where v is as defined above and V is the volume in liters available for relative translation of A and B excluding the reactive volume v. Then the effective molarity is

$$EM = K_{uni}k_2/K_{bi}k_2 = (LV)^{-1}$$
(39)

For the three systems in the rows 4-6 of Table II, and 3D unimolecular reactions, the activated (diffusional) effective molarities are, respectively, 0.40 (0.48 M), 27 (69 M), and 416 M (5060 M). These three systems differ only in the volume V available for unimolecular fragment diffusion outside the reactive volume v; the bimolecular reactions are the same for the three systems. The rate constant  $k_{uni}$  and the EM of the diffusion-controlled reactions increase more rapidly with decreasing V than do those of the activated reactions. This is due to the nonuniform distribution of reaction partners in the (nonequilibrium) diffusioncontrolled reaction.

# Conclusion

Simple diffusion-controlled reactions between spherical, isotropically reactive groups can display large rate enhancements when restrictive translational constraints are imposed on the unimolecular reaction. Additional rate enhancements occur when a reduction in dimensionality accompanies the translational constraint unless the latter is very restrictive. If the reactants are not isotropically reactive, the effective molarity will be further increased if the geometric constraints in the unimolecular system keep the reactive surfaces in a proper orientation for reaction. Very large rate enhancements can occur when an attractive potential operates between the reactive groups in the unimolecular system, corresponding to some form of internal strain relief upon reaction.

These simulation results indicate that highly elevated values of effective molarity are not likely to arise from mass transport considerations alone. To reach effective molarities greater than about 10<sup>3</sup>, it is necessary to have favorable energetics, modeled here by an attractive intramolecular potential, or geometries so constrained that the concept of reactants separated by a tether becomes questionable.

Acknowledgment. This work has been supported in part by NIH, NSF, and the Robert A. Welch Foundation. M.H.M. is supported by an NIH Traineeship under the Houston Area Biophysics Training Program. J.A.M. is the recipient of the 1987 Hitchings Award from the Burroughs Wellcome Fund.

# **Electric Field Effect on the Chemical Activation Processes of** 1,1,2,2-Tetrafluorocyclopropane

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The electric field effect on the decomposition and energy-transfer process of chemically activated 1,1,2,2-tetrafluorocyclopropane is studied. The apparent unimolecular rate constant is measured as a function of the electric field strength in the range 0-7.2 kV/cm. A significant dependence of the experimental constant on the electric field was observed up to a saturation value. Several explanations for this behavior are analyzed.

#### Introduction

In recent years there has been great theoretical and experimental interest in the influence of electric and magnetic fields on transport properties,<sup>1</sup> energy absorption,<sup>2</sup> radiative and nonradiative processes,<sup>3,4</sup> and reaction mechanism<sup>5,6</sup> of gases, microemulsions,<sup>7-10</sup> and crystals.<sup>6,11,12</sup> Unfortunately, many questions remain unsolved, mainly those concerned with highly excited polyatomic systems. In previous papers<sup>13-15</sup> we have studied the

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decomposition and deactivation of highly vibrationally excited 1,1,2,2-tetrafluorocyclopropane. We now report the characterization of this process in a dc electric field. The data show a strong dependence of the unimolecular rate constants with the electric field strength. The results are discussed in terms of the current understanding of unimolecular processes.

#### **Experimental Section**

Reactants were obtained and purified as described previously.<sup>13,14</sup> The samples were photolyzed with the unfiltered light of an OSRAM 500-W high-pressure mercury lamp, in cylindrical Pyrex vessels of diameter as small as possible compared with that of the electrodes. The diameter of the cell was typically 1-2 cm. In each experiment the cell was placed between two parallel circular plate electrodes made of polished aluminum, of 30 cm diameter, which were spaced 3 cm apart. The electrodes were connected to a HV power supply, which provided voltage in the range 0-30 kV, controlled to better than 5%. From the configuration used in this work, the dc electric field strength in the cell (E) can be related to the unperturbed field strength far from the Pyrex cell ( $E_0$ ) by  $E \sim 0.9E_0$ . In calculating this relation, using a similar formulation to that of Gozel and van den Bergh,<sup>2</sup> it has

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been assumed that the diameter of the cell is small compared to the diameter and distance between the electrodes. The zero-field measurements were made by keeping the cell between the electrodes with  $E_0 = 0$  and photolyzing under the same conditions as in the other experiments.

Three sets of experiments were carried out with reactant ratios  $CH_2CO:C_2F_4:O_2 = 1:16:2$ , on collisional basis, and total pressures of 67, 139, and 361 Torr. Another set was made adding  $CO_2$  as inert gas, in a ratio  $C_2F_4:CO_2 = 1:70$  at a total pressure of 157 Torr. All the experiments were carried out at room temperature in the range 0–7.2 kV/cm. After irradiation the samples were analyzed by gas chromatography. Further details of the experimental method can be found in ref 13–15. Some control experiments were made by changing the distance between the electrodes, the cell geometry, and the characteristics of the high power supply and the condensers. None of them had any noticeable effect on the experimental results, so that we conclude that they only depend on the total pressure and the electric field strength.

#### Results

The reaction products observed from the photolysis of ketene in the presence of  $C_2F_4$  and  $O_2$ , as a scavenger of triplet methylene, were  $CH_2$ == $CF_2$  and 1,1,2-2-tetrafluorocyclopropane (TFC).

The products are well explained by the following mechanism:

$$CH_{2}CO + h\nu \rightarrow :CH_{2} + CO$$
$$:CH_{2}(^{1}A_{1}) + C_{2}F_{4} \rightarrow TFC^{*}$$
$$TFC^{*} \rightarrow CH_{2} = CF_{2} + :CF_{2}$$
$$TFC^{*} + M \rightarrow TFC + M$$
$$:CF_{2} + C_{2}F_{4} \rightarrow c - C_{3}F_{6}$$
$$2(:CF_{2}) \rightarrow C_{2}F_{4}$$

$$:CH_2(^{3}B_1) + O_2 \rightarrow CO, CO_2, H_2, H_2O, ...$$

The asterisk denotes a chemically activated species. The excited TFC may either decompose to yield  $CH_2$ =CF<sub>2</sub> (D) or be deactivated by collisions to yield a stable molecule of TFC (S). As previously discussed, this last process is represented as taking place in one step although it is actually a multistep process.<sup>13</sup>

From the gas chromatographic analysis the ratio (D/S) was calculated and the apparent unimolecular rate constant for decomposition,  $k_a$ , was obtained through the following equations

$$k_{\alpha} = (D/S)\omega$$
, s<sup>-1</sup> or  $k_{\alpha} = (D/S)P$ , Torr

where  $\omega$  is the collision frequency and P is the total pressure.

In order to obtain  $\omega$  it is necessary to evaluate the collision number,  $k_{\rm M}$ . The values used were the same as in ref 13 and 14,  $k_{\rm M}(\rm C_2F_4) = 0.85 \times 10^7 \, \rm s^{-1} \, Torr^{-1}$  and  $k_{\rm M}(\rm CO_2) = 1.96 \times 10^7 \, \rm s^{-1} \, Torr^{-1}$ .

The rate constants  $k_{\alpha}$  were calculated assuming that  $k_{\rm M}$  does not change in the presence of the dc electric field.

In some experiments the amount of  $O_2$  was tripled in order to eliminate the presence of triplet methylene. The (D/S) ratios obtained were the same as before. In another set of blank experiments the cell with the reactants was subject to the highest available electric field strength but without irradiating with the lamp. Even though the duration of these experiments were much longer than the total duration of the longest experiment, no products were found. Some experiments were also made in order to check if the extent of reaction was dependent on the field strength. Despite the relatively large errors involved in the absolute quantification of the products, no evidence of that effect could be observed. The experimental results are shown in Figure 1 where the ratio of the unimolecular rate constants with and without the electric field,  $k_{\alpha}/k_{\alpha}^{0}$ , is plotted as a function of the squared electric field strength. Considering all the experimental uncertainties the highest limit of error in  $k_{\alpha}$  was estimated to be about 20%. Clearly, the variation in  $k_{\alpha}$  with the field strength is beyond the experimental error.



Figure 1. Relative experimental unimolecular rate constants as a function of the squared electric field strength (see text): (**D**) total pressure, 67 Torr;  $w = 5.7 \times 10^8 \text{ s}^{-1}$ ; (**O**) total pressure, 139 Torr;  $w = 1.2 \times 10^9 \text{ s}^{-1}$ ; (**A**) total pressure, 361 Torr;  $w = 3.1 \times 10^9 \text{ s}^{-1}$ ; (**D**) total pressure, 157 Torr;  $w = 3.1 \times 10^9 \text{ s}^{-1}$ , with CO<sub>2</sub> as inert gas.

The data show a relative decrease of  $k_{\alpha}$  with the electric field strength for E < 4 kV/cm. At higher field strengths the  $k_{\alpha}$  values are constant within the experimental uncertainties. Considering the experimental error, the results with CO<sub>2</sub> as inert gas do not differ significantly from those obtained at 192 and 361 Torr by using C<sub>2</sub>F<sub>4</sub> as the main collider. The saturation value of the field strength for the results at 67 Torr, which is much lower than the other results, cannot be explained without further investigation.

The experimental results were compared with model calculations for the decomposition and stabilization processes of the activated TFC as follows. The computation of the RRKM rate constants and the (D/S) values was done as before.<sup>13,16</sup> The vibrational frequencies for the activated complex were the same as in ref 15 and selected to fit the experimental Arrhenius parameters, i.e., log k (s<sup>-1</sup>) = 14.01-45154/(4.576T). The critical energy for decomposition was calculated to be  $E_0 = 44$  kcal/mol. A stepladder model was used in order to compute the collisional transition probabilities,  $P_{ij}$ . Other details may be found in ref 13-15.

The results at E = 0 kV/cm do agree with our previous data<sup>13</sup> and can be fit with a value of the critical energy for the reverse of the activation process  $E_m = 98 \pm 4 \text{ kcal/mol}$  and with a mean down energy transfer  $\langle \Delta E \rangle_d = 8 \pm 1 \text{ kcal/mol}$  for C<sub>2</sub>F<sub>4</sub> as deactivating gas.

A series of computations were made in order to analyze the effect of the different parameters involved. First,  $E_m = 98$  kcal/mol was used and  $\langle \Delta E \rangle_d$  was changed between 4 and 14 kcal/mol. Second,  $E_m$  was varied between 94 and 98 kcal/mol and  $\langle \Delta E \rangle_d$  was set as 8 kcal/mol. Two other series were computed as before but assuming that an excess energy is distributed in the vibrational modes of the CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>).<sup>15,17</sup> This energy (about 7 kcal/mol) is sufficient to populate the v = 1 and possibly the v = 2 level of CH<sub>2</sub>. This would result in a distribution of vibrational energy on the reacting CH<sub>2</sub>. We used only the most satisfactory distribution of the study of ref 17, i.e., 30% of the population in the level v = 1 ( $g_1 = 0.3$ ) and 70% in the ground state. In these calculations the influence of a variation of the Arrhenius parameters was also analyzed.

The computed results, for the first two series of calculations and  $C_2F_4$  as a bath gas, together with the experimental points are presented in Figures 2a and 3. Dashed and black points represent experiments at E = 0 kV/cm and E saturation values, respectively. The other points are experiments at increasing values of E. Figure 2a shows that the  $k_{\alpha}$  values for saturation field strength can be fitted with higher  $\langle \Delta E \rangle_{d,Es} - \langle \Delta E \rangle_{d,E=0}$  as a function of  $\omega$  is displayed in Figure 2b, where  $\langle \Delta E \rangle_{d,Es}$  is the mean down energy loss for

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Figure 2. (a, bottom) Comparison of experimental data with stepladder calculations using  $E_m = 98$  kcal/mol, the Arrhenius parameters and the distribution energy of singlet methylene of ref 15. Step sizes  $\langle \Delta E \rangle_d$  are given in kcal/mol for each curve. Total pressures are (O) 67 Torr, ( $\Delta$ ) 139 Torr, ( $\square$ ) 361 Torr. C<sub>2</sub>F<sub>4</sub> is the main collider. See text for details. (b, top) Increase of the  $\langle \Delta E \rangle_{\rm d}$  values for saturation fields, relative to  $\langle \Delta E_d \rangle = 8$  kcal/mol (best fit for E = 0 kV/cm) as a function of collisional frequencies and as a function of the product  $\alpha \omega$  (see text for details). The dashed point was calculated from the experiments with CO<sub>2</sub> as inert gas.



Figure 3. Comparison of experimental data with stepladder calculations using  $\langle \Delta E \rangle_d = 8 \text{ kcal/mol.}$  Curve 1:  $E_m = 98 \text{ kcal/mol}$ , the Arrhenius parameters of ref 15 and a distribution function for  $CH_2({}^1A_1)$ ,  $(g_1 = 0.3)$ . See text. Curve 2:  $E_m = 94 \text{ kcal/mol}$ , and the other conditions of curve 1. Curve 3:  $E_m = 94 \text{ kcal/mol}$ , and the Arrhenius parameters of ref 15.  $CH_2({}^1A_1)$  was considering as being in its fundamental vibrational level. Curve 4:  $E_m = 98$  kcal/mol, the distribution function of ref 15, log A = 13.76 and  $E_0$  = 44.04 kcal/mol. Total pressures are (O) 67 Torr, ( $\Delta$ ) 139 Torr, (**D**) 361 Torr.  $C_2F_4$  is the main collider. See text for details.

a field strength equal or higher than the saturation value, and  $\langle \Delta E \rangle_{d,E=0}$  is the corresponding value at zero field strength and equal to 8 kcal/mol. Alternatively, the results of Figure 3 show that the dependence of  $k_{\alpha}$  for saturation field strength with



Figure 4. Comparison of experimental data with stepladder calculations. The experimental points were obtained by using CO<sub>2</sub> as the main collider at a total pressure of 157 Torr. Curve 1:  $E_{\rm m} = 98 \text{ kcal/mol}, \langle \Delta E \rangle_{\rm d} =$ 4 kcal/mol, the distribution function for singlet methylene and the Arrhenius parameters of ref 15. Best fit for the data with E = 0 kV/cm. Curve 2:  $\langle \Delta E \rangle_d = 8$  kcal/mol and the other conditions of curve 1. Curve 3:  $E_{\rm m} = 94$  kcal/mol and the other conditions of curve 1. Curve 4:  $E_{\rm m}$ = 93 kcal/mol and the other conditions of curve 1. Curve 5:  $\log A =$ 13.76,  $E_0 = 44.04$  kcal/mol, and the other conditions are as for curve 1.

pressure can also be reproduced with a lower value of the excitation energy and keeping  $\langle \Delta E \rangle_d = 8 \text{ kcal/mol.}$  The best fit is obtained with  $E_{\min} = 94 \pm 1 \text{ kcal/mol.}$  Also a very good agreement with the experimental results is obtained by decreasing the preexponential factor for the decomposition reaction, irrespective of whether the density of states of the TFC or the sum of states of the activated complex is modified. Finally, Figure 4 shows the results for the calculations with  $CO_2$  as deactivating gas. Even though the experiments were made at only one value of total pressure (157 Torr), the same behavior as for  $C_2F_4$  is observed; that is, the saturation value of  $k_{\alpha}$  can be reproduced with a higher value of  $\langle \Delta E \rangle_d$  or with a lower excitation energy for TFC.

### Discussion

Experimental and theoretical studies of the influence of external magnetic and electric fields on transport properties of dilute polyatomic gases have been carried out extensively since 1962 (see, e.g., ref 1 and 18-26). This so-called Senftleben-Beenakker effect is explained by the anisotropies (or polarizations) produced in the angular momentum distribution in polyatomic gases. Such angular momentum dependent polarizations, which are produced in collisions because of nonspherical intermolecular potential, can be partially destroyed by applying an external field which will cause the molecules to precess around the field direction. This will alter the transport properties. The analysis of measured data on

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magnetic and electric field effects on the viscosity for saturation field strengths is less than 1%.24 A similar change could be expected on the collision number,  $k_{\rm M}$ , since the dependence of  $k_{\rm M}$ and viscosity on the  $\Omega^{2,2}$  integrals is the same.<sup>27</sup> So the large dependence of the unimolecular rate constants on the electric field cannot be explained only by a change in  $k_{\rm M}$ . The linear relationship of Figure 2b is rather surprising. But is must be pointed out that, considering the uncertainties in the estimated collision diameter and Lennard-Jones constants,<sup>28</sup> the ratio  $(\langle \Delta E \rangle_{d,Es})$  $\langle \Delta E \rangle_{d,E=0} / \langle \Delta E \rangle_{d,E=0}$  is essentially the same for C<sub>2</sub>F<sub>4</sub> and CO<sub>2</sub> as main collisional partners, comparing the results at the same collision frequency. This suggests that the relative increase in  $\langle \Delta E \rangle_{d}$  is independent of the bath gas at the same  $\omega$ . Another explanation can be obtained considering the polarizabilities of the bath gases. The polarizabilities are  $\alpha(C_2F_4) = (41.7-54) \times 10^{-25}$ cm<sup>3 29</sup> and  $\alpha$ (CO<sub>2</sub>) = 26.5 × 10<sup>-25</sup> cm<sup>3</sup>. Considering these values if the difference  $\langle \Delta E \rangle_{d,Es} - \langle \Delta E \rangle_{d,E=0}$  is plotted against the product  $(\alpha\omega)$ , then a linear relationship is obtained for both C<sub>2</sub>F<sub>4</sub> and CO<sub>2</sub>, as shown in Figure 2b. Regarding this point, it should be noted that recent experiments carried out in our laboratory on the infrared multiphoton decomposition of 1,1,2-trifluoro-2-trifluoromethylcyclopropane in the presence of a dc electric field showed no dependence of the collisional results with the electric field.<sup>30</sup> However, in this case the bath gas used was argon which is an inefficient collider and has a polarizability of  $16.3 \times 10^{-25}$ cm<sup>3</sup>, which is much lower than the value for  $C_2F_4$  and  $CO_2$ .<sup>31</sup>

A reasonable fit to the experimental data can be obtained with a lower  $E_{\rm m}$  value (Figure 3). As was just pointed out,  $E_{\rm m} = 94$  $\pm$  1 kcal/mol gives a good fit, even for the data with CO<sub>2</sub> as the mean collider (Figure 4). Within the large experimental error, the computational results with and without energy distribution for the reacting methylene are indistinguishable. Thus, it precludes any consideration about a change in the distribution of vibrational levels of singlet methylene.<sup>17</sup> Curve 4 in Figure 3 has been calculated with a new set of Arrhenius parameters for the decomposition reaction:  $\log k = 13.76-44.040/(4.576T)$ . This modification in the preexponential factor leads to a new sum of states for the activated complex of the decomposition reaction (about 40% lower) or an increase of about 75% in the density of states of the excited TFC.

In recent years many papers have reported studies on collision-induced intersystem crossing (CI-ISC),432-46 infrared mul-

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tiphoton ionization and dissociation,<sup>2,47-49</sup> predissociation,<sup>50</sup> and electric field induced spectra.<sup>51,52</sup> In all of them, the results have been explained within the framework of some mixing of states produced by the electric or magnetic field as a consequence of the spin-rotation decoupling. One of the most thoroughly studied systems is the CI-ISC of glyoxal in the presence of a weak magnetic field.<sup>32-40</sup> It was found that the magnetic quenching of the fluorescence intensity increases smoothly with the magnetic field and reaches saturation at a field strength of about 1000 G, where the fluorescence quenching rate is 40% higher than without the magnetic field. This value appears independent of the nature of the collision partner and the excitation wavelength. The situation seems to be similar here, in the sense that the electric field could mix singlet and triplet states of the CH<sub>2</sub> radical, resulting in a lower excitation energy of the TFC\* and hence a lower value of  $k_{\alpha}$ . However, this explanation is not unique, since a decreased preexponential A factor could also satisfactorily reproduce the experimental results. Also, the correlation of the change of  $\langle \Delta E \rangle_d$ with the polarizabilities of the bath gases suggests that a change in the interaction potential could be the reason for a more efficient transference of energy. Unfortunately, there is no information on highly vibrationally excited polyatomic molecules in the electronic ground state, like TFC, which has an average excitation energy of about 100 kcal/mol, i.e., 56 kcal/mol above the critical energy for unimolecular reaction.

Then, other considerations are speculative at present and more experimental data are desirable. Further discussion is postponed until the study with other systems is completed.

Acknowledgment. We thank Professor H. van den Bergh for helpful discussions and CONICET and CONICOR (Argentina) for their partial financial support.

Registry No. TFC, 3899-71-6; C<sub>2</sub>F<sub>4</sub>, 116-14-3; CH<sub>2</sub>CO, 463-51-4.

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