SELECTIVE PHOTOADDITION OF ICl TO ACETYLENE: PRESSURE, BUFFER AND WAVELENGTH DEPENDENCE OF ENRICHMENT

M. Stuke and E. Marinero

Max-Planck-Institut für biophysikalische Chemie, Abteilung Laserphysik, D-3400 Göttingen (F.R.G.)

The technique of selective photoaddition has shown to be very useful to obtain high single step enrichment factors [1]. Adding ICl to acetylene, enrichment of ^{35}Cl and ^{37}Cl up to $\beta = 100$ (≥ 97 % purity) could be obtained [2]. Monitoring the enrichment in the photoproduct C_2H_2ICl after completely selective cw single-mode dye laser excitation at different pressures (up to one atmosphere), buffers (He, Ne, Ar, Kr, N_2) and wavelengths (5854 - 6030 Å), detailed information about the reaction mechanism was obtained. The quantum yield of the reaction was determined.

The single-mode dye laser can be automatically tuned and stabilized to a wavelength of maximum excitation selectivity for one isotope. The experimental setup is shown in Fig. 1 and described in detail in [2]. Using a mixture of 0.1 Torr natural ICl and 0.1 Torr HC≡CH, irradiating it with 100 mW for 5 minutes, the photoaddition product is highly enriched in ^{35}Cl (Fig. 2a) or ^{37}Cl (Fig. 2b) depending on the excitation wavelength (around 5963.2 Å).

In order to investigate the reaction mechanism, mixtures of 0.5 Torr ICl, 0.5 Torr HC≡CH and buffer were irradiated and analyzed for different buffers and pressures (Fig. 3). The enrichment decreases towards high pressures, but even for pressures up to 700 Torr ($9.3 \cdot 10^4$ Pa), the selectivity is not completely lost. This can be explained by energy transfer processes from the ICl ($^3\Pi_1$) and from highly vibrationally excited ICl ($^1\Sigma_g^+$), which is formed by quenching by the buffer.

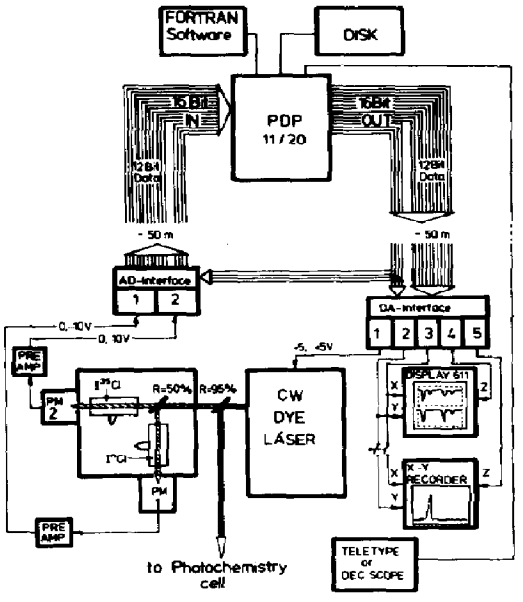

Fig. 1.

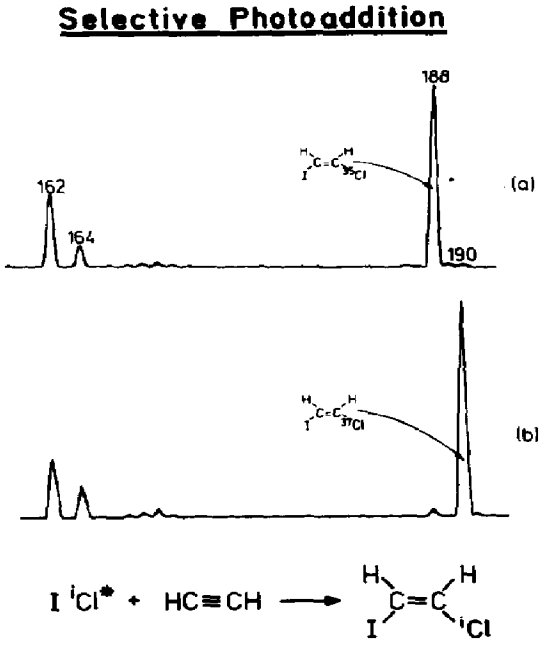

Fig. 2.

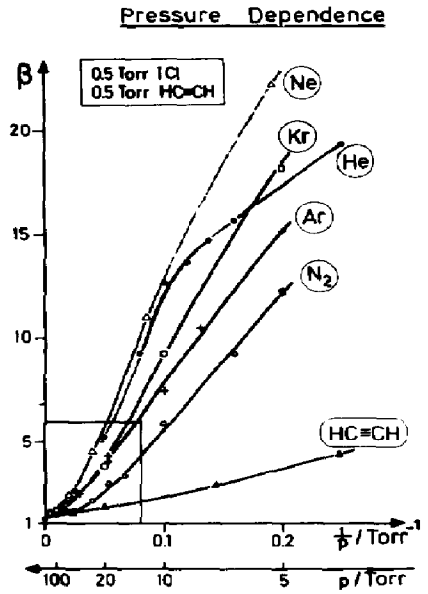

Fig. 3 (a).

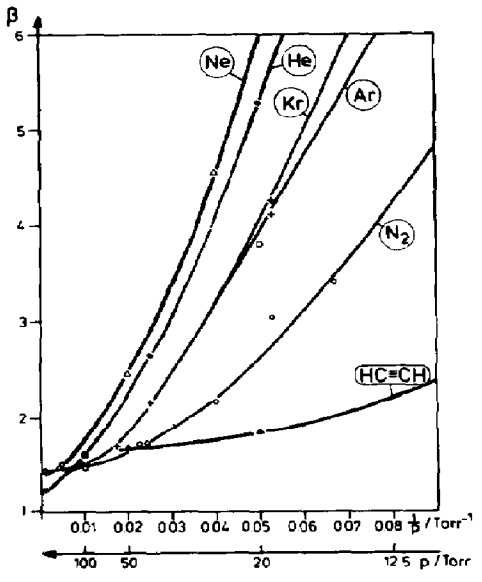

Fig. 3 (b).

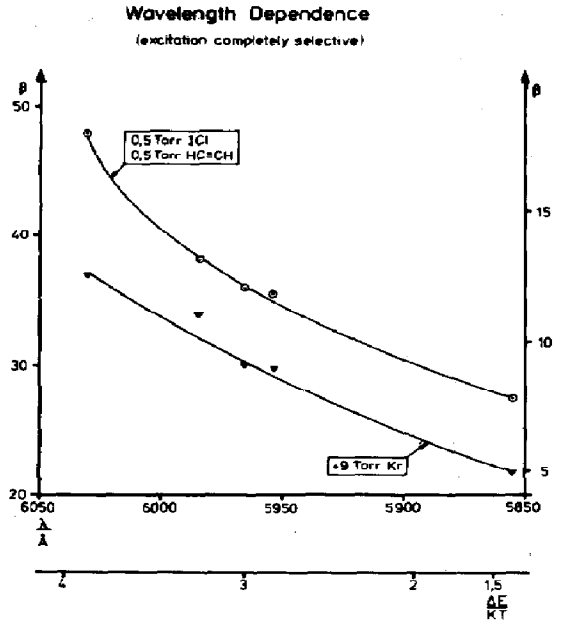

Fig. 4.

The wavelength dependence was studied between 5854 Å and 6030 Å, corresponding to an energy distance to the dissociation limit between 1.4 and 3.9 kT. Figure 4 shows, that the enrichment decreases towards the dissociation limit, even though the excitation is still completely selective, which was checked for each wavelength. These results indicate, that not only vibrational deactivation, but also dissociation after several collisions can occur, depending on the energy distance to the dissociation limit.

This method of injecting selectivity into a photochemical system and then watching its loss due to energy transfer processes, is very useful to get information about the reaction mechanism and energy transfer rates.

[1] M. Stuke, F. P. Schäfer: Chem. Phys. Lett. 48 (1977) 271
"Enrichment of chlorine isotopes by selective photoaddition of ICl to acetylene"

[2] M. Stuke, E. Marinero: Appl. Phys. 1978 (in press)
"On-line computer-controlled cw dye laser spectrometer for laser isotope separation"