# Kinetics and Thermodynamics of the Thermal Interconversion of Decafluoro-1,2-dimethylcyclobutene and Decafluoro-2,3-dimethylbutadiene-1,3

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**Abstract:** The kinetics of the reversible thermal interconversion of the isomeric decafluoro-1,2-dimethylcyclobutene and decafluoro-2,3-dimethylbutadiene-1,3 have been studied in the gas phase between 290 and 352° at reactant pressures between 4 and 150 cm. The equilibrium constant, defined for the opening of the ring of the dimethylcyclobutene to give the dimethylbutadiene, was determined up to 385°; for this reaction $\Delta H° = 0.40 \pm 0.20$ kcal/mole and $\Delta S° = 4.87$ eu. The reaction appears to follow reversible first-order kinetics and is probably a homogeneous unimolecular reaction. Defining the forward and reverse rate constants by the relation $K = k_1/k_2$, it is found that $(k_1 + k_2) = 10^{13.62} \exp[(-45.8 \pm 0.6 \text{ kcal})/RT] \text{ sec}^{-1}$. A significant difference of 11.3 kcal/mole is found on comparison of the $\Delta H°$ for this reaction with that previously reported for the isomerization of hexafluorocyclobutene to hexafluorobutadiene-1,3. This difference is interpreted as direct evidence against the view that changes in carbon–fluorine bond strengths attributable to changes in the hybridization of carbon are the principal sources of variance between the thermochemistry of reactions of fluoroolefins and the reactions of analogous hydrocarbons.

The thermochemistry and kinetics of a considerable number of hydrocarbon isomerization reactions have been reported. The isomerization and decomposition reactions of small ring compounds have proved to be particularly useful in studies of substituent effects of homologous series of compounds. A recent tabulation of many of these studies has been provided by Benson and DeMore.[1] The thermochemistry of these reactions seems to be relatively well understood. Methyl substitution, for example, appears to make little difference in the activation energies of the reactions of cyclopropanes and cyclobutanes. Fluorine substitution, however, makes a significant difference in the energetics, and relatively little is accurately known of fluorocarbon bond energies and heats of formation, as has been discussed by Patrick.[2] To date there have been few kinetic studies reported giving activation energies of fluorocarbon iomerizations. It is to be hoped that examination of the effects of fluorine substitution or the replacement of fluorine by fluoroalkyl groups will give some insights into the nature of bonding in fluorocarbons and possibly the nature of the transition states of the isomerization reactions. Schlag and Peatman recently published[3] a study of the isomerization of hexafluorocyclobutene to hexafluorobutadiene-1,3. The following is a report of the isomerization of decafluoro-1,2-dimethylcyclobutene to decafluoro-2,3-dimethyl-butadiene-1,3. The values found for $\Delta H°$ and $\Delta S°$ are significantly different from those for the reaction of the hexafluorocyclobutene, and are reported here along with a study of the kinetics of the isomerization reaction. Comparison of these results with those of Schlag and Peatman leads to a selection between opposing models for the effect of fluorine substitution on the enthalpy of formation of fluoroolefins.

## Experimental Section

**Materials.** Decafluoro-2,3-dimethylbutadiene-1,3 was provided through the courtesy of Dr. Walter Mahler of DuPont as a principal by-product mixture from a preparation[4] of the decafluorodimethylbicyclobutane. Separations of the dimethylbutadiene from this product mixture and all analyses of the reaction products of the thermal reactions reported here were effected using an 18-ft GE SF-96 silicone oil on firebrick glpc column at room temperature. The gas phase infrared spectrum of the dimethylbutadiene trapped from the purification procedures was in agreement with the spectrum furnished by Dr. Mahler for this compound. Decafluoro-1,2-dimethylcyclobutene was collected as a product of the pyrolysis of dimethylbutadiene and rechromatographed for use in runs starting with the cyclic isomer. The infrared spectrum of this pyrolysis product of the dimethylbutadiene was also in agreement with that for the authentic compound.

**Kinetic and Equilibrium Measurements.** The procedure was essentially that employed in a previous study of another system.[5] Reactions were carried out in sealed Pyrex ampoules of 1.5-ml average capacity. The ampoules were well evacuated and flamed before filling to remove surface water. The reactant at pressures between 0.1 and 5 mm in the vacuum manifold was condensed at liquid nitrogen temperatures in each ampoule. The manifold-to-ampoule volume ratio gave reactant pressures in the ampoules at room temperature of 2 to 12 cm for runs starting with the dimethylcyclobutene and 10 to 76 cm for runs starting with the dimethylbutadiene. Pyrex glass wool was packed in ampoules used in runs at the extremes of the temperature range covered in the kinetic experiments to test for surface effects. Kinetic runs were made by immersing the ampoules in a rapidly stirred and thermostated molten salt bath for the desired periods of time followed by rapid quenching of the ampoules on removal from the bath. Time errors for heating and quenching processes have been found to be insignificant except for runs under about 2 min. Temperature fluctuations varied from about 0.1° at the highest temperatures to as much as 0.4° at the lowest temperatures. Temperatures were monitored by means of a four-junction Chromel-P alumel thermocouple and Leeds and Northrup K-3 potentiometer. This thermocouple was compared in the bath with a Leeds and Northrup 8163 platinum resistance thermometer; absolute temperatures are probably accurate to 0.3°. Ampoules were broken *in vacuo* for sample transfer to the gas injection system of the glpc apparatus.

## Results

**Equilibrium Constant.** The equilibrium constant was determined with a series of nine samples which were allowed to come to equilibrium at temperatures be-

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[1] S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, **16**, 397 (1965).

[2] C. R. Patrick, *Advan. Fluorine Chem.*, **2**, 1 (1961).

[3] E. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.*, **86**, 1676 (1964).

[4] W. Mahler, *ibid.*, **84**, 4600 (1962).

[5] J. P. Chesick, *ibid.*, **85**, 2720 (1963).

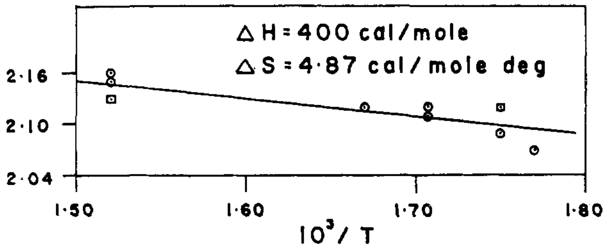
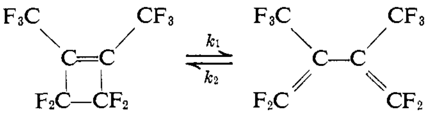


Figure 1. Temperature dependence of the equilibrium constant for the reaction perfluoro-1,2-dimethylcyclobutene → perfluoro-2,3-dimethylbutadiene-1,3: ⊙, approach equilibrium starting with perfluorodimethylbutadiene; ⊡, approach equilibrium starting with perfluorodimethylcyclobutene.

tween 291 and 385°. It is to be noted from Figure 1 that runs at two temperatures which employed the dimethylcyclobutene as starting material give essentially the same equilibrium mixture as those beginning with the dimethylbutadiene. For the reaction as written here we define the equilibrium constant $K$ = [dimethylbutadiene]/[dimethylcyclobutene].



For this reaction $\Delta H^\circ = 400 \pm 200$ cal/mole and $\Delta S^\circ = 4.87$ cal/mole deg.

**Rate Constants.** The kinetic analysis of a reversible first-order reaction gives the sum of the two first-order rate constants for the forward and reverse reaction, $(k_1 + k_2)$. The ampoule pressures at reaction temperatures for most of the runs starting with the perfluorodimethylcyclobutene were between 4 and 24 cm and the runs starting with the perfluorodimethylbutadiene were between 20 and 150 cm. These pressures are well above those for which deviations from first-order behavior would be expected for a unimolecular reaction of a molecule of this complexity, and the agreement between the data for the two reactant species as well as the independence of rate with gross variations in pressure for each reactant indicates that the values obtained for $(k_1 + k_2)$ are in fact pressure independent. Pyrolysis times were varied to provide data for periods ranging from about 0.5 to 2 half-lives; no systematic trend with conversion was seen in the rate constants. The ratio of chromatograph total peak area to pressure of reactant condensed from the manifold in preparation of the ampoule was likewise independent of degree of conversion to within the error of pressure measurements, usally about 5%.

Packing ampoules with Pyrex glass wool had no effect on the rate of reaction for one run starting with the dimethylbutadiene at the highest temperature employed for the kinetic measurements, 351°, and for runs starting with each of the isomeric reactant species at 294.3°, near the bottom of the temperature range. The surface-to-volume ratio was increased by factors of 40 and 80 for the packed ampoule experiments at the the temperatures. Schlag and Peatman[3] noted that the reaction of perfluorobutadiene to perfluorocyclobutene was also unusually clean and free from surface effects or side reactions. The reaction is practically thermoneutral, and therefore an Arrhenius plot, Figure 2, of the quantity $(k_1 + k_2)$ may be expected to appear

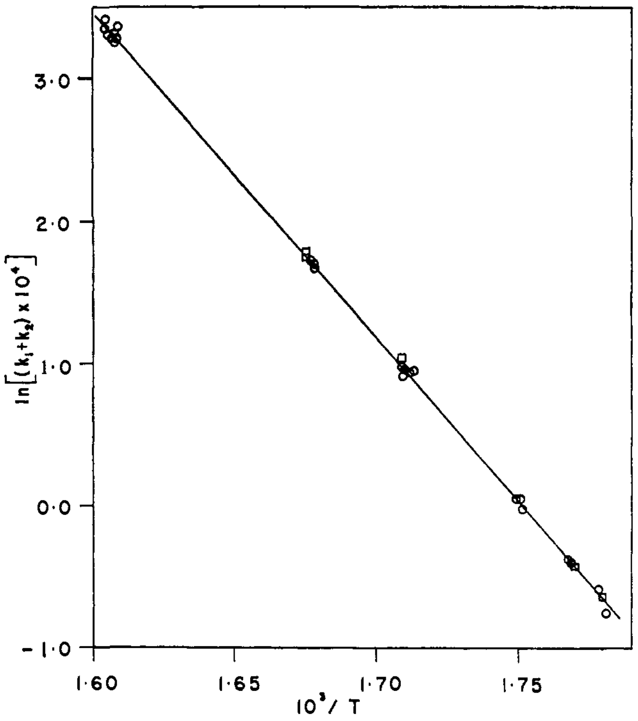


Figure 2. Arrhenius plot of rate constant sum: ⊙, runs starting with perfluorodimethylbutadiene; ⊡, runs starting with perfluorodimethylcyclobutene.

linear and to give a mean activation energy for the forward and reverse reactions. From Figure 2 is obtained

$$(k_1 + k_2) = 10^{13.62} \exp[(-45.8 \pm 0.6 \text{ kcal})/RT] \text{ sec}^{-1}$$

Combining this result with the equilibrium constant data and making the minor correction for the small $\Delta H^\circ$ of the reversible reaction, we obtain the following individual rate constants for the ring opening $(k_1)$ and ring closure $(k_2)$.

$$k_1 = 10^{13.64} \exp[(-46.0 \text{ kcal})/RT] \text{ sec}^{-1}$$

$$k_2 = 10^{12.57} \exp [(36.6 \text{ kcal})/RT] \text{ sec}^{-1}$$

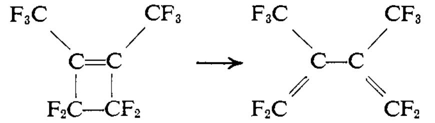
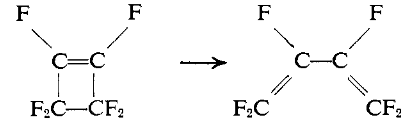
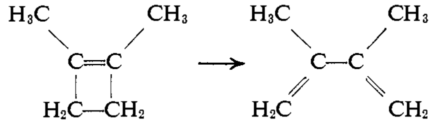
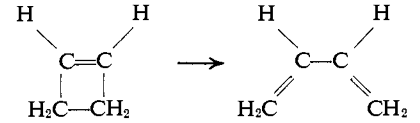
## Discussion

The thermochemistry of some reactions of hydrocarbons and their perfluoro analogs is summarized in Table I along with kinetic parameters, where known. Comparison of the heats of polymerization of tetrafluoroethylene and ethylene and comparison of the heats of cyclization of tetrafluoroethylene and ethylene to octafluorocyclobutane and cyclobutane, respectively, indicate that the fluorocarbon reactions are 16 to 18 kcal/$C_2$ unit more exothermic than the analogous hydrocarbon reactions.[2] Complete substitution of fluorine for hydrogen in ethylene destabilizes the $\pi$-electron system of the double bond and/or increases the strength of the $\sigma$-bond system in the ring or polymer forms by this amount of 16 to 18 kcal. This observation has been stated and discussed in detail by a variety of investigators.[2,3]

Schlag has noted the arguments of Peters[6] attributing these effects *solely* to changes in C–F bond energies through carbon hybridization effects. Peters estimated on this basis that the bond of a fluorine attached

(6) D. Peters, *J. Chem. Phys.*, **38**, 561 (1963).

**Table I.** Thermodynamics and Kinetic Parameters of Fluorocarbon and Hydrocarbon Reactions

| | | | Kinetic parameters | | |
|---|---|---|---|---|---|
| Reaction | $\Delta S$, cal/mole deg | $\Delta H$, kcal/mole | Log $A$ | $E$, kcal/mole | Ref |
|  | 4.9 | 0.4 | 13.64 | 46.0 | This work |
|  | 9.6 | 11.7 | 14.12 | 47.1 | 3 |
|  | | | 13.84 | 36.0 | *a* |
|  | 4.5 | −8 | 13.13 | 32.5 | *b* |

[a] K. M. Frey, *Trans. Faraday Soc.*, **59**, 1619 (1963). [b] W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958). The enthalpy change is estimated from heats of hydrogenation of cyclobutenes.

to a saturated $sp^3$ hybridized carbon is 4 kcal/mole stronger than that of a fluorine attached to an unsaturated or $sp^2$-hybridized carbon. Thus in comparison with the hydrocarbon reaction, Peters attributed the more exothermic (by 32 kcal/mole of cyclobutane formed) dimerization of tetrafluoroethylene to the stabilization of 4 kcal/mole for each of the eight CF bonds transformed from unsaturated carbon atoms to saturated carbon atoms. It was not possible in the systems studied by Schlag to distinguish definitively between this approach of Peters, and the view that the principal effect of substitution of fluorine for hydrogen in comparing fluorocarbon and hydrocarbon reactions was to destabilize the olefin $\pi$-electron system. The later work[7] suggested that the $\pi$-destabilization effect was a more probable explanation. Thus the difference between the $\Delta H$ values for the decyclization reactions of perfluorocyclobutene and cyclobutene (see Table I) could be attributed, using the two extreme points of view, either to the formation of an additional weaker double bond for the fluoro system or to the transformation of four bonds between fluorine atoms and saturated carbon atoms into four weaker bonds between fluorine atoms and olefinic carbon atoms.

From the data reported here we can add confirmatory evidence to the suggestion by Schlag[7] that the arguments of Peters attributing these energy differences solely to changes in $\sigma$-bond strengths on carbon rehybridization are incorrect. On comparing the reaction reported here with the isomerization of perfluorocyclobutene, we see that changes in the hybridization of carbon are the same for both the isomerization of perfluoro-1,2-didimethylcyclobutene to perfluoro-2,3-dimethylbutadiene-1,3 and the isomerization of perfluorocyclobutene to perfluorobutadiene-1,3. Thus if significant changes in C–F bond energies through changes in carbon hybridization determine the differences between the energetics of fluorocarbon and hydrocarbon reactions, there should be no difference in the values of $\Delta H$ for these two reactions, instead of the observed difference of 11.3 kcal/mole. We therefore feel justified in making the simplification that conjugative effects involving the $\pi$-electron systems are the principal quantities to be considered in examining the energetics of these isomerization and dimerization reactions of perfluoroolefins.

Schlag and Kaiser observed[7] that the barrier for the *cis–trans* isomerization of octafluorobutene-2 was 7.6 ± 1 kcal/mole less than for the analogous hydrocarbon. Assuming that the activation energy for this *cis–trans* isomerization is a reasonable measure of the energy to uncouple the $\pi$-electron system, then the decrease of 7.6 kcal/mole observed for the octafluorobutene-2 reaction may be taken to be the $\pi$-electron destabilization effect of replacing hydrogen by fluorine in butene-2. If the previously mentioned 16- to 18-kcal/mole difference in the thermochemistry of reactions of $C_2F_4$ and $C_2H_4$ is attributed to $\pi$-electron destabilization effects in the fluorocarbon, then for purposes of illustration we might expect the activation energy for the *cis–trans* reaction of an isotopically labeled tetrafluoroethylene to be 16 to 18 kcal/mole less than that for 1,2-dideuterioethylene,[8] or about 47 kcal/mole. Unfortunately the existence of only one isotope of fluorine makes this a difficult reaction to study. Replacement of two fluorines of tetrafluoroethylene by two $CF_3$ groups is then seen to increase the stability of the $\pi$-electron system by the difference between the $\pi$ destabilization in $C_2F_4$, 16 to 18 kcal/mole, and the value for the $\pi$-electron destabilization of octafluorobutene-2 deduced from the work of Schlag and Kaiser,[7] 7.6 kcal/mole, or a difference of 9.4 ± 1.5 kcal/mole.

Comparison of the value for $\Delta H$ of 0.4 kcal/mole for the opening of the ring in perfluoro-1,2-dimethylcyclo-

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(7) E. W. Schlag and E. W. Kaiser, Jr., *J. Am. Chem. Soc.*, **87**, 1171 (1965).

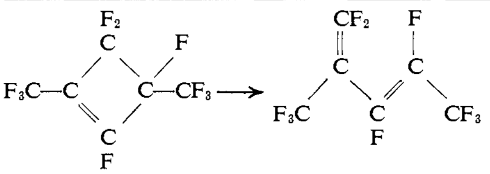
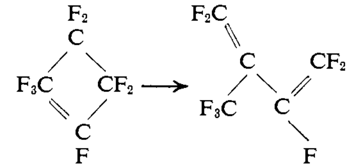
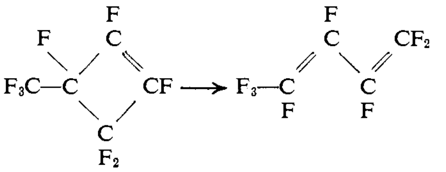
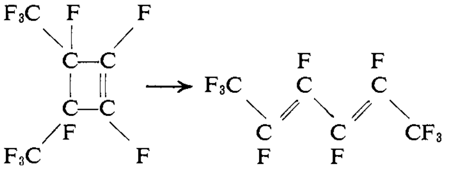
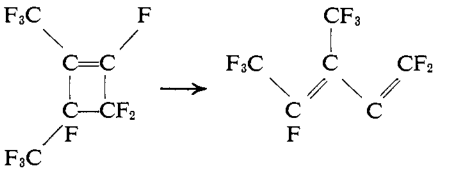
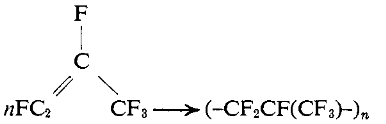
(8) J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315, (1955).

butene with the value of 11.7 kcal/mole obtained by Schlag for the similar opening of perfluorocyclobutene shows that the substitution of two $CF_3$ groups for fluorine atoms on two different double bonds of perfluorobutadiene has a 11.3 kcal/mole more negative effect on the energy of the diene system than does the substitution of two $CF_3$ groups for fluorines on the same double bond of the perfluorocyclobutene. If we assume that the effect of a single $CF_3$ substitution at a double bond would be approximately the same for both the diene and the cyclobutene, then a second substitution to form perfluoro-1,2-dimethylcyclobutene from perfluoro-1-methylcyclobutene apparently has little effect on the $\pi$-system energy. As a working rule which explains empirically the data reported by Schlag and that obtained in this work, we may assert that it is the first substitution of a $CF_3$ group for a fluorine at a double bond which causes the principal stabilization of the $\pi$-electron system to the extent of about 10 kcal/mole.

It should be noted that we are not attempting with this somewhat crude generalization to provide a detailed explanation of these effects considering the limited amount of data available. Various combinations of inductive and resonance effects could be invoked. There must certainly be some effects of a second substitution of a $CF_3$ group for a fluorine atom at a double bond; it is only suggested that the effect seems small compared to the value of 10 kcal/mole taken as the result of the first substitution. The differences in magnitude of the substituent effects discussed here for fluorocarbons and those encountered with hydrocarbon systems become more apparent if it is noted that relative to the value for ethylene, the gaseous heats of hydrogenation of propylene, butene-1, and *cis*- and *trans*-butene-2 are 3.0, 2.6, 4.3, and 5.3 kcal/mole, respectively.[9]

We can then summarize predictions of the thermochemistry of some reactions of related perfluoroolefins, taking the reaction of hexafluorocyclobutene as a reference (Table II). The reactions listed are probably also clean unimolecular isomerizations. Studies of these should provide useful data for evaluation of the relative effects of fluorine and $CF_3$ as substituents and the validity of the assumptions used in estimating the $\Delta H°$ values.

**Table II**

| Reaction | $\Delta H$, kcal/mole |
|---|---|
|  | +1 |
|  | +12 |
|  | +1 |
|  | −8 |
|  | +17 |
|  | −28/$C_3$ unit |

The similarity in the activation energies for the isomerization of perfluoro-1,2-dimethylcyclobutene and perfluorocyclobutene suggests that the effects of the $CF_3$ groups are apparent only in the final reorganization to the diene after the transition state has been passed. If the cyclobutene ring opening reactions listed were found also to have similar activation energies and to exhibit the predicted $\Delta H°$ values, then the difference between the activation energy for the hydrocarbon and fluorocarbon cyclobutene ring-opening reaction might be due to changes in carbon–carbon $\sigma$-bond strengths due to fluorination. It is now usually *assumed* that carbon–carbon $\sigma$ bonds in fluorocarbons are of the same strengths as in hydrocarbons. Inaccuracies in heats of formation of fluorocarbons and the inability to produce consistent data for fluorocarbon dissociation energies or heats of formation of fluoro radicals have made it impossible to provide definitive statements on this matter.

The magnitudes of conformational energy effects or nonbonded repulsion energies in fluorocarbons are also generally unknown. It might be argued that the 11.3-kcal energy difference in the enthalpies changes for the reactions of perfluoro-1,2-dimethylcyclobutene and perfluorocyclobutene is due to the relief of strain caused by the *cis*-trifluoromethyl groups on opening the ring of the former compound. However, the enthalpy change for the conversion of *trans*-octafluorobutene-2 to *cis*-octafluorobutene-2 was found to be only 0.8 kcal/mole,[7] suggesting that there is not a significant destabilization due to steric hindrance caused by placing a pair of trifluoromethyl groups in a *cis* configuration on a double bond of a fluoroolefin.

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(9) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.