$

the volume change on solution is given by

$$\Delta \bar{V}^0 = \frac{Ne^2}{r}\,\frac{\partial(1/\epsilon)}{\partial P} - Ne^2\left(1 - \frac{1}{\epsilon}\right)\frac{\partial(1/r)}{\partial P} \qquad (7)$$

If we consider the same ions in different solvents, the last term, involving the ionic radii, is constant, and it is evident that part of ΔV^* due to electrostriction depends upon $\partial\ (1/\epsilon)/\partial P$. As a first approximation, the change in dielectric constant with pressure is given by the Clausius–Mossotti formula

$$(\epsilon - 1)/(\epsilon + 2) = \text{density} \times \text{a constant} \qquad (8)$$

whence, to the same approximation, the negative contribution of electrostriction to ΔV^*'s in ionization processes should be largest in solvents of high compressibility. Unfortunately, there are few data available to test this hypothesis. Hammann and Strauss have observed that the effect of pressure on the ionization of piperidine is notably smaller in water than in methanol (the more compressible solvent).[18] Again, the older data of Gibson, Fawcett and Perrin indicates a larger pressure acceleration of the reaction between ethyl iodide and pyridine in hexane than in ethanol.[19]

While compressibility data have not been reported for all of the solvents employed in our work, compressibilities of organic liquids follow predictable regularities, increasing in the order glycols < alcohols < alkyl halides, ethers < hydrocarbons and decreasing with molecular weight as shown by the sample data in Table III. In comparison, the ΔV^* data in any of the columns of Tables I and II change very little from solvent to solvent, and differences in no way parallel either

TABLE III

COMPRESSIBILITIES OF ORGANIC LIQUIDS[20]

Compound	d ln V/dP × 10^6, (atm.$^{-1}$)
Ethylene glycol	35
Propylene glycol	32
Ethanol	111
1-Hexanol	90
Ethyl ether	149
n-Butyl bromide	140
Pentane	200
Decane	144

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(17) For discussion and references, *cf.* S. D. Hammann, "Physico-Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957, Ch. 9.

(18) S. D. Hammann and E. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955).

(19) R. G. Gibson, E. W. Fawcett and M. W. Perrin, *Proc. Roy. Soc. (London)*, **A150**, 223 (1935).

(20) Bridgeman's data; for summary *cf.* ref. 17, pp. 219–226.

solvent compressibility or variations in atmospheric pressure rates.

Scheme 2 is our understanding of the transition state proposed by White for the Claisen rearrangement.[6] In the extreme form it seems incompatible with our results, since other homolytic bond scissions of peroxides[21] and azo compounds[22] show positive ΔV^*'s of 5–12 cc./mole.

Scheme 3, in which bond-forming precedes bond breaking, we consider in the best accord with our results. Here ΔV^*s should be negative, and their upper values can be estimated from volumes differences between starting materials and cyclic products approximating the possible transition states. Molar volumes of some model systems are listed in Table IV. For the Claisen rearrangement the difference in molar volume of allyl phenyl ether and 1-chromene is 15.8 cc./mole at 15°, and would be somewhat larger at 160°. For two models of the Cope rearrangements (hexadienes cyclohexadienes) differences are 16–18 cc./mole. As we have seen, different methods of extrapolation to atmospheric pressure yield somewhat different values of ΔV^*s from our data, but the general range is smaller than the above differences, as would be expected for transition states in which two bonds are somewhat stretched.

TABLE IV

MOLAR VOLUMES (CC.) OF MODEL COMPOUNDS

Allyl phenyl ether	135.9[23]
1-Chromene	120.1[24]
4-Methylheptadiene-1,5	150.9[25]
2,6-Dimethylcyclohexadiene-1,3	132.5[25]
2,5-Dimethylhexadiene-1,5	146.4[25]
1,4-Dimethylhexadiene-1,3	130.0[25]

While our results thus favor cyclic transition states with marked bonding between fragments of the rearranging molecules for the two systems studied (which is certainly plausible, since the driving forces of the reactions must be chiefly the formation of new bonds), it must be kept in mind that the three schemes discussed represent limiting models of the possible transition states. Accordingly, contributions of other structures sufficient to account for phenomena such as the effects of substituents on reaction rates are certainly not ruled out. Indeed, in our present state of knowledge, it is difficult to make clean cut distinctions between largely "σ-bonded" transition states and species which are very tight ion pairs or charge transfer complexes, or even to say to what extent these formulations are operationally differentiable.

Experimental

Materials.—Solvents were commercial materials, distilled before use. Since most of our analyses of products involved absorption spectrometry, their optical absorption at the wave lengths involved was checked before use. **Allyl phenyl ether** was prepared by treating phenol with allyl bromide in acetone in the presence of potassium carbonate; b.p. 85° (19 mm.), $n^{25}\text{D}$ 1.5196. Reference samples of **2-allylphenol** were prepared by rearrangement of the ether by refluxing at 180° and extracting with alkali; b.p. 72° (3 mm.) $n^{25}\text{D}$ 1.5448.

Ethyl (1-Ethylpropenyl)-allylcyanoacetate, (VIII) was prepared in two steps from diethyl ketone, ethyl cyanoacetate and allyl bromide. The ketone and ester were condensed in the presence of acetic acid and ammonium acetate essentially as described in reference 26. The resulting ethyl (1-ethylpropylidene)-cyanoacetate, b.p. 123–125° (12 mm.) was alkylated with allyl bromide in the presence of sodium ethoxide, essentially as described by Cope and Hancock[27] for a series of similar compounds, to give VIII, b.p. 84–85° (0.7 mm.) $n^{25}\text{D}$ 1.4618. A sample of VIII was rearranged to **ethyl (1-ethyl-2-methyl-4-pentenylidene)-cyanoacetate (IX)** by heating 7 hr. at 170°; b.p. 147–148° (12 mm.), $n^{25}\text{D}$ 1.4775.

Apparatus and Technique.—All experiments were carried out in collapsible Teflon vessels in the high pressure apparatus used previously.[28] Aliquots of standard solutions were used in all runs, and reaction times were long enough, 5–8 hr., so that the short time required for samples to come to thermal equilibrium could be neglected. At the end of each experiment, samples were removed from the pressure system and analyzed as described below.

Analyses.—Early runs involving allyl phenyl ether were analyzed by acetylating the 2-allylphenol produced with a standard solution of acetic anhydride–pyridine, and back-titrating unreacted acetic anhydride with NaOH.[29] Subsequently it proved simpler to analyze samples by determining the optical density of aliquots, dissolved in 0.1 *N* NcOH in 50% ethanol, at 291 mμ using a Beckman DU spectrophotometer. Allyl phenyl ether is transparent at this wavelength, while the 2-allylphenoxy anion absorbs strongly $\epsilon = 3638$.

TABLE V

REARRANGEMENT OF ALLYL PHENYL ETHER IN 1-OCTANOL AT 160°

P, kg./cm.^{2}	Time, sec. × 10^3	Reacn., %	*k*, sec.$^{-1}$ × 10^6
1	25.2	6.33	2.59
1510	25.2	10.3	4.31
2130	25.25	11.8	4.97
2880	25.2	14.3	6.12
3620	25.3	16.7	7.23
4200	25.2	17.1	7.44
5030	24.75	19.3	8.66
5980	25.2	23.7	10.75

TABLE VI

REARRANGEMENT OF VIII IN 1-OCTANOL AT 119° (ALL RUNS 18,900 SEC.)

P, kg./cm.^{2}	Reacn., %	*k*, sec.$^{-1}$ × 10^5
1	19.3	1.13
1840	34.4	2.23
2210	36.6	2.41
2660	38.0	2.53
3430	42.7	2.94
3940	43.8	3.05
5100	50.5	3.72
5910	56.7	4.42

The conversion of VIII to IX was followed by determining the optical density at 238 mμ of aliquots dissolved in absolute ethanol. Although both materials absorb significantly at this wave length (for VIII, $\epsilon = 1045$, for IX, $\epsilon = 9789$) they differ sufficiently for analysis. In all analyses, three aliquots were made up independently, measured, and the average taken.

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(26) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 399.

(27) A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **60**, 2903 (1938).

(28) C. Walling and J. Pellon, *ibid.*, **79**, 4776, 4786 (1957).

(29) "Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1953, p. 24.

Treatment of Data.—Since this study was primarily a survey of reactions under a variety of conditions, rate constants were calculated from single experiments (*e.g.*, one point) for each pressure in each solvent, a procedure which appeared justified, since the first-order kinetics of Claisen and Cope rearrangements at atmospheric pressure are well established, and since the plots of rate *vs.* pressure (Figs. 1 and 2) give reasonably smooth curves. Original data for two sets of runs are listed in Tables V and VI. The values of $\Delta V^{\neq}$'s listed in Tables I and II were obtained from the slope of lines obtained by the method of least squares, and experimental errors given are standard deviations. No experimental errors are assigned to the Benson–Berson extrapolations, which involve plots of $(\log k/k_0)/P$ *vs.* $P^{0.523}$, since points often scattered badly and extrapolation seemed to involve a good deal of subjective judgment.

[CONTRIBUTION FROM THE INSTITUTE FOR CHEMICAL RESEARCH, KYOTO UNIVERSITY, YOSHIDA, KYOTO, JAPAN]

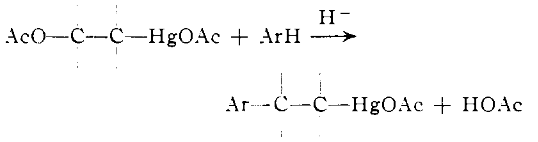
The Kinetics of the Reactions of β-Acetoxyethylmercuric, β-Acetoxypropylmercuric and β-Acetoxy-β-phenylethylmercuric Acetate with Aromatic Substances

BY KATSUHIKO ICHIKAWA, KOICHI FUJITA AND OSAMU ITOH

RECEIVED SEPTEMBER 5, 1961

The reaction rates of β-acetoxyethylmercuric, β-acetoxypropylmercuric and β-acetoxy-β-phenylethylmercuric acetate with aromatic substances have been studied in acetic acid–perchloric acid–water systems. The results showed that the reactivity order of various aromatics is the same with those in the usual electrophilic aromatic substitutions. The relative rates of the three mercurials mentioned above with anisole were 1.0, 1.3 and 710, respectively, under the same conditions. From these results, the mechanism is discussed as an electrophilic aromatic substitution. As a preliminary experiment for the rate study above, the stabilities of the mercurials in acetic acid containing perchloric acid have been studied and the stoichiometry, rates and mechanism of the decompositions are reported.

In previous papers,[1] it has been shown that β-acetoxyalkylmercuric acetates (obtained by the addition of mercuric acetate to olefins in acetic acid) react with aromatics by eq. 1. The kinetics and



$$\mathrm{AcO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}HgOAc + ArH \xrightarrow{H^-} Ar{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}HgOAc + HOAc} \quad (1)$$

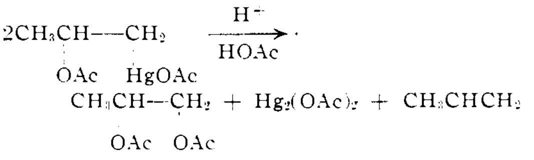
mechanism of this reaction between β-acetoxyethylmercuric acetate and anisole have been reported also.[2] It is desired, however, that the kinetic studies are extended to other mercurials and aromatics more extensively as a new type of aromatic substitution. In this paper, the results of the rate studies of the reactions of β-acetoxyethylmercuric (I), β-acetoxypropylmercuric (II) and β-acetoxy-β-phenylethylmercuric acetate (III) (prepared by the addition of mercuric acetate to ethylene, propylene and styrene in acetic acid) with various aromatic substances are reported.

Unfortunately, these mercurials are not always stable enough for the kinetic measurements of reaction 1 in the presence of perchloric acid which is one of the typical catalysts. As a preliminary study, therefore, the decompositions have been studied.

Stabilities of I, II and III in Acetic Acid Containing Perchloric Acid.—In 80% acetic acid containing perchloric acid up to 2 molar, I is stable indefinitely. At room temperature, no appreciable decomposition was observed even after 5 days. With II and III, however, a reaction to form mercurous salt was observed, while their acetic acid solutions containing no perchloric acid are much more stable.

Many examples of this type of reaction can be found in terpene chemistry, since the oxidation of terpene with mercuric acetate to form the corresponding diacetate and mercurous salt proceeds apparently through the formation of the addition compounds, *i.e.*, β-acetoxy mercuric compounds. The stoichiometry of this reaction, however, is not yet established, because these oxidations have been carried out in the presence of excess mercuric acetate usually. With the addition compounds of lower olefins, such as II, no detailed results have been reported.[3] Therefore, the product analysis and kinetics have been studied.

At room temperature, the solution (50 ml.) which contained 48.1 millimoles of II and 1.03 molar perchloric acid in 80% acetic acid gave 5.6 ml. (at N.T.P.) of gaseous product (5.1 millimoles as propylene). This gas was identified to be propylene by vapor phase chromatograph. The analysis of the liquid mixture showed that 5.1 millimoles of mercurous acetate was formed. Although the quantitative analysis of the liquid organic products was difficult, propylene glycol diacetate and its hydrolyzed product glycol were found to be formed which were expected from the results in terpene chemistry mentioned above (no acrolein was detected). These results show that the reaction of II in the presence of perchloric acid can be expressed by eq. 2. The results de-



$$\mathrm{2CH_3\underset{\underset{OAc}{|}}{CH}{-}\underset{\underset{HgOAc}{|}}{CH_2} \xrightarrow[HOAc]{H^+} CH_3\underset{\underset{OAc}{|}}{CH}{-}\underset{\underset{OAc}{|}}{CH_2} + Hg_2(OAc)_2 + CH_3CHCH_2} \quad (2)$$

scribed above were obtained in the range of less than about 20% reaction. At higher reaction percentages, the situation is much more complicated. The mercurous acetate produced may disproportionate to give metallic mercury and mercuric acetate which reacts with propylene to give II again. The reaction equation in this case might be expressed by the equation

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[1] K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, *J. Am. Chem. Soc.*, **80**, 6005 (1958); **81**, 3401 (1959).

[2] K. Ichikawa, K. Fujita and H. Ouchi, *ibid.*, **81**, 5316 (1959).

[3] The formation of acrolein by the reaction of propylene with mercuric sulfate in aqueous sulfuric acid (du Pont, U. S. Patent 2,197,258) appears to belong to a different type of reaction.