Thermodynamics of Cis–Trans Isomerizations. The Relative Stabilities of the 1,2-Dimethoxyethylenes

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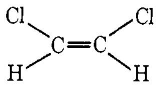
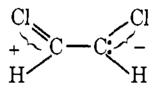
Abstract: Equilibrium constants for the mercuric acetate catalyzed reaction, *c*-MeOCH=CHOMe $\rightleftarrows$ *t*-MeOCH=CHOMe, have been determined in the liquid and vapor phase over the temperature range 30–175° by gas chromatographic analysis. From a screening of 29 catalysts, mercuric acetate, mercuric benzoate, and mercuric salicylate were found to be favorable isomerization catalysts. For the liquid phase reaction, $\ln K = (-799.8/T) + 0.6748$ with $\Delta H° = 1.549 \pm 0.019$ kcal/mol and $\Delta S° = 1.34 = 0.05$ eu/mol. For the vapor phase reaction, $\ln K = -(727.2/T) + 0.8335$ with $\Delta H° = 1.445 \pm 0.054$ kcal/mol and $\Delta S° = 1.66 \pm 0.15$ eu/mol. *cis*-1,2-Dimethoxyethylene (**3**) was more stable relative to its trans isomer (**4**) in both the liquid and vapor phase.

Vinyl ethers or enol ethers represent a class of compounds in which very little is known about the relative stabilities of the corresponding cis–trans pairs. There are examples of allyl to vinyl ether rearrangements involving 1,2 shifts in which the cis configuration predominates over the trans configuration.[1,2] As early as 1924, Crean[3] reported qualitatively on the predominance of the cis configuration at equilibrium for 1-chloropropene. Viehe[4] made similar observations for $HFC{=}CFH$, $CH_3CH{=}CHI$, and the mixed dihaloethylenes, such as, $HFC{=}CHI$, etc. Other studies in which preference for the cis configuration is indicated include $CH_3CH{=}CHBr$[5] and $HClC{=}CH\text{-}CN$.[6] None of these investigations were thermodynamic stability studies since equilibrium constants were measured at only one temperature. More recently heats of isomerization (cis $\rightleftarrows$ trans) were obtained for $CH_3CH{=}CHCl$ (0.700 kcal/mol)[7] and $CH_3CH{=}CHCN$ (0.17 kcal/mol).[8] These compounds were also found to be more stable in the cis configuration.



1a



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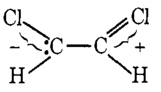

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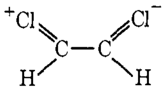
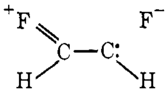


1d

The dihaloethylenes represent a class of compounds in which much data[9–11] have been accumulated testifying to the thermodynamic stabilities of the respective cis isomers. Pitzer and Hollenberg[9] have given a semiquantitative interpretation for the higher stability of *cis*-1,2-dichloroethylene (**1a**). Their argument was based on the importance of contributions from resonance structures such as **1b** and **1c** which were formulated to include the polarity of a carbon–carbon 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 **1b** and **1c**. The sizable negative charge on chlorine has been attributed to d-orbital participation[6,12] as in **1d**. Craig, *et al.*,[10,11] have shown that *cis*-1,2-difluoroethylene has a higher stability relative to its trans isomer (0.928 kcal/mol) than does *cis*-1,2-dichloroethylene (0.650 kcal/mol). They proposed structures (**2a** and **2b**) similar to the ones given by Pitzer and Hollenberg (**1b** and **1c**) for the dichloroethylenes. While d-orbital participation (**1d**) can be involved in resonance stabilization of the dichloro- and dibromoethylenes, it is not a necessary condition for cis isomer stability as evidenced by the high stability of *cis*-1,2-difluoroethylene relative to its trans isomer.



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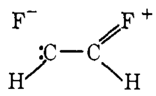
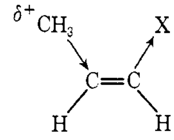


2b

Crumb[6] rationalized the preference for the cis configuration of the halopropenes in terms of permanent dipoles which caused a polar attraction between the C–H and C–X (X = Br, Cl) bonds.



The electron delocalization interpretation of the cis effect is far from complete.[10,11] It does not, however, afford a reasonable proposal for the dihaloethylenes, since the dipole attraction arguments, used for the monohalopropenes, will not serve to explain the cis effect in the symmetrically substituted dihaloethylenes

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(1) T. J. Prosser, *J. Amer. Chem. Soc.*, 83, 1707 (1961).

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

(3) M. Crean, Ph.D. Thesis, University of Brussels, 1924.

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

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

(6) J. W. Crumb, *J. Org. Chem.*, 28, 953 (1963).

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

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

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

(11) N. C. Craig and E. A. Entemann, *J. Amer. Chem. Soc.*, 83, 3047 (1961).

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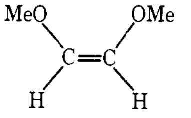
or the dimethoxyethylenes. This is due to the dipoles of the dihalo groups normally operating in the same direction.[6]

The intention of this paper is to demonstrate that enol ethers, the dimethoxyethylenes in particular, are thermodynamically more stable in the cis configuration than in their corresponding trans form, *cis*- and *trans*-1,2-dimethoxyethylene (**3** and **4**, respectively) represent a two-carbon enol ether system containing two adjacent methoxy groups, thereby, permitting analogies to the dihaloethylene series for which thermodynamic and equilibrium data are available.[10,11]



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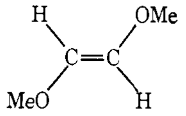

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Experimental Section

1,2-Dimethoxyethylenes. The preparations and characterizations of *cis*- and *trans*-1,2-dimethoxyethylene have been described before by the dechlorination of 1,2-dimethoxy-1,2-dichloroethane[13,14] and by the potassium *tert*-butoxide initiated elimination on substrate 1,1,2-trimethoxyethane.[15,16] However, a more convenient and novel preparation of the olefins has been obtained[17] by the continuous pyrolysis of 1,1,2-trimethoxyethane over alumina at 300°. This preparation was a modification of that used by McElvain[18] for the synthesis of the ethoxy derivative (1,2-diethoxyethylene), the details of which are being submitted in a separate paper.

Gas Chromatographic Analyses. All analyses were performed on a Varian 700-A gas chromatograph using a 10 ft × 0.25 in. column containing 25% THEED (tetrahydroxyethylethylenediamine) on Chromosorb W. Helium was used as a carrier gas and maintained at 115 to 120 ml/min. A detector filament current of 150 mA was used at a detector temperature of 210°. The column oven temperature was 100–120° with an injection temperature of 140°. Injection quantities were between 1.5 and 2.0 μl for liquids. A 10-ml gas syringe was used for vapors. The purity of *cis*-1,2-dimethoxyethylene (bp ~ 101°), established by vapor phase chromatography (vpc), was >99.9%. The corresponding trans isomer (bp ~ 94°) purity was >96% with the cis isomer as the main impurity. Equilibrium constants were determined from gas chromatograms by measuring peak weight ratios of the trans/cis isomer. Quantitative peak estimation was made by cutting and weighing the peaks (four significant figures) and by area triangulation (product of the band height and width at half-height). The experimental error for reproducibility of the measured weight ratios was ±0.0020. The results for area ratios were within experimental error since all the peaks were Gaussian shaped and separated. The chromatograms were calibrated by measuring area ratios (trans/cis) for four synthetic mixtures which had been prepared gravimetrically. The measured area ratios were 0.08249, 0.4442, 0.8992, and 1.915. The corresponding synthetic weight ratios were 0.1593, 0.4152, 0.9588, and 2.143. Therefore, the actual weight ratio of trans/cis = (area ratio)(1.100 ± 0.002).

Determinations of Equilibrium Constants. The samples were handled on a conventional vacuum system pumped to gauge pressure of 0.1 mm or less. At most temperatures, equilibrium was approached from both the cis-rich and trans-rich sides (Table I). The isomerizations were carried out in a constant temperature bath (±0.1°) using ~20% $Hg(OAc)_2$ as catalyst. The *cis*- and *trans*-1,2-dimethoxyethylenes (**3** and **4**, respectively) were transferred using a 1-ml syringe to a tared (±0.1 mg) ampoule containing catalyst. The filled ampoules were temporarily capped with a rubber serum cap, cooled down to −60°, sealed with an oxygen–methane torch, and allowed to equilibrate for 38 to 48 hr. The liquid (after equilibration) was transferred by quantitaive vpc. This ensured that the liquid portion was removed from any traces of catalyst, thereby preventing further isomerization on the chromatographic column. Controls were run without catalyst and no isomerization was observed. For the liquid phase, isomerizations were measured from 30 to 175°.

The techniques for the vapor phase were similar but more complex on a physical handling and transferring basis. Mercuric acetate was dissolved in benzene and added to a 500-ml standard tapered flask which contained 4-mm unglazed porcelain berl saddles. The solvent was removed by a rotary evaporating apparatus leaving the catalyst deposited on the berl saddles. The olefin samples (**3** or **4**) were added to the reaction flask by conventional vacuum transfer techniques. The 500-ml reaction flask was evacuated (<0.1 mm) on one leg of the vacuum system. The sample was placed in a 25-ml flask on a separate leg, cooled to −60°, then evacuated. After closing off the main leg of the system, the sample was allowed to warm up to room temperature and simultaneously expand into the reaction flask to a pressure of 30 mm. The reaction flask was removed from the vacuum system and was allowed to equilibrate in a constant temperature bath. After the isomerization was complete (40–48 hr), the contents of the flask were brought up to atmospheric pressure with nitrogen and analyzed by vpc using a 10-ml gas syringe.

Similar analyses were made by transferring the isomerized vapor (at the temperature of the run) directly on the vacuum system and condensing it into a preevacuated receiver at −60°. The liquid sample (free of catalyst) was analyzed by quantitative gas chromatography using 1.5-μl injection samples. Both methods of analysis gave results that were within experimental error.

An analysis of variance was performed on both sets of data (liquid and vaor phase). The confidence limits on $\Delta H°$ and $\Delta S°$ are at the 90% probability 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, which signifies that 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. An independent experimental error analysis was utilized to give an indication as to the minimal errors involved due to reproducibility of area ratios, temperature variation, etc. This was accomplished in the standard fashion by taking partial differentials of the van't Hoff equation. The results were consistent with the statistical error analysis.

From a screening of several catalysts, mercuric acetate, mercuric benzoate, and mercuric salicylate were found to be favorable isomerization catalysts. Other catalysts, such as AgF, HgF_2, $HgCl_2$, $CuCl_2$, $CuBr_2$, $PdCl_2$, I_2, and $Pd(OAc)_2$, polymerized the dimethoxyethylenes. The reactions were usually rapid and exothermic.

Below 175° side reactions are not extensive and the trans/cis ratio appears to be a reliable measure of the equilibrium constant. At temperatures above 175°, however, there was some indication as to side products (lower and higher boiling compounds) as evidenced by gas chromatography. In addition, there is considerable mercury formation above 175°. Fieser[19] observed that the addition of mercuric acetate to olefins, involving the stepwise reduction of mercury ($Hg^{2+} \rightarrow Hg^{+} \rightarrow Hg^{0}$) with the simultaneous oxidation of the olefin, required temperatures greater than 150°.

Infrared and Raman Spectra. Infrared spectra were obtained on a Perkin-Elmer grating spectrophotometer (Model 457), using NaCl cells with CCl_4 solvent (1% solution), neat (between NaCl disks) and in the vapor phase using a 10-cm gas cell (cesium iodide windows) at a pressure of 8 Torr. Raman spectra were obtained on a Beckman Model 700 laser raman spectrometer which employed a He–Ne laser. The average vibrational stretching frequencies in reciprocal centimeters for the previously unreported *cis*- and *trans*-1,2-dimethoxyethylenes (**1** and **2**, respectively) are: for **1**, $\nu_{C=C} = 1693$, $\nu_{\text{methyl C–H}} = 2902$, $\nu_{\text{vinyl C–H}} = 3031$, $\nu_{C-O} = 1116$; for **2**, $\nu_{C=C} = 1616$, $\nu_{\text{methyl C–H}} = 2948$, $\nu_{\text{vinyl C–H}} = 3084$, $\nu_{C-O} = 1084$. The C–H out-of-place bending vibrations (γ) for **1** and **2** are 718 and 960 cm^{-1}, respectively. Details of the spectra

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(13) H. Baganz, K. Praefcke, and J. Rost, *Chem. Ber.*, **96**, 2657 (1963).

(14) S. Iwatsuki, S. Iquchi, and Y. Yamashita, *Kogyo Kagaku Zasshi*, 68 (12), 2463 (1965); *Chem. Abstr.*, **65**, 3979e (1965).

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(19) F. L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 644–652.

and full assignments of the infrared- and Raman-active fundamentals for **1** and **2** are being submitted in a separate paper.

Results

1,2-Dimethoxyethylene Isomerization. The results of the isomerization equilibrium studies in the liquid phase for the reaction

$$c\text{-MeOCH}{=}\text{CHOMe} \underset{\text{Hg(OAc)}_2}{\rightleftharpoons} t\text{-MeOCH}{=}\text{CHOMe} \qquad (1)$$

3 **4**

are summarized in Table I. Figure 1[20] shows the temperature dependence of ln K over a 150° range for the liquid phase isomerization. A least-squares fit gives ln $K = (-779.8/T) + 0.6748$. Similarly, Figure 2 shows the temperature dependence of ln K over a 120° range for the vapor phase isomerization. The least-squares result is ln $K = (-727.1/T) + 0.8335$. The vapor phase data are summarized in Table II.[20]

Table I. Observed Equilibrium Constants for the Reaction $c\text{-CH}_3\text{OCH}{=}\text{CHOCH}_3\text{(l)} \underset{\text{Hg(OAc)}_2}{\rightleftharpoons} t\text{-CH}_3\text{OCH}{=}\text{CHOCH}_3\text{(l)}$

Temp,[a] °C	Time, hr	Number of runs Pure cis	 Pure trans	Equilibrium constant[b]
30	44	2	1	0.150 ± 0.004
40	38	3		0.162 ± 0.003
50	40	2	1	0.172 ± 0.002
60	48	3		0.192 ± 0.003
70	48	3		0.202 ± 0.004
80	36	2	1	0.213 ± 0.002
90	40	3		0.231 ± 0.007
100	38	2	1	0.246 ± 0.004
110	38	3		0.255 ± 0.006
120	40	3		0.273 ± 0.008
130	48	3		0.282 ± 0.008
150	36	2	1	0.315 ± 0.009
175	38	2	1	0.338 ± 0.009

[a] Temperatures were maintained to within ±0.1°. [b] All 39 values of the equilibrium constant were used in the least-squares analysis. The values shown here are the mean values.

The stability of the cis isomer (**3**) is slightly higher in the liquid phase ($\Delta H° = 1.549 \pm 0.019$ kcal/mol) than in the vapor phase ($\Delta H° = 1.445 \pm 0.054$ kcal/mol), as expected.[21,22] The positive values for the entropy change indicate that the trans isomer has a larger measure of randomness associated with it for both the vapor and liquid phase. Internal rotation (free rotation around the Me–O bond) occurs more freely for the trans isomer.[8,23] This occurence of free rotation was larger in the vapor phase ($\Delta S° = 1.66 \pm 0.15$ eu/mol) than in the liquid phase ($\Delta S° = 1.34 \pm 0.05$ eu/mol), as expected. These results are significant at the 90% probability level.

Discussion

A summary of relative stabilities in Table III compares the experimental enthalpies of isomerization ($\Delta H°$), temperature ranges, and range of equilibrium constants for the cis-to-trans isomerization of the dimethoxyethylenes, the dihaloethylenes, and related molecules. It is an extension of the compilation made by Craig, *et al.*,[10] on the thermodynamic quantities of the dihaloethylenes. In addition, the dimethoxyethylenes lend more supporting evidence for the cis effect (higher stability of the cis isomer relative to its trans isomer) as found in the haloethylenes and halopropenes.

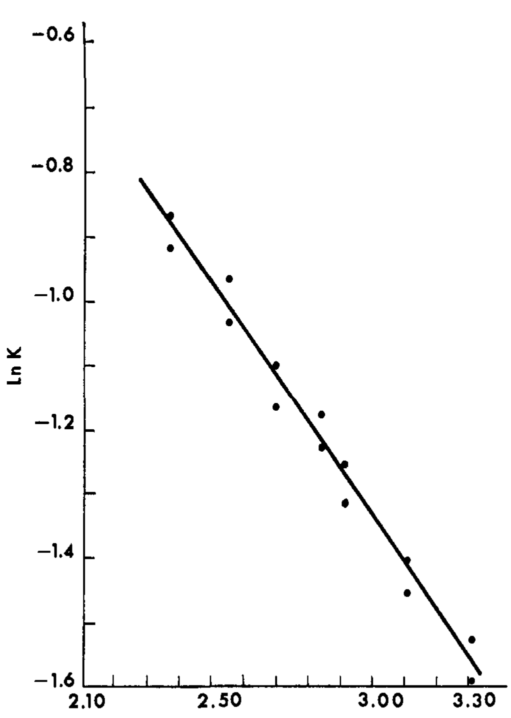
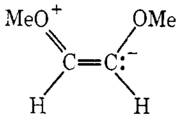


Figure 2. The temperature dependence of the equilibrium constant for the cis–trans isomerization of dimethoxyethylene in the vapor phase. The line is from least-squares analysis.

Resonance arguments similar to those of Pitzer[9] (**1b** and **1c**) and Craig[10,11] (**2a** and **2b**) could be advanced to justify the cis effect of the dimethoxyethylenes as shown in **5a**–**5d**. However, there is evidence



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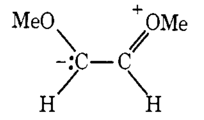

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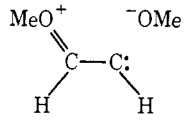

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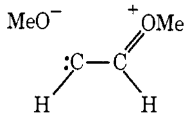

5d

that there is more involved than just resonance in explaining the greater preference (free energy) for the cis configuration in dimethoxy- and difluoroethylene since the gauche conformers of 1,2-dimethoxyethane[25] and 1,2-difluoroethane[21,26] are more stable than the trans conformers. Resonance arguments will not suffice for these saturated analogs.

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(20) See the paragraph at the end of the paper regarding supplementary material.

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

(22) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).

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

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

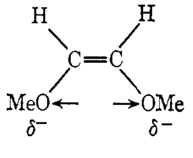
(26) R. J. Abraham and K. Parry, *J. Chem. Soc. B*, 539 (1970).

Table III. Thermodynamic Functions for Cis–Trans Isomerization of 1,2-Dimethoxyethylene and Related Compounds

Compound	Ref	Temp range, °K	$\Delta H°$, kcal/mol	Range of K's
$CH_3OCH{=}CHOCH_3$(l)	*a*	150	1.549 ± 0.019	0.150–0.338
$CH_3OCH{=}CHOCH_3$(g)	*a*	125	1.445 ± 0.054	0.210–0.410
$FN{=}NF$(g)	*b*, *c*, 19	75	3.00 ± 0.3	
$HFC{=}CFH$(g)	19, 20, 33	285	0.928 ± 0.029	0.401–0.582
$HFC{=}CClH$(g)	19, *d*	280	0.780 ± 0.020	0.485–0.669
$HClC{=}CClH$(g)	*e*, 24, 19,	90, 50	0.650 ± 0.070	0.577–0.683
$HBrC{=}CBrH$(g)	19, 20, *g*	60	0 ± 0.130	
$HBrC{=}CBrH$(l)	19, *f*	100	0.320 ± 0.200	
$HIC{-}CIH$(l)	*h*, *i*	30	-1.550 ± 1.0	0.681–0.792
$HIC{=}CIH$(g)	19, *j*	140	0 ± 0.2	
$HFC{=}CFCl$(g)	19, *k*		0.01 ± 0.180	
$HClC{=}CHCH_3$(g)	38	380	0.700 ± 0.064	0.297–0.600
$CH_3CH{=}CHCN$(g)	39	260	0.17 ± 0.12	0.640–0.833

[a] Experimental values determined in the present investigation. [b] C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Amer. Chem. Soc.*, **81**, 6397 (1959). [c] G. T. Armstrong and S. Marantz, *J. Chem. Phys.*, **38**, 169 (1963). [d] N. C. Craig, Y. S. Lo, L. G. Piper, and J. C. Wheeler, *J. Phys. Chem.*, **74**, 1712 (1970). [e] R. E. Wood and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 1650 (1941). [f] A. R. Olson and W. Maroney, *ibid.*, **56**, 1320 (1934). [g] R. M. Noyes and R. G. Dickinson, *ibid.*, **65**, 1427 (1943). [h] R. M. Noyes, R. G. Dickinson, and V. Schomaker, *ibid.*, **67**, 1319 (1945). [i] S. F. Miller, A. Weber, and F. F. Cleveland, *J. Chem. Phys.*, **23**, 44 (1955). [j] S. Furuyama, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, **72**, 3204 (1968). [k] N. C. Craig, D. A. Evans, L. G. Piper, and V. L. Wheeler, *ibid.*, **74**, 4520 (1970).

However, for 1,2-dibromo- and 1,2-dichloroethylene,[21] the trans conformers are more stable than the gauche conformers and resonance arguments alone are sufficient to justify the high cis isomer stability for their unsaturated analogs. 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.[27,28] 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 (**6**). 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 causes a shift in electron density toward the carbon–carbon single bond resulting in a higher stability for the gauche form.



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Nonbonded intramolecular interactions between the methoxy groups are important for the observed cis olefin stability. Bartell[29] and others[30] have pointed out that, although isomerization energies can be small resulting from small differences between large quantities, intramolecular nonbonded repulsions can be quite significant. A possible explanation for the higher $\Delta H°$ of isomerization for the dimethoxyethylenes, as compared with the difluoroethylenes (Table III), 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.

Table IV. Stretching Frequencies (C═C Bond) for the Dimethoxy- and Some Dihaloethylenes

Compound	Ref	Frequency, ν $\pm$ 1 cm^{-1}
c-MeOCH═CHOMe	*a*	1693
t-MeOCH═CHOMe	*a*	1661
c-HFC═CFH	*b*, *c*	1714
t-HFC═CFH	*b*, *c*	1694
c-HClC═CClH	*d*, *e*	1587
t-HClC═CClH	*d*, *e*	1576
c-HFC═CClH	*f*	1661
t-HFC═CClH	*f*	1647

[a] Values determined from the present study. [b] N. C. Craig and E. A. Entemann, *J. Chem. Phys.*, **36**, 243 (1962). [c] N. C. Craig and V. Overend, *ibid.*, **51**, 1127 (1969). [d] H. J. Berstein and D. A. Ramsay, *ibid.*, **17**, 556 (1949). [e] M. Hopper, Ph.D. Thesis, University of Minnesota, 1967. [f] N. C. Craig, Y. S. Lo, L. G. Piper, and J. C. Wheeler, *J. Phys. Chem.*, **74**, 1712 (1970).

In support of the above arguments, the nmr spectra for the dimethoxyethylenes[17] and the difluoroethylenes[31,32] indicate that the cis vinyl protons for both cases absorb at approximately 1 ppm upfield (higher field) from the corresponding trans isomer. The resolution of the spectra was ±0.5 cps (±0.01 ppm). This indicates that the electron density in the cis double bonds must be higher than in the corresponding trans double bond since the cis-vinyl protons absorbed at a higher field than the trans-vinyl protons.[13,32] Apparently the cis-vinyl protons are more effectively shielded[33] than the trans protons and this is an indication of a stronger C═C bond (higher electron density) for the cis isomer of both dimethoxy- and difluoroethylene.

Another indication for the stronger cis C═C bond in **3** is that the average C═C stretching frequency for **3** occurs at a higher frequency (1693 ± 1 cm^{-1}) than for **4** (1661 ± 1 cm^{-1}). 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. Table IV

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shows the average C=C stretching frequency for the dimethoxy- and some dihaloethylenes. In all cases, the stretching frequencies for the cis isomers occur at higher frequencies. A correlation was made between the enthalpies of isomerization (cis $\rightleftarrows$ trans) for dimethoxyethylene, $C_2H_2F_2$, C_2H_2ClF, $C_2H_2Cl_2$, and $C_2H_2Br_2$ (Table III), and the differences between the C=C stretching frequencies squared ($\Delta\nu^2_{C=C}$) for the corresponding cis and trans isomers as shown in Figure 3. A smooth curve can be drawn through the data indicating that the $\Delta\nu_{C=C}$ values between the cis–trans pairs are also reflected in the corresponding energies of isomerization. The major differences in $\Delta H°$ (preference for the cis configuration) are apparently associated with the stronger C=C bond in the cis olefins. However, the fact that the correlation is nonlinear suggests that not all of the energy differences reside in the differences in double bond strength. In the dimethoxy- and dihaloethylenes for example, smaller energy changes in the C–X, C–O, and C–H bond strengths are also involved.[17]

It is interesting to notice that a similar situation now exists for the group VIa series as was proposed for the dihaloethylene series on the basis of electronegativity differences.[10,11] Table III indicates an increase in relative stability of the cis isomers as the electronegativity of the halogen atom is increased. There is recent evidence which indicates that the isomerization of 3-substituted methacrylonitriles[24] yield 78% of the cis isomr at equilibrium when the substituent group is MeO– and only 68% cis isomer when it is EtS–. These results are consistent with and in the same direction as the halogen series.

In summary, the arguments presented above appear to show ample evidence for the preference of the cis configuration of 1,2-dimethoxyethylene. Explanations employing dipole–dipole repulsions between electronegative methoxy groups with resulting electron density shifts served to explain the apparent cis effect for both the saturated and unsaturated compounds. The nonbonded intramolecular interactions between the methoxy groups resulted in a stronger C=C bond for the cis isomer, as evidenced by nmr, infrared, etc., which resulted in an increase in relative stability for the cis isomer.

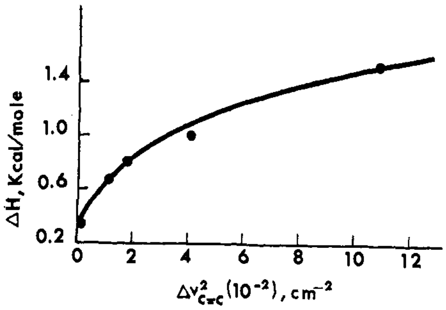

Figure 3. A plot of enthalpies of isomerization ($\Delta H°$) *vs.* the square of the difference between the carbon–carbon double bond stretching frequencies ($\Delta\nu^2_{C=C}$) for corresponding cis–trans pairs.

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Supplementary Material Available. Figure 1 (a plot of ln k *vs.* $1/T$ for the liquid phase) and Table II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche referring to code number JACS-73-5491.