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THE THERMAL ISOMERIZATION AND CLEAVAGE OF CIS-1,1,2,2-TETRAFLUORO-3,4-DIMETHYLCYCLOBUTANE

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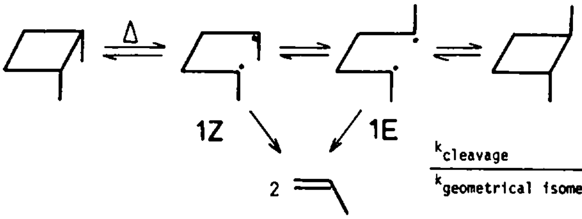
Abstract - The reversible isomerization of cis-1,1,2,2-tetrafluoro-3,4-dimethylcyclobutane 5 to trans-1,1,2,2-tetrafluoro-3,4-dimethylcyclobutane 6 at 435°-483° has been investigated: (Log $A=14.8\pm0.2$, $E_a=61.1\pm0.5$ kcal/mol). The irreversible cleavage of the cyclobutane ring leading to the formation of 1,1-difluoropropene is competitive with the isomerization, occurring at a relative rate of 0.12 at 435°C.

Cyclobutane thermolyses are considered to proceed via 1,4-tetramethylene diradical species such as 1. Such diradicals are known to generally exhibit a much greater propensity to undergo β-scission to form two ethylenic moieties than to undergo geometric isomerization via bond-rotation and recyclization,[1] thus making it difficult to obtain details as to the kinetic behavior of such diradicals.



$$\frac{k_{\text{cleavage}}}{k_{\text{geometrical isomerization}}} \cong 5$$

However, through studies of cyclobutane thermolyses,[1] azo compound decompositions[2] and [2+2] cycloaddition reactions,[3] it has been possible to derive significant insight into the nature of 1,4-tetramethylene species. The extent of effort in this area relative to that in probing its sister diradical, 1,3-trimethylene,[4] can likely be attributed to this problem of β-cleavage.

With the knowledge that a CF_2-CF_2 single bond is strengthened relative to its CH_2-CH_2 counterpart,[5] it was hoped that thermolyses of molecules of the basic structure **2** might

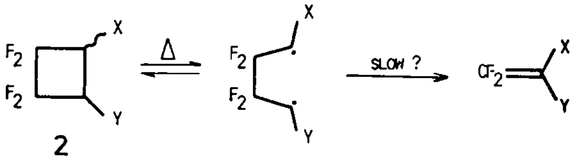
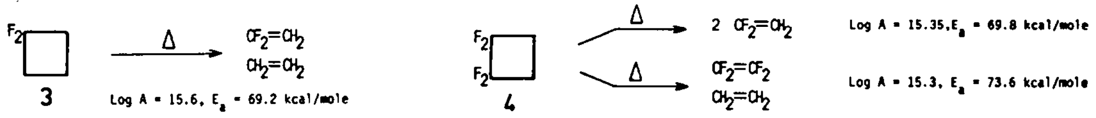


exhibit significant inhibition of the second, cleavage step so as to allow easy mechanistic probing of the respective tetramethylene diradicals. If a clean geometric isomerization process could be kinetically observed, there would be significant potential to gain insight into substituent effects on bond rotations, similar to those studies which have been carried out extensively on comparable cyclopropane systems.

Such a study would allow us moreover to test the overall effect of β-fluorine substituents on the bond dissociation energy of cyclobutane. It should be remembered that a CF_2 group in cyclopropane has been shown to exert a dramatic bond-weakening effect upon the opposite carbon-carbon bond, while having little effect upon the strength of adjacent bonds.[6]

Frey's kinetic studies on overall cleavage processes of 1,1-difluoro-cyclobutane, 3, and 1,1,2,2-tetrafluorocyclobutane, 4, certainly indicate a significant inhibition of the <u>overall</u> process, but provide no specific insight into the individual bond fragmentation steps.[7]



3

Log A = 15.6, E_a = 69.2 kcal/mole

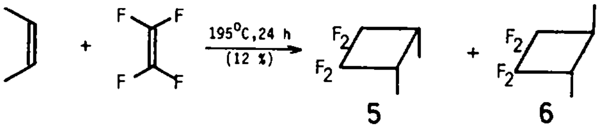
4

Log A = 15.35, E_a = 69.8 kcal/mole

Log A = 15.3, E_a = 73.6 kcal/mole

RESULTS

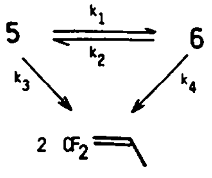
Cis- and trans-1,1,2,2-tetrafluoro-3,4-dimethylcyclobutane, 5 and 6, were prepared in an autoclave reaction via the [2+2] cycloaddition of cis- or trans-2-butene with tetrafluoroethylene (TFE) at 195°C. Coffman et al first reported this reaction, among others of TFE in 1949, while Bartlett et al later studied the stereochemistry of the reaction under such autoclave conditions.[9] The cycloaddition could also be carried out under more controlled conditions in the gas phase.[10]



5 6

$$\text{CIS-2-BUTENE} + \text{TFE} \xrightarrow[\text{gas phase}]{229^{\circ}\text{C}} \underset{1}{5} \; + \; \underset{2.2}{6}$$

$$\text{TRANS-2-BUTENE} + \text{TFE} \xrightarrow[\text{gas phase}]{229^{\circ}\text{C}} \underset{1}{5} \; + \; \underset{5.0}{6}$$



At temperatures >430°C, 5 and 6 were found to interconvert at a rate ~8.4 times that of cleavage to 1,1-difluoropropene. While constituting a dramatic improvement over the kinetic picture for the hydrocarbon system, kinetic analyses of the 5 6 equilibration data nevertheless still required utilization of the Simplex method of optimization. Using gas chromatographic analyses of the reaction mixtures, rates were obtained at eight temperatures between 434-483°C. Reactions were carried out in the gas phase, starting from pure 5, in a well-conditioned pyrex vessel immersed in a molten salt bath.[11] Using the basic mechanistic scheme below, the rate constants shown in Table I were obtained. Using these rate

Table I. Rate Constants for the thermolysis of cis-1,1,2,2-tetrafluoro-3,4-dimethylcyclobutane.

(°C)	k_1(sec^{-1})	k_2(sec^{-1})	k_3(sec^{-1})	k_4(sec^{-1})
434.75	9.19×10^{-5}	3.5×10^{-5}	1.09×10^{-5}	4.19×10^{-6}
444.7	1.63×10^{-4}	5.92×10^{-5}	2.13×10^{-5}	8.24×10^{-6}
450.2	2.305×10^{-4}	8.056×10^{-5}	2.89×10^{-5}	1.16×10^{-5}
461.3	4.26×10^{-4}	1.68×10^{-4}	5.67×10^{-5}	1.83×10^{-5}
467.25	6.15×10^{-4}	2.46×10^{-4}	9.4×10^{-5}	2.55×10^{-5}
472.2	7.74×10^{-4}	2.97×10^{-4}	1.07×10^{-4}	3.7×10^{-5}
479	1.17×10^{-3}	4.60×10^{-4}	1.62×10^{-4}	6.5×10^{-5}
483	1.48×10^{-3}	6.10×10^{-4}	1.90×10^{-4}	1.01×10^{-4}

Table II. Arrhenius Parameters for the 1,1,2,2-tetrafluoro-3,4-dimethylcyclobutane Thermolysis System.

Rate Constant	$E_a{}^a$	Log A	$\Delta H^{\neq a,b}$	$\Delta S^{\neq a,b}$	$\Delta G^{\neq a,b}$
k_1	61.1(0.5)	14.8(0.2)	59.6	5.5	55.6
k_2	63.3(1.2)	15.1(0.4)	61.9	6.6	57.0
k_3	63.8(1.5)	14.8(0.4)	62.4	5.2	58.6
k_4	65.8(3.8)	14.9(1.1)	64.3	5.9	60.0

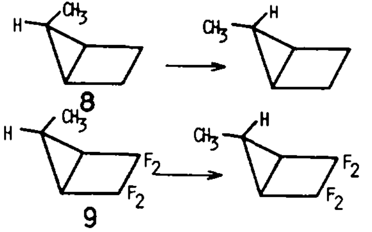
[a]kcal/mole [b]mean temperature=462.8°C

constants, the Arrhenius parameters in Table II were calculated. The relatively large errors observed for the k_3 and k_4 Arrhenius determinations can at least partially be attributed to the fact that the Simplex method of approximation has increasing difficulty in precise determination of rate constants which are much smaller than others in a scheme, as is the case with k_3 and k_4 with respect to k_1 and k_2.

DISCUSSION

It can be seen that the activation parameters for geometric isomerization of 5 (Log A=14.8±0.2, E_a=61.1±0.5 kcal/mole) are similar to those reported for the unfluorinated analog, cis-1,2-dimethylcyclobutane, 7 (Log A=14.0, E_a=60.1 kcal/mole).[11]

These results are moreover consistent with the related observation by Al-Fekri[12] that the activation energies for the thermal endo-exo isomerizations of fluorinated and unfluorinated[13]

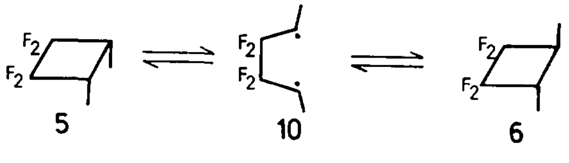


Log A = 15.0, E_a = 39.2 kcal/mole

Log A = 13.4, E_a = 39.4 kcal/mole

bicyclopentanes, 8 and 9, were also virtually identical.

Such geometric isomerizations are generally considered to proceed via initial homolytic cleavage of the cyclobutane ring into a tetramethylene diradical system (i.e. **10**), followed



by bond rotation and/or conformational interconversions within the system of diradicals **10**, leading finally to recyclization to either 5 or 6 or irreversible cleavage to 1,1-difluoro-propene.

The activation energies for such isomerizations of 5 and its unfluorinated analog 7 are therefore considered to be a good measure of the bond-dissociation energies of their respective C_3-C_4 bonds. Hence one should conclude, probably rightfully, that the presence of the four fluorine substituents has little net effect upon the C-C bond in question.

One must be careful however not to interpret the above results to necessarily indicate that the strain of the two molecules is identical. Indeed, the strain of 5 could be greater than or less than that of 7 and still give rise to the observed results. In fact it appears that perfluorocyclobutane is 8.5-12 kcal/mole less strained than cyclobutane itself.[14] If tetrafluorocyclobutanes such as 5 and 6 were to also reflect a surely reduced but analogous diminishment of strain, then a specific compensatory weakening of the C_3-C_4 bond of 5 and **6** would need to be invoked to explain our kinetic results.[15,16]

At this time, with no specific thermodynamic data on the tetrafluorocyclobutane system or on the $C(F)_2(C)(CF_2)$ group equivalent, it is best to defer making definitive conclusions until such data is available.

It should finally be mentioned that the energy required for C_3-C_4 bond homolysis of 5 is substantially less than the 64.2 kcal/mole that is required for the perfluoro-1,2-dimethylcyclobutane system,[17] a result which is consistent with expectations.

EXPERIMENTAL

All preparative GC separations were accomplished on a VARIAN AEROGRAPH 90-P chromotograph with helium as a carrier gas and fitted with a 20 ft. x 1/4 in. 20% SE-30 on CHROM-P60 column at 80°C.

All product ratio and kinetic data were obtained by GLPC using a Hewlett-Packard 5710A chromotograph fitted with flame ionization detector and gas injecting system, and coupled to a Hewlett-Packard 3380 integrator. In this case a 20 ft. x 1/8 in. 20% SEC-30 on CHROM-P60 column was used at 80°C.

NMR spectra were obtained in $CDCl_3$ at ambient temperature by using a VARIAN XL-100 instrument; 100.1 MHz for ^{1}Hnmr and 94.06 MHz for ^{19}F nmr; and JEOL FX90; - 25.2 MHz for ^{13}C proton decoupled spectra. The internal standard for ^{1}H and ^{13}C was $(CH_3)_4Si$ and for ^{19}F nmr $CFCl_3$.

Mass spectra were obtained on a AEI-MS30 spectrometer at 70eV.

Cis and trans-1,1,2,2-tetrafluoro-3,4-dimethylcyclobutanes (5 and 6) were prepared by procedure similar to that described previously.[11] A five hundred mL autoclave was charged with 44.2g(.442)moles) of tetrafluoroethylene. The autoclave was then placed in a bomb rocker and this mixture was then heated at 195°C for 24 hours. Pressures up to 2,000 lb/in were observed. The autoclave was then cooled to room temperature and opened to a dry ice trap, which was connected to a drying tower. After the autoclave pressure was close to atmoshperic, but slightly greater, the bomb was closed and then connected to a vacuum line. The bomb was then reopened and its contents transferred to a 200 mL round bottom flask equipped with a magnetic stirring bar. The round bottom flask was disconnected from the line and quickly stoppered and then connected to a distillation apparatus which was attached to a dry ice trap equipped with a drying tower. The flask was then allowed to warm to room temperature with stirring. The resultant mixture was transferred after an hour at room temperature on the vacuum line into another smaller round bottom flask which upon disconnecting was stoppered with a rubber septum. The mixture was then separated by GLPC.

Then 6.2g(9%) of the first eluting peak was collected and identified as trans-1,1,2,2-tetrafluoro-3,4-dimethylcyclobutane, 6: ^{1}H nmr, δ2.38-2.01(CH, broad multiplet, 2H), 1.18-1.01(CH_3, doublet, 6H); ^{19}F nmr, ϕ=123.89 ppm (midpoint), AB with further splitting, J_{ab}=197.9 Hz, $\Delta\upsilon_{ab}$=2175.6 Hz; ^{13}C nmr, decoupled, δ42.93-42.1(C_1, s complex multiplet), 122.4-114.0(C_3,C_4, doublet of virtual triplets, J_{CF}=278.74 Hz, $^2J_{CF}$=25.7 Hz), 10.4(C_5,C_6,s); Mass spectrum give M^+ 156.0543±.0019(12.3 ppm), calculated for $C_6H_8F_4$ 156.0562 dev -.0018(11.8 ppm).

Also 2.1g(3.1%) of cis-1,1,2,2-tetrafluoro-3,4-dimethylcyclobutane, 5, was collected: ^{1}H nmr, δ2.95-2.53(CH, broad multiplet, 2H), 1.18-1.01(CH_3, doublet, 6H); ^{19}F nmr, ϕ=123.46 ppm (midpoint), AB with further splitting, J_{ab}=185.9 Hz, $\Delta\upsilon_{ab}$=2159.6 Hz; ^{13}C nmr, decoupled, δ123.15-114(C_3,C_4, doublet of doublet of virtual triplets, J_{CF}=292.6 Hz, $^2J_{CF}$=25.4 Hz; 38.2-37.3(C_1,C_2, complex multiplet), 6.1-6(C_5,C_6 singlet). Mass spectrum gave M^+ 156.0552±.0017 (12ppm), calculated for $C_6H_8F_4$ 156.0562, dev -.001 (6.4ppm).

All spectroscopic data (^{1}H nmr, ^{19}F nmr, ^{13}C nmr, MS) of 1,1-difluoropropene were consistent with the reported values.[18]

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