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ARTICLES

Effect of NO on the Isotopically Selective Dissociation of CF_3Br with a Transversely Excited Atmospheric CO_2 Laser

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Mixtures of CF_3Br and NO have been irradiated with a transversely excited atmospheric (TEA) CO_2 laser under different experimental conditions. The isotopic composition of the undissociated CF_3Br has been analyzed by mass spectrometry. ^{13}C enrichment factor in the remaining CF_3Br and ^{13}C selectivity have been estimated and compared with those obtained with the pure substance and previous mixtures of $CF_3Br + X$ ($X = He, Ar, Xe, H_2, D_2, N_2, CF_4$). The presence of NO produces a remarkable improvement of the enrichment factor. The trapping ability of NO, due to its radical-like character, improves drastically the results obtained previously.

I. Introduction

The multiple photon dissociation (MPD) of polyatomic molecules has been studied by several authors.[1−9] We have studied the MPD of pure CF_3Br and mixtures with monatomic (He, Ar, and Xe), diatomic (H_2, D_2, and N_2), and polyatomic (CF_4) gases.[10,11] The experiments were carried out by irradiating with a transversely excited atmospheric (TEA) CO_2 laser, at different temperatures, pressures, and fluences. Mixtures of CF_3Br with different gases[12−16] have also been studied by MPD, following the effect of the presence of these gases on the carbon-13 enrichment. They observed that the enrichment factor tends toward 1 as the total pressure increases, when irradiating with laser lines between 1035 and 1050 cm^{-1}, as we do. Most studies have been carried out with static cells and sharp focusing, while in ours a wave guide is irradiated with constant fluence. Due to the different experimental conditions, it is difficult to compare in detail their results with ours. Avatkov et al. and Parthasarathy et al.[12,13] have observed, as we do,[10] that the dependence of the enrichment factor on the irradiation fluence is strong, and they used fluences between 2.6 and 3, while we use from 0.98 to 1.7 J/cm^2.

As we have reported previously,[10,11] the irradiation wavelength is the most important parameter for achieving selectivity, while decreasing the temperature from 295 to 188 K does not produce a remarkable effect on the enrichment factor.

The presence of different diatomic gases in the irradiated mixture produces an increase of the enrichment, especially when using H_2, while the presence of monatomic gases has no effect.[10,11]

However, none of these added molecules were able to avoid the recombination of the free radicals (CF_3 and Br) formed during the MPD process. This recombination results in a loss of selectivity of the process.

To avoid the undesired recombination, we thought of introducing NO, a highly reactive gas capable of trapping the generated radicals before they recombine and lose the selectivity achieved by the MPD process. In fact, NO has been successfully used previously in the MPD of other Freons.[17] The present work describes the results obtained in mixtures of $CF_3Br + NO$.

II. Experimental Section

Figure 1 shows the experimental apparatus that has been previously described.[10] The analysis of the products is performed with a SXP Elite mass spectrometer from Fisons, capable

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S1089-5639(98)00223-0 CCC: $15.00

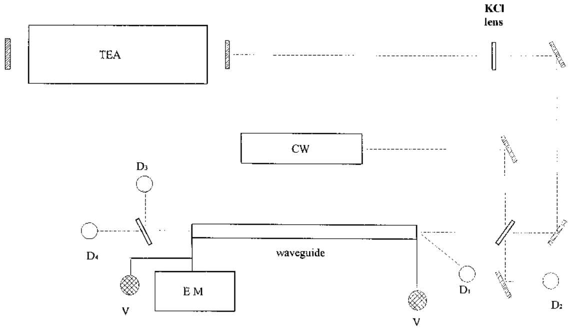

Figure 1. Experimental apparatus. (TEA, pulsed CO_2 laser; CW, continuous wave CO_2 probe laser; D_1, D_2, D_3, and D_4, IR detectors; V, vacuum and gas supply; MS, mass spectrometer).

of detecting 1 ppm of masses up to 300 amu. The electrons are accelerated with an energy of 70 eV, and the generated ions are positive.

CF_3Br has been supplied by PRAXAIR and NO by Air Liquide, and both have been used without further purification.

III. Results and Discussion

As in previous works, to measure the enrichment of the process, we use the enrichment factor of the residual CF_3Br, β, defined as

$$\beta = \frac{(I_{149}/I_{148})_{\text{after irradiation}}}{(I_{149}/I_{148})_{\text{before irradiation}}}$$

where I_{149} and I_{148} are, respectively, the mass peak intensities of $^{13}CF_3{}^{79}Br$ and $^{12}CF_3{}^{79}Br$.

The observed β values are smaller than 1, which shows that ^{13}C-bearing molecules are preferentially dissociated.

However, the enrichment factor of the reactant, β, by itself has limited quantitative significance since its value is influenced by many nonfundamental parameters such as the size of the reaction wave guide and the number of laser pulses. Therefore, when possible, we will estimate the selectivity factor, α_{13}, since it is a direct measurement of the reaction yield ratio for the two isotopic species of the reactant. It is defined as[18]

$$\alpha_{13} = \frac{V_{13}}{V_{12}} = 1 + \frac{\ln \beta_{\text{reactant}}}{\ln f}$$

where V_i is the reaction yield of $^iCF_3Br$ and $f = [^{12}CF_3Br]_{\text{after irradiation}}/[^{12}CF_3Br]_{\text{before irradiation}}$. The irradiation fluence was, in all cases, 1.4 J/cm^2, and, unless otherwise mentioned, the experimental conditions were as follows: total pressure, 0.5 Torr; temperature, 295 K; number of pulses per irradiation, 960; irradiation wavelength, 1046.9 cm^{-1} (9P20); and mixture composition, 1:6 CF_3Br + NO.

The results have been obtained as the averaging of three or more measurements, under the same experimental conditions, and the error bars reflect their statistical deviation.

Figure 2 shows that the optimum CO_2 laser line to achieve enrichment is the 9P20 that lies at 1046.9 cm^{-1} for the pure substance and all the mixtures previously studied. As always, this is the most important parameter to reach selectivity.

Figure 2 shows that lowering the temperature from 295 to 188 K increases the selectivity factor, α_{13}.

A. Effect of NO Addition. Mixtures 1:*x* (*x* = 2.2, 4, 6, and 7.3) of CF_3Br + NO have been studied. Figure 3 shows the selectivity factor for these mixtures as a function of total pressure. The observed increase is maximum when irradiating with the lines 9P28 (1039.4 cm^{-1}) and 9P18 (1048.7 cm^{-1}). In general, the selectivity factor values reach a maximum in the pressure range of 1−4 Torr. For higher pressures, α decreases abruptly and, as usual, the process stops being selective.

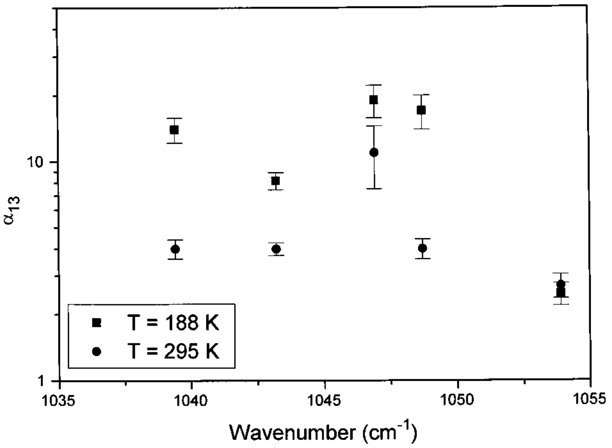

Figure 2. Selectivity factor versus wavelength for the 1:6 CF_3Br + NO mixture, at two different temperatures: 295 and 188 K.

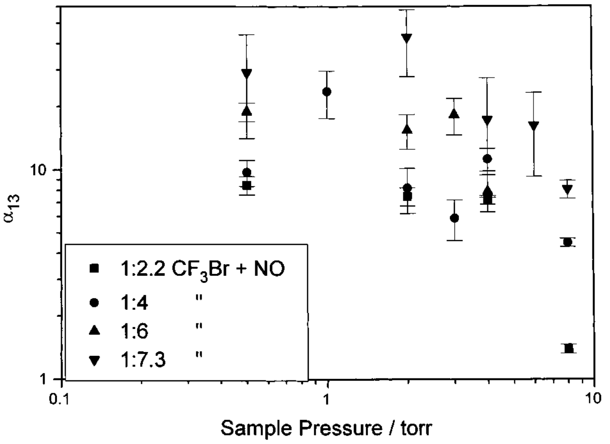

Figure 3. Selectivity factor versus total sample pressure for NO mixtures with different proportions: 9P20 irradiating line, room temperature, 1.4 J/cm^2 of fluence, and 960 pulses.

Maximum enrichment is achieved for the 1:7.3 mixture. More diluted samples have not been studied because the peak intensity corresponding to the mass 149 after irradiation is in the detection limit of the mass spectrometer. This is responsible for the large error bars in the measurements with 1:7.3 mixtures. However, the maximum possible enrichment is not reached under our experimental conditions.

Except at the lowest pressure measured, 0.5 Torr, best enrichments (measured as minimum β values) are always achieved in the NO mixtures (Figure 4). The improvement of the enrichment when adding NO is remarkable for total pressures between 1 and 4 Torr.

When the results of all of the mixtures studied are compared, the following conclusions are reached:

1. In general, the enrichment factor tends monotonically toward 1 when the total pressure is increased from 0.5 to 10 Torr, for the pure substance and the mixtures with all the gases studied, except NO. In this last case, β shows a minimum between 2 and 4 Torr.
2. Maximum enrichment is achieved in the presence of NO.
3. In the NO mixtures, the higher the NO mole fraction, the better the enrichment obtained.

The different behavior of NO could be based on its radical-like structure, which makes it an excellent species for capturing

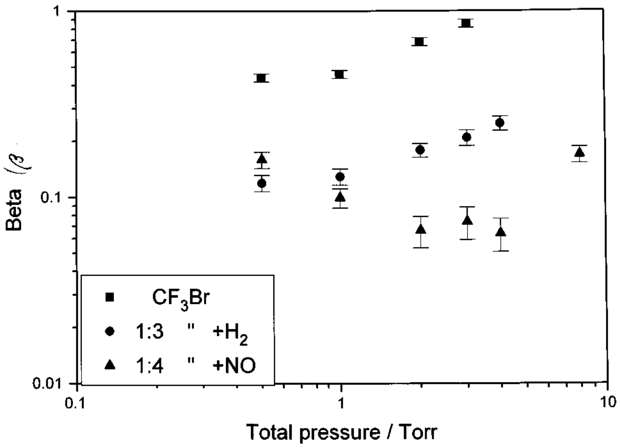

Figure 4. *β* values versus total presure for the pure substance, a 1:3 $CF_3Br + H_2$ mixture, and a 1:4 CF_3Br + NO mixture. The experimental conditions are the same as those in Figure 3.

TABLE 1: C_R Values (Torr) for the NO Mixtures Studied (Irradiating Line, 9P20; Room Temperature; 1.4 J/cm^2 of Fluence; 960 Pulses)

	C_R for given P_T (Torr) value, Torr						
mixture	8 Torr	6 Torr	4 Torr	3 Torr	2 Torr	1 Torr	0.5 Torr
1:2.2	3.50		9.00		4.69		1.33
1:4	7.20		9.04	3.54	3.30	4.74	0.98
1:6			4.51	7.85	4.43		1.33
1:7.3	12.96	19.56	13.92		10.33		1.75

the radical fragments of the photodissociation. It is believed that the following reactions take place:

$$CF_3Br + h\nu \rightarrow CF_3^{\bullet} + Br^{\bullet}$$

$$CF_3^{\bullet} + NO \rightarrow CF_3NO$$

$$Br^{\bullet} + NO \rightarrow BrNO$$

These reactions avoid the following recombination of the fragments:

$$CF_3^{\bullet} + Br^{\bullet} \rightarrow CF_3Br$$

This recombination reaction contributes to the loss of enrichment in the other mixtures studied, where the gases act as buffers (H_2, D_2, and N_2) or spectators (He, Ar, and Xe), but they do not trap the fragments formed.[10,11]

B. Efficiency of the Carbon Isotopic Separation Process. The carbon product of the photodissociation is CF_3. It is believed that, in the presence of NO, CF_3NO is formed. It is confirmed by the appearance among the products of $^{12}CF_3NO$, at mass 99 amu. However, there are three species at mass 100 amu, $^{12}C_2F_4$, $^{13}CF_3NO$, and ^{81}BrF, that in our results cannot be distinguished. Abdushelishvili et al.[17] attribute the peak at mass 100 to $^{12}C_2F_4$, in the MPD of CF_3I + NO. In our case, we cannot discard that $^{12}C_2F_4$ contributes to the peak intensity at mass 100 because we are not able to detect the peaks at masses 101 and 102 corresponding to $^{12}C^{13}CF_4$ and $^{13}C_2F_4$, respectively, due to their low concentration. The CF_3NO contribution to the mass 100 is only possible when NO is added to the sample. However, the mass 100 appears also with samples of pure CF_3Br and with similar intensity. Therefore, $^{13}CF_3NO$ is a minor contributor to this mass. We believe that the main contribution to mass 100 is due to ^{81}BrF since the peak at mass 98, corresponding to ^{79}BrF, is also observed and the ratio of the intensities matches the natural abundance of bromine atoms. The fact that the peak intensity at mass 100 is practically the same before and after the irradiation supports our assignment to a species not formed during irradiation.

We have not been able to decrease the intensity at mass 100 after several attempts of separating BrF by passing the commercial CF_3Br through a coil at −95 °C (slush bath of heptane with liquid nitrogen). Therefore, we think the BrF is generated as a fragment in the analysis by mass spectrometry of CF_3Br.

As we have already pointed out, our results were obtained from the remaining CF_3Br. To estimate the efficiency of the separation process in NO mixtures, the following function is defined:

$$C_R = \alpha_{13}[P_{CF_3Br}]_{\text{before irradiation}}$$

where the first factor takes account of the efficiency of the selective dissociation, and the second, the number of particles susceptible of dissociation.

We consider that the maximum values of C_R give the optimum pressure conditions for carbon isotopic separation. Table 1 shows the estimated values of this function in the mixtures studied. Under the present experimental conditions, best results are obtained for the most diluted samples, 1:7.3, and 6 Torr of total pressure.

IV. Conclusions

1. The irradiating wavelength is the crucial parameter in obtaining selectivity.
2. Although lowering the temperature does not influence noticeably the enrichment factor, *β*, its effect on the α values is significant.
3. The addition of a radical trapper like NO improves significantly the enrichment.
4. The MPD process is more selective than can be inferred from our previous results. The recombination of the radicals formed in the dissociation masks the selectivity of the initial MPD process. The presence of NO avoids this recombination, preserving the selectivity of the multiple photon dissociation.
5. Maximum possible enrichment is not reached in 1:7.3 CF_3Br + NO mixtures. However, at higher dilutions the number of CF_3Br molecules is so small that the efficiency of the process would be very poor.
6. An efficient experimental method for obtaining carbon isotopes has been established.

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