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Cycloaddition Reactions of CF with Unsaturated Hydrocarbons. Correlation of Activation Energies and Frequency Factors with the Hydrocarbon Ionization Energies

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Absolute rate coefficients of the elementary reactions of $CF(X^2\Pi, v{=}0)$ with a series of unsaturated hydrocarbons have been measured for the first time over an extended temperature range. The rate coefficients of the CF reactions with ethene, propene, isobutene and 2,3-dimethyl-2-butene, as well as with allene, 1,3-butadiene, isoprene, and propyne, have been determined at temperatures between 294 and 455 K and at pressures in the 2−10 Torr range, using pulse laser photolysis−laser-induced fluorescence (PLP-LIF) techniques. The rate constants of the reactions of CF with 1-butene, *cis*-2-butene, and *trans*-2-butene have been determined at 294 K. The $CF(X^2\Pi)$ radicals were generated by excimer laser multiphoton dissociation of CF_2Br_2 at 248 nm. Pseudo-first-order exponential decays of $CF(X, v{=}0)$ were monitored by LIF (excitation at the P_{11} band head of the $A^2\Sigma^+$, $v' = 1 \leftarrow X^2\Pi$, $v'' = 0$ transition) at varying concentrations of the coreactant, always in very large excess over CF. Pressure effects were not observed. The rate coefficients, in units of cm^3 $molecule^{-1}$ s^{-1}, can be expressed by the following Arrhenius equations: $k(CF+C_2H_4) = (8 \pm 1) \times 10^{-13} \exp\{(-700 \pm 96)/T\}$, $k(CF+C_3H_6) = (9.1 \pm 0.9) \times 10^{-13} \exp\{(-80 \pm 20)/T\}$, $k(CF+i\text{-}C_4H_8) = (1.1 \pm 0.1) \times 10^{-12} \exp\{(400 \pm 50)/T\}$, $k(\text{CF+2,3-dimethyl-2-butene}) = (1.6 \pm 0.5) \times 10^{-12} \exp\{(720 \pm 95)/T\}$, $k(\text{CF+allene}) = (3.4 \pm 0.4) \times 10^{-12} \exp\{(-1037 \pm 100)/T\}$, $k(\text{CF+1,3-butadiene}) = (9 \pm 2) \times 10^{-12} \exp\{(-560 \pm 140)/T\}$, $k(\text{CF+isoprene}) = (1.2 \pm 0.2) \times 10^{-11} \exp\{(-190 \pm 80)/T\}$, and $k(\text{CF+propyne}) = (3 \pm 1) \times 10^{-12} \exp\{(-860 \pm 200)/T\}$. For the other butenes, the following rate constants were measured at $T = 294$ K: $k(\text{CF+1-butene}) = (8.28 \pm 0.83) \times 10^{-12}$, $k(\text{CF+}cis\text{-2-butene}) = (5.22 \pm 0.52) \times 10^{-12}$, and $k(\text{CF+}trans\text{-2-butene}) = (5.56 \pm 0.56) \times 10^{-12}$. For the alkenes, as well as for the alkanedienes, linear correlations were observed between the Arrhenius activation energy and the ionization potential (IP) of the corresponding hydrocarbon and likewise between the Arrhenius frequency factors and the IP. Ample evidence is presented that the title reactions are electrophilic cycloaddition reactions.

Introduction

Fluorocarbon radicals are important in many aspects of modern society and technology. One major area of importance concerns the dry-etching techniques for the fabrication of ULSI microcircuits, using fluorocarbon-based plasmas to etch semiconductor and/or oxide layers. The chemistry of these plasmas is extremely complex, featuring a multitude of different species (including CF and CF_2), each involved in several chemical reactions. CF and CF_2 are specifically involved in the regeneration of active etching species through reactions in the gas phase (e.g., regeneration of F atoms through reaction of CF with F_2 produced by heterogeneous recombination of F atoms) and the formation of inhibiting carbon polymer films on the etched substrate. In the latter process, the (cyclo)addition of CF to larger, unsaturated fluorocarbons is of likely importance. Determination of the kinetic coefficients of several of these reactions is a key step toward the elucidation and characterization of the chemical mechanisms involved.

As part of ongoing research on the reactivity and kinetics of the CF radical in this laboratory,[1] we presently report the results of absolute rate coefficient determinations for the reactions of CF with several alkenes and alkanedienes, as well as with propyne. From a fundamental viewpoint, it will also be instructive to compare the reactivity of $CF(X^2\Pi)$ with that of the related (halo)carbyne radicals CCl, CBr, and CH.

The only other direct determinations of rate constants for CF + alkene reactions known to us are those of Ruzsicska et al.,[2] who used flash photolysis of $CHFBr_2$ for the generation of the CF radicals and kinetic absorption spectroscopy for their detection. Their results can be found in Table 1. On the basis of their experimental results, Ruzsicska et al. suggest that the reaction of CF with alkenes is an electrophilic cycloaddition, forming a vibrationally excited fluorocyclopropyl adduct in the primary reaction step.

In a comprehensive study on the gas phase chemistry of carbynes, James et al. [3] observed a linear anticorrelation between the logarithm of the $k(T{=}295\text{ K})$ rate coefficients for the reactions of CCl and CBr with alkenes and the ionization potential (IP) of the alkene concerned. They attribute this correlation to a decreasing activation energy as the IP of the alkene decreases, facilitating the electrophilic attack of the carbyne on the double bond.

One objective of the work presented here was to verify this correlation for CF + alkene reactions and to establish whether the activation energy of these reactions increases indeed with the IP of the alkene. To this end, the rate coefficients of the reactions of CF with ethene, propene, 1-butene, isobutene, *trans*-2-butene, *cis*-2-butene, and 2,3-dimethyl-2-butene have been determined at temperatures ranging from 295 to 455 K.

With a similar goal, the rate coefficients of the reactions of CF with allene, 1,3-butadiene, isoprene, and propyne were measured in the same temperature range.

All rate coefficient determinations were carried out under pseudo-first-order conditions using pulse-laser photolysis and time-resolved laser-induced fluorescence (PLP-LIF). Possible dependences of the rate coefficients on pressure in the range

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TABLE 1: Absolute Rate Constants for the Reactions of (Halo)methylidynes with Several Alkenes and with Propyne at Room Temperature (*k* in 10^{-13} cm^3 molecule^{-1} s^{-1})

coreactant	CF	CCl	CBr	CH
ethene	0.7 ± 0.2^b	2.7 ± 0.2^b	8.6 ± 0.3^b	2230 ± 300^d
	0.7 ± 0.07^a	2.2 ± 0.2^c		
propene	5 ± 2^b	17 ± 2^b	50 ± 5^b	
	7 ± 0.7^a	42^b		
1-butene	7 ± 2^b	28 ± 3^b	58 ± 5^b	
	8 ± 0.8^a			
isobutene	18 ± 5^b	58 ± 5^b	133 ± 17^b	
	41 ± 4^a			
trans-2-butene	18 ± 3^b	43 ± 3^b	123 ± 13^b	
	51 ± 5^a			
cis-2-butene	52 ± 5^a	159^e		
2,3-dimethyl-2-butene	171 ± 17^a			
propyne	1.5 ± 0.2^a	37 ± 3^f	80 ± 1^f	4600 ± 1500^h
		40 ± 3^g		

[a] This work. [b] Reference 2. [c] Reference 17. [d] Reference 9. [e] Reference 18. [f] Reference 3. [g] Reference 19. [h] Reference 20.

2−10 Torr and on the fluence of the photolysis laser pulse have been investigated as well.

Experimental Section

The apparatus and most of the experimental procedures have been described in detail previously,[1] and only a brief summary is given here.

Ground-state CF radicals were generated in a blackened stainless steel LIF cell by photodissociation of CF_2Br_2 at 248 nm using a pulsed KrF excimer laser (Lambda Physik EMG 101E MSC; $E_p \approx 200$ mJ/pulse, $t_p \approx 20$ ns, pulse rate = 10 s^{-1}), with the beam section reduced to 0.8 × 0.3 cm^2 by cylindrical optics. The CF ($X^2\Pi, v''=0$) radicals were probed by a pulsed tunable dye laser pumped by a Nd:YAG laser (Quantel Datachrom 5000 system), at $\lambda = 223.88$ nm ($E_p \approx 1.5$ mJ/pulse, $t_p \approx 10$ ns, bandwidth ≈ 0.2 cm^{-1}) exciting the strong P_{11} band head of the $A^2\Sigma^+ \leftarrow X^2\Pi$ (1,0) transition. The resulting fluorescence was detected by a 0.22 m double grating Spex 1680 Spectramate monochromator at 268.4 nm, corresponding to the A → X (1,6) band; the slit widths of the monochromator were 3 mm each, resulting in a bandwidth of 6 nm. The Hamamatsu R928 photomultiplier output signal was fed to a Stanford Research Systems SR250 boxcar integrator. Data acquisition/reduction was achieved by a Macintosh II computer. A programmable, microprocessor-based digital delay generator (0.1 μs resolution) controlled the delay between the photodissociation pulse and the probe laser pulse; it allowed an adjustable rate of change of the delay over a very wide range.

All experiments were carried out under quasi-stagnant conditions. Gases were fed into the system through calibrated MKS mass flow controllers. The concentrations of molecular species were determined from their fractional flows and from the total pressure. The pressure was measured by a Datametrics Barocel absolute pressure sensor.

Total flows varied from 200 to 850 sccm at total pressures from 2 to 10 Torr. The flow rates were sufficiently high to refresh the gas in the irradiated volume between successive laser pulses. Kinetic measurements were carried out in the temperature range 294−455 K. The reaction cell was heated by means of a heating mantle. The temperature in the reaction volume at the center of the cell was measured by a movable chromel−alumel thermocouple.

Gases fed to the LIF cell were (i) Ar (99.9996%) or CF_4 (43.4% in He(UHP)) used as diluent, (ii) a mixture of 5% CF_2Br_2 in He(UHP), (iii) C_2H_4 (99.99%), C_3H_6 (99.93%), 1-C_4H_8 (99.0%), or certified mixtures of *i*-C_4H_8 (9.9% in He(UHP)), *trans*-2-C_4H_8 (10% in He(UHP)), *cis*-2-C_4H_8 (9.75% in He(UHP)), 2,3-dimethyl-2-butene(5.02% in Ar(UHP)), C_3H_4 (allene, 5.0% in He (UHP)), C_4H_6 (1,3-butadiene, 9.97% in He(UHP)), and C_3H_4 (propyne, 4.80% in He (UHP)).

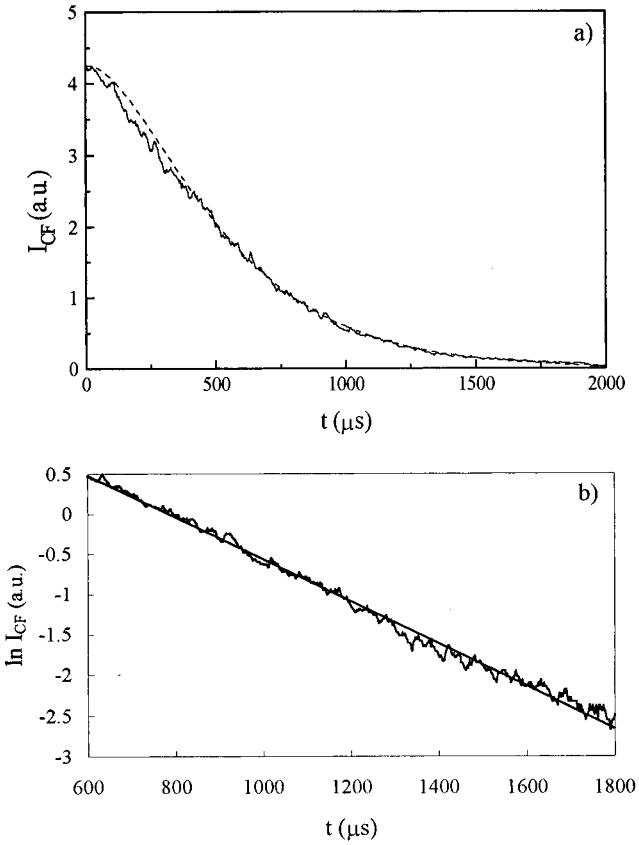


Figure 1. (a) Plot of typical CF fluorescence signal, in arbitrary units, vs reaction time. (b) Semilog plot of (a). Experimental conditions: reaction with 2,3-dimethyl-2-butene at $T = 295$ K and a total pressure of 10 Torr with CF_4 as bath gas, [23DM2B] = 1.53×10^{14} molecules/cm^{-3}.

Results

Decays of the CF($v=0$) LIF signals, I_{CF}, as a function of the delay time *t* between the photolysis laser and probe laser pulses were recorded under pseudo-first-order conditions with the coreactant always in very large excess. The initial $[CF(v=0)]_0$ concentration was estimated to be $\sim 10^{11}$ molecules cm^{-3} from the absolute LIF intensity.[1b] Coreactant concentrations ranged from 10^{13} to 5×10^{16} molecules cm^{-3}; in each case they were varied over about an order of magnitude.

The magnitudes of the CF fluorescence signals measured immediately after the photolysis laser pulse were essentially the same in the absence or presence of coreactants, indicating that any interference by a possible precursor + coreactant reaction was negligible.

Figure 1 shows the typical shape of the CF($v=0$) decay curves in the alkene + CF experiments. The initial biexponential behavior is due to $CF^\dagger(v \geq 1) \rightarrow CF(v=0)$ vibrational relaxation, as discussed in detail below. At larger reaction times, the I_{CF} decays always closely obey a simple exponential law, usually over more than three 1/e lifetimes (see Figure 1b as an example).

Pseudo-first-order rate constants for CF($v=0$) removal, k_{obs}, were generally derived from the slopes of the final, linear portions of the ln I_{CF} vs *t* plots: $k_{obs} \equiv -\mathrm{d}\ln[CF(v=0)]/\mathrm{d}t$, for large *t*. Base lines obtained by switching off the excimer laser or the PM power supply correspond with the signal at

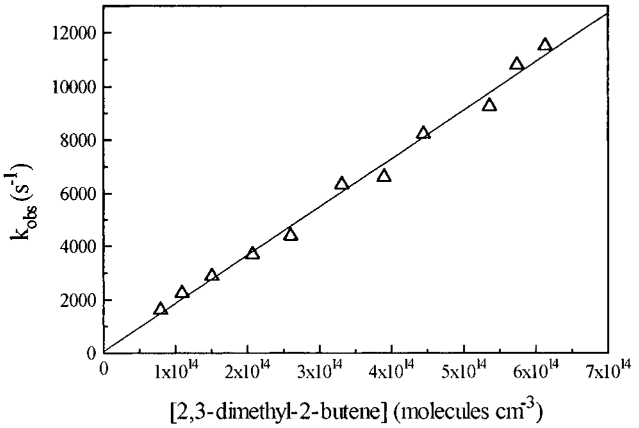


Figure 2. Pseudo-first-order rate constants k_{obs} plotted vs [2,3-dimethyl-2-butene] for the reaction CF + 2,3-dimethyl-2-butene, at $T = 295$ K and $p = 10$ Torr. The solid line represents a weighted linear least-squares fit.

$t \to \infty$. The slope k_{obs} for each decay was computed using a least-squares routine, with weights proportional to local noise.[1]

The bimolecular rate constant k(CF+A) for each reaction was obtained from the slope of a plot of k_{obs} vs the coreactant concentration [A]. The slopes $k = \mathrm{d}k_{obs}/\mathrm{d}[A]$ were also computed using a weighted least-squares routine. Figure 2 shows an example of a k_{obs} vs [coreactant] plot. The small ordinate intercepts are attributed to convection and diffusion of CF out of the probed volume.[1]

Systematic errors on the bimolecular rate constants due to inaccuracies in the absolute coreactant concentrations and in other experimental parameters are normally estimated at about 10%. In the few cases where vibrational relaxation effects hamper a sufficiently precise determination of the limiting slope d ln[CF(v=0)]/dt, the estimated systematic error on k is significantly higher.

Vibrational Relaxation Effect. The initial portions of the CF(v=0) decay curves exhibit a marked biexponential behavior (see Figure 1), as already observed and discussed in our earlier study of the CF + Cl_2 reaction.[1a] This phenomenon, which is more pronounced at higher total pressures, is due to collisional relaxation of CF radicals generated initially in excited vibrational states to the $v = 0$ state. As can be expected, the effect is stronger for reactions without energy barrier, such as CF + 2,3-dimethyl-2-butene (see below); for processes involving a barrier, the CF(v≥1) states react more rapidly than CF(v=0), and therefore the relative importance of $v \geq 1 \to v = 0$ relaxation will be limited.

The process of collisional relaxation of population from the $v \geq 1$ levels into the $v = 0$ state, combined with simultaneous chemical reactions with a coreactant A, can be approximated[5] by the simplified scheme

$$\mathrm{CF}(v{\geq}1) \xrightarrow{\mathrm{M}} \mathrm{CF}(v{=}0) \qquad k_{1a}$$

$$\mathrm{CF}(v{\geq}1) \xrightarrow{\mathrm{A}} \text{products} \qquad k_{1b}$$

$$\mathrm{CF}(v{=}0) \xrightarrow{\mathrm{A}} \text{products} \qquad k_{2}$$

where k_{1a}, k_{1b}, and k_2 are pseudo-first-order rate constants for a given bath gas density [M] and coreactant concentration [A]. For such a scheme one has

$$[\mathrm{CF}(v{=}0)](t) = [\mathrm{CF}(v{=}0)]_0 \mathrm{e}^{-k_2 t} + [\mathrm{CF}(v{\geq}1)]_0 \frac{k_{1a}}{k_1 - k_2}(\mathrm{e}^{-k_2 t} - \mathrm{e}^{-k_1 t}) \qquad \text{(I)}$$

where $k_1 = k_{1a} + k_{1b}$; the subscript zero refers to the initial concentrations. The expression above can be represented by

$$I_{\mathrm{CF}} = P\mathrm{e}^{-k_2 t} + Q\mathrm{e}^{-k_1 t} \qquad \text{(II)}$$

in agreement with the observations. The dashed curve in Figure 1a is an example of a fit of the logarithm of $I_{\mathrm{CF}}(t)$ by the logarithm of eq II, plotted as a normal signal vs time plot.

The rate coefficient of relevance to the CF(v=0) reaction kinetics of interest here is of course k_2, and hence experimental conditions must be chosen such that the term $Q\mathrm{e}^{-k_1 t}$ is either negligible or decays much more rapidly than $P\mathrm{e}^{-k_2 t}$, which implies that $k_1 > k_2$. The latter is easily achieved by using an efficient vibrational energy acceptor, at a high pressure, as bath gas. Moreover, one can easily verify whether $k_1 > k_2$. First, one then always has $P > 0$ and $Q < 0$, which entails that the second derivative $\mathrm{d}^2 I_{\mathrm{CF}}/\mathrm{d}t^2$ increases as a function of time, i.e., that I_{CF} will show an inflection point. Second, the limiting slope $-$d ln I_{CF}/dt for larger times—denoted above as k_{obs}—is then equal to k_2, and will therefore be directly proportional to [A]. Observation of both the above provides sufficient proof that $k_1 > k_2$ such that the limiting slope $-$d ln I_{CF}/dt is indeed equal to k_2.

Therefore, the majority of the decay experiments were carried out with CF_4 as bath gas (a 43% mixture in He), at a total pressure of 10 Torr. CF_4 is an efficient vibrational energy acceptor here since its C−F stretch frequencies closely match that of the CF molecule. However, in order to verify that the rate coefficients of the CF + alkene/alkyne reactions are independent of pressure—as is theoretically expected (see below)—decay experiments were carried out also at lower pressure with a fairly inefficient third body, argon, as bath gas. In this way, for both CF + propene and CF + isobutene, room temperature measurements were made at 2 Torr of Ar, 10 Torr of Ar, and 10 Torr of CF_4/He. In all the experiments it was verified that $k_1 > k_2$, and therefore k_2 was always derived from the limiting slope $-$d ln I_{CF}/dt. Generally, the vibrational relaxation effect was found to be the least pronounced at 2 Torr of Ar and most pronounced at 10 Torr of CF_4/He, but in the latter case compressed into a shorter time span. The rationalization is obvious. At 2 Torr of Ar the vibrational quenching constant k_{1a} is so small that the second term of eq I is only of minor importance. At 10 Torr of Ar the vibrational relaxation effect proved to be most troublesome: its magnitude is less than at 10 Torr of CF_4/He, but it is stretched out over a longer time span; the sum $k_{1a} + k_{1b}$ is only slightly larger than k_2—especially for the larger alkenes where there is no energy barrier to the reaction with CF—and the limiting slope $-$d ln $I_{\mathrm{CF}}/\mathrm{d}t = k_2$ is attained only at fairly long times such that the experimental "k_{obs}" should be considered here rather as a lower limit of k_2. Therefore, the k_2 values at 10 Torr of Ar were also derived from the data in an alternative way, by fitting them by the biexponential function, eq II. For these k_2 values, the systematic error was estimated at 20%.

Reaction with Alkenes. The results obtained for the kinetic coefficients of the CF reactions with the various alkenes and over the temperature range 294−455 K are listed in Table 2. All listed data are based on first-order rate constants k_{obs} obtained from the slope $-$d ln I_{CF}/dt at large reaction times for experiments where it was verified that $k_1 > k_2$.

TABLE 2: Summary of the Rate Constants Obtained in This Work

coreactant	P_{tot} (Torr)	bath gas[a]	T (K)	k (cm^3 molecule^{-1} s^{-1})
ethene	10	CF_4	294	7.40×10^{-14}
	10	CF_4	325	8.24×10^{-14}
	10	Ar	376	1.25×10^{-13}
	10	Ar	398	1.28×10^{-13}
	10	Ar	425	1.56×10^{-13}
	10	Ar	428	1.75×10^{-13}
propene	2	Ar	295	6.87×10^{-13}
	10	Ar	295	6.45×10^{-13}
	10	CF_4	295	6.88×10^{-13}
	10	CF_4	342	7.22×10^{-13}
	10	CF_4	397	7.32×10^{-13}
	10	CF_4	428	7.58×10^{-13}
	10	CF_4	457	7.59×10^{-13}
1-butene	2	Ar	294	8.28×10^{-13}
	10	Ar	294	8.05×10^{-13}
isobutene	2	Ar	294	4.06×10^{-12}
	10	Ar	294	3.71×10^{-12}
	10	CF_4	294	4.28×10^{-12}
	10	CF_4	358	3.42×10^{-12}
	10	CF_4	392	3.13×10^{-12}
	10	CF_4	421	2.90×10^{-12}
	10	Ar	457	2.57×10^{-12}
trans-2-butene	2	Ar	294	5.58×10^{-12}
	10	Ar	294	4.58×10^{-12}
cis-2-butene	2	Ar	294	5.22×10^{-12}
	10	Ar	294	4.43×10^{-12}
	10	CF_4	294	5.12×10^{-12}
2,3-dimethyl-2-butene	2	CF_4	295	1.88×10^{-11}
	10	CF_4	295	1.71×10^{-11}
	10	CF_4	331	1.47×10^{-11}
	10[b]	CF_4	331	1.31×10^{-11}
	10	CF_4	368	1.15×10^{-11}
	10[b]	CF_4	368	1.15×10^{-11}
	10	CF_4	395	9.68×10^{-12}
	10	CF_4	427	8.19×10^{-12}
allene	10	CF_4	295	1.02×10^{-13}
	10	CF_4	359	1.90×10^{-13}
	10	CF_4	397	2.50×10^{-13}
	10	CF_4	440	3.31×10^{-13}
1,3-butadiene	10	CF_4	295	1.41×10^{-12}
	10[b]	CF_4	295	1.54×10^{-12}
	10	CF_4	349	1.77×10^{-12}
	10	CF_4	392	2.10×10^{-12}
	10	CF_4	440	2.71×10^{-12}
isoprene	10	CF_4	294	6.50×10^{-12}
	10	CF_4	334	7.06×10^{-12}
	10	CF_4	370	7.20×10^{-12}
	10	CF_4	409	7.46×10^{-12}
	10	CF_4	442	8.37×10^{-12}
propyne	10	CF_4	296	1.53×10^{-13}
	10	CF_4	355	2.14×10^{-13}
	10	CF_4	395	3.12×10^{-13}
	10	CF_4	445	3.99×10^{-13}

[a] CF_4 as a 43% mixture in helium. [b] Experiments with photodissociation laser fluence reduced (see text).

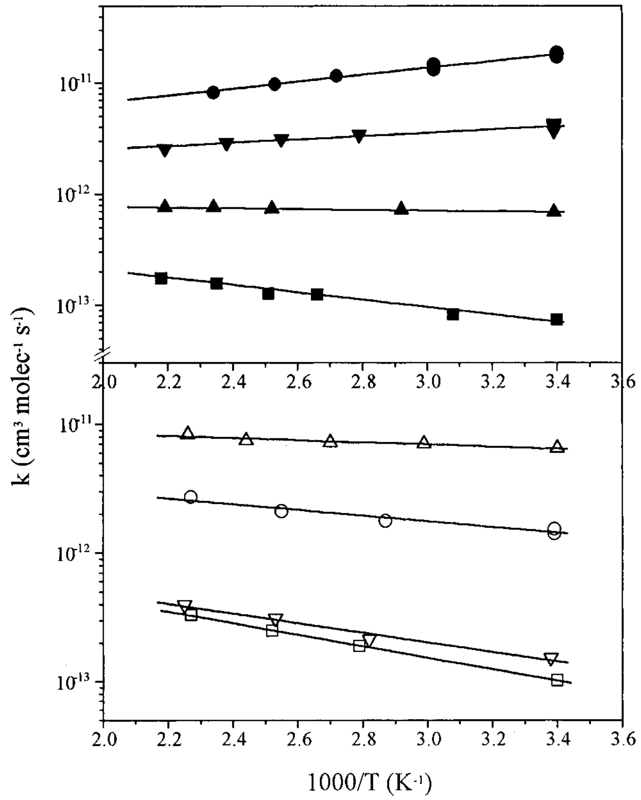


Figure 3. Arrhenius plot for the various reactions studied (total pressure = 10 Torr): ■, CF + ethene; ▲, CF + propene; ▼, CF + iso-butene; ●, CF + 2,3-dimethyl-2-butene; □, CF + allene; ○, CF + 1,3-butadiene; △, CF + isoprene; ▽, CF + propyne. The solid lines represent weighted linear-least squares fits.

The reactions of CF with the smaller alkenes were found to be independent of pressure between 2 and 10 Torr, within the experimental error. As an example, Table 2 lists $k(T=295$ K) data for C_3H_6 at 2 and 10 Torr of Ar and at 10 Torr with the CF_4/He mixture as bath gas. In earlier work on the C_2H_4 reaction, Van Hoeymissen[4] likewise found rate constants independent of pressure in the range 2−10 Torr of Ar at $T = 295$ K; his absolute values were about 15% higher than our present results at 10 Torr of CF_4/He. For the higher alkenes the rate constant obtained with Ar as bath gas appears to decrease slightly when raising the pressure from 2 to 10 Torr, but this is clearly due to the effects of vibrational relaxation affecting the k_{obs} data at 10 Torr of Ar, as discussed above. Indeed, as seen for the isobutene and *cis*-2-butene cases, the data at 10 Torr of CF_4/He—a bath gas that compresses the vibrational relaxation into a short time span—are nearly identical to the results at 2 Torr of Ar. Moreover, a biexponential analysis of the decay curves for the CF + isobutene case at 10 Torr of Ar led to k_2 values some 10−20% higher that the limiting slope k_{obs}. Therefore, it can be stated that the observed, small pressure effects are artifacts. For obvious reasons, most of the rate constant measurements at higher temperatures were carried out at 10 Torr of CF_4/He.

After a few thousand excimer laser pulses a sooty deposit formed on the inside surface of the windows. The deposit speed was independent of the alkene concentration but showed a pronounced correlation with the number of C atoms of the alkene. The possibility of this evident dissociation of the alkene influencing the measured value of the rate constants prompted us to determine a rate constant at two different photolysis laser fluences. "Low-fluence" experiments (5×10^{17} photons/cm^2 pulse) for the CF + 2,3-dimethyl-2-butene reaction at 331 and 368 K yielded essentially the same bimolecular rate constants k as the "normal" fluence measurements (10^{18} photons/cm^2 pulse), thus indicating that the fraction of alkenes dissociated under influence of 248 nm excimer light is extremely small. This result is in agreement with absorption data.[6,7]

The rate constants obtained at room temperature are in good agreement with the measurements of Ruzsicska et al.[2] (Table 1), except for the reactions with 2-butenes for which our k values are about 3 times higher. A reasonable explanation for this remarkable difference was not found.

The rate coefficients obtained for the CF + alkene reactions in the $T = 300−450$ K range can be represented by Arrhenius relations $k = A \exp(-E_a/RT)$. The kinetic coefficients are summarized in an Arrhenius plot in Figure 3. The A factors and experimental "activation energies" E_a are listed in Table

TABLE 3: Summary of the Obtained Arrhenius Parameters for the Various Reactions and Ionization Energy (IP) of the Coreactants[a]

coreactant	IP (eV)	A (cm^3 molecule^{-1} s^{-1})	E_a (kcal/mol)
ethene	10.51	$(8 \pm 1) \times 10^{-13}$	1.39 ± 0.19
propene	9.74	$(9.1 \pm 0.9) \times 10^{-13}$	0.16 ± 0.04
iso-butene	9.23	$(1.1 \pm 0.1) \times 10^{-12}$	-0.81 ± 0.10
2,3-dimethyl-2-butene	8.30	$(1.6 \pm 0.5) \times 10^{-12}$	-1.43 ± 0.19
allene	9.65	$(3.4 \pm 0.4) \times 10^{-12}$	2.06 ± 0.06
1,3-butadiene	9.20	$(9 \pm 2) \times 10^{-12}$	1.11 ± 0.28
isoprene	8.85	$(1.2 \pm 0.2) \times 10^{-11}$	0.38 ± 0.16
propyne	10.36	$(3 \pm 1) \times 10^{-12}$	1.71 ± 0.40

[a] The stated error margins are 95% confidence intervals.

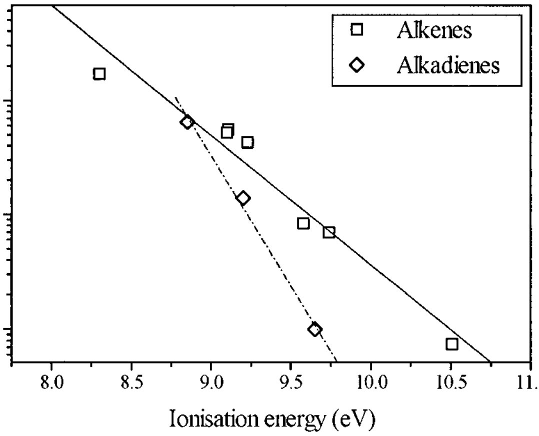


Figure 4. Plots of k vs the hydrocarbon ionization energy for the CF + alkene and CF + alkanediene reactions at $T = 295$ K.

3, together with the alkene ionization potential (IP). The A factors are fairly low, and the E_a values are small; the latter are even negative for the larger alkenes. Both the E_a and A correlate well with the IP.

The rate constant results at room temperature confirm that a linear correlation as observed earlier by James et al. [3] between ln k of the CCl/CBr + alkene reactions and the IP of the corresponding alkene is also valid for CF + alkene reactions (Figure 4). Also, the derived Arrhenius parameters confirm that the E_a for these reactions decreases progressively with increasing alkyl substitution on the alkenic carbons.

Reaction with Alkanedienes. The rate constants obtained for the reactions of CF with the three alkanedienes are listed in Table 2. For the reaction of CF with isoprene (2-methyl-1,3-butadiene), an adsorption/desorption effect of isoprene on the wall of the reaction cell reduced the accuracy and precision of its concentration. We therefore adopted a systematic error of 20% for the measured rate constant of this reaction.

The reaction of CF with 1,3-butadiene has been studied at two different excimer laser fluences at room temperature, to determine the influence of a possible photodissociation of the alkanediene on the measured rate constant. As with the alkenes, this did not result in a significantly different result, indicating that alkanediene photolysis is unimportant in our experimental conditions. This is confirmed by the work of Haller and Srinivasan,[8] who find the major products of the photodissociation of 1,3-butadiene to be C_2H_6, C_2H_4, and C_2H_2, all stable species which react very slowly with CF.[1]

It is seen that the rate constants of these reactions follow the same trend as the alkene reactions, increasing with alkyl substitution on the alkenic carbons. As with the alkene reactions, there is a linear correlation between log k for the CF + alkanediene reactions and the IP of the alkanediene (Figure 4), indicating that these reactions likewise proceed via electrophylic cycloaddition.

Arrhenius plots are displayed in Figure 3. The parameters A and E_a can be found in Table 3. Again, as with the alkenes, both E_a and A correlate well with the IP.

Reaction with Propyne. The rate coefficients obtained for the reaction of CF with propyne at temperatures between 295 and 455 K are given in Table 2. The Arrhenius plot is shown in Figure 3, and the Arrhenius parameters are given in Table 3.

Discussion

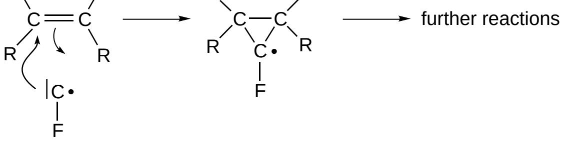
Reaction with Alkenes. The reactions of CF with alkenes are the slowest of all known carbyne + alkene reactions (Table 1); e.g., the reaction of CF with ethene has a rate constant at room temperature of 7.4×10^{-14} cm^3 molecule^{-1} s^{-1} while the analogous CH reaction has a rate constant of 2.2×10^{-10} cm^3 molecule^{-1} s^{-1},[9] a difference of almost 4 orders of magnitude.

The high reactivity of CH in this type of reactions can be explained by its particular electronic properties.[1] The strongly electron-deficient carbon atom has (besides an unpaired electron) a lone-pair orbital together with a vacant π-orbital. This combination favors insertion reactions, since it allows the formation of two new σ-bonds at the expense of breaking one σ- or π-bond, without net charge transfer. The carbyne family shares this particular feature with the closely related singlet carbenes CX_2. The latter species are also well-known for their insertion reactions, into σ- or π-bonds.

The initial step of the reaction of CH with alkenes, for example, is an insertion of CH in the π-bond, forming a cyclopropyl adduct. The zero-point energy of the initially formed adduct lies roughly 100 kcal/mol below that of the reactants, leading to a fast reaction with a negligibly small entrance barrier and an "early" and loose transition state, resulting in a high frequency factor.

In the halocarbynes though, this particular orbital combination breaks down partially, due to back-donation from the pπ-orbitals of the halogen atom to the vacant π-orbital of the carbon atom.[1,3] This back-donation effect is most pronounced in CF, where the overlap of the halogen and carbon π-orbitals is largest, producing an exceptionally stable C−F bond, as evidenced by (i) its high dissociation energy of ~130 kcal/mol[12] compared to an average C−F bond energy in for example CF_4 of 116 kcal/mol and (ii) the "inverse" C^-F^+ dipole moment of 0.65 D.[13] As a result, CF has the lowest reactivity of all halocarbynes toward this type of compound (Table 1).

The reaction of CF with alkenes probably proceeds similarly to the CH + alkene reaction, via an electrophilic cycloaddition of CF onto the π-bond of the alkene as the first reaction step, forming a (vibrationally excited) fluorocyclopropyl adduct that can undergo further unimolecular isomerisation and/or fragmentation:



That CF + alkene reactions do not proceed by insertion in a C−H σ-bond can be concluded from the finding that the reactions of CF with alkanes are at least 1 order of magnitude slower.[1]

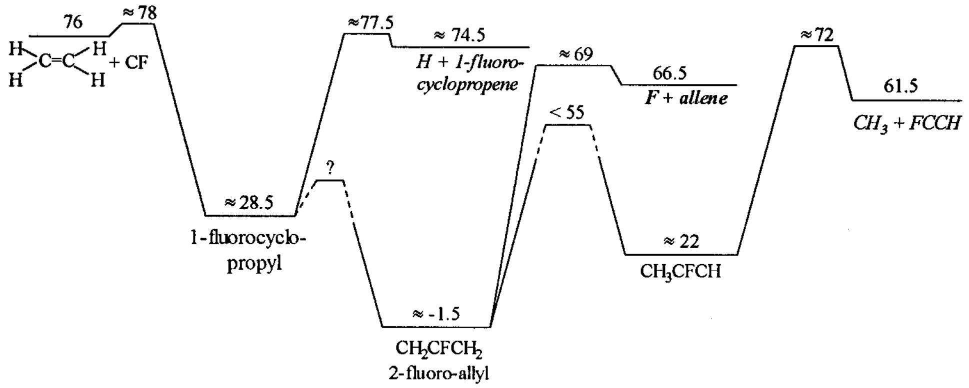


Figure 5. Approximate energy diagram of the CF + C_2H_4 reaction.

Figure 5 shows an approximate potential energy diagram of the CF + C_2H_4 reaction. The energies ($\Delta H^0_{f,0}$) of the reactants and of the products of the most facile fragmentation path, F + allene, are well-known.[10,11] Energies of intermediates and other end products had to be estimated by comparison with analogous compounds,[10,11] but their precise values are of little importance here. The energy of the transition state (TS) connecting the fluoroallyl radical with the end products F + allene is of particular importance, however. By considering the reverse reaction, i.e., the addition of F to allene, it is seen that this can be only a few kcal/mol above 66.5 kcal/mol, which is almost 10 kcal/mol below the TS of the entrance channel. That the TS for at least one exit channel lies so much lower than the entrance TS entails that the redissociation of the initial cycloadduct back into C_2H_4 + CF is much slower than its further unimolecular isomerization/fragmentation into products (F + allene, possibly others). This implies that the formation of the initial adduct is the only rate-controlling step and hence that collisional stabilization at higher pressures can only alter the product distribution, but can have no influence on the total phenomenological rate constant. Therefore, pressure dependence of the bimolecular rate constant can be excluded a priori on a theoretical basis. This is confirmed by the experimental results.

Since alkyl substitution is expected to have an equal effect on the energies of ethene and allene, the argument above should be valid for CF + alkene reactions in general. It also follows that the likely if not dominant fate of the initial adduct will be isomerization to a resonance stabilized 2-fluoroallyl type radical, which will eventually dissociate into an F atom and a substituted allene.

Alkyl groups have electron-donating properties, so that increasing the alkyl substitution on the alkenic carbons results in a more electron-rich π-bond, as witnessed by the concomitant IP drop. This should facilitate the electrophilic attack of the electron-deficient CF and thus result in a faster reaction with a lower energy barrier. The expected decrease of the activation energy with increasing alkyl substitution is fully confirmed by our experimental results. Indeed, our E_a data exhibit a strong correlation with the alkene IP (Table 3). This constitutes further proof that the reaction in question is an electrophilic cycloaddition process. The observed linear correlation between log k and the IP can thus be attributed to a corresponding change of barrier height.

We also observe a correlation between the Arrhenius frequency factor A and the IP, the A values increasing significantly from ethene to 2,3-dimethyl-2-butene (Table 3). This correlation can be traced back to the E_a−IP correlation as well: a lowering of the energy barrier results in an "earlier" and less rigid transition state, leading to a higher frequency factor. Nevertheless, even when the barrier almost vanishes, the A value remains rather low, indicating an entropically unfavorable or highly ordered transition state, again consistent with a cycloaddition process.

Finally, for the reactions of CF with isobutene and most prominently with 2,3-dimethyl-2-butene, we observe a negative temperature dependence of the rate coefficient, and hence a negative Arrhenius "activation energy" E_a. This indicates that the actual energy barrier for these reactions, and specifically for the latter reaction, is probably vanishingly small. According to transition state theory, the temperature dependence of the rate coefficient will in such a case be determined solely by the T dependence of the frequency factor $B(T) = k_bT/h \times F_‡/(F_{CF}F_{alkene})$, where the F_i represent the partition functions for transition state and reactants. A simple evaluation of this formula, assuming CF in its electronic and vibrational ground states but accounting for the $^2\Pi_{3/2}$ state that lies approximately 77 cm^{-1} above the $^2\Pi_{1/2}$ electronic ground state,[14] results in $B(T) \propto T^{-1.6}$. Yet, the rate coefficient data for CF + 2,3-dimethyl-2-butene show that $B(T) \propto T^{-2}$, indicating that the simple evaluation above is not sufficient.

The transition state in "barrierless" reactions is variational; the "most difficult passage" on the reaction coordinate is determined by mainly entropic factors (as opposed to enthalpic factors) and lies at the bottleneck of the TS partition function, where the sum of accessible states is the lowest. It can be shown[15] that this variational TS always lies inside (i.e., at separations smaller than) the so-called centrifugal maximum, the energy maximum resulting from relative rotation of the reactants. According to Waage and Rabinovitch,[16] the location of this centrifugal maximum on the reaction coordinate, r_m, varies with temperature according to $T^{-1/\sqrt{3}}$ for a Lennard-Jones (6,12) potential energy function. Via the rotational partition function for the complex at the centrifugal maximum, proportional to $r_m{}^2$, this introduces an additional $T^{-1/3}$ factor in the temperature dependence for the frequency factor, leading to the observed T^{-2} dependence. It must be added though, that the actual potential energy drop of the CF + 2,3-dimethyl-2-butene reaction surface is probably much steeper than given by a Lennard-Jones function, limiting the above to a semiquantitative interpretation. Nevertheless, the argumentation provides an acceptable theoretical justification for the experimentally determined negative temperature dependence.

Reaction with Alkanedienes. As the reactions of CF with alkanedienes follow the same trend as those with alkenes, we can conclude that the reaction mechanism in question is similar: CF will attack one of the π-bonds of the alkanediene (cycloaddition), forming a vibrationally excited cyclic adduct, which can undergo further unimolecular isomerization and fragmentation reactions. Again, as with the alkenes, the manifest correlations between log k, E_a, and log A, on one hand, and the ionization energy of the alkanediene on the other (Figure 4 and Table 3), can be traced back to a larger affinity of the electrophilic CF toward a more electron-rich double bond.

Although these correlations exist for both the alkenes and the alkanedienes, the precise functional dependences differ for the two reaction classes. The reason behind this is twofold: (i) the IP of the alkanedienes is significantly lowered by resonance stabilization in the positive ion, a stabilization which, although much less pronounced, also features in the alkanediene molecule itself, but (ii) is no longer present in the TS of CF + alkanediene reactions. This should lead to a higher energy barrier and lower rate constant than for a reaction with an alkene that has an identical IP. Our results confirm this, consistently showing a higher activation energy for CF + alkanediene reactions than for reactions of CF with alkenes having a comparable IP.

On the other hand, the frequency factors for the CF + alkanediene reactions are higher than those for CF + alkenes. This can be explained by the larger size of the π-electron cloud of the alkanedienes, increasing the chance of successful interaction between CF and the alkanediene. In fact, for the conjugated dienes, with their delocalized π-cloud, the frequency factor is already so much higher that it can compensate for the higher energy barrier, as seen in Figure 4.

Reaction with Propyne. This reaction will probably proceed similarly through cycloaddition of CF on the triple bond, forming a vibrationally excited fluorocyclopropenyl adduct, that will very quickly undergo fast unimolecular dissociation. The cycloaddition mechanism can explain the markedly slower CF + propyne reaction as compared to the CF + propene reaction: the π-bond in alkynes is ~25 kcal/mol stronger than that in alkenes, which will lower the exoergicity and raise the energy barrier for the CF + propyne reaction, resulting in a lower rate constant.

Further research in this laboratory is planned to verify the log k − IP correlation for CF + alkyne reactions that James et al.[3] observed for CCl and CBr + alkynes; the relation between the activation energy and the alkyne ionization energy will also be addressed.

Conclusion

The reactions of CF with unsaturated hydrocarbons are found to be electrophilic cycloaddition reactions. For both the alkene and alkanediene classes, the activation energy as well as the frequency factor was found to correlate with the ionization energy of the hydrocarbon. These correlations can be traced back to the electrophilic character of CF, resulting in an increase of the reaction rate as the π-electron density increases by alkyl substitution on the alkenic carbons.

Although these correlations exist for both the alkene and alkanediene classes, they differ quantitatively. This is because, compared to reactions with an alkene with a similar IP, the alkanediene reactions have (i) a higher energy barrier due to resonance stabilization of the alkanediene and (ii) a higher frequency factor due to their larger π-electron cloud. This leads to rate coefficients which are lower than those of reactions with alkenes with similar IP. From the conjugated dienes onward though, the frequency factor will increase so much that the resulting rate coefficient might become higher than those of the alkene reactions.

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