

Intramolecular Perturbations in Small Molecules in the Presence of a Continuous Electric Field

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Neste trabalho foi estudado o efeito de um campo elétrico na decomposição UV da cetena. Foi determinada experimentalmente a relação entre os principais produtos $[C_2H_4]/[C_2H_6]$, que é proporcional a $[CH_2(^1A_1)]/[CH_2(^3B_1)]^2$, como função da intensidade do campo elétrico no intervalo 0 - 4 kV/cm. Observou-se uma significativa dependência desta relação com o campo elétrico até um valor de saturação.

The electric field effect on the UV decomposition of ketene is reported. The ratio of the main products $[C_2H_4]/[C_2H_6]$ which is proportional to $[CH_2(^1A_1)]/[CH_2(^3B_1)]^2$ was measured as a function of the electric field strength in the range 0 - 4 kV/cm. A significant dependence of this ration on the electric field was observed up to a saturation value.

Key words: *small molecules; ketene; electric field.*

In recent years many papers has been published on the influence of electric and magnetic fields on transport properties, energy absorption, radiative and non-radiative processes and reaction mechanisms^{1,2}. Also the electric field effect on fluorescence and lifetimes of formaldehyde has been studied^{3,5} and numerical calculations have been performed⁶.

In this note we report the effect of an electric field on the singlet/triplet methylene ratio obtained in the UV decomposition of ketene. The results were interpreted in terms of the energy levels of methylene and collisional induced transitions between perturbed states. These results illustrate a description of radiationless process which seems to be common to all small molecules.

In all experiments a constant partial pressure of ketene was used (5 Torr) and argon was added up to the desired total pressure. The samples were photolyzed in a Pyrex cell, with Corning 707 windows, placed between two parallel circular plates electrodes connected to a HV power supply, which provided voltage in the range 0 - 30 kV, controlled to better than 2%. The value of the d.c. electric field

strength in the cell was calculated as in Ref. 1. The samples were irradiated (5 min) with the unfiltered light of an Osram high pressure Hg lamp, focused with quartz lenses. The zero field measurements were made by keeping the cell between the electrodes with $E = 0$ kV/cm and photolizing under the same conditions as in other experiments.

Some control experiments were made by photolyzing 30 min. and others by changing the distance between the electrodes and none of them had any noticeable effect on the experimental results. Also, dark experiments with 5 Torr of ketene and argon up to 111 Torr were performed at 3.5 kV/cm field strength for 10 min. No products were observed so that we concluded that the observed results were not caused by free electrons created by the field.

After irradiation, the samples were analyzed by gas-chromatography with a Varian 3700 apparatus equipped with a flame ionization detector. The major condensable products obtained were ethane and ethylene. Also minor quantities of allene and trace quantities of acetylene were formed. A complete analysis of the products was not done since it has been one of the objects of very detailed previous works^{7,8}

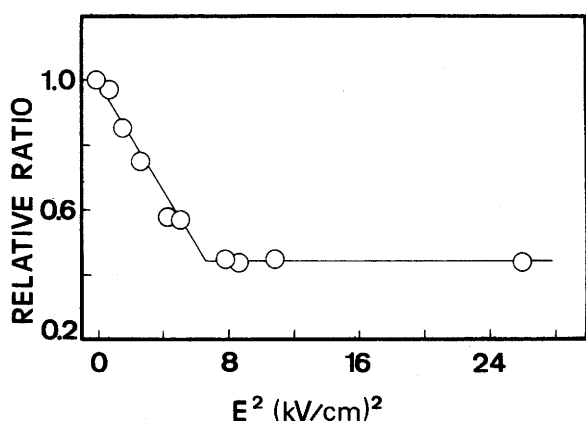


Figure 1. Relative experimental $[C_2H_4]/[C_2H_6]$ ratios as function of the squared electric field strength at III Torr of total pressure. The ratios are relative to the value at $E=0$ KV/cm.

and the main interest here was to determine the singlet/triplet ratio at different d.c. electric field strengths.

On the basis of the mechanism of Reference 8, differential kinetic equations for this system were written and solved by a numerical integration method⁹. From these results the following relation was obtained:

$$R[C_2H_4]/R[C_2H_6] \cong k_a + k_b [CH_2(^1A_1)]/[CH_2(^3B_1)]^2 \quad (1)$$

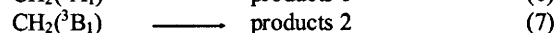
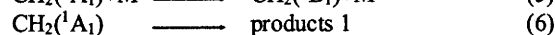
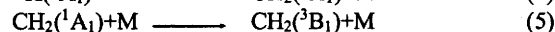
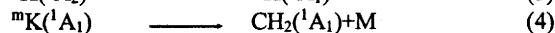
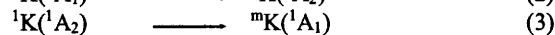
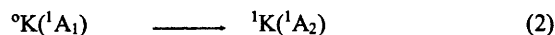
where k_a and k_b are global constants which depend on the individual rate constants for the individual steps, and the concentration of ketene (which may be taken as a constant, since the conversion was kept lower than 2%). Even more, a steady state treatment for radicals and excited species, gave the same result.

Considering all the experimental uncertainties the highest limit of error in the $[C_2H_4]/[C_2H_6]$ ration was estimated to be about 20%. Clearly, the variation of this ratio with the field strength is beyond experimental error.

The total amount of formed products was also checked. Within experimental uncertainties it is the same for all field strengths, which indicates that the electric field does not change the total amount of methylene formed during photolysis.

It is quite well established that the 308-320 nm photolysis of ketene proceeds via a vibronically allowed excitation to the 1A_2 state, followed by fast internal conversion to high vibrational levels of the ground state. The vibrationally excited ketene ($^mK(^1A_1)$) dissociates to $CH_2(^1A_1)$, which can further react or pass to $CH_2(^3B_1)$ by collisional induced intersystem crossing^{9,10}.

That is:



Present experiments in the presence of a d.c. electric field show that the $[CH_2(^1A_1)]/[CH_2(^3B_1)]^2$ ratio diminishes with the field strength reaching saturation at $E \cong 3.5$ kV/cm

This effect can be explained in terms of the collision induced intersystem crossing (CI ISC) eq. 5, and the fact that the rotational levels of the 1A_1 (0,0,0) and (0,1,0) vibronic states are heavily perturbed by nearby rovibrational levels of the ground triplet state. That is, singlet methylene is never in a pure spin state and always has some triplet character in its wave function. This perturbation has been demonstrated by the magnetic tuning of singlet levels seen in LMR spectra¹¹ and by visible $^1B_1 \rightarrow ^1A_1$ magnetic rotation spectra¹².

The spin-orbit interaction between the 1A_1 and 3B_1 states occurs in first order and it has been found that nearly 60% of the assigned 1A_1 (0,0,0) rotational levels are perturbed by the (0,2,0) and (0,3,0) 3B_1 vibronic states¹³.

Within this description, which is similar to the mixed-state model of Gelbart and Freed for small molecules, the cross section of CI ISC is approximately^{14,15}.

$$\sigma_{isc}^a = \langle \beta^2 \rangle n_s n_t \sigma_{rot}^t$$

where $\langle \beta^2 \rangle$ is the averaged mixing coefficient of the initially excited rovibronic level, n_s and n_t are the number of the zero order singlet and triplet states involved in the processes and σ_{rot}^t is the rotational relaxation cross section of the pure triplet electronic state. This mixing coefficient, β , depends on the field, which causes the decoupling of spin and rotation and as a consequence leads to a complete mixing of the triplet sublevels (which are only partially mixed by rotation at zero field)¹⁶. That is, the electric field which induces remixing of the triplet sublevels might increase the density of final states in the singlet-triplet transition.

The possibility of field ionization due to population of Rydberg levels of ketene seems quite interesting. Nevertheless, spectroscopic and theoretical studies suggest that the first Rydberg series initiates at 54680 cm^{-1} , by the $\tilde{X}^1A_1 - 2^1A_1$ transition. Since the excitation energy in this work is about 32467 cm^{-1} , those states can not be reached¹⁷.

Further efforts are presently being done to elucidate all the remaining questions. Nevertheless two important conclusions can be pointed out. First, the details of the intersystem crossing are directly related to the mixed character of the molecular states. Second, the electric field perturbs the CI ISC process. These conclusions may, in principle, be extended to other small molecules which show significant intrinsic interactions. In that sense, quantitative information on the extent of singlet-triplet interaction will be needed to obtain a correct modeling of observed collision induced intersystem crossing processes and of the kinetics of singlet and triplet reactions.

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