DIRECT MEASUREMENTS OF REMOVAL RATES OF CHF($\tilde{X}^1 A'(0,1,0)$) BY SIMPLE ALKENES

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Direct measurements of the rate constants for collisional removal of CHF($\tilde{X}^1 A'(0,1,0)$) by argon (Ar), ethylene (C_2H_4), propene (C_3H_6), 1-butene (1-C_4H_8), iso-butene (i-C_4H_8), 1,3-butadiene (C_4H_6), are reported. CHF($\tilde{X}^1 A'(0,1,0)$) was prepared by IRMPD of precursor CH_2F_2. Fluence independence removal rate constants by Ar, ethylene and propene are: 0.0045, 2.70 and $2.46 \times 10^{-11} \, cm^3 \, molecule^{-1} \, s^{-1}$, faster than the rates for the vibrational ground state. 1,3-butadiene was measured at a fluence of $42 \, J \, cm^{-2}$, yielding a value of $0.81 \times 10^{-11} \, cm^3 \, molecule^{-1} \, s^{-1}$. Iso-butene has fluence dependence removal rates, given 1.28 and $0.92 \times 10^{-11} \, cm^3 \, molecule^{-1} \, s^{-1}$ for fluences of 50 and $32 \, J \, cm^{-2}$ respectively. For 1-butene a non-linear Stern-Volmer behaviour has been observed and attributed to fast resonant vibrational-to-vibrational (V-to-V) intermolecular energy transfer. The influence of this V-to-V energy transfer on the removal rates is discussed.

KEY WORDS: Removal rates of CHF transients, IRMPD, energy transfer.

INTRODUCTION

Singlet carbenes react with simple molecules leading to insertion and cycloaddition compounds.[1,2] Several decades ago competitive kinetic experiments of state non-selective transient CTF with olefins leading to a stereospecific addition and with saturated hydrocarbons, where direct insertion in primary and secondary C-H linkages was established, were reported.[3–6] In particular, monofluorocarbene reactions with alkenes were shown to proceed through the cycloaddition channel.[7] Empirical correlations based on thermochemistry properties did help to characterize the philicity (electrophilic, ambiphilic and nucleophilic behaviour) of carbenes, while frontier molecular orbital theory provided the framework to rationalize and predict the experimental kinetic results. Developments in instrumentation, including the use of the extensive laser ancillary and leading to direct measurements of reactivity, improvements in preparative organic chemistry methods for new precursors and carbenes and progress in computational facilities make the field as broad and interesting as it had been in the last few decades.[1–4,8–11] Applications to atmospheric chemistry, astrophysics and semiconductor etching have enhanced their interest.[12–15]

Ground electronic CHF transient was first prepared by infrared laser-induced multiple photon dissociation (MPD) of precursors CH_2FCl and CH_2F_2[16–18] and its vibrational, rotational and translational energies have been characterized

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recently.[19,20] Direct removal rates of state selective $CHF(\tilde{X}^1A'(0,0,0))$—referred henceforth as either $CHF(\tilde{X}(0,0,0))$ or $CHF(\tilde{X})$ according to conveniences—with noble gases, simple molecules[21–23,17] and radicals[18,24] have been reported in the last few years.

Removal rates of CHF transient and its vibrational states in the electronic $\tilde{X}$ and $\tilde{A}$ states with alkenes[16–26] have often been stated to be half way between fast methylene, CH_2[27–31] and slow difluorocarbene CF_2[24,32–33] transients. This rough statement is to be looked at with suspicion, particularly when several removal channels enter into play. In fact, in the lowest singlet $CH_2(\tilde{a}^1A_1)$ this average behaviour is blurred by the influence and perturbation of ground state triplet $(\tilde{X}^3B_1)$. The total reactivity of the singlet is composed by the proper chemical reactivity of the transient and the physical quenching consequence of the singlet-triplet perturbation. A considerable interest has developed in this subject in the last few years.[29–31]

In this paper a kinetic study of the state selected transient $CHF(\tilde{X}(0,1,0))$, produced in the IRMPD of precursor CH_2F_2, with some selected simple alkenes (ethylene (C_2H_4), propene (C_3H_6), 1-butene $(1\text{-}C_4H_8)$, iso-butene $(i\text{-}C_4H_8)$, 1,3-butadiene (C_4H_6)) and with Ar is presented. Alkenes have vibrational bands near resonance of the CHF bending mode $(1406\,cm^{-1})$[34] so that $V\text{-}to\text{-}V$ intermolecular energy transfer is expected to compete with the cycloaddition chemical channel. In addition, the long lifetimes of the alkene vibrational states[35] and the low efficient $V\text{-}to\text{-}V$ intermolecular energy transfer of these alkenes make the problem challenging.
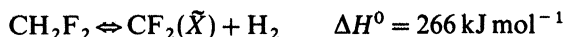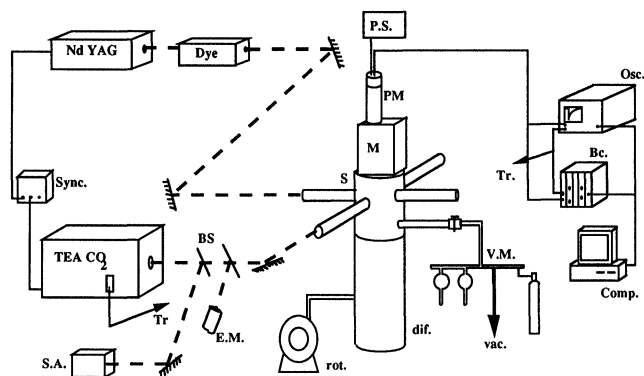

EXPERIMENTAL

The experimental set up used to probe the state selected transients and later to measure the removal rates, is shown in Figure 1. Briefly, the beam of a dissociation laser (TEA-CO$_2$ laser, Lumonics K-103), that oscillate in a optical cavity made by a R35% germanium output coupler and a master ruled grating set at the R(20) of the $(0,2^0,0)$–$(0,0^0,1)$ band of CO_2 (at $\lambda = 9.27\,\mu m$), was directed, dumped and split when appropriate, and focused to a 0.5 mm diameter spot, into the sample cell center. Fluences were varied in the range from 50 to 12 J cm^{-2}. The sample cell was filled with precursor CH_2F_2 (5 mTorr), buffer gas (Ar, 2 Torr) and the selected reactant partner at variable pressures (usually up to 100 mTorr). Precursor pressure was selected as a compromise to get sizeable emission signals and low noise background due to luminiescence (caused[27] either by collisional dissociation of precursor molecules following infrared laser multiple photon absorption or by reaction/energy transfer of MPD transients with or to the added gases).

Infrared MPD of precursor CH_2F_2 in the conditions mentioned is known to follow a three center elimination channel:

$$CH_2F_2 \Leftrightarrow CHF(\tilde{X}, v'') + HF(v'', R) \qquad \Delta H^0 = 341\,kJ\,mol^{-1}$$
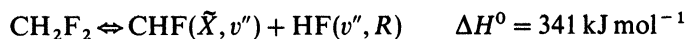
in preference to thermodynamically favoured channel

$$CH_2F_2 \Leftrightarrow CF_2(\tilde{X}) + H_2 \qquad \Delta H^0 = 266\,kJ\,mol^{-1}$$

Figure 1 Experimental set up to study the product state distributions and the removal of IRMPD produced free radicals. The system works as follows: A CO_2 laser pulse of known fluence and shape is sent to the vacuum chamber where an appropriate mixture of precursor and argon has been introduced. Absorption of high intensity infrared radiation leads to precursor photodissociation and the fragments are probed with a dye laser coupled to a 15 ns pulsed Nd:YAG laser in a perpendicular configuration. The emitted light from the excited photofragments is selected with a monochromator, captured with a photomultiplier and routed through an oscilloscope or boxcar integrator to a PC-computer were data are fitted to appropriate models and delivered as hard copy. The following abbreviations are used: Nd:YAG: pulsed Nd:YAG laser. Bc: Boxcar integrator. BS: Beam splitter. Comp: Personal computer, plotter and printer. Dye: Tunable dye laser. E.M.: Energy Monitor. M: Monochromator/Filter (interference or cut off). Osc: Digital Oscilloscope. PM: Photomultiplier. S: Sample space. S A: (CO_2 laser) spectrum analyzer. SYNC: Electronic laser synchronization. TEA CO_2:Transversely excited CO_2 laser. Tr: Trigger. VAC: Vacuum system. V M: Vacuum manifold.

that plays a minor role.[25] At high infrared fluences, bimolecularly created fragments, C_2 and CH have been detected.[19] CHF is produced at a vibrational temperature of 750 ± 50 K[19,20] as measured in its bending mode, yielding a population ratio, $\tilde{X}(0,1,0)/\tilde{X}(0,0,0)$ of 0.067, that has probed to be large enough to allow the detection and time resolved study of the vibrational selected transient.

State selected CHF($\tilde{X}(0,1,0)$) was probed by a Nd:YAG/Dye laser coupled system (Quantel 581 and Datachrom) set at 592.3 nm, corresponding to the CHF($\tilde{A}(0,1,0) \leftarrow \tilde{X}(0,1,0)$) transition, where the experimental intensity factor is 0.38.[25] Spectra were recorded with a delay between the photodissociation and probe lasers of 3 μs, long enough to finish the rotational relaxation. Emission was consistently observed through a monochromator set at 546.9 nm (CHF($\tilde{A}(0,1,0) \rightarrow \tilde{X}(0,0,0)$) transition[25]) with a fast side-on photomultiplier (Hamamatsu R928). Crossed laser beams, in a perpendicular configuration, has been used throughout after checking its lower luminescence level. Time decays were captured with a 150 MHz digital oscilloscope, Tektronix 2430A, IEEE interfaced with a PC-computer, where time resolved removal rate constants were obtained by non-linear fitting and, alternatively, integrated between selected times to simulate a boxcar integrator, so that the laser induced fluorescence spectra was scanned. In both cases, care was taken in the subtraction of background luminescence signals. The laser resolution used either for still or time resolved measurements was 0.08 cm^{-1}.

The increase in the magnitude of the luminescence signals with the molecular size of the alkene and with the fluence induced a careful search for CH_2 fragments in the IRMPD of 1-butene and of 1,3-butadiene by themselves and in presence of Ar. Pump and probe lasers delays were set from 1 to 6 μs and probe wavelength scanned in the range from 589 and 593 nm. Indeed, no traces of CH_2 were detected.

Precursor CH_2F_2 and all alkenes were freeze-thaw cycled in a vacuum manifold in order to be purified. Mixtures of degassed precursor, buffer gas and the selected olefin partner at the appropriate pressures (as measured with a capacitance manometer, Datametrics $10 - 0.001$ Torr) were homogenized in a balloon under magnetic stirring for a minimum of 30 minutes just before flowing into the reaction vessel.

All experiments were done at room temperature. Chemicals used were of the highest commercially available purity and include: CH_2F_2(>97.0 vol%, Fluorochem Ltd), Ar(99,9995%, SEO), C_2H_4(99.7%, Matheson), C_3H_6(99.5%, Matheson), 1-butene (99.0%, Matheson), *i*-butene (99.0%, Matheson) and 1,3-butadiene (99.7%, Matheson).

RESULTS AND DISCUSSION

The LIF spectrum of transient molecules generated by high intensity IRMPD of precursor CH_2F_2 in Argon (20 mTorr/1 Torr ratio) at room temperature and 3 μs delay between dissociation and probe lasers, at wavelengths in the range from 591.0 to 593.0 nm is shown in Figure 2. The spectrum is readily assigned[36] to the $\tilde{A}(0,1,0) - \tilde{X}(0,1,0)$ transition of CHF transient. CHF($\tilde{X}$) is a bent molecule (101.6°) with a CF stretch vibrational mode at 1181.5 cm^{-1} (in Ar) and a bending mode in Ar of 1406 cm^{-1}.[34] The triplet state CHF ($\tilde{a}^3A''$) has an energy estimated to be $T_0 < 5140\,cm^{-1}$ above the electronic ground level and, presumably, it does not affect
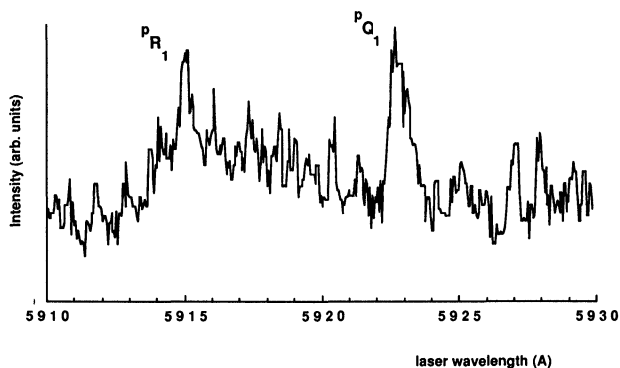
Figure 2 Laser induced excitation spectra and assignation of the CHF($\tilde{X}^1A'(0,1,0)$) transient in the 591 to 593 nm region. $^PQ_1$ transition(s) by 592.24 nm have been consistently used to study the removal rates of vibrational excited CHF($\tilde{X}$) with alkenes.

or perturb the first (and second) vibrational excited state.

Kinetic removal rates were consistently determined by probing the time evolution of CHF($\tilde{X}(0,1,0)$) at 592.3 nm (emission at 546.9 nm). For the quenching of CHF($\tilde{X}(0,1,0)$) by Ar, the removal rate constants at pressures up to 6 Torr were fitted to

$$k = k_0 + k_1[CH_2F_2] + k_{Q,Ar}[Ar] + \beta'/P_{Ar} \tag{1}$$

where the first two terms on the right hand side correspond to the non-collisional removal of the CHF bending mode and the quenching by CH_2F_2 (partial pressure: 4 mTorr) respectively. CH_2F_2 is an efficient physical quencher for CHF[19] and in the plot of k versus [Ar] shifts the rate constant upwards by an (irrelevant) constant quantity. Finally, β' is the diffusion coefficient[37] of CHF in Ar. Figure 3 shows the contribution of the collisional and diffusional removal rates. The fit to the experimental results yields:

$$k_{v,Ar} = 4.5 \pm 0.5 \times 10^{-14}\, cm^3\, molecule^{-1}\, s^{-1}$$

$$\beta' = 2540 \pm 250\, s^{-1}\, Torr$$

that show a sizable quenching rate of the first vibrational state when compared to that of the ground state. The diffusion coefficient gives, for the experimental conditions employed in the study of the removal rates (0.5 Torr of Ar and decays shorter than 100 μs), an estimated root mean square distance of 0.07 cm, a figure that allows to neglect the diffusional contribution in the determination of the kinetic rates of alkenes. Consequently, the collisional quenching fits the simple relation

$$k' = k'_0 + k_Q\,[alkene] \tag{2}$$

were k_Q is the removal rate constant at each partial pressure of the selected partner. Figure 4(a, b) shows two examples of decay traces of the removal of CHF($\tilde{X}(0,1,0)$)
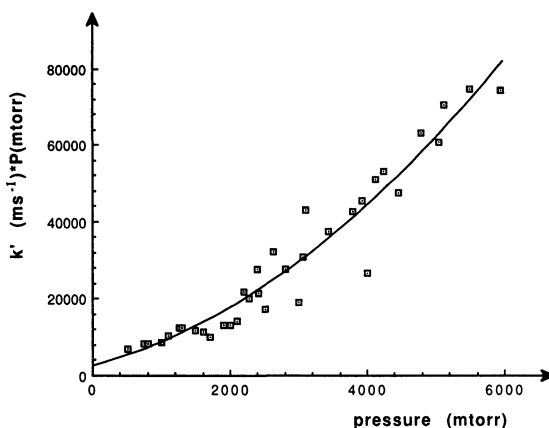
Figure 3. Plot of the removal rates times pressure versus quencher pressure in the quenching of CHF($\tilde{X}(0,1,0)$) by Argon. Fitting of the experimental values to equation (1) yields the diffusion coefficient and the removal rate (see text).
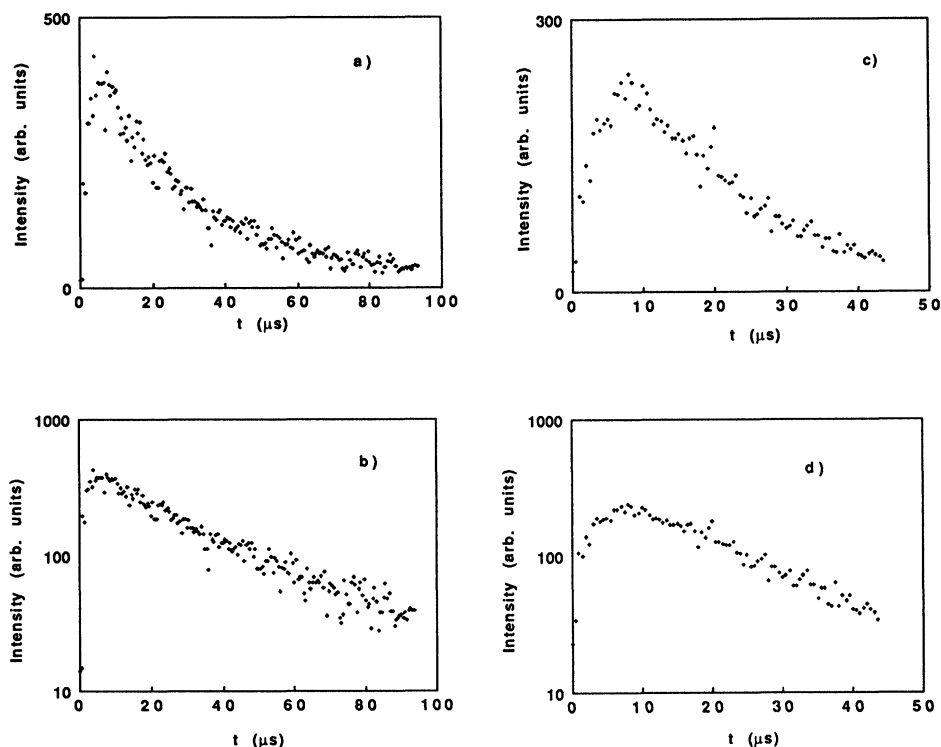
Figure 4 Examples of linear (a, b) and semilogarithm (c, d) decay curves of the quenching of ethylene and 1-butene respectively. The experimental pressures of the reactants were: (CH_2F_2: 4 mTorr; ethylene: 10 mTorr; Ar: 0.5 Torr) and (CH_2F_2: 4 mTorr; 1-butene: 10 mTorr; Ar: 0.5 Torr).

by 10 mTorr of ethylene and by 90 mTorr of 1-butene respectively. The corresponding semilogarithmic plots are also shown in order to visualize the correlation to a straight line of the fit.

Removal rate constants of $CHF(\tilde{X}(0,1,0))$ by ethylene and propene follow simple Stern-Volmer type plots, i.e. independent of the fluence. An example is presented in Figure 5a. Quenching rates by 1,3-butadiene at fluences of 50 and 20 J cm^{-2} show large experimental scattering measurements and are not reported. However, the removal rates at a fluence of 42 J cm^{-2} fits quenching rate of $0.82 \pm 0.08 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} with a correlation coefficient of 0.87. Isobutene have fluence dependent removal rates, as shown in Figure 5b. Finally, 1-butene, have proved to be difficult to measure due to nonlinear dependence of the removal rates versus the pressure, and the results reported were extrapolated to very low pressures. *Table 1* collects the measured removal rates.

The correlation[38,39] of the logarithm of the removal rate constants or cross sections of the quenching of CHF versus the root square of the intermolecular well depth of the reactant partner has been often used to rationalize the kinetic behaviour of
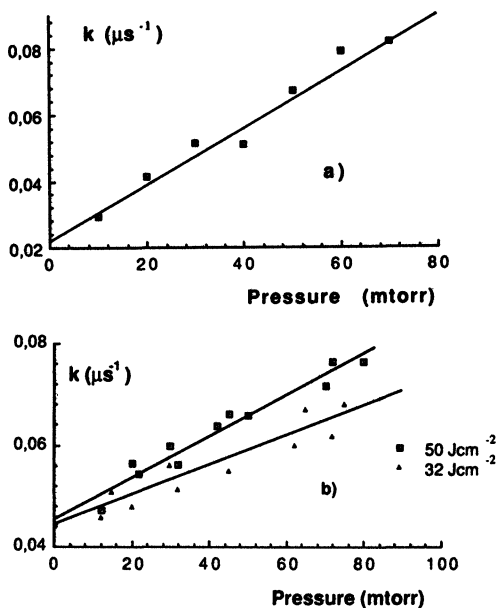
Figure 5 Stern-Volmer type plots for the determination of the removal rates of the reaction between transient CHF($\tilde{X}(0,1,0)$) and (a) ethylene and (b) isobutene at CO_2-laser fluences of 50 and 32 J cm^2.

Table 1 Removal rates in 10^{-11} cm^3 molecule^{-1} s^{-1} units, of transient selective state CHF($\tilde{X}(0,1,0)$) by five simple alkenes (in 0.5 mTorr of Ar) as a function of TEA-CO_2 laser fluence

Fluence:	50 J cm^2	42 J cm^2	32 J cm^2	Range (mTorr)
Ar	$(4.5 \pm 0.5)10^{-3}$			
Ethylene	2.76 ± 0.28	2.5 ± 0.25	3.17 ± 0.58	10–170
Propene	2.53 ± 0.23	—	2.39 ± 0.22	10–80
1-Butene	0.74 ± 0.08^a	—	0.91 ± 0.13^a	10–170
1,3-Butadiene	—	0.81 ± 0.08	—	15–90
Isobutene	1.28 ± 0.10	—	0.92 ± 0.12	10–80

^{a} Slope at low pressures (see text).

electronic and vibrational CHF ground state,[19,20] its first electronic excited state[26,25] and the ground and excited states of other carbenes.[27,28] For the kinetics of CHF($\tilde{A}$), reactants as different as noble gases, alkenes, NO, etc, fits to a straight line, so that physical and chemical quenching channels cannot be distinguish.

In the reactions of vibrational state selected CHF($\tilde{X}(0,1,0)$) with alkenes an additional V-to-V intermolecular energy transfer channel is introduced. Removal rate through this channel are expected to be high as a consequence of the near resonant alkene vibrations ((CH_2 bending (in plane), CH_2 bending and CH_3 symmetric deformation) with the CHF bending at 1406 cm^{-1}. Indeed, a comparison of the

removal rates of vibrational ground and first excited states with the simplest alkene used, ethylene, leads to the conclusion that energy transfer of $CHF(\tilde{X}(0,1,0))$ to the CH_2 bending (in plane) of C_2H_4 is 2–5 times faster than the cycloaddition of $CHF(\tilde{X}(0,0,0))$ with double bonds.

Comparing the removal rates of $CHF(\tilde{X}(0,1,0))$ among the alkenes studied (*Table 1*) one is tempted to assign partial *V*-to-*V* removal rate constants to specific vibrational modes of the alkene.[40] So, the transfer to the CH_2 bending (in plane) is far more efficient than the transfer to $>CH_2$ bending and CH_3 symmetric deformation. However, the slight changes of vibrational transitions of alkenes respect to the $1406\,cm^{-1}$ energy of the $CHF(\tilde{X}(0,1,0))$ and the few number of molecules studied so far makes premature the task of a quantitative approach.

Within the difficulties of interpretation of the experimental results it is worth mentioning the competitive effects found in the removal of $CHF(\tilde{X}(0,1,0))$ by 1-butene, were a saturation effect of the kinetic constants for high alkene pressures is observed (Figure 6). Vibrational ground state $CHF(\tilde{X}(0,0,0))$ reacts with 1-butene to yield a cyclopropane derivative at an absolute rate measured to be $1.7 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$, slightly faster than the quenching of $CHF(\tilde{X}(0,1,0))$.
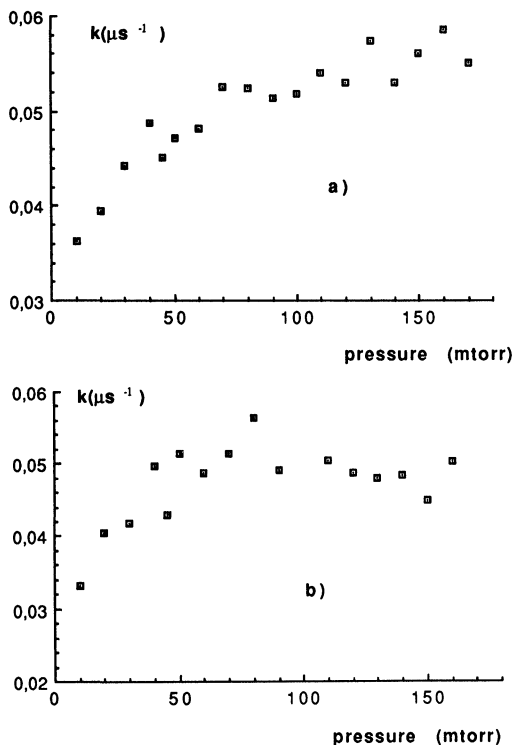
Figure 6 Plot of the experimental decays of the reaction $CHF(\tilde{X}(0,1,0))$ with 1-butene versus pressure for two fluences: (a) $50\,J\,cm^2$ and (b) $32\,J\,cm^2$. Note the non-linear dependence.

This result, as well as those of the removal rates of i-butene and butadiene can be readily interpreted as a decrease of efficiency in the cycloaddition by bending excited CHF. On the other hand, the saturation effect seems to be related to the long radiative lifetimes of the 1-butene in the $1400 \, cm^{-1}$ region.[41-43] Indeed, if the 1-butene would behave as a reservoir of vibrational energy, and had a very efficient V-to-V inermolecular energy transfer, the concentration of $CHF(\tilde{X}(0,1,0))$, in systems with low alkene pressure, would disappear at a rate proportional to the alkene concentration. For high concentrations of alkene, the fast first part of the reaction is set before firing the second laser and the observed rate would correspond to the quenching of the steady state concentration of $CHF(\tilde{X}(0,1,0))$ in equilibrium with vibrationally excited 1-butene, i.e. slow and nearly constant (Figure 6). A quantitative explanation of the experimental findings would require measurements with controlled CO_2-laser pulse widths and shapes, shorter laser pulses delays, simultaneous time-measurements of state selected reactants and products etc.

Acknowledgements

References

1. R. A. Moss, *Acc. Chem. Res.* **22**, 15 (1989).
2. R. A. Moss, *Acc. Chem. Res.* **13**, 58 (1989).
3. P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.* **78**, 5430 (1956).
4. W. v. E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.* **80**, 5274 (1958).
5. M. Kirmse (ed.), *Carbene Chemistry*. 2nd ed. Academic (1971).
6. C. Wentrup, *Reactive Molecules*. Wiley-Interscience (1984).
7. Y. N. Tang and F. S. Rowland, *J. Am. Chem. Soc.* **89**, 6420 (1967).
8. S. R. Cain, R. Hoffman and E. R. Grant, *J. Phys. Chem.* **85**, 4046 (1981).
9. L. B. Harding, H. B. Schlegel, R. Krishnan and J. A. Pople, *J. Phys. Chem.* **84**, 3394 (1980).
10. C. Sosa and H. B. Schlegel, *J. Am. Chem. Soc.* **106**, 5847 (1984).
11. M. Moreno, J. M. Lluch, A. Oliva and J. Bertran, *J. Phys. Chem.* **92**, 4180 (1988).
12. R. Wayne, *Chemistry of the atmospheres*. Oxford U.P. (1985).
13. G. Herzberg, *The Spectra and Structures of Simple Free Radicals*. Dover (1988).
14. S. J. Moss and A. Ledwith, eds., *The Chemistry of the Semi-conductor Industry*. Blackie (1986).
15. H. Okabe, *Photochemistry of Small Molecules*. Wiley-Interscience (1978).
16. M. N. R. Ashfold and G. Hancock, *Spec. Period. Rep., Gas Kinetics and Energy Transfer* **4**, 73 (1982).
17. G. Hancock and G. W. Ketley, *J. C. S., Faraday Trans.* 2 **78**, 1283 (1982).
18. G. Hancock, G. W. Ketley and A. J. MacRobert, *J. Phys. Chem.* **88**, 2104 (1984).
19 A. Ortiz de Zarate, *Ph.D. Thesis.* Univ. Pais Vasco (1991).
20. A. Ortiz de Zarate, F. Castaño, J. A. Fernandez, M. N. Sanchez Rayo and G. Hancock, JCS. Faraday Transactions. Accepted.
21. G. W. Ketley, *D. Phil. Thesis.* Oxford University (1983).
22. K. G. McKendrick, *D. Phil. Thesis.* University of Oxford (1985).
23. A. Ortiz de Zarate, F. Castaño, *Anales de Química.* **87**, 167 (1991)
24. G. Hancock and D. E. Heard, *Chem. Phys. Lett.* **158**, 167 (1989).
25. G. Dornhoffer and W. Hack, *J.C.S. Faraday 2* **84**, 441 (1988).

26. A. Ortiz de Zarate, F. Castaño, J. A. Fernandez, M. N. Sanchez Rayo and G. Hancock, *Chem. Phys. Lett.* Accepted.
27. M. N. R. Ashfold, M. A. Fullstone, G. Hancock and G. W. Ketley, *Chem. Phys.* **55**, 245 (1981).
28. M. Castillejo, J. M. Figuera, I. Garcia-Moreno and J. Medina, *Chem. Phys. Lett.* **157**, 41 (1989).
29. W. Hack, M. Koch, R. Wagener and H. G. Wagner, *Ber. Bunsenges. Phys. Chem.* **93**, 165 (1989).
30. R. Wagner and H. G. Wagner, *Ber. Bunsenges. Phys. Chem.* **94**, 1096 (1990).
31. M. Koch, F. Temps, R. Wagener and H. G. Wagner, *Z. Naturforsch.* **44a**, 195 (1989).
32. J. Edelbuettel-Einhauss, K. Hogermann, G. Rhode, H. G. Wagner and W. Hack, *Ber. Bunsenges. Phys. Chem.* **93**, 1413 (1989).
33. G. Dornhoffer, W. Hack, K. Hayermann and G. Rhode, *Ber. Bunsenges. Phys. Chem.* **94**, 468 (1990).
34. M. E. Jacox, *J. Phys. Chem. Ref. Data* **19**, 1387 (1990); **17**, 269 (1988) and references therein.
35. A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules and Ions.* Springer-verlag (1985).
36. A. J. Merer and D. N. Travis, *Can. J. Phys.* **44**, 1541 (1966).
37. A. C. G. Mitchell and M. W. Zemanski, *Resonance Radiation and Excited Atoms.* Cambridge (1934).
38. H. M. Lin, M. Seaver, K. Y. Tang, A. E. W. Knigth and C. Parmenter, *J. Chem. Phys.* **70**, 5442 (1979).
39. C. Parmenter and M. Seaver, *J. Chem. Phys.* **70**, 5458 (1979).
40. F. Beitia, F. Castaño and D. Husain, *J.C.S. Faraday Trans.* **85**, 795 (1990).
41. N. Sheppard, *J. Chem. Phys.* **17**, 74 (1949).
42. G. Herzberg, *Molecular Spectra and molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules.* Van Nostrand Rheinhold (1945).
43. L. M. Sverdlov, M. A. Kovner and E. P. Krainov, *Vibrational Spectra of Polyatomic Molecules.* Wiley (1974).