10.1071/CH17440_AC

Australian Journal of Chemistry

SUPPLEMENTARY MATERIAL

Internal Energy Deposition in Dielectric Barrier Discharge Ionization is Significantly Lower than in Direct Analysis in Real Time Mass Spectrometry

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Table S1. Calculated 4-substituted benzylamine proton affinities (PA) and benzylammonium BDEs (kJ mol^{-1}; 298 K) using CAM-B3LYP/6-311++G(d,p) from the literature.[1]

Substitution	PA	BDE
$-C(CH_3)_3$	930.4	134.5
$-CH_3$	927.7	139.7
-H	919.2	163.4
-F	906.5	152.8
$-CF_3$	883.6	184.5

Table S2. Fitting parameters and uncertainty values for the best fit curves using a sigmoid function for the data in Figures 3 to 7; $f(x) = 1/(1+\exp[(x_0-x)/m])$.

	Figure	x_0	m
Fig. 3	LTP (blue)	126.13±8.24	35.74±8.12
	APCI (brown)	189.62±5.25	24.52±4.67
	DART (red)	251.66±3.07	37.67±1.44
Fig. 4	150ºC (red line)	162.11±6.57	31.89±6.45
	250ºC (dashed red line)	251.66±3.07	37.67±1.44
Fig. 5	Water (blue)	162.12±6.66	31.91±6.54
	Methanol (brown)	169.29±5.38	26.23±4.50
	Acetonitrile (red)	178.02±4.01	21.58±3.94
Fig. 6	25 mm (blue)	151.96±5.21	27.12±4.91
	18 mm (brown)	161.45±5.11	25.43±4.72
	10 mm (red)	166.21±5.97	28.25±5.64
Fig. 7	150ºC (blue)	149.39±5.64	27.83±5.35
	250ºC (brown)	155.19±5.33	27.11±5.02
	350ºC (red)	169.57±5.48	28.55±5.16

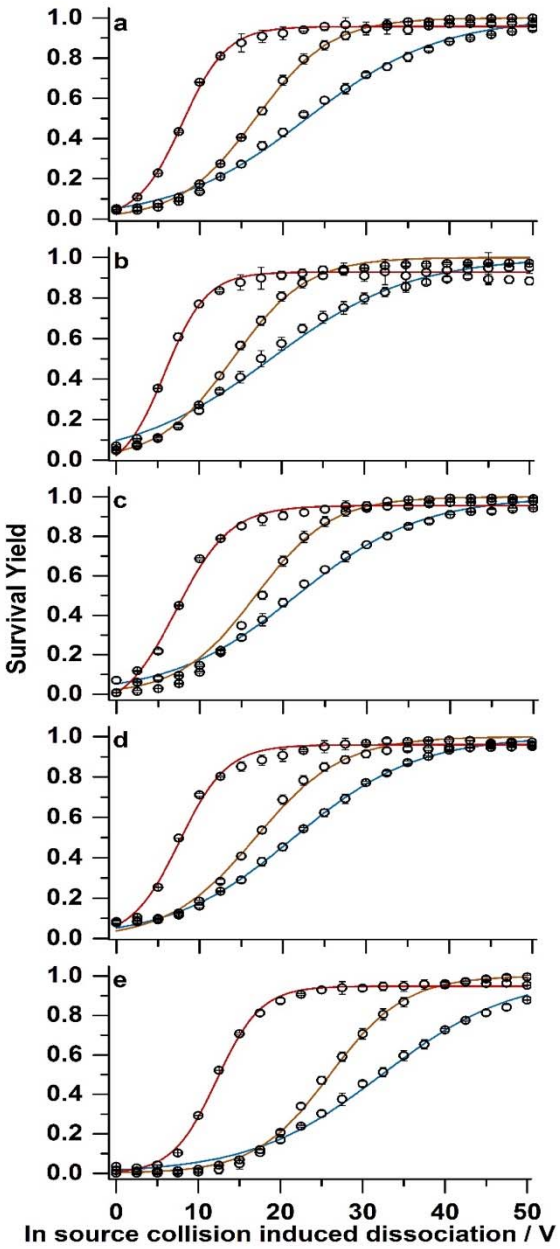

Figure S1. Survival yield vs. in-source collision-induced dissociation (CID) voltage of five benzylammmonium thermometer ions: (a) 4-tertbutylbenzylammonium, (b) methylbenzylammonium, (c) benzylammonium, (d) 4-fluorobenzylammonium, and (e) 4-trifluoromethylbenzylammonium that were formed from an aqueous solution containing the corresponding 4-subtituted benzyl amine (R = –H, $–CH_3$, –F, $–C(CH_3)_3$, and $–CF_3$; 100 µM each) using DART (red), APCI (orange) and DBDI (blue). The capillary entrance to the MS was set to 150 °C.

[1] E. R. Stephens, M. Dumlao, D. Xiao, D. Zhang, W. A. Donald. *Journal of the American Society for Mass Spectrometry*. **2015**;*26*(12):2081-2084.