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Supplementary Information for

Reaction rates and product formation during advanced oxidation of ionic liquid cations by UV/peroxide, UV/persulfate, and UV/chlorine

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Contents

S1 Chemicals	2
S2 Control experiments, quenching, and quantifying free chlorine	3
S3 Product identification procedure	5
S4 Kinetic Results	6
S5 Tentatively identified transformation products	10
S6 References	18

S1 Chemicals

Eight ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium chloride (C₂-imidazolium, 99%, Acros Organics), 1-butyl-3-methylimidazolium chloride (C₄-imidazolium, 99%, Acros Organics), 1-hexyl-3-methylimidazolium chloride (C₆-imidazolium, 98%, Sigma-Aldrich), 1-octyl-3-methylimidazolium chloride (C₈-imidazolium, 99%, Acros Organics), 1-decyl-3-methylimidazolium chloride (C₁₀-imidazolium, 98%, Sigma-Aldrich), N-butylpyridinium chloride (C_4 -pyridinium, 98%, Alfa Aesar), 1butyl-1-methylpyrrolidinium chloride (C₄-pyrrolidinium, 99%, TCI America), and 1-butyl-1-methylpiperidinium bromide (C_4 -piperidinium, 99%, TCI America), were used as received. Hydrogen peroxide (H₂O₂, 30%, Fisher Scientific), potassium persulfate (K₂S₂O₈, 99.5%, Fisher Scientific), sodium hypochlorite (NaClO, 13% w/v, Fisher Scientific), benzoic acid (99.5%, Sigma-Aldrich), nitrobenzene (99%, Sigma-Aldrich), and tert-butyl alcohol (t-BuOH, 99%, Sigma-Aldrich) were used in irradiation experiments. Sodium phosphate monobasic monohydrate ($NaH_2PO_4 \cdot H_2O_1$) 98%, Fisher Scientific), sodium hydroxide (NaOH, 98%, Macron), and hydrochloric acid (HCl, TraceMetal Grade, Fisher Scientific) were used for preparing buffers. Sodium sulfite (Na_2SO_3) anhydrous, 99%, Mallinckrodt), potassium iodide (KI, 99%, Fisher Scientific) and 2,2'-azino-bis(3ethylbenzothiazoline-6-sulphonic acid) (ABTS, 98%, TCI America) were used for quenching and quantifying free chlorine (see section S2). All stock solutions and buffers were prepared in ultrapure water (18.2 MΩ·cm, EMD Millipore Corp.). Methanol (99.9% HPLC grade, Fisher Scientific). ultrapure water, ammonium acetate (97%, Macron), and glacial acetic acid (99%, BDH) were used for HPLC analysis. Methanol (Optima LC/MS grade, Fisher Scientific), ultrapure water, and ammonium acetate (99%, Sigma-Aldrich) were used for LC/MS analysis. Acetonitrile, water, formic acid, and ammonium acetate (all Optima LC/MS grade, Fisher Scientific) were used for LC/HRAM-MS/MS analysis.

S2 Control experiments, quenching, and quantifying free chlorine

Control experiments in the absence of light were conducted with C_4 -imidazolium, C_{10} -imidazolium, and C_4 -pyridinium in 15 mL buffer solutions (10 mM NaH₂PO₄, pH 7.0) with and without 370 μ M NaClO (281 μ M HClO and 89 μ M ClO⁻). Sub-samples of 900 μ L were removed daily over a time period of 7 days and immediately mixed with 100 μ L Na₂SO₃ (20 g L⁻¹) to quench free chlorine. Concentrations of IL cations were analyzed simultaneously in all samples at the end of the experiment. The apparent increase in C_{10} -imidazolium concentrations over time in experiments with and without NaClO was probably due to a slow reaction of C_{10} -imidazolium with Na₂SO₃ leading to a decrease in concentration between sampling and analysis time (see right panel in Fig. S2). The fact that similar concentration trends were observed in experiments with and without NaClO indicates no significant reactivity of C_{10} -imidazolium towards free chlorine. The concentrations of the other two IL cations were not significantly influenced by the presence of Na₂SO₃ (see Figs. S2-S1).

Total free chlorine concentrations in the above mentioned control experiments as well as in one UV/chlorine experiment with C_4 -imidazolium were quantified with a colorimetric assay adapted from Pinkernell *et al.*¹ (see Figs. S2-S1 for results). Depending on expected free chlorine concentrations, samples of 0.1 – 1.5 mL were diluted in buffer solution (10 mM NaH₂PO₄, pH 7.0) to make up a total volume of 2.43 mL. These dilute samples were mixed in 1-cm quartz cuvettes with 360 μ L phosphate buffer (0.5 M, pH 6.1), 120 μ L ABTS (1 g L⁻¹), and 90 μ L potassium iodide (0.2 mM). Absorption at 405 nm was measured with a Shimadzu UV-1601PC spectrophotometer after 5 min and corrected for base-line absorption of ABTS in samples without free chlorine. Total free chlorine concentrations were calculated assuming the formation of two molecules of ABTS-radicals (ABTS^{-•}) per molecule of HClO or ClO⁻ and a molar extinction coefficient of 28500 M⁻¹ cm⁻¹ for ABTS^{-•}.¹



Fig. S1 Concentration trends of free chlorine (HCIO) during UV-irradiation (left panel) as well as C_{10} -imidazolium and HCIO during control experiments in the absence of light (right panel). Blue circles represent free chlorine concentrations, green triangles are C_{10} -imidazolium concentrations during HCIO-free controls, and red squares show concentrations of C_{10} -imidazolium in the presence of HCIO. The solid line indicates a pseudo-first order kinetic fit.



Fig. S2 Concentration trends of free chlorine (HCIO), C_4 -imidazolium (left panel) and C_4 -pyridinium (right panel) during control experiments in the absence of light. Green triangles indicate IL cation concentrations during HCIO-free controls, red squares show concentrations of IL cations in the presence of HCIO, and blue circles are free chlorine concentrations. Concentration trends of HCIO were identical in the absence of IL cations.

S3 Product identification procedure

Molecular formulas of potential transformation products were obtained by analyzing LC-HRAM-MS/MS raw data with Compound Discoverer 1.0 (Thermo Fisher Scientific) according to a workflow published by Gulde et al.². This work-flow automatically extracts and filters peaks/features and assigns molecular formulas according to the measured accurate masses with a mass tolerance of 5 ppm. Both the suspect-screening and non-target part of the work-flow were used, however, MS/MS data were not evaluated with Compound Discoverer because permanently charged compounds are not handled well with this software. For the suspect screening, the work-flow looks for transformation products that correspond to specific changes in accurate mass (molecular structure) compared to the parent compound. We included molecular changes corresponding to oxidation/hydroxylation (+O), reduction (+2H), hydration $(+H_2O)$, desaturation (-2H), dehydration $(-H_2O)$, chlorination (+Cl, -H), and any combinations thereof. The resulting list of potential transformation products was manually refined by eliminating features with maximum peaks areas below 15000 and features with peak areas not exceeding corresponding peak areas in blank sample by at least 5 fold. In addition, the peak shapes of the remaining product peaks were manually checked in Thermo Xcalibur 3.0 (Thermo Fisher Scientific). Potential transformation products without reasonable peak shape and retention time (compared to parent compound considering molecular changes) were eliminated from further consideration. All the remaining potential transformation products are listed in Tables S2-S6.

Potential transformation products were assigned confidence levels according to Schymanski et al.³ based on (i) matches between observed and predicted isotopic pattern and (ii) comparison between observed and predicted MS/MS fragments. Isotopic patterns were generated for all potential transformation products listed in Tables S2-S6 with enviPat Web 2.2⁴ and compared to observed isotopic pattern in full scan data with Xcalibur. For all potential transformation products listed in Tables S2-S6 with recorded MS/MS spectra, in silico MS/MS fragment prediction was performed with MassFrontier 7.0 (Thermo Fisher Scientific) for all reasonable structural isomers of a molecular formula. Confidence Level 5 was assigned to transformation products (accurate mass only). that showed no match between observed and predicted isotopic pattern. Level 4 was assigned to transformation products (molecular formula) with matching isotopic pattern but without available or usable MS/MS spectra. Level 3 was assigned to transformation products (tentative structures) with MS/MS spectra that could be compared to MS/MS fragments predicted by MassFrontier. Structures shown in Tables S2-S6 correspond to the structure(s) that had the largest number of matches between observed and predicted fragments. Due to the lack of reference MS/MS spectra in publicly available databases and the fact that for many of the structural isomers the set of predicted fragments were very similar, none of the transformation products were assigned to Level 2 (probable structure supported by library spectrum match or unambiguous diagnostic evidence).

S4 Kinetic Results

Table S1 Steady-state concentrations (\pm 95%-confidence intervals) of hydroxyl radicals calculated based on pseudo-first order reaction kinetics of nitrobenzene experiments during UV/peroxide, UV/persulfate, and UV/chlorine experiments shown in Fig. 1 of the main manuscript and below. ^a

reactant (Figure)	Hydroxyl radical steady-state concentration (10^{-14} M)				
	UV/peroxide	UV/persulfate	UV/chlorine		
C_4 -imidazolium (Fig. 1)	22 ± 7.9	25 ± 5.4	76 ± 15		
C_4 -pyridinium (Fig. 1)	14 ± 2.1	21 ± 4.9	76 ± 16		
C_2 -imidazolium (Fig. S6)	11 ± 2.5		21 ± 4.9		
C_6 -imidazolium (Fig. S6)	14 ± 2.1		4.8 ± 2.5		
C_8 -imidazolium (Fig. S7)	8.6 ± 3.1		4.2 ± 1.4		
C_{10} -imidazolium (Fig. S7)	8.3 ± 1.6	16 ± 3.0	63 ± 26		
C_4 -pyrrolidinium (Fig. S8)			29 ± 12		
C_4 -piperidinium (Fig. S8)			28 ± 9.3		
benzoate (Fig. S5)	63 ± 26	16 ± 3.0	12 ± 1.9		
nitrobenzene (Fig. S5)	63 ± 26	16 ± 3.0	12 ± 1.9		

 $^{\rm a}$ Hydroxyl radical steady-state concentrations in UV/persulfate experiments with tert-butyl alcohol were $\leq 1.8\cdot 10^{-14}$ M



Fig. S3 Log-normalized concentration trends of C_4 -imidazolium during direct photolysis with a 220 nm (red circles) and a 280 nm (green triangles) cut-off filter and indirect photolysis with 1 mM H_2O_2 (purple squares). The solid lines represent linear regressions with corresponding pseudo-first order rate constants shown in brackets in the legend.



Fig. S4 Log-normalized concentration trends of C_4 -pyridinium during irradiation experiments with either a 220 nm (left panel) or a 280 nm (right panel) cut-off filter. Red circles and green triangles show concentrations during direct photolysis controls, blue diamonds and purple squares show concentrations during indirect photolysis experiments with 1 mM H_2O_2 , and solid lines represent linear regressions with corresponding pseudo-first order rate constants shown in brackets in the legend.



Fig. S5 Normalized concentration trends of benzoate (BZA, left panel, $c_0=10 \ \mu$ M) and nitrobenzene (NB, right panel, $c_0=10 \ \mu$ M) during UV only controls (blue squares), in dark controls with $K_2S_2O_8$ (grey triangles, BZA only), in UV/peroxide experiments (green diamonds), in UV/persulfate experiments (purple pentagons), in UV/persulfate experiments with *t*-BuOH (red circles), and in UV/chlorine experiments (yellow starts). Solid lines show fits to pseudo-first order kinetics.



Fig. S6 Normalized concentration trends of C₂-imidazolium (left panel, $c_0=20 \ \mu$ M) and C₆-imidazolium (right panel, $c_0=10 \ \mu$ M) during UV only controls (blue squares), in dark controls with K₂S₂O₈ (grey triangles), in UV/peroxide experiments (green diamonds), in UV/persulfate experiments with *t*-BuOH (red circles), and in UV/chlorine experiments (yellow starts). Solid lines show fits to pseudo-first order kinetics.



Fig. S7 Normalized concentration trends of C_8 -imidazolium (left panel, $c_0=10 \ \mu$ M) and C_{10} -imidazolium (right panel, $c_0=10 \ \mu$ M) during UV only controls (blue squares), in dark controls with $K_2S_2O_8$ (grey triangles), in UV/peroxide experiments (green diamonds), in UV/persulfate experiments (purple pentagons, C_{10} -imidazolium only), in UV/persulfate experiments with *t*-BuOH (red circles), and in UV/chlorine experiments (yellow starts). Solid lines show fits to pseudo-first order kinetics.



Fig. S8 Normalized concentration trends of C₄-pyrrolidinium (left panel, $c_0=20 \ \mu$ M) and C₄-piperidinium (right panel, $c_0=20 \ \mu$ M) during UV only controls (blue squares), in UV/persulfate experiments with *t*-BuOH (red circles), and in UV/chlorine experiments (yellow starts). Solid lines show fits to pseudo-first order kinetics.



Fig. S9 The left panel shows log-normalized concentrations trends of C_4 -imidazolium during UV/chlorine experiments in pH 7.0 phosphate buffer (blue squares), UV control experiments (> 280 nm) in pH 7.0 phosphate buffer (red circles), UV/peroxide experiments in pH 10 carbonate buffer (green diamonds), and UV/chlorine experiments in pH 10 carbonate buffer (green diamonds), and UV/chlorine experiments order rate constants shown in brackets in the legend. The right panel shows log-normalized concentrations of C_4 -and C_{10} -imidazolium vs. log-normalized concentrations of nitrobenzene during various UV/chlorine experiments. Red squares and triangles represent UV/chlorine experiments in pH 7.0 phosphate buffer, blue circles represent a UV/chlorine experiment in pH 8.2 phosphate buffer, and purple diamonds represent a UV/chlorine experiment in pH 7.0 phosphate buffer with 1 mM *tert*-butyl alcohol (t-BuOH). Solid lines represent linear regressions.

S5 Tentatively identified transformation products

Table S2 List of tentatively identified transformation products of C_4 -imidazolium (parent compound information given in first line) with confidence levels according to Schymanski *et al.*³.

accurate mass	molecular formula	RT (min)	$\frac{\mathbf{detected}}{\mathbf{in}^{\mathrm{a}}}$	confidence level	proposed structure
139.1227	$\mathrm{C_8H_{15}N_2}$	24.2	A, B, C	Level 1	
205.0737	$\mathrm{C_8H_{14}N_2O_2Cl}$	25.7	C^{\pm}	Level 3	
173.0837	$\mathrm{C_8H_{14}N_2Cl}$	23.1	C^{\pm}	Level 3	
171.1125	$\mathrm{C_8H_{15}N_2O_2}$	23.0	A^+	Level 3	
		24.5	A^+, B^{\pm}	Level 3	N N N N
155.1176	$\mathrm{C_8H_{15}N_2O}$	26.9	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^\pm$	Level 3	N-T []
		30.0	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^\pm$	Level 3	№ + он
		31.3	A^+, C^{\pm}	Level 3	
153.1019	$\mathrm{C_8H_{13}N_2O}$	24.7	A^+, B^{\pm}	Level 4	
		07.4	A+ D+ C+	I 10	
		27.4	$A^{\perp}, B^{\perp}, C^{\pm}$	Level 3	
137.1070	$\mathrm{C_8H_{13}N_2}$	29.4	A^+, C^{\pm}	Level 4	

accurate mass	molecular formula	RT (min)	${f detected}$ in $^{ m a}$	confidence level	proposed structure
223.2169	$\mathrm{C}_{14}\mathrm{H}_{27}\mathrm{N}_{2}$	20.1	А, В, С	Level 1	
273.1723	$\mathrm{C}_{14}\mathrm{H}_{26}\mathrm{ON}_{2}\mathrm{Cl}$	22.5	C^{\pm}	Level 4	
		24 5	C^+	Level 3	
271.2013	C14HazO2Na	24.8	A ⁺ . B [±]	Level 4	
211.2010	0141127 031 02	25.5	A^+, B^{\pm}	Level 4	
271.1568	$C_{14}H_{24}ON_2Cl$	22.0	C±	Level 4	
257.1773	$\mathrm{C}_{14}\mathrm{H}_{26}\mathrm{N}_{2}\mathrm{Cl}$	20.6	C^{\pm}	Level 3	
255.2063	$\mathrm{C}_{14}\mathrm{H}_{27}\mathrm{O}_{2}\mathrm{N}_{2}$	21.0	$A^{\pm}, B^{\pm}, C^{\pm}$	Level 3	
		26.1	C^+	Level 4	
		28.8	C^+	Level 4	
		30.8	A^+, B^\pm, C^\pm	Level 3	
255.1618	$\mathrm{C}_{14}\mathrm{H}_{24}\mathrm{N}_{2}\mathrm{Cl}$	21.2	C^{\pm}	Level 4	
253.1908	$\mathrm{C}_{14}\mathrm{H}_{25}\mathrm{O}_{2}\mathrm{N}_{2}$	21.8	$\mathrm{A}^{\pm},\mathrm{B}^{\pm},\mathrm{C}^{+}$	Level 4	
		24.1	A^+, C^+	Level 4	
		25.1	A^+, B^\pm, C^+	Level 4	
		25.7	$A^{\pm}, B^{\pm}, C^{\pm}$	Level 4	

Table S3 List of tentatively identified transformation products of C_{10} -imidazolium (parent compound information given in first line) with confidence levels according to Schymanski *et al.*³.

		26.9	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^+$	Level 3	
	-	28.3	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^+$	Level 3	
239.2114	$\mathrm{C}_{14}\mathrm{H}_{27}\mathrm{ON}_2$	21.6	A^{\pm}, C^{\pm}	Level 3	
	-	22.9	A^\pm,B^\pm,C^\pm	Level 3	
		24.6	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^\pm$	Level 3	
237.1959	$\mathrm{C}_{14}\mathrm{H}_{25}\mathrm{ON}_2$	22.7	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^\pm$	Level 3	
235.1803	$\mathrm{C}_{14}\mathrm{H}_{23}\mathrm{ON}_2$	25.3	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^+$	Level 4	
221.2011	$\mathrm{C}_{14}\mathrm{H}_{25}\mathrm{N}_{2}$	21.0	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^\pm$	Level 4	
209.2007	$\mathrm{C_{13}H_{25}N_2}$	20.6	A^{\pm}, C^{\pm}	Level 4	
158.9962		32.8	$\mathbf{A}^{\pm},\mathbf{B}^{\pm},\mathbf{C}^{\pm}$	Level 5	

accurate mass	molecular formula	RT (min)	${f detected}$ in $^{ m a}$	confidence level	proposed structure
136.1117	$\rm C_9H_{14}N$	25.5	A, B, C	Level 1	
186.0676	$C_9H_{13}ONCl$	26.2	C^+	Level 4	
170 0727	CeHeeNCl	94 9	C^+	Level 3	
168.1016		23.4	A^+, B^{\pm}	Level 5	
	$\mathrm{C_9H_{14}O_2N}$	25.0	A^+, B^{\pm}	Level 4	
154.0415	C_8H_9NCl	26.5	C^+	Level 4	
152.1066	$C_9H_{14}ON$	26.8	A^{+}, B^{+}, C^{+}	Level 3	×N ↓ OH
		30.7	A^{+}, B^{+}, C^{+}	Level 3	√
150.0911	$C_9H_{12}ON$	24.9	A^+, B^+, C^+	Level 3	- N +]
		27.8	A^{+}, B^{+}, C^{+}	Level 3	
		32.5	$\mathrm{A}^+,\mathrm{B}^\pm,\mathrm{C}^+$	Level 3	
134.0961	$\rm C_9H_{12}N$	28.8	$\mathrm{A^+,B^+,C^\pm}$	Level 4	
		30.8	$\mathrm{A^+,B^+,C^\pm}$	Level 4	

Table S4 List of tentatively identified transformation products of C_4 -pyridinium (parent compound information given in first line) with confidence levels according to Schymanski *et al.*³.

accurate mass	molecular formula	RT (min)	detected in ^a	confidence level	proposed structure
142.1585	$C_9H_{20}N$	26.3	A, B, C	Level 1	
208.1095	$\mathrm{C}_{9}\mathrm{H}_{19}\mathrm{O}_{2}\mathrm{NCl}$	27.3	C^{\pm}	Level 3	OH CI
190.0990	$C_9H_{17}ONCl$	27.3	C^{\pm}	Level 4	
184.9853	$\mathrm{C_4H_6O_6Cl}$	32.4	$\mathrm{A}^{\pm},\mathrm{B}^{+},\mathrm{C}^{+}$	Level 4	
176.1197	$C_9H_{19}NCl$	24.4	C^{\pm}	Level 3	
174.1484	$C_9H_{20}O_2N$	23.2	A^{\pm}	Level 3	
		25.5	A^{\pm}, B^{+}	Level 3	HO +N OH
		29.8	$A^{\pm}, B^{\pm}, C^{\pm}$	Level 3	*N (OH)2
172.9768		34.3	\mathbf{A}^+	Level 5	
158.1535	$\rm C_9H_{20}ON$	25.3	A^{\pm}, C^{\pm}	Level 3	· N € OH
		27.4	A^{\pm}, C^{\pm}	Level 3	
		31.7	$\mathrm{A}^{\pm},\mathrm{B}^{+},\mathrm{C}^{\pm}$	Level 3	f.,_]
		32.5	A^{\pm}, C^{\pm}	Level 3	− Ц+№
156.1379	$\rm C_9H_{18}ON$	23.2	A^{\pm}, B^{\pm}	Level 3	
		25.5	\mathbf{A}^{\pm}	Level 3	

Table S5 List of tentatively identified transformation products of C_4 -pyrrolidinium (parent compound information given in first line) with confidence levels according to Schymanski *et al.*³.

	28.4	A^{\pm}, B^{\pm}	Level 3	
	29.9	$A^{\pm}, B^{\pm}, C^{\pm}$	Level 3	
142.1223	25.5	$A^{\pm}, B^{\pm}, C^{\pm}$	Level 5	

accurate molecular \mathbf{RT} detected confidence proposed mass formula (min) in $^{\rm a}$ level structure 156.1742 $C_{10}H_{22}N$ 25.9A, B, CLevel 1 $C_{10}H_{21}O_2NCl$ 222.125223.0 $\mathbf{C}+$ Level 4 \mathbf{C}^{\pm} 26.9Level 4 A^+, C^+ 204.159226.3Level 5 B^+ 190.987334.3Level 5 \mathbf{C}^{\pm} $C_{10}H_{21}NCl$ Level 3 190.135522.4 \mathbf{C}^{\pm} ·CI 24.0 Level 3 $C_{10}H_{22}O_2N$ A^+, B^+ 188.164323.1Level 4 A^{\pm}, B^{+}, C^{\pm} 25.5Level 3 A^{+}, B^{+}, C^{\pm} 29.5Level 3 +он \mathbf{C}^+ Level 3 31.7186.1486 A^+, C^{\pm} Level 4 $C_{10}H_{20}O_2N$ 26.5 A^+, C^{\pm} 29.9Level 4ŧон 32.9 A^+, C^+ Level 3 A^+, B^\pm, C^\pm 172.976634.3Level 5 $C_{10}H_{22}ON$ 172.169325.8 A^+, C^{\pm} Level 3 A^+, C^{\pm} 27.5Level 3

Table S6 List of tentatively identified transformation products of C₄-piperidinium (parent compound information given in first line) with confidence levels according to Schymanski *et al.*³.

	_	31.5	$\mathrm{A^+,B^+,C^\pm}$	Level 3	*N
		32.5	$\mathrm{A^+,B^+,C^\pm}$	Level 3	
170.1536	$C_{10}H_{20}ON$	24.0	A^+, B^+	Level 4	
					+ N (
	_	25.5	$\mathrm{A^+,B^+,C^\pm}$	Level 3	
					+ N (
	_	28.2	A^+, B^+	Level 3	└_/ [`
					~ + N ~ ~ ~
		29.5	C^{\pm}	Level 3	0// ~ ~
156.1384	$\rm C_9H_{18}ON$	25.5	A^+, B^{\pm}	Level 4	
118.0859	$\mathrm{C_5H_{12}O_2N}$	32.5	\mathbf{A}^+	Level 4	

S6 References

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