

On the photodissociation of propadienylidene, $l\text{-C}_3\text{H}_2$

Supplementary Material

Synthesis of 3-Bromo-1-Iodopropyne

The synthesis was carried out following Ref. ¹. Two solutions were prepared separately: 9.66 g propargyl bromide solution (80%) in toluene (7.73 g pure propargyl bromide, 65.0 mmol) and a solution of 16.5 g iodine (65.0 mmol) in 16 ml of saturated aqueous KI solution. Both solutions were added within an hour simultaneously from separate dripping funnels to a solution of 14.6 g (260 mmol) NaOH in 98 ml of water with agitation at 0-5°C. After 3 h the product is extracted from the yellow reaction mixture with 3 times 20 ml of diethyl ether, dried over MgSO_4 and distilled under inert gas over a Vigreux column. The yield of the colourless product was 28% (4.48 g, 18.3 mmol) and can be stored at -20°C under argon (b.p.: 59-60°C at 3 mbar).

Synthesis of 1,3-Diiodopropyne

1,3-Diiodopropyne was prepared from 3-bromo-1-iodopropyne by the Finkelstein reaction². 1.00 g (4.08 mmol) of 3-bromo-1-iodopropyne was slowly added at 5°C to 20 ml of a saturated solution of KI in acetone. Immediate precipitation of KBr was noticeable. After 1 h at 5°C the reaction mixture was distilled over a Vigreux column under argon. The yield of the colourless product was quantitative (b.p. 52-55°C at 2 mbar).

Wavenumbers in cm^{-1} for RRKM-computations:

The reactand-wavenumbers were taken from the literature³.

$l\text{-C}_3\text{H}_2$: 3168, 3091, 2043, 1485, 1147, 1052, 1042, 293, 233

TS: $l\text{-C}_3\text{H}_2 \rightarrow c\text{-C}_3\text{H} + \text{H}$:

3252, 1677, 1251, 956, 892, 869, 615, 593, -869

The isomerisation between linear and cyclic C_3H_2 was computed to be much faster than the dissociation. Thus according to the Curtin-Hammett principle the cyclic intermediate can be ignored. The transition state for dissociation was defined as suggested by ⁴. The following geometry was calculated:

Atomic Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
6	C	0.592771	-0.517872	0.000000
6	C	-0.649148	-0.089986	0.000000
6	C	0.307613	0.905155	0.000000
1	H	-2.895264	-0.536148	0.000001
1	H	1.387845	-1.247635	0.000001

TS: $\text{l-C}_3\text{H}_2 \rightarrow \text{l-C}_3\text{H} + \text{H}$:

3301, 2032, 1237, 847, 744, 662, 348, 224, -841

The transition state was defined as suggested by ⁴. The following geometry was calculated:

Atomic Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
6	C	0.414582	-0.977540	0.000000
1	H	-1.126387	-2.671504	0.000000
1	H	1.325344	-1.550311	0.000000
6	C	0.000000	0.231301	0.000000
6	C	-0.447742	1.449875	0.000000

TS: $\text{l-C}_3\text{H}_2 \rightarrow \text{C}_3 + \text{H}_2$:

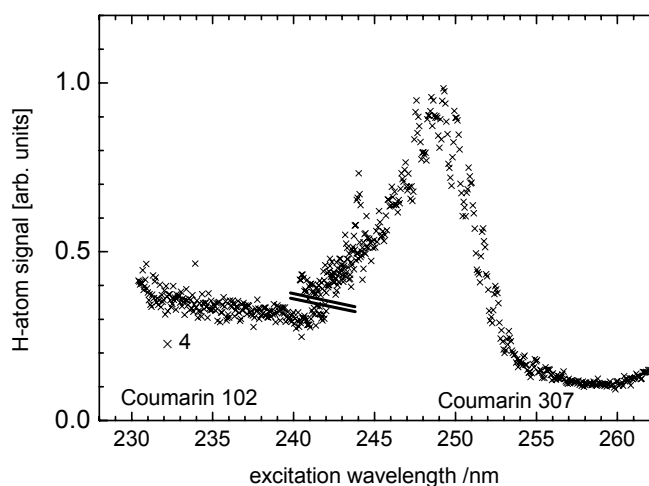
3133, 2388, 1747, 1124, 903, 520, 427, 259

The wavenumbers were taken from the literature³.

H-Atom Action Spectrum

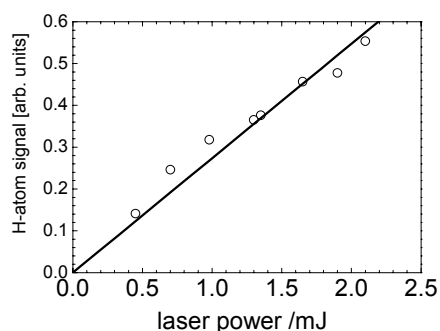
The H-atom signal was recorded as a function of excitation wavelengths. The H-atom signal rises between 260 and 255 nm and reaches a maximum around 249 nm. Note that the signal intensity below 238 nm (Coumarin 102) cannot be compared to that recorded at longer wavelengths (Coumarin 307) When compared with the spectrum recorded in a rare gas matrix^{5,6} it has a similar appearance in the red. However, the matrix spectrum reaches its maximum around 237 nm and vibronic structure is discernible. Two reasons might be responsible for the differences: First, our experimental approach is sensitive to only one possible reaction channel, no information is available on the loss of a H₂ molecule. Second, at the very high temperatures corresponding to figure 5 in the manuscript the stability of the pyrolysis source might not be sufficient for a long scan over a large energy range, thus a

complete conversion of both precursor and IC₃H₂ intermediate cannot be ensured. This could lead to a contribution of vibrationally hot carbenes that obscure the vibronic structure.



Laser Power

The H-atom signal depends linearly on the excitation laser power at 250 nm.



References

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- ² H. Finkelstein, *Chem. Ber.*, 1910, **43**, 1528.
- ³ A. M. Mebel, W. M. Jackson, A. H. H. Chang, and S. H. Lin, *J. Am. Chem. Soc.*, 1998, **120**, 5751.
- ⁴ R. G. Gilbert and S. C. Smith, 'Theory of Unimolecular and Recombination Reactions', Blackwell Scientific, 1990.
- ⁵ R. A. Seburg, E. V. Patterson, J. F. Stanton, and R. J. McMahon, *J. Am. Chem. Soc.*, 1997, **119**, 5847.
- ⁶ J. F. Stanton, J. T. DePinto, R. A. Seburg, J. A. Hodges, and R. J. McMahon, *J. Am. Chem. Soc.*, 1997, **119**, 429.