

kilocalorie difference in the results is thus due to experimental error and not to a change in ΔH with temperature. An average value of 20.8 kcal. \pm 1 at 100° probably best represents the experimental results.

The entropy change found from statistical treatment of the molecular constants falls between the experimental values of 40 and 45 e.u. The experimental determinations show no significant temperature dependence, however, probably as a result of the relative magnitudes of experimental error and the real effect. The agreement among the three values is fair when the large effect of small systematic errors is considered.

The average ΔH of 20.8 kcal./mole \pm 1 kcal. found in this work corresponds to the N-N bond dissociation energy in N_2F_4 . The existence of a low bond energy has precedent³ in N_2O_4 (14.6 kcal.) and in N_2O_3 (10.2 kcal.). The similarity in behavior of these three systems may be taken as support of both the experimental enthalpy change and the estimated bond strength.

Loughran and Mader¹⁴ have reported an N-N bond dissociation energy in N_2F_4 of 30 kcal./mole from the results of an electron bombardment study. However, this value is based on the assumption of an ionization process which does not occur in significant proportion under their experimental conditions. In view of our suggestion that the NF_2^+ peak is derived directly from NF_2 radicals, Loughran and Mader have reappraised¹² their calculations and now find an N-N bond strength of 20 ± 5 kcal. in agreement with our results.

Herron and Dibeler¹⁵ recently have published the results of an appearance potential study on

(14) E. D. Loughran and C. Mader, *J. Chem. Phys.*, **32**, 1578 (1960).

(15) J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.*, **82**, 1555 (1960).

N_2F_4 in which a mass spectrometer with an "open" ion source was used. The fragmentation pattern they find is essentially that we observe using an unheated source and likewise represents the tetrafluorohydrazine-difluoramino equilibrium displaced toward the radical by the low pressure only. Using literature data,^{16,17} they derive an N-N bond dissociation energy in N_2F_4 of 56 kcal. by a method which involves $D(NF_2-F)$. This value of $D(NF_2-F)$ used by Herron and Dibeler results from an arbitrary division by Reese and Dibeler¹⁷ of the N-F bond energy in NF_3 into an initial strong bond and two lesser bonds by analogy with ammonia.

We find that two methods of calculation using the relations $\Delta H_f(NF_2) = \Delta H_f(NF_3) + D(NF_2-F) - \Delta H_f(F)$ and $A(NF_2^+) = D(F_2N-F) + I(NF_2)$ ¹⁸ give estimates of 55 and 57 kcal., respectively, for $D(NF_2-F)$. The remaining two N-F bond energies in NF_3 then average 70.4 kcal. (using the average of the two estimates above). This value is in excellent agreement with the average N-F bond strengths calculated for tetrafluorohydrazine (70.3 kcal. using N-N of 20.8 kcal.) and for the difluoramino radical (70.1 kcal. using $\Delta H_f(NF_2) = 9.4$ kcal). The relatively facile preparation of tetrafluorohydrazine from NF_3 in the presence of a variety of fluorine acceptors may be taken as qualitative evidence that the first N-F bond in NF_3 is weaker than the remaining two.

Acknowledgments.—The authors wish to thank Mr. Al Kennedy for the mass spectral data and help in the calculation of bond energies. We are also grateful to Mr. Don Strahm for his assistance with the spectrophotometric work and to Dr. Carl Bumgardner for his interest and helpful discussions.

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(18) $A(NF_2^+) = 14.2$ e.v. and $I(NF_2) = 11.8$ e.v.^{12,14}

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OBERLIN COLLEGE, OBERLIN, OHIO]

Thermodynamics of *cis-trans* Isomerizations. The 1,2-Difluoroethylenes

BY NORMAN C. CRAIG AND ERIC A. ENTEMANN

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Equilibrium constants for the iodine-catalyzed reaction, *cis*-HFC=CFH = *trans*-HFC=CFH, have been determined over the temperature range 477–762°K. by gas chromatographic analysis. For this reaction, $\log K = -202.8/T + 0.02919$, $\Delta H^0 = 928$ cal./mole, and $\Delta S^0 = 0.134$ e.u./mole. The lower energy of *cis*-HFC=CFH compared with *trans*-HFC=CFH is considered in relation to previous results for the other symmetrically dihalogenated ethylenes. Previously unreported *trans*-HFC=CFH has been characterized.

Introduction

cis-trans Isomerizations are of considerable interest because of the simplicity of the reaction. From this point of view a particularly interesting series of such isomers is that of the dihalogenated ethylenes. For the *cis-to-trans* reaction, ΔH_0^0 for the 1,2-diodoethylenes¹ is about 2 kcal./mole exothermic, ΔH_0^0 for the 1,2-dibromoethylenes² is within 0.1 kcal./mole of being zero, but ΔH_0^0 for the 1,2-

dichloroethylenes³ is nearly 0.5 kcal./mole endothermic. This last value may also be contrasted with those for the stilbenes,⁴ decalins,⁵ 2-butenes⁶ and other *cis-trans* pairs in which the enthalpy of the *trans* isomer is also smaller. Pitzer and Hollenberg³ have given a semi-quantitative interpretation of the lower energy of *cis*-1,2-dichloro-

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

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

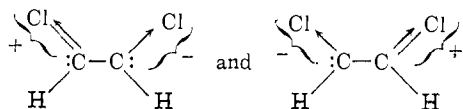
(5) N. L. Allinger and J. L. Coke, *ibid.*, **81**, 4080 (1959).

(6) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935); E. J. Prosen, F. W. Maron and F. D. Rossini, *J. Research Natl. Bur. Standards*, **46**, 106 (1951).

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

(2) J. M. Dowling, P. G. Puranik, A. G. Meister and S. I. Miller, *ibid.*, **26**, 233 (1957).

ethylene. Their argument is based on the importance of contributions from the structures, so formu-



lated to include the polarity of the carbon-chlorine σ -bond. If, as has been argued,⁷ a fluorine atom participates to a greater extent than a chlorine atom in double bond character, presumably because of the availability of 2 p orbitals, and since it is more electronegative than chlorine, one would then predict that *cis*-difluoroethylene would have an even lower relative energy. First reports of the preparation^{8,9} of 1,2-difluoroethylene recently appeared making it possible to examine this isomerization.

We have used iodine as a catalyst for this reaction. Its role is presumably that supported by rate studies of the iodine-catalyzed isomerizations of the dichloroethylenes¹⁰ and the diiodoethylenes.¹¹ An iodine atom, produced thermally, adds to one of the carbon atoms, giving a free radical with a carbon-carbon single bond. Isomerization then occurs by internal rotation, followed by loss of the iodine atom. As is known to be the case for ethylene diiodide,¹² the diiodide of difluoroethylene is presumed to be essentially unstable in the temperature range we have studied.

Experimental

Preparation of *cis*- and *trans*-1,2-Difluoroethylene.—A mixture of *cis*- and *trans*-difluoroethylene was prepared by means of reactions reported by Haszeldine and Steele⁹ and by Park, Sharrah and Lacher.¹³ Matheson chlorotrifluoroethylene and Matheson hydrogen bromide, reacted in a flow system on a charcoal catalyst at about 200°, gave crude 1-bromo-2-chloro-1,1,2-trifluoroethane in 75% yield. After fractionating, the ethane (b.p. 52.5°, uncorr; n_D^{20} 1.3684) was dehalogenated with zinc dust in refluxing ethanol. The product, trifluoroethylene, was collected in a Dry-Ice-cooled trap in 70% yield and was of high purity except for some ethanol. This trifluoroethylene (b.p. -61.5°, uncorr; lit., -60.5°¹⁴) and an excess of hydrogen bromide were metered into a quartz flask irradiated with ultraviolet light from a mercury lamp. Of the 55% yield of product ethanes, 1-bromo-1,1,2-trifluoroethane and 1-bromo-1,2,2-trifluoroethane, only one half was the desired isomer. (This reaction was also attempted with a charcoal catalyst but only gave high yields of the unwanted isomer.) In the final step, 1-bromo-1,2,2-trifluoroethane was dehalogenated by zinc dust in refluxing ethanol. This reaction involving the removal of a fluorine atom was quite slow requiring refluxing for several hours, while collecting the mixture of difluoroethylenes in a Dry-Ice-cooled trap. In this step the yield of mixed difluoroethylenes was about 70%, one fifth being the *trans* isomer. Larger quantities of the *trans* isomer were obtained from iodine-catalyzed

isomerizations of the *cis* isomer in a flow system at about 420°. The *cis* isomer (b.p. -26.0°) was readily separated from the *trans* isomer (b.p. -53.1°) by fractional distillation. Pure *cis* and pure *trans* isomers were stored at room temperature in darkened flasks for periods up to six months at pressures of 100-900 mm. without significant isomerization or decomposition.

Molar weights of the difluoroethylenes were determined by the Dumas method. Obsd: 64.6 g. for *cis*; 64.6 g. for *trans*. Calcd: 64.0 g. The infrared spectrum of the *cis* isomer was the same as that reported by Haszeldine and Steele⁹ for the "*cis-trans*" mixture but confirmed as the *cis* isomer by Coyle, Stafford and Stone.¹⁵ The identity of the 1-bromo-2-chloro-1,1,2-trifluoroethane¹⁶ and the trifluoroethylene¹⁷ were also confirmed by their infrared spectra.

The normal boiling points were calculated from Clausius-Clapeyron equations fitted to measured vapor pressure data. Melting points were observed as the on-set of fusion of 0.5 ml. samples immersed in a well-stirred acetone bath in an unsilvered dewar flask. For these measurements a calibrated Leeds and Northrup four-lead resistance thermometer and associated G-1 Mueller bridge were used. Samples were 99.8% pure. The observed melting point of the *trans* isomer was identical with that calculated from the intersection of the vapor pressure equations for the solid and liquid. *cis*-Difluoroethylene: m.p. 172.1 \pm 0.2°K. b.p. 247.2 \pm 0.1°K. *trans*-Difluoroethylene: m.p. 135.0 \pm 0.1°K. b.p. 220.1 \pm 0.1°K.

Gas Chromatographic Analyses and Fractionations.—Gas chromatography was used for analysis as well as for isolation of highest purity samples. For the difluoroethylenes, 1 cm. \times 3.9 m. copper columns packed with 30% dibutyl phthalate on firebrick, hydrogen carrier gas and a Gow-Mac hot wire thermal conductivity detector were employed. For fractionations, gas samples were put through the column at 0°. Analyses were, however, run at 100° as well as 0° to emphasize higher boiling components. For the isomerization equilibrium studies analyses were made at 0° with gas samples of about 1 ml. NTP and carrier gas flow rates of 60-100 ml. NTP/min. At a flow rate of 100 ml. NTP/min. retention times were 6 min. for the *trans*-difluoroethylene and 18 min. for the *cis*-difluoroethylene.

On a typical chromatogram in the equilibrium studies the area under the *trans*-difluoroethylene band was about 55 cm.² whereas that under the *cis*- was about 95 cm.² Areas of these near Gaussian-shaped bands were calculated as the product of the band height and width at half-height. The chromatograms were calibrated by measuring the ratios of areas (*trans/cis*) for two synthetic mixtures, which had been prepared manometrically. (1) Measured area ratio, four samples: 0.4083 \pm 0.0005 S.D.; synthetic pressure ratio: 0.4109; correction: +0.0026. (2) Measured area ratio, six samples: 0.5807 \pm 0.0033 S.D.; synthetic pressure ratio: 0.5841; correction: +0.0034. This small, but apparently significant positive correction of 0.61% was applied to the ratios reported in Table I.

Gas chromatographic analysis and purification also were used in preparing samples of the ethanes and other ethylenes for infrared spectra. 1,1-Difluoroethylene, a side-product in the thermal isomerization, was isolated as described above for the 1,2-difluoroethylenes on the 0° column. Retention time was 2.5 min. 1-Bromo-1,1,2-trifluoroethane (I) and 1-bromo-1,2,2-trifluoroethane (II) also were handled on a dibutyl phthalate-firebrick column but at 100°. Relative retention time: (I)/(II) = 0.55.

Infrared Spectra.—Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. Samples were contained in a 10 cm. gas cell at pressures ranging from 200 to 4 mm. as required to bring out the band shapes. Previously unreported spectra, expressed in microns, are: *trans*-1,2-difluoroethylene (99.9% pure): 3.20s; 3.50w; 4.36m; 4.96w; 5.84, 5.92m; 6.03, 6.09m; 6.85w; 7.08, 7.23w; 7.80, 7.90s; 8.57, 8.63, 8.70vs, 11.45s (type C band¹⁸). 1-Bromo-1,1,2-trifluoroethane (99.8% pure): 3.34, 3.37m;

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(18) R. M. Badger and L. R. Zumwalt, *ibid.*, **6**, 711 (1938).

TABLE I
 ISOMERIZATION EQUILIBRIUM DATA

Pressure range, mm.	Sampling time, hr. ^a	No. of equil. samples	Corr. av., <i>trans/cis</i> ^b	Stand dev. of ratio × 10 ^a	T, °K., av. and range	% CF ₂ CH ₂ , last sample
126-83	29 ^c -39 ^d	2	0.401	..	477.2 ± 1.3	..
164-138	71-83	3	.430	3	507.1 ± 0.9	..
155-98	7 ^e -12	4	.454	2	541.8 ± .6	..
169-138	19-27	3	.469	7	567.4 ± .6	..
161-134	11-19	3	.468	4	567.5 ± .5	..
169-100	16-27	4	.500	8	623.0 ± .9	..
181-88	12-48	6	.504	5	629.0 ± 1.8	..
191-102 ^f	48-55 ^e	4	.525	4	656.2 ± 1.3	1.0
189-94 ^f	1.5-24	5	.544	10	689.3 ± 0.9	1.2
201-122 ^f	1 3 ^c -18	4	.550	7	691.7 ± 1.0	1.4
207-112 ^f	0.17-0.93	5	.582	6	761.5 ± 0.3	0.45

^a Samples withdrawn during this time interval showed no trend in *trans/cis* ratio. ^b Average corrected ratio of *trans* band area to *cis* band area. ^c Samples were withdrawn previous to this time interval and were not found to be at equilibrium. ^d Started run with the sample equilibrated at 507°K., having a ratio of 0.430. ^e Reported temperature range maintained during last 31 hr. ^f Measurable excess fall-off in pressure during run.

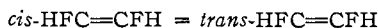
3.47w; 4.59w; 4.69w; 6.86m; 7.17m; 7.51w; 7.92s; 8.14s; 8.57s; 8.77s; 9.04s; 9.20, 9.27s; 10.31w; 10.52, 10.62vs; 11.80w; 12.67vs; ~15.0s. 1-Bromo-1,2,2-trifluoroethane (99.5% pure): 3.38s; 4.52w; 4.66m; 5.95w; 6.42w; 7.20, 7.30s; 7.45, 7.50m; 7.75m; 8.03m; 8.55s; 8.91vs; 9.31s; 10.32m; 11.16m; 11.80w; 13.05, 13.13, 13.21vs. Details of the spectra and assignments of the infrared-active fundamentals of the *cis* and *trans*-difluoroethylenes as well as the mono- and di-deuterated analogs are being submitted in a separate paper. The interpretation of the spectra confirms the identifications of the *cis* and *trans* isomers given in the present paper.

Determinations of Equilibrium Ratios.—For the isomerization equilibrium studies the reactants and products were handled in a conventional vacuum system. Before each experiment the system was pumped to a McLeod gage pressure of 10⁻⁶ mm. or less. The 173 ml. Pyrex reaction vessel with a capillary inlet was mounted in a close-fitting and substantial aluminum cylinder. This whole assembly was supported in a thermostat. The calibrated resistance thermometer described above was held in a tight-fitting hole deep in the aluminum cylinder.

In an equilibrium run, iodine vapor (0.3 mm.) was admitted into the reaction vessel. *cis*-Difluoroethylene was allowed to expand into the reaction vessel to a pressure of 150-210 mm. After closing off the reaction vessel, a 9 ml. section of tubing including a capillary manometer was evacuated. Pressure measurements and samples for analysis were obtained by venting the reaction vessel into this 9 ml. section. Samples were transferred to the gas chromatography apparatus by quantitative distillations into liquid-nitrogen-cooled traps. In the course of these transfers iodine vapor was removed with copper turnings. Separate experiments showed that no significant photochemically induced isomerization occurred at room temperature under normal lighting during the time of these transfers.

Results

The results of the isomerization equilibrium studies are summarized in Table I. Since the equilibrium expression for the reaction



is $K = p_{trans}/p_{cis}$, the equilibrium constants are given by the *trans/cis* ratios in column four. In accord with the van't Hoff equation, $\log K$ is plotted versus $1/T$ in Fig. 1. Within the indicated limits of scatter of the experimental points, this equilibrium data, which spans a 285°K. range in temperature, can be fitted with a straight line. The least squares result is

$$\log K = -202.8/T + 0.02919$$

From this equation, $\Delta H^0 = 928$ cal./mole and $\Delta S^0 = 0.134$ e.u./mole.

Although evidence of side reactions was obtained, the *trans/cis* ratios appear to be reliable equilibrium constants. At temperatures below 656°K. the difluoroethylenes are quite stable thermally in the presence of small amounts of iodine. However, at 656°K. measurable amounts of 1,1-difluoroethylene were observed on the gas chromatograms (as confirmed by the infrared spectrum¹⁹

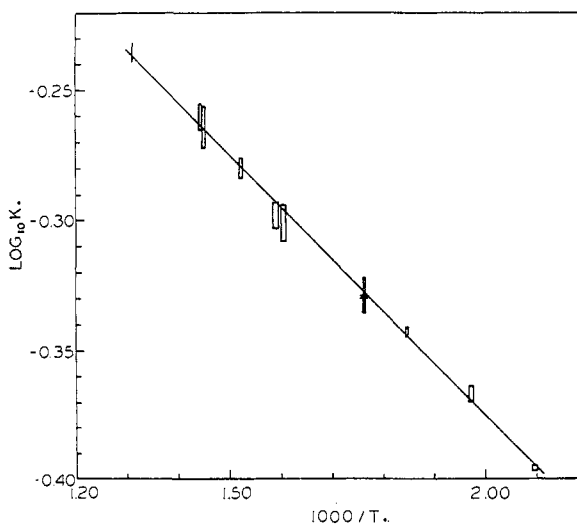


Fig. 1.—Dependence of isomerization equilibrium constant on temperature. The standard deviation of the equilibrium constant and the range of temperature are indicated by the dimensions of each rectangle.

of a sample trapped from a longer, higher temperature run). In addition, a noticeable excess pressure fall-off occurred in 55 hr. Above 656°K. the rate of production of 1,1-difluoroethylene increased, as shown in Table I by comparison of columns two and seven. The rate of pressure fall-off also increased with temperature rise. In an experiment at 760°K. with 0.7 mole per cent. of iodine present, in 10 min. equilibrium was already established and 0.25 mole % of 1,1-difluoroethylene was produced. Two other side products in smaller amount were also evident on the 0° gas chro-

(19) American Petroleum Institute Research Project 44, "Catalog of Infrared Spectral Data," National Bureau of Standards, No. 1004.

matogram. The excess pressure drop during this time was less than 1%.

From this data a semiquantitative estimate of the relative rate of isomerization to the rate of side reactions can be made. We assume that the iodine atom concentration remains effectively constant and thus the rate of isomerization varies only with the olefin concentration. In the same time interval that the *cis-trans* isomerization was at least 99.5% complete, the side reactions had proceeded to about 1.5%, as estimated from the excess pressure fall-off and the build-up of 1,1-difluoroethylene. The relative rate of *cis-trans* isomerization to side reactions is then approximately $[\log(1/0.005)]/2(0.015) = 80$. At lower temperatures, where side reactions are relatively less important, the rate ratios are more favorable.

One experiment was also run at 760°K without iodine. In 25 min. 2.5 mole per cent. of 1,1-difluoroethylene formed, the pressure diminished 30%, and *cis-trans* equilibrium was not achieved. A number of other side products in addition to 1,1-difluoroethylene were observed on chromatograms at 0° and 100° but were not readily identified. (Similar chromatograms also were obtained from prolonged heating in the presence of iodine.) Comparison of this experiment with the one in the presence of iodine described above shows that small amounts of iodine are effective in suppressing side reactions as well as catalyzing the *cis-trans* isomerization. These side reactions are thus apparently mostly free radical processes as the effectiveness of iodine as an inhibitor of free radical chains is well known.²⁰

Discussion

Table II compares the enthalpies and entropies of *cis-trans* isomerization of the 1,2-dihaloethylenes. Unfortunately, ΔH_0^0 and general statis-

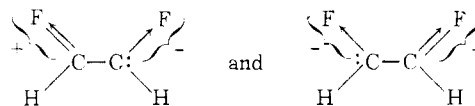
TABLE II
COMPARISON OF ENTHALPIES AND ENTROPIES OF ISOMERIZATION OF THE DIHALOETHYLENES
cis-HXC=CXH \rightarrow *trans*-HCX=CXH

	Ref.	Temp. range, °K.	ΔH^0 , cal./mole	ΔS^0 , e.u./mole	ΔH_0^0 , cal./mole
HFC=CFH	..	480-760 ^d	928	0.134
HCIC=CCIH	3, ^a ^b	458-548 ^d 573-628 ^e	720 480	.26 ^g	445 \pm 20
HBrC=CBrH	2, ^c	417-451 ^d	130	.60 ^h	-100 \pm 160
HIC=CIH	1, 11	403-432 ^{d, f}	-1550	2.4 ⁱ	-1700 \pm 1000

^a R. E. Wood and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 1650 (1941). ^b A. R. Olson and W. Maroney, *ibid.*, **56**, 1320 (1934). ^c R. M. Noyes and R. G. Dickinson, *ibid.*, **65**, 1427 (1943). ^d Iodine catalysis. ^e No catalysis. ^f Liquid phase with decalin as solvent. ^g From tabulated entropies of Pitzer and Hollenberg³; 0.49 e.u./mole found by Wood and Stevenson. ^h From tabulated entropies of Dowling, *et al.*²; 0.34 e.u./mole found by Noyes, *et al.*¹¹ ⁱ Calculated from the revision given by Miller, *et al.*¹

(20) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, Ltd., London, 1955, p. 234.

tical thermodynamic values are not calculable at this time for the difluoroethylenes due to limitations in the rotational and vibrational spectral data now available. Nonetheless, it appears that the 1,2-difluoroethylenes continue the trend toward lower electronic energy for the *cis* isomer. This result supports the predictions based on the valence bond treatment of Pitzer and Hollenberg,³ involving the resonance structures



In going down the series from fluorine to iodine such structures should become less important as participation in double bond character diminishes and electronegativity decreases. Furthermore, although carbon-halogen dipole repulsions also diminish down the series, repulsions due to steric overlap should also increase as the halogen atoms increase in size.

The enthalpy difference between the rotational isomers of 1,2-difluoroethane recently has been determined by Klaboe and Nielsen.²¹ The trend in the enthalpy difference, $H_{(gauche)}^0 - H_{(trans)}^0$, in the dihaloethane series parallels that in the dihaloethylene series. In the gas phase, for H_2FC-CF_2 , $\Delta H^0 = 0$, for $H_2ClC-CClH_2$, $\Delta H^0 = 1.2$ kcal./mole and for $H_2BrC-CBrH_2$, $\Delta H^0 = 1.5$ kcal./mole.²¹ Since the repulsion between the carbon-fluorine dipoles is about 0.8 kcal./mole²² greater for the *gauche* isomer than the *trans* isomer, it appears that some contribution to the electronic energy is lower for the *gauche* isomer. This contribution which is independent of the presence of a double bond is probably also involved in the relatively lower energy for *cis*-isomer of difluoroethylene.

NOTE ADDED IN PROOF.—H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960), has recently reported "approximate" measurements of the *cis-trans* equilibrium for the 1,2-difluoroethylenes, the 1-chloro-2-fluoroethylenes, the 1-bromo-2-fluoroethylenes, and the 1-fluoro-2-iodoethylenes. In the 373-573°K. temperature range, it is found that the *cis* isomer is more stable in these mixed dihaloethylenes as well as in difluoroethylene. Furthermore, additional literature data are cited for other halogenated ethylenes in which the *cis* isomer predominates at equilibrium. The spectrum reported for *trans*-difluoroethylene is in excellent agreement with that given in the present paper.

Acknowledgments.—Some preliminary isomerization equilibrium measurements were made by Mr. Rolf Sternglanz. We thank Research Corporation for support of this research through a Frederick Gardner Cottrell Grant. E.A.E. was supported by a National Science Foundation Undergraduate Research Participation summer stipend.

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

(22) For this calculation we have used: $r(C-F) = 1.37 \text{ \AA}$, $r(C-C) = 1.54 \text{ \AA}$, $\angle CCF = 109.5^\circ$ and $\mu(C-X) = 1.45D$.²¹