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The preparation of CIS- and trans-1,2-dimethoxyethylene. The study of the CIS-trans-rearrangement and evaluation of equilibrium constants

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THE PREPARATION OF CIS- AND TRANS-1,2-DIMETHOXYETHYLENE. THE STUDY OF THE CIS-TRANS-REARRANGEMENT AND EVALUATION OF EQUILIBRIUM CONSTANTS.

BY

JAMES WALDRON

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APPROVAL OF DISSERTATION

THE PREPARATION OF <u>CIS</u>- AND <u>TRANS</u>-1,2-DIMETHOXYETHYLENE THE STUDY OF THE <u>CIS</u>-<u>TRANS</u> REARRANGEMENT AND EVALUATION OF EQUILIBRIUM CONSTANTS.

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FOR

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NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMITTEE

APPROVED: CHAIRMAN

NEWARK, NEW JERSEY

SEPTEMBER, 1972

ABSTRACT

Equilibrium constants for the mercuric acetate-catalyzed reaction, cis-$CH_3OCH{=}CHOCH_3 \rightleftharpoons$ trans-$CH_3OCH{=}CHOCH_3$, have been determined in the liquid and vapor phase over the temperature range 30° - 175°C by gas chromatography analysis. A novel synthesis of the cis- and trans-isomers of 1,2-dimethoxyethylene is discussed. From a screening of 29 catalysts, mercuric acetate, mercuric benzoate, and mercuric salicylate were found to be favorable isomerization catalysts. For the liquid phase reaction,

$$\ln K = -779.8/T + 0.6748$$

with $\Delta H^{\circ} = +1.549 \pm 0.019$ Kcal/mole
and $\Delta S^{\circ} = +1.34 \pm 0.05$ e.u./mole

Similarly, for the vapor phase reaction,

$$\ln K = -727.2/T + 0.8335$$

with $\Delta H^{\circ} = +1.445 \pm 0.054$ Kcal/mole
and $\Delta S^{\circ} = +1.66 \pm 0.15$ e.u./mole

A linear regression analysis, employing a least-squares curve fit and an analysis of variance, was performed on the data. An independent experimental error analysis (for uncertainties in measurement, reproducibility, etc.) was performed using partial differentials and was consistent with the above findings.

cis-1,2-Dimethoxyethylene was more stable relative to its trans-isomer in both the liquid and vapor phase. The greater amount of cis-isomer present at equilibrium (the cis-effect) is discussed in terms of dipole-dipole interactions with a resultant increase in the C=C bond strength for the *cis*-isomer due to electron density shifts. The dimethoxyethylenes are correlated with previous results found in the literature for related systems (e.g. dihaloethylenes, etc.). Additional arguments are also advanced.

ACKNOWLEDGEMENT

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DEDICATION

To my friend, Phillip Snell

INTRODUCTION

Compounds known as the vinyl ethers or enol ethers represent a class of compounds in which very little is known as to the relative stabilities of the corresponding cis-trans-pairs. The main criteria for enol ether structure is an olefinic carbon to which an alkoxy group is attached (i.e. $\rangle C=C\langle^{OR}$). The cis-trans-isomerization of enol ethers constitutes an interesting and relatively unexplored area of organic chemistry.

There are examples of allyl to vinyl ether rearrangements involving 1,2-shifts in which the cis-configuration predominated over the trans-configuration.[1,2]

$$ROCH_2CH=CH_2 \xrightarrow[KO\text{-}\underline{tert}\text{-}Bu]{} ROCH=CHCH_3$$

R = phenyl, n-hexyl, tert-butyl, 2-hydroxypropyl, 1-methyl-2-hydroxyethyl.

C. C. Price and W. H. Snyder[2] have shown in the course of investigating the prototropic rearrangement of allyl ethers to their propenyl analogs employing potassium tert-butoxide as catalyst that the cis-isomer was formed almost exclusively (greater than 99% in some cases). This is considerably in excess of the equilibrium concentration of about 65% cis.[3]

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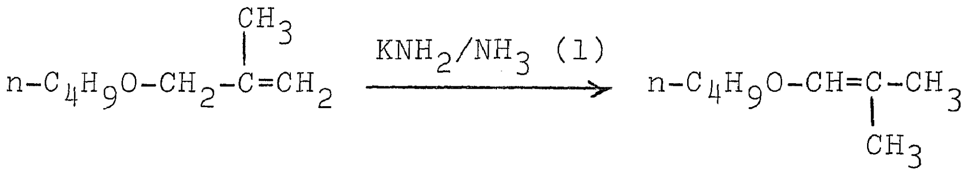
(1) T. J. Prosser, J. Am. Chem. Soc., 83, 1701 (1961).

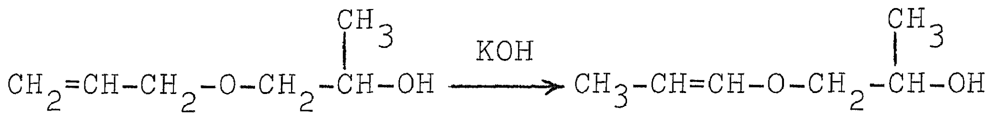
(2) C. C. Price and W. H. Snyder, J. Am. Chem. Soc., 83, 1773 (1961).

Earlier investigations have shown that allyl vinyl ether isomerizes to propenyl vinyl ether[4] and that allyl aryl ethers isomerize to aryl vinyl analogs.[5] Birch[6] has found that 3 *n*-butoxy-2-methylpropene is rearranged to 1-*n*-butoxy-methylpropene with potassium amide in liquid ammonia.



$$n\text{-}C_4H_9O\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{=}CH_2 \xrightarrow{KNH_2/NH_3\ (1)} n\text{-}C_4H_9O\text{-}CH\text{=}\underset{\underset{\displaystyle CH_3}{|}}{C}\text{-}CH_3$$

The partial rearrangement of 1-allyloxy-2-propanol to the propenoxy derivative by refluxing the allyl derivative with potassium hydroxide has been reported.[7] Simons and Verbanc[7] described this rearrangement as incomplete, so they postulated a reversible equilibrium.



$$CH_2\text{=}CH\text{-}CH_2\text{-}O\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{-}OH \xrightarrow{KOH} CH_3\text{-}CH\text{=}CH\text{-}O\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{-}OH$$

G. J. Dege *et al*.[8] have shown the amount of *cis*-propenyl unsaturation formed in the synthesis of

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(3) W. H. Snyder, Ph. D. Dissertation, University of Pennsylvania, 1961.

(4) R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim. France*, *121* (1950).

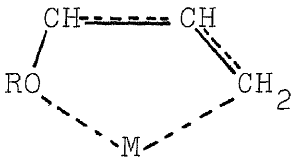
(5) M. Julia and M. Baillarge, *Compt. rend.*, *21*, 2793 (1959).

(6) A. J. Birch, *J. Chem. Soc.*, 1642 (1947).

(7) D. Simons and J. Verbanc, *J. Polymer Sci.*, *34*, 303 (1960).

polypropylene glycol increased with increasing reaction temperature and catalyst concentration. If this was an indication of thermodynamic equilibrium, the cis-isomer would be less stable since it increased with increasing temperature. However, this was not the case since equilibrium conditions were not obtained.[1]

Prosser[1,9] investigated several mono- and polyfunctional allyl and methallyl ether rearrangements to the corresponding propenyl and isobutenyl ethers by treatment at 150° - 175° in the presence of a basic catalyst (usually 2 - 15% potassium tert-butoxide). He concluded that the ultimate degree of rearrangement was not an indication of an equilibrium condition as Dege et al.[8] had observed but a stereoselective isomerization dependent only on initial catalyst concentration and independent of reaction temperature. It was found that the rearrangement gave almost exclusively the cis-propenyl isomer in all cases examined. A stabilized cis-allylic carbanion incorporating the cation of the basic catalyst was postulated to account for the formation of cis-propenyl ether.



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(8) G. J. Dege, R. L. Harris, J. S. Mackenzie, J. Am. Chem. Soc., 81, 3374 (1959)

(9) T. J. Prosser, U. S. Patent 3,168,575 (1965).

The rearrangement was irreversible since pure *trans*-propyl propenyl ether gave no *cis*-ether upon treatment under isomerization conditions. Propyl allyl ether does rearrange to *cis*-propyl propenyl ether under the usual conditions.[1]

cis-Propenyl ethers appear to predominate regardless of the method of preparation. The acid-catalyzed de-alcoholation of 1,1-dipropoxypropane is reported to give a mixture of 75% *cis*- and 25% *trans*-propyl propenyl ether.[10] A similar preponderance of the *cis*-isomer has been noted in methyl- and butyl-1-butenyl ethers prepared through the corresponding butyrals.[11,12]

In many cases, the stereospecific nature of the allyl to vinyl ether rearrangement has been used in order to explain the abundance of the *cis*-isomer. In the allyl to propenyl ether rearrangement the oxygen atom in position 4 participates in stabilizing the *cis*-carbanion by attracting the α-hydrogen to the alkoxide oxygen. By movement of a proton only, the complex with the hydrogen in the following position results:[2]

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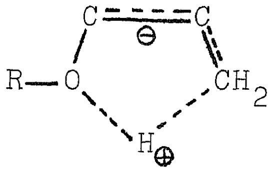
(10) W. Rottig and O. Lieben, German Patent 1,019,090 (1957).

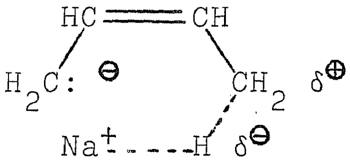
(11) R. L. Longly, U. S. Patent 2,667,517 (1954).

(12) R. H. Hall, A. R. Philpotts, E. S. Stern and W. Thain, *J. Chem. Soc.*, 3341 (1951).



Under similar conditions of isomerization, the allyl amines furnished the cis-isomers.[13,14]

Similarly, W. Haag and H. Pines[15] suggested a resonance stabilized carbanion intermediate in the prototropic isomerization of 1-butene where the initial, rate-controlled product is predominantly cis-2-butene.



The catalysts employed were sodium deposited on alumina, lithium-on-alumina, and a sodium dispersion. To account for the somewhat lower stereoselectivity observed in the lithium-catalyzed reaction (less cis-isomer produced), models demonstrated that a sodium ion fits just in between the two terminal groups of the cis-butenyl anion, while lithium does not have complete contact.

---

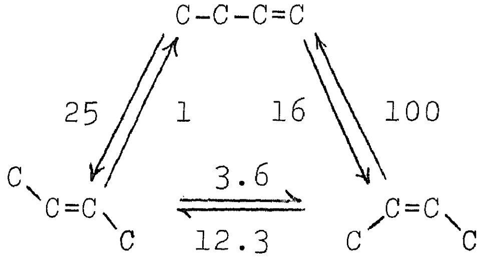
(13) C. C. Price and W. H. Snyder, Tetrahedron Letters, No. 2, 69 (1962).

(14) M. Riviere and A. Lattes, Bull. soc. chim. France, 4430 (1968).

(15) W. O. Haag and H. Pines, J. Am. Chem. Soc., 82, 387 (1960)

These workers indicated that the products were kinetically controlled. For instance in the isomerization of 1-butene, the thermodynamically less stable _cis_-2-butene was produced four times faster than the _trans_-isomer. If allowed to reach thermodynamic equilibria, the _trans_-isomer would predominate. The relative rate constants indicate that _trans_-2-butene undergoes _trans_-to-_cis_ conversion at a faster rate than double bond shift, while the reverse is true for _cis_-2-butene.[15]

catalyst, Na-Al_2O_3, 30°C



Other investigators[16] have shown that the butene isomerizations involved more than geometric factors and stereospecific considerations. They felt that the major, decisive role was primarily associated with the acidity and basicity of the catalytic materials. The acidic and basic catalysts employed ranged from potassium hydroxide to sulfuric acid. They postulated that the _cis_-butenyl

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(16) N. F. Foster and R. J. Cvetanovic, _J. Am. Chem. Soc._, _82_, 4274 (1960).

carbanion would predict essentially exclusive double bond shift with the butene-2 isomers and not *cis-trans*-isomerization as was observed.[16] Their work was limited to small conversions to determine initial ratios of the isomers formed. With potassium hydroxide they found initially exclusive formation of *cis*-2-butene from 1-butene and 1-butene from either *cis*- or *trans*-2-butene. Sulfuric acid, on the other hand, gave a less pronounced selective formation of *cis*-2-butene from 1-butene and initially exclusive *cis-trans*-isomerization from either *cis*- or *trans*-2-butene rather than a double bond shift.

What is important in the above findings is that for initial rate isomerizations, basic catalysis leads to exclusive 1,2-shifts whereas acidic catalysis proceeds by exclusive *cis*-/*trans*-conversions. A combination of the two processes is operative if equilibrium conditions are reached.

The high stereoselectivity for this base-catalyzed isomerization parallels the high stereoselectivity in the polymerization of styrene by Ziegler type catalysts.[17] The acidic catalysts produce an atactic (randomly oriented)

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(17) F. Dannusso, *Chim. and Ind.*, *41*, 13 (1959).

polymer by a cationic mechanism while the basic catalysts yield an isotactic (highly oriented) polymer by an anionic mechanism, i.e., the basic catalyst gives a highly stereoselective reaction.

More recently, S. Bank, *et al.*[18] have suggested that the earlier work of W. O. Haag and H. Pines[15] with the butenes is analogous to the vinyl and propenyl ether systems[1,2,13] in that the rearrangements are often accompanied by unexpected kinetic control to the *less* stable *cis*-form.

There is thermodynamic evidence for higher *trans*-stability in the case of the 2-butenes as will be discussed in the following section. Bank *et al.*,[18] however, present no evidence for postulating higher *trans*-stability in the case of the enol ethers. They did suggest that for simple olefins the *cis*-allylic anion was thermodynamically more stable than the *trans*-form.

$$\begin{tikzcd}
 & \underline{\text{cis}}\text{-anion} \arrow[r, shift left, "k_3"] \arrow[dd, shift left, "k_5"] \arrow[dl, shift left, "k_{-1}"] & \underline{\text{cis}}\text{-olefin} \arrow[l, shift left, "k_{-3}"] \\
\text{1-olefin} \arrow[ur, shift left, "k_1"] \arrow[dr, shift left, "k_2"] & & \\
 & \underline{\text{trans}}\text{-anion} \arrow[r, shift left, "k_4"] \arrow[uu, shift left, "k_{-5}"] \arrow[ul, shift left, "k_{-2}"] & \underline{\text{trans}}\text{-olefin} \arrow[l, shift left, "k_{-4}"]
\end{tikzcd}$$

---

(18) S. Bank, A. Schriesheim, and C. Rowe, *J. Am. Chem. Soc.*, *87*, 3244 (1965).

They postulated that if $k_{-5} > k_5$ the cis-allylic anion is more stable than the trans-form. Both k_{-5} and k_5 were taken to be small; nonetheless the allylic anions once formed are expected largely to maintain their geometry.[19] Then with $k_{-3} > k_{-4}$ the reaction would initially produce more cis-olefin, but if allowed to reach thermodynamic equilibrium the more stable trans-olefin would predominate. To extend this reasoning to the vinyl ethers and vinyl amines was short-sighted in that they had no thermodynamic evidence for claiming higher trans-stability.

A more recent investigation by C. Cerceau, et al.[20] has shown that for 1,2-rearrangements with 1-olefins and potassium tert-butoxide, that the cis-olefin predominated by stereoselective isomerization but the cis/trans-ratio decreased as a function of temperature. This indicates higher cis-olefin stability. Likewise, Snyder et al.[21] explained the greater preference for the cis-configuration

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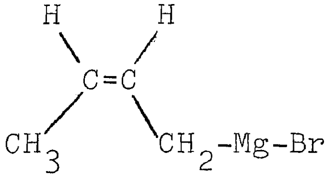
(19) D. H. Hunter and D. J. Cram, J. Am. Chem. Soc., 86, 5478 (1964).

(20) C. Cerceau, M. Laroche, A. Pazdzerki and B. Blouri, Bull. soc. chim. France, 405, 2323 (1970).

(21) W. H. Snyder, K. J. Taylor, N. S. Chu, and C. C. Price, Trans. N.Y. Acad. Sci., 24, 341 (1962)

of propenyl ethers based on energy differences of the conformers. Equally convincing support for the stability of the *cis*-carbanion is found in quenching butenyl Grignard reagents.[22] There is evidence that the butenyl Grignard reagent is actually present in the *cis*-form,[23] as shown below.



When *trans*-cinnamyl methyl ether was treated with potassium *tert*-butoxide in dimethoxyethane the *cis*-2-benzylvinyl methyl ether was produced exclusively.[24] Similarly, when diallyl ether was treated with potassium *tert*-butoxide *cis*-*cis*, *cis*-*trans* and *trans*-*trans*-dipropenyl ether was produced.[25] The *cis*-*cis*-dipropenyl ether was formed in excess of the other isomers. Some preliminary work with the pure *cis*-*cis*-isomer suggested that mercuric acetate possibility could be used for a *cis*-*trans* isomerization catalyst.[25]

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(22) W. G. Young, S. Winstein, and A. N. Prater, *J. Am. Chem. Soc.*, *58*, 289 (1936).

(23) K. W. Wilson, J. D. Roberts and W. G. Young, *J. Am. Chem. Soc.*, *72*, 218 (1950).

(24) I. Elphimoff-Felkin and J. Huet, *Comptes rendus*, *268*, 2210 (1969).

(25) W. H. Snyder, unpublished results.

From the above considerations, there is no certainty for enol ether systems as to whether the *cis*-isomer is more thermodynamically stable than the *trans*-isomer. The findings presented above are quite mixed in the following fashion:

a) the question of attainment of equilibria for the propenyl ethers in the 1,2-rearrangements,[1,8]

b) the importance or unimportance of stereospecific effects involving substrate, solvent, and catalyst,[1,2,20]

c) the basicity or acidity of the catalyst resulting in 1,2-shifts and/or *cis*-*trans* isomerization,[16]

d) the effect of catalyst concentration, solvent[1,9] and independence of temperature on *cis*/*trans* ratios,

e) opposite findings on temperature dependence with respect to *cis*/*trans* ratios,[8,20]

f) misinterpretation of kinetic control for thermodynamic control.[15,18]

In the examples considered above, the base catalyzed rearrangement to enol ethers involve at least a three-carbon prototropic system. Since many of the *cis*-*trans* isomerizations occur simultaneously with 1,2-rearrangements, it is difficult to isolate and study one effect alone.

On the other hand, the investigation of the *cis*-*trans* isomerization of a two carbon enol ether system can be as fruitful as the study of dihaloethylenes. Relative *cis*-*trans* stabilities can be deduced from thermodynamic equilibrium data. The corresponding dihaloethylenes have received more intensive investigation because they are generally more readily available.

The dialkoxyethylenes (vinyl diethers) are representative of the enol ether or vinyl ether class. No one has investigated the relative stabilities of the *cis*-*trans* pairs for the dialkoxy olefins nor studied the *cis*-*trans* isomerization for this system. The present research was concerned with the synthesis and separation of pure *cis*- and *trans*-1,2-dimethoxyethylene and investigating the *cis*-*trans* isomerization. In particular it was desired to find equilibrium data as a function of temperature and in addition to ascertain whether the *cis*-isomer was indeed the more stable.

cis-trans Isomerization and Stability of Related Compounds.

cis-*trans* Isomerization are of considerable interest because of the simplicity of the reaction. In general, *trans*-olefins are thermodynamically more stable than the corresponding *cis*-olefin.[26,27] In the 1930's, Kistiakowsky and his co-workers at Harvard made a series of precise

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(26) F. H. Westheimer, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, p. 554.

(27) G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, *58*, 766 (1936).

measurements of enthalpies of hydrogenation from which accurate resonance energies and energies of isomerization were made for the *cis*- and *trans*-2-butenes.[28] They found that the heat of isomerization at 355°K for the reaction

$$\text{cis-2-butene(g)} \rightleftharpoons \text{trans-2-butene(g)}$$

was -950 ± 120 cal/mole.

Other substituted ethylenes for which isomerization energies have been found, include -940 cal/mole for MeHC=CH(i-Pr),[29,30] -4220 cal/mole for EtOOCHC=CHOOEt,[31] -5700 cal/mole for PhHC=CHPh,[31] and -9370 cal/mole for (*tert*-Bu)HC=CH(*tert*-Bu).[30] In these cases, the *trans*-configuration has the lower energy and is the more stable isomer.[32,33] These energy differences for the isomeric ethylenes are a part of the experimental basis for the concept of steric crowding, which is apparently important even in the case of 2-butenes.[26,34]

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(28) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.*, *57*, 876 (1935).

(29) R. B. Turner, D. E. Nettelton, and M. Perelman, *J. Am. Chem. Soc.*, *85*, 260 (1963).

(30) R. B. Turner, D. E. Nettelton, and M. Perelman, *J. Am. Chem. Soc.*, *80*, 1430 (1958).

(31) R. B. Williams, *ibid.*, *64*, 1395 (1942).

(32) G. M. Wyman, *Chem. Reviews*, *55*, 625 (1955).

(33) W. W. McCarthy and J. Turkevich, *J. Chem. Phys.*, *12*, 405 (1944).

More recently, equilibrium studies were made for the *cis*- and *trans*-2-butene isomerization.[35,36] Equilibrium constants were calculated as a function of temperature from which isomerization energies were calculated. The amount of *trans*-isomer at equilibrium conditions diminished as the temperature increased, again indicating that the *trans*-2-butene was the more thermodynamically stable isomer.[37]

In contrast to the above, there is a growing body of experimental data on haloethylenes (and a diazene) strongly suggesting that the *cis*-isomers are the more stable. Examples of *cis*-olefin stability include the 1,2-difluoroethylenes,[38,39,40,41] the 1,2-dichloroethylenes,[42,43,44]

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(34) G. W. Wheland, *Advanced Organic Chemistry*, John Wiley and Sons, Inc., New York, 1960, pp. 408-515, 354-357, 428.

(35) S. W. Benson and A. N. Bose, *J. Am. Chem. Soc.*, *85*, 1385 (1963).

(36) D. M. Golden, K. E. Egger, S. W. Benson, *ibid.*, *86*, 5415 (1964).

(37) H. H. Vogue and N. C. May, *J. Am. Chem. Soc.*, *68*, 550 (1946).

(38) N. C. Craig and Eric A. Entemann, *J. Am. Chem. Soc.*, *83*, 3047 (1961).

(39) N. C. Craig and Eric A. Entemann, *J. Chem. Physics*, *36*, 243 (1962).

(40) N. C. Craig and V. Overend, *ibid.*, *51*, 1127 (1969).

(41) H. G. Viehe, *Chem. Ber.*, *93*, 1697 (1960).

(42) R. E. Wood and D. P. Stevenson, *J. Am. Chem. Soc.*, *63*, 1650 (1941).

the 1,2-difluorodiazenes,[45,46] the 1,chloro-2-fluoroethylenes,[47,48] and the 1,2-difluoro-1-chloroethylenes.[49] The equilibrium measurements for the 1,2-dibromoethylenes are questionable,[38,47,50] although in the liquid phase the polar *cis*-isomer is favored (K = 0.59 - 0.67 at 25-150°)[51] over the gas phase as expected.[52]

It is interesting to notice that the diiodoethylenes are more stable in the *trans*-configuration than in the *cis*-configuration. Liquid phase isomerization data has shown that for the *cis*⇄*trans* equilibrium, the enthalpy

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(43) H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, *17*, 556 (1949).

(44) K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, *76*, 1493 (1954).

(45) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Am. Chem. Soc.*, *81*, 6397 (1959).

(46) G. T. Armstrong and S. Marantz, *J. Chem. Phys.*, *38*, 169 (1963).

(47) N. C. Craig, L. G. Piper, and V. L. Wheeler, *J. Phys. Chem.*, *75*, 1453 (1971).

(48) N. C. Craig, Y-S Lo, L. G. Piper, and J. C. Wheeler, *J. Phys. Chem.*, *74*, 1712 (1970).

(49) N. C. Craig, D. A. Evans, L. G. Piper, and V. L. Wheeler, *J. Phys. Chem.*, *74*, 4520 (1970).

(50) R. M. Noyes and R. G. Dickinson, *J. Am. Chem. Soc.*, *65*, 1427 (1943).

(51) A. R. Olson and W. Maroney, *J. Am. Chem. Soc.*, *56*, 1320 (1934).

of reaction is approximately - 1550 cal/mole.[53,54] Recent measurements in the gas phase, however, show no significant temperature dependence over a 140° range.[55]

For the above isomerizations (*cis*$\rightleftarrows$*trans*), enthalpy differences range from +250 to +3000 cal/mole, clearly indicating the high stability for the *cis*-isomers. By looking at a few values, we can see a definite trend: FN=NF (3.0 Kcal/mole), HFC=CFH (0.928 Kcal/mole), HClC=CClH (0.650 Kcal/mole), HBrC=CBrH (-0.09 to 0.320 Kcal/mole), and HIC=CIH (-1.55 Kcal/mole). We observe an increase in stability of the *cis*-olefin relative to the *trans*-olefin as the electronegativity of the halogen atom increases. In the case of 1,2-difluorodiazene, the preference for the *cis*-configuration is very high (approx. 3000 cal/mole).

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(52) P. Klaboe and J. R. Nielson, *J. Chem. Phys*., *33*, 1764 (1960).

(53) R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Am. Chem. Soc*., *67*, 1319 (1945).

(54) S. F. Miller, A. Weber, and F. F. Cleveland, *J. Chem. Phys*., *23*, 44 (1955).

(55) S. Furuyama, D. M. Golden, and S. W. Benson, *J. Phys. Chem*., *72*, 3204 (1968).

(56) D. V. Gardner and D. E. McGreer, *Can. J. Chem*., *48*, 2104 (1970).

(57) J. W. Crump, *J. Org. Chem*., *28*, 953 (1963).

There are a few other examples reported in the literature where the *cis*-configuration predominates over the *trans*-configuration.[56] These include: $HClC{=}CHCH_3$ (700 cal/mole),[41,57,58] $HBrC{=}CHCH_3$,[59] $HClC{=}CHCN$,[57] $CH_3CH{=}CHCN$ (170 cal/mole),[57,60] and some propenyl ethers ($ROCH{=}CHCH_3$).[1-3] Heats of isomerization for the propenyl ethers ($ROCH{=}CHCH_3$), $HClC{=}CHCN$ and $HBrC{=}CHCH_3$ were not available since the equilibrium constants were determined at only one temperature.

It appears that in these cases the *cis*-isomers are somewhat more stable if there is at least one strongly electronegative atom or group attached to the double-bond carbon.[2,57,59] The above mentioned compounds are the total number of compounds studied to date in which the *cis*-isomer has the lower energy (thermodynamically more stable).

Comparison of *cis*- and *trans*-1,2-Dimethoxyethylene to the Dihaloethylenes.

Another *cis*-*trans* system has been synthesized, namely, the 1,2-dimethoxyethylenes which appear to be more stable in the *cis*-configuration.

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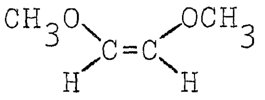
(58) M. Craen, Ph. D. Dissertation, University of Brussels, 1924.

(59) K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, *77*, 1682 (1955).

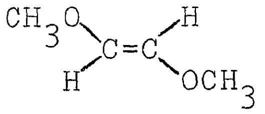
(60) J. N. Butler and R. D. McAlpine, *Can. J. Chem.*, *41*, 2487 (1963).

cis-1,2-dimethoxyethylene,



(I);

trans-1,2-dimethoxyethylene,



(II).

Both of these isomers are examples of vinyl ethers (vinyl diethers to be more exact). The early predictability of the more stable *cis*-isomer arose from reaction yield investigations and from NMR data.[61]

In a base catalyzed elimination reaction using potassium *tert*-butoxide on the substrate 1,1,2-trimethoxyethane (III) at 165°C, *cis*- and *trans*-1,2-dimethoxyethylene were produced in a 2:1 ratio (*cis*-isomer/*trans*-isomer). In this case, the *cis*-formation probably proceeds by a lower energy mechanism with one conformation of the substrate predominating.

The NMR spectra of the *cis*- and *trans*-dimethoxyethylenes suggest higher *cis*-isomer stability if an analogy is made to the NMR spectra[62,63] of the *cis*- and *trans*-difluoroethylenes in which it is known that

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(61) J. Waldron, M.S. Thesis, Newark College of Engineering, 1967.

(62) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, *150*, 743 (1961).

(63) G. W. Flynn, M. Matsushima, J. D. Baleschivieler, and N. C. Craig, *J. Chem. Phys.*, *38*, 2295 (1963).

the *cis*-isomer has the lower energy.[38,40,47] The τ values for the vinyl protons of *cis*- and *trans*-difluoroethylene are 3.75 (2.78).[64] For the *cis*- and *trans*-dimethoxyethylenes (I and II), the τ values (CCl_4) relative to tetramethylsilane are 4.88 (3.85)[64] for the vinyl protons.

The *cis*-vinyl protons for both cases absorb at approximately 1 ppm upfield (higher field) than the *trans*-isomer suggesting that *cis*-DME (I) has a higher stability as does *cis*-1,2-difluoroethylene. Apparently the electron density in the *cis*-double bonds must be higher in those cases where the *cis*-vinyl protons absorb at higher field than the *trans*-vinyl protons.[63,65] This infers that the *cis*-protons are more effectively shielded than the *trans*-protons.[66]

Normally, electron withdrawing groups attached to an olefin exert an opposite and more pronounced deshielding effect in the *cis*-isomer than in the *trans*-isomer. This is true for the dichloroethylene[66] although the difference is negligible. τ Values for the vinyl protons of *cis*- and *trans*-1,2-dichloroethylene are 3.72 (3.77).[64] Likewise, the

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(64) *trans*-values are in parenthesis.

(65) H. Baganz, K. Praefeke, and J. Rost, *Ber.*, *96*, (10) 2657 (1963).

(66) E. B. Whipple, W. E. Stewart, G. S. Reddy, and J. H. Goldstein, *J. Chem. Phys.*, *34*, 2136 (1961).

stability of the *cis*-isomer relative to the *trans*-isomer is less pronounced for the dichloroethylenes than for the difluoroethylenes.

It appears by this analogy that the methoxy groups in I and II are more related to the difluoroethylenes than to the dichloroethylenes. Oxygen and fluorine have similar electronegativities which are higher than chlorine. Also, the C=C stretching frequency for I occurs at higher frequency than for II which implies that it takes more energy to break the *cis*-double bond than the *trans*-double bond. This is a measure of stability again indicating higher stability for the *cis*-configuration.

Coyle *et al.*,[62] in 1961, made some interesting observations on the relative stabilities of the *cis*- and *trans*-1,2-difluoroethylenes *before* the stabilities of these two isomers were known. In the reaction between diborane and tetrafluoroethylene[67] and in the classical dehalogenations,[68] *cis*-1,2-difluoroethylene was the exclusive product formed.[62] He deduced that the appearance of only one isomer in the reaction products may be due

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(67) Bartocha, Graham, and Stone, *J. Inorg. Nuclear Chem.*, *6*, 119 (1958).

(68) R. N. Hoszeldine and B. R. Steel, *J. Chem. Soc.*, 2850 (1957).

to the thermodynamic factors and may not reflect any geometric specifity in the formation of the difluoroethylenes.

Similar reasoning leads one to believe that cis-1,2-dimethoxyethylene was the more stable isomer and initiated an investigation into the synthesis and isomerization of these isomers.

DISCUSSION AND RESULTS

Although the *cis*-*trans* isomerization of haloethylenes and the butenes have been studied in great detail, and the base and acid catalyzed 1,2-rearrangements of allyl ethers have been studied in some detail, very little work has been done on the *cis*-*trans* isomerizations of enol ethers. It was felt that an investigation into this area might provide novel contributions and confirmation of *cis*-enol ether stability.

cis- and *trans*-1,2-Dimethoxyethylene were chosen because they contained two adjacent methoxy groups on a two carbon unsaturated system, therby, permitting analogies to the dihalo ethylene series for which thermodynamic and equilibria data were available.[47] It was considered possible that molecules of this type were more stable in the *cis* than in the *trans*-configuration, as the difluoroethylenes.

1. Synthesis of 1,1,2-Trimethoxyethane.

1,1,2-Trimethoxyethane $CH_3OCH_2-CH(OCH_3)_2$ (III), was synthesized from bromoacetaldehyde dimethyl acetal, $Br-CH_2-CH(OCH_3)_2$ (IV) and sodium methoxide via a Williamson ether synthesis employing a modification of that used by S. M. McElvain[69] *et al*. for the 1,1,2-triethoxy derivative.

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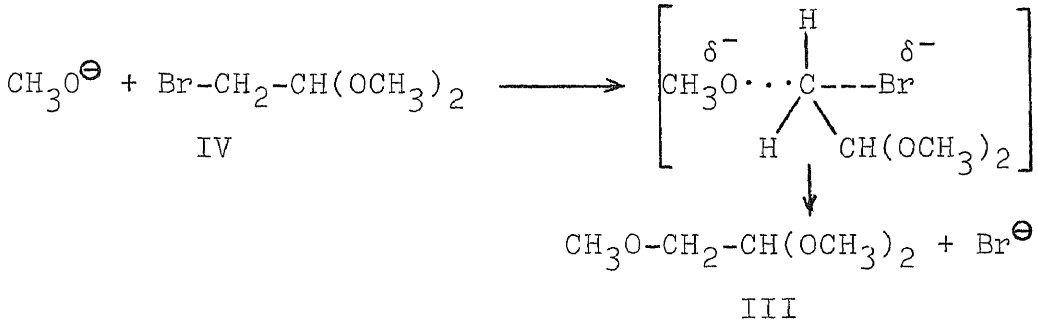
(69) S. M. McElvain and C. H. Stammer, *J. Am. Chem. Soc.*, 73, 915 (1951).

The reaction involved was characteristic of an S_N2-type displacement with the strong base, methoxide ion (CH_3O^-) displacing bromide ion from IV.[70.71]

(1)



The mechanism for the formation of bromoacetaldehyde dimethyl acetal from vinyl acetate, bromine, and methanol is more complex in that an addition and substitution reaction take place.[72,73] N-bromosuccinimide could also be used as the brominating reagent.[74]

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(70) E. S. Gould, Mechanism and Structure in Organic Chemistry, Holt, Rinehart and Winston, New York, 1959, pg. 250.

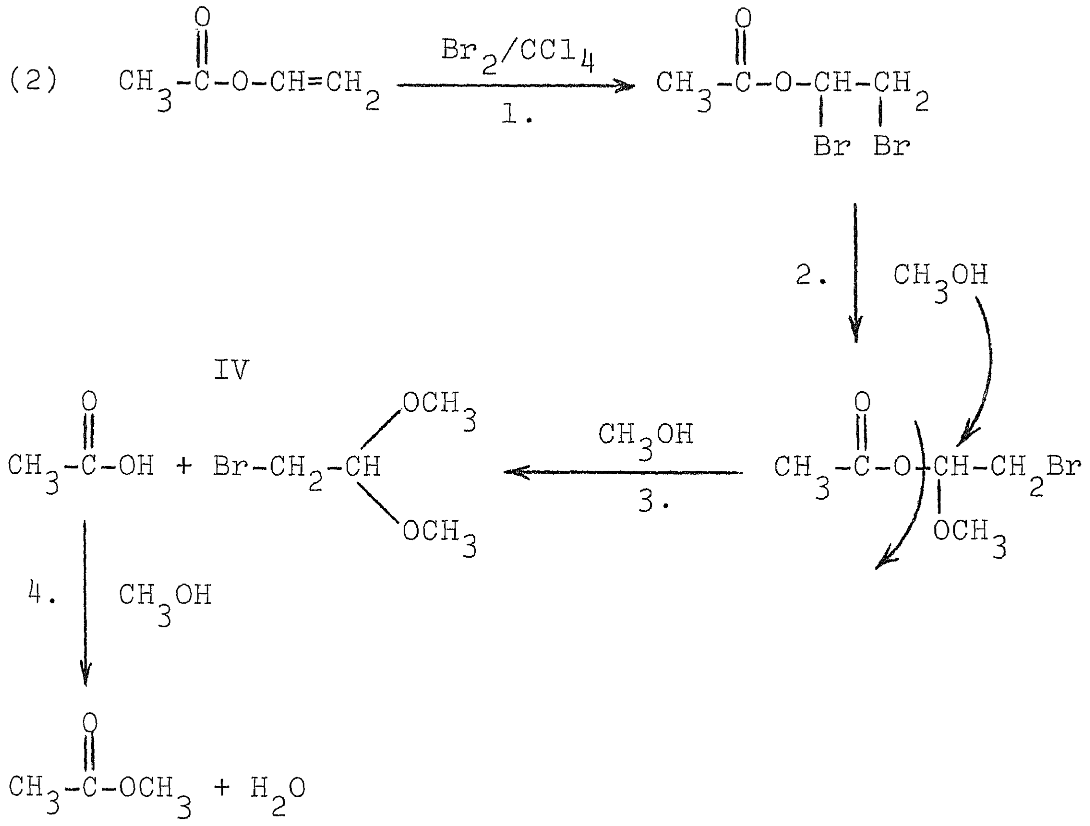
(71) C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, New York, 1953, pg. 306.

(72) E. M. Filachione, J. Am. Chem. Soc., 61, 1705 (1939).

(73) S. M. McElvain and D. Kundiger, Org. Synthesis, Coll. Vol. 3, 123 (1951).

(74) E. N. Marvell and M. J. Joncich, J. Am. Chem. Soc., 73, 973 (1951).

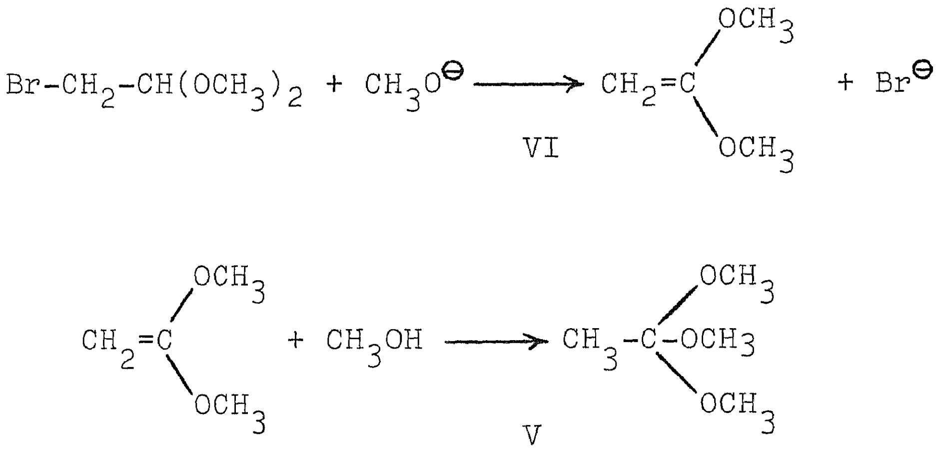
(2)



Step (1) is the addition of bromine to the double bond. Step (2) is an S_N1-type substitution with methanol displacing bromine on the α-carbon. Step (3) can be viewed as either an S_N1-type substitution with methanol as the attacking nucleophile displacing the acetoxy group from the α-carbon or as an alkyl-oxygen cleavage ($A_{AL}1$)-type transesterification. The final step (4) is a simple esterification of methanol and acetic acid yielding methyl acetate. The final products from the reaction were methyl acetate and bromoacetaldehyde dimethyl acetal.

The yield of 1,1,2-trimethoxyethane (III) from reaction (1) was 52%. The conversion of a bromoacetal (limiting reagent) was 95% based on the amount of sodium bromide formed. A major side product, 1,1,1-trimethoxyethane (the trimethyl ester of orthoacetic acid) was formed in over 40% yield. This product was compared to an authentic sample (same boiling point of 109°C., identical vpc retention times and identical IR spectra) for confirmation of structure.

A mechanism was postulated for the formation of 1,1,1-trimethoxyethane, $CH_3\text{-}C(OCH_3)_3$ (V), based on an initial E_2-type elimination reaction with subsequent addition of methanol to the double bond.



$$Br\text{-}CH_2\text{-}CH(OCH_3)_2 + CH_3O^{\ominus} \longrightarrow CH_2{=}C(OCH_3)_2 + Br^{\ominus}$$

VI

$$CH_2{=}C(OCH_3)_2 + CH_3OH \longrightarrow CH_3\text{-}C(OCH_3)_3$$

V

This seemed likely in that a strong base such as sodium methoxide and relatively non polar conditions (5.6 molar solution of sodium methoxide in methanol) is favorable for elimination conditions.[70] The expected product, ketene dimethyl acetal (VI), would then add methanol rapidly producing the trimethyl orthoacetate (V). The direction of this addition follows Markovnikov's rule.

McElvain[75,76] has shown that ketene dimethyl acetal or any of the ketene acetal series does indeed add methanol to the double bond producing the corresponding trimethyl orthoester. He also showed that ethanol, n-propanol, isopropanol, etc. reacted similarly with the exception of _tert_-butanol, an important point in that potassium _tert_-butoxide was generally employed as the base for the dehydrohalogenation of haloacetals to produce VI.[75,77,78]

A different approach was tried in which the mode of addition of reagents was reversed. Initially, the bromoacetal was added to the sodium methoxide/methanol solution which kept the base concentration high at all times and the solvent polarity of reaction medium relatively low. These conditions favored E_2-type eliminations. On the other hand, when the sodium methoxide/methanol solution was added slowly in a dropwise fashion to a solution of bromoacetal in methanol, the yield of III increased considerably to 75%. Conversion of bromoacetal was 95% of theory. In the latter

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(75) S. M. McElvain, _Chem. Reviews_, 455 (1949).

(76) S. M. McElvain and W. R. Davie, _J. Am. Chem. Soc_., _73_, 1400 (1951).

(77) S. M. McElvain and G. R. McKay, _J. Am. Chem. Soc_., _77_, 5601 (1955).

(78) P. R. Johnson, H. M. Barnes, and S. M. McElvain, _J. Am. Chem. Soc_., _62_, 964 (1940).

case, the increased solvent polarity of the reaction medium and the low base concentration favored bimolecular substitution (S_N2) at the expense of elimination.[79] As expected, the S_N2/E_2 ratio increased. The results are summarized in Table I.

It should also be pointed out that the sodium methoxide solution must be prepared from fresh sodium and absolute methanol since commercially available sodium methoxide had sodium carbonate and sodium hydroxide contamination due to exposure to moisture, CO_2, etc.

2. Batch Reactor Synthesis of *cis*- and *trans*-1,2-Dimethoxyethylene (I and II respectively).

McElvain and Stammer[69] described the preparation of 1,2-diethoxyethylene from ethoxyacetal and alumina. They reported a 39% yield. The *cis*-olefin was obtained exclusively.

To investigate the feasibility of the reaction with methoxyacetal(III) and alumina (Al_2O_3), a batch reactor set-up was used initially in-lieu-of a continuous operation. The reaction investigated was a dealcoholation, from which methanol was eliminated from the substrate III.

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(79) E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, Rinehart and Winston, New York, 1959, pg. 489.

TABLE I

The Synthesis of 1,1,2-Trimethoxyethane (III) from Bromoacetaldehyde Dimethyl Acetal (IV) and Sodium Methoxide/Methanol.

				Reactants			Products			
Run No.	T, °C	Rate of Addition, ml./hr.	Reflux Time, hr.	$NaOCH_3$ g. (moles)	CH_3OH g. (moles)	IV g. (moles)	III g. (moles)	V[a] g. (moles)	Yield of III, wt. %[b]	X_A %[c]
1[d]	82	750	48	352 (6.51)	1120 (35.0)	957 (5.66)	353 (2.94)	271 (2.26)	52	95
2[e]	73	200	48	368 (6.81)	2415 (75.5)	1150 (6.81)	613 (5.10)	123 (1.02)	75	96

a. major side product (1,1,1-trimethoxyethane)

b. The yield of III was based on the limiting reactant, bromoacetal (IV).

c. The conversion of IV was based on the total amount of sodium bromide formed.

d. In run 1, IV was added to sodium methoxide/methanol.

e. In run 2, sodium methoxide/methanol was added to IV/methanol.

$$\underset{\text{III}}{CH_3OCH_2\text{-}CH(OCH_3)_2} \xrightarrow[Al_2O_3]{} CH_3OCH{=}CHOCH_3 + CH_3OH$$

A partial take-off method was used in which the olefins (b.p. 94° - 101°C.) were removed as soon as they formed. The higher boiling methoxyacetal (III), b.p. 126°C., was returned to the batch reactor by total reflux. A slow stream of nitrogen facilitated this operation by entrainment of the more volatile olefins and methanol. These were condensed in a cold trap. As the products were removed from the reaction site, the reaction was driven to completion. After approximately 72 hours, the entire reaction mixture and products of reaction were condensed in the cold trap bypassing the first partial take-off condenser due to nitrogen entrainment.

The danger in using a total reflux operation (Dewar condenser) was that as the olefin formed it would be returned to the reactor causing long contact times with the alumina. This would lead to some decomposition of desired products. Pyrolysis of vinyl ethers over alumina yielding aldehydes and other degradation products are known reactions.[80,81,82]

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(80) S. M. McElvain, H. I. Anthes, and S. H. Shapiro, *J. Am Chem. Soc.*, 64, 2525 (1942).

(81) C. Frisell and S. O. Lawesson, *Org. Synthesis*, 43, 55 (1963)

The results of 3 runs are described in Table II and III. Since it was very difficult to control contact times via the partial take-off technique, low yields of olefins were produced. It was felt that a continuous process such as, pyrolysis, would give increased yields of dimethoxyethylene.

3. The Continuous Pyrolysis of 1,1,2-Trimethoxyethane (III)

A better approach to the synthesis of the *cis* and *trans* olefins was desired. McElvain and Stammer[69] did some preliminary work on the ethoxy derivatives which seemed promising as a starting point.

The first few runs were encouraging since, at 220°C, the yield of both *cis*- and *trans*-dimethoxyethylene (I and II respectively) was 44%, based on unrecovered III. The *trans*/*cis* ratio was 0.07. At 320°C, the total yield of I and II was 64% based on unrecovered III. The *trans*/*cis* ratio was 0.27. (See Tables IV and V). The ratio of the *trans*-isomer to the *cis*-isomer increased with higher temperature.

In the earlier runs, batch and continuous, the *cis*-isomer was formed almost exclusively. Similarly, in the

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(82) J. March, *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, McGraw-Hill Book Co., New York, 1968, pg. 756.

TABLE II

Batch Reaction Synthesis of cis- and trans-1,2-Dimethoxyethylene (I and II respectively) from 1,1,2-Trimethoxyethane (III)

			Reactant	------Reaction Products------				
Run No.	Temp. (°C)	Time (hr.)	III g. (moles)	I g. (moles)	II g. (moles)	Methanol g. (moles)	Yield of I (%)	Conversion of III (%)[a]
1	126	12	64.0 (0.533)	13.6 (0.155)	0.6 (0.007)	10.4 (0.323)	30.4	60.6
2	126	80	64.0 (0.533)	7.1 (0.081)	0.4 (.004)	10.7 (0.334)	15.2	62.6
3	126	72	159.3 (1.33)	11.1 (0.127)	1.23 (0.014)	15.7 (0.492)	9.5	37.0

a. Conversion was based on amount of methoxyacetal converted to methanol.

TABLE III

Product Distribution from Batch Reactor Synthesis[a]

Run No.	Products I[b] (wt. %)	 II[c] (wt. %)	 Methanol (wt. %)	Reactant III[d] (wt. %)	Amount[e] recovered, g.	Wt.% Recovered
1	34.1	1.6	25.2	39.1	39.8	62.2
2	24.7	1.3	37.2	36.8	28.7	44.8
3	14.7	1.6	20.7	63.0	75.8	47.6

a. Wt. % based on recovered material from reaction mixture.

b. I = *cis*-1,2-dimethoxyethylene

c. II = *trans*-1,2-dimethoxyethylene

d. III = 1,1,2-trimethoxyethane (unreacted starting material)

e. Total amount of reactants and products recovered.

TABLE IV

Continuous Pyrolysis of 1,1,2-Trimethoxyethane (III)

Run No.[a]	Temp. °C.	Reactant	Products			Rate of Addition of III, g./hr.	Conversion of III, (%)[d]
		III g. (moles)	I[b] g. (moles)	II[c] g. (moles)	Methanol g. (moles)		
1	220	38.2 (0.318)	3.87 (0.043)	0.3 (0.003)	5.7 (0.178)	19.1	55.6
2	320	57.3 (0.478)	12.5 (0.143)	3.4 (0.039)	12.1 (0.378)	57.3	79.1
3	360	57.3 (0.478)	9.6 (0.109)	1.9 (0.022)	11.1 (0.347)	57.3	72.6
4	310	50.0 (0.417)	11.7 (0.133)	2.9 (0.033)	13.1 (0.411)	57.0	98.6
5	310	190.0 (1.583)	71.0 (0.807)	11.3 (0.128)	27.7 (.865)	87.0	54.6
6	300	296.0 (2.467)	169.8 (1.930)	20.6 (0.234)	66.9 (2.090)	114.0	84.7 (87.7)[e]

a. The nitrogen rate was not measured by a flow meter for the first 3 runs. The outlet gas rate measured by an outlet bubbler was 1-2 bubbles/sec. For runs 4-6, the nitrogen input rate was 90 ml./min.

b. *cis*-1,2-dimethoxyethylene

c. *trans*-1,2-dimethoxyethylene

d. Conversion is based on amount of III converted to methanol.

e. Conversion is based on amount of III converted to olefins I and II.

TABLE V

Product Distribution from Continuous Pyrolysis of 1,1,2-Trimethoxyethane (III)[a]

	Products			Reactant		
Run No.	I[b] (wt. %)	II[c] (wt. %)	Methanol (wt. %)	III[d] (wt. %)	Amount[e] recovered, g.	Wt.% Recovered
1	14.1	1.2	21.4	63.3	26.8	70.2
2	33.4	8.9	32.1	25.6	37.7	65.8
3	28.8	5.8	33.5	31.9	33.2	57.9
4	42.5	10.7	46.8	0.0	27.5	55.0
5	52.6	8.4	20.5	18.5	135.0	71.1
6	66.0	8.0	26.0	0.0	257.2	86.9

a. Wt. % based on recovered material from reaction mixture.

b. *cis*-1,2-dimethoxyethylene

c. *trans*-1,2-dimethoxyethylene

d. 1,1,2-trimethoxyethane (unreacted starting material)

e. Total amount of reactants and products recovered.

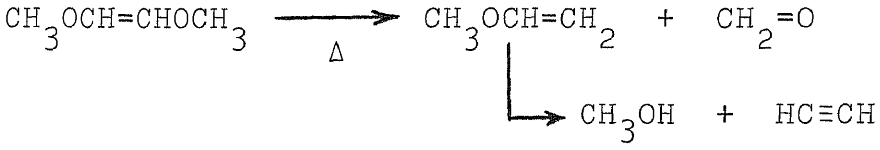
potassium *tert*-butoxide initiated elimination[61] on substrate III, the *cis*-to-*trans* ratio was approximately 2:1. One could conclude that this is not necessarily an indication of *cis*-olefin thermodynamic stability but is, at the very minimum, an indication that *cis*-formation probably proceeds by a lower energy mechanism with one conformation of the substrate reacting preferentially over the other. But as the temperature of the pyrolysis reaction was raised, more *trans*-isomer relative to the *cis*-isomer was formed. Since the *least* stable isomers are favored thermodynamically at *higher* temperatures, we had another independent indication of the higher stability for the *cis*-enol ether (I).

Coyle *et al.*,[62] with less evidence, used this type of deductive reasoning to infer higher stability for *cis*-difluoroethylene. *cis*-*trans* Equilibrium data with measured heats of isomerization, etc. would confirm the above hypothesis. This will be shown in later sections of this work.

Other runs were performed at different oven temperatures. There appeared to be a lower conversion to the olefins when the temperature was raised from 320°C to 360°C. (Table IV) Temperatures as high as 500°C were tried but many decomposition products were formed either as a smoke or non-condensable gases. Some of the pyrolysis degredation products may have been formed by the elimination of methanol from dimethoxyethylene yielding methoxyacetylene.[83]

(1) $CH_3OCH{=}CHOCH_3 \xrightarrow[\Delta]{} CH_3OH + CH_3OCH{\equiv}CH$

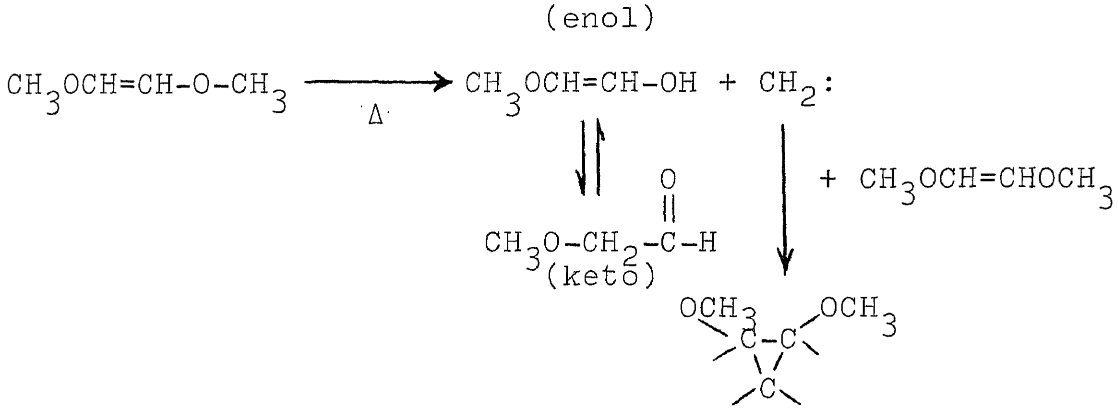
Also, methyl vinyl ether can form which could then undergo elimination to acetylene, as shown below.

(2) 

$$CH_3OCH{=}CHOCH_3 \xrightarrow[\Delta]{} CH_3OCH{=}CH_2 + CH_2{=}O$$
$$CH_3OCH{=}CH_2 \rightarrow CH_3OH + HC{\equiv}CH$$

Formaldehyde would also be formed by this mode of reaction. McElvain[69] found trace quantities of acetaldehyde in his work with the ethoxy derivative.

Vinyl ethers are also known to pyrolyze with alkyl-oxygen cleavage.[81,84] Methoxyacetaldehyde and/or 1,2-dimethoxycyclopropane would be the expected products if that were the case.

(3) 

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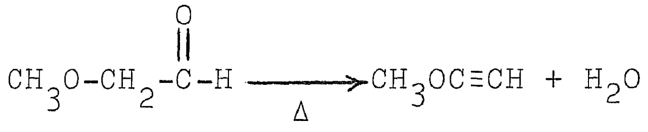
(83) E. R. Jones, G. Eglinton, M. C. Whiting and B. L. Shaw, Org. Synthesis, Coll. IV, 404 (1965).

The previous reaction paths are plausible explanations for the formation of low boiling pyrolytic degradation products. They were not collected or identified except as trace quantities appearing on gas chromatograms from the low boiling distillation cuts. These products were usually in the form of smoke or fog entrained in nitrogen and were not condensed.

At high reaction temperatures (360° - 500°C), the alumina was charred black and burnt unevenly. When lower temperatures were again employed, as in runs 1 and 2, the results were not reproducible. Decomposition products, non-condensibles, etc. were formed resulting in 2-phase product mixtures (a large aqueous phase) and a marked lowering in olefin yield. The water can result from the elimination of water from methoxyacetaldehyde (Eqn. 3),

(4)



$$CH_3O\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \xrightarrow[\Delta]{} CH_3OC\equiv CH + H_2O$$

again resulting in methoxyacetylene (Eqn. 1).

There appeared to be a problem of reaction optimization and defining certain reaction parameters that should

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(84) W. L. Howard and N. B. Lorette, Org. Synthesis, 42, 14, (1962).

be known and accurately measurable. Once they became measurable, the parameters could be varied until certain optimum conditions were obtained and held constant. Such variables as nitrogen input rate (not output rate since gases were evolved from the pyrolysis), catalyst temperatures within the bed, addition rate of reactant, and amount of catalyst were picked as parameters to optimize.

The pyrolysis apparatus went through many evolutionary changes before the optimum conditions of run 6 were achieved. Instead of measuring small flow rates of nitrogen with an exit bubbler, two flow meters (low and high range) were used before the apparatus. The addition of methoxyacetal (III) could not be measured accurately by vaporizing it from a boiling flask into the pyrolysis tube since the rate of vaporization would change as a function of the liquid left in the flask, surface area, nitrogen entrainment, etc. It was decided to add III in a dropwise fashion from an addition funnel into a hot empty flask whereby it vaporized rapidly on contact and was carried into the tube furnace by nitrogen. The optimum addition rate was found to be 1 - 2 ml./min.

The amount of alumina varied from 70 g. to 115 g. The best results were obtained with 75 g. The catalyst could be used from run to run unless hot spots developed in the reaction creating burnt catalyst spots. This would lead to more decomposition products. After a successful run, the catalyst appearance was usually light to medium brown throughout. Initially the catalyst is white and for the first hour or so of a run some decomposition products were noticed in the form of a two phase product mixture. A light yellow-green liquid was obtained initially. When the run was operating sucessfully (high olefin yields), the product mixture condensed as a light golden liquid. Apparently the catalyst must be slightly deactivated before high olefin yields are realized.[15,85-87] This type of catalyst deactivation has been described for analogous elimination reactions utilizing alumina for the dehydration of alcohols.[88-90]

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(85) Nikolesku and N. Chiok, Kinetika i Kataliz, 10, 910 (1969).

(86) L. V. Nicolescu, A. Nicolescu, M. Gruia, A. Terleck-Baricevic, M. Dordan, E. Angelescu, and A. Ionescu, Fourth International Congress on Catalysis, Moscow, (1968).

(87) J. W. Myers, Chem. Eng. Prog. Symposium Series,(1970).

(88) L. Freidlin, V. Z. Sharf, G. I. Samakhvalov, and Y. N. German, Neftekhimiya, 6, 887 (1966).

(89) W. O. Haag and H. Pines, J. Am. Chem. Soc., 83, 2847 (1961).

(90) J. Turkevich and R. K. Smith, J. Chem. Physics, 16, 466 (1948).

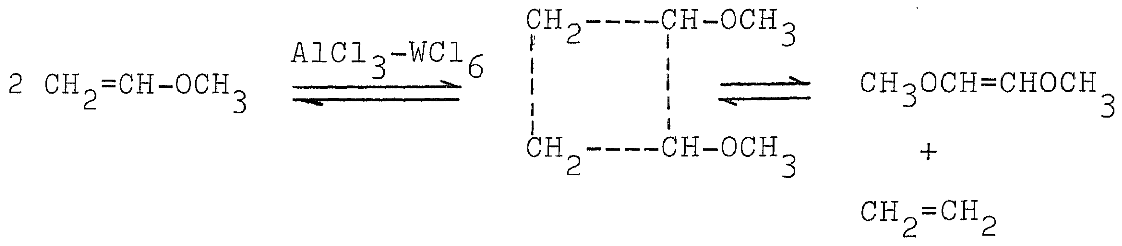
The reaction products were initially collected from a Dewar condenser at -60°C. The Dewar condenser was followed by a cold trap to reduce losses. There was still 30% to 50% losses. The pyrolysis vapors exited from the reactor tube at 300° to 400°C and were subjected to "thermal shock" on contacting the walls of the cold Dewar condenser. This caused excessive fogging due to fine droplet formation (rain) with nitrogen entrainment. To reduce the mechanical losses a better condenser system was designed. The hot vapors were first subjected to a 30 cm. air condenser packed with porcelin Raschig rings. This was followed by a water condenser and finally the original Dewar condenser and cold trap. With this scheme, the hot vapors were cooled more gradually resulting in better simultaneous heat and mass transfer. The mechanical losses due to fogging, nitrogen entrainment, etc., were reduced approximately 3-fold to only 14%. Tables IV and V contain summaries for the 6 runs. Run 6, performed at the most optimum conditions, gave nearly a 90% yield of olefins from 1,1,2-trimethoxyethane.

The pyrolysis of III was a convenient route to the preparation of the _cis_-olefin. However, the _trans_-olefin was obtained in much lower yield due to the high ratios of _cis_-olefin/_trans_-olefin produced (Tables IV and V). Many of the runs were combined and distilled to produce enough _trans_-olefin to investigate the _cis_$\rightleftarrows$_trans_ equilibrium from both sides.

Another reaction scheme could be utilized which results in a greater proportion of trans-isomer. The dechlorination of 1,2-dimethoxy-1,2-dichloroethane has been described.[65,91] A 50% yield of 1,2-dimethoxyethylene was reported in which the isomer distribution was 68% trans- and 32% cis-olefin.[65]

N. Calderon[92] has recently discussed olefin metathesis reactions which can be utilized to disproportionate olefins using catalyst systems such as WCl_6-C_2H_5OH-$C_2H_5AlCl_2$ or $AlCl_3$-WCl_6. A possible alternate route to the synthesis of dimethoxyethylene could involve the reaction of methyl vinyl ether with an active metathesis catalyst mentioned above.

(5)



$$2\ CH_2{=}CH\text{-}OCH_3 \xrightleftharpoons{AlCl_3\text{-}WCl_6} \begin{array}{ccc} CH_2 & \text{----} & CH\text{-}OCH_3 \\ \vdots & & \vdots \\ CH_2 & \text{----} & CH\text{-}OCH_3 \end{array} \rightleftharpoons \begin{array}{c} CH_3OCH{=}CHOCH_3 \\ + \\ CH_2{=}CH_2 \end{array}$$

Again, larger proportions of trans-isomer may possibly be obtained by that reaction scheme (Eqn. 5).

---

(91) S. Iwatsuki, S. Iquchi, and Y. Yamashita, Kogyo Kagaku Zasshi, 68 (12), 2463 (1965).

(92) N. Calderon, Accounts of Chemical Research, 5, 127 (1972).

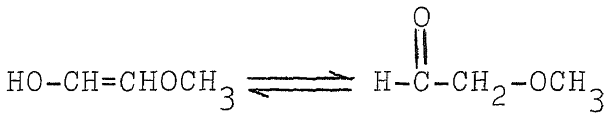
4. Reaction of *cis*-1,2-Dimethoxyethylene (I) with Potassium *tert*-Butoxide (VII)

It was felt from an earlier investigation[61] that the substituted product, methyl *tert*-butyl ether (VIII) was produced by substitution of potassium *tert*-butoxide on dimethoxyethylene (a reaction product) and/or by substitution on substrate 1,1,2-trimethoxyethane (initial reactant). At that time, only microliter quantities of dimethoxyethylene were available and the reaction could not be studied.

Since a sufficient quantity of the *cis*-olefin (I) became available using the synthetic route outlined in the text (Section 3), it was desirable to study the reaction in more detail (Eqn. 1). The major product from the reaction of *cis*-dimethoxyethylene with potassium *tert*-butoxide was methyl *tert*-butyl ether. This was clearly an indication of an S_N2-type reaction involving a strong base on the enol ether substrate (I).

$$(1)\quad \underset{\text{VII}}{(CH_3)_3C\text{-}O^{\ominus}} + \underset{\text{I}}{CH_3OCH{=}CHOCH_3} \longrightarrow \underset{\text{VIII}}{CH_3O\text{-}C(CH_3)_3} + \underset{\text{IX}}{\overset{\ominus}{O}\text{-}CH{=}CHOCH_3}$$

Methyl *tert*-butyl ether was observed in 40.5% yield. The leaving group in the above reaction is the electron delocalized enolate ion (IX) of methoxyacetaldehyde.



$$HO\text{-}CH{=}CHOCH_3 \rightleftharpoons H\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}OCH_3$$

A small (8.5%) yield of tert-butanol (X) was most likely produced by an E2-type elimination with the strong base (potassium tert-butoxide) abstracting a proton from the cis-olefin (I) with simultaneous departure of methoxide ion (poor leaving group).[93]

$$(2) \quad \underset{VII}{(CH_3)_3C\text{-}O^{\ominus}} + \underset{I}{CH_3OCH{=}CHOCH_3} \longrightarrow \underset{X}{(CH_3)_3C\text{-}OH} + CH_3OC{\equiv}CH + CH_3O^{\ominus}$$

A trace quantity of a low boiling material (possibly methoxyacetylene) was observed as a small peak when the liquid products were subjected to gas chromatographic analysis. However, it was not identified.

tert-Butanol contamination of the potassium tert-butoxide could also explain the presence of small quantities of tert-butanol in the product mixture. Although potassium tert-butoxide was prepared in the absence of tert-butanol using dimethoxyethane as a solvent (Eqn. 3), tert-butanol could form if potassium tert-butoxide initiated an elimination on the solvent as shown in Eqn. 4.[93]

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(93) W. H. Snyder, J. Parascandola, M. Wolfinger, J. Org. Chem., 31, 2037 (1966).

$$(3)\quad 2K + (CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \xrightarrow[\text{Dimethoxy-}\atop\text{ethane}]{} 2KOCH(CH_3)_3$$

$$(4)\quad (CH_3)_3C\text{-}O^{\ominus} + CH_3OCH_2\text{-}CH_2OCH_3 \longrightarrow \underset{X}{(CH_3)_3C\text{-}OH} + CH_2{=}CHOCH_3 + CH_3O^{\ominus}$$

The above series of reactions are known and have been reported.[93]

The total recovery of liquid and solid products was 95%. The liquid fraction (transferred on a high vacuum system) was analyzed by quantitative gas chromatography. The results are shown in Table VI. The solid products (1.7989 g.) were found to contain 14.5 meg. of base. The theoretical yield of solids from reactions (1) and (2), S_N2 and E2-type reactions respectively, was 1.3245 g. containing 13.42 meg. of base (Table VI).

An important result was that an S_N2 type substitution product, methyl tert-butyl ether (VIII), was produced in reasonably high yield from reaction (1). In the potassium tert-butoxide initiated elimination on 1,1,2-trimethoxyethane (III), there was some doubt as to whether methyl tert-butyl ether was produced by direct substitution on III or on the cis- and trans-dimethoxyethylenes (I and II respectively).[61] It appears now that substitution on the olefins is a more likely path. That would explain the low

TABLE VI

Reaction of cis-1,2-Dimethoxyethylene (I) and Potassium tert-Butoxide (VII)

	------Reactants------		------Products------			
Temp. °C	I g. (moles)	VII g. (moles)	t-BuOCH$_3$ [a] g. (moles)	t-BuOH [b] g. (moles)	I [c] g. (moles)	Conversion [d] (XA) (%)
120	5.0325 (0.05188)	1.5032 (0.01342)	0.4784 (0.00544)	0.0849 (0.00115)	3.8474 (0.0437)	49.0

Analysis of Solid Product Residue

Theory:	g.-moles	grams
KOCH$_3$	0.001148	0.08036
KO-t-Bu	0.006837	0.76573
Potassium salt of enolate ion	0.005436	0.47837
	0.013421	1.32446 g.
	= 13.42 meq	

Found: 1.7989 g. (14.5 meq)[e]

a. The methyl tert-butyl ether yield was 40.5% based on potassium tert-butoxide.
b. The tert-butanol yield eas 8.5%.
c. unreacted cis-olefin (I)
d. conversion of limiting reactant, potassium tert-butoxide
e. total basicity by titration with standard 1.00 N HCl

olefin yields. If the amount of tert-butanol is assumed to come from elimination only, the moles of tert-butanol produced would equal the moles of I, II and VIII. This was indeed the case.[61]

If the total amount of both cis and trans-olefins (I and II) that formed, equalled the amount of tert-butanol produced exclusively, a conversion of 44% (S_N2 substitution of potassium tert-butoxide on I and II) would give the total amount of methyl tert-butyl ether formed. In the reaction just considered (Eqn. 1) with potassium tert-butoxide and cis-dimethoxyethylene (I) the conversion to methyl tert-butyl ether was 49% (Table VI). This appeared to be confirming evidence for assigning the substrate undergoing substitution to the cis and trans-olefins (I and II) and not methoxyacetal (III).

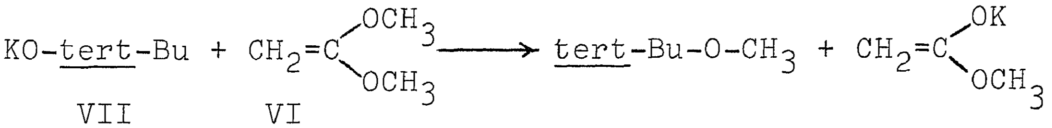
5. The Reaction of Bromoacetal (IV) with Potassium tert-Butoxide

Although the presence of ketene dimethyl acetal (VI) was never observed in the reaction with potassium tert-butoxide (VII) and methoxyacetal (III),[61] it could be argued that VI was formed and underwent substitution with VII producing methyl tert-butyl ether (VIII). If that were the case, VI (a reaction intermediate) would not be observed.

(1) $$\text{KO-}\underline{\text{tert}}\text{-Bu} + CH_3OCH_2\text{-}CH_2(OCH_3)_2 \longrightarrow CH_2{=}C(OCH_3)_2 + \underline{\text{tert}}\text{-BuOH} + KOCH_3$$

VII III VI

VIII

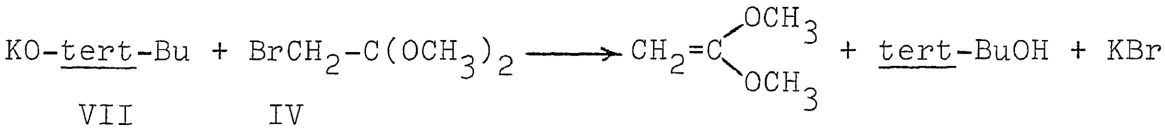
(2) 

$$\text{KO-}\underline{\text{tert}}\text{-Bu} + CH_2{=}C\begin{matrix}\diagup OCH_3\\ \diagdown OCH_3\end{matrix} \longrightarrow \underline{\text{tert}}\text{-Bu-O-}CH_3 + CH_2{=}C\begin{matrix}\diagup OK\\ \diagdown OCH_3\end{matrix}$$

VII VI

To confirm that the substitution product, methyl *tert*-butyl ether (VIII), resulted from nucleophilic attack on *cis*- or *trans*-dimethoxyethylene (I and II) and not from attack on ketene dimethyl acetal (VI), VI was prepared in-situ in a bomb reactor and allowed to sit in the presence of excess potassium *tert*-butoxide at 120°C for 8 hours.

VI

(3) 

$$\text{KO-}\underline{\text{tert}}\text{-Bu} + BrCH_2\text{-}C(OCH_3)_2 \longrightarrow CH_2{=}C\begin{matrix}\diagup OCH_3\\ \diagdown OCH_3\end{matrix} + \underline{\text{tert}}\text{-BuOH} + KBr$$

VII IV

The yield of ketene dimethyl acetal (VI) was 52% (Table VII). No methyl *tert*-butyl (VIII) ether was observed. This was confirmed by gas chromatography using an authentic sample of VIII.

TABLE VII

Reaction of Bromoacetal (IV) with Potassium *tert*-Butoxide (VII)

	Reactants		Solvent	Products			
Temp. °C.	IV g. (moles)	VII g. (moles)	X[a] g. (moles)	VI[b] g. (moles)	X[c] g. (moles)	IV[d] g. (moles)	Yield of VI (%)
120	0.8623 (0.00510)	1.1256 (0.01005)	6.4422 (0.0871)	0.2335 (0.00265)	0.1698 (0.00225)	0.4140 (0.00245)	52

a. *tert*-butanol

b. ketene dimethylacetal

c. *tert*-Butanol was a solvent and also a product of the elimination reaction.

d. unreacted bromoacetal

e. The yield of ketene dimethyl acetal based on limiting reactant, bromoacetal (IV).

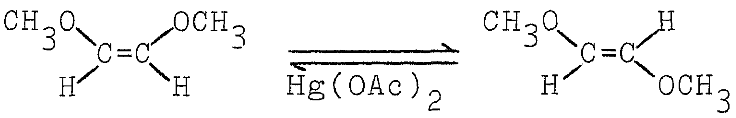
McElvain *et al*. has used this proceedure to produce a series of ketene acetals.[73,75,77] He also observed that ketene dimethyl acetal remains unaffected if heated alone for 6 hours at 200°C.[80]

The above results were expected in light of the work that was done recycling ketene dimethyl acetal through a strong base, $NaO\text{-}C(CH_3)_2\text{-}\phi$, at 175° - 185°C.[77] No substitution or elimination products were observed. It appeared unlikely that a strong base would effect a substitution reaction on ketene dimethyl acetal.

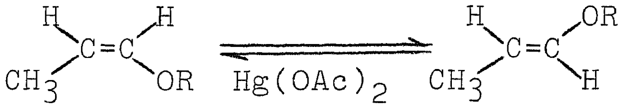
Therefore, if Eqn. 1 did take place, VI would be observed. The absence of VI indicates that Eqn. 2 and Eqn. 1 did not take place. It can be concluded that all the methyl *tert*-butyl ether (VIII) formed resulted from substitution on *cis*- and *trans*-dimethoxyethylene.

6. Catalyst Screening for the *cis*- and *trans*-1,2-Dimethoxyethylene Isomerization

From the results of some early exploratory runs, it appeared that mercuric acetate could be employed as a catalyst for isomerization of *cis*- or *trans*-1,2-dimethoxyethylene.



It has been shown[3] in some preliminary work with propenyl ethers that indeed mercuric acetate did effect a cis-trans interconversion.



Basic catalysts are usually employed for allyl to vinyl ether rearrangements but in these cases at least a 3 carbon system is employed and the prototropic rearrangement is very complicated by cis-trans isomerization leading to contradictory information in the literature about the stereochemistry of the prototropic shift.[94]

There is ample information on the catalysis of unsaturated paraffins leading to 1,2-rearrangements, cis-trans isomerizations and skeletal rearrangements.[94-96] The catalysts employed were palladium and platinum complexes,[96-100]

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(94) L. D. Yanovskaya and K. Shakhidayatov, Russian Chem. Reviews, 39, 10 (1970).

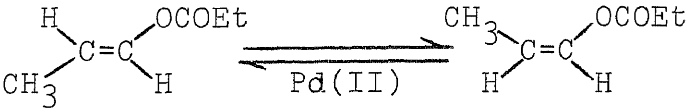
(95) J. Levisalles, Chimie and Industrie (French), Review Article, 526 (1970).

(96) F. R. Hartley, Chem. Reviews, 69, 779 (1969).

(97) W. H. Clement and T. Speidel, Ind. Eng. Chem. Prod. Res. Develop., 9, 220 (1970).

bismuth molybdate,[101] nickel alkyl compounds,[102] rhodium complexes,[103] complexes of the Group VIII elements,[104] and other transition-metal complexes.[105] In a series of papers, Asinger and Fell[106] described these types of isomerizations in detail.

The only closely related isomerization catalyst found in the literature[107] was a Pd(II)-catalyzed *cis-trans* isomerization of enol propinates using $Li_2Pd_2CL_6$.



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(98) N. R. Davies, Rev. *Pure and Appl. Chem.*, *17*, 83 (1967).

(99) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.*, *A*, 190 (1968).

(100) J. Blum and Y. Pickholtz, *Isreal J. Chem.*, *7*, 723 (1969).

(101) P. Batist, P. Van Der Heigden, and G. Schuit, *J. of Catalysis*, *22*, 411 (1971).

(102) J. Thomson and M. C. Baird, *Can. J. Chem.*, *48*, 3443 (1970).

(103) R. Cramer, *J. Am. Chem. Soc.*, *89*, 4621 (1967).

(104) G. C. Bond, *Anna. Rep. Prog. Chem.*, *63*, 27 (1966).

(105) J. E. Lyons, *J. Org. Chem.*, *36*, 2497 (1971).

(106) V. F. Asinger and B. Fell, *Erdol and Kohle. Erdgas. Petrochemie*, *19*, 177-181, 258-264, 345-348, 406-414, 500-502 (1966). (This represents a 5 part series.)

Also, Calderon[92] discussed catalyst systems for olefin disproportionation and *cis*⇄*trans*-isomerization which could have possible value for enol ether isomerizations.

Since no catalysts for the isomerization of enol ethers have been reported it was decided to investigate catalysts similar to mercuric acetate (weak Lewis acids) by a process of catalyst screening.[108]

Elemental iodine caused a rapid exothermic reaction followed by rapid polymerization. Potassium triiodide, however, gave some isomerization and no polymerization. The KI_3 sample which was not oven dried resulted in approximately 3% *trans*-isomer, whereas the oven dried sample gave only 1.7% *trans*-isomer.

Metal salts containing anions of weak acids (i.e. fluorides) were tried as catalysts possibilities. The cations had the highest oxidation state (stronger Lewis acid) thereby allowing complex-formation with the π-bond of the olefins as in the mercuric (II) acetate catalysis. All the inorganic salts tested were anhydrous unless other wise indicated (Table VIII).

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(107) P. H. Henry, *J. Am. Chem. Soc*., **93**, 3547 (1971).

(108) V. R. Choudhary and L. K. Doraiswamy, *J. of Catalysis*, **23**, 54 (1971).

TABLE VIII

Catalyst Screening[a]

	Anion								
Cation	I_3[b]	tert-BuO	OAc	F	Cl	Br	OBz	Salicylate	Succinate
K^+	X								
Al^{+3}[c]		N.R.	N.R.				N.R.		
Hg^{+2}			I	R.P.	R.P.	R.P.	I	I	X
Cu^{+2}			N.R.	N.R.	R.P.			T	
Ag^{+1}			X	P			X		
Fe^{+3}			N.R.	N.R.					
Zn^{+2}				N.R.			N.R.		
Cd^{+2}			N.R.	N.R.					
Pd^{+2}			P		P				

P = Polymerization
R.P. = Rapid exothermic reaction with Polymerization
N.R. = No Reaction (No *trans*-isomer formed)

T = Trace of *trans*-DME formed
I = equilibrium Isomerization of *cis*-*trans*-DME
X = Less than 5% *trans* formed

a. Reaction time was 24-36 hours at 110°C.
b. I_2 gave rapid exothermic polymerization.
c. Al_2O_3 gave no reaction.

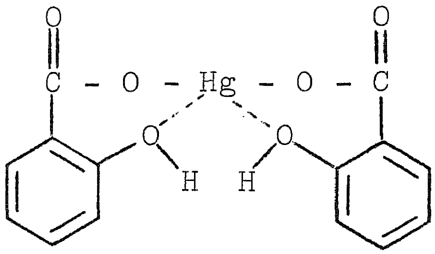
Silver fluroide (AgF) and mercuric fluoride (HgF_2) resulted in polymerization of the olefin. Cupric fluoride (CuF_2), ferric fluoride (FeF_3), zinc fluoride (ZnF_2) and cadmium fluoride (CdF_2) gave no reaction or isomerization. It was thought that Zn^{2+} and Cd^{2+} cations would be good Lewis acids and have less tendency to form the free metal (more negative electrode potential) but this was not the case. They were rejected as catalyst possibilities for this system.

Some chlorides and one bromide were tried but in all cases polymerization of the olefin resulted. This was not surprising since chloride ion is an anion of a stronger acid (HCl as opposed to HF or HOAc). Mercuric chloride ($HgCl_2$) and cupric chloride ($CuCl_2$) and cupric bromide ($CuBr_2$) resulted in rapid exothermic polymerization (hard clear polymer) where as palladium chloride ($PdCl_2$) polymerized slowly at 115°C. After 24 hours the sample containing $PdCl_2$ was put on a high vacuum system. No liquid was transferred over at 0.1 mm. Hg at a 100°C. An IR spectrum of the sample showed disappearance of the C=C stretching frequency at 1691 cm^{-1} for the cis-1,2-dimethoxyethylene. The liquid was viscous and dark brown.

There was no isomerization with regular or basic washed alumina (Al_2O_3) or aluminum tri tert-butoxide ($Al(O\text{-}tert\text{-}Bu)_3$), although the catalytic use of alumina for 1-butene rearrangements[15,16,33,90] and for cis-trans isomerizations[88,90] have been discussed in the literature.

Other acetates were investigated. Basic aluminum diacetate ($Al(OH)OAc_2$), cupric acetate ($Cu(OAc)_2 \cdot H_2O$), ferric acetate ($Fe(OAc)_3$) and cadmium acetate ($Cd(OAc)_2$) were rejected as catalyst possibilities since no trans-isomer was observed. Silver acetate (AgOAc) at 100°C gave small amounts of trans-isomer (3.5%) compared with 20% trans-isomer from mercuric acetate at 100°C. A silver mirror was observed after a few hours at room temperature and at 100°C. Palladium acetate ($Pd(OAc)_2$) caused polymerization. (Similar to palladium chloride).

Anions other than acetate were tried with Hg^{II}. Mercuric salicylate and mercuric benzoate gave results similar to mercuric acetate (approximately 20% trans-isomer at 110°C). Mercuric succinate, however, resulted in only 5% trans-isomer. Cupric salicylate gave trace quantities of the trans-isomer (less than 2%). These three anions were tried since different structural possibilities were available with the cation, Hg^{2+}. In the benzoate example, the anion is from a slightly stronger acid than mercuric acetate (Ka of benzoic acid = 6.3×10^{-5}, Ka of acetic acid = 1.76×10^{-5}). In the mercuric salicylate case, there was the possibility of chelation of the mercuric ion, rendering it less reactive to the double bond. However, it reacted as similar as mercuric acetate.



Likewise, mercuric succinate involved only one anion for the 2^+ oxidation state of mercury.

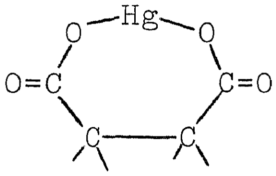
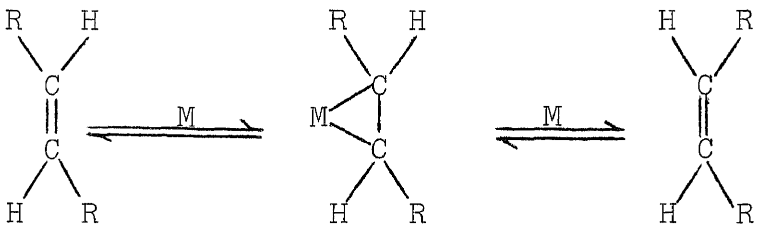
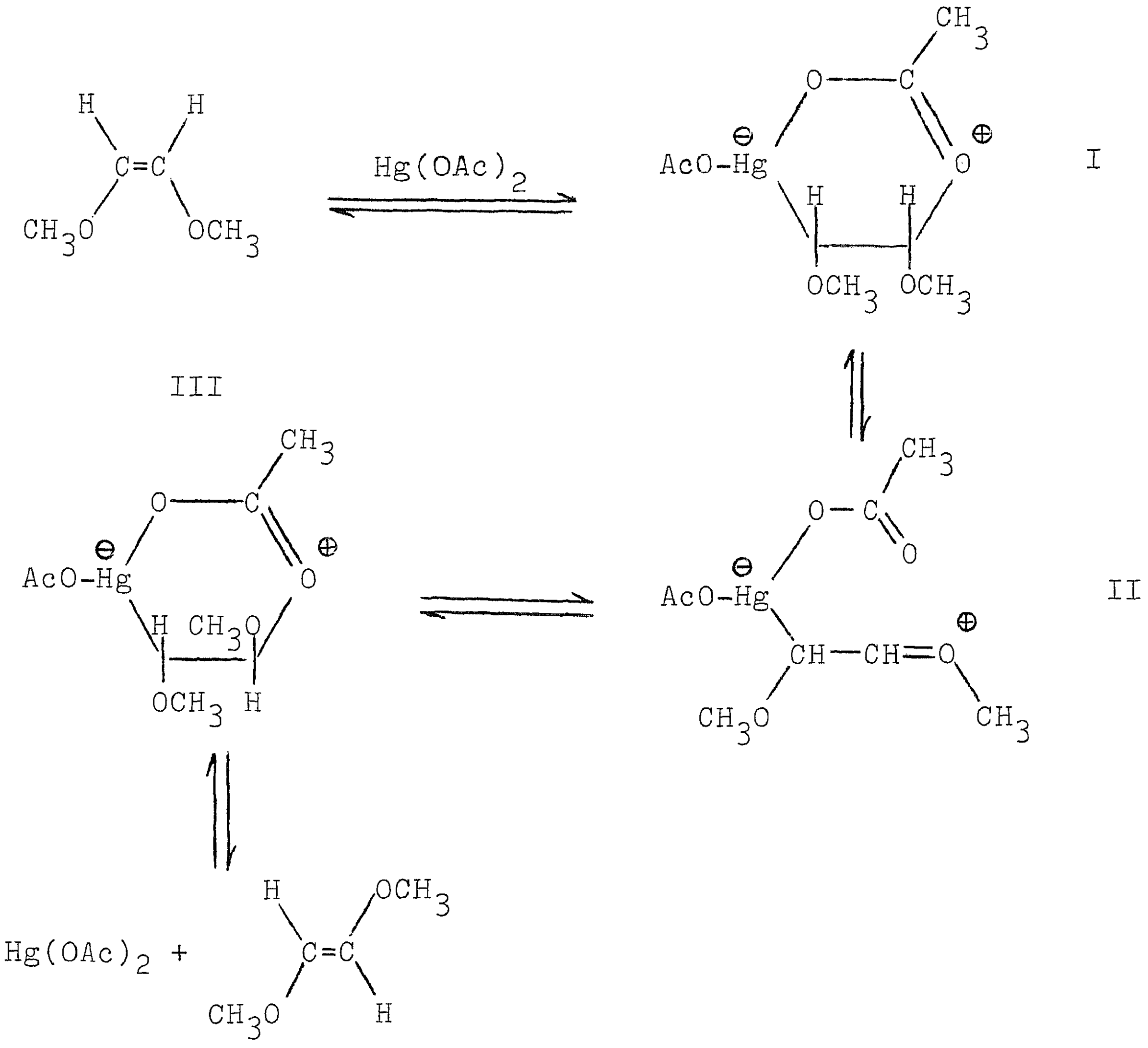


Table VIII summarizes the results from the catalyst screening. A total of 29 different catalysts were investigated. Mercuric acetate was the catalyst of choice since no other catalyst investigated gave better results. Mercuric benzoate and mercuric salicylate could also be used as enol ether catalysts.

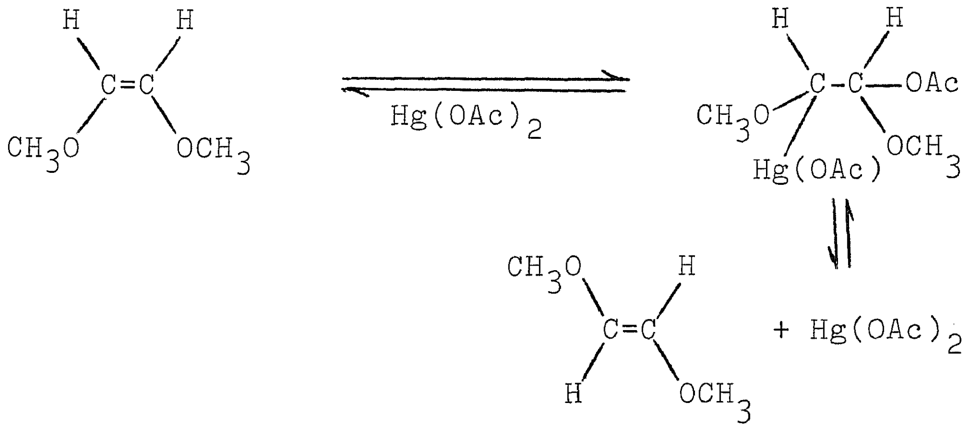
Levisalles[95] proposed a simple, non-detailed mechanism for general cis-trans isomerizations.



A more detailed mechanism was proposed for the reversible addition of mercuric acetate to the double bond.[3] A similar mechanism, as applied to dimethoxyethylene, is presented.

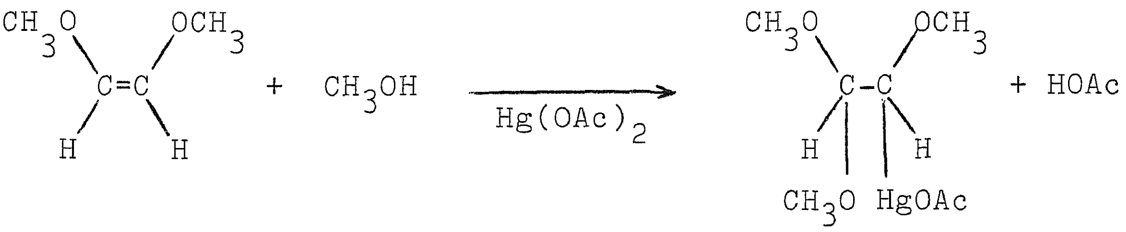


"The reversible interconversion of I and III through the intermediate oxonium ion II, followed by elimination of mercuric salt, explains the cis-trans interconversion."[29] Apparently, mercuric fluoride and mercuric chloride cannot participate in resonance stabilized structures such as I and II and underwent polymerization with this substrate. Free rotation around the carbon-carbon single bond (IV) permits the cis-trans isomerization to take place. Another similar mechanism was postulated.



IV

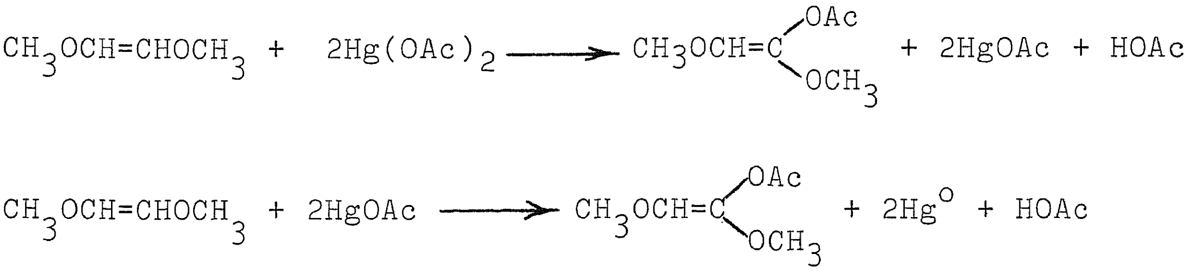
If impurities were present, small amounts of decomposition products and mercury were observed. This could be an indication of competing side reactions. When the cis- and trans-1,2-dimethoxyethylenes were relatively pure, these side reactions were eliminated. Methanol could be a possible impurity since dimethoxyethylene was prepared from the dealcoholation of 1,1,2-trimethoxyethane. The mechanism for the addition of methanol is one of electrophilic addition.[109]



Similarly it can be looked at as a nucleophilic substitution with methanol displacing acetate ion from intermediate IV.

All mercuric salts gave trace amounts of mercury formation, which were of negligable quantity to affect isomerization results. If the temperature exceeded 175°C, these side reactions became objectionable. The isomerization runs were performed from 30° to 175°C. The data was consistant for this range, as will be shown in the next section, for both the liquid and vapor phase.

The reduction to elemental mercury, however, can be explained by the following sequence of reactions.[109]



$$CH_3OCH{=}CHOCH_3 + 2Hg(OAc)_2 \longrightarrow CH_3OCH{=}C\begin{smallmatrix}OAc\\OCH_3\end{smallmatrix} + 2HgOAc + HOAc$$

$$CH_3OCH{=}CHOCH_3 + 2HgOAc \longrightarrow CH_3OCH{=}C\begin{smallmatrix}OAc\\OCH_3\end{smallmatrix} + 2Hg^0 + HOAc$$

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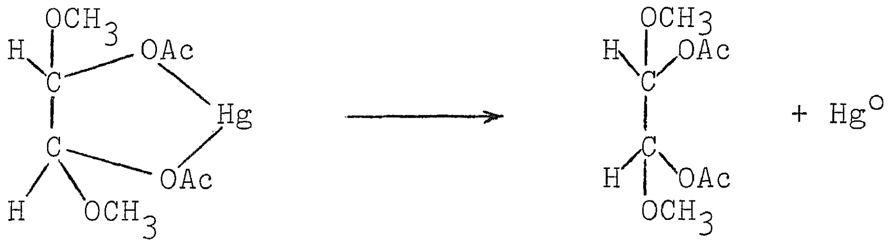
(109) F. L. Fieser and M. Fieser, Reagents for Organic Synthesis, John Wiley and Sons, Inc., New York, 1967 pp. 644-652.

This scheme involves the stepwise reduction of mercury ($Hg^{+2} \rightarrow Hg^{+1} \rightarrow Hg^{0}$) and simultaneous oxidation of the olefin. Fieser[109] observed that reactions similar to the one above require temperatures greater than 150°C.

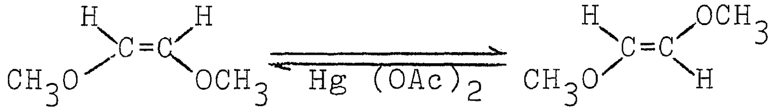
Another mechanism, similar to Hartley's[96] explanation for palladium acetates, is the following:



The diacetoxy derivative would be formed in this case. This was not isolated.

7. The Thermodynamics of the Liquid and Vapor Phase Isomerization for the 1,2-Dimethoxyethylenes

The reaction investigated was the *cis-trans* isomerization of 1,2-dimethoxyethylene (and an enol diether) catalyzed by mercuric acetate.

(1)


In order to establish a basis and definition for equilibrium constants as applied to the above isomerization, a brief introduction to some applicable thermodynamic definitions and underlying assumptions is offered.

For any reaction such as

$$bB + cC \rightleftarrows rR + sS$$

The equilibrium constant is defined as

$$K_a = \frac{a_R{}^r a_S{}^s}{a_B{}^b a_C{}^c}$$

where a_R, a_S, a_B, and a_C are the activities of the products and reactants. The change in free energy is given by

$$\Delta G = \Delta G^o + RT \ln \left(\frac{a_R{}^r a_S{}^s}{a_B{}^b a_C{}^c} \right) \tag{2}$$

where ΔG^o = free energy change of the reaction in the standard state. At equilibrium, $\Delta G = 0$, and

$$\Delta G^o = -RT \ln \left(\frac{a_R{}^r a_S{}^s}{a_B{}^b a_C{}^c} \right) = -RT \ln K_a \tag{3}$$

For gases, this expression can be represented in terms of fugacities.

$$\Delta G^o = -RT \ln \left(\frac{f_R{}^r f_S{}^s}{f_B{}^b f_C{}^c} \right) = -RT \ln K_f \tag{4}$$

The ratio of fugacities of component i in any state compared to its fugacity in the standard state is called the activity (a_i).

$$(a_i)_T = (f_i/f_i)_T$$

When the standard state for a gas is chosen as its ideal state at 1 atm., the fugacity is unity when expressed in atmospheres ($f_i^o = 1$) and the activity of a component gas in a mixture becomes equal to its fugacity expressed in atmospheres.

$$a_i = f_i/f_o = f \qquad \text{and} \qquad K_a = K_f \quad \text{(see eqn. 4)}$$

For ideal gases, the fugacity is equal to the pressure. For mixtures showing ideal gas behavior the activity of each component becomes equal to its partial pressure. At low pressures, real gases exhibit ideal behavior, since $\lim f/P = 1$, as $P \to 0$. This standard state is used in dealing with equilibrium in chemical reactions.[110] For liquids the standard state can also be chosen as the pure component at a pressure of 1 atm.

From eqn. (4), the equilibrium constant can be defined in terms of partial pressures.

$$\Delta G^o = -RT \ln K_p$$

If gas ideality is assumed or if low pressures are involved, $K_p = K_a$.

For gaseous reactions in which there is no change in the number of moles of products and reactants ($\Delta n_g = 0$), $K_c = K_p$. K_c is the equilibrium constant defined in terms of concentration. K_c and K_p are related by $K_p = K_c(RT)^{\Delta n_g}$. Similarly K_y is defined in terms of mole fractions. For isomerization reactions, as in eqn. (1), $\Delta n_g = 0$ and $K_p = K_c = K_y$.

The standard change in Gibbs free energy (ΔG^o) may also be calculated from values of ΔH^o and ΔS^o.[111]

(5) $$\Delta G^o = \Delta H^o - T\Delta S^o$$

Where ΔG^o, ΔH^o, and ΔS^o are the changes in free energy, enthalpy, and entropy, respectively, that accompany the stoichiometric reaction with all reactants and products in their standard states. By use of equations (3) and (5), the equilibrium constant is defined at any given temperature by the van't Hoff equation.

(6) $$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

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(110) O. A. Hougen, K. M. Watson and R. A. Ragatz, Chemical Process Principles - Part II, John Wiley & Sons, Inc. New York, 1964 (pg. 868).

The enthalpy change (heat of isomerization for eqn. 1) is also a function of temperature,

$$\left[\frac{\partial(\Delta H^{o})}{\partial T}\right]_{p} = \Delta C_{p}$$

where ΔC_p is the difference in the heat capacities between the products of reaction and the reactants. This can be integrated to give

$$\Delta H^{o} = \int \Delta C_{p} dt + I$$

where I is a constant of integration.

The heat of reaction at constant pressure (ΔH) is equal to the heat of reaction at constant volume (ΔE) if the pressure-volume changes are small as for liquids and solids.[112]

$$\Delta H = \Delta E + \Delta(Pv)$$

For gases, $$\Delta H = \Delta E + \Delta n_{g}RT$$

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(111) E. A. Moelwyn-Hughes, Physical Chemistry, the Macmillan Co., New York, 1964 (pp. 992-996).

(112) S. H. Maron and C. F. Prutton, Principles of Physical Chemistry, The Macmillan Co., New York, 1958 (pp. 256-350).

and for isomerization reactions similar to eqn. (1), $\Delta ng = 0$ and $\Delta H = \Delta E$.

In general, for isomerization reactions, especially for molecules as similar as cis-trans pairs, the heat capacity changes are usually negligible.[38,47] There have only been a few isomerization studies on similar systems, such as, the dihaloethylenes[43,53,55] and halopropenes[41,56,57,59,113] and in all cases the enthalpy change was taken to be constant in the van't Hoff equation.[51] Olson and Brittain[114] made heat capacity measurements for the dibromoethylenes and found ΔC_p to be zero within the limits of their experimental error. Linearity in the ln K vs 1/T plot is a good indication of the thermodynamic consistancy in ΔH.[115] Over small temperature intervals, ΔH is usually considered temperature independent even if the above considerations aren't applicable (e.g., reactions which produce many complex products, etc.). Similarly, if calculations are made using group contributions from a model paraffin system for ΔC_p changes (products - reactants) for cis-trans pairs,

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(113) H. Kalof and K. Kirchhoff, Tetrahedron Letters, 42, 3861 (1971).

(114) A. R. Olson and F. W. Brittain, J. Am. Chem. Soc., 55, 4063 (1933).

(115) D. F. Eggers, N. W. Gregory, G. D. Halsey, B. S. Rabinovitch, Physical Chemistry, John Wiley & Sons, Inc., New York, 1964, pg. 313.

such as enol ethers, the difference is zero.

For the *cis-trans* isomerization shown in eqn. (1), the equilibrium constant was calculated from the ratio of $|$*trans*-isomer$|$ / $|$*cis*-isomer$|$ for both the liquid and vapor phase. For a detailed description of the experimental procedures see Section 2 and 12 of the Experimental Section.

The results of the isomerization equilibria studies in the liquid phase for the reaction,

$$\text{\underline{cis}-}CH_3OCH{=}CHOCH_3(l) \rightleftharpoons \text{\underline{trans}-}CH_3OCH{=}CHOCH_3(l)$$

are summarized in Table IX. Figure 1 shows the temperature dependence of ln K over the 150° range for the liquid phase isomerization. A least-squares fit gives (see Appendix A)

$$\ln K = \frac{-779.8}{T} + 0.6748$$

from which $\Delta H^{\circ} = 1549 \pm 19$ cal/mole and $\Delta S^{\circ} = 1.34 \pm 0.05$ cal/deg.-mole.

The results of the vapor phase isomerization studies are summarized in Table X. In accord with the van't Hoff equation, ln K is plotted *versus* 1/T in Figure 2 over a 120° range. The least-squares result is

$$\ln K = -727.1/T + 0.8335$$

From this equation, $\Delta H^{\circ} = 1445 \pm 54$ cal/mole and $\Delta S^{\circ} = 1.66 \pm 0.15$ cal/deg.-mole.

TABLE IX

Observed Equilibrium Constants for the Reaction

$$\underline{cis}\text{-}CH_3OCH{=}CHOCH_3\ (l) \xrightleftharpoons[Hg(OAc)_2]{} \underline{trans}\text{-}CH_3OCH{=}CHOCH_3\ (l)$$

Temp, °C [a]	Time hr.	---- Number of Runs ----- Pure cis	Pure trans	Equilibrium Constant, K [b]
30	44	2	1	0.150 ± .004
40	38	3	-	0.162 ± .003
50	40	2	1	0.172 ± .002
60	48	3	-	0.192 ± .003
70	48	3	-	0.202 ± .004
80	36	2	1	0.213 ± .002
90	40	3	-	0.231 ± .007
100	38	2	1	0.246 ± .004
110	38	3	-	0.255 ± .006
120	40	3	-	0.273 ± .008
130	48	3	-	0.282 ± .008
150	36	2	1	0.315 ± .009
175	38	2	1	0.338 ± .009

a. Temperatures were maintained to within ± 0.1°C.

b. All 39 values of the equilibrium constant were used in the least-squares analysis. The values shown here are the mean values.

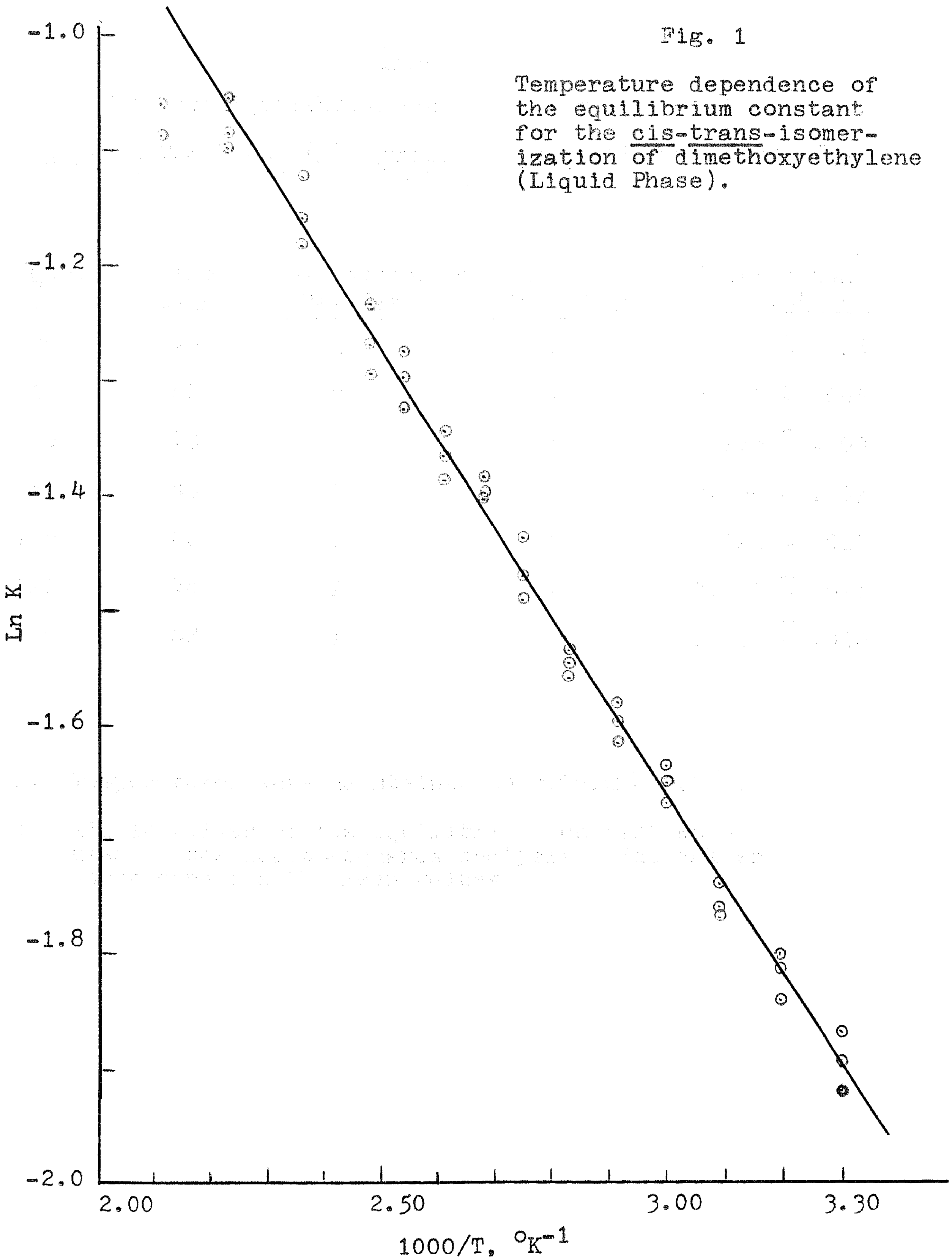


Fig. 1

Temperature dependence of the equilibrium constant for the cis-trans-isomerization of dimethoxyethylene (Liquid Phase).

TABLE X

Observed Equilibrium Constants for the Reaction

$$\underline{\text{cis}}\text{-}CH_3OCH{=}CHOCH_3\ (g) \underset{Hg(OAc)_2}{\rightleftharpoons} \underline{\text{trans}}\text{-}CH_3OCH{=}CHOCH_3\ (g)$$

Temp,[a] °C	Time hr.	---- Number of Runs ----- Pure *cis*	Pure *trans*	Equilibrium Constant, K[b]
30	48	1	1	0.210 ± .008
50	48	2	-	0.239 ± .006
70	40	1	1	0.276 ± .009
80	40	2	-	0.300 ± .007
100	40	1	1	0.322 ± .011
120	44	2	-	0.367 ± .011
150	48	1	1	0.410 ± .010

a. Temperatures were maintained to within ± 0.1°C.

b. All 14 values of the equilibrium constant were used in the least-squares analysis. The values shown here are the mean values.

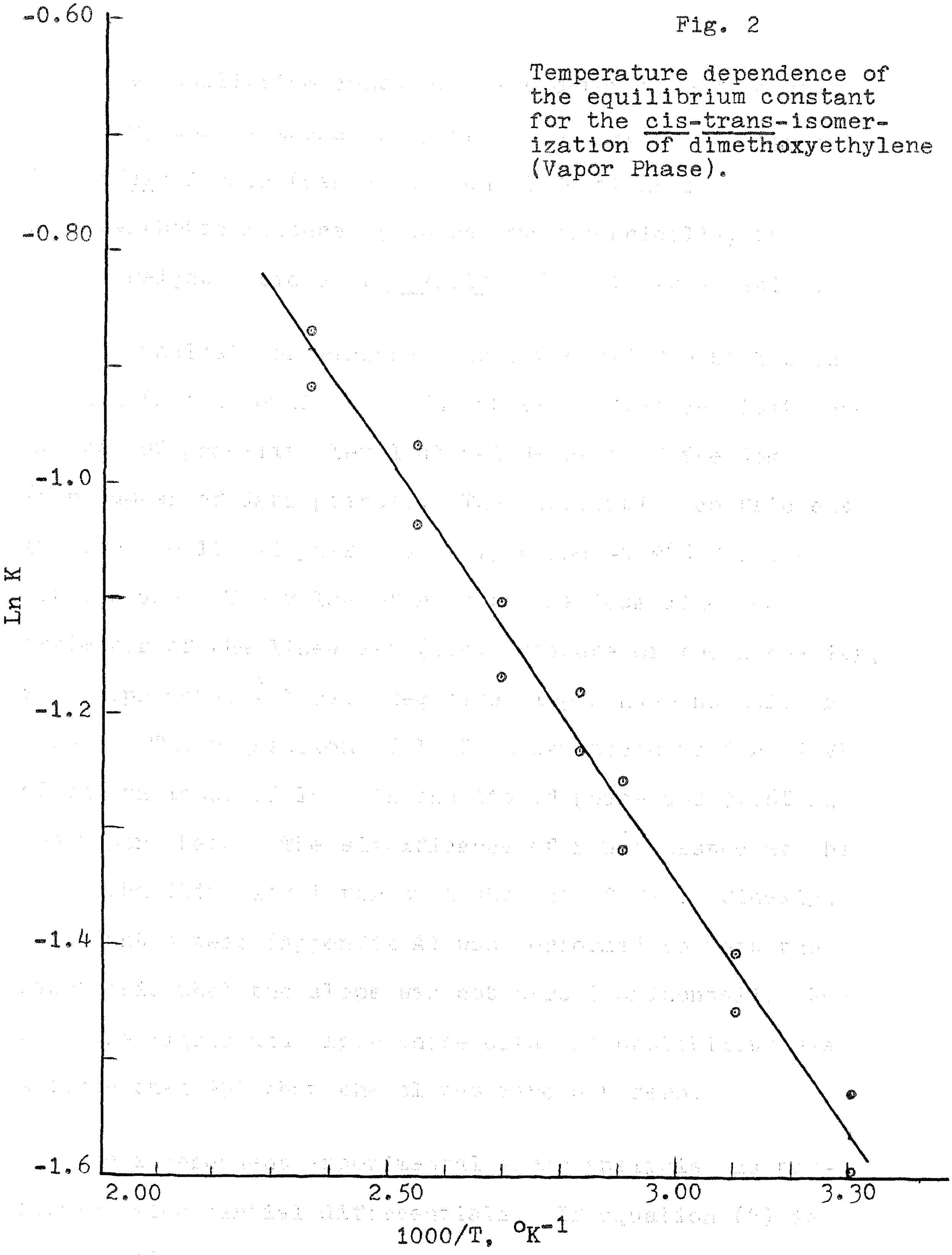


Fig. 2

Temperature dependence of the equilibrium constant for the *cis-trans*-isomerization of dimethoxyethylene (Vapor Phase).

The equilibrium constants were determined from gas chromatograms by measuring peak weight ratios of <u>trans</u>-isomer/<u>cis</u>-isomer (see Experimental Sections 1 and 12). From synthetic mixtures prepared gravimetrically, the actual weight ratio of <u>trans</u>/<u>cis</u> = (1.10) (Area ratio).

An analysis of variance was performed for both sets of data (see Appendix A). The above confidence limits are at the 90% probility level at N-2 degrees of freedom. (N = number of data points). The correlation coefficient (r) for the liquid phase was -0.996 and -0.988 for the vapor phase. The value of r is the maximum likelihood estimator of the linearity (i.e., measure of the linearity, as r approaches ± 1.0). Negative slopes have negative r values. The regression of ln K on 1/T accounts for 99.2% of the variance of ln K in the liquid phase and 97.6% in the vapor phase. The significance of r was tested at the 99% probability level for straightness of fit. Finally, a Student t test (Appendix A) was performed to test the hypothesis that the slope was not zero (horizontal). For both the liquid and vapor phase data the probability was greater than 99% that the slopes were not zero.

An independent experimental error analysis was performed using partial differentials. If equation (6) is rearranged

$$\Delta H = -RT \ln K + T\Delta S$$

and differentiated with respect to temperature at constant ln K, the following expression is obtained.

$$\left(\frac{\partial \Delta H}{\partial T}\right)_{\ln K} = -R \ln K + \Delta S = \frac{\Delta H}{T}$$

Similarly,

$$\left(\frac{\partial \Delta H}{\partial \ln K}\right)_{T} = -RT = \frac{-R(\Delta H)}{\Delta S - R \ln K}$$

The minimum experimental error in ΔH is defined as

$$|\Delta(\Delta H)| = \left(\frac{\partial \Delta H}{\partial T}\right)_{\ln K} \Delta T + \left(\frac{\partial \Delta H}{\partial \ln K}\right)_{T} \Delta \ln K$$

where $|\Delta(\Delta H)|$ is the variation in ΔH due to errors in weighing peaks (reliability of measured K's, temperature deviation, etc.)

Therefore, for the liquid phase (see Appendix B),

$$|\Delta(\Delta H)| = \pm\ 11.2 \text{ cal/mole} = \pm\ 0.011 \text{ Kcal/mole}$$

and

$$|\Delta(\Delta\ S)| = \pm\ 0.026 \text{ cal/deg.-mole}$$

For the vapor phase data

$$|\Delta(\Delta H)| = \pm 26.2 \text{ cal/mole} = 0.026 \text{ Kcal/mole}$$

and

$$|\Delta(\Delta S)| = \pm 0.06 \text{ cal/deg. mole}$$

There was good agreement between the statistical error analysis and the experimental error analysis (Appendix A and B). Below 175°C, side reactions were not extensive. The <u>trans/cis</u> ratio appeared to be a reliable measure of the equilibrium constant. At temperatures above 175°C, there was some indication as to degradation products (lower and higher boiling compounds) as evidenced by gas chromatography. In addition, there was considerable mercury formation above 175°C. Figure 3 is a composite of both liquid and vapor phase equilibrium constants using the mean values of ln K. However, all 54 values of the equilibrium constants were used to obtain the least-squares lines. Figures 1 and 2 show individual liquid and vapor phase equilibrium constants (all values) on an extended ordinate to indicate the scatter in the data.

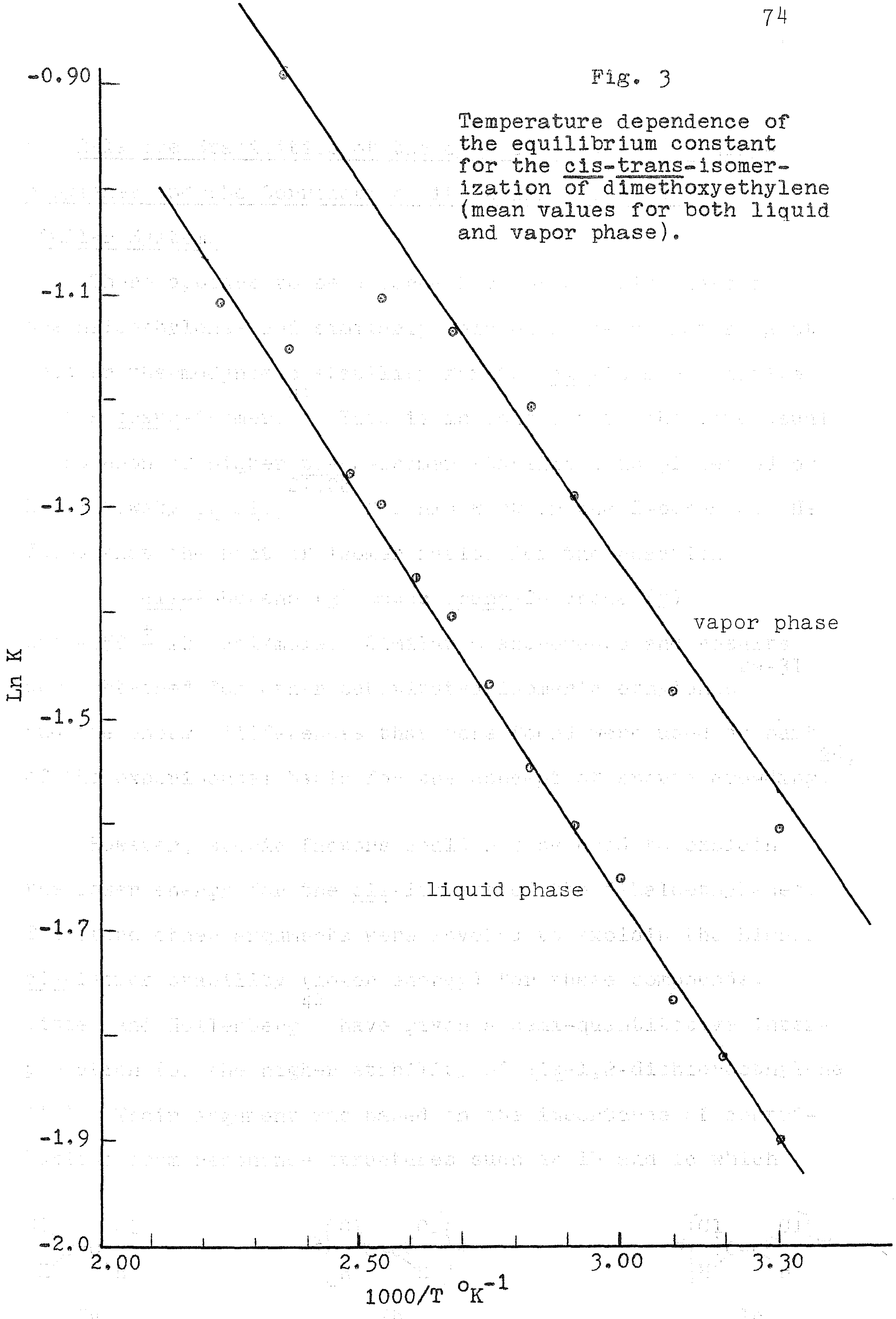


Fig. 3

Temperature dependence of the equilibrium constant for the *cis*-*trans*-isomerization of dimethoxyethylene (mean values for both liquid and vapor phase).

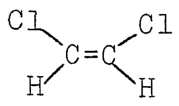
8. Relative Stabilities of the *cis*- and *trans*-Dimethoxyethylenes and the Correlation with Available Data for Similar Systems

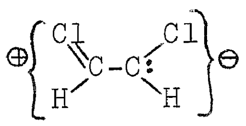
There appears to be a large body of existing data on the haloethylenes and similarly related systems that suggest greater thermodynamic stability for the *cis*-isomer relative to its *trans*-isomer.[47] This is in contrast to the more usual phenomenon of higher *trans*-isomer stability, as pioneered by Kistiakowsky *et al.*,[27,28] for his work on the 2-butenes. He found that the heat of isomerization for the reaction

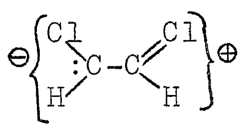
cis-2-butene (g) $\rightleftharpoons$ *trans*-2-butene (g)

was -950 ± 120 cal/mole. Similar measurements and results were obtained for other substituted isomeric ethylenes[29-31] and the energy differences that were found were used as part of the experimental basis for the concept of steric crowding.[26,34]

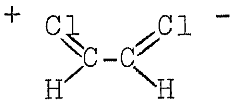
However, steric factors could not be used to explain the lower energy for the *cis*-isomers of the dihaloethylenes. Therefore other arguments were invoked to explain the higher *cis*-isomer stability (lower energy) for these compounds. Pitzer and Hollenberg[44] have given a semi-quantitative interpretation for the higher stability of *cis*-1,2-dichloroethylene (Ia). Their argument was based on the importance of contributions from resonance structures such as Ib and Ic which


Ia


Ib


Ic

were formulated to include the polarity of the carbon-chlorine σ-bond. They concluded that the anomalous stability of the cis-isomer of dichloroethylene was associated with the unlike charges on the chlorine atoms in the resonance structures Ib and Ic. The sizeable negative charge on chlorine has been attributable to d-orbital participation[51] as in Id.



Id

The heats of isomerization for the dihaloethylenes (cis ⇄ trans) have been reported. These include + 0.928 Kcal/mole for HFC=CFH (g),[38,41,47] + 0.780 Kcal/mole for HFC=CClH (g),[47,48] + 0.650 Kcal/mole for HClC=CClH (g),[42,44,47,48] 0.0 - 0.130 Kcal/mole for HBrC=CBrH (g),[38,47,50] + 0.320 Kcal/mole for HBrC=CBrH (l),[47,51] and - 1.550 Kcal/mole for HIC=CIH (l).[53,54] These compounds have a higher stability in the cis-configuration than in the trans-configuration with the exception of diiodoethylene. The shift in stability of the latter is ascribed to the large amount of steric crowding in the cis-isomer.[47] For the gas phase isomerization of diiodoethylene, Furuyama *et al*. found no significant temperature dependence over a 140° range.[55] The liquid phase isomerization results of diiodoethylene are doubtful since the 30° temperature range used was insufficient to accurately determine a small heat of reaction.[47] Similarly, the vapor phase result for dibromoethylene is questionable.[38,47]

There have been a few other studies in which preference for the *cis*-configuration was indicated. They were not thermodynamic stability studies since equilibrium constants were measured at only one temperature.[56] These included: $CH_3CH=CHBr$,[59] $HCl=CHCN$,[57] and some propenyl ethers ($ROCH=CHCH_3$).[1-3] As early as 1924, Craen[58] reported qualitatively the predominance of the *cis*-configuration at equilibrium for 1-chloropropene. Viehe[41] made similar observations for $HFC=CFH$, $CH_3CH=CHI$ and the mixed dihaloethylenes, such as, $HFC=CHI$, etc. More recently, heats of isomerization (*cis* ⇄ *trans*) were obtained for $CH_3CH=CHCl$ (0.700 Kcal/mole)[116] and $CH_3CH=CHCN$ (0.17 Kcal/mole).[60] These compounds were found to be more stable in the *cis*-configuration. It appeared that in these cases the *cis*-isomer was somewhat more stable if there was at least one strongly electronegative atom or group attached to the double bond.

The reaction investigated in the present study was the isomerization of 1,2-dimethoxyethylene shown in Eqn. (1).

$$(1) \qquad \textit{cis}\text{-}CH_3OCH=CHOCH_3 \underset{Hg(OAc)_2}{\rightleftharpoons} \textit{trans}\text{-}CH_3OCH=CHOCH_3$$

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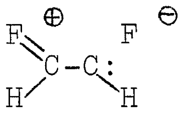
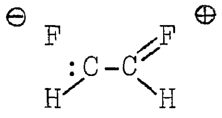
(116) L. A. Shevtsova and P. N. Andreevsku, *Izv. Vyssh. Vcheb. Zaved. Khim. Tekhnol.*, **14** (5), 718 (1971).

In the liquid phase, the experimental heat of isomerization was +1.549 ± 0.019 Kcal/mole and for the vapor phase it was +1.445 ± 0.054 Kcal/mole. Dimethoxyethylene was also more stable in the *cis*-configuration. The dimethoxyethylene case is the first reported example of *cis*-olefin stability for enol ethers. The justification for the *cis*-stability (*cis*-effect) will become apparent when correlated with available data for haloethylenes. Additional arguments will also be advanced.

Craig *et al.*[38,47] have shown that *cis*-1,2-difluoroethylene has a higher stability relative to its *trans*-isomer (0.928 Kcal/mole) than does *cis*-1,2-dichloroethylene (0.650 Kcal/mole). They proposed structures (IIa and IIb) similar to the ones given by Pitzer and Hollenberg (Ib and Ic) for the dichloroethylenes.



IIa



IIb

While d-orbital participation (Id) can be involved in resonance stabilization of the dichloro and dibromoethylenes it is not a necessary condition for *cis*-isomer stabilization as shown by the high stability of *cis*-1,2-difluoroethylene relative to its *trans*-isomer. Pauling[117] has argued that a fluorine atom participates to a greater extent than a chlorine atom in double bond character, because of the availability of 2 p-orbitals. He deduced that the C-F bond has 8 to 19 percent double bond character compared to 3 to 8 percent for C-Cl and C-Br bonds and that multiple bonds with first row elements are more stable than those with heavier atoms. Also, the C-F bond has a larger amount of ionic character (43 percent) than the other carbon-halogen bonds (6 percent or less) which is in the same direction as the electronegativity increase of the halogen series. As the electronegativity of the halogen atoms increase, an increase in the stability of the *cis*-olefin relative to the *trans*-olefin is observed. This is consistent with the structures proposed by Pitzer[44] (Ib and Ic) which take into account the polarity of the carbon-halogen σ-bond. A summary of relative stabilities is given in Table XI which compares the enthalpies of isomerization, temperature ranges, and the range of equilibrium constants for the dimethoxyethylenes, haloethylenes, 1-chloropropene and difluorodiazine. These have been the only compounds observed in which the *cis*-isomer is more thermodynamically stable.

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(117) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 3 rd. edition, 1960, pg. 314.

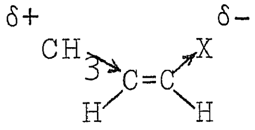
TABLE XI

Thermodynamic Functions for cis-trans-Isomerization of 1,2-Dimethoxyethylene and Related Compounds

Compound	Temp Range °K	ΔH Kcal/mole	Range of K's	Ref.
$CH_3OCH{=}CHOCH_3$ (l)	150	1.549±0.019	0.150-0.338	a
$CH_3OCH{=}CHOCH_3$ (g)	125	1.445±0.054	0.210-0.410	a
FN=NF (g)	75	3.00 ± 0.3	-	45,46,47
HFC=CFH (g)	285	0.928±0.029	0.401-0.582	38,41,47
HFC=CClH (g)	280	0.780±0.020	0.485-0.669	47,48
HClC=CClH (g)	90 & 50	0.650±0.070	0.577-0.683	42,44,47,51
HBrC=CBrH (g)	60	0 ±0.130	-	38,47,50
HBrC=CBrH (l)	100	0.320±0.200	-	47,51
HIC=CIH (l)	30	-1.550± 1.0	0.681-0.792	53,54
HIC=CIH (g)	140	0 ± 0.2	-	47,55
HFC=CFCl (g)	-	0.01 ±0.180	-	47,49
$HClC{=}CHCH_3$ (g)	380	0.700±0.064	0.297-0.600	116
$CH_3CH{=}CHCN$ (g)	260	0.17 ± 0.12	0.640-0.833	60

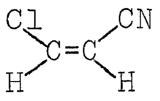
a. Experimental values determined in present investigation.

Crumb[57] rationalized the preference (free energy) for the <u>cis</u>-configuration of the halopropenes, in terms of permanent dipoles which caused a polar attraction between C-H and C-X (X = Br, Cl) bonds (III).



III

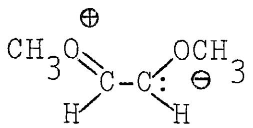
A dipole attraction argument will not serve, however, to explain the effect in the symmetrically substituted haloethylenes or the dimethoxyethylenes. Crumb similarly concluded that the simple dipole hypothesis was not sufficient to explain the preference for the <u>cis</u>-configuration of <u>cis</u>-3-chloroacrylonitrile (IV) since



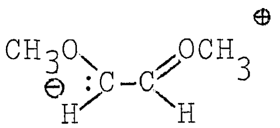
IV

the dipoles of the chloro and nitrile group normally operate in the same direction.[57] The justification for <u>cis</u>-stability of IV was analogous to the resonance arguments used by Pitzer[44] (Ib and Ic) and Craig[38,47] (IIa and IIb) for the dichloro and difluoroethylenes respectively.

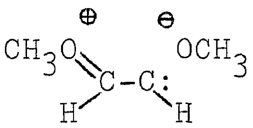
Similar resonance arguments can be applied to the dimethoxyethylenes as shown in Va to Vd.



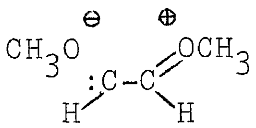
Va



Vb

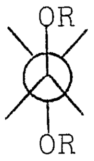


Vc



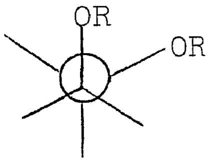
Vd

However, there is evidence that there is more involved than just resonance in explaining the greater preference for the *cis*-configuration in difluoro and dimethoxyethylene[52,118] since the *gauche*-conformers of 1,2-difluoroethane and 1,2-dimethoxyethane[119] (VIa and VIb) are more stable than the *trans*-conformers.



trans

VIa



gauche

VIb

For 1,2-dibromo and 1,2-dichloroethane, the *trans*-conformers are more stable than the gauche-conformers[52] and resonance arguments alone are sufficient to justify the high *cis*-isomer stability for their unsaturated analogs.

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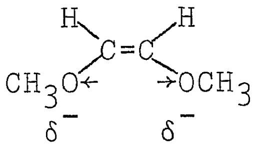
(118) R. J. Abraham and K. Parry, *J. Chem. Soc.*, B, 539 (1970).

(119) T. M. Conner and K. A. McLauchlan, *J. Phys. Chem.*, *69*, 1888 (1965).

The electron delocalization arguments employing resonance structures (I-V) will not suffice to explain the apparent cis-effect (cis-stability) in saturated compounds (VIb). Craig et al.[38,47] concluded that some contribution which lowers the energy of the gauche-conformer relative to the trans-conformer of 1,2-difluoroethane is probably also involved in the relatively lower energy for the cis-isomer of difluoroethylene. This contribution was not forthcoming. He suggested that although the electron delocalization interpretation of the cis-effect (based on resonance) was far from complete, it appeared the most reasonable proposal for the haloethylenes. A weakness in the electron delocalization argument can be found from the heat of isomerization values in Table XI for the haloethylenes. Craig found that the ΔH values for the haloethylenes did not decrease in proportion to the presumed weakening of the p-p overlap between carbon and larger halogen atoms. There was no obvious trend.

In view of the present investigation with the dimethoxyethylene isomerization, adjacency or nearness of two neighboring highly electronegative methoxy groups is apparently important for the high stabilization of the cis-isomer relative to its trans-isomer. As was mentioned earlier, the presence of one strongly electronegative atom or group attached to the double bond (as in a halopropene, propenyl ether, etc.) is important for cis-stability and can be justified.

There is a high electron density around both oxygen atoms in dimethoxyethylene. In the cis-isomer, both methoxy groups repel each other and push electron density either toward the vinyl C-O bond or into the C=C bond (VII).



VII

The resultant charge density around both oxygen atoms is reduced resulting in a higher stability for the cis-isomer.

Similarly, the nearness of two neighboring electronegative methoxy groups in the gauche-conformer (VIb) causes a shift in electron density toward the carbon-carbon single bond. This reduction of charge density around the methoxy groups results in a higher stability for the gauche-conformer (VIb) of 1,2-dimethoxyethane. Similar reasoning can be applied to the very strong C-C bonds in the perfluoroalkanes such as teflon, C_2F_6, etc. where the highly electronegative, neighboring fluorine groups repel each other and push electron density back into the carbon chain. These explanations, not employing resonance but dipole-dipole repulsions with resulting electron density shifts, serve to explain the apparent cis-effect in both the saturated and unsaturated compounds. Nonbonded intramolecular interactions between the methoxy groups are important for cis-olefin stability. Bartell[120] and others[121] have pointed out that although isomerization energies can be small (resulting from small differences between large quantities) intramolecular nonbonded repulsions can be quite significant. The dipole-dipole repulsive forces in the cis-isomer cause a reduction in charge density around the methoxy groups which result in an increase in stability relative to its trans-isomer. A possible explanation for the higher ΔH of isomerization for the dimethoxyethylenes, as compared to the difluoroethylenes (Table XI), rests on the many nonbonded intramolecular interactions possible for the dimethoxyethylenes (i.e., interactions between methoxy groups). This is not the case for the dihaloethylenes since atoms, not groups, are involved.

In support of the above arguments, the NMR spectra for the dimethoxyethylenes[61] and the difluoroethylenes[62,63] indicate that the cis-vinyl protons for both cases absorb at approximately 1 ppm upfield (higher field) than the corresponding trans-isomer. The resolution of the difluoroethylene spectra[62] was ± 0.5 cps (± 0.01 ppm). This indicates that the electron density in the cis-double bonds must be higher than in the *trans*-double bond since the *cis*-vinyl protons absorbed at a higher field than the *trans*-vinyl protons.[63,65] In this situation the *cis*-protons are more effectively shielded than the *trans*-protons. This is an indication of a stronger C=C bond (higher electron density) for the *cis*-isomers of dimethoxy and difluoroethylene, which again supports the high stability for these isomers.

Another indication for the stronger *cis*-C=C bond is the differences in the C=C stretching frequencies for the *cis* and *trans*-isomers.

The average C=C bond stretching frequencies are shown below.

	average stretching frequency, $\bar{\nu}$ ± 1 cm^{-1}
cis-$CH_3OCH=CHOCH_3$	1693
trans-$CH_3OCH=CHOCH_3$	1661
cis-HFC=CFH[39,40]	1714
trans-HFC=CFH[39,40]	1694
cis-HClC=CClH[37,43]	1587
trans-HClC=CClH[37,43]	1576
cis-HFC=CClH[48]	1661
trans-HFC=CClH[48]	1647

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(120) L. S. Bartel, E. J. Jacob, and H. B. Thompson, *J. Chem. Phys.*, *47*, 3736 (1967).

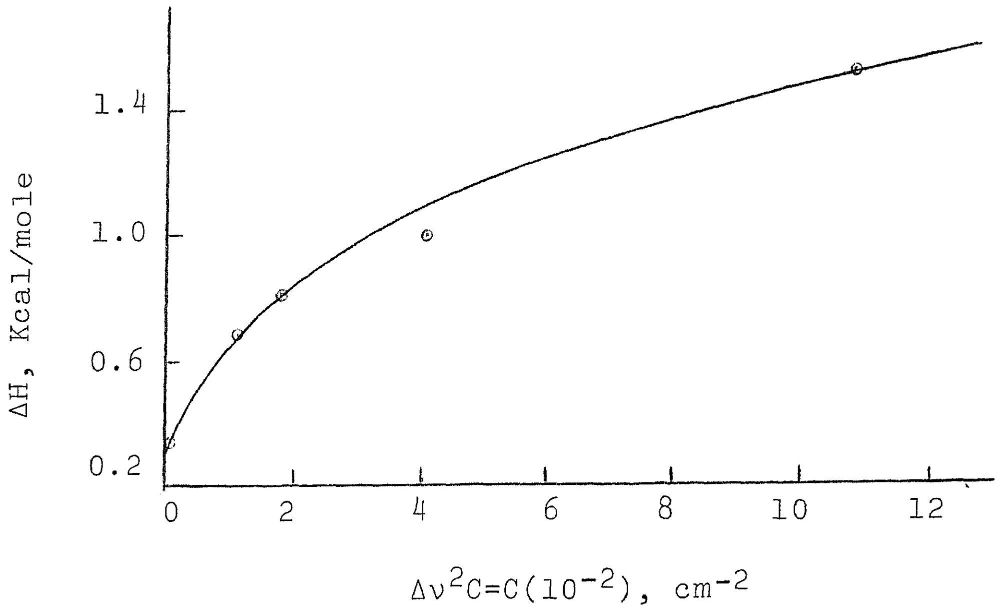
(121) M Cignitti and T. Allen, *J. Chem. Phys.*, *43*, 4472 (1965).

The C=C stretching frequencies for the cis-isomers occur at higher frequencies than the corresponding trans-isomers. This implies that it takes more energy to break the cis-double bond than the trans-double bond, since the force constant (k) is proportional to the frequency squared (see Appendix C).

A correlation was made between the heats of isomerization (cis $\rightleftarrows$ trans) for dimethoxyethylene and some dihaloethylenes (Table XI) and the differences between the C=C stretching frequencies squared for the corresponding cis-and-trans isomers.

	ΔH, Kcal/mole	$\Delta\nu^2$C=C, cm^{-2}
$CH_3OCH{=}CHOCH_3$ (g)	1.445	1089
$C_2H_2F_2$ (g)	0.928	400
C_2H_2ClF (g)	0.780	196
$C_2H_2Cl_2$ (g)	0.650	121
$C_2H_2Br_2$ (g)	0.320	47 0

A smooth curve can be drawn through the data indicating a similar trend between the heats of isomerization and the differences between the C=C stretching frequencies for the cis-and-trans isomers.



Apparently, the preference for the cis-configuration in these compounds (cis-effect) is certainly associated with the stronger C=C bond in the cis-olefins. The major differences in ΔH are apparently associated with the stronger C=C bond for the cis-olefin. However, the fact that the correlation is non-linear suggests that not all of the ΔH differences reside in the differences in double bond strength. In the dihaloethylenes for example, smaller changes in the C-X and C-H bond strength are also involved. A tabulation of all the bond strengths (based on stretching frequency data) for the haloethylenes and the dimethoxyethylenes are given in Appendix C.

Some additional data found for the dimethoxyethylenes can be used to explain a few shortcomings in the literature. In the dihaloethylene series, heats of isomerization were determined for one phase only,[47] usually the vapor phase due to the high vapor pressures of the compounds studied, etc. If the stability of the *cis*-isomer relative to the *trans*-isomer was higher in the vapor phase, it was *inferred* that the liquid phase *cis*-isomer stability would be even greater.[47,52] This is usually the case, since according to Onsager's[122] theory of dielectrics, the polar *cis*-isomer should have lower potential energy in the liquid than in the gas, while the nonpolar *trans*-isomer should not suffer a change in potential energy on going from the gas to liquid. This is obvious when one considers that the liquid state has much more of an effect on a polar structure than on a non-polar structure due to the close proximity of molecules. These are qualitative judgements however. For dimethoxyethylene, the heats of isomerization were determined for both the liquid phase (1.55 ± 0.019 Kcal/mole) and the vapor phase (1.45 ± 0.054 Kcal/mole). This was an experimental indication that the *cis*-olefin was slightly more stable in the liquid phase than in the vapor phase. This result is significant at the 90% probability level (see Appendix A).

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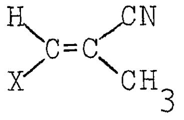
(122) L. Onsager, *J. Am. Chem. Soc.*, *58*, 1486 (1936).

(123) W. G. Dauben and K. S. Pitzer, *Steric Effects in Organic Chemistry*, Edited by M. Newman, John Wiley & Sons, Inc., New York, 1965, pg. 58.

The entropy change (cis $\rightleftarrows$ trans) was +1.34 ± 0.05 e.u./mole for the liquid phase and +1.66 ± 0.15 e.u./mole for the vapor phase. The positive value for the entropy change (higher entropy for the trans-isomer) indicated that the trans-isomer had a larger measure of randomness associated with it for both the vapor and liquid phase. This indicated that internal rotation (free rotation around the CH_3-O bond) occurred more freely for the trans-isomer.[60,123] This occurrence of free rotation was even more likely in the vapor phase than in the liquid phase (larger ΔS^o), as expected.

A similar argument can be proposed for the Group VIa series as was proposed earlier for the dihaloethylene series (Group VIIa) on the basis of electronegativity differences. One observed an increase in stability of the cis-olefin relative to the trans-isomer as the electronegativity of the halogen atom increased (Table XI). In going down the Group VIa series, a similar trend is observed. This is evidenced by the isomerization of the 3-substituted methacrylonitriles.[56] The cis-configuration is defined as,



since the methyl group has a larger steric requirement than the nitrile group. When X = CH_3O, 78% of the cis-isomer was found at equilibrium and when X = C_2H_5S, 68% of the cis-isomer was found. These results are consistent with the halogen series.

In addition, stretching frequencies for the haloethylenes[37,39,40,43] and dimethoxyethylene were used to predict heats of atomization for the respective compounds. This was used to calculate heats of isomerization. The method used is outlined in Appendix C along with a discussion of the applicable error treatments. The stretching frequencies for the haloethylenes are also listed in Appendix C. It suggests that the calculations may be indicative of the same trend as found experimentally for the heats of isomerization (Table XI). However, because of the large uncertainties in the calculated heats of isomerization, comparisons can not be made.

	ΔH,Kcal/mole(exp.)	ΔH,Kcal/mole(calc.)
$CH_3OCH{=}CHOCH_3$ (g)	1.445 ± 0.054	2.04 ± 2.9
HFC=CFH (g)	0.928 ± 0.029	1.10 ± 1.4
HClC=CClH (g)	0.65 ± 0.07	0.73 ± 1.6

In summary, the arguments presented above appear to show ample evidence for the preference of the cis-configuration of dimethoxyethylene. Although electron delocalization arguments could have been advanced, as was discussed earlier for the haloethylenes, this did not take into account the high stability of the saturated *gauche*-analogs. Explanations employing dipole-dipole repulsions between electronegative groups with resulting electron density shifts served to explain the apparent *cis*-effect for both the unsaturated and saturated compounds. The nonbonded intramolecular interactions between the methoxy groups resulted in a stronger C=C bond for the *cis*-isomer as evidenced by IR, NMR, etc. The stronger double bond of the *cis*-isomer resulted in an increase in stability of the *cis*-isomer relative to the *trans*-isomer. Finally a correlation was made for the heats of isomerization and the corresponding differences between the C=C stretching frequencies ($\Delta\nu C=C$) for the respective *cis*-and-*trans* isomers. A trend was obtained which indicated that the $\Delta\nu C=C$ values were also reflected in the corresponding energies of isomerization.

It is now evident that the major product (*cis*-dimethoxyethylene) obtained from the elimination reactions (dealcoholation) on the substrate, 1,1,2-trimethoxyethane, yielded the thermodynamically more stable isomer. This was found to be the case for the pyrolysis over alumina and for the base-initiated elimination using potassium *tert*-butoxide.[61,124]

In each of the above examples, the isomer obtained in higher yield was the more stable isomer.

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(124) W. H. Snyder and J. Waldron, Paper presented at 154 th. National Meeting of the American Chemical Society, Sept., 1967, Chicago, Ill.

EXPERIMENTAL

1. General Proceedures

Infrared spectra were obtained (with sodium chloride cells) in CCl_4 solvent (1% solution), neat (between sodium chloride disks) or in the gas phase using a 10 cm. gas cell (cesium iodide windows) at a pressure of 8 torr. The spectra were obtained on a Perkin-Elmer grating spectrophotomer (Model 457). A normal slit width and medium or slow scan speeds were employed. A polystyrene spectrum was used to check the wavelength accuracy. Raman spectra were obtained on a Beckman Model 700 Laser Raman Spectrometer which employed a He-Ne laser.[125]

Routine evaporation of solvents was carried out using a water or oil bath by means of a rotary evaporating apparatus (Rinco-Roto·Vap) connected to either a water aspirator or connected directly to a vacuum pump depending on the particular situation.

All gas chromatograms were run on a Varian 700-A unit using a 10 ft. 1/4 inch analytical column containing 25% THEED (tetrahydroxyethyl ethylene diamine) on chromosorb W.

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(125) The Raman spectra were obtained with the cooperation of Beckman personnel at Beckman Labs, Springfield, New Jersey.

The helium flow rate was maintained at 115 to 120 ml./min. A detector filament current of 150 milliamperes was used at a detector temperature of 210°C. The column oven temperature was maintained at 120°C or 100°C. The injection oven temperature was 140°C. Injection quantities were between 1.5 and 2.0 microliters for liquids with the voltage attenuator (sensitivity) set at 4X so that components could be kept on the recorder chart.

To measure reaction product distributions, for the dealcohoation of methoxyacetal, quantitative vapor phase chromatography (vpc) techniques were employed. A standard was chosen which was always present in high yield as a reaction product. Methanol was chosen as the standard since methanol, methoxyacetal, and the cis- and trans-dimethoxyethylenes were present in the final reaction mixture. This is analogous to the method of internal standards, except that methanol was not weighed in as a standard. A limitation of this technique is the calculation of absolute quantities of reaction products if side reactions occur to an appreciable extent. This was not the case since only small amounts of water formed from the pyrolysis reaction in addition to the 4 major components of the product mixture. The water was removed prior to analysis with calcium hydride. Trace amounts of a low boiler (degradation product) were formed in negligable quantities and did not alter the product distribution.

Samples were prepared with known weight ratios with respect to methanol. Although special attention was made to prepare standards with similar weight ratios as they appeared in the actual reaction product ratios, an entire range was prepared from 0 to 100%, for each sample. From this data, a straight line was drawn correlating vpc area ratios with known weight ratios. The actual weight percent of the reaction products were calculated from these graphs. A synthetic mixture was made consisting of the same distribution as found for one of the dealcoholation runs. The detector sensitivity was identical. The standards were rerun each time a reaction sample was analyzed. The equations found were:

wt. ratio of methoxyacetal/methanol = (1.95) (Area ratio)
wt. ratio of *cis*-DME/methanol = (1.60) (Area ratio)
wt. ratio of *trans*-DME/methanol = (1.76) (Area ratio).

A similar correlation was done for the *cis*- and *trans*-dimethoxyethylenes.

wt. ratio of *trans* DME/*cis*-DME = (1.10) (Area ratio)

Quantitative peaks estimation was made by cutting and weighing the peaks (4 significant figures) or by measuring the peak areas (multiplying the base at one half the height by the height of the peak). The results were within a few percent of each other since all the peaks were Gaussian-shaped and were separated. Regular triangulation or planimeter methods are 2 to 3% more in error than the above methods used.[126]

Routine distillations and vacuum distillations were performed on a 40 cm. vacuum jacketed column using 1/8 inch glass, single-turn helices. A Todd column (a semi-micro distillation apparatus) was employed when more efficient distillation conditions were needed. A metal spiral band (5 mm. I. D. x 90 cm. length) was used in the Todd column when the sample was small (less than 100 ml.) since the column hold-up was negligable (1-2 ml.). A glass-helices (4 mm.) packed column (12 mm. I. D. with vacuum jacket x 90 cm.) was employed when larger samples were distilled.

The distillations were monitored by qualitative gas chromatography. When a distillate fraction assayed greater than 99% purity it was collected as the main cut (e.g., the cis- and trans-dimethoxyethylenes were purified in this manner.).

The constant temperature baths used throughout this work were maintained to within ± 0.1°C. A water bath was used for isomerization studies from 30°C to 60°C. A small

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(126) Varian Aerograph Instrument Nomagraph, 1971.

oil layer was used on top of the water to prevent evaporation. A solid state thermoregulator with thermistor probe was used to maintain constant temperature via control of the heaters. A Fisher Hi-Temp oil bath was used for temperature ranges of 70°C to 200°C. Dow silicone fluid was used for the heating medium. The oil had a vapor pressure of 0.01 mm. Hg at 200°C and could be used to 300°C before smoking. The oil bath had its own internal heater, but an additional Fisher immersion heater (with thermostat removed) was used as a second heater for finer temperature control. This heater was controlled by the thermoregulator-thermistor. Sufficient stirring in both baths allowed temperatures to be controlled to within ± 0.1°C.

The thermometer employed had ranges of 0° to 99° and 99° to 200° in tenth degree intervals. Both thermometers were checked and calibrated against N.B.S. Standard Thermometers.

Throughout most of this work, precautions were taken to ensure dryness in most operations, since water and traces of acid could be deleterious to the types of compounds sought after (vinyl ethers, ketene acetals, etc.) Nitrogen was used in all synthetic operations (usually in low flow-rates) when reactions were taking place or as a blanket in stored reaction mixtures. All glassware was base-washed with sodium hydroxide or sodium carbonate in any reaction set-up. Reaction intermediates or solvents, such as, methoxyacetal or dimethoxyethane were stored over freshly pressed sodium ribbon.

Ether reactants and solvents such as 1,1,2-trimethoxyethane and 1,2-dimethoxyethane were tested for peroxides before distillation purification or before their use in general reactions to prevent possible explosive hazards due to peroxide formations. The ether compounds were treated with potassium hydroxide and potassium iodide (5% by wt. of solvent) and distilled. This procedure demonstrates the presence of peroxides (yellow-brown color) and simultaneously destroys them.

2. General Description of Liquid and Vapor Transfer Procedures for Liquid and Vapor Phase Isomerization.

For the catalyst screening work and most of the routine liquid phase isomerization runs, 2 ml. ampules were employed. The ampules were tared on a Saritorius balance and small amounts of catalyst were added (10% - 20%). The *cis*-1,2-dimethoxyethylene was transferred using a 1 ml. syringe. If the *trans*-isomer was used, only 0.3 to 0.5 ml. were used since this isomer was available in much smaller supply. The quantities were weighed to within 0.1 mg. The filled ampules were temporarily capped with a rubber serum cap, cooled down to -60°C, and sealed with an oxygen-methane torch.

The sealed ampules were placed in a constant temperature bath and allowed to reach equilibrium (36 - 48 hours). Equilibrium was approached with both the pure *cis* and *trans*-isomer. After 36 - 48 hours, identical *trans*/*cis* ratios were obtained. For routine catalyst screening, the ampules were heated at 110°C for 24 - 36 hours. After cooling to -60°C, the ampules were opened and the contents placed in a small standard tapered flask maintained at -60°C. The flask was put on a leg of the vacuum system and the contents were transferred free of catalyst under vacuum (less than 0.1 mm. Hg) to a prevacuated, cooled receiver. The liquid was analyzed by quantitative gas chromatography. Injection samples of 1.5 microliters were used.

The techniques for the vapor-phase runs were similar but more complex on a physical handling and transferring basis since a vapor is harder to transfer than a gas. One definition of a gas is a substance above its critical temperature. In this work, the vapor (DME) was used which made transferring more difficult. A given quantity of a true gas will occupy a certain volume at a certain pressure. To transfer a gas is a relatively simple procedure at atmospheric pressure, whereas, a vapor must be transferred under vacuum (at very low pressures so that the boiling point is below room temperature). At these low pressures, the occupied volume is very large for a relatively small quantity of vapor. Two different procedures were found which worked very well and which gave results within experimental error.

The vapor phase isomerization runs were done in a 500 ml., round bottom, standard tapered flask. The catalyst (mercuric acetate) was dissolved in benzene and added to the flask which contained 4 mm. unglazed porcelin berl saddles. The solvent was removed by a rotary evaporating apparatus.

The dimethoxyethylene (DME) was added to the flask by two techniques. The first involved the evacuation of the reaction flask down to a pressure of less than 0.1 mm. Hg on a leg of the vacuum system. The DME was cooled down to -60^{o}C in a small micro, standard tapered flask (25 ml.) and also evacuated to 0.1 mm. Hg. The main leg of the vacuum system was closed off to the pump at this point. The DME was then allowed to warm up to room temperature and simultaneously expanded into the reaction flask which was also under vacuum. The pressure, measured by an open-end mercury manometer, equilibriated at the vapor pressure of DME at room temperature (30 mm. Hg). The stop cock on the reaction flask was closed and the flask was taken off the vacuum system. It was then immersed in a constant temperature bath and allowed to equilibriate. After the isomerization was complete (36 - 48 hours), the flask was brought up to atmospheric pressure with nitrogen. The vapor was analyzed by gas chromatography using a 10 ml. gas syringe. Aliquots were taken through a serum cap in the reaction flask.

Another technique for the vapor phase, employed a small liquid sample of DME (0.5 to 0.75 ml.) found from elementary PV = nRT relationships. It was found that at temperatures greater than 70° to 80°C, a 500 ml. flask full of DME vapor would be produced from approximately 0.5 ml. of DME liquid. Again, mercuric acetate was deposited on a support as in the above procedure, and approximately 0.5 ml. of liquid DME was introduced into the flask. The flask was cooled down to -40°C and evacuated on the vacuum system. The main leg to the system and the stop cock on the flask was shut off, and the reaction flask removed from the vacuum system. It was placed in a constant temperature bath and allowed to reach equilibrium. As soon as the flask was heated the small liquid sample vaporized. After equilibrium was attained, the flask assembly was transferred to the vacuum system which already had a small 25 ml. flask pre-evacuated to less than 0.1 mm. Hg in a cold bath at -60°C. The vapor in the reaction flask was transferred directly on the vacuum system and condensed into the receiver. The liquid was analyzed by quantitative gas chromatography using 1.5 micro-liter injection samples.

3. Preparation of Sodium Methoxide

150 g. (6.51 g.-atoms) of sodium were added slowly over a 2 hour period to 1420 ml. of absolute methanol placed in a 5 liter 3-necked round bottom flask fitted with a stirrer, large Friedrich condenser, and nitrogen inlet. A slow stream of nitrogen was maintained throughout the addition. A cold trap was used after the reflux condenser to condense any entrained methanol vapors. The sodium was added slowly at first until boiling started, then at a rate to maintain a steady state reflux of methanol. A nitrogen blanket was kept over the solution until ready for use.

A 5:1 molar excess of methanol to sodium methoxide was used which was less than the 11:1 molar excess used by McElvain[69] for the sodium ethoxide preparation. Since sodium ethoxide is less soluble in ethanol than sodium methoxide is in methanol, smaller ratios of MeOH/MeONa were possible.

The sodium was cut and weighed into a tared beaker containing paraffin oil. It could be stored in this condition prior to addition to the reaction flask. The sodium was wiped free of oil with paper towels before addition to methanol. Paraffin oil was used to prevent any possible contamination since some of the desired products in this work have boiling points between 95° to 126°C.

4. Purification of Bromoacetaldehyde Dimethyl Acetal (IV)

The bromoacetal (IV), as purchased from Chemical Procurement Labs in N.Y.C., contained many impurities. It was analyzed by gas chromotography and showed approximately a 50 - 60% purity. When the compound was vacuum distilled the presence of low boilers in the mixture prevented evacuation below 40 mm. Hg. Large quantities of methyl acetate distilled over at 23°C/100 mm. Hg. It appeared that this was the reaction mixture and not pure bromoacetal since methyl acetate is a product of the reaction (see page 24).

Two kg. of crude bromoacetal (dark yellow in color) were washed in 2 liters of ice-water in a 4 liter beaker. The organic layer was separated and washed in a saturated solution of sodium bicarbonate with constant stirring to remove any traces of acidity (from HBr, etc.). The heavier organic layer was again separated, using a large separatory funnel, and rewashed in 2 liters of cold distilled water. The organic layer was finally separated and vacuum distilled in a 2000 ml. flask through a 40 cm. jacketed distillation column containing 1/8" glass, single turn helices. The reflux ratio was 10:1.

The distillate was clear and had a boiling point of 49.5°C at 18 mm. Hg. The known b.p. is 48 - 51°C/18 mm. Hg.[72] The pure bromoacetal (1150 g.) was recovered (55%) and dried with 34 g. $CaCl_2$ (5 g. $CaCl_2$ per mole of bromoacetal).

5. Synthesis of 1,1,2-Trimethoxyethane (III)

A solution of sodium methoxide (58°C), prepared by the reaction of 150 g. (6.51 g.-atoms) of sodium with 1120 g. of absolute methanol (1420 ml.), was placed under nitrogen in a 3-necked, 5-liter round bottomed flask fitted with stirrer, Friedrich condenser and a Claisen adapter. The Claisen adapter was fitted with a thermometer (0 - 200°C) and a large 500 ml. addition funnel. The addition funnel had a gas tube as a side arm so that nitrogen could be introduced at the top of the funnel using a gas inlet tube which obviated the need for a stopper. To this solution, 957 g. (5.66 g.-moles) of bromoacetaldehyde dimethyl acetal (IV) was added over a period of 1 hour.

The temperature of the reaction mixture after addition was complete was 48°C. The reaction was <u>not</u> noticeably exothermic. A slow stream of nitrogen, measured by a nitrogen exit bubbler (1 - 2 bubble/sec.), was passed over the mixture while it was heated under reflux for

48 hours at 82°C. The nitrogen rate was kept low to prevent entrainment; it was used mainly as a nitrogen blanket to prevent moisture or air from contaminating the sodium methoxide. The condenser was followed by a cold trap receiver in chilled isopropanol (-40°C) to condense vapors due to nitrogen entrainment. A drying tube, containing indicating Drierite was placed after the cold trap. All the joints in the above apparatus were secured with appropriate tension hooks.

The reaction mixture was cooled down to 25°C with an ice bath and allowed to stand 4 - 5 days under a nitrogen blanket before it was worked-up. The precipitated sodium bromide was filtered off through Whatman 90 (24 cm.) filter paper and dissolved in 750 ml. of distilled water. It was stirred for 1 - 2 hours. The theoretical yield of sodium bromide was 582 grams and the solubility at 0°C is 80 g./ 100 ml., therefore 750 ml. water was approximately 100 ml. in excess of the amount necessary to dissolve all the sodium bromide formed. The sodium bromide solution was saved for ether extraction. The filtered reaction mixture was distilled from a 3-liter flask to remove methanol. The reflux ratio was 1:1 (take-off rate of methanol was 3 ml./min.) until the head temperature reached approximately 70°C (most of the methanol was removed).

As the distillation proceeded, sodium bromide continued to precipitate out. All the sodium bromide that formed as the distillation progressed was saved and dissolved in the same water used initially for the extraction work-up. A total of 550 g. of sodium bromide was collected which accounted for a 95% conversion of bromoacetal (limiting reagent) based on the total amount of sodium bromide formed. The sodium bromide solution was extracted with a 1-liter continuous ether extraction apparatus for 5 to 7 days. N.F. extraction grade diethyl ether was used. The ether vapors were never more than 1/3 into the reflux condenser, since the condenser was of a high efficiency, non-flooding design especially made for the apparatus.

When all the methanol was distilled (R = 1:1) from the main reaction mixture, the reflux ratio was changed to 10:1 until the head temperature reached 108° - 110°C. This was the boiling point of the major side product, the trimethyl orthoacetate (V). At this point, the reaction mixture was transferred to the Todd column to affect a more efficient separation. A reflux ratio of 50:1 was used until all of the orthoester (b.p. 109°C) was removed. The cut (30 g.) from 110°C to 125°C (half orthoester - half methoxyacetal) was saved for further purification with the ether extract work-up. When the distillate temperature reached 125°C it was assayed by gas chromatography until the purity obtained was greater than 99%. Since all of the orthoester had been removed, the reflux ratio was adjusted back down to 10:1. A total of 180 g. of pure methoxyacetal distilled over (b.p. 126.4°C). The distillation data is summarized in Table XII.

The ether extract was distilled off at a reflux ratio of 1:1 until the diethyl ether (b.p. 35°C) and the methanol (b.p. 65°C) were removed. The reflux ratio was changed to 5:1 after the methanol was removed. A cut was obtained from 108°C - 125°C (50 g.) consisting of the methoxyacetal and the orthoester in a 70:30 ratio respectively. The main fraction (b.p. 126°C) consisted of pure methoxyacetal (115 g.). It appeared that pure methoxyacetal occluded preferentially to the sodium bromide precipitate to the exclusion of the orthoester since the sodium bromide/water - ether extraction gave almost exclusively pure methoxyacetal (150 g.) with only a slight amount of the orthoester (15 g.).

Another run was performed reversing the mode of addition. The apparatus was essentially the same as described above. To 1120 g. of methanol (1450 ml.), 156 g. (6.81 g.-atoms) of sodium were added. This solution was placed in an addition funnel and added slowly over a 6 hour period to 1150 g. (6.81 g.-atoms) of bromoacetal (IV) in 1000 ml. of methanol. It was allowed to reflux gently for 48 hours at a pot temperature of 73°C.

TABLE XII

Methoxyacetal Distillation on Todd Column[a]

Reflux Ratio	Pot Temp.	Bottom Column Heater, °C	Top Column Heater, °C	Distillate Temp., °C
50:1	122	120	110	109[b]
50:1	130	128	120	110 - 125[c]
10:1	140	130	128	126.2[d]

a. Todd column dimensions: 12 mm. I.D. with vacuum jacket x 90 cm. The packing consisted of 4 mm. single-turn pyrex glass helices. The product mixture (460 g.) was distilled from a 1-liter flask.

b. The major side product was trimethyl orthoacetate (b.p. 109°C), 230 g.

c. 50:50 mixture of orthoester and methoxyacetal, 30 g.

d. pure methoxyacetal (b.p. 126.2°C), 180 g.

Again, the work-up was essentially the same as the first run giving a total of 613 g. of methoxyacetal (75% yield) and 123 g. of trimethyl orthoacetate. The conversion of bromoacetal was 96% based on the total amount of sodium bromide (672 g.) in the water extraction layer after removal of water by a rotary evaporating apparatus.

A summary of results of both runs are found in Table I. The boiling point of pure methoxyacetal was 126.4°C with a $n_D^{29} = 1.3932$. The methoxyacetal was stored over sodium ribbon.

6. Batch Reactor Synthesis of *cis*- and *trans*-1,2-Dimethoxyethylene, (I and II respectively)

In a 100 ml. 3-necked round bottom flask, was placed 64 g. (0.524 g.-moles) of methoxyacetal (III) and 25 g. (0.245 g.-moles) of alumina. The alumina was basic washed and had a 50 - 200 mesh distribution. The flask was fitted with a reflux condenser, stirrer, thermometer, and nitrogen inlet tube. The reflux condenser was followed by a cold trap (250 mm. x 41 mm.), drying tube and nitrogen bubbler. The cold trap was maintained at -40°C. A slow stream of nitrogen was used to effect a partial take-off procedure. The reaction products and unreacted starting material were collected in the cold trap after 12 hours. The temperature of the refluxing reaction medium was 126°C.

The mixture was analyzed by quantitative gas chromatography. The results are given in Tables II and III. Similarly, two other runs were performed. Identical quantities were used in run No. 2. The weight ratio of methoxyacetal: alumina was 2.56:1 (mole ratio 2.12:1). In run No. 3, 62.5 g. of alumina (0.614 g. moles) and 159.3 g. of III (1.33 g.-moles) were used. The weight ratio of III: alumina was 2.55:1 (mole ratio 2.17:1). Since very little trans-isomer was produced, the three runs were combined and distilled on a semi-micro distillation apparatus giving 15 g. of cis-1,2-dimethoxyethylene (b.p. 101°C).

7. The Continuous Pyrolysis of 1,1,2-Trimethoxyethane (III)

Initial exploratory runs were made using a horizontal tube furnace containing a pyrolysis tube (2 ft. in length and 1 inch in diameter) custom made by Scientific Glass Co. with a standard tapered ₸ 24/40 female joint at one end. The tube was packed with alumina (Alcoa grade, regular, 8 - 14 mesh) into which pure 1,1,2-trimethoxyethane (III) was slowly dropped from an addition funnel. The wt. ratio of III to alumina was 2.56:1. This ratio differed from the earlier batch runs (0.535:1) because the entire oven space was filled with alumina.

In run 1, 71.3 g. of alumina (Al_2O_3) was charged to the 2 foot pyrolysis tube and 38.2 g. of III added slowly by dropwise addition over a 2 hour period. The furnace temperature was maintained at 220°C. A dropping funnel, used for the addition of III, was fitted with a standard tapered right angle adopter which was wrapped with heating tape for approximately 6 inches. Nitrogen was introduced by a gas inlet adapter fitted on the addition funnel and was measured by a paraffin oil bubbler at the end of the apparatus. The exit gas rate was 1 - 2 bubbles/ sec. The nitrogen was used to maintain dry, inert conditions and to act as a carrier gas for the carry over (by entrainment) of methoxyacetal (III). The products (26.8 g.) were collected in a cold trap (-60°C) and analyzed by quantitative gas chromatography. The product distribution was 14.1% cis-1,2-dimethoxyethylene (I), 1.2% trans-1,2-dimethoxyethylene (II), 21.4% methanol and 63.3% unreacted III. The results are in Tables IV and V. The product mixture was fractionated on an efficient semi-micro distillation apparatus. The b.p. of cis-1,2-dimethoxyethylene (I) was 101°C. The trans-isomer (II) azeotroped with methanol at 64°C. II was later purified by an azeotropic distillation with benzene (Section 8 - Experimental).

Another experiment was performed (run 2) in which 57.3 g. of methoxyacetal (III) was vaporized directly (over a 1 hour period) from a 3-necked 100 ml. round bottom flask directly into the pyrolysis tube containing 72.5 g. alumina. Again a slow stream of nitrogen was used to facilitate the carry over of methoxyacetal vapors into the tube furnace. Heating tape was employed near the tube entrance. The reaction products (37.7 g.) were collected in a cold trap, analyzed and fractionated as in run 1. The product distribution was 33.4% I, 8.9% II, 32.1% methanol and 25.6% unreacted III. In run 3, the same quantities were used as for run 2 but the tube furnace temperature was raised to 360°C (oven thermostat setting of 1.4). The oven was turned on at least 2 - 3 hours before a run was started for temperature stabilization since a long time delay was observed between the actual oven temperature and the oven pyrometer. A large Dewar condenser (300 mm. x 75 mm.) was added to the apparatus to facilitate the removal of reaction products (for vpc analysis, etc.). It was placed at the exit of the pyrolysis tube and maintained at -60°C with isopropanol and a refrigeration coil. This was followed by a cold trap (-40°C) used previously to collect the reaction products. There was some smoking (non-condensibles) observed in the Dewar condenser. The reaction products (33.2 g.) were analyzed and fractionated as above (Tables IV and V).

Additional runs were tried at higher temperatures (400° - 500°C) but decomposition products in the form of smoke and non-condensables provided for extremely poor yields. Products exiting from the tube furnace were in two phases. There was a large water phase. The catalyst bed (black) was unevenly burnt in many places. Yellow-green decomposition products were observed near the exit of the pyrolysis tube and on the walls of the Dewar condenser.

In the next experiment (run 4), the apparatus was modified greatly. A copper constantan thermocouple probe (3 feet) was placed in a 3 ft. by 3/16 inch pyrex tube which had one end sealed. The individual thermocouple wires were stripped of their insulation (to prevent the insulation from melting at high temperatures) and placed inside small diameter teflon tubes to prevent shorting due to contact. A junction was made and the assembly was moved back and forth inside the pyrex tube to monitor the actual catalyst temperature inside the bed along the length of the tube. The pyrolysis tube was filled with alumina (75.0 g.) with the tube held in the middle bed resulting in an annular temperature probe. Methoxyacetal (50.0 g.) was added dropwise through an addition funnel to a preheated 3-necked 250 ml. round bottom flask and vaporized rapidly on contact. The addition rate was 1 ml./min. The glass surface temperature was 190°C as measured by a copper-constantan thermocouple. Heating tape was placed around the tube entrance and the right angle adapter for approximately 8 inches of length to prevent condensation of vapors. The entrance and exit portions (1 inch) of the pyrolysis tube were packed with large glass helices to prevent hot acetal or reaction product vapors from condensing on catalyst. The nitrogen was monitored before the apparatus with 2 flow meters (high and low ranges). The input rate was 90 ml./min. The oven temperature (setting 1.0) was 300° - 310°C. The interior catalyst temperature was 280°C - 320°C during the reaction. The oven was turned on 4 hours before the run commenced to stabilize the temperature. The reaction products (27.5 g.) were condensed from the Dewar condenser (-60°C) into a 3-necked 100 ml. flask (ice-cooled). The Dewar condenser was followed by a cold trap (-40°C) to reduce product losses. A small amount of water was formed from the pyrolysis reaction and was subsequently removed by drying the reaction mixture over calcium hydride prior to fractionation. The reaction products were analyzed and fractionated as in runs 1 - 3. The product distribution was 42.5% I, 10.7% II, and 46.8% methanol. The conversion of methoxyacetal was 98.6%.

The nitrogen was left on at a low rate overnight between runs to prevent moisture from entering the system. A similar run was made (run 5) with the same catalyst (light brown color throughout) as used for run 4. 190 g. of III was added at a rate of 1 1/2 ml. per minute. The furnace temperature was maintained at 320°C (setting 1.0) and the movable thermocouple probe registered catalyst temperatures of 290 - 310°C throughout the reaction. The nitrogen input rate was 90 ml./min. A total of 135.0 grams were collected (12.8 g. from cold trap and 122.2 g. from Dewar condenser) for a 71.1% recovery. The product mixture was dried over calcium hydride and distilled. The final reaction product distribution was 52.6% I, 8.4% II, 20.5% methanol, and 18.5% unreacted III.

A final pyrolysis was made (run 6) in which the apparatus was similar to that described above except between the Dewar condenser and exit tip of pyrolysis tube. Two condensers were placed in series. The first was an air condenser (30 cm. long and 2 cm. in diameter) filled with porcelin Raschig rings (for heat transfer to hot vapors). The second condenser (30 cm. x 2 cm.) was water cooled. See Figure 4 for a schematic diagram of the final apparatus set-up. A slow steady stream of nitrogen was maintained 3 - 4 hours before the refrigeration apparatus was turned on in the Dewar condenser. This prevented moisture and ice from forming inside the condenser walls and contaminating the reaction product mixture. Similarly, the oven furnace was turned on during this "warm up" phase. This is an important point since the presence of water caused a 2-phase azeotrope (b.p. 84°C) to form upon fractionation of the final product mixture. Table XIII gives a summary of the distillation

Figure 4

Pyrolysis Apparatus

STAGE #1

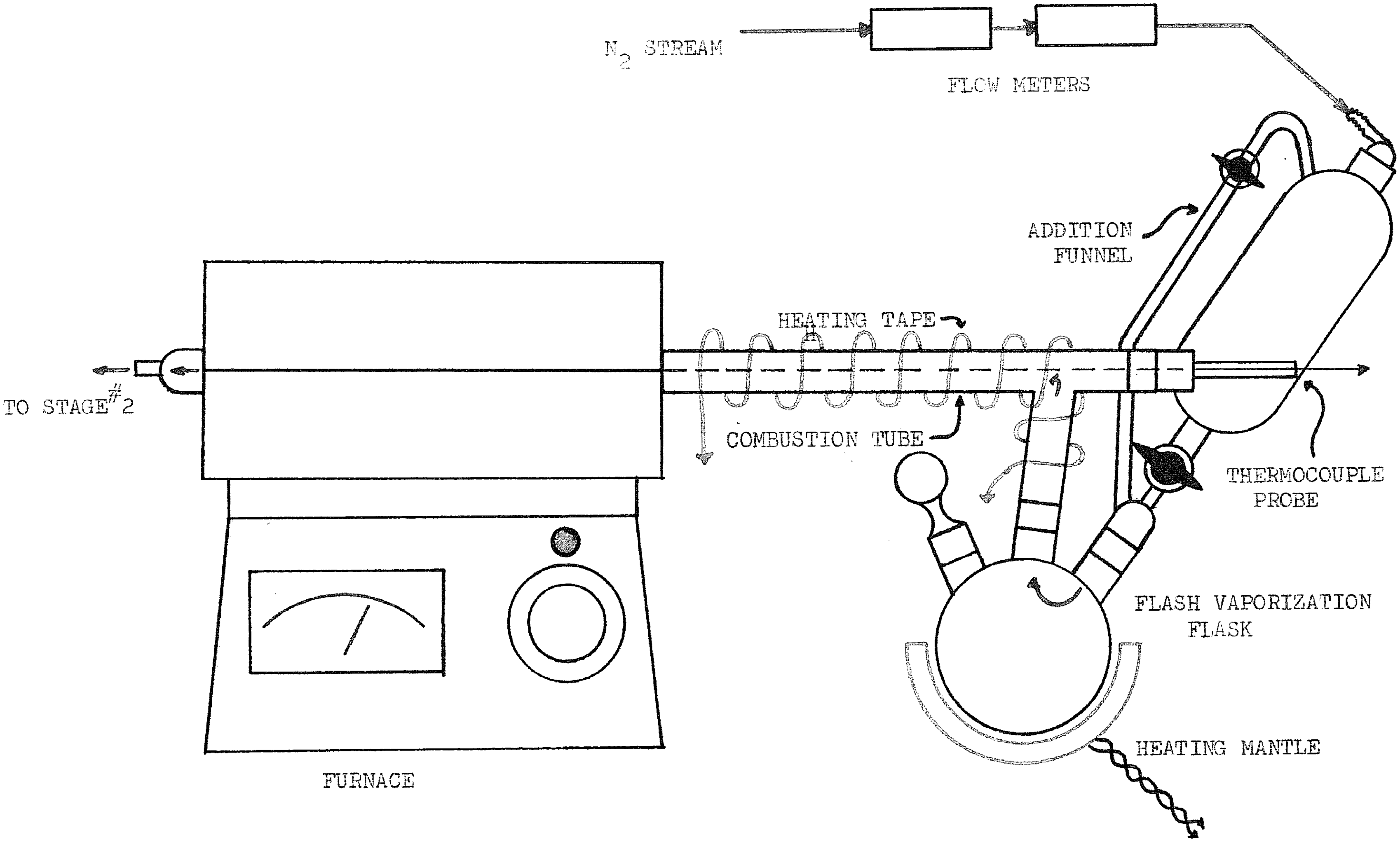


Figure 5

STAGE #2

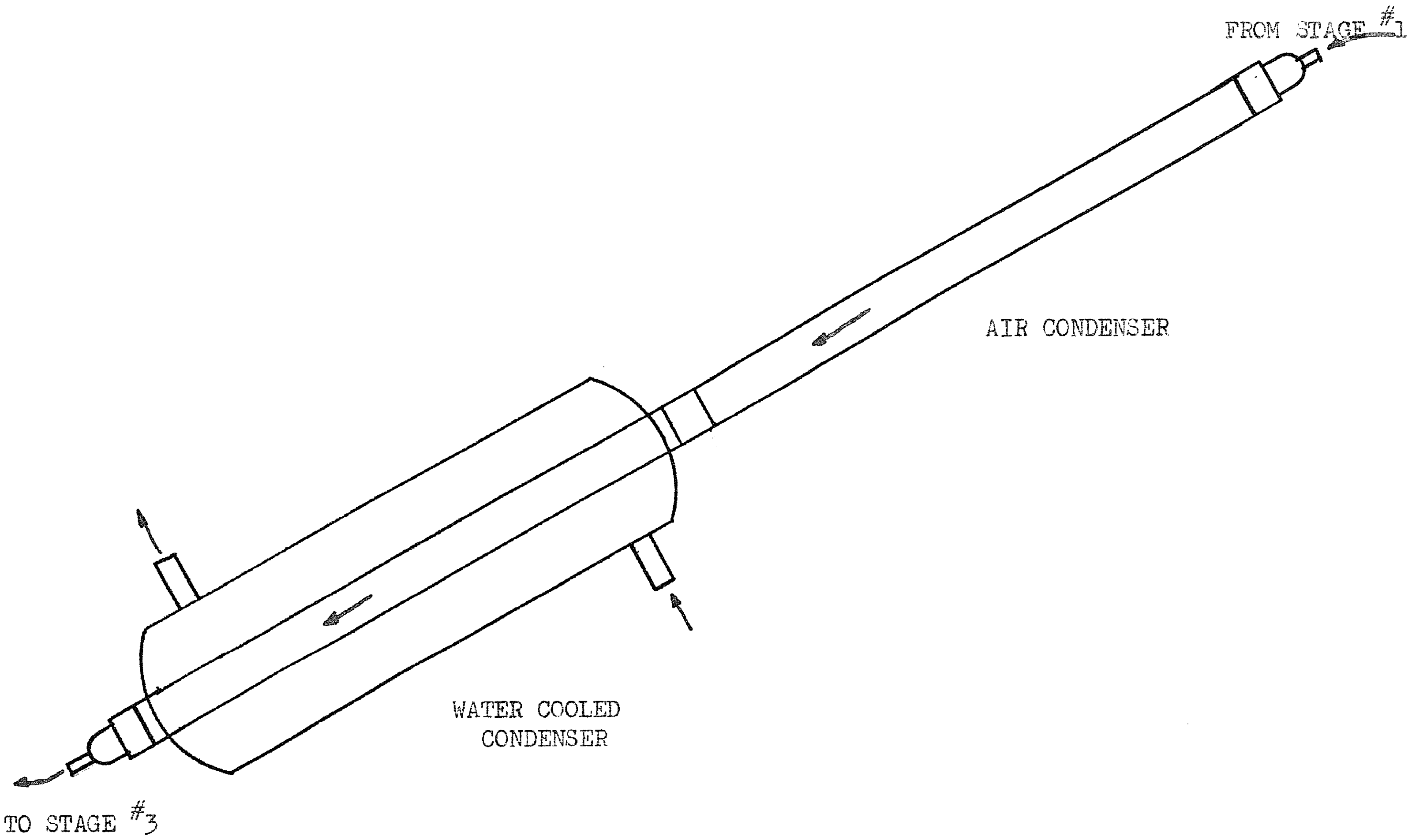
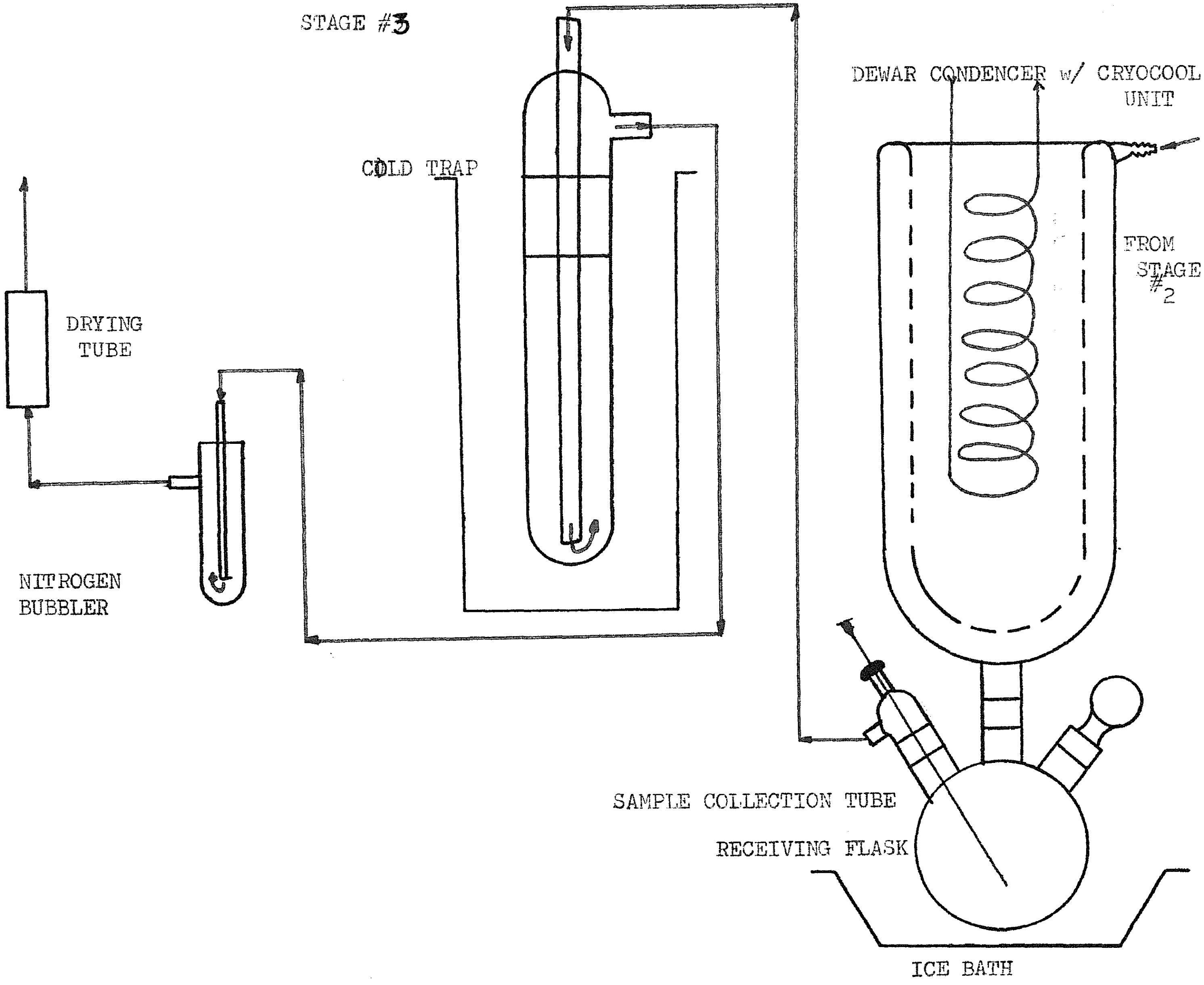


Figure 6

STAGE #3



data for the pyrolysis products (dealcoholation) of methoxyacetal.

Fresh alumina (75.0 g.) was charged to the pyrolysis tube and 296.0 g. of III were added at an average rate of 2 ml./min. to the preheated vaporization flask. The nitrogen input rate was 90 ml./min. There was some fogging in the Dewar condenser but it was considerably less than the former runs. Initially there was some trace amounts of yellow-green product formed near the exit tube. During the first hour of the run a 2-phase mixture was collected. One phase was water. After the first hour the reaction products were homogeneous (one phase) and golden yellow in color. The oven furnace was maintained at 290° - 320°C. A total of 257.2 g. of reaction products was collected (34.6 g. from the cold trap and 222.6 from the Dewar condenser) for a total recovery of 86.9%. The final reaction product distribution was 66.0% I, 8.0% II, 26.0% methanol. The conversion of methoxyacetal was 84.7%. The reaction mixture was dryed with calcium hydride and distilled. Tables IV and V contain a summary of results (pp. 33 - 34).

8. The Purification of *trans*-1,2-Dimethoxyethylene (II) by Azeotropic Distillation

Fractionation of the pyrolysis reaction products (Table XIII) gave a constant boiling azeotrope of methanol *trans*-dimethoxyethylene (II) at 64°C. Benzene was chosen as an

TABLE XIII

Distillation of Reaction Products from Dealcoholation of Methoxyacetal[a]

Reflux Ratio	Pot Temp.	Bottom Column Heater, °C	Top Column Heater, °C	Distillate Temp., °C
25:1	74	80	47	50-63[b]
25:1	82	81	66	64[c]
50:1	84	81	68	65-83[d]
	94	91	86	
50:1	103	96	86	84[e]
50:1	104	97	86	85-100[f]
	110	105	97	
50:1	112	105	98	101[g]
	127	115	98	
50:1	127	115	100	102-125[h]
	132	128	128	
10:1	132	129	128	126.2[i]
	135	132		

a. Todd column dimensions: 12 mm. I.D. with vacuum jacket x 90 cm. The packing consisted of 4 mm. pyrex glass helices. The product mixture from runs 4 and 5 (162 g.) was distilled from a 250 ml. flask.

TABLE XIII (continued)

b. relatively small low boiling cut containing approx. 4 degradation products, some trans-DME and methanol (2.0 g.)

c. constant boiling azeotrope (64°C) of trans-DME and methanol containing 18% trans-DME (50 g.)

d. small midrange cut depending on efficiency of separation (4 g.)

e. a heterogeneous 2-phase azeotrope containing water. If the pyrolysis reaction is run at temperatures greater than 300°C, water is produced. The composition of the organic phase is 30% cis-DME, 40% trans-DME, and 30% methanol. This phase can be eliminated if all the water is removed initially with calcium hydride before reaction mixture is distilled (1 - 3 g.).

f. small midrange cut (3 g.)

g. pure cis-DME (b.p. 101°C) (72 g.)

h. small midrange cut (1 - 2 g.)

i. pure methoxyacetal (b.p. 126.2°C). The size of this cut depends essentially on the initial conversion. If the reaction went essentially to completion there would be no methoxyacetal left to distill over. In that case, O-xylene was charged to the still pot and used as a distillation "chaser" to prevent olefin loses due to column hold-up (25 g.).

azeotropic solvent since it forms an azeotrope with methanol at 58°C. The composition of the benzene-methanol azeotrope is 60.5% benzene and 39.5% methanol. The trans-DME (II) - methanol azeotrope was found to contain 17.8% II and 82.2% methanol by quantitative gas chromatography. A 50 g. distillation cut (b.p. 64°C) contained 9.0 g. of II and 41.0 g. of methanol. 64 g. of benzene was added which was 1 g. in excess of the theoretical amount necessary to azeotrope-out all the methanol present in the 50 g. sample.

o-Xylene was used as a distillation "chaser". The trans-olefin (II) was the highest boiling component in the mixture; to prevent mechanical losses due to column hold-up some o-xylene (20 ml.) was added to the batch.

The mixture was fractionated on a Todd column at 50:1 reflux ratio since the methanol-benzene azeotrope (b.p. 58°C) distills near the methanol-trans-olefin (II) azeotrope (b.p. 64°C). Table XIV shows a summary of the distillation procedure and results. Approximately 8 g. of relatively pure II (>96%) were obtained.

9. Reaction of cis-1,2-Dimethoxyethylene (I) with Potassium tert-Butoxide

The solvent, dimethoxyethane, was used to prepare potassium tert-butoxide. It was tested for peroxide content with potassium iodide and potassium hydroxide (50 g. of KI

TABLE XIV

The Purification of trans-Dimethoxyethylene (DME) by Azeotropic Distillation[a,b]

Reflux Ratio	Pot Temp.	Bottom Column Heater, °C	Top Column Heater, °C	Distillate Temp., °C
50:1	62-100	60	59	58[c]
		70	60	
50:1	108	97	64	60-93[d]
	142	128	110	94[e]
50:1	144	128	110	95-100[f]

[a] The starting composition was a binary azeotrope (50 g.) of 18% trans-DME and 82% methanol. This binary azeotrope was "broken" by adding the calculated amount of benzene (64 g.) to give a new azeotrope (b.p. 58°C) containing 60.5% benzene and 39.5% methanol.

[b] Todd column dimensions: 12 mm. I. D. with vacuum jacket x 90 cm. The packing consisted of 4 mm. pyrex glass helices.

[c] methanol/benzene azeotrope, b.p. 58°C (60.5% benzene), 103 g.

[d] midrange cut, contains some methanol, benzene, and trace quantities of trans-DME (3 g. total)

[e] pure trans-DME (b.p. 94°C), 7 g.

[f] A small trans-rich cut, containing trace amounts of cis-DME (1 g.). At this point the distillate temperature dropped since the next fraction up the column would be the much higher boiling O-xylene (b.p. 142°C) used as a distillation "chaser". The distillation was stopped at this point.

and 50 g. KOH per liter of ether). Dimethoxyethane was distilled at a reflux ratio of 1:1 (b.p. 84°C) and stored over sodium ribbon. Approximately 1-liter was collected. Potassium metal was dissolved in dimethoxyethane. The di-tertiary butyl peroxide was then added slowly. This yielded potassium tert-butoxide with no tert-butanol contamination.[93] The resulting dimethoxyethane was 2.3 molar in potassium tert-butoxide as determined by titration with standard hydrochloric acid (1 ml. of solution consumed 23.0 ml. of 0.100 N HCl). The solvent was removed with a rotary evaporating apparatus connected to a vacuum pump. Initially the solvent was taken off without heat (5 mm. Hg). Finally a hot water bath (90°C) was used to remove the last traces of dimethoxyethane (1 mm. Hg). The solid was dried for 3 hours.

Potassium tert-butoxide (0.2302 g.) was dissolved in 25 ml. of water and titrated with 19.9 ml. of 0.100 N HCl, (phenolphthalein end-point). The purity was 96.8%. The dry potassium tert-butoxide was stored under nitrogen.

A small Parr bomb reactor, fitted with a pressure gauge, was charged with 1.5032 g. (0.01342 g.-moles) of potassium tert-butoxide and 5.0325 g. (0.05188 g.-moles) of cis-dimethoxyethylene (I). The reactor was placed in a 120°C ± 0.1°C constant temperature oil bath for 8 hours. The final pressure was 100 psig. The reactor was cooled down to room temperature and vented. The reaction mixture was transferred to a 25 ml. flask and the liquid portion transferred on a high vacuum system. The total recovery of solids and liquid was 95% (6.2096 g.). The liquid portion was analyzed by quantitative gas chromatography (Table VI). The solid products (1.7989 g.) were dissolved in water and titrated with standard HCl (14.5 ml. of 1.00 N HCl). This represented 14.5 meq. of base from the solid products.

In a preliminary experiment, equal molar quantities of potassium _tert_-butoxide and I were added to a 1 ml. ampule. The ampule was sealed and heated for 24 hours at 175°C. It was cooled to -60°C and opened. A violent explosion occurred, due to either pressure build-up in the ampule or actual detonation (the former was more likely). It was decided to use an excess (4:1) of _cis_-olefin (I), and a bomb reactor apparatus (experiment described above). The reaction was followed by the pressure gauge and was stopped when the gauge pressure was 100 psig. This was 10 psig in excess of the vapor pressure (at 120°C) of methyl _tert_-butyl ether (major product of reaction) at 120°C.

10. The Reaction of Bromoacetal (IV) with Potassium _tert_-Butoxide (VII)

A Parr reaction bomb was charged with 1.1256 g. (0.0101 g.-moles) of VII, 6.4422 g. (0.0871 g.-moles) of _tert_-butanol, and 0.8623 g. (0.0051 g.-moles) of IV. The reactor was heated at 120°C ± .1°C for 8 hours. The final pressure reading was 30 psig. The reactor was cooled down to room temperature and vented. The product mixture was transferred on a high vacuum system and the liquid products were collected in a cooled (-60°C) receiver at 0.1 mm. Hg. The liquid portion was analyzed by quantitative gas chromatography (Table VII). The total recovery of solid and liquid was 8.1359 g. (3 1/2% losses).

An experiment was performed in which pure potassium _tert_-butoxide was added to bromoacetal in an ampule without the presence of solvent (_tert_-butanol). The reaction was too exothermic and could not be controlled. For this reason, excess _tert_-butanol (8.7:1 molar ratio) was added to potassium _tert_-butoxide.

11. Preparation of Potassium Triiodide (KI_3)

To 100 ml. of distilled water, 10 g. (0.06 g.-moles) of potassium iodide was added and dissolved, followed by the addition of 15 g. (0.06 g.-moles) of elemental iodine. The solution turned dark brown indicating the formation of KI_3.

$$KI + I_2 \rightleftharpoons KI_3$$

An excess of 5 g. of potassium iodide was added to dissolve the remaining iodine. The water was removed by a rotary evaporating apparatus at 90° connected to a water aspirator

(25 mm. Hg). When the water was removed, part of the sample was oven dried at 120°C and the remaining portion was left as recovered.

The sample from the oven gave off purple vapors upon grinding. After grinding in a hood for 5 - 10 min., all the iodine vapors appeared to have been removed. KI_3 was probably unstable at those conditions and broke down to KI and I_2. Both samples of KI_3 were used in the catalyst screening work.

12. Liquid and Vapor Phase Isomerization of 1,2-Dimethoxyethylene

Mercuric acetate (20%) was added to a small sample of pure (>99%) *cis*-1,2-dimethoxyethylene (1 ml.) and sealed in a 2 ml. ampule. For confirmation of equilibria, the *trans*-isomer was used (0.5 ml.) throughout the range of temperatures employed.

The isomerizations were carried out in a constant temperature bath ($\pm$ 0.1°C). The liquid (after equilibration) was transferred on a high vacuum system and analyzed by quantitative gas chromatography. This insured that the liquid portion was removed from any traces of catalyst, so as not to isomerize further on the column. Controls were run with no catalyst (using pure olefin samples). No isomerization products were observed with the control runs.

A detailed description of the liquid and vapor transfer procedures are described in Section 2 of Experimental.

For the liquid phase, isomerizations were measured from 30°C to 175°C (at 10° intervals). Temperature control was ± 0.1°C. Three isomerizations and one control were performed at each temperature. The pure trans-isomer was employed at 30°, 50°, 80°, 100°, 120°, 150°, and 175°C for confirmation of equilibria. The sampling time was 36 - 48 hours.

The vapor phase isomerizations were measured over the same temperature range using two catalyst samples and one control at each temperature. The pure cis-isomer was isomerized at 30°, 50°, 70°, 80°, 100°, 120°, and 150°C. The trans-isomer was isomerized at 30°, 70°, 100°, and 150°C.

At most temperatures, equilibrium was approached from both the pure cis- and pure trans-sides. The gas chromatographic peaks had Gaussian shapes. Areas of the peaks were calculated by triangulation (the height times the base at half the height) and by weighing the peaks and gave results for area ratios within experimental error. The chromatograms were calibrated by measuring the ratios of areas (trans/cis) for four synthetic mixtures, which had been prepared gravimetrically. The measured area ratios were 0.08249, 0.44423, 0.89917, and 1.91498. The corresponding synthetic wt. ratios were 0.15934, 0.41515, 0.95876, 2.14286. Therefore, the actual wt.-ratio of trans/cis = (1.100) (Area ratio). The experimental error for reproducibility of the measured wt. ratios was ± 0.002.

The samples were equilibrated for two days and showed no evidence for volatile side products. Although there was some evidence of a minor side reaction due to trace amounts of free mercury formation, the trans/cis ratios appear to be a reliable measure of the equilibrium constants at temperatures up to 175°C.

CONCLUSIONS

(1) From a screening of 29 different catalysts, mercuric acetate, mercuric benzoate and mercuric salicylate were found to be favorable isomerization catalysts for the *cis*-*trans* interconversion of 1,2-dimethoxyethylene.

(2) A novel synthesis for the *cis*-and-*trans* isomers of dimethoxyethylene was found via a continuous pyrolysis of 1,1,2-trimethoxyethane over alumina.

(3) Equilibrium constants along with enthalpies (ΔH) and entropies (ΔS) of isomerization have been determined for the liquid and vapor phase reaction

$$\underline{\text{cis}}\text{-}CH_3OCH{=}CHOCH_3 \underset{Hg(OAc)_2}{\rightleftharpoons} \underline{\text{trans}}\text{-}CH_3OCH{=}CHOCH_3$$

over the temperature range 30° - 175°C. A linear regression analysis employing a least-squares curve fit and an analysis of variance were performed on the data. For the liquid phase isomerization,

$$\ln K = -779.8/T + 0.6748$$

where $\Delta H^o = +1.549 \pm 0.019$ Kcal/mole

and $\Delta S^o = 1.34 \pm 0.05$ e.u./mole

Similarly, for the vapor phase,

$$\ln K = -727.2/T + 0.8335$$

where $\Delta H^{o} = +1.445 \pm 0.054$ Kcal/mole

and $\Delta S^{o} = +1.66 \pm 0.15$ e.u./mole

An independent experimental error analysis was performed and was consistent with the above findings.

(4) cis-1,2-Dimethoxyethylene was more stable relative to its trans-isomer in both the liquid and vapor phase. Also, the cis-stability was highest in the liquid phase. This was the first reported example of enol ether stability.

(5) The entropy change accompanying the isomerization (cis $\rightleftarrows$ trans) was positive for both the liquid and vapor phase. The positive value for the entropy change (higher entropy for the trans-isomer) indicated that the trans-isomer had a larger measure of randomness associated with it for both the vapor and liquid phase. This indicated that internal rotation (free rotation around the CH_3-O bond) occurred more freely for the trans-isomer. This occurrence of free rotation was even more likely in the vapor phase than in the liquid phase (larger ΔS^{o}) as expected.

(6) The greater preference for the cis-configuration at equilibrium (the cis-effect) was discussed in terms of nonbonded dipole-dipole interactions with resultant electron density shifts. The shift in charge density toward the carbon-carbon double bond for the cis-isomer resulted in an increase

in the C=C bond strength for the *cis*-isomer and an increase in relative stability. Also, the dimethoxyethylenes were correlated with available data from related systems found in the literature to justify contributing factors effecting the stabilities.

APPENDIX A

Statistical Error Analysis

For the equation

$$\ln K = -\Delta H^{o}/RT + \Delta S^{o}/R$$

A least-squares fit was performed for the plot of ln K vs. 1/T.

The equation is of the form

$$y = a + bx$$

where $y = \ln K$

$a = \text{intercept} = \Delta S/R$

$b = \text{slope} = \Delta H/R$

A linear regression analysis gives[127]

$$b = \frac{n\Sigma x_i y_i - \Sigma x_i y_i}{n\ x_i^2 - (\Sigma x_i)^2}$$

where n = number of data points (39 for liquid phase, 14 for vapor phase)

$x_i = 1/T$

$y_i = \ln K$

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(127) E. L. Crow, F. A. Davis, and M. W. Maxfield, Statistics Manual, Dover Publications, Inc., New York, 1968, pp. 152 - 163.

Similarly,

$$a = \overline{y} - b\overline{x}$$

where

$$\overline{y} = \Sigma y_{i/n} \quad \text{and} \quad \overline{x} = \Sigma x_{i/n}$$

The calculations were performed on a Wang calculator. For the liquid phase runs:

$b = -779.8 = \text{slope} = -\Delta H/R$

$a = 0.6748 = \text{intercept} = \Delta S/R$

The equation is

$$\ln K = -779.8/T + 0.6748$$

where $\Delta H = 1549$ cal/mole = 1.549 Kcal/mole

and $\Delta S = 1.341$ cal/deg.-mole

The confidence limits at the 90% probability level were determined for the slope (b) and the intercept (a). For the slope the confidence limits are

$$b \pm t\alpha/_{2,n-2}(s_b)$$

where t is the value of the Student t distribution[127] at the 100 (1 - α)% confidence limit at n-2 degrees of freedom. The standard error of the regression coefficient b is

$$s_b = \frac{s_{y|x}}{s_x \sqrt{n-1}}$$

where $s_{y|x}$ is the standard error of the estimate and s_x is the standard deviation (s_x^2 = variance of x)

$$s^2_{y|x} = \frac{n-1}{n-2}\left(s_y^2 - b^2 s_x^2\right)$$

$$s_{y|x} = 0.021801 \text{ and } s_x = 3.165 \times 10^{-4}$$
(from program)

Therefore,

$$s_b = \frac{0.021801}{3.165 \times 10^{-4} \sqrt{38}} = 11.18$$

and $t_{.05,37} = 1.684$

$$\Delta H = 1549 \pm 1.684\ (11.18)$$

$$\Delta H = 1549 \pm 19 \text{ cal/mole} = 1.549 \pm 0.019 \text{ Kcal/mole}$$

For the intercept, the confidence limits (90%) are

$$\Delta S \pm t_{\alpha/2,n-2}(s_{y|x})\sqrt{1/n + \frac{(X - \bar{x})^2}{(n-1)\ s_x^2}}$$

where $X = 0$ and $\bar{x}$ = mean value of $1/T = 2.770 \times 10^{-3}$. The error in estimating the true mean ordinate is smallest at $X = \bar{x}$ and increases greatly as $|X - \bar{x}|$ increases. When $X = 0$ ($T = \infty$, since $x = 1/T$), the error estimation is the largest since we are extrapolating to infinite temperature to determine the intercept value.

$$S = 1.341 \pm 1.684\ (0.021801) \sqrt{\frac{1}{39} - \frac{(2.770 \times 10^{-3})^2}{38\ (1.001 \times 10^{-7})}}$$

$$S = 1.341 \pm 1.684\ (0.0218)\ (1.43)$$

$$S = 1.34 \pm 0.05 \text{ cal/deg.-mole}$$

The regression coefficient[128] (r) was calculated for the liquid phase runs.

$$r = \frac{\Sigma(x_i - \bar{x})\ (y - \bar{y})}{(n-1)\ \ s_x s_y}$$

The value of r is the maximum likelihood estimator of the linearity. Negative r values indicate negative slopes. It has values between ± 1 (measure of the linearity as r approaches ± 1). For the liquid phase isomerizations, $r = -0.996$. From r^2, the regression of ln K on 1/T accounts for 99.2% of the variance of ln K. The value of r was tested at the 99% critical level for straightness of fit. The test was positive.

For the vapor phase runs, similar analyses were performed. The equations are

$$y = a + bx$$

where $b = -727.1 = \text{slope} = -\Delta H/R$

$a = 0.8335 = \text{intercept} = \Delta S/R$

Therefore $$\ln K = -727.1/T + 0.8335$$

$\Delta H = 1445$ cal/mole

$\Delta S = 1.656$ cal/deg.-mole

$s_{y|x} = 0.033515$

$s_x = 3.0865 \times 10^{-4}$

$\bar{x} = 2.819 \times 10^{-3}$

$$s_b = \frac{s_{y|x}}{s_x\sqrt{n-1}} = \frac{0.033515}{3.0865 \times 10^{-4}}\left(\frac{1}{\sqrt{13}}\right) = 30.09$$

at 90% confidence limit, $t_{.05,12} = 1.782$

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(128) P. G. Hoel, Introduction to Mathematical Statistics, John Wiley and Sons, Inc., New York, 1966 pp. 160 - 175.

therefore

$$\Delta H = 1445 \pm 30.09\ (1.782)$$

$$\Delta H = 1445 \pm 54 \text{ cal/mole} = 1.445 \pm .054 \text{ Kcal/mole}$$

Similarly,

$$\Delta S = 1.656 \pm 1.782\ (0.0335)\sqrt{\frac{1}{14} - \frac{(2.819 \times 10^{-3})^2}{13\ (9.527 \times 10^{-8})}}$$

$$\Delta S = 1.656 \pm 1.782\ (0.0335)\ (2.545)$$

$$\Delta S = 1.66 \pm 0.15 \text{ cal/deg.-mole}$$

The regression coefficient was found to be $r = -0.988$. From r^2, the regression of ln K on 1/T accounts for 99.2% of the variance of ln K. The test at 99% critical level was positive for straightness of fit.

APPENDIX B

Experimental Error Analysis

An experimental error analysis gives a good indication as to the minimal errors involved due to reproducibility of area ratios, temperature variation, etc. There have been examples in the literature where experimental values from statistical correlations have been reported beyond the accuracy that could be measured.[38,47] The errors involved in reporting confidence limits on experimentally measured values are at least as great or greater than the reliability of the measurements. If this condition is not met, the statistical analysis is not significant. Usually the confidence limits from a statistical regression analysis or analysis of variance are greater than the minimum experimental error, since a correlation of data is being fit at the 90 - 95% probability level. Therefore, the variance, from run to run, should be greater than the minimum allowable experimental error.

The van't Hoff equation can be rearranged in terms of ΔH.

$$\Delta H = -RT \ln K + T\Delta S \tag{1}$$

The minimum experimental error in ΔH is defined as

$$|\Delta(\Delta H)| = \left(\frac{\partial \Delta H}{\partial T}\right)_{\ln K} T + \left(\frac{\partial \Delta H}{\partial \ln K}\right)_{T} \Delta \ln K$$

The confidence limits on ΔH sould be larger than $|\Delta(\Delta H)|$ since $|(\Delta H)|$ is the error expected from human judgement, area reproducibility, etc. as mentioned above.

Eqn. (1) can be differentiated with respect to temperature at constant ln K and with respect to ln K at constant temperature.

$$(2) \qquad \left(\frac{\partial \Delta H}{\partial T}\right)_{\ln K} = -R \ln K + \Delta S = \frac{\Delta H}{T}$$

$$(3) \qquad \left(\frac{\partial \Delta H}{\partial \ln K}\right)_{T} = \frac{-R(\Delta H)}{\Delta S - R \ln K} = -RT$$

Therefore,

$$(4) \qquad |\Delta(\Delta H)| = \left(\frac{\Delta H}{T}\right)\Delta T + RT\ (\Delta \ln K)$$

A synthetic mixture of cis- and trans-1,2-dimethoxyethylene was prepared gravimetrically and analyzed 4 times by quantitative gas chromatography to determine the reproducability of measurement. The trans/cis ratio was 0.1852 g./1.0325 g. = 0.1794. The actual weight ratio of trans/cis = 1.10 times the peak wt. ratio. Therefore, 0.1794/1.10 = 0.1631 (peak wt. ratio). From the 4 measurements, the peak wt. ratios were 0.1643, 0.1660, 0.1637, 0.1628. The average ratio ($\bar{K}$) = 0.164 ± 0.002. To determine ln K, K_1 = 0.162 with ln K_1 = -1.7958 and K_2 = 0.166 with ln K_2 = -1.8202. Therefore, ln K = ± 0.0122.

The temperature deviation was ± 0.1°C. Eqn. (4) was solved using the highest temperature run (448°K) since the error would be a maximum. For the liquid phase runs,

$$|\Delta(\Delta H)| = \frac{1549}{448}(0.1) + 1.987\,(448)\,(0.0122)$$

$$|\Delta(\Delta H)| = \pm 11.2 \text{ cal/mole} = \pm 0.011 \text{ Kcal/mole}$$

Likewise, the van't Hoff equation can be arranged in terms of ΔS.

$$(5) \quad \Delta S = \Delta H/T + R \ln K$$

as before,

$$\left(\frac{\partial \Delta S}{\partial T}\right)_{\ln K} = \frac{-\Delta H}{T^2}$$

$$\left(\frac{\partial \Delta S}{\partial \ln K}\right)_{T} = R$$

The minimum allowable arror in ΔS is defined as

$$(6) \quad |\Delta(\Delta S)| = \frac{\Delta S}{T}_{\ln K} \Delta T + \frac{\Delta S}{\ln K}_{T} \Delta \ln K$$

therefore,

$$(7) \qquad |\Delta(\Delta S)| = \left(\frac{\Delta H}{T^2}\right)\Delta T + R(\Delta \ln K)$$

$$|\Delta(\Delta S)| = \frac{1549(0.1)}{(303)^2} + 1.987\ (0.0122)$$

$$|\Delta(\Delta S)| = \pm\ 0.0259 = \pm\ 0.026 \text{ cal/deg.-mole}$$

To determine the reproducability of measurement for the vapor phase, the same synthetic mixture was analyzed as a vapor by quantitative gas chromatography. The liquid was transferred on a high vacuum system. The peak wt. ratios were 0.1618, 0.1569, 0.1671, and 0.1625.

The average ratio ($\overline{K}$) = 0.162 ± 0.005.

To determine ln K, K_1 = 0.167 with ln K_1 = -1.7898

and K_2 = 0.157 with ln K_2 = -1.8515.

Therefore ln K = ± 0.0308

Solving Eqn. (4), for the vapor phase runs at T = 423°K,

$$|\Delta(\Delta H)| = \frac{(1445)(0.1)}{423} + 1.987\ (423)\ (0.0308)$$

$$|\Delta(\Delta H)| = \pm\ 26.2\ \text{cal/mole} = \pm\ 0.026\ \text{Kcal/mole}$$

Similarly, from Eqn. (7)

$$|\Delta(\Delta S)| = \frac{(1445)\ (0.1)}{(303)^2} + 1.987\ (0.0308)$$

$$|\Delta(\Delta S)| = \pm\ 0.063\ \text{cal/deg.-mole}$$

APPENDIX C

Predictability of Bond Energies and Heats of Atomization Including Sample Calculations for Reference Molecules and Related Molecules Using Available Thermochemical and Stretching Frequency Data.

An equation was developed using the classical harmonic oscillator model and empirical reduced mass relationships to predict bond energies of polyatomic models using infrared and Raman stretching frequencies.[129] From the classical harmonic oscillator model for a diatomic molecule[130]

$$\bar{v} = \frac{1}{2\pi c}\sqrt{k/u} \tag{1}$$

where $c = 3 \times 10^{10}$ cm/sec

k = force constant (dynes/cm)

u = reduced mass (m_1m_2/m_1+m_2)

$\bar{v}$ = frequency (cm^{-1})

The force constant is a measure of the strength of a chemical bond. If the bond energy is a measure of the force constant, then $D_e \propto \bar{v}^2$ from equation (1). An equation was developed such that $D_e^s = f(\bar{v}^2)$.

$$D_e^s = \frac{\bar{v}_c^{\,2}}{n_i c} \tag{2}$$

where $\bar{v}_c$ = corrected frequency (corrected to reduced mass of hydrogen)

D_e^s = bond energy determined from spectroscopic data (Kcal/mole)

c = 7.8212×10^4 (empirically derived constant using a value of n = 2.00 for the hydrogen molecule)

n_i = constant for each type of bond under consideration

Values of n_i for other types of bonds (value of 2.00 arbitrarily assigned to hydrogen) were determined from actual data using the most recent values for thermochemical heats of formation[131] and infrared and Raman assignments[132] for the various reference molecules. Maximum uncertainties in the thermochemical data and in the frequency assignments were used to calculate errors in the values of n_i and the bond energies (D_e^s).

A sample calculation is presented to determine the n value for the C-H bond. Methane was used as the reference molecule. On the next page is a list of n values for other bonds and their corresponding uncertainties. The molecules in paranthesis were the reference compounds used to calculate the corresponding n values.

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(129) W. H. Snyder, unpublished results.

(130) G. M. Barrow, Molecular Spectroscopy, McGraw-Hill, Inc., New York, 1962, p. 29.

(131) D. D. Wagner, W. H. Evans, V. B. Parker, I. Hallow, S. M. Barley, and R. H. Schumms, Selected Values of Chemical Thermodynamic Properties (Rossini), 1968.

Bond Type	n	n
C-H (CH_4)	2.039	± 0.002
C=C(C_2H_4, CH_4)	3.715	± 0.087
C-F (CF_4)	2.224	± 0.052
C-CL (CCl_4)	1.391	± 0.096
O-H (H_2O)	2.847	± 0.002
C-O (CH_3OH, H_2O, CH_4)	2.269	± 0.042

Sample Calculation: C-H bond (Methane)

$$\Delta H \text{ atom} = \Delta H^o_{f\ (prod)} - \Delta H^o_{f\ (react)}$$

$$CH_4 \longrightarrow C^{\cdot} + 4H\cdot$$

$$\Delta H \text{ atom} = 171.29 + 52.1(4) - (-17.88)$$

$$\Delta H \text{ atom} = 397.57 \text{ Kcal/mole}$$

from Eqn. (2), to determine the error in n

$$|\Delta n| = \left(\frac{\partial n}{\partial \bar{v}c}\right)_{D_e} \Delta \bar{v}_c + \left(\frac{\partial n}{\partial D_e}\right)_{\bar{v}_c}^{2} \Delta D_e$$

$$(3) \quad |\Delta n| = \frac{n(\ 2)\Delta \bar{v}_c}{\bar{v}c} + \frac{n(\ 1)}{D_e} \Delta D_e$$

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(132) T. Shimanouchi, Tables of Molecular Vibrational Frequencies, Parts 1, 2, and 3, NBS circulars, (NBS - 17, NBS - 6, NBS - 11), 1968.

Similarly, the error in the bond energy is

$$|\Delta D_e| = \left(\frac{\partial D_e}{\partial \bar{v}_c}\right)_n \Delta \bar{v}_c + \left(\frac{\partial D_e}{\partial n}\right)_{\bar{v}_c} \Delta n$$

$$(4) \quad |\Delta D_e| = \left(\frac{2D_e}{\bar{v}_c}\right) \Delta \bar{v}_c + \left(\frac{D_e}{n}\right) \Delta n$$

The uncertainty in the heat of atomization of methane is ± 0.11 Kcal/mole.[131]

$$D_{ref.} = \Delta H \text{ atom}/4 = 99.393 \pm 0.028 \text{ Kcal/mole}$$

The 4 C-H stretching frequencies are:

$\bar{v}_{C-H} = 3019 \pm 1\ cm^{-1}$ CH_4 degenerate stretch (triply deg.)

$\bar{v}_{C-H} = 2917 \pm 1\ cm^{-1}$ CH_4 symmetric stretch

The C-H stretching frequencies are summed and divided by 4 to give an average C-H stretching frequency ($\bar{v}$).

$$\bar{v} = \frac{\Sigma \bar{v}}{4} = 2993.5 \pm 1\ cm^{-1}$$

The zero point energy (εo) is added to the average thermochemical bond energy (D_{ref}).

$$\varepsilon_0 = \frac{2993.5}{699.672} = 4.278 \text{ Kcal/mole}$$

$$D_e = D_{ref} + \varepsilon_0 = 103.671 \pm 0.028 \text{ Kcal/mole}$$

The average C-H frequency ($\bar{v}$) is corrected for the reduced mass of hydrogen.

$$\bar{v}_c = 2993.5 \frac{\sqrt{u_{C-H}}}{\sqrt{u_{H-H}}} = 2993.5\ (1.3583)$$

$$\bar{v}_c = 4066.1\ \text{cm}^{-1}$$

The uncertainty in the frequency is also corrected for the reduced mass of hydrogen.

$$\bar{v}_c = \pm\ 1(1.3583) = \pm\ 1.358\ \text{cm}^{-1}$$

from Eqn. (2)

$$n = \frac{\bar{v}_c^{\,2}}{D_e c} = \frac{16.111 \times 10^6 \text{cm}^{-2}}{(103.576)(78212)} + 2.039$$

The uncertainty in n is obtained from Eqn. (3)

$$|\Delta n| = \frac{2.039\ (2)\ (1.36)}{4066.1} + \frac{2.039\ (0.028)}{103.671}$$

$$|\Delta n| = \pm\ 0.002$$

Therefore

$$n = 2.039 \pm 0.002$$

The calculations become more involved with more complex molecules. To calculate the n value for the C=C bond, ethylene was used as a reference molecule. The calculations are basically the same as in the above example. The heat of atomization of ethylene was calculated from thermochemical data. The 4 C-H stretching frequencies were averaged. The corrected frequency ($\bar{v}_c$) was calculated and an average bond energy was obtained using equation (2) with n = 2.039.

$$D_e^s = \frac{\bar{v}_c^{\,2}}{nc} = \frac{17.2311 \times 10^6}{2.039(78212)} = 108.049 \text{ Kcal/mole}$$

This was corrected for zero point energy.

$$D^s = D_e^s - \varepsilon_0 = 103.681 \text{ Kcal/mole}$$

The uncertainty in the C-H bond energy was obtained from Eqn. (4).

$$|\Delta D_e| = \pm 0.124 \text{ Kcal/mole}$$

The value of D^s was multiplied by 4 (4 C-H bonds) and subtracted from the heat of atomization of ethylene (538.49 Kcal/mole) to give the C=C bond energy.

$$\begin{aligned} \Delta H \text{ atom} &= 538.49 \pm 0.13 \\ -4(D^{s}_{C-H}) &= \underline{414.72 \pm 0.50} \\ D^{s}_{C=C} &= 123.77 \pm 0.63 \end{aligned}$$

$D^{s}_{C=C}$ was corrected for the zero point energy of the carbon-carbon double bond.

$$D_e^s = D^s + \varepsilon_0 = 126.09 \pm 0.63 \text{ Kcal/mole}$$

Similarly, Eqn. (2) was solved for n and Eqn. (3) was solved for Δn.

$$n_{C=C} = 3.715 \pm 0.087$$

Similar calculations were performed on the other reference molecules. The uncertainties are high for the C=C and C-Cl bond, since the uncertainties in the assigned frequencies were high for the reference molecules (± 15 to ±30 cm^{-1}).

Large uncertainties in frequency assignments or in thermochemical data from reference compounds limit the accuracy of the n values obtained (Eqn. 3). This is an important point since bond energies obtained from Equation (2) for a particular compound can be summed to give an estimate of the total heat content of that compound from infrared and

Raman vibrational frequencies. When absolute values of heats of atomization are desired, reasonable results are obtained. For example, the heats of atomization of acetone and acetaldehyde were calculated[133] and the results agreed with thermochemical data.

For acetone,

$$\Delta H \text{ atom (Eqn. 2)} = 935.8 \pm 10.9 \text{ Kcal/mole}$$

$$\Delta H \text{ atom (thermo)} = 938.5 \pm 1.7 \text{ Kcal/mole}$$

For acetaldehyde,

$$\Delta H \text{ atom (Eqn. 2)} = 645.5 \pm 9.0 \text{ Kcal/mole}$$

$$\Delta H \text{ atom (thermo)} = 650.4 \pm 1.3 \text{ Kcal/mole}$$

In acetone, for example, the maximum error obtained in summing up all the calculated bond energies is ± 10.9 Kcal/mole. This is on the order of ± 1 Kcal/mole per bond since 9 bonds were considered. The error is quite small since some cases the frequency uncertainty was as high as $\pm 30 \text{ cm}^{-1}$.

In calculating heats of isomerization using stretching frequency data, the uncertainties obtained were large if both the variance of n and ν_c (Eqn. 4) were included. For example, in the reaction

$$\underline{\text{cis}}\text{-HClC=CClH} \rightleftharpoons \underline{\text{trans}}\text{-HClC=CClH}$$

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(133) J. Waldron and W. H. Snyder, The Stability of Simple Keto-Enol Systems, paper presented at Am. Chem. Soc. Meeting, Metrochem 1971, San Juan, Puerto Rico.

the calculated ΔH was +0.73 ± 36.8 Kcal/mole. The maximum absolute uncertainty in the ΔH atom for each isomer was on the order of ± 18 Kcal/mole. In using Equation (2) to predict heats of isomerization (for molecules as similar as cis-trans pairs) a more resonable estimate of the error is obtained by assuming an absolute value of n ($\Delta n = 0$ in Eqn. 4). The uncertainty in ΔH is then reflected only by the variance in the frequency data ($\Delta\bar{\nu}_c$) for the similar cis-trans isomers. There is no physical justification for this assumption however, and both variances, for example, are given for the dichloroethylenes. However, the variance in n is essential when calculating absolute heats of atomization as was done above for acetone and acetaldehyde.

The n values obtained from reference compounds were used to calculate the heats of atomization of cis- and trans-1,2-difluoroethylene, cis- and trans-1,2-dichloroethylene, and cis- and trans-1,2-dimethoxyethylene. Accurate assignments from the literature were used for the difluoroethylenes[39,40] and the dichloroethylenes.[37,43] The updated vibrational assignments of Hopper[134] were used for confirmation of the dichloroethylene assignments. The vibrational stretching frequencies[135] for cis- and trans-1,2-dimethoxyethylene are listed in Tables XV and XVI.

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(134) M. Hopper, Ph. D. Thesis, University of Minnesota, 1967.

(135) H. Kimmel, W. H. Snyder, J. Waldron, paper to be published.

TABLE XV

Vibrational Frequencies for cis-1,2-Dimethoxyethylene

Raman (cm^{-1})	Infrared (cm^{-1})			Assignment
Liquid	Liquid	CCl_4	Gas	
	3105 (sh)	3105 (sh)		
3065 (m)	3060 (m)	3065 (m)	3065 (m)	ethylenic C-H stretch
3015 (m)	3015 (s)	3020 (s)	3020 (s)	
			2965 (vs)	
2960 (vs)	2955 (vs)	2955 (vs)	2955 (sh)	methyl C-H stretch
2910 (m)	2920 (m)	2920 (s)	2932 (sh)	
2860 (vs)	2850 (vs)	2860 (vs)	2865 (s)	
2815 (m)	2820 (m)	2825 (m)	2835 (m)	
		2730 (w)	2740 (w)	
		2650 (w)		
	2595 (w)	2595 (w)	2605 (w)	
	2500 (w)	2500 (w)		
		2430 (sh)		
	2395 (w)	2400 (w)		
	2360 (vw)	2360 (w)		
	2315 (vw)	2320 (w)		
	2280 (vw)	2285 (vw)	2290 (vw)	
	2250 (vw)	2190 (w)	2200 (vw)	
	2130 (w)	2130 (w)	2145 (w)	
		2110 (sh)		
	2015 (w)	2030 (w)	2045 (w)	

TABLE XV (continued)

Raman (cm^{-1}) Liquid	Infrared (cm^{-1}) Liquid	CCl$_4$	Gas	Assignment
	1935 (vw)			
1825 (vw)	1843 (vw)	1850 (vw)	1870(vw,b)	
			1768 (vw)	
			1758 (vw)	
		1735 (w)		
1720 (s)	1700 (m)	1702 (m)	1715 (w)	C=C stretch
1690 (vs)	1690 (sh)	1680 (sh)	1690 (sh)	C=C stretch
	1675 (m)	1672 (m)	1680 (m)	
	1655 (sh)	1655 (sh)	1655 (sh)	
		1648 (sh)		
		1638 (sh)		
	1562 (w,b)		1590 (vw,b)	
			1495 (w)	
			1475 (sh)	
1470 (w)	1460 (s)	1462 (sh)	1465 (m)	
1455 (w)		1455 (m)		
		1440 sh)		
1385 (vw)			1388 (s)	
	1377 (vs)	1375 (vs)	1378 (s)	
1300 (m)	1305 (sh)	1310 (m)	1310 (m)	
	1292 (m)	1288 (m)		
1220 (vw)	1220 (vs)	1218 (s)	1220 (vs)	C-O stretch

TABLE XV (continued)

Raman (cm^{-1})	----------Infrared (cm^{-1})--------			Assignment
Liquid	Liquid	CCl_4	Gas	
1195 (vw)	1188 (sh)	1190 (sh)		
1165 (vw)		1168 (w)		
1120 (vw)	1115 (vs)	1120 (vs)	1133 (vs)	C-O stretch
		1095 (sh)	1105 (sh)	C-O (IR- only) stretch
1030 (vw)	1028 (m)	1028 (w)	1033(w)	
			991 (w)	
980 (vw)	978 (w)	978 (w)	980 (w)	
925 (s)			925 (w)	C-O (Raman - only)stretch
	911 (m)	913 (m)	913 (w)	
			889 (w)	
885 (w)	878 (w)	878 (w)	881 (w)	
860 (w)		855 (vw)		
		840 (vw)		
790 (vw)			785 (w)	
745 (w)			740 (m)	
	725 (m)		731 (m)	
		665 (sh)		
	615 (s)	615 (w)	615 (w)	
550 (w)				
380 (s)				

TABLE XVI

Vibrational Frequencies for trans-1,2-Dimethoxyethylene

Raman (cm^{-1})	Infrared (cm^{-1})			Assignment
Liquid	Liquid	CCl_4	Gas	
	3120 (sh)	3120 (sh)	3120 (sh)	
3105 (m)	3105 (sh)	3100 (sh)	3100 (w)	ethylenic C-H stretch
3080 (w)	3085 (m)	3085 (w)	3090 (w)	
3050 (w)	3055 (m)	3050 (w)	3055 (m)	methyl C-H stretch
3015 (m)	3020 (m)	3015 (m)	3020 (s)	
2945 (m)	2960 (s)	2950 (m)	2960 (s)	
2915 (sh)	2925 (s)	2915 (m)	2930 (s)	
			2855 (m)	
2845 (vs)	2850 (s)	2845 (m)	2845 (m)	methyl C-H stretch
	2805 (sh)			
	2600 (vw)		2600 (vw)	
	2430 (vw)	2430 (vw)	2445 (vw)	
	2370 (vw)	2360 (vw)		
	2325 (vw)	2325 (vw)		
	2240 (vw)		2260 (vw)	
	2145 (w)	2150 (vw)	2170 (w)	
	2110 (vw)	2110 (vw)	2130 (w)	
	2070 (vw)	2070 (vw)	2090 (w)	
	1980 (vw)	1985 (vw)	1995 (vw)	
	1935 (vw)			
	1855 (vw)	1850 (vw)		

TABLE XVI (continued)

Raman (cm^{-1})		Infrared (cm^{-1})		Assignment
Liquid	Liquid	CCl_4	Gas	
	1822 (vw)	1825 (vw)		
	1770 (sh)			
	1737 (w)	1737 (vw)		
1688 (m)			1690 (sh)	
1675 (s)			1678 (w)	
1655 (sh)	1670 (m)	1668 (w)	1670 (w)	C=C stretch
		1655 (vw)	1655 (sh)	
			1475 (sh)	
1460 (w)	1467 (m)	1463 (m)	1465 (m)	
	1455 (m)	1452 (m)		
			1385 (w)	
	1375 (w)	1372 (w)	1375 (w)	
1330 (w)	1333 (vw)	1330 (vw)		
1310 (m)	1310 (m)	1310 (w)	1310 (sh)	
	1300 (sh)	1300 (sh)	1298 (m)	
	1292 (m)	1290 (w)	1288 (m)	
1215 (vw)	1218 (vs)	1218 (vs)	1225 (vs)	C-O stretch
			1182 (s)	
			1178 (s)	
1170 (vw)	1172 (vs)	1172 (vs)	1172 (s)	
1155 (vw)				
1125 (vw)	1135 (vs)	1137 (vs)	1145 (vs)	C-O stretch
			1100 (sh)	

TABLE XVI (continued)

Raman (cm^{-1})	Infrared (cm^{-1})			
Liquid	Liquid	CCl_4	Gas	Assignment
1025 (vw)	1020 (sh)	1020 (sh)	1005 (sh)	
995 (w)	995 (m)	995 (m)	992 (m)	C-O stretch
			968 (m)	
	957 (s)	957 (m)	958 (m)	C-O stretch
945 (w)	945 (m)	945 (m)		
			901 (m)	
910 (vw)	900 (s)	897 (m)	892 (m)	
785 (w)	785 (w)		782 (w)	
	735 (vw)	730 (w)	730 (w)	
		672 (vw)	670 (vw)	
		665 (vw)		
635 (vw)				
605 (vw)	605 (w)	605 (w)		
475 (vw)				
365 (vw)				
320 (vw)				
290 (vw)				
225 (vw)				
190 (vw)				

The heats of atomization were used to calculate the enthalpy changes for the corresponding *cis*-*trans*-isomerizations.

The results for *cis*-HClC=CClH $\rightleftharpoons$ *trans*-HClC=CClH are:

cis-HClC=CClH	*trans*-HClC=CClH
For the C-H bond	
$\bar{v} = 3082 \pm 1\ cm^{-1}$	$\bar{v} = 3080 \pm 1\ cm^{-1}$
$\varepsilon_o = 4.40$ Kcal/mole	$\varepsilon_o = 4.40$ Kcal/mole
$\bar{v}_c = 4186.4 \pm 1.36\ cm^{-1}$	$\bar{v}_c = 4183.6 \pm 1.36\ cm^{-1}$
$D_e^s = 109.90$ Kcal/mole	$D_e^s = 109.75$ Kcal/mole
$D^s = 105.49 \pm 0.072$ Kcal/mole	$D^s = 105.35 \pm 0.072$ Kcal/mole
For the C=C bond	
$\bar{v} = 1587 \pm 1\ cm^{-1}$	$\bar{v} = 1576 \pm 1\ cm^{-1}$
$\varepsilon_o = 2.27$ Kcal/mole	$\varepsilon_o = 2.25$ Kcal/mole
$\bar{v}_c = 5701.5 \pm 3.59\ cm^{-1}$	$\bar{v}_c = 5661.9 \pm 3.59\ cm^{-1}$
$D_e^s = 111.87$ Kcal/mole	$D_e^s = 110.33$ Kcal/mole
$D^s = 109.61 \pm 0.141$ Kcal/mole	$D^s = 108.08 \pm 0.140$ Kcal/mole
For the C-Cl bond	
$\bar{v} = 785.5 \pm 1\ cm^{-1}$	$\bar{v} = 787.5 \pm 1\ cm^{-1}$
$\varepsilon_o = 1.12$ Kcal/mole	$\varepsilon_o = 1.13$ Kcal/mole
$\bar{v}_c = 3407.3 \pm 4.34\ cm^{-1}$	$\bar{v}_c = 3415.9 \pm 4.34\ cm^{-1}$
$D_e^s = 106.70$ Kcal/mole	$D_e^s = 107.35$ Kcal/mole
$D^s = 105.58 \pm 0.272$ Kcal/mole	$D^s = 106.12 \pm 0.270$ Kcal/mole

ΔH atoms $= \Sigma D^s$

cis-HClC=CClH	*trans*-HClC=CClH
ΔH atom $= 531.8 \pm 0.82$ Kcal/mole	ΔH atom $= 531.02 \pm 0.82$ Kcal/mole

Therefore:

$\Delta H_{(isom)} = +\ 0.73 \pm 1.65$ Kcal/mole (calc.)

$\Delta H_{(isom)} = +\ 0.65 \pm 0.07$ Kcal/mole (observed)[47]

For the reaction, *cis*-HFC=CFH $\rightleftharpoons$ *trans*-HFC=CFH

cis-HFC=CFH	*trans*-HFC=CFH
For the C-H bond	
$\bar{v} = 3133 \pm 1\ cm^{-1}$	$\bar{v} = 3112.5 \pm 1\ cm^{-1}$
$\varepsilon_o = 4.48$ Kcal/mole	$\varepsilon_o = 4.45$ Kcal/mole
$\bar{v}_c = 4255.6\ cm^{-1}$	$\bar{v}_c = 4227.8\ cm^{-1}$
$D_e^s = 113.46$ Kcal/mole	$D_e^s = 11.98$ Kcal/mole
$D^s = 108.98 \pm 0.072$ Kcal/mole	$D^s = 107.53 \pm 0.072$ Kcal/mole
For the C=C bond	
$\bar{v} = 1714 \pm 1\ cm^{-1}$	$\bar{v} = 1694 \pm 1\ cm^{-1}$
$\varepsilon_o = 2.45$ Kcal/mole	$\varepsilon_o = 2.42$ Kcal/mole
$\bar{v}_c = 6155.7\ cm^{-1}$	$\bar{v}_c = 6085.9\ cm^{-1}$
$D_e^s = 130.11$ Kcal/mole	$D_e^s = 127.09$ Kcal/mole
$D^s = 127.66 \pm 0.15$ Kcal/mole	$D^s = 124.67 \pm 0.15$ Kcal/mole

cis-HFC=CFH	trans-HFC=CFH
For the C-F bond	
$\bar{v} = 1129 \pm 1\ \mathrm{cm^{-1}}$	$\bar{v} = 1141 \pm 1\ \mathrm{cm^{-1}}$
$\varepsilon_o = 1.61$ Kcal/mole	$\varepsilon_o = 1.63$ Kcal/mole
$\bar{v}_c = 4419\ \mathrm{cm^{-1}}$	$\bar{v}_c = 4465.9\ \mathrm{cm^{-1}}$
$D_e^s = 112.25$ Kcal/mole	$D_e^s = 114.64$ Kcal/mole
$D^s = 110.63 \pm 0.20$ Kcal/mole	$D^s = 113.01 \pm 0.20$ Kcal/mole

$$\Delta H\ \mathrm{atom} = \Sigma D^s$$

$\Delta H\ \mathrm{atom} = 566.85 \pm 0.69$ Kcal/mole	$\Delta H\ \mathrm{atom} = 565.75 \pm 0.69$ Kcal/mole

Therefore:

$\Delta H_{(\mathrm{isom})} = +1.10 \pm 1.39$ Kcal/mole (calc.)

$\Delta H_{(\mathrm{isom})} = +0.928 \pm 0.029$ Kcal/mole (observed)[47]

For the reaction, cis-$\mathrm{CH_3OCH{=}CHOCH_3} \rightleftharpoons$ trans-$\mathrm{CH_3OCH{=}CHOCH_3}$

cis-$\mathrm{CH_3OCH{=}CHOCH_3}$	trans-$\mathrm{CH_3OCH{=}CHOCH_3}$
For the vinyl C-H bonds	
$\bar{v} = 3031 \pm 1\ \mathrm{cm^{-1}}$	$\bar{v} = 3083.8 \pm 1\ \mathrm{cm^{-1}}$
$\varepsilon_o = 4.33$ Kcal/mole	$\varepsilon_o = 4.41$ Kcal/mole
$\bar{v}_c = 4117\ \mathrm{cm^{-1}}$	$\bar{v}_c = 4188.6\ \mathrm{cm^{-1}}$
$D_e^s = 106.28$ Kcal/mole	$D_e^s = 110.02$ Kcal/mole
$D^s = 101.95 \pm 0.07$ Kcal/mole	$D^s = 105.61 \pm 0.07$ Kcal/mole

For the C=C bond

cis-$CH_3OCH{=}CHOCH_3$	trans-$CH_3OCH{=}CHOCH_3$
$\bar{v} = 1693 \pm 1\ cm^{-1}$	$\bar{v} = 1660.8 \pm 1\ cm^{-1}$
$\varepsilon_o = 2.42$ Kcal/mole	$\varepsilon_o = 2.37$ Kcal/mole
$\bar{v}_c = 6082.9\ cm^{-1}$	$\bar{v}_c = 5967.1\ cm^{-1}$
$D_e^s = 127.35$ Kcal/mole	$D_e^s = 122.54$ Kcal/mole
$D^s = 124.93 \pm 0.15$ Kcal/mole	$D^s = 120.17 \pm 0.15$ Kcal/mole

For the methyl C-H bond

cis-$CH_3OCH{=}CHOCH_3$	trans-$CH_3OCH{=}CHOCH_3$
$\bar{v} = 2902 \pm 1\ cm^{-1}$	$\bar{v} = 2948.2 \pm 1\ cm^{-1}$
$\varepsilon_o = 4.14$ Kcal/mole	$\varepsilon_o = 4.21$ Kcal/mole
$\bar{v}_c = 3941.8\ cm^{-1}$	$\bar{v}_c = 4004.6\ cm^{-1}$
$D_e^s = 97.43$ Kcal/mole	$D_e^s = 100.56$ Kcal/mole
$D^s = 93.28 \pm 0.07$ Kcal/mole	$D^s = 96.35 \pm 0.07$ Kcal/mole

For the $\overline{avg}$ C-O bond

cis-$CH_3OCH{=}CHOCH_3$	trans-$CH_3OCH{=}CHOCH_3$
$\bar{v} = 1116 \pm 1\ cm^{-1}$	$\bar{v} = 1084.4 \pm 1\ cm^{-1}$
$\varepsilon_o = 1.59$ Kcal/mole	$\varepsilon_o = 1.55$ Kcal/mole
$\bar{v}_c = 4295.8\ cm^{-1}$	$\bar{v}_c = 4174.4\ cm^{-1}$
$D_e^s = 103.99$ Kcal/mole	$D_e^s = 98.19$ Kcal/mole
$D^s = 102.39 \pm 0.19$ Kcal/mole	$D^s = 96.64 \pm 0.18$ Kcal/mole

$$\Delta H \text{ atom} = \Sigma D^s$$

cis	trans
ΔH atom $= 1298.07 \pm 1.45$ Kcal/mole	ΔH atom $= 1296.03 \pm 1.42$ Kcal/mole

Therefore:

$\Delta H_{(isom)} = +2.04 \pm 2.9$ Kcal/mole (calc.)

$\Delta H_{(isom)} = +1.445 \pm 0.054$ Kcal/mole (observed)

The calculated results agree fairly well with the observed results. The uncertainties in the heats of isomerization are high since large heats of atomization with their respective uncertainties were used to predict rather small enthalpy differences (small differences between large numbers). Large uncertainties in vibrational assignments (± 30 cm^{-1}) and in thermochemical data for reference molecules, such as carbon tetrachloride, etc., limit the accuracy of the n values used in Eqn. (2). Although more reasonable estimates of heats of isomerization uncertainty are obtained by including only the variance in $\bar{\nu}$ and neglecting the variance in n for similar *cis* - *trans* pairs, the resulting error is high in either case.

It should be pointed out that even for semi-empirical "magic formula" calculations developed by Mulliken[137] for energies of atomization, the accuracy was no better than ± 1 to ± 2 Kcal/mole per bond.[121] Errors on this order of magnitude were obtained when Eqn. (2) was used to calculate the heats of atomization of acetone and acetaldehyde as mentioned above.

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(137) R. S. Mulliken, *J. Phys. Chem.*, *56*, 295 (1952).