Carbon isotope separation by multiphoton dissociation of CF₃I

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A selective multiphoton dissociation process has been used to enrich carbon-13 in CF₃I. A separation factor of nearly 600 has been achieved for irradiation of 0.1 torr of CF₃I at -80°C with the R(14) line of the 9.6 μ CO₂ laser transition. An investigation of the dependence of the enrichment factor on pressure indicates that collisions during the dissociation are effective in destroying the selectivity. The multiphoton dissociation is quite efficient. At laser energy fluences of 1.2 J/cm², one in every 11 absorbed photons contributes its energy to the breaking of the C-I bond.

I. INTRODUCTION

Multiphoton dissociation of molecules using pulsed infrared lasers has been the object of extensive investigation following the observation by Isenor and Richardson of dissociation in the intense field of a TEA CO₂ laser. An important application of this technique is to the separation of isotopically labeled molecules, as reviewed in Refs. 11-14. Enrichment in the isotopes of H, B, C, Si, Cl, S, and Os has been reported.

In this paper we report the multiphoton dissociation of CF₃I. We have used this dissociation to separate carbon isotopes. Multiphoton dissociation in the structurally similar molecules CCl₃F and CF₃Cl has recently been reported by Dever and Grunwald. These authors used a focused CO₂ laser to obtain up to 1,6% conversion of the parent molecule per flash at about 60 torr of pressure. No investigation of the isotopic selectivity was reported. Lyman and Rockwood enriched carbon-13 by multiphoton dissociation of CF₃Cl₂ (Freon-12). The ¹²C/¹³C ratio of the starting material was increased by a factor of 1.65 by selectively dissociating ¹³CF₃Cl₂. Our use of CF₃I for investigation of the multiphoton process offers several advantages. Carbon is the only element of this molecule for which more than one isotope occurs naturally. This property considerably simplifies the mass spectral analysis. In addition, CF₃I can be dissociated at intensities as low as 5 MW/cm². An unfocused TEA CO₂ laser gives sufficient power so that a measurable fraction of starting material may be dissociated in fewer than 100 shots at one torr in a reasonable cell volume. Finally, very high isotope separation factors may be achieved in CF₃I. In excess of 15% of the molecules in the beam can be dissociated per laser pulse at high intensities, and enrichment factors of nearly 600 have been obtained.

The interaction of CO₂ laser radiation with CF₃I has been reported previously. By using a microwave-infrared double resonance scheme, Jones and Kohler have shown that the R(16) line of the 9.6 μ CO₂ band is coincident with the K=2, F'=19/2-21/2 transition of the ν₁ CF₃I band. The absorption coefficient can be inferred from their data to be on the order of 0.23 cm⁻¹torr⁻¹. By using an infrared-infrared double resonance scheme, Petersen et al. have observed an increase in absorption at 1052 cm⁻¹ following the excitation of CF₃I at 1075 cm⁻¹ with a pulsed CO₂ laser. This observation indicates that an appreciable excited state population in CF₃I may be obtained.

II. EXPERIMENTAL

CF₃I dissociation was achieved with a grating tuned CO₂ TEA laser (Tachisto Corporation model 215 laser head) producing a maximum of 1 J single line output in 60 nsec FWHM. Roughly half of the total energy appears in a 400 nsec tail following the main pulse. A 30 cm focal length sodium chloride lens was used to focus the radiation through polished NaCl windows into cylindrical Pyrex sample cells. The dimensions of the cells were adjusted to meet requirements of individual experiments. Cell lengths ranged from 5 to 30 cm when focusing was used, and from 5 to 114 cm when the laser was used unfocused. Species identification, concentrations, and isotope ratios were determined with a Perkin Elmer model 821 grating infrared spectrometer and a Consolidated Engineering Corporation type 21-103A mass spectrometer.

Laser power was measured with a Scientech model 360001 laser power meter. The pulse intensity was taken to be one-half of the measured energy per pulse in 60 nsec over the mean irradiated area of a sample. Beam areas were recorded on thermal sensing paper stock and were not corrected for laser mode structure or external diffraction effects. An intracavity aperture near the output mirror was used to restrict lasing to low order transverse modes, and an external aperture was generally used to reduce the beam area to 0.5 cm².

Trifluoromethyl iodide was used as supplied by PCR Incorporated after out-gassing at 77°C. K, and sample pressures were measured with an MKS Instruments capacitance manometer.

III. RESULTS AND DISCUSSION

A. Definitions

For pressures below 1.0 torr, the multiphoton process selectively dissociates ³⁵CF₃I. We define below the parameters necessary to describe this selectivity.

Following Lyman and Rockwood and Benedict and Pigford, let b₁ be the ratio of reactant isotope abundances before and after irradiation.
\[ \beta = \frac{[n_{12}/n_{13}]/[n_{12}(0)/n_{13}(0)]}{,} \]

where \( n_{12} \) and \( n_{13} \) is the number density of \(^{12}\text{CF}_3\text{I} (^{12}\text{CF}_3\text{I})\) molecules and \( n_i(0) \) refers to the initial number of each species. The laser preferentially dissociates \(^{12}\text{CF}_3\text{I} \) so that \( \beta \) increases as the bulk dissociation proceeds.

In a similar fashion, we define \( \beta_p \) as the isotope ratio in the products, \( n_{12} \) and \( n_{13} \), compared to the ratio expected for a nonselective process:

\[ \beta_p = \frac{[n_{12}(0)/n_{13}(0)]}{,} \]

Both \( \beta \) and \( \beta_p \) increase with increasing selectivity.

The parameters \( \beta \) and \( \beta_p \) whose values depend on the number of laser pulses, are useful macroscopic indicators of the selectivity. The microscopic information concerning the selectivity is contained in the parameter \( \alpha \), defined as follows. After each laser pulse, small increments \( \Delta n_{12} \) and \( \Delta n_{13} \) of \( n_{12} \) and \( n_{13} \) will be converted to the products \( n_{12} \) and \( n_{13} \). The isotope ratio in the increment of products will thus be given by \( \Delta n_{12}/\Delta n_{13} \). Since a completely nonselective process would give an incremental isotope ratio equal to the current value of \( n_{12}/n_{13} \), we measure the microscopic selectivity by the parameter

\[ \alpha = \frac{[n_{12}(0)/n_{13}(0)]}{,} \]

If \(^{12}\text{CF}_3\text{I} \) molecules are preferentially dissociated, then \( \alpha \) will be larger than one.

We define \( f \) to be the fraction of starting material remaining after irradiation of the sample with several pulses,

\[ f = \frac{[n_{12} + n_{13}]/[n_{12}(0) + n_{13}(0)]}{,} \]

where the approximate holds for \( n_{12} \gg n_{13} \). Assuming that \( n_{12} \gg n_{13} \) and that \( \alpha \) is constant during the course of the photolysis, the quantities \( f, \alpha, \) and \( \beta \) are related by the equation

\[ \beta = f^{(1-\alpha)/\alpha} \].

Combination of Eqs. (2) and (3) and integration from \( f = 1 \) to \( f' = f \) to obtain \( \beta \) yields

\[ \beta = \frac{\alpha^2}{2\alpha - 1} \left[ (1 - f^{(1-\alpha)/(1-f)})/(1-f) \right]. \]

In principle, \( \alpha \) may be calculated from \( \beta \) and \( f \), from \( \beta_p \) and \( f \), or from \( \beta_p \) and \( \beta \).

Finally, we will need to know how \( f \) varies with \( N \), the number of laser pulses. Let us at first assume that the fraction of \(^{12}\text{CF}_3\text{I} \) dissociated in the beam per pulse, \( \Delta f \), is constant throughout the irradiation. For a cell of volume \( V_c \) and a homogeneously irradiated volume \( V_{irr} \), \( \Delta f \) is related to \( f \) by

\[ f = (1 - \gamma \Delta f)^N, \]

where \( \gamma = V_{irr}/V_c \) and \( N \) is the total number of laser pulses.

B. Kinetic scheme

The \(^{12}\text{CF}_3\text{I} \) and \(^{12}\text{CF}_3\text{I} \) radicals formed by multiphoton dissociation of \(^{12}\text{CF}_3\text{I} \) recombine to yield \(^{12}\text{CF}_3\text{I} \), \(^{12}\text{CF}_3\text{I} \), and \(^{12}\text{CF}_3\text{I} \).

These are the only species observed in either infrared or mass spectra of samples irradiated at intensities below 25 MW/cm². In particular, \(^{12}\text{CF}_3\text{I} \) and other products which arise from breaking a C-F bond are not observed. We propose below a kinetic scheme for the purpose of discussing our results. While this scheme is not exhaustive, it completely accounts for our observations.

The dissociation is described by three processes:

1. \(^{12}\text{CF}_3\text{I} + \text{photon} \rightarrow ^{12}\text{CF}_3\text{I}^*, \)  
2. \(^{12}\text{CF}_3\text{I}^* + \text{photon} \rightarrow ^{12}\text{CF}_3\text{I} + ^{12}\text{CF}_3\text{I} \)  
3. \(^{12}\text{CF}_3\text{I}^* + ^{12}\text{CF}_3\text{I} \rightarrow ^{12}\text{CF}_3\text{I} + ^{12}\text{CF}_3\text{I} \)  

In these equations \( p \) and \( q \) are integral numbers of photons totaling enough energy to break the C-I bond (\( \Delta H_{298}^0 = 55 \text{ kcal/mole; } p + q \geq 18 \text{ photons} \)). Equations (8) and (9) may actually consist of several individual steps.

Dissociation is followed by recombination of radicals to yield products or reactants:

1. \(^{12}\text{CF}_3\text{I} + ^{12}\text{CF}_3\text{I} \rightarrow ^{12}\text{CF}_3\text{I} + ^{12}\text{CF}_3\text{I} \)  
2. \(^{12}\text{CF}_3\text{I} + ^{12}\text{CF}_3\text{I} \rightarrow ^{12}\text{CF}_3\text{I} + ^{12}\text{CF}_3\text{I} \)  

C. Isotopic selectivity as a function of pressure

A summary of the experimental results is given in Table I. Runs 1–12 investigate the dependence of \( \beta_p \) on pressure. As shown in Fig. 1, \( \beta_p \) increases dramatically from unity as the pressure of \(^{12}\text{CF}_3\text{I} \) is reduced below 1.0 torr. The \( R(14) \) line of the 9.6 μCi CO₂ laser transition selectively dissociates \(^{12}\text{CF}_3\text{I} \). It may be noted from the table that the fraction of \({}^{12}\text{CF}_3\text{I}\) remaining undissociated,  

FIG. 1. Selectivity of product formation as a function of pressure. Laser intensity was 5.5 MW/cm².
TABLE I. Summary of experimental results.

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<th>(P) (torr)</th>
<th>(I^b) (MW/cm²)</th>
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\(^a\)For dissociation with the \(R(14)\) line of the 9.6 \(\mu\) CO₂ laser transition.
\(^b\)Energy/cm²=\(I(0,12)\).
\(^c\)\(f_s=\frac{(\text{CF}_3 \text{I}) + (\text{CF}_3 \text{I} + \text{CF}_3 \text{I})_{\text{initial}}}{(\text{CF}_3 \text{I} + \text{CF}_3 \text{I})_{\text{initial}}}\).
\(^d\)\(V_{\text{eff}}=V_{\text{LX}}\).
\(^e\)\(\text{MeOH}-\text{LX} \text{ slush on side arm.}\)
\(^f\)\(\text{\(-80^\circ\)C dry ice jacket on cell.}\)

\(f_s\) is always greater than 0.73 for these runs. Expansion of Eq. (6) under the condition that \(f_s>0.73\) yields \(\beta_s=\alpha\) to within 14%. Thus, for CF₃I, \(\alpha\) increases as the pressure, \(P\), decreases.

For dissociation of SF₆, a proportionality between \(\ln \beta_s\) and \(P^{-1}\) has been noted by Ambartzumian et al.\(^{29}\) An increase in \(\beta_s\) as \(P\) decreases has also been observed for dissociations of CF₅Cl₂, BCl₃, and SiF₆.\(^{26}\) From Eq. (5) it may be shown that, at a given fractional dissociation, the fact that \(\beta_s\) increases as \(P\) decreases implies that \(\alpha\) increases as \(P\) decreases. Since this behavior seems to be common to a variety of multiphoton systems, one might reasonably conclude that the dependence of \(\alpha\) on \(P\), shown for CF₃I in Fig. 1, is related to the mechanism of multiphoton dissociation and not to the specific case at hand. This implies that Reaction (10) must be at least partly responsible for the scrambling.

The differential equations corresponding to Reactions (8)-(10) may be used to predict the dependence of \(\ln \beta_s\) on \(P\). These equations can be solved to yield the time dependence of \(^{12}\text{CF}_3\)I and \(^{13}\text{CF}_3\)I. The amounts of each radical formed per laser pulse of duration \(t_0\) may then be solved by integration of the equations for \(^{12}\text{CF}_3\)I and \(^{13}\text{CF}_3\)I from \(t=0\) to \(t=t_0\). The result gives an expression for \(\alpha\) which simplifies to

\[
\alpha = \left( \frac{k_5}{k_{10}P} \right) \left( n_{12} + n_{13} \right) + 1, \quad (16)
\]

under the assumptions that \(k_5\) is large compared to \(k_{10}^{-1}\) and that no scrambling occurs after the dissociation.

Consequently, the simple model presented by Reactions (8)-(10) explains why \(\alpha\) increases as \(P\) decreases. More explicitly, substitution of Eq. (16) into Eq. (5) predicts that \(\ln \beta_s\) should increase as \(P^{-1}\):

\[
\ln \beta_s = \ln (1/f) \left[ 1 + P \left( \frac{k_5 n_{12}}{k_{10} n_{13} + n_{12}} \right) \right]^{-1}. \quad (17)
\]

Although it is not clear that the fractional dissociation, \(f_s\), was constant in their experiments, an increase in \(\ln \beta_s\) with \(P^{-1}\) was observed by Ambartzumian et al.\(^{29(a)}\)

For CF₃I the dependence of \(\alpha\) on pressure is somewhat stronger than the \(P^{-1}\) dependence of Eq. (16). This may be due to the fact that collisional scrambling following dissociation, Reaction (15), also depends on pressure.

Dever and Grunwald\(^{7}\) have suggested in their study of CC₁₄F and CF₃Cl that the energy provided by the laser stays predominantly in one vibrational mode prior to dissociation. Their operating pressures exceeded 60 torr. While the question of intramolecular energy transfer prior to dissociation remains unanswered, our data strongly suggest that, at one torr, intermolecular energy transfer occurs sufficiently often to scramble the isotopic selectivity before dissociation. At 60 torr we would expect a large degree of collisional redistribution of the energy among the vibrational modes prior to dissociation.

D. Optimization of the selectivity

As the products of the multiphoton dissociation of CF₃I become enriched in \(^{12}\text{C}\), the remaining reactants become
enriched in $^{13}$C. For a given value of $\alpha$ the limit of enrichment in the reactants depends through Eq. (5) on their remaining fraction, $f$. In order to obtain an efficient separation we would like $f$ to fall as rapidly as possible with the number of pulses, $N$.

Figure 2 shows the dependence of $f$ on $N$. The upper line (circles) is a fit to the experimental data for a cell temperature of 298 K, while the dashed line is the prediction of Eq. (7), where $\Delta f$ has been chosen to fit the region of low $N$. The middle line (triangles) shows the effect of cooling the cell to $-80^\circ$C. It is evident that cooling increases the rate of decomposition with $N$. This increase may be due to at least two effects: 1) Cooling may place more population in the absorbing levels and, therefore, increase the fractional dissociation. 2) Cooling may also affect the fractional dissociation through inhibition of the Reaction (14), which would otherwise cause a decrease in $\Delta f$ with $N$ as $I_g$ accumulated in the cell. The rate of Reaction (14) has been reported to be $5 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. At $-80^\circ$C the vapor pressure of $I_g$ is below $10^6$ torr, whereas the vapor pressures of CF$_3$I and CF$_2$I are both larger than our operating pressures. Thus, at this temperature Reaction (14) should be effectively eliminated; $I_g$ will condense at the cell walls between laser pulses (0.5 Hz). Since it is unlikely that radicals will reach the cell walls (radius = 2 cm) before recombining, other effects of cooling must be attributable to the temperature variation of the recombination rates. The source of residual deviation between the $-80^\circ$C curve and the predicted curve of Fig. 2 is still under investigation.

By cooling the cell to $-80^\circ$C we have achieved a 590-fold enrichment of $^{13}$CF$_3$I. Naturally occurring CF$_3$I ($^{12}$C/$^{13}$C = 1/99) at 0.1 torr was irradiated with 2000 pulses on the $R(14)$ line of the 0.664 CO$_2$ laser band. The peak intensity was 25 MW/cm$^2$ corresponding to an energy fluence of 3 J/cm$^2$. Mass spectral analysis showed that 86% of the residual reactant was $^{12}$CF$_3$I. These data are summarized in Table I, Runs 13–15.

E. Efficiency of the multiphoton process

By measuring both the amount of energy absorbed by the sample and the number of product molecules, it is possible to determine the quantum efficiency of the multiphoton dissociation. We have examined the efficiency as a function of incident intensity over the range 1–10 MW/cm$^2$.

A substantial uncertainty in the efficiency arises from the kinetics. If Reaction (12) and (14) occur faster than Reaction (11), then the net number of products created or reactants consumed will be substantially less than the number of dissociations. This will result in a lower apparent efficiency for dissociation than that which would be obtained in the absence of these reactions. Of the set of Reactions (11)–(14), Reaction (13) is known to be slow$^{22}$ under our experimental conditions. The rate for Reaction (11) has been reported$^{35–36}$ to be in the range $5 \times 10^{-12}$–$3.8 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, while that for Reaction (12) has been reported$^{37–39}$ to be in the range $(1,5–6,5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Based on the value of $5 \times 10^{-12}$ for Reaction (11), Andreeva et al.$^{39}$ have found that Reaction (12) has a rate of $(1,5–2,5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. It would thus appear that roughly 80% of the CF$_3$ radicals recombine with I to form CF$_3$I. The remainder form CF$_2$I unless the pressure of I$_g$ is high enough to allow Reaction (14) to occur ($k_{I_g} = 5 \times 10^{-12}$).$^{35}$ Consequently, the fractional dissociation will actually be five times larger than the apparent value we measure. The fractional dissociation per shot and the efficiency reported below have not been corrected by this factor, since there is still some uncertainty in the relative rates of Reactions (12) and (13).

The first step in determining the efficiency of the multiphoton dissociation process is to determine the fraction of molecules dissociated in the beam per pulse, $\Delta f$. If we ignore the effect of Reaction (14), $\Delta f$ may be determined from $N$ and the measured value of $f$ using Eq. (7). In Table I, Runs 16–24 give the results for 0.5 torr of CF$_3$I and a range of incident intensities. These are plotted in Fig. 3. The fractional dissociation exhibits a threshold below 2 MW/cm$^2$ (0.24 J/cm$^2$) and then increases with intensity. At an intensity of 10 MW/cm$^2$ (1.2 J/cm$^2$), roughly 8.4% of the molecules in the beam are dissociated per pulse, while at 16 MW/cm$^2$ (1.9 J/cm$^2$) the fraction increases to 15%.

The fractional dissociation in the beam per pulse may be converted to an efficiency if the amount of energy absorbed by the sample is measured. For 0.5 torr of CF$_3$I absorption could conveniently be measured in the intensity range below 11 MW/cm$^2$. The resulting curve was interpolated to yield the values listed in the column of Table I headed $E_{abs}$. Since the CF$_2$I bond strength
is 55 kcal/mole and roughly equal to the energy of 18 laser photons, we define an efficiency of 1.0 to correspond to one dissociation for every 18 photons absorbed. Division of $\Delta f$ by $E_{abs}$ (in photons/molecule in the beam) and multiplication by 18 yields the efficiencies listed in Table I. At 10 MW/cm$^2$ (1.2 J/cm$^2$) the efficiency is found to be 9.1%. Thus, one in every 11 photons absorbed contributes its energy to the dissociation process at this intensity. The actual efficiency may be much higher, considering the relative rates of Reactions (12) and (13).

IV. CONCLUSION

Multiphoton dissociation of CF$_3$I has been shown to be an isotropically selective and efficient process. Enrichment of carbon-13 by a factor of nearly 600 has been achieved. At 10 MW/cm$^2$ (1.2 J/cm$^2$) the observation that at least 8.4% of the molecules in the beam are dissociated leads to the conclusion that at this intensity at least one in every 11 absorbed photons contributes its energy to the breaking of the CF$_3$I bond. These values may be as much as five times higher, considering the relative rates and Reactions (12) and (13). We are currently investigating the dependence of the selectivity and efficiency on wavelength and pressure of added gases.

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