

The Thermal *trans*-*cis* Isomerization of Octafluorobutene-2

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The kinetics of this isomerization has been studied at a pressure of about 5 mm., the unimolecular high pressure region. The reaction appears to be a clean, homogeneous, reversible unimolecular isomerization. The *trans*-*cis* reaction was studied, and the rate constant was found to be $k_1 = 10^{13.53 \pm 0.11} e^{-56.4 \pm 0.16/RT}$ sec.⁻¹. The equilibrium constant for the reaction was also studied; $\Delta H = 816.8 \pm 44.1$ cal./mole and $\Delta S = -0.486 \pm 0.026$ e.u., the *trans* form being more stable. Fluoroolefin addition reactions are known to be more exothermic than their hydrocarbon counterparts. This has been interpreted variously either as an increased destabilization of the olefin or as an increased stabilization of the carbon-fluorine bond for a saturated carbon atom. The value of the activation energy for the isomerization studied here is interpreted as direct evidence for the destabilization of the double bond by fluorine substitution. The relatively large lowering of the activation energy (6-8 kcal./mole) with respect to that for the corresponding hydrocarbon is of the order of the relative exothermicities observed for addition reactions.

Addition reactions of fluoroolefins to form saturated compounds are well known to be more exothermic than the corresponding hydrocarbon reactions. One such example is the quantitative cyclization of hexafluorobutadiene to hexafluorocyclobutene at 200°,^{2a} whereas under similar conditions the corresponding hydrocarbon reaction is known to proceed quantitatively in the opposite direction.^{2b,c}

A second example is the heat of dimerization of tetrafluoroethylene³ which is exothermic by 50 kcal./mole; for chlorotrifluoroethylene⁴ this is reduced to 40 kcal./mole, and for ethylene, to 18 kcal./mole.⁵ Two hypotheses have been offered to explain this fluorine effect: (a) an increased stabilization owing to fluorine atoms attached to saturated carbon atoms as compared to their attachment to unsaturated carbon atoms or (b) a destabilization of the olefin owing to fluorine substitution on the unsaturated carbon atoms and a consequent weakening of the carbon-carbon double bond.

Peters⁶ has argued the double bonds are essentially similar and that this increased exothermicity is to be attributed to (a). A consideration of double bond-no bond resonance⁷ would favor (a) since the stabilization effect is much more important when several fluorine atoms are attached to the same saturated carbon atom

than when they are attached to an unsaturated carbon atom. Alternatively, the observed greater reactivity of CF₂=CClF with fluorine as compared with CF₂=CCl₂ has been interpreted by Miller and co-workers⁸ in terms of the greater olefin instability of the more highly fluorinated olefin. Similarly, the relative heats of polymerization of gaseous tetrafluoroethylene to a solid linear polymer, which is 17 kcal./mole more exothermic than the corresponding ethylene reaction, has been interpreted by Bartlett and co-workers⁹ as being due to a destabilization of the double bond. Similarly, Patrick⁵ compares the high heats of saturation of various fluoroolefins and concludes that it is tempting to attribute this to a weakness of the carbon-carbon double bond in these compounds.

Arguments involving bond energy relationships are not yet on firm enough ground for fluorocarbons to allow any decision between these hypotheses. Thermochemical arguments are necessarily ambiguous about such hypotheses since they involve both the opening of the double bond and the formation of new, saturated linkages. For this reason it is never clear to what extent each of these two processes plays a role in determining the heat of the reaction.

The present work attempts to split the thermochemical problem by studying separately the energy necessary for just part of the over-all reaction, namely, the "uncoupling" of the double bond. The assumption is that, for a thermal *cis*-*trans* isomerization of olefins, the activation energy is a better measure of the uncoupling energy for the double bond, though, of course, there may still be some overlap of the p-electrons in the transition state.

Experimental

Materials. Perfluorobutene-2 was obtained from Peninsular ChemResearch and introduced into the system by a bulb-to-bulb distillation. The *trans* isomer was obtained from this equilibrium mixture by gas-liquid chromatographic separation. The gas thus obtained was analyzed by gas-liquid chromatography and contained no detectable impurity (0.2% impurity is detectable). Nitric oxide (Matheson 99.0%) was distilled from a slush bath at -160°. Oxygen was used as received from Linde. Cyclopropane (Matheson 99.5%) was twice distilled from a -108° slush.

Apparatus and Procedure. A conventional vacuum system was employed. The reactor was a 330-cc. quartz vessel in an air furnace adjusted to a vertical temperature gradient of $\pm 0.15^\circ$ or less. Temperatures were measured with a calibrated (melting points of zinc, lead, and tin) chromel-alumel thermocouple and a Leeds and Northrup K-2 potentiometer. The analysis

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- (2) (a) E. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.*, **86**, 1676 (1964); (b) W. P. Hauser and W. D. Walters, *J. Phys. Chem.*, **67**, 1328 (1963); (c) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).
- (3) (a) B. Atkinson and A. B. Trenwith, *J. Chem. Soc.*, 2082 (1953); (b) J. N. Butler, *J. Am. Chem. Soc.*, **84**, 1393 (1962).
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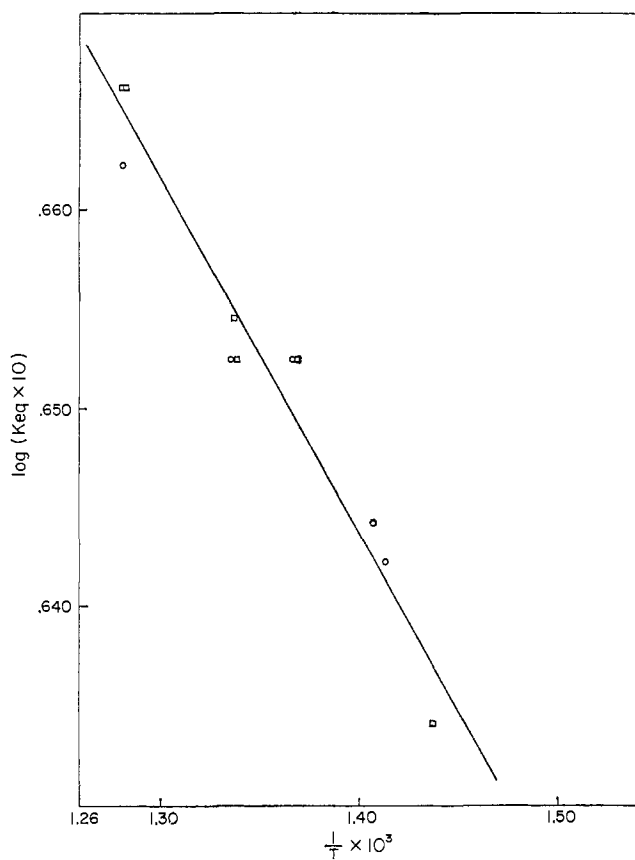


Figure 1. Equilibrium constant plot: □, approaching equilibrium from *cis* side; ○, approaching equilibrium from *trans* side.

was made by g.l.c. employing a thermistor cell as the detector. The column was 35 ft. long and was packed with 40–60 mesh firebrick coated with 10% by weight of Kel-F 1 polymer oil. The column was maintained near -35° . Only peak ratios were used. The g.l.c. analysis was calibrated with standard samples containing *cis* and *trans* isomers in a range from 0.68 to 0.88. From these results it was ascertained that, in order to obtain a 1:1 correspondence between the area per mole of the *cis* and *trans* isomers, the area of the *cis* isomer had to be increased by 3%.

The reaction was allowed to proceed continuously, samples being withdrawn at periodic intervals (25–75% reaction) for analysis. Samples were taken by expansion into a 20-cc. vessel. The consequent reduction in pressure did not produce any falloff in the rate constant. Expansions into 50- and 70-cc. volumes were made in order to assess the dead-space effect. No significant change in rate constant was observed, and, hence, no correction was necessary. In some low pressure runs, the entire sample was trapped from the furnace with liquid nitrogen.

Results

Identification of Product. The compounds were separated by g.l.c., and infrared spectra were taken of each fraction. The *trans* sample was pure, and the *cis* sample contained a small *trans* impurity, as determined by a rerun of the purified components by g.l.c. The *trans* sample showed no absorption at 5.8μ . Such an absorption at 5.8μ is typical for *cis* fluorolefins¹⁰ and, hence, forms the basis for the structural

assignment. Such an assignment was also used in the n.m.r. analysis of the 1,2-difluoroethylene spectrum.¹¹ Furthermore, the order of appearance of the peaks on the g.l.c. column is the same as for the hydrocarbon. On the basis of this, it was found that *trans*-octafluorobutene-2 is more stable than the *cis* isomer by $\Delta H = 817$ cal./mole. This is reasonable since *cis*-1,2-difluoroethylene is more stable than the *trans* isomer by only 928 cal./mole¹²; if one adds to this a reasonable value for trifluoromethyl group repulsions, one accounts for the 817 cal./mole found in this work.

Handling of the Data. Rate constants obtained over a temperature range of 430 – 477° were calculated from the equation for first-order, reversible reactions and are listed in Table I. Equilibrium constants were ob-

Table I. List of Rate Constants

| Run ^a | Temp., °C. | $(k_0)_{av}$ $\times 10^4$, sec. | $(k_0)_{av}$ cor. to 740°K . $\times 10^3$, sec. |
|------------------|---------------|--------------------------------------|---|
| A1 | 461.3 | 17.8 | 2.34 |
| A3 | 474.9 | 34.7 | 2.28 |
| A4 | 475.7 | 36.3 | 2.29 |
| A5 | 474.6 | 37.3 | 2.49 |
| A6 | 458.8 | 16.5 | 2.48 |
| AN2 | 460.5 | 17.7 | 2.43 |
| BN1 | 473.0 | 32.2 | 2.33 |
| BN2 | 474.4 | 34.3 | 2.31 |
| B1 | 469.3 | 26.0 | 2.27 |
| B2 | 443.8 | 7.18 | 2.41 |
| B3 | 431.5 | 3.52 | 2.34 |
| B4 | 467.8 | 25.9 | 2.43 |
| B5 | 433.2 | 3.76 | 2.27 |
| B6 | 433.8 | 3.98 | 2.33 |
| B7 | 475.5 | 35.6 | 2.27 |
| B8 | 437.6 | 4.83 | 2.28 |
| B9 | 434.1 | 4.08 | 2.34 |
| C1 | 477.0 | 39.5 | 2.34 |
| C2 | 477.1 | 39.3 | 2.32 |
| C3 | 443.9 | 6.98 | 2.33 |
| P2 | 471.0 | 29.3 | 2.34 |
| P3 | 432.0 | 3.80 | 2.46 |
| P4 | 432.6 | 3.92 | 2.43 |
| O1 | 468.1 | 27.6 | 2.57 |
| O2 | 473.1 | 35.0 | 2.53 |
| NS | 475.5 | 40.4 | 2.60 |
| BC1 | 470.6 | 28.4 | 2.34 |
| BC2 | 445.5 | 7.61 | 2.34 |
| BC4 | 437.0 | 5.09 | 2.48 |
| LP1 | 438.7 | 5.07 | |
| LP2 | 438.8 | 5.03 | |
| LP3 | 438.8 | 5.20 | |
| LP4 | 438.5 | 4.91 | |
| LP5 | 438.5 | 5.11 | |
| LP6 | 438.2 | 5.20 | |
| LP7 | 471.4 | 28.9 | |
| LP8 | 471.8 | 30.2 | |
| LP9 | 472.0 | 29.8 | |
| LP10 | 472.0 | 30.0 | |

^a A, B, and C denote separate seasonings; N denotes nitric oxide run; P denotes packed vessel; O denotes oxygen added; BC1, BC2, and BC4 expanded into 50, 50, and 70 cc., respectively; NS denotes unseasoned reactor; LP denotes low pressure.

tained for the process $trans \rightleftharpoons cis$ over the 425 – 510° temperature range. Identical values for the equilibrium constants were obtained approaching equi-

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librium from either direction, and both are plotted in Figure 1. Heat of reaction and activation energies were calculated from these data by a least-squares reduction carried out on an IBM 709 computer.

Reactor Seasoning. Effective poisoning of the walls was obtained by allowing ~ 20 cm. of pressure of cyclopropane to remain in the reactor for ~ 15 hr. at $\sim 465^\circ$. The reactor was reseasoned three separate times in this manner after having in each case been previously burned out for ~ 15 hr. with oxygen. The results from these seasonings indicate that this process leads to reproducible rate constants.

Three attempts were made to season the vessel with the reactant. Twice, rate constants were obtained which were in agreement with those following cyclopropane seasoning. One reactant seasoning yielded a higher rate constant. Since adequate cyclopropane seasoning was very easily reached while reactant seasoning was a difficult process, cyclopropane was used for the remainder of the study.

Side Reactions. In a clean, unpacked vessel, no indication of side reactions was evidenced upon g.l.c. analysis. However, it was determined that, following many seasonings and a large number of experimental runs, an unidentified peak appeared on the g.l.c. chart. Unfortunately, too little of this product was formed (5% of the reaction product) for chemical analysis, but, owing to its short retention time on the chromatographic column, it may be inferred that it is a low molecular weight product. When the vessel was removed, a small amount of a black, carbonaceous-appearing deposit was found. The vessel was then washed and etched out with NH_4HF_2 to obtain a clean surface and was returned to the system. When this newly cleaned vessel was properly seasoned, there was no evidence of side reaction. It should be mentioned that the presence of side reactions had no effect on the rate constants obtained for the *trans* \rightarrow *cis* isomerization. However, none of the data obtained when side reactions were present was used in the calculations presented in this paper.

Effect of Addends and Other Variables

Nitric Oxide. When about 30% of nitric oxide was added to the reactant, no change in the isomerization rate was noted (see Figure 2), and no side products were visible upon g.l.c. analysis.

Oxygen. It was found that a pressure of 5×10^{-3} mm. of oxygen caused an increase of $\sim 8\%$ in the rate constant for isomerization (see Figure 2). Since all runs were performed in the $3\text{--}7 \times 10^{-6}$ mm. region, it may be presumed that oxygen catalysis has been minimized. The vacuum was measured statically in the reactor section with a cold-cathode discharge gauge.

Packed Reactor. The reactor was packed with 2.17 g. of Amersil fine quartz wool (average diameter 5–7 μ) to increase the surface-to-volume ratio by a factor of at least 23. Within experimental error, this produced no change in the rate of isomerization (see Figure 2). However, a trace of side reactions was evidenced amounting to only 3% of the reaction product.

Autocatalysis. When the reaction was studied at high pressures (16 mm.) in the range of 25–85% reaction a small upward trend in the rate constant (22%) was observed. No systematic change in rate

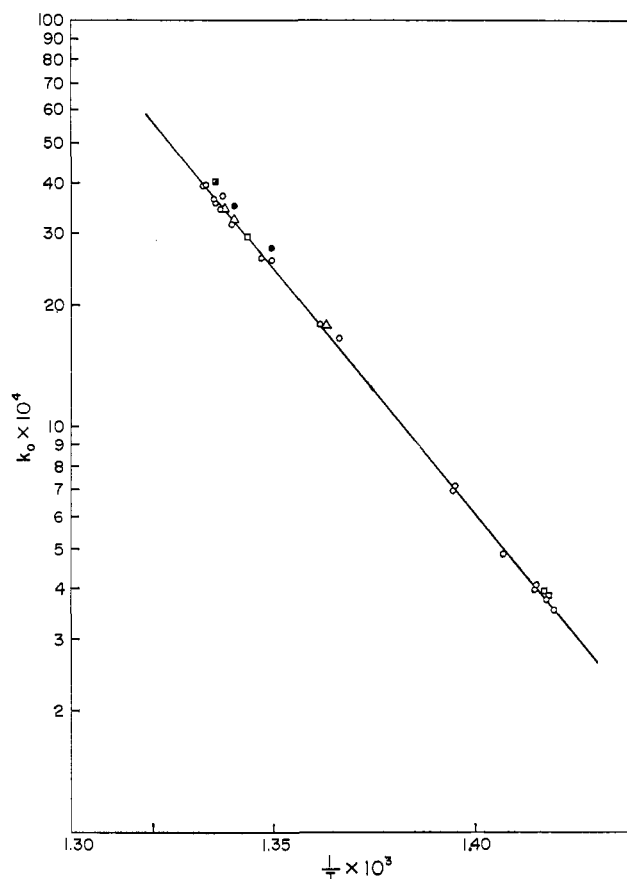


Figure 2. Activation energy plot: ○, normal point, and △, NO added (both used in E_a and A determination); □, packed vessel run; ●, oxygen added; ■, unseasoned vessel.

constants was observed during the course of a run under normal pressures (~ 4 mm.), the typical spread in values being about 5%. Rabinovitch and Michel¹³ noted an acceleration of the rate constant at high pressures also, but this was over a smaller extent of reaction. This autocatalytic effect resulted in a lowering of their activation energy, below the value reported at 1.76 mm., by about 10 kcal./mole. Hence, it became of interest to see if a similar problem could exist for the reaction reported here; a series of runs was carried out at ~ 0.5 mm., *i.e.*, a pressure-lowering of about a factor of 8. This yielded the same energy of activation (Table II). While this latter value is not of as great a statistical significance as the high pressure value, it indicates that at 4 mm. the reaction is probably free of autocatalytic effects noted for the hydrocarbon reaction.

Variation of Pressure. It should also be noted that the values of the rate constants obtained at 0.5 mm. showed no significant lowering in comparison with the values obtained at 4 mm. This indicates that at 4 mm. the values of the rate constants are arbitrarily close to the high pressure limit, and no correction is needed. This is, of course, expected for a molecule of this complexity and vibrational frequency pattern.

Equilibrium Constant. The value of the equilibrium constant was determined in a slightly higher temperature region (see above) to facilitate the experimental procedure. The heat of reaction was found to be

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Table II. Arrhenius Parameters for the *trans-cis* Isomerization of Perfluorobutene-2

| | No. of (<i>k</i> , <i>T</i>) data | <i>E_a</i> , cal./mole | log <i>A</i> |
|--|---|-------------------------------------|----------------|
| High pressure ^a | | | |
| (<i>k</i> ₀) _{av} ^b | 21 | 55,870 ± 267 | 13.873 ± 0.184 |
| <i>k</i> ₀ | 102 | 55,860 ± 157 | 13.869 ± 0.108 |
| <i>k</i> ₁ | 102 | 56,430 ± 157 | 13.528 ± 0.108 |
| <i>k</i> ₂ | 102 | 55,610 ± 157 | 13.633 ± 0.108 |
| Low pressure ^a | | | |
| (<i>k</i> ₀) _{av} | 10 | 55,980 ± 308 | 13.893 ± 0.214 |
| <i>k</i> ₀ | 10 | 55,980 ± 308 | 13.893 ± 0.214 |
| <i>k</i> ₁ | 10 | 56,500 ± 297 | 13.539 ± 0.207 |
| <i>k</i> ₂ | 10 | 55,740 ± 308 | 13.660 ± 0.214 |

^a The high pressure *E_a* was determined at pressures varying from 3.8 to 4.8 mm. The low pressure *E_a* was determined at pressures varying from 0.35 to 0.55 mm. ^b *k*₀ = *k*₁ + *k*₂; *k*₁ is the rate constant for the formation of the *cis* isomer, and *k*₂ is the rate constant for the reverse process. (*k*₀)_{av} is the average value of the individual values of *k*₀ for a given run. The uncertainties refer to the probable error.

816.8 ± 44.1 cal./mole, and Δ*S* = -0.486 ± 0.026 e.u.; *i.e.*, the *trans* form of octafluorobutene-2 is slightly more stable.

Elementary Nature of Isomerization. It would appear that in a properly seasoned vessel the reaction studied is a simple unimolecular isomerization in the high pressure region at pressures of ~4 mm. This is evidenced by several facts: (1) side reactions are absent in the unpacked vessel; (2) the kinetics are unaffected by a large addition of nitric oxide which would change the rate if free radicals are involved; (3) the packing of the vessel does not change the kinetics although some side reaction is present; (4) low pressure (0.5 mm.) values of the rate constants and activation energy are identical with those observed at 4 mm.

Discussion

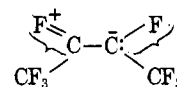
The activation energy found here for the *trans-cis* isomerization of octafluorobutene-2 is 56.4 kcal./mole. This is 6.4 kcal./mole lower than the corresponding value for the reaction of the hydrocarbon butene-2, which was found to be 62.8 kcal./mole.^{13,14}

The value for butene-2 is somewhat in doubt even though it was found in two different laboratories. It was found in both laboratories that a maximum in the activation energy was observed at a pressure of 1.76 mm., beyond which the value decreased again. This behavior is contrary to the known behavior of unimolecular reactions, a behavior which agrees with the present theory of unimolecular reactions,¹⁵ imperfect though it may be. Furthermore, the falloff of the reaction shows anomalies with respect to theory not otherwise observed.¹⁵ All this casts some doubt on the elementary unimolecular nature of the isomerization of the hydrocarbon. Somewhat in support of the hydrocarbon value, one may cite the data on the isomerization of 1,2-dideuterioethylene which also has a reported activation energy of 65 kcal.¹⁶ This

would then be an activation energy lowering of 8.6 kcal./mole.

Hence, the results of this study indicate a lowering of the π-uncoupling energy in fluoroolefins when compared to the corresponding hydrocarbons. Such a change in the uncoupling energy can be attributed to a destabilization of the double bond or to a stabilization of the transition state in the fluoroolefin, or both. It is unlikely that the latter effect can be solely responsible for this effect. The relevant carbon atoms in the transition state are probably closer to sp² than sp³ in character. It appears likely that fluorine atoms attached to sp³-carbon atoms are more effective in removing an electron than when they are attached to an sp²-carbon atom.⁶ A stabilization value for the transition state of 8 kcal./mole would be typical⁶ were these sp³-carbon atoms, and, hence, a value far less than this would be reasonable if the transition state has more s-character. The experimental value is 6-8 kcal./mole, hence indicating that this shift in uncoupling energy cannot be just due to the relative stability of the transition states, but, rather, that a considerable destabilization of the double bond appears to be involved.

Such a lowering of the π-uncoupling energy in fluoroolefins may be attributed to the participation of structures such as



which would tend to lower the energy for rotation about the double bond although they might not lead to a lengthening of the carbon-carbon bond.¹⁷ Such structures have been postulated to explain the higher stability of *cis*-dichloroethylene¹⁸ as well as the higher stability of *cis*-difluoroethylene¹² as compared to their *trans* isomers. (For the isomerization reported here, the *trans* isomer is more stable, which is what one might expect from methyl group repulsions.) Similarly, in an n.m.r. study of C¹³ shifts, the high-field shift owing to an *ortho* fluorine atom was taken as evidence for the presence of ionic structures of this type.^{19,20} The similarity in the force constants for C=C in ethylene and tetrafluoroethylene again does not necessarily mean that the bonds have equal strengths as judged by their energy of rotation about the C=C bond.

In conclusion, it is shown that the lowering in the activation energy of the *cis-trans* isomerization of octafluorobutene-2 when compared to butene-2 is 6-8 kcal./mole. It is reasonable to say that this represents a measure of the lowering of the π-uncoupling energy owing to fluorine atom substitution, an effect which must also be considered in the relative exothermicities of addition reactions to fluoroolefins.

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