

CO₂ Laser Induced Telomerization of C₂H₄ + CF₃I

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Many concepts on laser chemistry are only successful at low pressures in the gas phase. In contrast, for synthesis of larger produced quantities it is desirable to work at fairly high pressure (e.g. above 500 mbar). At such pressures the reaction is collision dominated and the laser is more or less only a heating source. To apply a laser may thus be uneconomical. To justify the use of a laser, one tries to find advantages over conventional heating sources. Alternatively one tries to obtain a high quantum yield to reduce the costs; then even a minor advantage could be sufficient to favor the laser chemical process. Some cases which permit good quantum yield may be identified as follows. 1. For a reaction which can run at high temperature, raising the temperature will improve the quantum yield. This will be demonstrated below. 2. For a thermally initiated chain reaction, often the propagation rate is high and initiation rate is low at low temperature. In this case the system can be heated by a laser for initiation of the chain and then be quenched to lower temperature for the chain propagation. 3. For a thermally initiated exothermic reaction, if the volume to surface ratio of the reaction zone is large enough, the heat produced by the reaction can compensate the heat loss, then the reaction will be self-sustained.

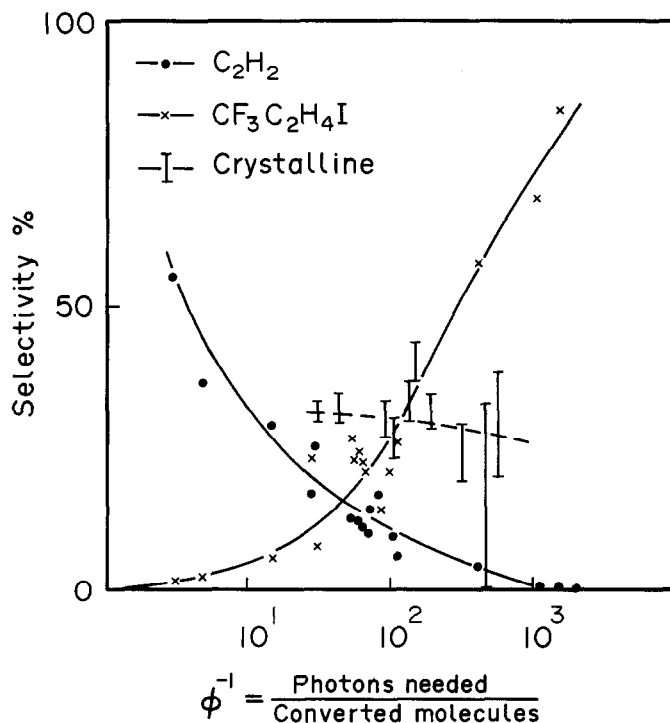
The insertion of one or more C₂H₄ into CF₃-I (telomerization) is an exothermic chain reaction. The propagation steps here consist primarily in transfer of I from CF₃I to CF₃(C₂H₄)_n. Using a pulsed CO₂ laser, we studied this reaction as a model to demonstrate the above mentioned principles. Besides, the products CF₃(C₂H₄)_nI (and CF₃C_{2n}H_{4n-1}) as well as those of similar reactions have practical interest as synthetic intermediates. The conventional technique for this kind of reaction employs liquid phase, high pressure (~ 100 bar) and moderate temperature and requires an initiator. We worked in gas phase at pressures up to 1.6 bar.

In the experiment the laser beam was weakly focused into the reaction cell. The conversion of reactants was measured by IR spectrometry. The products were analyzed by gas chromatography and identified by mass spectroscopy.

The experimental results show that CF₃I + C₂H₄ reacts and produces several products (mainly CF₃(C₂H₄)_nI, CF₃C₂H₃, C₂H₂, CF₃H, C₂F₆) at all the investigated CO₂ laser wavelengths (9R24 to 10P28). The quantum yields (ϕ = converted reactant molecules/consumed photons) at the different wavelengths can be correlated with the absorption: The more absorption, the higher the quantum yield.

For optimizing the selectivity S (S = produced product/converted reactant) and the

quantum yield ϕ , we investigated the influence of laser energy density (1.0 - 3.5 J/cm²), total pressure (125 - 1600 mbar), reactant composition ($C_2H_4/CF_3I = 7:1$ to 2:6) and laser wavelength (9R12 to 10P20). These results are summarized in the figure. This figure shows that, as a tendency, high selectivity for $CF_3C_2H_4I$ is incompatible with high quantum yield. However, the selectivity for the crystalline products (according to mass spectroscopy, they consist of $CF_3C_2H_4I$, $CF_3C_4H_8I$, $CF_3C_6H_{12}I$, $CF_3C_6H_{11}$) is nearly constant for all quantum yields. It is probable that the crystalline products are produced at lower temperature.



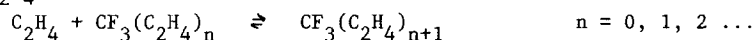
Typical experimental results, $C_2H_4/CF_3I = 5:3$, laser line 10P20, 80 laser pulses, TEA CO_2 laser, 6 - 8 J/pulse, focussed to 2 - 3 J/cm² applied in one run, laser beam diameter 2 cm, reactor diameter 3.3 cm.

P	E	conv. ^a		Selectivity %						quantum yield
				to conv. C_2H_4		to conv. CF_3I		to conv. Reactant		
mbar	J	C_2H_4	CF_3I	C_2H_2	C_2H_3I	$CF_3C_2H_3^b$	$CF_3C_2H_3^b$	$CF_3C_2H_4I$	crystalline ^c	
820	7.5	95	102	11	2	50	42	24	36	1.1×10^{-2}
1580	6.3	190	91	7	1	27	53	20	32	1.7×10^{-2}

- a) unit: mbar cm³/pulse
- b) CF₃C₂H₃ yield is a little bit higher than the actual value, because the quantity of CF₃C₂H₃ was calculated from its G.C. peak, which overlaped slightly with the C₂H₄ peak.
- c) weight %.

The results show the adducts (CF₃C₂H₄I + crystalline products) selectivity is about 50 - 60 %. Including CF₃C₂H₃ which is also useful as a reagent for synthesis, the total selectivity of these products together is more than 90 %. To increase the quantum yield, one can either prolong the time before the reaction is quenched by cooling (e.g. by an increased volume to surface ratio of reaction zone), or accelerate the propagation reaction (e.g. by increased pressure or temperature).

For C₂H₄ telomerization, the reaction temperature is limited because of the equilibrium



The equilibrium temperature T_c (under standard conditions, C₂H₄ gas phase, radical in condensed phase) is 422 °C, whereas for the analog C₂F₄ system, T_c is 750 °C. Thus C₂F₄ will be more favorable than C₂H₄, because higher temperatures here permit more conversion during the limited reaction time. A corresponding reaction has already been induced by a laser, but at low pressure [1], where the production rate must be limited.

Reference

- [1] Bagratashvili V.N. et al.: J. Phys. Chem. 88 (1984) 5780-5786.