

ylide **4** is trapped by the addition of a large excess of CH₃I to the solution to give the monoalkylated product **8a**, mp 151–152 °C.⁹ A mixture of **8a** and **8b**¹⁰ was observed by NMR when a slight excess of CH₃I was added under similar conditions. These findings clearly indicate **4** to be an intermediate in these methylation reactions.

Further work on the structure of **4** and its reactions with other electrophiles is underway in our laboratory.

Acknowledgment. This research was supported in part by a grant from the National Cancer Institute (CA 13963) and in part by fellowships from Abbott Laboratories, the Uniroyal Co., and the University of Illinois for P.H.W.L.

References and Notes

- (1) Paper 30 in a series on sulfuranes. For paper 29 in this series, see P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, in press.
- (2) (a) W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3838 (1960); (b) W. Kwasnik, F.I.A.T. Review of German Science (1939–1946), "Inorganic Chemistry", Vol. 1, 1948; (c) H. Jonas, *Z. Anorg. Allg. Chem.*, **265**, 273 (1951); (d) F. B. Dudley, G. H. Gady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956); (e) S. P. von Halasz and O. Glemser, *Chem. Ber.*, **103**, 594 (1970); (f) S. P. von Halasz, O. Glemser, and M. F. Feser, *ibid.*, **104**, 1242 (1971); (g) J. M. Shreeve, *Acc. Chem. Res.*, **6**, 387 (1973); (h) G. H. Sprenger and A. H. Cowley, *J. Fluorine Chem.*, **7**, 333 (1976); (i) E. F. Perozzi and J. C. Martin, *J. Am. Chem. Soc.*, **94**, 5519 (1972); (j) J. C. Martin and E. F. Perozzi, *ibid.*, **96**, 3155 (1974); (k) E. F. Perozzi, J. C. Martin, and I. C. Paul, *ibid.*, **96**, 6735 (1974); (l) L. J. Adzima and J. C. Martin, *ibid.*, **99**, 1657 (1977).
- (3) Anal. (C₁₇H₂₆O₃S) C, H, S. ¹H NMR (CDCl₃-pyridine-d₅): δ 7.36 (s, 2, ArH), 3.68 (s, 3, SCH₃), 1.58 (s, 6, OCCH₃), 1.54 (s, 6, OCCH₃), 1.42 (s, 9, t-C₄H₉). IR (CHCl₃): 1182 cm⁻¹ (s, S=O stretch).
- (4) Diol **5** was prepared from the corresponding diacid by successive treatment with thionyl chloride, ethanol and pyridine, and methylmagnesium bromide in ether. The diacid was synthesized from 2,6-dimethyl-4-tert-butylbromobenzene as follows: Dimethylbromobenzene was oxidized to the dicarboxylic acid with KMnO₄, which in turn was treated with sodium hydrosulfide to convert the bromo substituent to thiol. The diacid thiophenol was methylated at sulfur with dimethyl sulfate in aqueous NaOH.
- (5) A. W. Herriott and D. Picker, *Tetrahedron Lett.*, 1511 (1974).
- (6) Anal. (C₁₇H₂₆O₂S) C, H, S. ¹H NMR (CDCl₃, 220 MHz): δ 7.25 (s, 2, ArH), 3.33 (s, 3, SCH₃), 1.51 (s, 6, OCCH₃), 1.49 (s, 6, OCCH₃), 1.41 (s, 9, t-C₄H₉).
- (7) All exchange experiments observed by NMR were followed by observing the disappearance of the S-methyl proton peak. No other changes in the spectra were noted.
- (8) Anal. (C₁₇H₂₆O₃S) C, H, S. ¹H NMR (CDCl₃): δ 7.30 and 7.04 (AB pattern, 2, J_{AB} = 1.7 Hz, ArH), 5.37 (br s, 1, OH), 5.04 (br m, 1, olefinic CH), 4.65 (br m, 1, olefinic CH), 3.41 (s, 3, SO₂CH₃), 2.23 (br s, 3, CH₃ at olefinic carbon), 1.71 (s, 6, OCCH₃), 1.30 (s, 9, t-C₄H₉).
- (9) Anal. (C₁₈H₂₈O₃S) C, H, S. ¹H NMR (CDCl₃-pyridine-d₅, 220 MHz): δ 7.35 (s, 2, ArH), 3.89 (q, 2, J = 7 Hz, SCH₂CH₃), 1.57 (s, 12, OCCH₃), 1.41 (s, 9, t-C₄H₉), 1.31 (t, 3, J = 7 Hz, SCH₂CH₃). IR (CHCl₃): 1176 cm⁻¹ (s, S=O stretch).
- (10) Compound **8b** was observed by ¹H NMR but not isolated.

Patrick H. W. Lau, J. C. Martin*

Roger Adams Laboratory, Department of Chemistry
 University of Illinois, Urbana, Illinois 61801

Received April 29, 1977

Frequency Dependence of Laser-Initiated Reaction Rates of CF₂CICF₂Cl

Sir:

In an earlier communication,¹ we reported on a large difference in the reaction rates of CF₂CICF₂Cl induced by con-

tinuous (CW) laser radiation for two frequencies (921 and 1051 cm⁻¹) corresponding to the centers of different absorption bands of the compound. Since the two absorption peaks have nearly the same strength, with the slightly stronger 1051-cm⁻¹ band actually giving the smaller reaction rate, the implication drawn was that significant compartmentalization of energy in vibrational modes was taking place, despite V-V transfer.

We wish to correct this interpretation as a result of further studies of the compound. In the earlier work, the optical absorptions used for band comparison were obtained with a standard spectrophotometer, where the incident intensity is low and the sample is at room temperature. Under laser radiation, the conditions are quite different, and band profiles are strongly altered. We have now measured reaction rates and optical absorptions under the same conditions as rate measurements for a series of frequencies covering the 921- and 1051-cm⁻¹ bands of CF₂CICF₂Cl.

The results show that the basis of comparison used in our earlier work is not the proper one. Reaction rates maximize at frequencies considerably below the absorption peaks of 921 and 1051 cm⁻¹, an effect termed "red shift". If we compare maximal rates for the two bands, they differ by only a factor of three, indicating little, if any, mode energy compartmentalization. Moreover, the 1051-cm⁻¹ band is now the one with the higher maximal rate.

However, there is strong evidence that the reaction is vibrationally enhanced, i.e., nonthermal. This comes from a comparison of reaction rate and laser-induced optical absorption as a function of frequency, with corroborating evidence from experiments using a "temperature probe" gas.

All measurements were made on 200 Torr of CF₂CICF₂Cl in a glass cell with KCl windows. The cell is 9.6 cm between windows along the laser path and has an inner diameter of 2.2 cm. There is also a cross arm 4.9 cm long for infrared diagnostics during laser irradiation. The laser beam for all measurements had a diameter of 0.1 cm, which was essentially constant over cell path, and an incident power of 4 W that was virtually all absorbed within the cell. Optical absorptions were measured in a shorter cell over a 1.3-cm path, providing ~30% transmission. In the latter case, a comparison of the diameters of incident and transmitted beams showed little evidence of self-focussing effects.² Reaction rates of CF₂CICF₂Cl were measured by monitoring the growth of absorption of the 1331-cm⁻¹ band of the product C₂F₄, which appears to be a primary product in all our experiments to date. Maximum rates did not exceed ~10⁻¹ Torr/s (measured over cell volume). Only initial rates are reported, corresponding to small percentage product concentrations.

As shown by the curves R in Figure 1, the reaction rate of CF₂CICF₂Cl maximizes at frequencies ~30 cm⁻¹ below ground-state absorption peaks. This "red shift" effect has been observed³ in the laser-driven reaction of BCl₃ with B(CH₃)₃, where a shift of 15 cm⁻¹ was noted, and has been ascribed to vibrational anharmonicity, with laser excitation taking place between states that are considerably above ground vibrational state. The maximum rate associated with the 1051-cm⁻¹ band is approximately three times as large as that of the 921-cm⁻¹ band. This factor is quite different from that obtained by comparing rates at the band-center frequencies, as done in our earlier report.⁴

The standard absorption band profiles are shown by the dashed curves α₀ in Figure 1. Laser-induced absorption is indicated by the curves α, measured for the same conditions as reaction rates, namely, a 4-W beam incident on 200 Torr of CF₂CICF₂Cl. Both α and α₀ are given in the same normalized units (cm⁻¹ Torr⁻¹) for comparison, but the laser-induced α is actually an average over the path length, since it is intensity dependent and, to a lesser degree, pressure dependent. Our

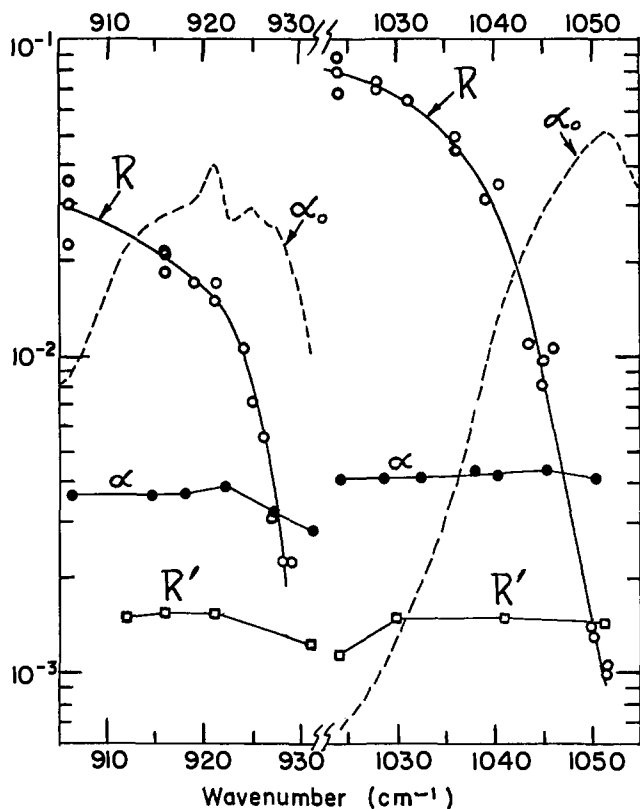


Figure 1. Data for various frequencies through two bands of $\text{CF}_2\text{ClCF}_2\text{Cl}$. Curves α_0 are the "ground-state" optical absorption coefficients (in units of $\text{cm}^{-1} \text{Torr}^{-1}$). Curves α are absorption coefficients ($\text{cm}^{-1} \text{Torr}^{-1}$) induced by a 4-W, 1-mm-diameter laser beam in 200 Torr of $\text{CF}_2\text{ClCF}_2\text{Cl}$. Curves R are the reaction rates (arbitrary units) of 200 Torr of $\text{CF}_2\text{ClCF}_2\text{Cl}$ for a 4-W, 1-mm-diameter laser beam. Curves R' are the reaction rates (arbitrary units) of the "temperature probe" gas PFB.

measurements show that α varies only weakly with intensity for incident powers exceeding 1 W, so that Beer's law is approximately satisfied over the path length.

Figure 1 shows that α is essentially independent of laser frequency in both bands. Similar results are obtained for pressures at least as low as 20 Torr. According to standard equations for steady-state heat flow, temperatures in the beam region are determined (all other factors equal) by the power absorbed per unit volume, which is proportional to αI , where I is the intensity. Since α does not change with frequency, neither should the temperature.

Reaction rates, on the other hand, increase sharply with decreasing frequency. We consider the contrast of rate with absorption as strong evidence for a nonthermal, vibrationally enhanced reaction route. The results are consistent with the above-mentioned interpretation of the red shift, where frequencies below band centers are favored for excitation to higher vibrational states.

Very little of the absorbed power is drained by the reaction, since the rates are sufficiently low for 4-W radiation. Nearly all absorbed power is carried to the cell walls. Accordingly, the frequency behavior of α is essentially unaffected by that of the reaction rate.

Since the magnitude of α is nearly the same for both bands while the maximal rates differ by a factor of three, a small difference in mode energy content may be indicated.

To corroborate the results, we introduced a small amount (2.44%) of a "temperature probe" gas,⁵ perfluorobutadiene (PFB), which converts thermally to perfluorocyclobutene (PFCB) according to known kinetics.^{6,7} The PFB does not absorb at the frequencies used here⁸ and alone reacts negligibly under radiation at these frequencies. Therefore, PFB should

serve as a temperature probe in the mixture, since most but not all of the input energy is expected to lie in modes of $\text{CF}_2\text{ClCF}_2\text{Cl}$ that are already equilibrated at the translational temperature.

Curves R' in Figure 1 show the rates of cyclization of PFB, obtained by monitoring absorption at the 1416-cm^{-1} band of PFCB. These rates are nearly independent of frequency. If indeed the probe is measuring mainly translational temperature, then the results are entirely consistent with those for absorption α of $\text{CF}_2\text{ClCF}_2\text{Cl}$, namely, constant translational temperature over the frequency ranges.

It should be noted that for frequencies in the range $1024\text{--}1036\text{ cm}^{-1}$, the high intensity absorption α exceeds the low intensity absorption α_0 . This induced absorption can be ascribed to anharmonicity and the onset of excited-state transitions, in concurrence with the explanation of the red shift of reaction rates. Induced absorption has been observed in SF_6 and other compounds.⁹ The lack of a corresponding effect for the 921-cm^{-1} band may be due to the onset of absorption by another band at 883 cm^{-1} .

More extensive data and the results of continued studies of this compound will appear later.

Acknowledgment. This work was supported in part by the National Science Foundation through Grant No. CHE 76-01162.

References and Notes

- (1) R. N. Zitter and D. F. Koster, *J. Am. Chem. Soc.*, **98**, 1614 (1976).
- (2) Self-focussing is produced by refractive index variations across the beam profile.
- (3) R. Rinck, R. Bachmann, H. Noth, and K. L. Kompa, in a talk presented by K. L. Kompa at the Ninth International Conference on Quantum Electronics (Digest), Amsterdam, Netherlands, June 14-18, 1976.
- (4) The factor 160 given in ref 1 for the ratio of $921\text{--}1051\text{-cm}^{-1}$ (band centers) reaction rates must be amended to a more correct number, 25, resulting from a more careful analysis of the shape of time-decay curves in the experiment.
- (5) The use of a probe gas for temperature has been reported by H. R. Bachmann, H. Noth, R. Rinck, and K. L. Kompa, *Chem. Phys. Lett.*, **33**, 261 (1975).
- (6) M. Prober and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **71** 598 (1949).
- (7) The reverse reaction induced by a TEA CO_2 laser has been reported by A. Yoge and R. M. J. Benmair, *Chem. Phys. Lett.*, **46**, 290 (1977).
- (8) PFB has an absorption band at 969 cm^{-1} .
- (9) U. P. Oppenheim and P. Meiman, *IEEE J. Quant. Elect.*, **QE-7**, 426 (1971); A. V. Nowak and J. L. Lyman, *J. Quant. Spectrosc. Radiat. Transfer*, **15**, 945 (1975); A. B. Peterson, J. Tsee, and C. Wittig, *Opt. Commun.*, **17**, 259 (1976).

Robert N. Zitter*

Department of Physics and Astronomy
Southern Illinois University
Carbondale, Illinois 62901

David F. Koster*

Department of Chemistry and Biochemistry
Southern Illinois University
Carbondale, Illinois 62901

Received March 3, 1977

Multiple Frequency (Field) Carbon-13 Spin-Lattice Relaxation Studies. Probe to Cooperativity of Complex Molecular Motions

Sir:

Variable frequency (and hence, variable field) ^1H spin-lattice relaxation time (T_1) measurements contain dynamics information that is not available from single frequency T_1 experiments.¹ ^1H T_1 data obtained at only one spectrometer frequency may only give information about one or more individual correlation times, τ_s , which are assumed to follow from a simple description of exponential decay of the autocorrelation function,² $G(\tau)$. By contrast, ^1H T_1 data obtained at more than