

Acetylene Oligomerization with a Bis(imino)pyridine Iron(II) Catalyst

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Cooligomerization of C₂H₂ and C₂D₂: Calculation of Expected Benzene Molecular Weight Distribution

Consideration of the different combinations in which a 1:1 mixture of C₂H₂ and C₂D₂ can be cotrimerized by either mechanism leads to the uncorrected benzene isotopomer ratios shown in Table S1.

Table S1. Benzene isotopomer ratios expected for metallacycle and hydride mechanisms.

Model	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆
Metallacycle	1	0	3	0	3	0	1
Hydride	3	2	9	4	9	2	3

No attempt has been made to incorporate a kinetic isotope effect, as this does not lead to H/D scrambling (new isotopomers) but would simply skew the predicted distribution somewhat. The final results indicate that a KIE is small to absent. A critical correction arises however because of the mass spectral (electron ionisation) fragmentation pattern of benzene. Normal benzene, C₆H₆, gives rise to a significant [M-1]⁺ signal at 77 Da; 24% of the intensity of the [M]⁺ signal at 78 Da. In addition, the [M+1]⁺ signal has an intensity of 8.9% relative to [M]⁺. In benzenes containing both H and D, the probability of H or D loss is proportional to the relative abundance of H and D in the molecule. Additionally, past work¹ has shown that D loss has a reduced probability and should be scaled by 0.67. For example, the isotopomer C₆H₄D₂ would give rise to the following mass spectral signals:

C ₆ H ₄ D ₂	→	[M] ⁺ @ 80 Da	100%
		[M-H] ⁺ @ 79 Da	4/6 × 24% = 16%
		[M-D] ⁺ @ 78 Da	2/6 × 24% × 0.67 = 5.4%
		[M+1] ⁺ @ 81 Da	8.9%

The scaling factor for D loss has been included for completeness, but its effect is very small and leaving this out makes no significant difference to the conclusions, as found previously.¹ The [M+1]

peak can for the most part be accounted for by the natural ^{13}C contribution, so is kept at 8.9% for all isotopomers (ie. assumed to be unaffected by the amount of H or D in the molecule).

Applying these corrections to the raw predicted distributions in Table S1 leads to the corrected distributions in Table S2. The experimental data is included as well, and the distributions are scaled such that the peaks at 82 Da are equal. This data gives rise to Figure 2 in the main article. The experimental mass spectrum for benzene isotopomers obtained in this experiment is shown in Figure S1, in which the spectrum is averaged across the whole GC signal.

Table S2. Corrected model and experimental molecular weight distributions.

	MW	77	78	79	80	81	82	83	84	85
Model										
Metallacycle		0.24	1.16	0.56	3.32	0.51	3.16	0.27	1.00	0.09
Hydride		0.24	1.23	1.28	3.38	1.84	3.16	0.89	1.01	0.09
Experimental		0.36	1.37	0.63	2.67	0.59	3.16	0.29	1.23	0.09

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Spectrum Plot - 1/30/2012 3:54 PM

1 A Scan 408 from c:\brukerws\data\chemistry\dm231111 benzenes.xms

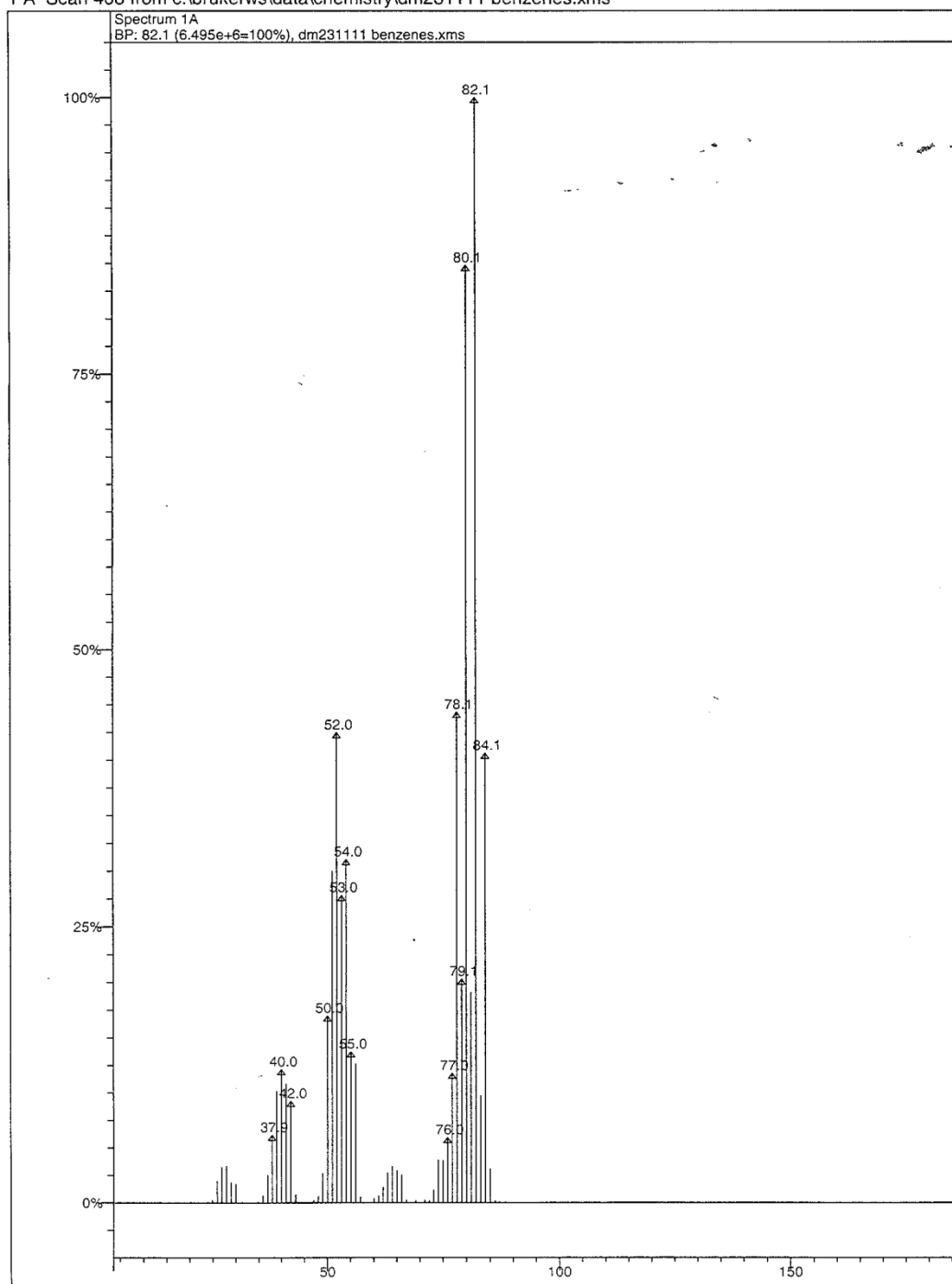


Figure S1. Mass spectrum of benzene isotopomers obtained from co-oligomerization of C_2D_2 and C_2H_2 .

¹ C. H. Patterson and R. M. Lambert, *J. Phys. Chem.* **1988**, 92, 1266.