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Bimolecular Kinetic Studies with High-Temperature Gas-Phase ^{19}F NMR: Cycloaddition Reactions of Fluoroolefins[†]

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Abstract: A gas-phase NMR kinetic technique has been used for the first time to obtain accurate measurements of rate constants of some bimolecular, second-order cycloaddition reactions. As a test of the potential use of this technique for the study of second-order reactions, the rate constants and the activation parameters for the cyclodimerization reactions of chlorotrifluoroethylene (CTFE) and tetrafluoroethylene (TFE) were determined in the temperature range 240−340 °C, using a commercial high-temperature NMR probe. Obtaining excellent agreement of the results with published data, the technique was then applied to the reaction of 1,1-difluoroallene with 1,3-butadiene, the results of which indicate that the use of gas-phase NMR for reaction kinetics is particularly valuable when a reagent is available only in small amounts and in cases where there are several competing processes occurring simultaneously. The major processes observed in this reaction are regioselective [2+2] and [2+4] cycloadditions, whose rates and activation parameters were determined [$k_2 = 9.3 \times 10^6$ exp(-20.1 kcal mol^{-1}/RT) L/mol^{-1} s^{-1} and $k_3 = 1.2 \times 10^6$ exp(-18.4 kcal mol^{-1}/RT) L/mol^{-1} s^{-1}, respectively] in the temperature range 130−210 °C.

Introduction

Rate constants for second-order gas-phase reactions have been commonly measured by monitoring pressure changes in constant volume systems and by concomitant chemical analyses typically involving gas chromatography. The latter requires periodic sample extractions causing mass loss and extensive standardization with authentic materials, and it is time-consuming. For carrying out quantitative vapor-phase kinetic studies, gas-phase NMR is an efficient alternative technique, the potential of which has been largely overlooked. The substantial literature on gas-phase NMR[1] mainly deals with physical studies (spin relaxation, conformational analysis, hydrogen bonding, hindered rotation, tautomerism, etc.) with little mention of reaction product analysis or kinetics[2] until our recent publications.[3] The kinetic measurements are simplified due to the automation of modern NMR spectrometers that allows unattended runs, fast processing of spectra, remote viewing of the progress of the reaction, and easy construction of kinetic reaction profiles showing the time evolution of the concentrations of all reaction components that contain the detected nucleus. Unlike conventional techniques for vapor-phase kinetics, gas-phase NMR is an in situ technique, specific for each detected molecule within the limitations of spectral resolution, which does not require periodic sample extractions and extensive calibrations of analytical instruments. In essence, a sealed glass ampule containing micromolar amounts of reagents, estimated so as not to produce excessive pressure after complete vaporization, is placed into the probe of the spectrometer, which is maintained at the desired reaction temperature. Spectra are then acquired automatically at prearranged time intervals to follow the chemical changes that are taking place inside the ampule.

The major difference between liquid- and gas-phase NMR is that NMR absorptions in the gas phase are broader than in liquids because of shorter T_1 nuclear spin relaxation times caused by efficient spin-rotation interaction. There is, therefore, a reduction in signal intensity for the same number of spins per unit volume that can be easily compensated for by faster signal averaging made possible by the shorter T_1 relaxation times. For fluorine detection, several hundred pulses in a minute are commonly used. Since lines are broader there is no need to spin the samples, and field homogeneity is much less important than for high-resolution NMR. Furthermore, since acquisition times are shorter, a distinct advantage for kinetic work, there is also no need for deuterium field locks. The fluorines of a prototypical CF_3 group have T_1 values of 30−50 ms corresponding to line widths of about 40 Hz at a pressure of about 1 atm. Narrower lines can be observed for other types of fluorines. A decrease in line width is observed as the pressure and the molecular size are increased due to the effects of intermolecular collisions. Resolution can thus be improved by increasing reactant con-

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(1) For reviews see: (a) Govil, G. *Appl. Spectrosc. Rev.* **1973**, *7*, 47. (b) Harris, R. K. *Org. Magn. Reson.* **1983**, *21*, 580. (c) Armstrong, R. L. *Magn. Reson. Rev.* **1987**, *12*, 91. (d) Jameson, C. J. *Chem. Rev.* **1991**, *91*, 1375. (e) Jameson, C. J. In *Encyclopedia of NMR*; Grant, D. M., Harris, R. K., Eds.; Wiley: New York, 1996; Vol. 4, p 2179. (f) True, N. S. In *Encyclopedia of NMR*; Grant, D. M., Harris, R. K., Eds.; Wiley: New York, 1996; Vol. 4, p 2173. (g) LeMaster, C. B. *J. Prog. Nuclear Magn. Spectrosc.* **1997**, *31*, 119.

(2) (a) Haugh, M. J.; Dalton, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 5674. (b) Costello, F.; Dalton, D. R.; Poole, J. A. *J. Phys. Chem.* **1986**, *90*, 5352.

(3) (a) Kating, P. M.; Krusic, P. J.; Roe, D. C.; Smart, B. E. *J. Am. Chem. Soc.* **1996**, *118*, 10000. (b) Roe, D. C.; Kating, P. M.; Krusic, P. J.; Smart, B. E. *Top. Catal.* **1998**, *5*, 133. Krusic, P. J.; Roe, D. C.; Smart, B. E. *Isr. J. Chem.* **1999**, *39*, 117−123.

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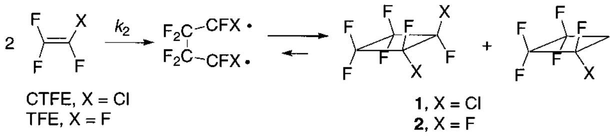
centrations or by the addition of an inert buffer gas within the limits of safe internal pressures in the ampule and complete vaporization required for quantitative analysis. The reduced resolution in gas-phase ^{19}F NMR is usually of little consequence because of the wide dispersion of the chemical shifts for fluorine nuclei in different chemical environments.[4] A wide bore magnet allowing the use of 10 mm OD ampules is a definite advantage for kinetic gas-phase NMR, as is a commercial high-temperature probe with an upper temperature limit of 400 °C.[5] No other specialized equipment is required beyond a conventional vacuum system with an accurate pressure transducer and inexpensive ampules that are now commercially available.[6]

The aim of the current study was, first, to validate gas-phase ^{19}F NMR as a technique for making reliable kinetic measurements of second-order reactions and, second, to use the method to study the kinetics of the cycloaddition reactions of 1,1-difluoroallene with 1,3-butadiene, for which no kinetic data are available.[7,8] The latter reaction is of considerable kinetic and mechanistic interest because [2 + 2] and [2 + 4] cycloadditions, mechanistically quite distinct, are in competition with each other and, to our knowledge, no experimental kinetic data or activation parameters for allene cycloadditions are presently available.[9]

To carry out the validation of this kinetic technique, it was decided to reexamine the kinetics of two prototypical cyclodimerization reactions involving fluoroolefins, those of chlorotrifluoroethylene and tetrafluoroethylene, whose rates and kinetic activation parameters have been determined quite accurately. The kinetics of the thermal cyclodimerization of chlorotrifluoroethylene (CTFE)[10,11] and tetrafluoroethylene (TFE)[10,11b,12] have been studied by several investigators by measuring the pressure changes during the course of the reaction in heated vessels of 250 mL to 1 L volume. At pressures of 1 atm or less, these cyclodimerizations (eq 1) are well-behaved homogeneous second-order reactions, with rates that are independent of pressure and unaffected by heterogeneous wall reactions. The reactions are believed to proceed via a mechanism involving biradical intermediates.[13,14] The cyclodimerization of CTFE at temperatures below 410 °C is remarkably regioselective, giving almost exclusively *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane, **1**, which are formed initially at equal rates. Equilibration favoring the thermodynamically more stable trans isomer occurs at higher temperatures. Above 420 °C the dimers begin to dissociate into starting CTFE at rates that have also been previously measured. The dimerization of TFE to octafluorocyclobutane also proceeds quite cleanly at pressures of less than 1 atm, showing signs of reversibility at around 500 °C. Above this temperature the dimer dissociates into other products, including hexafluoropropylene, by complex carbene mechanisms.



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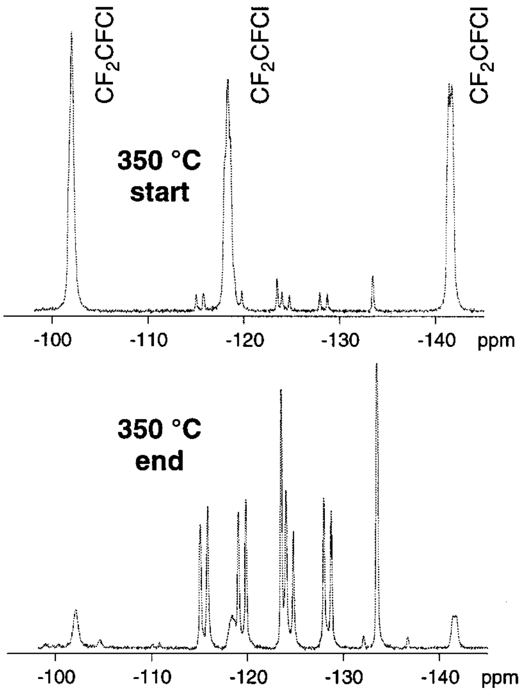

Figure 1. CTFE dimerization: ^{19}F NMR near the start of the reaction (top); ^{19}F NMR near the end of the reaction (bottom).

Results and Discussion

CTFE and TFE Cyclodimerizations. Figure 1 (top) shows the ^{19}F NMR spectrum that was obtained a few minutes after inserting a sealed, 3.8 mL internal-volume ampule containing 100 μmol of CTFE into the probe at 350 °C. The initial concentration of CTFE is 0.026 mol/L and the approximate initial pressure, calculated by the ideal gas law at 350 °C, is 1.3 atm.[15] Tests demonstrated that temperature equilibration in these experiments requires no more than 3 min, a time that is very short compared to the time scale of the reactions that are being considered here. The three major resonances with partially resolved spin–spin coupling for the three vinylic fluorines agree well with published data in solution. In this case, rather exceptionally, the NMR spectrum was also studied in the gas phase to provide information on the ^{19}F nuclear magnetic shielding for the three different vinylic environments in

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[4] T_1 values are longer for protons in the gas phase with typical line widths of a few hertz.

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[7] Dolbier, W. R., Jr.; Piedrahita, C. A.; Houk, K. N.; Strozier, R. W.; Gandour, R. W. *Tetrahedron Lett.* **1978**, *26*, 2231–2234.

[8] Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1984**, *49*, 2381–2386.

[9] For relevant computational studies see, e.g.: (a) Rastelli, A.; Bagatti, M.; Gandolfi, R. *J. Am. Chem. Soc.* **1995**, *117*, 4965–4975. (b) Halevi, E. A.; Wolfsberg, M. *J. Chem. Soc., Perkin Trans.* 2 **1993**, 1493–6.

[10] Lacher, J.; Tompkin, G. W.; Park, J. D. *J. Am. Chem. Soc.* **1952**, *74*, 1693–1696.

[11] (a) Atkinson, B.; Stedman, M. *J. Chem. Soc.* **1962**, 512–519. (b) Atkinson, B.; Tsiamis, C. *Int. J. Chem. Kinet.* **1979**, *11*, 585–593. (c) Ivanova, S. M.; Zemlyanskaya, N. V.; Volkov, G. V.; Boikov, Yu. A.; Barabanov, V. G.; V'yunov, K. A. *Kinet. Katal.* **1986**, *27* (5), 1236–1237.

[12] (a) Atkinson, B.; Trenwith, A. B. *J. Chem. Soc.* **1953**, 2082. (b) Drennan, G. A.; Matula, R. A. *J. Phys. Chem.* **1968**, *72*, 3462–3468. (c) Buravtsev, N. N.; Grigor'ev, A. S.; Kolbanovskii, Yu. A. *Kinet. Katal.* **1985**, *26* (1), 7–14.

[13] Bartlett, P. D. *Science* **1968**, *159*, 833.

[14] Buravtsev, N. N.; Kolbanovskii, Y. A.; Ovsyannikov, A. A. *Mendeleev Commun.* **1994**, 48–50. Buravtsev, N. N.; Kolbanovsky, Y. A. *J. Fluorine Chem.* **1999**, *96*, 35–42.

[15] Attention must be paid not to create excessive pressures in sealed gas-phase ampules at elevated temperatures. We routinely calculate the pressures that would be generated at the reaction temperature by the ideal gas law from the total moles of reactants that were sealed in the ampule taking into account the stoichiometry of the gas-phase reactions. We consider that our ampules, now availble commercially (see ref 5), can safely withstand ~3 atm internal pressure since they did not explode in barricaded tests with a calculated 10 atm of CF$_4$.

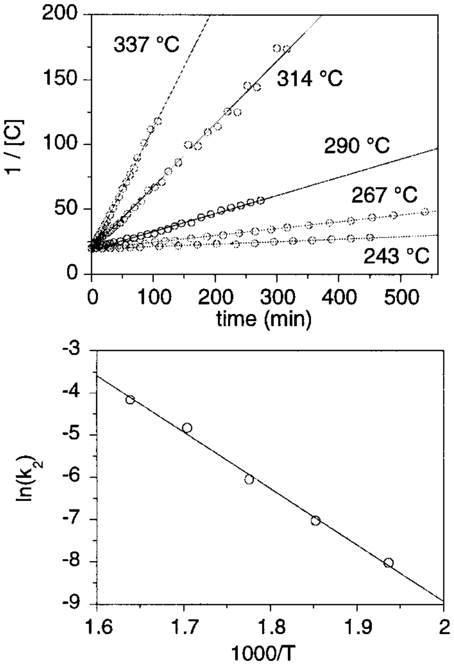

Figure 2. CTFE dimerization: second-order plots of rate data (top); Arrhenius plot (bottom).

CTFE.[16,17] Already quite visible are the narrower lines belonging to a 1:1 mixture of *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane whose solution spectra have also been studied before.[11a,18] These lines grow at the expense of the CTFE resonances, as can be seen graphically by viewing the set of spectra obtained automatically according to a prearranged time schedule. A spectrum near the end of the reaction is shown in Figure 1 (bottom). The CTFE multiplets at each end of the spectrum have no overlap with the product spectra and can be integrated for the entire set of acquired spectra by using the automation features available in modern spectrometers. After scaling the resulting integrals by the initial concentration, a plot of 1/(concentration, mol/L) vs time gives a good straight line representing the disappearance of CTFE, the slope of which is the rate constant. The experiment was repeated for several temperatures between 240 and 340 °C, each leading to similar linear plots (Figure 2), and the resulting rate constants were used to construct the Arrhenius plot that is shown in Figure 2.[19]

An analogous procedure was followed with TFE (100 μmol in a 3.8 mL ampule). The only fluorine resonances that can be detected are two single resonances belonging to TFE and octafluorocyclobutane ($\delta \sim -134$ ppm relative to $CFCl_3$). Unfortunately, they overlap substantially and ordinary integration cannot be used as above to follow the disappearance of TFE with time. The chemical shift difference of the two resonances is also slightly temperature dependent, tending to decrease resolution at higher temperatures ($\Delta\delta = 0.7$ ppm at 25 °C and 0.3 ppm at 325 °C). Recourse can be made to spectral deconvolution that is available in the software of modern spectrometers: the overall absorption is fitted by least-squares methods as a superposition of two Lorentzian curves to obtain their integral area values, which are proportional to the NMR signal intensity of each reaction component. Figure 3 shows the fits for two kinetic points at two different temperatures. Obviously, a complication of this kind is time-consuming since each kinetic point requires a computer fit, and it is fortunate that in practice such situations do not occur very frequently. Most molecules, unlike TFE and octafluorocyclobutane, have more than one NMR resonance that can be used to follow the kinetics. The 1/[C] (mol/L) vs time plot for the disappearance of TFE at 225 °C, giving the rate constant as the slope,[19] is shown in Figure 4 (top) together with the Arrhenius plot for the dimerization of TFE in the temperature range 220−300 °C (Figure 4, bottom).

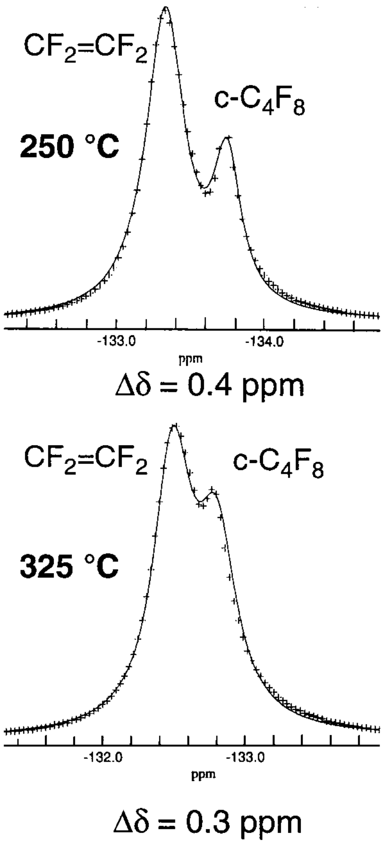

Figure 3. TFE dimerization: ^{19}F NMR spectrum deconvolution at 250 (top) and at 325 °C (bottom).

The Arrhenius activation parameters extracted from the Arrhenius plots of Figures 2 and 4 are compared with previously published values in Table 1. The agreement is excellent, particularly as regards the Arrhenius activation energies, despite the widely different reactors used with widely different surface-to-volume ratios: 250 mL to 1 L in the previous work vs ampules of less than 4 mL internal volume in this study.[20] To complete the comparison, the entropy and heats of activation for the two reactions were determined as in ref 10a,b, using the transition-state theory expression for the rate constant of eq 2 with a transmission coefficient of unity. $R_1 = 0.08205$ atm L K^{-1} mol^{-1}, $R = 1.987$ cal K^{-1} mol^{-1}, and the standard states are at 1 atm of pressure.[21,22] Using the logarithmic form of eq 2 with $\Delta n^{\ddagger} = -1$, a plot of $\ln(kh/k_BT(R_1T))$ vs $1/T$ gives a straight line. The activation enthalpy is obtained from the slope and the activation entropy from the intercept. The resulting

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[16] The chemical shifts in solution and in the gas phase are not identical but the differences are generally small. We calibrate the chemical shift scale by adding to the ampule about 10 mol % of Freon11 or chemically more inert CF_4 ($\delta = -63.5$ ppm).

[17] Jameson, C. J.; Jameson, A. K.; Oppusunggu, D. *J. Chem. Phys.* **1985**, *83*, 5420−5424.

[18] Gazzard, V. J.; Harris, R. K. *Org. Magn. Reson.* **1974**, *6*, 404−406.

[19] See Supporting Information for rate constant data.

[20] We often test for wall catalysis by carrying out the NMR kinetic runs in the presence of crushed ampule glass.

[21] Cf.: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; J. Wiley and Sons, Inc.: New York, 1976.

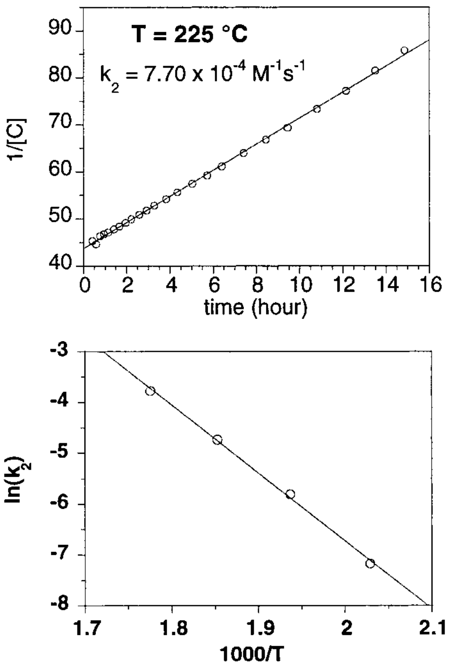

Figure 4. TFE dimerization: typical second-oder plot derived from deconvolution (top); Arrhenius plot (bottom).

values (Table 1) compare in a very satisfactory manner with previous work, from which we conclude that gas-phase NMR

$$k\,(\mathrm{L\ mol^{-1}\ s^{-1}}) = \frac{k_{\mathrm{B}}T}{h}(R_1T)^{-\Delta n^{\ddagger}}\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)\left(\frac{\Delta S^{\ddagger}}{RT}\right) \quad (2)$$

is a very attractive alternative to conventional techniques for quantitative vapor-phase chemical kinetics of second-order reactions, requiring minute amounts of materials and much less tedious work.

The substantial reduction in entropy of the order of 30 entropy units in going from reactants to the transition state for these cyclodimerization reactions, as seen in Table 1, is a reflection not only of the obvious associative nature of these reactions but also of the fact that for the olefins to react they must be properly oriented with respect to each other.

Reaction of Difluoroallene with 1,3-Butadiene. 1,1-Difluoroallene (DFA) has been shown to react with a number of 1,3-dienes by competing [2 + 4] and [2 + 2] reactions, the Diels−Alder cycloaddition mechanism being presumably concerted, whereas the [2+2] cycloaddition apparently proceeds via a diradical intermediate.[7,8]

Previous studies of such reactions were carried out by using the time-honored sealed tube method, which required laborious product analyses. No quantitative kinetic information was reported in these studies. Our technique also involves sealed tubes but provides immediate analytical and kinetic information with micromolar amounts of materials. Preliminary experiments, aided by the analytical information from previous work, including expected NMR chemical shifts,[7,8] indicated that the major processes in the reaction between 1,3-butadiene and DFA can be represented by Scheme 1 in the temperature range 100−210 °C. The major reaction components have simple ^{19}F NMR spectra in the vapor phase as illustrated for a single kinetic point at 145 °C in Figure 5 that also shows the appropriate assignments. Preliminary work indicated that the dimerization of DFA, giving **5** and **6**, was competitive with DFA's [2 + 2] and [2 + 4] cycloadditions as shown in Scheme 1. Moreover, **6** underwent further Diels−Alder reaction rapidly with butadiene to give **7**, a result that obscured the [2 + 2] and [2 + 4] cycloadditions of interest.

The measured integral of the strong singlet at −99.5 ppm corresponding to the endocyclic $-CF_2-$ group of dimer **5** is significantly greater than expected for the 2F which correspond to the $=CF_2$ (doublets at −83 and −91 ppm) of dimer **5**. Therefore, we consider that this signal must consist of two overlapping signals that are not resolved in the gas-phase ^{19}F NMR spectrum. Indeed, when the ^{19}F NMR for the mixture was measured in $CDCl_3$ solution after the gas-phase reaction at 145 °C, two signals (1.8:1) were able to be resolved. In $CDCl_3$, the larger peak at −97.88 (tt, $^4J_{\mathrm{F-H}} = 4.2$, 3.1 Hz) was assigned to the exocyclic $=CF_2$ group of 1-difluoromethylene-3-vinylcyclobutane [2 + 2] adduct **8**, which has magnetically equivalent fluorines with small $^4J_{\mathrm{F-H}}$ couplings. The smaller, adjacent peak at −98.37 ppm (tt, $J = 10.1$, 2.7 Hz) is consistent the $-CF_2-$ signal for head-to-tail dimer **5**. In the GC/MS examination of the product mixture, products **3**, **4,** and **8** apparently eluted close to one another, with one major and one satellite peak (95:5) having similar mass spectra. The concentration of adduct **8** in the gas-phase reactions was, therefore, derived by subtracting the 2F integral of $=CF_2$ (−82.5 and −91 ppm) of dimer **5** from the integral of the −99.5 ppm signal (Figure 5). According to ^{19}F NMR, in the 1:10 DFA−butadiene reaction, adduct **8** is formed in 5−9% yield.

Using a 10-fold molar excess of butadiene reduced the importance of the DFA dimerization to 10−17% of the reaction, but it also required much smaller amounts of DFA to ensure safe internal pressures and to ensure that all components were in the vapor phase. Thus the initial concentration of DFA, under these conditions, was only 6.3×10^{-3} M. Although the signal-to-noise factor was consequently substantially reduced, the kinetic profiles were nevertheless quite adequate for kinetic analysis, albeit showing more scatter than customary. A typical reaction profile obtained under these conditions (Figure 6, top) shows the decay of DFA as a result of the three major reactions that use it and the formation of the products of interest, **3**, **4**, and **8**, at 132 °C. These products contribute 81−86% to the total mass balance, with **8** contributing only 5−9%.

The decay of DFA follows pseudo-first-order kinetics over the entire temperature range used as can be seen in Figure 6 (middle) by the linearity of the $\ln(C/C_0)$ vs time plots.[23]

The slopes of the linear plots yield values for k_1 that are needed below for the determination of k_3 and k_4 (k_8 will be neglected henceforward).[19] As shown in the Supporting Information section, k_3 and k_4 were obtained as the slopes of the linear plots obtained by plotting the cycloadduct concentrations vs $[C_4H_6]\{[\mathrm{DFA}]_0 - [\mathrm{DFA}]\}/k_1$ at six different temperatures. The resulting rates were used to construct the very satisfactory Arrhenius plots of Figure 6 (bottom), yielding log A and the activation energy E_a. Application of the transition state theory equation (eq 2) afforded linear plots yielding the activation enthalpies and activation entropies listed in Table 2. Note that the formation of the [2 + 2] DFA-butadiene adduct **4** prevails over the formation of the [2 + 4] adduct **3** at temperatures above 160 °C, whereas the [2 + 4] adduct **3** is preferred at lower temperatures.

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[22] Modern usage prefers a treatment of the transition state theory based on standard states at 1 mol L^{-1} (cf.: Maskill H. *The Physical Basis of Organic Chemistry*; Oxford University Press: Oxford, UK, 1985; Chapter 6). Slightly different values for the activation entropy and enthalpy are obtained with this approach.

[23] See Supporting Information for a more detailed kinetic analysis.

Table 1. Activation Parameters for CTFE and TFE Dimerizations

	activation parameters			
reaction	log *A*	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol[c]	$\Delta S^{\ddagger}$, cal/kmol[c]
TFE + TFE	8.38 ± 0.40[b] (8.01)[12a] (8.22)[10]	26.5 ± 1.0 (25.4)[12a] (26.3)[10]	23.7 ± 1.0[a] (22.2)[12a]	-34.0 ± 1.8[a,b] (-38.4)[12a]
CTFE + CTFE	7.40 ± 0.42[b] (7.63)[11a] (7.55)[10]	$26.5 \pm 1.0 \pm 0.3$ (26.6)[11a] (26.3)[10]	23.7 ± 1.0[a] (23.9)[11a]	-38.4 ± 1.9[a,b] (-38.6)[11a]

[a] Enthalpies and entropies of activation are calculated for the standard state of 1 atm at 700 K. [b] The log *A* and $\Delta S^{\ddagger}$ are derived from the rate of dimer formation: $k(\text{formation}) = k(\text{disappearance})/2$. [c] The same $\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$ values for the standard state of 1 atm can be obtained according to ref 21, pp 8−11, 146: since $\Delta S^{\ddagger}_p = \Delta S^{\ddagger}_c + R\,\Delta n^{\ddagger} \ln(R'T)$, $A_c = (k_BT/h)(R'T)^{-\Delta n^{\ddagger}}e^2 \exp(\Delta S_p^{\ddagger}/R)$, and $\Delta H_p^{\ddagger} = \Delta H_c^{\ddagger} + \Delta n^{\ddagger}RT$, where $\Delta n^{\ddagger} = -1$ for the second-order reaction and A_c is expressed in concentration units ($M^{-1}\,s^{-1}$). For 1 mol/L standard state $A_c = (k_BT/h)e^2 \exp(\Delta S_c^{\ddagger}/R)$ and $\Delta H_c^{\ddagger} = E_a - RT$ applies. Therefore, for 1 mol/L standard state for TFE: $\Delta H_c^{\ddagger} = 25.1$ kcal/mol, $\Delta S_c^{\ddagger} = -25.9$ eu, and for CTFE: $\Delta H_c^{\ddagger} = 25.1$ kcal/mol and $\Delta S_c^{\ddagger} = -30.4$ eu.

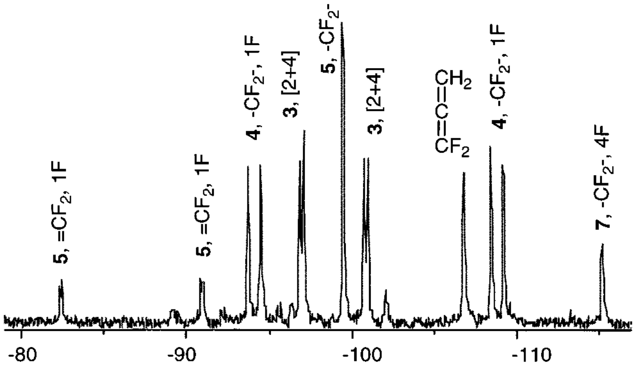
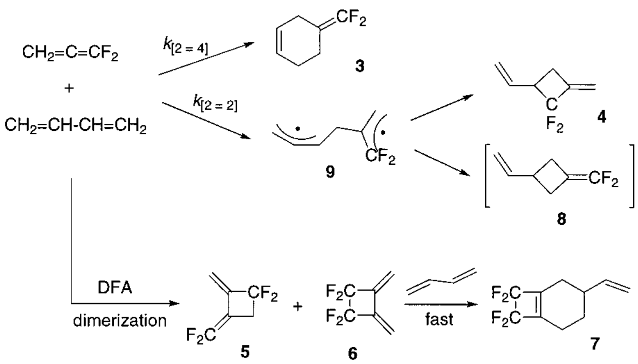


Figure 5. DFA reaction with 1,3-butadiene: ^{19}F NMR spectrum of product mixture.

Scheme 1

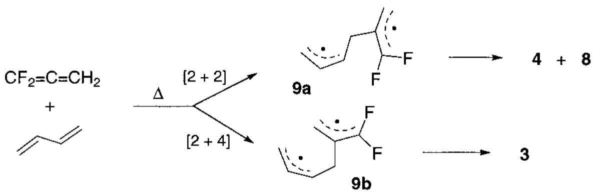


It is generally accepted that the [2 + 4] cycloadditions of 1,1-difluoroallene and other allenes are mechanistically concerted, pericyclic processes, whereas their [2 + 2] cycloadditions are considered to be nonconcerted reactions, proceeding through diradical intermediates. Although the smaller activation enthalpy and larger negative entropy of activation for the [2 + 4] cycloadditions than those observed for the [2 + 2] cycloadditions of DFA can be considered consistent with such proposed mechanistic differences, there is nevertheless no way that such small differences in activation parameters can be considered *convincing* evidence for the respective concerted and stepwise mechanisms.

Because the observed activation parameters for the [2 + 4] and [2 + 2] reactions *are clearly different*, what *can* be said with some certainty is that the two mechanisms *do not have a common rate-determining step, nor can they involve a common intermediate*. The latter conclusion derives from our extensive earlier studies of allene cycloadditions,[24] including those involving interconversion of [2 + 2] adducts such as **4** and **8**,[25] which indicate that diradicals such as **9** in Scheme 1 are not reversibly formed, that is they do not revert to allene (DFA) in competition with their cyclization processes (i.e., formation of **4** and **8**). Therefore, the rate-determining steps in DFA's reaction with 1,3-butadiene are the initial, bimolecular processes, and they are different for the [2 + 4] and [2 + 2] reactions.

The lack of regiospecificity exhibited in the [2 + 2] process combined with earlier isotope effect evidence[24] are consistent with a probable stepwise mechanism for this reaction, involving extended diradical intermediate **9**. The activation enthalpy for formation of [2 + 2] adduct **4** (−38.7 cal/deg) is consistent with values generally obtained for [2 + 2] cycloaddition processes, including the values of −34.0 and −38.4 cal/deg, which we obtained for the dimerizations of TFE and CTFE, respectively.

On the other hand, the evidence for a concerted mechanism for the [2 + 4] process is by no means definitive. The somewhat larger entropy of activation for formation of [2 + 4] adduct **3** is consistent with values that have been observed for other Diels Alder reactions. However, the enthalpy of activation for this supposedly "concerted" process is very similar to that of the acknowledged diradical [2 + 2] process that forms product **4**. Thus, there is no evidence of a significant "enthalpy of concert" for this reaction. Such enthalpy of concert is often invoked as convincing evidence for concerted, pericyclic mechanisms.[26] To play the devil's advocate in this particular case, one could readily attribute the slightly more entropically demanding, rate-determining step of the [2 + 4] reaction to initial formation of the isomeric, *cisoid* diradical **9b**, which could rapidly cyclize to product.



The major argument against such an explanation involving "competing diradical formation" is the observed total, contrathermodynamic regiospecificity that is observed for the [2 + 4] reaction, which results in exclusive formation of **3**. Such regiospecificity is consistent with computational models of the concerted reaction,[7,27] and it is not readily rationalized otherwise.

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(24) (a) Dolbier, W. R., Jr. *Acc. Chem. Res.* **1991**, *24*, 63−69. (b) Dolbier, W. R., Jr.; Dai, S. H. *J. Am. Chem. Soc.* **1972**, *94*, 3946.

(25) Dolbier, W. R., Jr.; Piedrahita, C. A.; Al-Sader, B. H. *Tetrahedron Lett.* **1979**, 2957.

(26) Roth, W. R.; Lennartz, H.-W.; Doering, W. v. E.; Birladeanu, L.; Guyton, C. S.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, *112*, 1722.

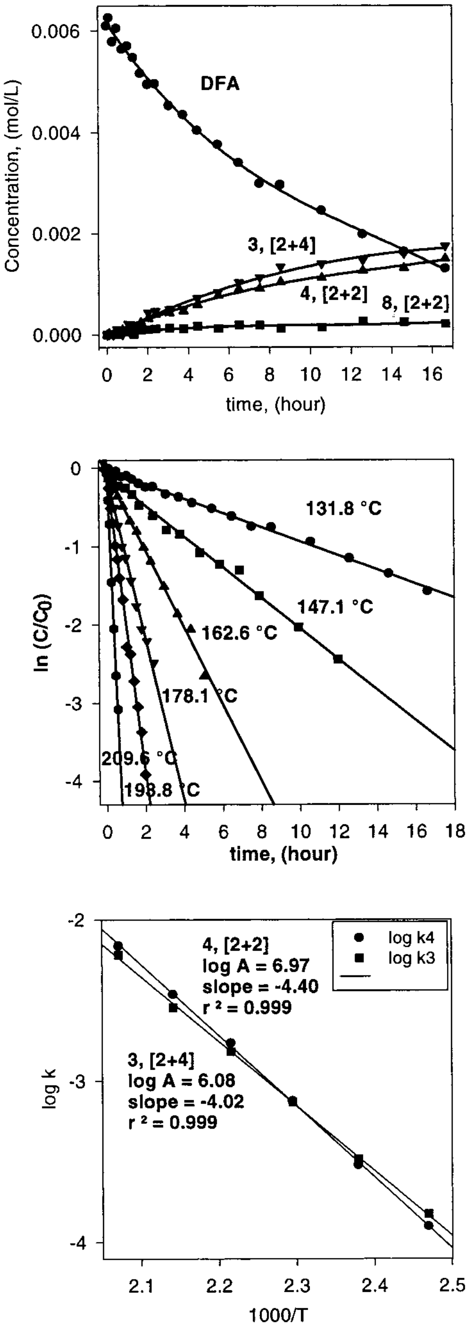

Figure 6. DFA reaction with 1,3-butadiene: concentration of components versus time (top); pseudo-first-order plot of decay of DFA (middle); Arrhenius plots for major cycloaddition products (bottom).

Table 2. Activation Parameters for DFA/1,3-Butadiene Cycloaddition Reactions

	activation parameters[a,b]			
adduct	log *A*	ΔE_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol[c]	$\Delta S^{\ddagger}$, cal/kmol[c]
4, [2 + 2]	6.97 ± 0.11	20.1 ± 0.2	18.3 ± 0.2	−38.7 ± 0.5
3, [2 + 4]	6.08 ± 0.12	18.4 ± 0.25	16.6 ± 0.25	−42.7 ± 0.6

[a] Enthalpies and entropies of activation are calculated for the standard state of 1 atm at 450 K. [b] See Table 4 in the Supporting Information for rate constants. [c] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are calculated as described in ref 23. The values for 1 mol/L standard state are different: for the formation of [2 + 2] product $\Delta H_c^{\ddagger} = 19.2$ kcal/mol, $\Delta S_c^{\ddagger} = -31.4$ eu, and for [2 + 4] adduct $\Delta H_c^{\ddagger} = 17.5$ kcal/mol and $\Delta S_c^{\ddagger} = -35.5$ eu.

All in all, we consider the available evidence, both experimental and computational, to be most consistent with the [2 + 4] reaction of DFA with 1,3-butadiene proceeding via a concerted mechanism.

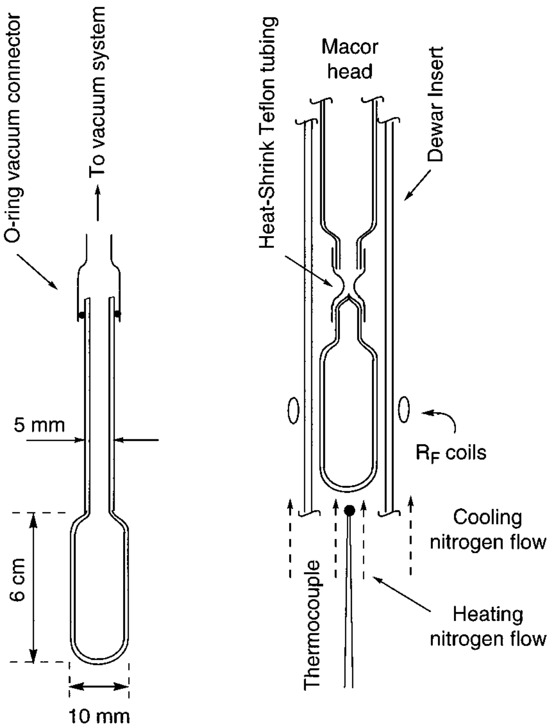

Figure 7. Diagrams of the gas-phase NMR ampule attached to a vacuum system before being sealed off with a propane torch (left) and seated in a commercial high-temperature NMR probe (right).

Conclusions

In conclusion, a novel gas-phase NMR methodology has been used to obtain accurate kinetic measurements for three bimolecular, second-order cycloaddition reactions. The derived activation parameters obtained for the thermal dimerizations of chlorotrifluoroethylene and tetrafluoroethylene were consistent with those that had previously been reported in the literature. The activation parameters that were obtained for the competing [2 + 2] and [2 + 4] cycloadditions of difluoroallene with 1,3-butadiene are to our knowledge the first such parameters obtained for a cycloaddition of an allene species. They indicate highly restricted transition states for both processes, with the [2 + 4] cycloaddition being somewhat more entropy demanding, while being less enthalpy demanding.

Experimental Section

Chlorotrifluoroethylenene and 1,3-butadiene were obtained from Aldrich and TFE was a DuPont product contained in a small cylinder at low pressure. 1,1-Difluoroallene was prepared according to published procedure.[28] It was found to be 90−97% pure by ^{1}H NMR containing 3−10% of *n*-butane from the BuLi reagent used in the synthesis.

The NMR reaction vessel is an ampule made from a short section of a 10 mm NMR tube with a coaxial 5 mm tube extension to allow quick attachment to a high-vacuum system via an O-ring adapter for sealing NMR tubes (Figure 7). These gas-phase NMR ampules are now available commercially at low cost.[6] Gases are metered using the ideal gas law by isolating a 53 mL bulb with the appropriate pressure of the gaseous reagent, measured with an MKS Baratron capacitance pressure

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(27) (a) Domelsmith, L. N.; Houk, K. N.; Dolbier, W. R., Jr.; Piedrahita, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6908. (b) Manoharan, M.; Venuvanalingam, P. *J. Fluorine Chem.* **1995**, *73*, 171−174. (c) Manoharan, M.; Venuvanalingam, P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1423−1427.

(28) Dolbier, W. R. J.; Burkholder, C. R.; Piedrahita, C. A. *J. Fluorine Chem.* **1982**, *20*, 637.

transducer (±0.1 Torr), for the desired number of micromoles followed by bulb-to-bulb transfer into the ampule. Alternatively, the number of moles of gas transferred can be obtained from the pressure drop in the manifold of known volume when the latter is opened to the evacuated compartment containing the ampule. When all gaseous reactants are loaded, the ampule kept in liquid nitrogen is sealed off with a flame at its neck so as to leave a short stub that facilitates the attachment by means of a short piece of heat-shrink Teflon tubing (Figure 7) to a matching stub of a 10 mm NMR tube attached to the ceramic head that seals the high-temperature probe. This method of holding the ampule in the probe is surprisingly effective even at probe temperatures close to 400 °C where the Teflon connector softens but continues to hold the ampule. An internal volume of 3.8 mL can be obtained reproducibly by sealing the ampules at the same height of the 5 mm extension. The main purpose of a short ampule is to minimize temperature gradients by restricting the sample volume to the thermostated region of the probe. We measure temperature gradients of 2 to 3° inside the ampule (vide infra). Great attention must be paid not to create *excessive pressures in sealed ampules at elevated temperatures*. A safe upper limit of 250 μmol of volatiles is obtained from the ideal gas law with an ampule volume of 3.8 mL and with a safe internal pressure of 3 atm at 400 °C.

The high-temperature probe is a Nalorac 10 mm probe for a wide bore magnet with an upper temperature limit of 400 °C. Heating is achieved by flowing into the probe hot nitrogen gas whose temperature is regulated by a controller. Another nitrogen flow in an anular space is used for cooling the probe externals. The probe comprises also a cylindrical Macor ceramic head that thermally seals the heated probe compartment and which accepts a flanged 10 mm NMR tube. The temperature was calibrated by positioning a thin thermocouple in the center of a dummy ampule identical to those used for actual kinetic runs except for a small hole at the end of the 5 mm stub. Repeated calibrations indicate that the temperature in the ampule is defined within 1 to 2 °C. To initiate a kinetic run, the Macor head carrying the sample assembly is lowered into the probe kept at the desired temperature with a string. Automatic NMR data acquisition starts as soon as the sample is seated in the probe according to a script that defines the time steps in the repetitive spectral sampling.

^{19}F NMR spectra were obtained with a GE Omega 300 MHz spectrometer. No field lock was used, and the ampules were not spun. A small flip angle of the magnetization vector (typically 10 to 15°) was used for a more uniform power distribution over the wide ^{19}F NMR spectral widths. Very short pulse delays of 50 ms allowed the acquisition of 512 transients in about 1 min.

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Supporting Information Available: Derivation of kinetic expressions and tables of kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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