Excited-State N Atoms Transform Aromatic Hydrocarbons into N-Heterocycles in Low-Temperature Plasmas

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Supporting information for

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Calculating the gas-phase concentration of the aromatic hydrocarbons using the liquid infusion system

A sample of pure (99.9% or higher) hydrocarbon sample was placed in a glass HPLC vial and pressurized with 0.5 bar of N_2 (technical grade) and forced through a capillary (ID: 30 µm, OD: 100 µm, Length: 63 cm) to a heated chamber infused with 3.0 L/min N_2 (technical grade). Assuming laminar flow through the capillary, the volumetric flowrate of the hydrocarbon analyte $Q_{vol,ana}$ was calculated using the Hagen-Poiseuille supp. equation 0:

$$Q_{vol,ana} = \frac{\pi \cdot R^4 \cdot \Delta P}{8 \cdot \mu \cdot L} \tag{1}$$

With the following constants:

R	capillary inner radius	1.5 E-5 m

ΔP	pressure difference between two ends of capillary	5.0 E4 Pa
L	capillary length	6.3 E-1 m
μ	dynamic viscosity of liquid	*x* Pa·s

The dynamic viscosity of the hydrocarbon analyte is given in supplementary table NO. The gas phase concentration of the hydrocarbon analyte was calculated in ppm (mol/mol) in nitrogen.

$$ppm = \frac{Q_{mol,ana}}{Q_{mol,gas}} \times 10^{-6} \tag{2}$$

The mol of analyte $Q_{mol,ana}$ were determined using the calculated volumetric flowrate of the hydrocarbon analyte $Q_{vol,ana}$, liquid density ϱ_{ana} (at 298 K) and molecular weight MW_{ana} (supplementary formula 3). The molecular weights and liquid densities of the hydrocarbon analytes are given in table S1.

$$Q_{mol,ana} = \frac{Q_{vol,ana} \cdot \varrho_{ana}}{MW_{ana}} \tag{3}$$

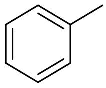
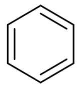
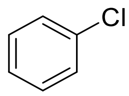
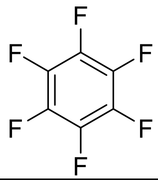
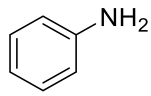
The mol of N_2 gas was determined using the known volumetric flowrate of the gas $Q_{vol,gas}$, gas density (at 400 K) and molecular weight (supplementary formula 4).

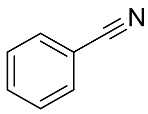
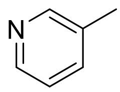
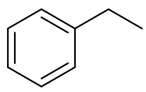
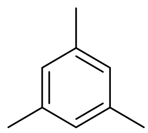
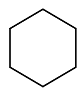
$$Q_{mol,gas} = \frac{Q_{vol,gas} \cdot \varrho_{gas}}{MW_{gas}} \tag{4}$$

The following values were used for the gas calculations:

$Q_{vol,gas}$	volumetric gas flow, determined by mass flow controller setting	5.0 E-5 m^3/s
ϱ_{gas}	density of N_2 gas at 400 K[1]	8.5 E-1 kg/m^3
MW_{gas}	molecular weight of N_2	2.8 E-2 kg/mol

Table S1: Values used for aromatic hydrocarbons, with dynamic viscosities μ in Pa·s from ref[2], molecular weights MW_{ana} in kg/mol and densities ϱ_{ana} in kg/m^3 from ref[3]

	toluene	benzene	chlorobenzene	hexafluoro benzene	aniline
					
μ	5.53E-04	6.03E-04	7.58E-04	9.33E-04	3.50E-03
MW_{ana}	9.21E-02	7.81E-02	1.13E-01	1.86E-02	9.31E-02
ϱ_{ana}	8.63E+02	8.75E+02	1.11E+03	1.61E+03	1.02E+03
IE (eV)	8.8	9.2	9.07	9.90	7.72
Proton affinity (kJ/mol)	784.0	750.4	753.1	648.0	882.5
Gas phase basicity (kJ/mol)	756.3	725.4	724.6	624.4	850.6

	benzonitrile	3-methyl benzene*	ethylbenzene	mesitylene	cyclohexane
					
μ	1.28E-03	8.00E-04	6.29E-04	6.57E-04	8.98E-04
MW_{ana}	1.03E-01	9.31E-02	1.06E-01	1.20E-01	8.42E-02
ϱ_{ana}	1.00E+03	9.57E+02	9.10E+02	8.65E+02	7.78E+02
IE (eV)	9.73	9.0	8.7	8.4	9.9
Proton affinity (kJ/mol)	811.5	943.4	788.0	836.2	686.9
Gas phase basicity (kJ/mol)	780.9	911.6	760.3	808.2	666.9

*3-methylbenzene data not available so averaged values of 2- and 4-methylbenzene were used.

Table S2: Overview of known rate reactions of reactive nitrogen species to form NO^+ and their rate constants[4]

Reaction	Rate constant
$N(^2P) + O(^3\Sigma_g^-) \rightarrow NO^+(X^1\Sigma^+) + O(^1D)$	NA SIFT (ref 6481)[5]
$N^+ + H_2O \rightarrow NO^+ + H_2$	4.20×10^{-9} SIFT
$N^+ + O_2 \rightarrow NO^+ + H_2$	2.36×10^{-10} SIFT
$N_2^+ + O \rightarrow NO^+ + N$	1.30×10^{-10} Eval (ref 9399)
$N_3^+ + O_2 \rightarrow NO^+ + N_2 + O$	2.36×10^{-10} HPMS (ref 8940)
$N_3^+ + CH_3OH \rightarrow NO^+ + N_2 + CH_4$	2.00×10^{-10} SIFT (ref 8012)
$O_2^+ + N \rightarrow NO^+ + O$	1.00×10^{-10} SIFT (ref 9803)

Scheme S1: Electrophilic aromatic substitution

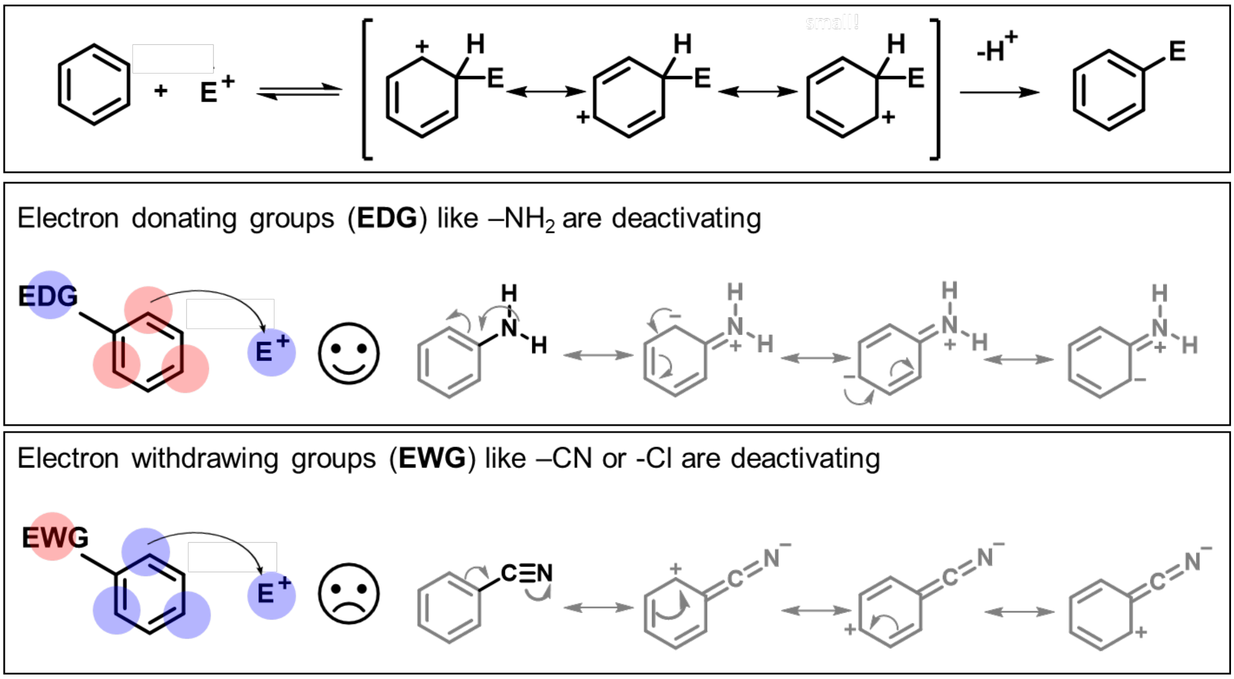


Table S3: Peak listings and suggested composition of aromatic hydrocarbons (5 ppmv) infused through DBDI source into Orbitrap mass spectrometer at high voltage (3.44 kV_{pp})

Benzene	***C_6H_{12}***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
65.0386	1.33E+06	3.81	-0.37	C5 H5	[M-CH]+
78.0463	1.68E+06	4.8	-0.97	C6 H6	[M]·+
80.0494	1.94E+07	55.38	-0.69	C5 H6 N	[M-C+N]+
81.0447	3.32E+06	9.48	-0.91	C4 H5 N2	[M-2C+2N]+
92.0494	3.50E+07	100	-0.65	C6 H6 N	[M+N]+
94.065	9.64E+05	2.76	-1.32	C6 H8 N	[M+NH2]+
104.0494	3.27E+06	9.33	-0.97	C7 H6 N	[M+CN]+
105.0446	5.79E+06	16.56	-0.77	C6 H5 N2	[M-H+2N]+
107.0602	1.67E+06	4.76	-1.45	C6 H7 N2	[M+N2H]+
109.0758	1.29E+06	3.68	-1.79	C6 H9 N2	[M+N2H2]+
119.0603	1.77E+07	50.67	-0.22	C7 H7 N2	[M+CN+NH]+
132.0554	1.40E+06	4.01	-1.94	C7 H6 N3	[M+CN+2N]+
143.0853	2.36E+06	6.76	-1.39	C11 H11	[2M-CH]+
144.0804	1.00E+06	2.86	-2.5	C10 H10 N	[2M-C2H2+N]+
156.0804	1.10E+06	3.14	-2.27	C11 H10 N	[2M-CH2+N]+
170.0964	1.15E+07	32.79	-0.05	C12 H12 N	[2M+N]+
171.0917	6.77E+06	19.35	0.16	C11 H11 N2	[2M-CH+2N]+
183.0915	2.72E+06	7.79	-0.98	C12 H11 N2	[2M-H+2N]+
210.1023	2.19E+06	6.25	-1.33	C13 H12 N3	[2M+CN+2N]+

Toluene	**C_7H_8**				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
80.0494	2.86E+06	5.92	-1.03	C5 H6 N	[M-C2H2+N]+
91.0541	1.20E+06	2.47	-1.3	C7 H7	[M-H]+
94.0651	3.96E+07	81.92	-0.74	C6 H8 N	[M-C+N]+
95.0603	1.84E+06	3.81	-1.07	C5 H7 N2	[M-C2H+2N]+
106.065	4.83E+07	100	-0.78	C7 H8 N	[M+N]+
107.0602	1.09E+06	2.25	-1.47	C6 H7 N2	[M-CH+2N]+
107.0726	1.62E+06	3.36	-2.83	C7 H9 N	[M+NH]+
108.0807	5.99E+06	12.4	-0.95	C7 H10 N	[M+NH2]+
119.0602	2.11E+06	4.36	-1.35	C7 H7 N2	[M-H+2N]+
121.0759	4.34E+06	8.97	-0.91	C7 H9 N2	[M+N2H]+
133.0759	7.33E+06	15.16	-0.58	C8 H9 N2	[M+CN+NH]+
184.1117	1.66E+06	3.43	-2.21	C13 H14 N	[2M-CH2+N]+
198.1276	6.53E+06	13.51	-0.77	C14 H16 N	[2M+N]+
199.1229	7.24E+06	14.99	-0.3	C13 H15 N2	[2M-C2H+2N]+
211.1228	4.73E+06	9.79	-0.81	C14 H15 N2	[2M-H+2N]+
213.1381	1.46E+06	3.03	-2.42	C14 H17 N2	[2M+N2H]+
226.1333	1.05E+06	2.16	-2.43	C14 H16 N3	[2M+N3]+
238.1335	1.49E+06	3.09	-1.57	C15 H16 N3	[2M+CN+N2]+

Ethylbenzene	***C_8H_{10}***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion

80.0494	1.66E+06	2.98	-1.02	C5 H6 N	[M-C3H4+N]+
91.0542	2.10E+06	3.78	-0.72	C7 H7	[M-CH3]+
94.065	1.55E+06	2.78	-0.99	C6 H8 N	[M-C2H2+N]+
105.0697	1.56E+06	2.79	-1.41	C8 H9	[M-H]+
106.0651	1.58E+07	28.34	-0.31	C7 H8 N	[M-CH2+N]+
108.0807	3.79E+07	68.02	-0.43	C7 H10 N	[M-C+N]+
119.0603	2.18E+06	3.91	-0.77	C7 H7 N2	[M-CH3+2N]+
120.0808	5.57E+07	100	-0.14	C8 H10 N	[M+N]+
121.0883	3.00E+06	5.38	-2.17	C8 H11 N	[M+H+N]+
122.0964	6.72E+06	12.06	-0.14	C8 H12 N	[M+NH2]+
135.0916	5.29E+06	9.5	-0.46	C8 H11 N2	[M+N2H]+
147.0917	5.95E+06	10.68	-0.14	C9 H11 N2	[M+CN+NH]+
198.1273	1.34E+06	2.4	-2.34	C14 H16 N	[2M-C2H4+N]+
225.1386	3.54E+06	6.36	-0.3	C15 H17 N2	[2M-CH3+2N]+
226.1589	4.24E+06	7.6	-0.57	C16 H20 N	[2M+N]+
227.1544	6.00E+06	10.77	0.37	C15 H19 N2	[2M-CH+2N]+
239.1539	1.44E+06	2.58	-1.42	C16 H19 N2	[2M-H+2N]+
241.1695	1.19E+06	2.14	-1.57	C16 H21 N2	[2M+N2H]+
Chlorobenzene	***C_6H_5Cl***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
80.0494	8.82E+06	12.12	-0.6	C5 H6 N	[M-CCl+NH]+
92.0494	2.03E+07	27.96	-0.36	C6 H6 N	[M-Cl+NH]+
105.0447	3.72E+07	51.13	-0.52	C6 H5 N2	[M-Cl+2N]+
107.0602	3.49E+06	4.79	-1.51	C6 H7 N2	[M-Cl+N2H2]+
114.0104	9.19E+06	12.62	-0.87	C5 H5 N Cl	[M-C+N]+
126.0105	7.28E+07	100	-0.31	C6 H5 N Cl	[M+N]+
128.0075	2.21E+07	30.37	-1.49	C6 H5 N 37Cl	[M+N]+
141.0211	3.51E+06	4.83	-2	C6 H6 N2 Cl	[M+N2H]+
153.0213	1.31E+07	17.95	-0.53	C7 H6 N2 Cl	[M+CN+NH]+
156.0805	3.02E+06	4.15	-2.02	C11 H10 N	[2M-CCl+N]+
181.076	2.11E+07	29	-0.29	C12 H9 N2	[2M-HCl2+2N]+
190.0414	4.50E+06	6.18	-0.7	C11 H9 N Cl	[2M-CHCl+N]+
202.0413	3.04E+06	4.17	-1.7	C12 H9 N Cl	[2M-HCl+N]+
203.049	2.29E+06	3.14	-2.6	C12 H10 N Cl	[2M-Cl+N]+
217.0524	7.79E+06	10.7	-0.05	C12 H10 N2 Cl	[2M-Cl+2N]+
229.0524	5.35E+06	7.35	-0.32	C13 H10 N2 Cl	[2M-Cl+CN+N]+
238.0183	6.19E+06	8.5	-0.88	C12 H10 N Cl2	[2M+N]+
Aniline	***C_6H_7N***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
80.0493	6.80E+06	16.59	-1.82	C5 H6 N	[M-CH]+
82.0649	1.25E+06	3.04	-2.47	C5 H8 N	[M-C+H]+
93.0572	1.55E+07	37.81	-1.47	C6 H7 N	[M]+
94.065	2.11E+07	51.51	-1.72	C6 H8 N	[M+H]+
95.0602	2.20E+07	53.62	-1.52	C5 H7 N2	[M-C+N]+
96.0554	1.28E+06	3.13	-2.35	C4 H6 N3	[M-C3H+2N]+
106.0648	1.34E+06	3.28	-2.69	C7 H8 N	[M+CH]+
107.0602	4.10E+07	100	-1.76	C6 H7 N2	[M+N]+

108.0679	4.51E+06	11.01	-2.63	C6 H8 N2	[M+NH]+
109.0758	5.14E+06	12.55	-1.98	C6 H9 N2	[M+NH2]+
122.0711	4.36E+06	10.64	-1.67	C6 H8 N3	[M+N2H]+
134.071	3.47E+06	8.48	-2.11	C7 H8 N3	[M+CN+NH]+
183.0913	4.73E+06	11.54	-1.84	C12 H11 N2	[2M-3H]+
184.0992	1.05E+07	25.66	-1.53	C12 H12 N2	[2M-2H]+
185.107	1.85E+07	45.27	-1.76	C12 H13 N2	[2M-H]+
198.102	1.66E+06	4.06	-2.19	C12 H12 N3	[2M-2H+N]+
199.1098	1.80E+06	4.38	-3.12	C12 H13 N3	[2M-H+N]+
200.1176	2.22E+06	5.41	-2.88	C12 H14 N3	[2M+N]+
Benzonitrile	***C_7H_5N***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
80.0493	3.67E+06	3.23	-1.71	C5 H6 N	[M-2C+H]+
93.0446	2.31E+06	2.03	-1.87	C5 H5 N2	[M-2C+N]+
103.0415	8.61E+06	7.57	-1.28	C7 H5 N	[M]+
104.0493	1.14E+08	100	-1.64	C7 H6 N	[M+H]+
105.0446	2.58E+07	22.72	-0.86	C6 H5 N2	[M-C+N]+
117.0446	5.61E+07	49.29	-1.19	C7 H5 N2	[M+N]+
118.0523	7.65E+06	6.73	-2.11	C7 H6 N2	[M+NH]+
119.0601	4.87E+06	4.28	-1.94	C7 H7 N2	[M+NH2]+
132.0553	2.40E+06	2.11	-2.6	C7 H6 N3	[M+N2H]+
134.0711	1.61E+07	14.12	-1.16	C7 H8 N3	[M+N2H3]+
144.0552	2.07E+06	1.82	-3.23	C8 H6 N3	[M+CN+NH]+
193.0757	1.04E+07	9.13	-1.65	C13 H9 N2	[2M-CH]+
205.0755	5.00E+06	4.39	-2.36	C14 H9 N2	[2M-H]+
219.0784	1.98E+06	1.74	-3.08	C14 H9 N3	[2M-H+N]+
220.0867	2.33E+07	20.5	-1.05	C14 H10 N3	[2M+N]+
221.0819	6.17E+06	5.42	-1.27	C13 H9 N4	[2M-CH+2N]+
233.0816	2.38E+06	2.1	-2.55	C14 H9 N4	[2M-H+2N]+
Mesitylene	***C_9H_{12}***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
93.0699	3.99E+06	1.85	0.56	C7 H9	[M-C2H3]+
108.0809	2.76E+07	12.83	1.03	C7 H10 N	[M-C2H2+N]+
120.0934	4.15E+06	1.93	0.06	C9 H12	[M]+
121.1012	8.38E+06	3.9	0.59	C9 H13	[M+H]+
122.0966	5.91E+07	27.47	1.37	C8 H12 N	[M-C+N]+
133.076	1.62E+06	0.75	-0.54	C8 H9 N2	[M-CH3+N2]+
134.0966	2.15E+08	100	1.22	C9 H12 N	[M+N]+
136.1122	1.39E+07	6.46	1.23	C9 H14 N	[M+NH2]+
147.0914	1.38E+06	0.64	-1.62	C9 H11 N2	[M-H+N2]+
149.1075	1.30E+07	6.05	1.16	C9 H13 N2	[M+N2H]+
161.1073	3.16E+06	1.47	-0.35	C10 H13 N2	[M+CN+NH]+
241.1697	2.02E+06	0.94	-0.8	C16 H21 N2	[2M-C2H3+2N]+
Hexafluorobenzene	***C_6F_6***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
170.0022	1.97E+06	0.57	-0.69	C5 H N F5	[M-C+NH]+
183.0102	6.49E+06	1.88	0.01	C6 H2 N F5	[M-F+NH2]+

185.9901	1.24E+08	35.89	1.13	C6 F6	[M]+
199.9932	3.45E+08	100	1.23	C6 N F6	[M+N]+
213.9957	8.65E+05	0.25	-1.26	C6 N2 F6	[M+N+2N]+
218.0036	5.22E+06	1.52	0.51	C6 H2 O N F6	[M+H2ON]+
Cyclohexane	***C_6H_{12}***				
m/z	Intensity	Relative	Delta (ppm)	Composition	Suggestion
55.0542	1.86E+06	12.08	-0.38	C4 H7	
56.0495	1.97E+06	12.78	-0.34	C3 H6 N	
68.0494	6.09E+05	3.95	-1.12	C4 H6 N	
69.0698	5.40E+05	3.5	-1.19	C5 H9	
70.0399	9.02E+05	5.85	-1	C2 H4 N3	
70.0651	1.61E+06	10.42	-1.01	C4 H8 N	
81.0698	2.38E+06	15.46	-1.45	C6 H9	[M-3H]+
83.0854	1.38E+07	89.52	-1.41	C6H11	[M-H]+
84.0806	9.83E+05	6.38	-1.71	C5 H10 N	[M-CH2+N]+
96.0806	2.89E+06	18.73	-1.35	C6 H10 N	[M-2H+N]+
98.0963	1.54E+07	100	-1.37	C6 H12 N	[M+N]+
100.0755	1.40E+06	9.06	-1.68	C5 H10 O N	[M-CH2+NO]+
110.0962	1.22E+06	7.89	-1.96	C7 H12 N	[M+CN]+
111.0914	6.87E+05	4.46	-2.39	C6 H11 N2	[M-H+2N]+
112.1118	7.30E+05	4.74	-2.46	C7 H14 N	[M+CNH2]+
125.1071	1.29E+06	8.37	-1.79	C7 H13 N2	[M+CN2H]+
180.1744	1.88E+06	12.22	-1.53	C12 H22 N	[2M-2H+N]+

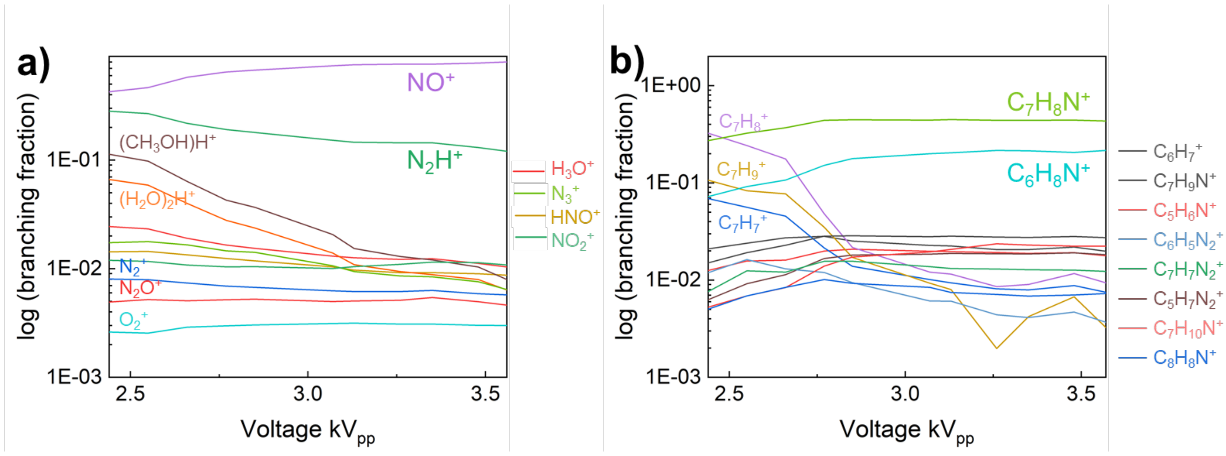


Figure S1: Variation in the branching fraction (logarithmic scale) of **a)** reactive nitrogen species in the low temperature plasma discharge alone and **b)** toluene product ions with increasing applied voltage (kVpp)

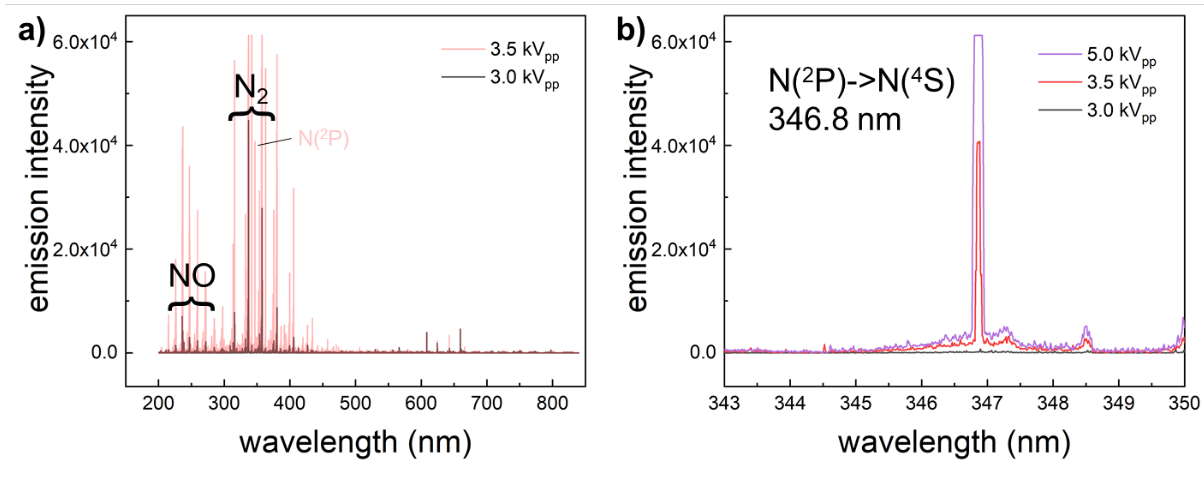


Figure S2: Optical emission spectra (Echelle Spectra Analyzer ESA 3000 EV, LLA Instruments GmbH, Berlin-Adlershof, Germany) of the DBDI source operated with nitrogen gas with a sine modulated high voltage (11 kHz, 3-5 kV_{pp}). **a)** Full spectrum at 3.0 (black) and 3.5 kV_{pp} (red), and zoom in on **b)** the $N(^2P)$->$N(^4S)$ transition at 346.8 nm, which is absent at 3.0 kV_{pp} (black), present at 3.5 kV_{pp} (red), and elevated with increasing voltage of 5.0 kV_{pp} (purple).

Table S4: Reactions and rate constants[4] used for modelling the reactive nitrogen species in the FALP-TOF

Type	Reaction	Reference type	Modelled Rate Constant
association	$He^{+}+He+He \rightarrow He_2^{+}+He+He$	MS	1.00E-27
charge transfer	$He_2^{+}+N_2 \rightarrow N_2^{+}+He+He$	eval	1.20E-09
penning ionization	$He^{*}+N_2 \rightarrow N_2^{+}+e^{-}+He$		7.00E-11
association	$He^{+}+N_2 \rightarrow N_2^{+}+He$	ICR	5.20E-10
charge transfer	$He^{+}+N_2 \rightarrow N^{+}+N$	ICR	7.80E-10
association	$N^{+}+N_2+He \rightarrow N_3^{+}+He$	HPMS	1.15E-29
association	$N_2^{+}+N_2+He \rightarrow N_4^{+}+He$	MS	8.00E-30
charge transfer	$N_3^{+}+N \rightarrow N_2^{+}+N_2$		8.00E-10
disproportionation	$N_3^{+}+N^{*} \rightarrow N_2^{+}+N_2$		8.00E-10
neutralization	$N_3^{+}+e^{-} \rightarrow N_2+N^{*}$		5.00E-07
neutralization	$N_4^{+}+e^{-} \rightarrow N_3+N^{*}$		1.00E-06
neutralization	$N_2^{+}+e^{-} \rightarrow N+N^{*}$	CRYING[6]	1.10E-7
neutralization	$N_2^{+}+e^{-} \rightarrow N^{*}+N^{*}$	CRYING[6]	1.10E-7
charge transfer	$N_4^{+}+N \rightarrow N_3^{+}+N_2$	NA[7,8]	7.50E-10

Table S5: Reactions and rate constants used for modelling the toluene product ions in the FALP-TOF

Type	Reaction	Reference type	Modelled Rate Constant
charge transfer	$C_7H_8 + N^+ \rightarrow C_7H_7^+ + N_2$	SIFT	1.80E-9
charge transfer	$C_7H_8 + N_2^+ \rightarrow C_7H_7^+$ + neutrals	measured	1.80E-9
association	$C_7H_8 + C_7H_7^+ \rightarrow C_8H_9^+$		2.00E-11
charge transfer	$C_7H_8 + N_3^+ + \rightarrow C_7H_8^+ + N + N_2$	measured	1.71E-09
charge transfer	$C_7H_8 + N_4^+ \rightarrow C_7H_8^+ + 2\ N_2$	measured	1.62E-9
addition	$C_7H_8 + N_4^+ \rightarrow C_7H_8N^+ + N_3$	measured	4.00E-11
association	$C_7H_8^+ + N \rightarrow C_7H_8N^+$		9.00E-11
neutralization	$C_7H_8^+ + e^- \rightarrow C_7H_8$		6.00E-7
neutralization	$C_7H_7^+ + e^- \rightarrow C_7H_7$		6.00E-7
neutralization	$C_7H_9^+ + e^- \rightarrow C_7H_9$	HPMS	6.00E-7
neutralization	$C_6H_8N^+ + e^- \rightarrow$ neutrals		6.00E-7
neutralization	$C_7H_8N^+ + e^- \rightarrow$ neutrals		3.00E-7
neutralization	$HCNH^+ + e^- \rightarrow$ neutrals		2.00E-7
proton transfer	$C_7H_7^+ + C_7H_8 \rightarrow C_7H_9^+$	MS	8.10E-12
replacement	$C_7H_8 + N^* \rightarrow C_6H_8N^+ + C$		5.32E-11
addition	$C_7H_8 + N^* \rightarrow C_7H_8N^+$		2.00E-10
fragmentation	$C_7H_8^+ + N \rightarrow C_6H_6 + HCNH^+$		1.01E-10
neutralization	$C_7H_9^+ + C_7H_8 \rightarrow C_7H_7^+$ + neutrals	MS	2.50E-11

Table S6: Zero-point corrected energies of the indicated product channels relative to reactants in eV. Energies for channels which are formally spin-forbidden are shown in brackets

			N-Addition		N-Replacement	
Reactants		Co-product	^{1}c-$C_6H_5(CHNH_2)^+$	^{3}c-$C_6H_5(CHNH_2)^+$	^{3}C + $^{1}C_6NH_8^+$	^{1}C + $^{1}C_6NH_8^+$
N (^{4}S)	$^2C_7H_8^+$	-	*{-6.16}*	-3.64	0.36	*{1.62}*
N (^{2}D)	$^2C_7H_8^+$	-	-8.55	-6.03	-2.02	-0.76
N (^{2}P)	$^2C_7H_8^+$	-	-9.74	-7.22	-3.22	-1.95
N^+ (^{3}P)	$^1C_7H_8$	-	*{-12.25}*	-9.73	-5.73	*{-4.47}*
$^2N_2^+$	$^1C_7H_8$	^{4}N	*{-3.83}*	-1.31	2.69	*{3.95}*
$^1N_3^+$	$^1C_7H_8$	$^1N_2$	-9.71	*{-7.19}*	*{-3.19}*	-1.93
$^2N_4^+$	$^1C_7H_8$	$^2N_3$	-1.99	0.53	4.53	5.80

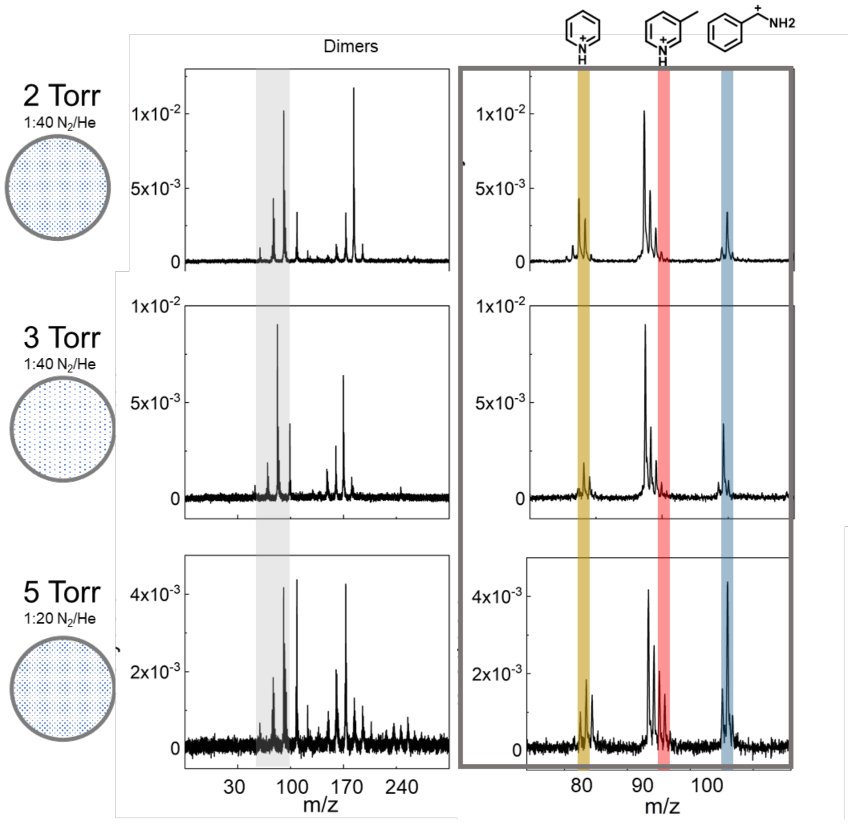
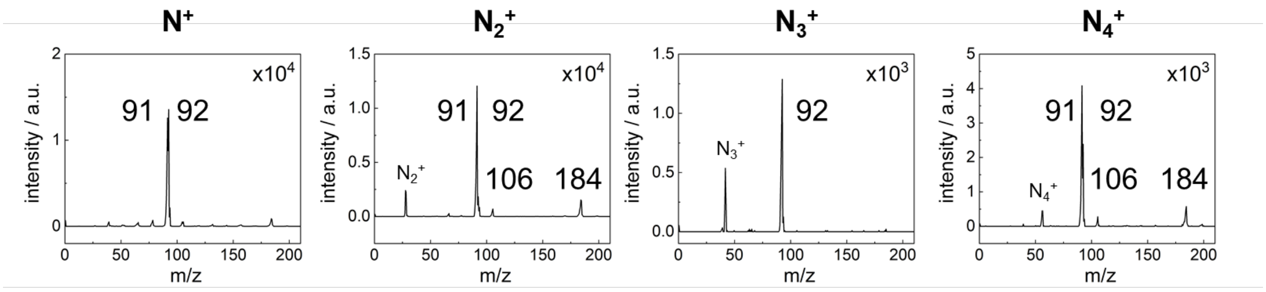


Figure S3: Mass spectra of nitrogen-plasma products of toluene in the FALP-TOF with varying pressure and flow conditions. As the pressure inside the flow tube and microwave cavity is increased from 2 to 5 Torr, there is a decrease in the intensity of the product ions overall, but an increase in the ratio of the N-addition (blue), N-replacement (red) products, and the pyridine fragment (yellow) relative to the radical cation/tropylium ion at 91 and 92 m/z, respectively. The decrease in intensity is due to lower diffusion through the flow tube to the detector, the increase in the nitrogen product ions is likely due to an increase in reaction time.



2.24×10^{-9} (lit)	**2.24×10^{-9}**	**1.96×10^{-9}**	**1.81×10^{-9}**

m/z	%	m/z	%	m/z	%	m/z	%
65	1	66	1				
78	2						
90	8						
91	**34**	**91**	**34**	**91**	**23**	**91**	**45**
92	**39**	**92**	**47**	**92**	**57**	**92**	**27**
93	6	93	5				
106	1	106	4			106	3
184	3	184	11			184	1

Figure S4: Spectra of the toluene products formed with selected ions N^+, N_2^+, N_3^+, and N_4^+, the overall rate constant of the reaction, and the relative quantities of the m/z of the products detected.

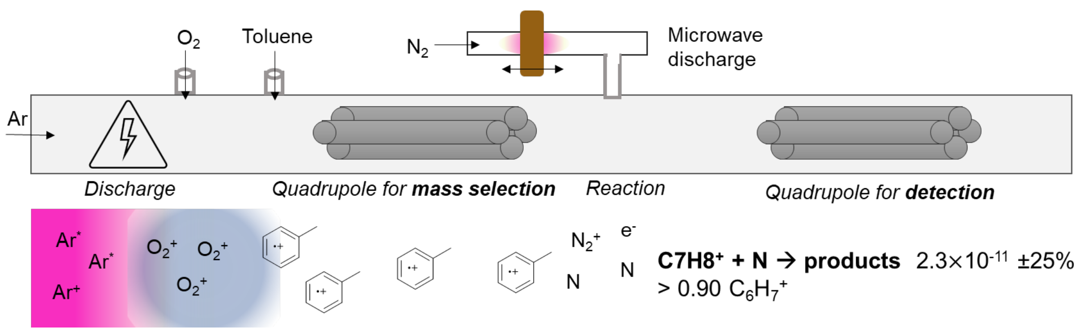


Figure S5: Schematic diagram of the modified SIFT experiment to test the reaction of nitrogen atoms with toluene radical cations. The major product detected was protonated benzene with a rate constant of 2.3×10^{-11}.

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