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Thermodynamics of cis-trans Isomerizations. II. The

1-Chloro-2-fluoroethylenes, 1,2-Difluorocyclopropanes, and Related Molecules¹

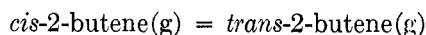
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For the cis-to-trans reaction of 1-chloro-2-fluoroethylene the equilibrium constant over the temperature range 475–760°K is given by $\log K = -171.0^\circ\text{K}/T + 0.0462$. As a consequence $\Delta H^\circ_{615} = 780 \pm 20$ cal/mol and $\Delta S^\circ_{615} = 0.21 \pm 0.04$ cal/deg-mol. For the cis-to-trans reaction of 1,2-dichloroethylene $K = 0.645 \pm 0.013$ at 562°K. This gas chromatographically derived value confirms previous dielectric constant measurements. Critically evaluated electronic energy differences for a series of cis-trans isomerizations in the gas phase are: N_2F_2 , 3050 \pm 400; $\text{C}_2\text{F}_2\text{H}_2$, 1080 \pm 120; C_2ClFH_2 , 870 \pm 110; $\text{C}_2\text{Cl}_2\text{H}_2$, 720 \pm 160; $\text{C}_2\text{Br}_2\text{H}_2$, 250 \pm 330; and $\text{C}_2\text{F}_2\text{ClH}$, 80 \pm 230 cal/mol. In each case the cis isomer has the lower energy. This cis effect is rationalized in terms of "nonbonded" forces. The synthesis of the cis and trans isomers of 1,2-difluorocyclopropane is described. A preliminary value for the equilibrium constant for the cis-to-trans isomerization of these isomers is 11.7 ± 0.5 at 585°K, from which it appears that the trans isomer has the lower energy. This result is remarkable in view of $H^\circ_{\text{gauche}} - H^\circ_{\text{trans}} = 0$ for 1,2-difluoroethane as well as the low energy of cis- $\text{C}_2\text{F}_2\text{H}_2$.

In the 1930's Kistiakowsky and his coworkers at Harvard made a series of precise measurements of enthalpies of hydrogenation from which accurate resonance energies and energies of isomerization were derived. In particular, for the reaction



they found that the energy change at 355°K was -950 ± 120 cal/mol.² Subsequent application of this method to more elaborately substituted ethylenes has given values for isomerization energies which include -940 cal/mol for $\text{MeHC}=\text{CH}(i\text{-Pr})$,^{3a} -4220 for $\text{Et-OOCHC}=\text{CHCOOEt}$,^{3b} -5700 for $\text{PhHC}=\text{CHPh}$,^{3b} and -9370 for $(\text{tert-Bu})\text{HC}=\text{CH}(\text{tert-Bu})$.^{3a} The presently available spectroscopic and thermodynamic data are, however, insufficient to permit separation of the electronic energy contribution in ΔE° from the contributions due to other degrees of freedom of the molecules. Nonetheless, it seems likely that the nonelectronic contributions nearly cancel out (*vide infra*), and thus the trans configuration has the lower electronic energy. These electronic energy differences for 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.⁴

In contrast to the foregoing examples, a growing body of experimental data on haloethylenes (and a diazene) strongly suggests that cis isomers can have the lower electronic energy. Reasonably well established gas-phase examples of this effect include the 1,2-dichloroethylenes,⁵ the 1,2-difluoroethylenes,^{1,6} and the 1,2-difluorodiazene.⁷ Fragmentary data exist for many others.^{5,8} In mixed dihaloethylenes the preference (free energy) for the cis configuration is sustained

throughout the series C_2FCIH_2 to C_2FIH_2 .^{6,8a,b} Enthalpy differences ranging from 700 to 3000 cal/mol are found in fluorine- and chlorine-substituted species. Haloethylenes are sufficiently simple that complete spectroscopic data may be confidently sought and employed to isolate the electronic energy change. In addition to giving experimental results from the isomerization equilibrium of the 1-chloro-2-fluoroethylenes and, secondarily, confirmatory data for the 1,2-dichloroethylenes, the main purpose of the present paper is to provide a thorough analysis for the whole series of halogenated ethylenes (and a diazene) for which reasonably complete data are now available.

(1) Part I: N. C. Craig and E. A. Entemann, *J. Amer. Chem. Soc.*, **83**, 3047 (1961).

(2) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **57**, 876 (1935). See also E. J. Prosen, F. W. Maron, and F. D. Rossini, *J. Res. Natl. Bur. Stand.*, **46**, 106 (1951), who obtained -750 ± 580 cal/mol from enthalpies of combustion.

(3) (a) R. B. Turner, D. E. Nettleton, and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958); (b) R. B. Williams, *ibid.*, **64**, 1395 (1942); (c) for values for other ethylenes see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962.

(4) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. Newman, Ed., Wiley, New York, N. Y., 1956.

(5) (a) L. Ebert and R. Bull, *Z. Phys. Chem. Abt. A*, **152**, 451 (1931); (b) A. R. Olson and W. Maroney, *J. Amer. Chem. Soc.*, **56**, 1320 (1934); (c) R. E. Wood and D. P. Stevenson, *ibid.*, **63**, 1650 (1941).

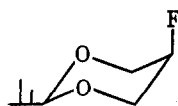
(6) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

(7) (a) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Amer. Chem. Soc.*, **81**, 6397 (1959); (b) G. T. Armstrong and S. Marantz, *J. Chem. Phys.*, **38**, 169 (1963).

(8) (a) H. Van der Walle, *Bull. Soc. Chim. Belges*, **47**, 217 (1938); (b) H. G. Viehe and E. Franchimont, *Chem. Ber.*, **96**, 3153 (1963); (c) H. G. Viehe, J. Dale, and E. Franchimont, *ibid.*, **97**, 244 (1964); (d) A. Demiel, *J. Org. Chem.*, **30**, 2121 (1965); (e) N. C. Craig and D. A. Evans, *J. Amer. Chem. Soc.*, **87**, 4223 (1965).

Preference (free energy) for the *cis* configuration is apparently not limited to halogenated ethylenes. It is also found in 1-halopropylenes⁶ with 1-chloropropylene⁹ and 1-bromopropylene¹⁰ being the best documented examples in the recent literature. For crotononitrile ($\text{CH}_3\text{HC}=\text{CHCN}$), Butler and McAlpine have obtained a positive enthalpy change for the *cis*-to-*trans* reaction from the temperature coefficient of the equilibrium constant.¹¹ These propylene examples have been rationalized in terms of polar attraction between CH and CX bonds with and without hyperconjugation. Such an explanation has also been given for the remarkably low barriers for CH_3 -group rotation in *cis*-1-fluoropropylene¹² and in *cis*-1-chloropropylene.¹³ A dipole attraction argument will not serve, however, to explain the effect in the symmetrically substituted haloethylenes.

There is evidence that the double bond is not required for an apparent net attraction to occur between two identical (or neighboring) halogen atoms.¹⁴ From vibrational spectroscopic studies Klaboe and Nielsen deduced a 0 ± 200 cal/mol energy difference between *gauche* and *trans* conformers of 1,2-difluoroethane near room temperature.¹⁵ Abraham and Parry have alluded to unpublished nmr observations¹⁶ that support the conclusions of Klaboe and Nielsen. El Bermami and Jonathan found only -200 ± 80 cal/mol for the *gauche*-to-*trans* conversion in 1-chloro-2-fluoroethane.¹⁷ These particular ethane cases are made all the more noteworthy by the failure of Abraham and Parry's empirical potential function to account for the rotational energy differences. In contrast, their function which includes an ethane-like threefold barrier term, a pair of Buckingham-like van der Waals terms, and a dipole term, was moderately successful in accounting for conformational energy differences in many other halogenated ethanes.¹⁶ Yet, Dellepiane and Zerbi have recently shown that similar empirical potential functions for internal rotation give a poor account of the shape of the barrier for a number of experimentally well-developed cases.¹⁸ Nmr studies, supported by a partial vibrational assignment, also suggest that 1,2-dimethoxyethane is another example in which the *gauche* configuration is of lower energy than the *trans*.^{19,20} Further evidence for a *cis* preference in the absence of a double bond comes from the studies by Eliel and Kaloustian of the equilibrium for the *cis*-*trans* isomerization of 5-substituted 2-isopropyl-1,3-dioxanes such as



for which $\Delta G^\circ_{298} = 830$ cal/mol for the *cis*-to-*trans* conversion in benzene.²¹

It has seemed to us that a thorough investigation of the 1,2-difluorocyclopropanes, which are spectroscopi-

cally manageable and configurationally well defined, would clarify the importance of the double bond in the *cis* effect. Models show that the FF distance in the *cis* and *trans* isomers of these cyclopropanes should be within 0.1 Å of the corresponding distances in the 1,2-difluoroethylenes and 1,2-difluoroethanes. Preliminary results of the cyclopropane study are reported in this paper.

Experimental Section

1-Chloro-2-fluoroethylenes. The preparation and characterization of the *cis* and *trans* isomers of C_2FClH_2 have been described before.²² As in the earlier study of the $\text{C}_2\text{F}_2\text{H}_2$ isomerization equilibrium,¹ gas chromatography was employed to analyze the equilibrium mixtures of the iodine-catalyzed, gas-phase isomerization. Samples were handled on a vacuum system as described before, but the oven was improved. A Bayley Instrument Co. (Model 117) controller was installed with its resistance element in the aluminum cylinder which enclosed the reaction cell, and three chromel-alumel thermocouples were positioned in and around the cell to check for temperature uniformity. At most the temperature varied about 1° over the cell volume. At each temperature equilibrium was approached from both the *cis*-rich and *trans*-rich sides. Gas chromatographic analyses were performed at 65° on a 4-m column packed with dibutyl phthalate on firebrick. Peaks representing the two isomers were well separated and had near-Gaussian shapes. Areas of the peaks were calculated by the triangle approximation after initial planimeter measurements gave the same results for ratios of areas within experimental error. Measurements on prepared mixtures showed that no correction was needed to observe *trans*/*cis* ratios within 0.5%. In most cases samples were equilibrated for several days and showed little evidence of volatile side products and only slow pressure decreases due to polymerization.

- (9) J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963).
- (10) (a) K. E. Harwell and L. F. Hatch, *J. Amer. Chem. Soc.*, **77**, 1682 (1955); (b) P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).
- (11) J. N. Butler and R. D. McAlpine, *Can. J. Chem.*, **41**, 2487 (1963).
- (12) R. A. Beaudet and E. B. Wilson, Jr., *J. Chem. Phys.*, **37**, 1133 (1962).
- (13) (a) R. A. Beaudet, *ibid.*, **40**, 2705 (1964); (b) V. W. Weiss, P. Beak, and W. H. Flygare, *ibid.*, **46**, 981 (1967).
- (14) R. G. Ford and R. D. Beaudet, *ibid.*, **48**, 1352 (1968); **48**, 4671 (1968).
- (15) P. Klaboe and J. R. Nielsen, *J. Chem. Phys.*, **33**, 1764 (1960).
- (16) R. J. Abraham and K. Parry, *J. Chem. Soc. B*, 539 (1970).
- (17) M. F. El Bermami and N. Jonathan, *J. Chem. Phys.*, **49**, 340 (1968).
- (18) G. Dellepiane and G. Zerbi, *J. Mol. Spectrosc.*, **24**, 62 (1967).
- (19) T. M. Connor and K. A. McLauchlan, *J. Phys. Chem.*, **69**, 1888 (1965).
- (20) R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, **23A**, 391 (1967).
- (21) E. L. Eliel and M. K. Kaloustian, *Chem. Commun.*, 290 (1970).
- (22) N. C. Craig, Y.-S. Lo, L. G. Piper, and J. C. Wheeler, *J. Phys. Chem.*, **74**, 1712 (1970).

Pressures in the reaction vessel ranged from 100 to 300 Torr.

1,2-Dichloroethylenes. Samples of Aldrich Chemical Co. *cis*-C₂Cl₂H₂ and *trans*-C₂Cl₂H₂ were used without further purification other than degassing and vacuum distillation. The equilibrium study at 288° followed the same procedure as for the 1-chloro-2-fluoroethylenes. For the gas chromatographic analyses a 4-m column packed with silicone oil on firebrick was used at 90°. Sketching was employed to untangle the small region of overlap between the two peaks, and areas were measured with a planimeter. Side reactions were not extensive.

1,2-Difluorocyclopropanes. *cis*- and *trans*-1,2-difluorocyclopropane were prepared by a photolytic reaction between diazomethane²³ and 1,2-difluoroethylene (source, Peninsular Chem Research Co.). Photolysis of approximately 1:1 mixtures of diazomethane and olefin in the liquid phase at -80° gave a yield of cyclopropanes of about 20%.²⁴ The vented reaction tube was immersed in an ethanol-Dry Ice mixture in an un-silvered Pyrex dewar flask and irradiated from the outside with light from a medium pressure mercury arc. Pure samples of *cis* and *trans* isomers were obtained by gas chromatographic fractionation on a 4-m column packed with tricresyl phosphate on firebrick. After the *trans* isomer (bp ~11°) was eluted at room temperature, the column temperature was raised to 75° to hasten the elution of the *cis* isomer (bp ~46°). Identities of the isomers were established by means of vapor densities, proton nmr, and infrared spectra.²⁵ The exploratory isomerization studies were carried out in a tube furnace with temperature control of ±5°. Both *cis*-rich and *trans*-rich samples were equilibrated. At temperatures below 300° the reaction was too slow even with iodine catalysis. Above 340° side reactions were overwhelming. Relatively large amounts of iodine were used. Gas chromatographic analyses were done at a constant temperature of 57° on the tricresyl phosphate column.

Statistical Thermodynamic Calculations. Calculations based on the rigid-rotor, harmonic oscillator model²⁶ were performed with program STATHEM on an IBM 360/44 computer. Input consisted of Cartesian coordinates and masses for atoms, vibrational fundamentals, and rotational symmetry numbers. Output included principal moments of inertia as well as tables of thermodynamic functions from 100 to 2000°K in 100° intervals. Tables of output data are on file.

Results

For the reaction

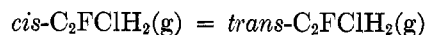


Table I summarizes the equilibrium constant measurements and Figure 1 shows the temperature dependence of log *K* over the 280° range. A least-squares fit gives

$$\log K = (-171.0 \pm 4.9^\circ\text{K})/T + (0.0462 \pm 0.0083)$$

from which $\Delta E^\circ_{620} = 780 \pm 20$ cal/mol and $\Delta S^\circ_{620} = 0.21 \pm 0.04$ cal/deg-mol. Figure 1 also includes two "ungefährer" values of the equilibrium constant reported by Viehe.⁶ They were not used in the least-squares analysis. A rigid-rotor, harmonic-oscillator treatment of the spectroscopic data gives $\Delta S^\circ_{620} = 0.24 \pm 0.2$ cal/deg-mol, $\Delta E^\circ_{\theta 620} = 185 \pm 20$ cal/mol, and $\Delta E_{zp} = -270 \pm 70$ cal/mol.^{22,27} As a consequence $\Delta E_e = \Delta E^\circ_{620} - \Delta E^\circ_{\theta 620} - \Delta E_{zp} = 860 \pm 110$ cal/mol. The excellent agreement between the entropy change derived from the equilibrium constant measurements and the entropy change calculated from the spectroscopic data is reassuring. The ±0.2 uncertainty in the calculated ΔS° is due primarily to the estimated uncertainties in the assignments of the vibrational fundamentals.

Table I: Observed Equilibrium Constants for the Reaction *cis*-C₂FClH₂(g) = *trans*-C₂FClH₂(g)

Temp, °K	—Number of analyses ^a —		Equilibrium constant ^b
	<i>cis</i> - rich	<i>trans</i> - rich	
474	1		0.485
		3	0.485 ± 0
540	4		0.536 ± 0.003
		4	0.549 ± 0.002
		5	0.527 ± 0.003
		3	0.533 ± 0.005
554	4		0.544 ± 0.011
		5	0.558 ± 0.007
615	5		0.587 ± 0.007
		6	0.576 ± 0.007
681	5		0.621 ± 0.007
		3	0.630 ± 0.003
756	5		0.661 ± 0.004
		2	0.669 ± 0.002

^a After mixture had apparently reached equilibrium. ^b With average difference from the average. All 55 values of the equilibrium constant were used in the least-squares analysis.

(23) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963). *N*-Methyl nitrosourea was obtained from Columbia Organic Chemical Co.

(24) This methylene reaction was not stereospecific. No reaction was observed in repeated attempts to photolyze ketene-difluoroethylene mixtures in the liquid phase at -80°. Gas-phase photolysis of the ketene-ethylene mixtures gave complex product mixtures and low yields of the difluorocyclopropanes.

(25) Paper II4, 23rd Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, September 1968. Principal gas-phase ir bands, *cis*-c-C₃F₂H₄: 3103B, 3063C, 1449B, 1346A, 1225B, 1150A, 1136C, 1060A, 1047C, 860B, 785B, 739A, 621A, 468C, 318A, ~210 cm⁻¹; *trans*-c-C₃F₂H₄: 3110C, 3070A, 1457 distorted B?, 1304A, 1159A, 1072A, 1003C, 961B, 842B, 782A, 452A, 414B, ~300 two bands overlapped.

(26) G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, "Thermodynamics," 2nd ed, McGraw-Hill, New York, N. Y., 1961, Chapter 27.

(27) θ = thermal energy; zp = zero point vibrational energy; and e = electronic energy.

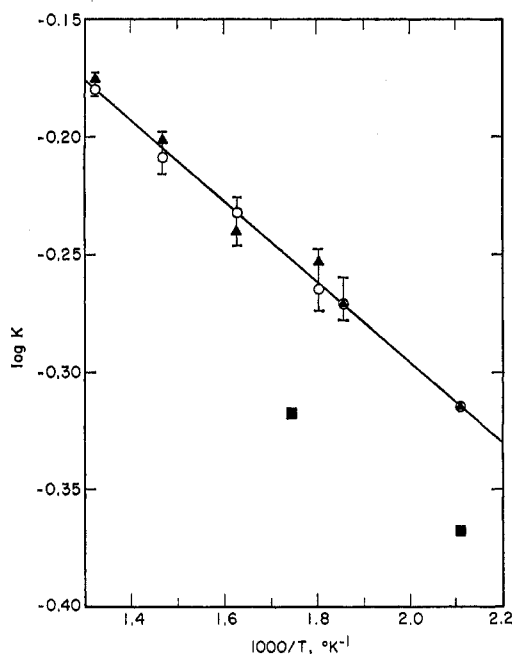
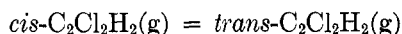


Figure 1. Temperature dependence of the equilibrium constant for the cis-trans isomerization of $C_2Cl_2H_2$. Viehe (ref 6) ■, this research: cis-rich, ○; trans-rich, ▲. Line is from least-squares analysis.

Figure 2 is a composite of all of the published values for the equilibrium constant for the reaction



Our single equilibrium constant measurement, $K = 0.645 \pm 0.013$ at $562 \pm 1^\circ K$, is also included. The agreement of this gas chromatographically derived value with the ones based on dielectric constant measurements decreases the possibility that the latter method was confounded by side reactions (*vide infra*). All of the published values save the one of Ebert and Büll^{5a} were obtained from dielectric constant measurements. The line in Figure 2 was drawn by eye. In drawing this line the single value of Ebert and Büll, based on boiling point measurements, was disregarded as were the two high temperature measurements of Maroney.²⁸ Side reactions were probably significant at these high temperatures. Nonetheless, the line fits the two high temperature values reasonably well. The equation for this line is

$$\log K = (-141^\circ K)/T + 0.066$$

from which $\Delta E^\circ_{540} = 650 \pm 70$ cal/mol and $\Delta S^\circ_{540} = 0.30 \pm 0.20$ cal/deg-mol. The upper limits on these values are based on the line which fits the data of Wood and Stevenson alone.^{5c}

From the published spectroscopic data we calculate $\Delta S^\circ_{540} = 80.40 - 80.05 = 0.35 \pm 0.2$ cal/deg-mol, $\Delta E^\circ_{540} = 8010 - 7800 = 210 \pm 20$ cal/mol, $\Delta E_{zp} = 20500 - 20775 = -275 \pm 80$ cal/mol. Consequently, ΔE_e is 720 ± 160 cal/mol. The small differences be-

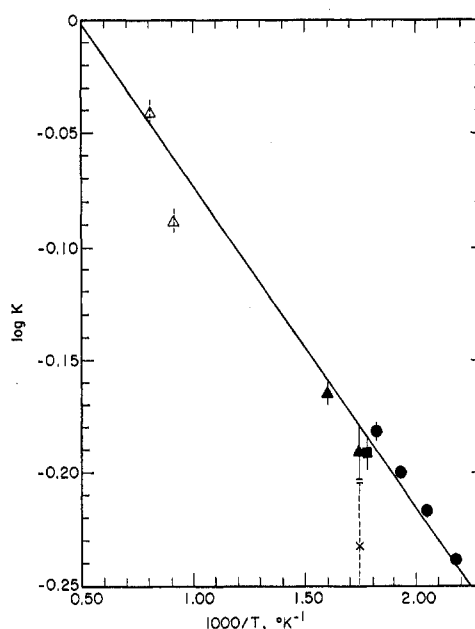


Figure 2. Temperature dependence of the equilibrium constant for the cis-trans isomerization of $C_2Cl_2H_2$: ●, Wood and Stevenson (ref 5c); ▲, Olson and Maroney (ref 5b); △, Maroney (ref 28); ×, Ebert and Büll (ref 5a); ■, this research.

tween these statistical thermodynamic quantities and those given by Pitzer and Hollenberg²⁹ are due to the use of the updated vibrational assignment of Hopper³⁰ and the geometric parameters preferred by Bernstein and Ramsay.³¹

The present value of 650 cal/mol for ΔE°_{540} is consistent with the value of $\Delta E^\circ_{300} = 200 \pm 500$ cal/mol obtained from the enthalpy of combustion of $C_2Cl_2H_2$ isomers in the liquid phase^{32a} and the enthalpies of vaporization.^{32b} Compared with the present value of $\Delta E^\circ_0 = 440$ cal/mol, values of 530 and 500 were calculated from Wood and Stevenson equilibrium constant data alone^{5c,31} and a value of 445 was calculated from the combined lower temperature data.²⁹

Statistical thermodynamic calculations were also carried out for cis- and trans- N_2F_2 . The vibrational fundamentals were from King and Overend's assignment^{33a} augmented with gas-phase Raman bands for the

(28) W. Maroney, *J. Amer. Chem. Soc.*, **57**, 2397 (1935).

(29) K. S. Pitzer and J. L. Hollenberg, *ibid.*, **76**, 1493 (1954).

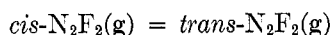
(30) M. Hopper, Ph.D. Thesis, University of Minnesota, 1967. For *cis*- $C_2Cl_2H_2$: (*a*₁) 3077¹, 1587, 1183¹, 714, 173¹; (*a*₂) 876¹, 406¹; (*b*₁) 3087, 1303, 857, 571; (*b*₂) 697. For *trans*- $C_2Cl_2H_2$: (*a*_g) 3071¹, 1576¹, 1270¹, 844¹, 349¹; (*a*_u) 895, 226; (*b*_g) 758¹; (*b*_u) 3090, 1200, 817, 245 cm^{-1} . 1 = liquid-phase values; others for gas phase.

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

(32) (a) L. Smith, L. Bjellerup, S. Krook, and H. Westermarck, *Acta Chem. Scand.*, **7**, 65 (1953); (b) J. A. A. Ketelaar, P. F. Van Velden, and P. Zahm, *Recl. Trav. Chim. Pays-Bas*, **66**, 731 (1947).

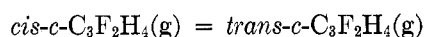
(33) (a) S.-T. King and J. Overend, *Spectrochim. Acta*, **23A**, 61 (1967); (b) J. Shamir and H. H. Hyman, *ibid.*, **23A**, 1191 (1967); *cis*- N_2F_2 : (*a*₁) 1525, 896, 341; (*a*₂) ~550; (*b*₁) 952, 737; *trans*- N_2F_2 : (*a*_g) 1523, 1018, 603; (*a*_u) 364; (*b*_u) 990, 423 cm^{-1} . All except the ~550 cm^{-1} band of the *cis* isomer are for the gas phase.

trans isomer observed by Shamir and Hyman.^{33b} Separate geometric parameters used for the two isomers were those reported by Bohn and Bauer from an electron diffraction study.³⁴ Microwave measurements concur on the cis geometry,³⁵ and high resolution infrared measurements concur on the trans.³⁶ For use with $\Delta E^\circ_{298} = 3000 \pm 300$ cal/mol obtained by Armstrong and Marantz from enthalpies of reduction with ammonia,^{7b} $\Delta E^\circ_{\theta 298} = 2915 - 2850 = 65 \pm 40$ cal/mol, and $\Delta E_{zp} = 7030 - 7145 = -115 \pm 75$ cal/mol. Also $\Delta S^\circ_{298} = 62.60 - 61.85 = -0.25 \pm 0.2$ cal/deg-mol. The difference in electronic energy between the two isomers is 3050 ± 400 cal/mol. All of these thermodynamic quantities are for the reaction



Colburn and coworkers have reported several measurements of the cis-trans equilibrium at 558°K .^{7a} From the average equilibrium constant, $K = 0.152$, and calculated values of $\Delta S^\circ_{560} = -0.15$ cal/deg-mol and $\Delta H^\circ_{560} - \Delta H^\circ_{298} = 40$ cal/mol, one calculates $\Delta E^\circ_{298} = 1990$ cal/mol. Given the difficulty of making equilibrium measurements on this highly reactive system, this value appears to be in reasonable agreement with the thermochemical one.

For the iodine-catalyzed reaction



at $586 \pm 5^\circ\text{K}$, the equilibrium constant is 11.7 ± 0.5 , from which $\Delta G^\circ_{585} = -2900 \pm 200$ cal/mol. Although considerable infrared and Raman data are in hand, we do not yet have a complete assignment of the fundamentals for the two isomers. Therefore, for the present we assume $\Delta S^\circ_{585} \approx 0$ and $\Delta E_e \approx \Delta E^\circ_{585} \approx \Delta G^\circ_{585}$. In this cyclopropane case, the trans isomer has lower electronic energy. In view of the difficulties in observing equilibrium in this system we consider this result to be preliminary.

Discussion

Table II is a compilation of thermodynamic quantities for the cis-to-trans isomerization of haloethylenes (and difluorodiazene) for which rather complete spectroscopic and thermodynamic data are available. The quantity of particular interest, the difference in electronic energy of the two isomers, is given in the last column. In addition to the data for difluorodiazene, chlorofluoroethylene, and dichloroethylene which were presented in the Results section, Table II includes data for 1,2-difluoroethylene, 1,2-dibromoethylene, 1,2-diiodoethylene, and one trihaloethylene.

Pertinent thermodynamic quantities for the iodine-catalyzed isomerization of $\text{C}_2\text{F}_2\text{H}_2$ have been reported previously.^{1,37} A shock tube study of the rate of isomerization from both the cis and trans directions gives $\Delta E^\circ_{1200} = 2700 \pm 2400$ cal/mol³⁸ in general agree-

ment with the value derived from the temperature dependence of the equilibrium constant.

Two sets of measurements of the gas-phase, iodine-catalyzed isomerization of $\text{C}_2\text{Br}_2\text{H}_2$ have been reported.^{39,40} The 80° temperature range is too small to reveal a believable temperature dependence of the equilibrium constant. In choosing $K = 0.960 \pm 0.06$, for the cis-to-trans reaction we have placed somewhat greater weight on the more recent measurements, which are based on gas chromatographic analysis. Statistical thermodynamic values of $\Delta S^\circ_{475} = 0.58 \pm 0.3$ cal/deg-mol and $\Delta E^\circ_{\theta 475} = 220 \pm 40$ cal/mol⁴¹ have been used to extract ΔE°_{475} and ΔE_e from ΔG°_{475} . Dowling and coworkers gave $\Delta E^\circ_0 = -100 \pm 160$ cal/mol (present value 90 ± 240) based on the dubious ΔE° calculated by Noyes and Dickinson.³⁹ In the liquid phase the polar, cis isomer is favored ($K = 0.59\text{--}0.67$ at $25\text{--}150^\circ$)^{5b} over the gas phase as expected.¹⁵

The published spectroscopic data for the diiodoethylenes do not permit meaningful statistical thermodynamic calculations. Although the assignment for the trans isomer⁴² appears to be sound, the assignment for the cis isomer is in doubt. The cis assignment is based on spectra measured on the eutectic mixture (20% trans, 80% cis).⁴³ A number of bands of the two isomers are overlapped. The standing assignment gives $\Sigma_i \nu_i(\text{cis}) < \Sigma_i \nu_i(\text{trans})$ in contrast to all of the other dihalo cases considered in this paper. Also two of the frequencies for *cis*- $\text{C}_2\text{I}_2\text{H}_2$ ($\nu_6 \approx 664$ and $\nu_7 = 176$ cm^{-1}) fall below values that would fit the group frequency pattern established by the other dihaloethylenes. In contrast, a similar group frequency comparison for the trans isomer is satisfactory.⁴²

Furuyama, Golden, and Benson have recently reported the equilibrium constant ($K = 1.69 \pm 0.13$) for the gas phase isomerization (inherently iodine catalyzed) and have found no significant temperature dependence over a 140° range.⁴⁴ They give $\Delta E^\circ_{590} =$

(34) R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, **6**, 369 (1967). Calculated moments of inertia were: *cis*- N_2F_2 : $I_a = 26.58$, $I_b = 64.04$, $I_c = 90.62$; *trans*- N_2F_2 : $I_a = 6.633$, $I_b = 109.80$, $I_c = 116.42$.

(35) R. L. Kuczkowski and E. B. Wilson, Jr., *J. Chem. Phys.*, **39**, 1030 (1963).

(36) S.-T. King and J. Overend, *Spectrochim. Acta*, **23A**, 2875 (1967).

(37) N. C. Craig and J. Overend, *J. Chem. Phys.*, **51**, 1127 (1969).

(38) P. M. Jeffers and W. Shaub, *J. Amer. Chem. Soc.*, **91**, 7706 (1969).

(39) R. M. Noyes and R. G. Dickinson, *ibid.*, **65**, 1427 (1943).

(40) Viehe and Franchimont (ref 8b) have shown an equilibrium is established between $\text{HBrC}=\text{CBrH}$, $\text{HBrC}=\text{CIH}$, and $\text{HIC}=\text{CIH}$, all of which were present in significant amounts in their system. We have not observed any such halogen exchange in the fluorochloroethylene systems.

(41) J. M. Dowling, R. G. Puranik, A. G. Meister, and S. I. Miller, *J. Chem. Phys.*, **26**, 233 (1957). Most of the frequencies used in the statistical thermodynamic calculations were liquid phase values.

(42) R. H. Krupp, E. A. Piotrowski, F. F. Cleveland, and S. I. Miller, *Develop. Appl. Spectrosc.*, **2**, 52 (1962).

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

Table II: Thermodynamic Functions for *cis-trans* Isomerization of Haloethylenes
cis-HXC=CXH(g) = *trans*-HXC=CXH(g)

	Temperature, °K	$\Delta S^\circ_{\text{obsd.}}$ cal/deg-mol	$\Delta S^\circ_{\text{calcd}}$	$\Delta E^\circ_{\text{obsd.}}$ cal/mol	ΔE°	ΔE_{elect}
FN=NF	300		-0.25 ± 0.2	3000 ± 300	2930 ± 330	3050 ± 400
HFC=CFH (480-760)	620	0.14 ± 0.03	-0.01 ± 0.2	930 ± 20	780 ± 40	1080 ± 120
HFC=CClH (475-760)	615	0.21 ± 0.04	0.24 ± 0.2	780 ± 20	600 ± 40	870 ± 110
HClC=CClH (460-620)	540	0.30 ± 0.20	0.32 ± 0.2	650 ± 70	440 ± 90	720 ± 160
HBrC=CBrH (420-500)	475		0.58 ± 0.3	$(320 \pm 200)^a$	90 ± 240	250 ± 330
HIC=CIH (470-610)	540	1.1 ± 0.1		0 ± 200		
HFC=CFCl	590		-0.12 ± 0.3	$(10 \pm 180)^a$	30 ± 20	80 ± 230

^a Calculated from a single equilibrium and $\Delta S^\circ_{\text{calcd}}$. Literature citations are given in the text.

0 ± 200 cal/mol and $\Delta S^\circ_{590} = 1.1 \pm 0.1$ cal/deg-mol. It is disturbing, however, that equilibrations at 400-430°K in the liquid phase in decalin gave $\Delta E^\circ = -1550$ cal/mol.⁴³ However, this liquid phase value is a recalculated one. In the original report the eutectic mixture was mistaken for pure *cis*.⁴⁵ Further doubt is introduced by the fact that a 30° temperature range is insufficient to accurately determine a small ΔE° .

The thermodynamic values in Table II for the one trihaloethylene, 1,2-difluoro-1-chloroethylene, are from a previous paper.⁴⁶ Error estimates have been revised somewhat as a consequence of the present comparative analysis.

Although much of the evidence for the *cis* effect depends on small differences between large numbers, the data in Table II, considered as a whole, provide rather strong support for the existence of this effect. The pattern of the entropy and energy values is reasonable, and, where checks on the entropy change from second-law and third-law treatments are possible, the agreement is good. Of course, contributions from second-order effects including anharmonicity, rotation-vibration interaction, Fermi resonance, and gas nonideality have been neglected in the statistical thermodynamic calculations. It is reasonable, however, to assume that these contributions tend to cancel out for molecules as similar as pairs of *cis-trans* isomers.

At first thought gas nonideality, particularly in the form of strong hydrogen bonding between pairs of *cis* isomers, is of greater concern. Qualitatively, dimerization of *cis* isomers (an exothermic process) could produce an apparent positive temperature coefficient for the overall *cis*-to-*trans* isomerization that could dominate a true negative temperature coefficient (exothermic) for the simple isomerization involving monomers. Evaluation of expressions for the competing equilibria with representative values for the overall temperature coefficient and *trans/cis* ratio showed that

the necessary degree of dimerization of the *cis* isomer would be unreasonably large. At room temperature the dimerization would be essentially complete. Yet, separate gas density measurements for the *cis* (and *trans*) isomers of $\text{C}_2\text{F}_2\text{H}_2$ gave molar weights within a few per cent of ideal gas values.¹ Also, enthalpies and entropies of vaporization are normal for both *cis*- and *trans*- $\text{C}_2\text{Cl}_2\text{H}_2$ ^{32b} and *cis*- and *trans*- $\text{C}_2\text{F}_2\text{H}_2$.⁴⁷

In every instance in Table II the observed, composite ΔE° reflects the difference in electronic energy rather well, as has been often assumed. Since $\Delta S^\circ \approx 0$, particularly for the fluoro systems, the approximation $\Delta E^\circ \approx \Delta G^\circ$ is useful.

At least one kind of nonthermodynamic evidence exists in support of the *cis* effect. It is the difference in torsional force constants for *cis*- and *trans*- $\text{C}_2\text{F}_2\text{H}_2$ ³⁷ and *cis*- and *trans*- C_2ClFH_2 .²² In both cases the *cis* isomer has the larger force constant for incipient torsion around the double bond. The difference is well outside the uncertainty in these force constants as calculated by a normal coordinate analysis of complete hydrogen-deuterium isotopic sets. In contrast, the force constants for CH out-of-plane wagging are very nearly the same in each case. The larger torsional force constant for *cis* isomer presumably reflects some additional force holding this isomer in the planar configuration.

Though more supporting evidence would be desirable, the *cis* effect in haloethylenes now seems to be rather

(44) S. Furuyama, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, **72**, 3204 (1968). The *cis-trans* isomerization competes with the dehalogenation reaction, $\text{HIC}=\text{CIH} \rightarrow \text{I}_2 + \text{CH}\equiv\text{CH}$. In the bromiodo system (ref 40) the equilibrium constant for the *cis-trans* isomerization of $\text{C}_2\text{I}_2\text{H}_2$ was found to be 2.13 (175°) and 2.07 (225°).

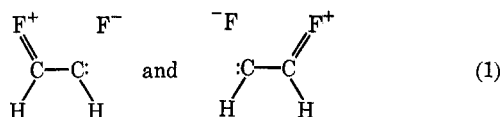
(45) R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Amer. Chem. Soc.*, **67**, 1319 (1945).

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

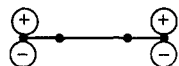
(47) From unpublished vapor pressure equations, for *cis*- $\text{C}_2\text{F}_2\text{H}_2$: $\Delta H^\circ = 5450$ and $\Delta S^\circ = 22.0$; for *trans*- $\text{C}_2\text{F}_2\text{H}_2$: $\Delta H^\circ = 4970$ cal/mol and $\Delta S^\circ = 22.6$ gibbs/mol.

well established in experiment. Rationalizations for it are, however, a much more uncertain matter. At first glance the 3000 cal difference in energy between the isomers of N_2F_2 (Table II) appears anomalously large compared with the 1100 cal difference for the isomers of $C_2F_2H_2$. However, in $C_2F_2H_2$ the repulsion energy between the CF bond dipoles is approximately 1400 cal greater in the cis isomer.⁴⁸ The corresponding difference in dipole-dipole repulsion in N_2F_2 must be considerably smaller since the cis isomer has a dipole moment of only 0.16 D.³⁵ Thus, for comparative purposes each for the electronic energy difference for a dihaloethylene pair in Table II should be increased from about 1400 to 400 cal, the latter being for $C_2I_2H_2$.¹⁶

At the present time no quantum mechanical calculations appear to be available that are sufficiently precise to corroborate the experimental evidence for the cis effect and to explain it. However, Pitzer and Hollenberg²⁹ and others have ascribed this effect to contributions from resonance structures of the type



More recently Hoffmann and Olofson⁴⁹ have argued for a preferred cis structure of electronically excited or anionic butadiene due to overlap of the p orbitals in the π HOMO



This molecular orbital argument applies to *cis*- $C_2F_2H_2$, which may be considered to have a six-electron π system if a nonbonded pair from each fluorine atom is involved. Both the valence bond and the MO arguments require double bond character in the CX bonds at the expense of the unshared pairs on each of the halogen atoms. The nuclear quadrupole coupling constants for chloroethylenes have been interpreted as indicating about 5% double bond character for CCl bonds.⁵⁰ The corresponding double bond character for *cis*- $C_2Cl_2H_2$ is not exceptional, however, and no data are available for *trans*- $C_2Cl_2H_2$. An apparent weakness in this electron delocalization explanation is the trend in the ΔE_e values in Table II. These ΔE_e values do not seem to decrease in proportion to the presumed weakening of the p-p overlap between carbon and larger halogen atoms. Steric repulsion of nonbonding electrons might also be expected to add to this rate of decrease in ΔE_e .¹⁶ However, these effects are offset to some extent by the previously cited decrease in the CX dipole-dipole repulsion. If the polar valence bond structures (1) were important, the cis effect would be marked in the mixed chlorofluoroethylenes. Yet, the electronic energy differences for the two chlorofluoro examples in Table II seem to fit a smooth trend between CFH=CFH and

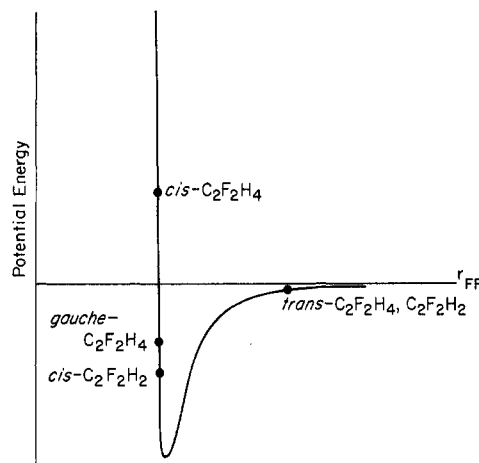


Figure 3. An approximation to the van der Waals intramolecular potential function for FF interaction. Estimated FF distances are shown for molecular structures of interest.

CClH=CClH. (The fragmentary data for CFH=CBH and CFH=CIH suggest otherwise, however.^{6,8} Although the case for the electron delocalization interpretation of the cis effect is far from complete, it seems the most reasonable proposal for haloethylenes (and diazenes).⁵¹

The electron delocalization argument will not serve to explain the apparent cis effect in saturated compounds. Although $H^\circ_{\text{gauche}} - H^\circ_{\text{trans}} = 0$ for 1,2-difluoroethane, allowance for about 1000 kcal/mol greater CF dipole-dipole repulsion in the gauche conformer makes $\Delta H^\circ = 0$ more significant. It must be emphasized, however, that $\Delta H^\circ = 0$ for the $C_2F_2H_4$ conformers is tentative, and further, ΔE_e might yet prove to favor the trans form. However, on the basis of presently available data (see the Introduction for other examples) a nonbonded, van der Waals attraction between the halogen atoms may be important. van der Waals attractions based on potential energy parameters obtained from noble gases are too small to support this hypothesis,¹⁶ although it is possible that noble gas parameters are inadequate for bound halogen atoms. Thus, for 1,2-dihaloethanes containing fluorine Abraham and Parry's calculations were 0.5–1.0 kcal too low for the gauche-to-trans conversion. Figure 3 is a schematic representation of the location of various fluorocyclopropanes on a deepened $-F \cdots F-$ potential curve. Based on rotation barriers in various fluoroethanes¹⁶ it appears that the cis (eclipsed) form of $C_2F_2H_4$ falls in the repul-

(48) Estimated from a point charge model based on the geometry and dipole moment from the microwave study (ref 35). Neglect of moment for the CH bond favors the cis isomer.

(49) R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

(50) (a) J. H. Goldstein, *J. Chem. Phys.*, **24**, 106 (1956); (b) R. G. Stone and W. H. Flygare, *J. Mol. Spectrosc.*, **32**, 233 (1969).

(51) For 1-halopropylenes simple dipole-dipole attraction seems to be an adequate explanation as shown by Abraham and Parry's calculation for rotamers of 1-halopropanes (ref 16).

sive region. Of course, the steepness of the potential curve on the repulsive side implies that small differences in geometry would cause sizeable changes in the van der Waals interaction energy. Unfortunately, the fact that the rotation barrier in *cis*-1-fluoropropylene is little different from that for 1,1-difluoropropylene,^{13a} in which the apparent equilibrium HF distance is 0.05 Å longer, seems to contradict this explanation—if the $-\text{H}\cdots\text{F}-$ van der Waals potential is anything like that for $-\text{F}\cdots\text{F}-$. For *cis* haloethylenes both double bond induced and direct van der Waals attractions may be involved, since the FF distance in *cis*-1,2- $\text{C}_2\text{F}_2\text{H}_2$ ⁵² is close to that in *gauche*-1,2- $\text{C}_2\text{F}_2\text{H}_4$.

cis-1,2-Difluorocyclopropane with a predicted FF distance⁵³ close to that of *gauche*- $\text{C}_2\text{F}_2\text{H}_4$ might be expected to exhibit the single bond *cis* effect alone. However, our preliminary equilibrium constant value implies a remarkably low energy for the *trans* configuration. Of course, it is possible that the true FF distance in the *cis*-cyclopropane is sufficiently small to place it well up the repulsive side of the van der Waals potential. Such a shortened FF distance could possibly be related to diminished opportunity for steric relief in the cyclopropane, which should be reflected in a large HCF bending force constant. It is also possible that the difluorocyclopropane result is the only one permitting direct interpretation, in which case the true *cis* effect is

only to be found along with double bonds. In the near future we expect to have more critical vibrational and thermodynamic data on the difluorocyclopropanes. It is also hoped that the *trans* cyclopropane isomer has a sufficient dipole moment to make possible a detailed microwave investigation of it as well as the *cis* isomer.⁵⁴

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(52) FF distance in *cis*- $\text{C}_2\text{F}_2\text{H}_2$ is 2.74 Å [V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963)]; in the corresponding *trans* isomer it is 3.56 Å. Based on the geometric parameters (ref 15): $r_{\text{CF}} = 1.37$, $r_{\text{CC}} = 1.54$ Å, $\angle\text{CCF} = 109.5^\circ$, and dihedral angle in *gauche* of 60° ; the FF distance in *cis*- $\text{C}_2\text{F}_2\text{H}_4$ is 2.45 Å, in *gauche*- $\text{C}_2\text{F}_2\text{H}_4$ is 2.77 Å, and in *trans*- $\text{C}_2\text{F}_2\text{H}_4$ is 3.56 Å.

(53) With $r_{\text{CF}} = 1.33$, $r_{\text{CC}} = 1.52$ Å, $\angle\text{CCC} = 60^\circ$, $\angle\text{HCF} = 118^\circ$, and $\angle\text{CCF} = 116.5^\circ$, the FF distance in *cis*- $\text{C}_2\text{F}_2\text{H}_4$ is 2.71 Å. See Hs. H. Günthard, R. C. Lord, and T. K. McCubbin, Jr., *J. Chem. Phys.*, **25**, 768 (1956), for cyclopropane geometric parameters.

(54) NOTE ADDED IN PROOF. D. Sianesi and R. Fontanelli, *Ann. Chim. (Rome)*, **55**, 850 (1965), have measured the bromine-catalyzed isomerization of 1*H*-pentafluoropropylene over the temperature range 300–550°. For the *cis*-to-*trans* reaction $\Delta H^\circ = 3.9$ kcal/mol (sign changed to conform to the data) and $\Delta S^\circ = 1.45$ cal/deg-mol.