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Impact of Chemical Environment on the Radiation Chemistry of *Di*-2-ethylhexylbutyramide (DEHBA) and Plutonium Retention

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Steady-State Gamma Irradiation Figures

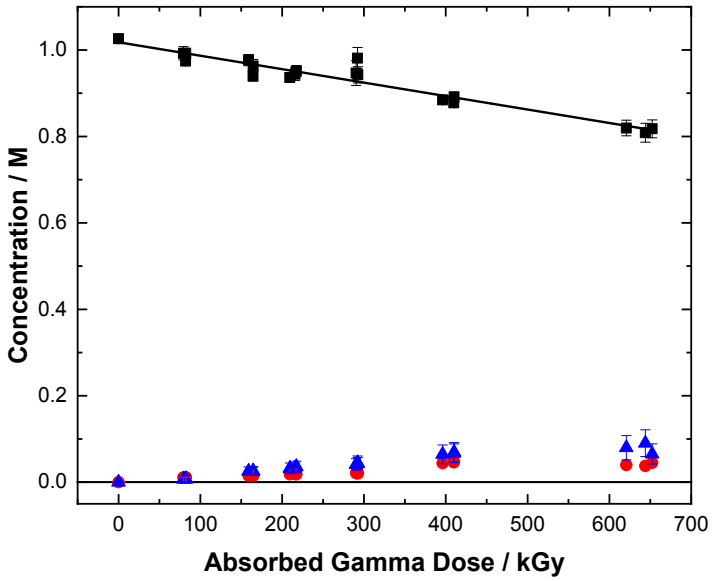

Fig. S1 Gamma irradiation (0.82 Gy s^{-1}) of organic only 1.0 M DEHBA *n*-dodecane solution: DEHBA (■), MEHBA (●) and b2EHA (□). Fitted line from linear least squares fits to data, *G*(DEHBA) = -0.31 ± 0.02 µmol J^{-1}.

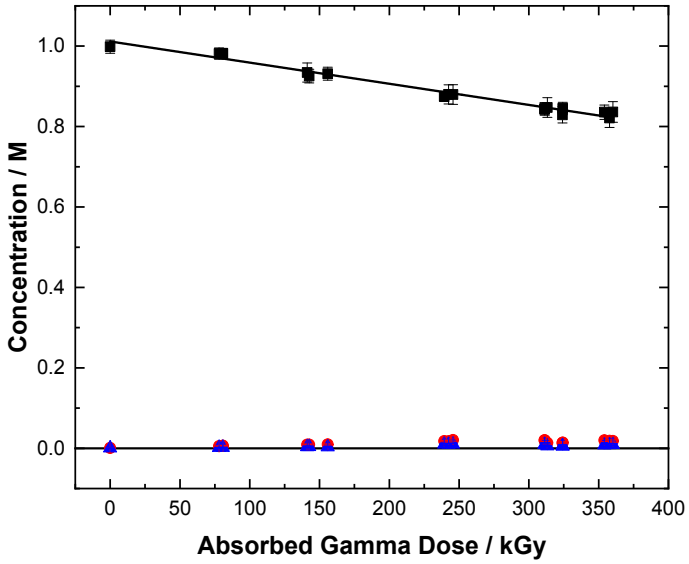

Fig. S2 Gamma irradiation (0.82 Gy s^{-1}) of biphasic 0.1 M HNO_3 contacted 1 M DEHBA *n*-dodecane solution: DEHBA (■), MEHBA (ꝏ) and b2EHA (□). Fitted line from linear least squares fits to data, *G*(DEHBA) = -0.53 ± 0.02 µmol J^{-1}.

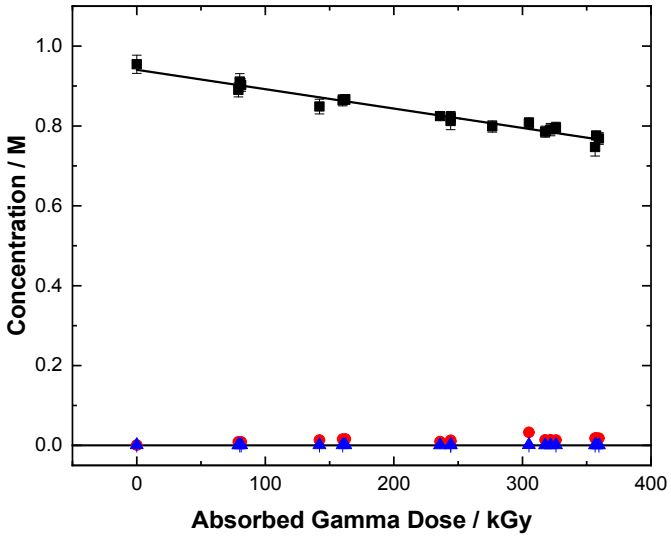

Fig. S3 Gamma irradiation (0.82 Gy s^{-1}) of biphasic 3.0 M HNO_3 contacted 1 M DEHBA *n*-dodecane solution: DEHBA (■), MEHBA (ꝏ) and b2EHA (□). Fitted line from linear least squares fits to data, *G*(DEHBA) = -0.49 ± 0.02 µmol J^{-1}.

Reaction Kinetics

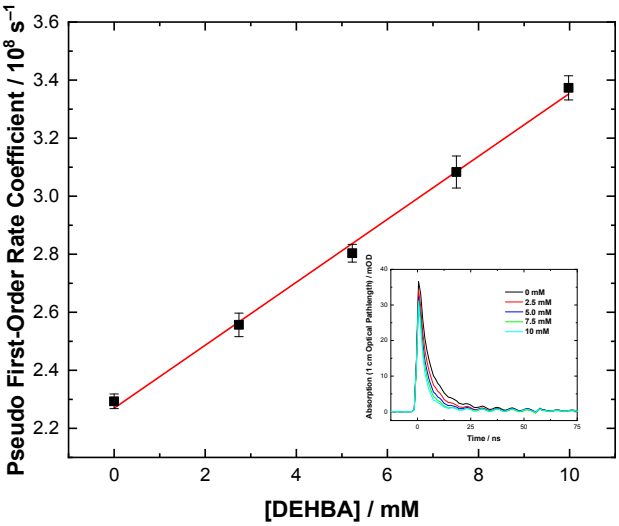

Fig. S5 Second-order determination of the rate coefficient for the dodecane radical cation reaction with DEHBA. Solid line is a weighted linear fit, with slope corresponding to the second-order rate coefficient, $k = (1.08 \pm 0.03) \times 10^{10}$ M^{-1} s^{-1}. *Inset:* Transient kinetic decays of the dodecane radical cation in *n*-dodecane solution containing 0.5 M dichloromethane in the presence of 0 (**Black**), 2.5 (**Red**), 5.0 (**Blue**), 7.5 (**Green**) and 10.0 (**Cyan**) mM DEHBA.

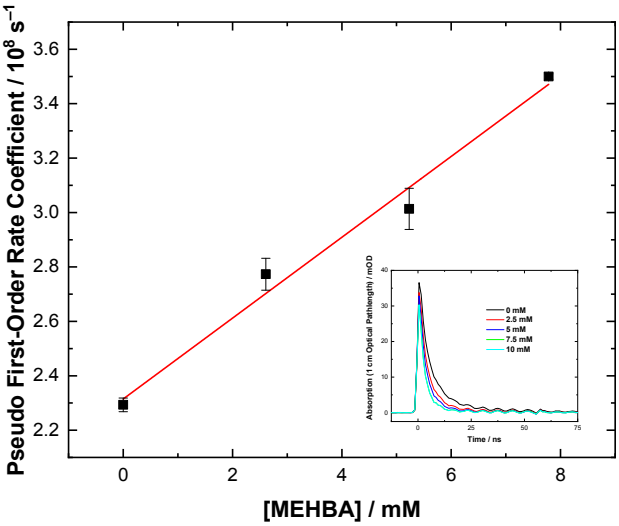

Fig. S6 Second-order determination of the rate coefficient for the dodecane radical cation reaction with MEHBA. Solid line is a weighted linear fit, with slope corresponding to the second-order rate coefficient, $k = (1.49 \pm 0.08) \times 10^{10}$ M^{-1} s^{-1}. *Inset:* Transient kinetic decays of the dodecane radical cation in *n*-dodecane solution containing 0.5 M dichloromethane in the presence of 0 (**Black**), 2.5 (**Red**), 5.0 (**Blue**), 7.5 (**Green**) and 10.0 (**Cyan**) mM MEHBA.

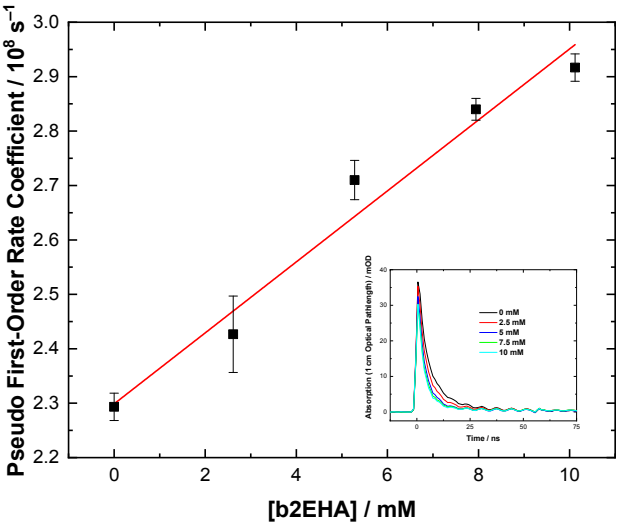

Fig. S7 Second-order determination of the rate coefficient for the dodecane radical cation reaction with b2EHA. Solid line is a weighted linear fit, with slope corresponding to the second-order rate coefficient, $k = (6.52 \pm 0.40) \times 10^9\ M^{-1}\ s^{-1}$. *Inset:* Transient kinetic decays of the dodecane radical cation in *n*-dodecane solution containing 0.5 M dichloromethane in the presence of 0 (**Black**), 2.5 (**Red**), 5.0 (**Blue**), 7.5 (**Green**) and 10.0 (**Cyan**) mM b2EHA.

Mass Balance

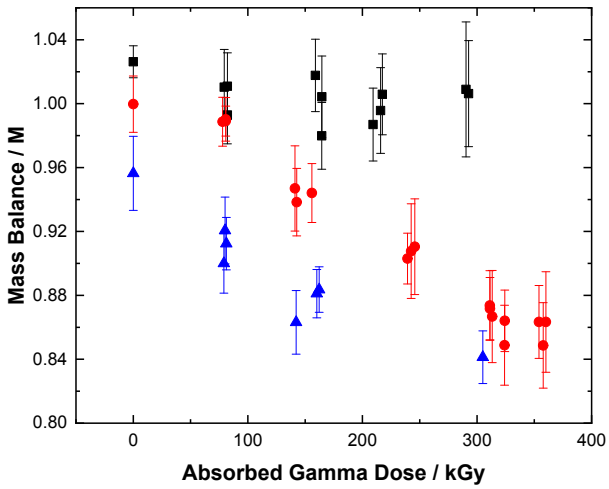

Fig. S8 Mass balance, assuming radiolysis of a single DEHBA molecule yields either one MEHBA or one b2EHA molecule, from the gamma irradiation (0.82 Gy s^{-1}) of 1.0 M DEHBA *n*-dodecane solution: organic only (■), and biphasic contact with 0.1 (ꝏ) and 3.0 (□) M HNO_3.

Mass Spectrometer Parameters

Source Parameters

End Plate Offset: 500 V

Capillary: 4500 V

Nebulizer Pressure: 4.0 bar

Dry Gas flow rate: 9.0 L min^{-1}

Dry Gas temperature: 220 °C

Mass Range: 40-800 *m/z*

Tune Parameters

Funnel 1 RF: 200 Vpp

Funnel 2 RF: 200 Vpp

IsCID Energy: 0.0 eV

Hexapole RF: 121.4 Vpp

Quadrupole Ion Energy: 4.0 eV

Low Mass Cutoff: 40.00 *m/z*

Collision Energy: 8.0 eV

Collision RF: 227.8 Vpp

Transfer Time: 80.8 µs

Pre-Pulse Storage Time: 5.0 µs

Mass Calibration

The tune mixture was composed of formic acid (Fisher Optima) and 1 M sodium hydroxide (Fisher, prepared in Fisher Optima LC/MS grade water) diluted in 50/50 water/2-propanol with a volume ratio of 1:5:100 (formic acid:1 M NaOH:50/50 water/2-propanol). The tuning mix was infused from 0.1 – 0.3 minutes and from 9.0 – 10.0 minutes in the run. Mass calibration was preformed using Bruker Data Analysis software using Automatic Internal Calibration the data at 9.5 – 10 minutes with the HPC calibration algorithm. The mass accuracy of the tune mix peaks infused from 0.1 – 0.3 minutes are used to verify the stability of the mass calibration throughout the run.

Degradation Product Analysis

Table S1. Compounds observed in the organic phase as a function of experimental conditions. 'L' stands for DEHBA.

m/z	Formula	Unirradiated	0.1 M HNO_3	4.0 M HNO_3
130.1	$[C_8H_{17}NH_2]\ H^+$			*
171.1	Contaminant	*		
200.2	**$[C_{12}H_{24}NO]H^+$ (MEHBA)**	*	*	*
242.2	**$[C_{16}H_{35}N]\ H^+$ (b2EHA)**		*	*
256.2	**$[C_{16}H_{33}NO]H^+$**	*	*	
270.2	$[C_{16}H_{31}NO_2]H^+$		*	
310.2	**$[C_{20}H_{39}NO]H^+$**		*	*
312.2	**LH+ (DEHBA)**	*	*	*
326.0	**$[C_{20}H_{39}NOO]H^+$**			*
328.0	$[C_{20}H_{40}NOOH]H^+$			*
334.2	LNa^+			*
350.0	LK^+			*
357.3	**$[C_{20}H_{40}N_2O_3]H^+$** (+NO2)			*
354.3	Contaminant	*	*	*
368.3			*	
379.2				*
382.3			*	
410.5	$[C_{28}H_{59}N]H^+$		*	
422.4			*	
447.3		*		
480.5	$[C_{32}H_{65}NO]H^+$		*	
533.5			*	*
551.7	$[C_{36}H_{74}N_2O]H^+$		*	
553.6	$[(C_{20}H_{41}NO)(C_{16}H_{35}N)]H^+$ **(adduct)**			*
621.6	$[C_{40}H_{80}N_2O_2]H^+$		*	
623.6	L_2H^+	*	*	*
645.5	L_2Na^+	*	*	*
661.1	L_2K^+			*

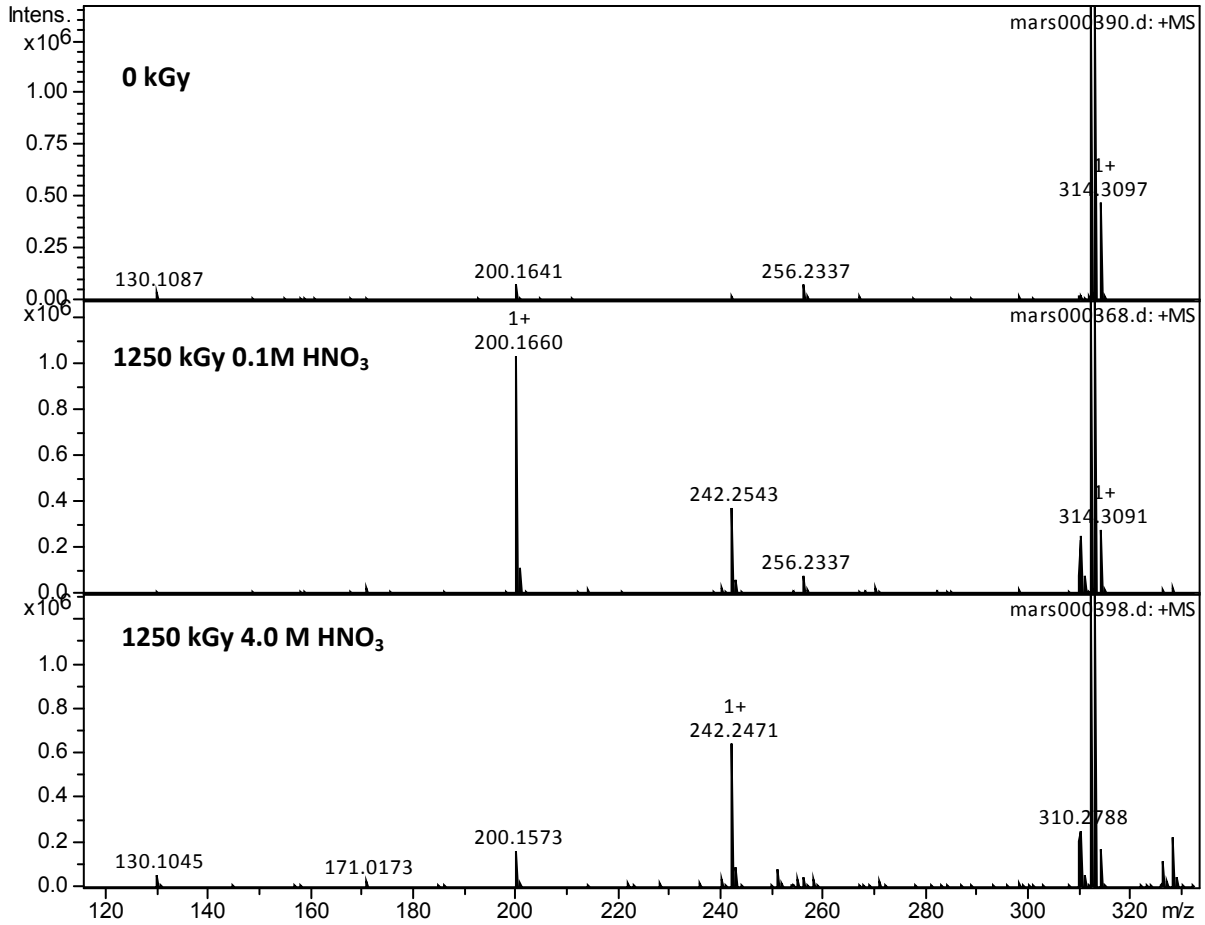

Fig. S9. ESI-MS spectra of organic phases of 1.0 M DEHBA *n*-dodecane solution before and after irradiation (1.25 MGy) in contact with either 0.1 or 4.0 M HNO_3. *In order to detect the minor peaks, the intensity of the peak corresponding to DEHBA is cut.*

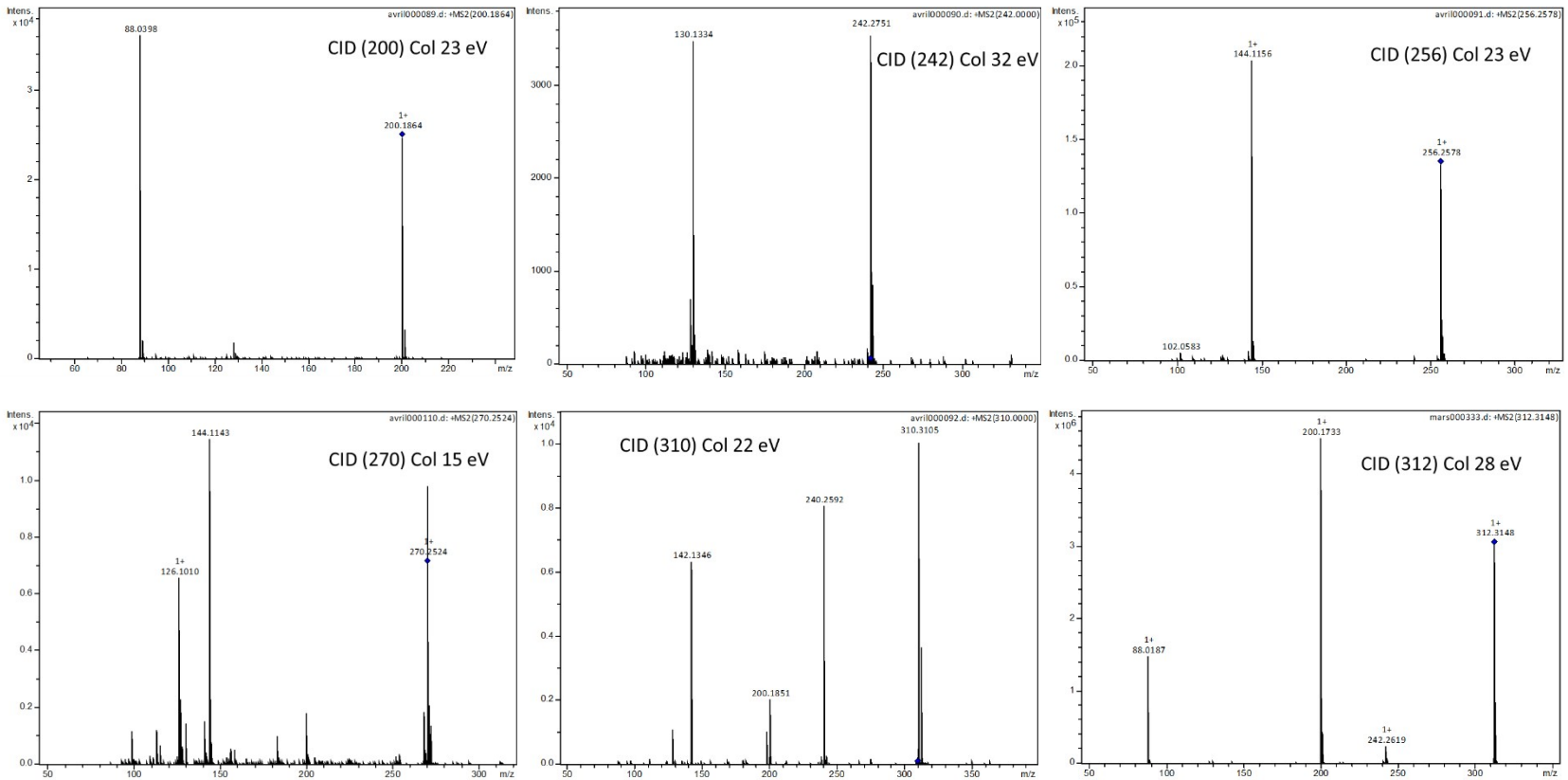

Fig. S10 CID spectra for the main ions at 200, 242, 256, 270, 310, and 312.

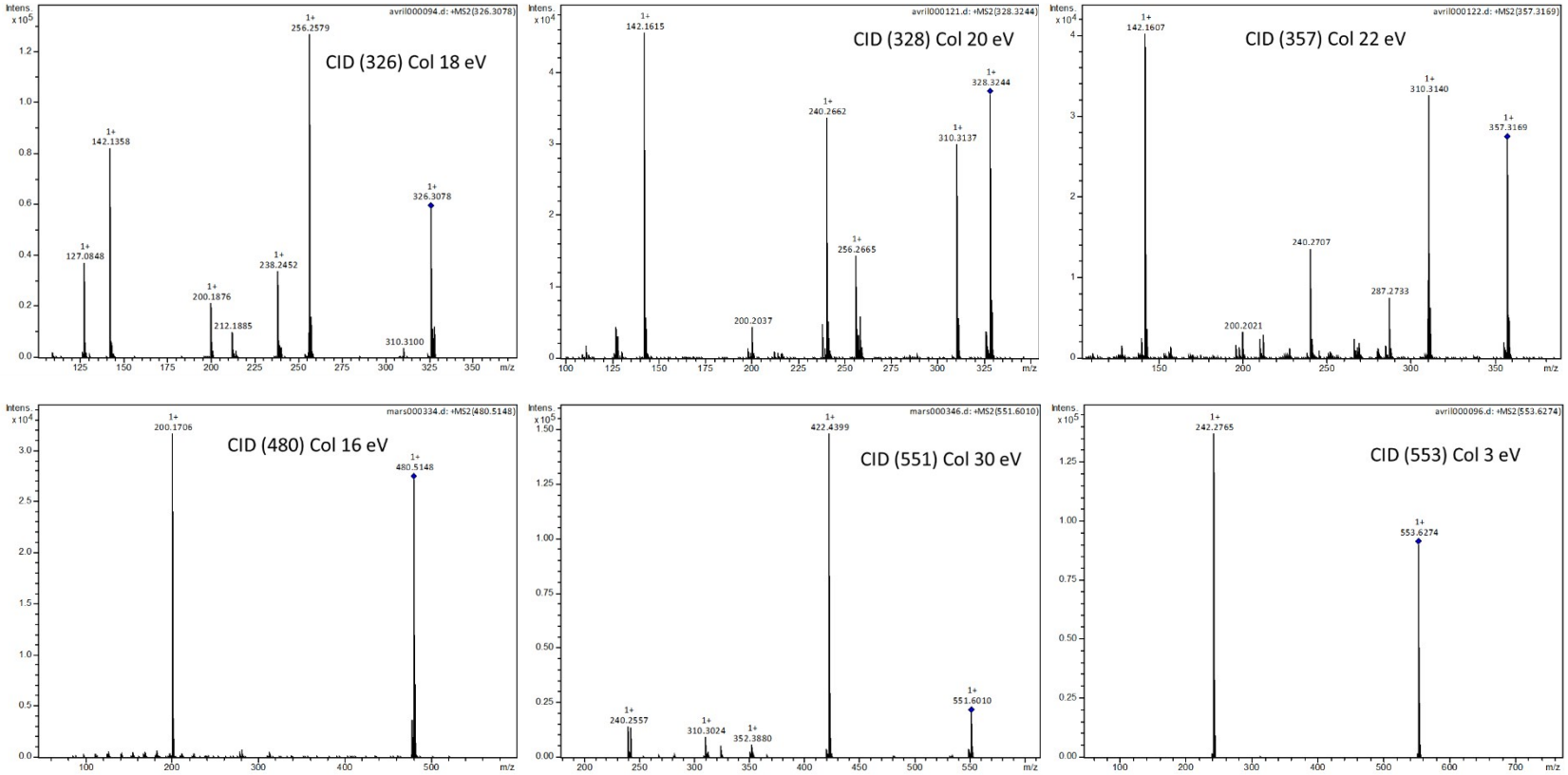

Fig. S11 CID spectra for the main ions at 326, 328, 357, 480, 551, and 553.

Degradation Schemes

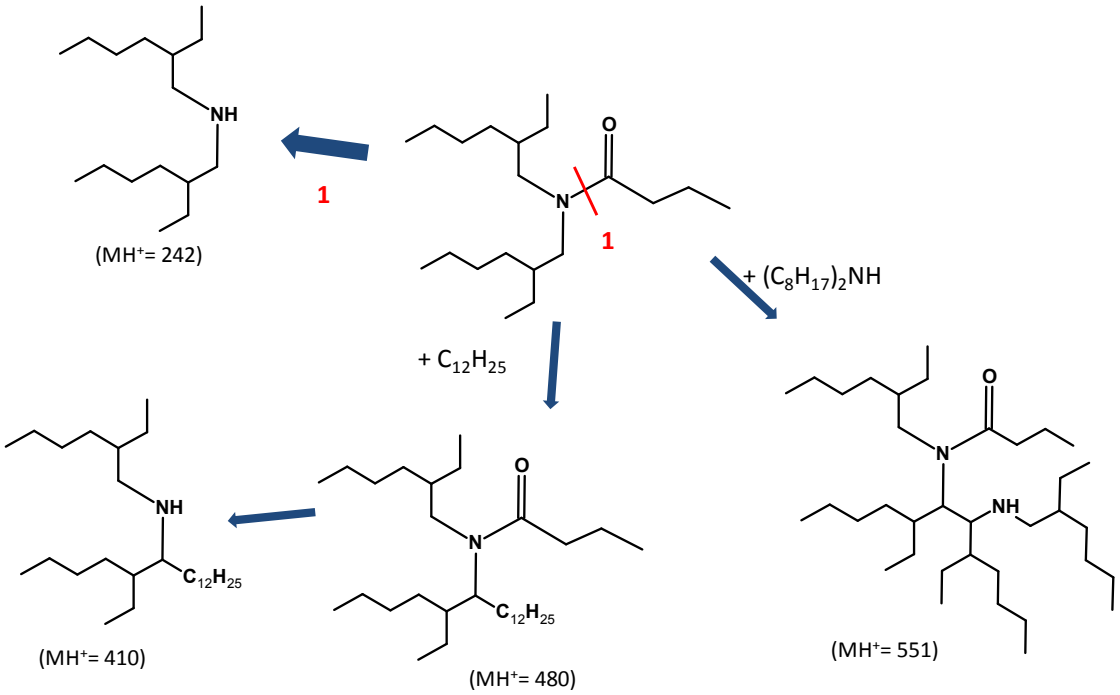

Fig. S12 Proposed radiation-induced DEHBA degradation pathways in the presence of low 0.1 M HNO_3, informed by degradation product analysis.

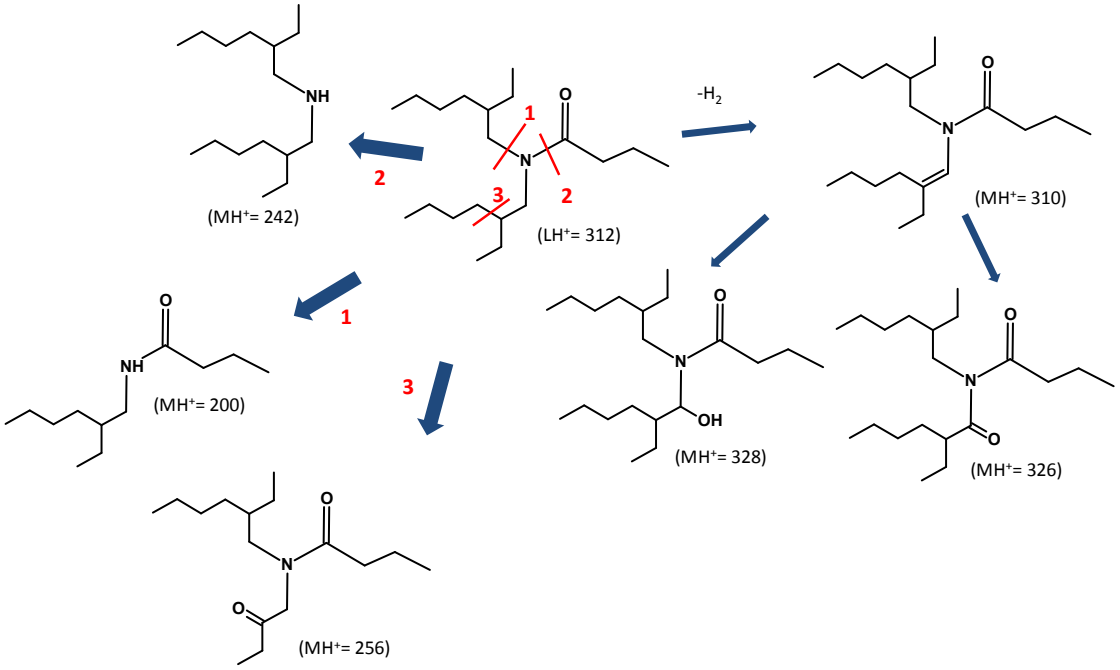

Fig. S13 Proposed radiation-induced DEHBA degradation pathways in the presence of 3.0 HNO_3, informed by degradation product analysis.

Colour Development

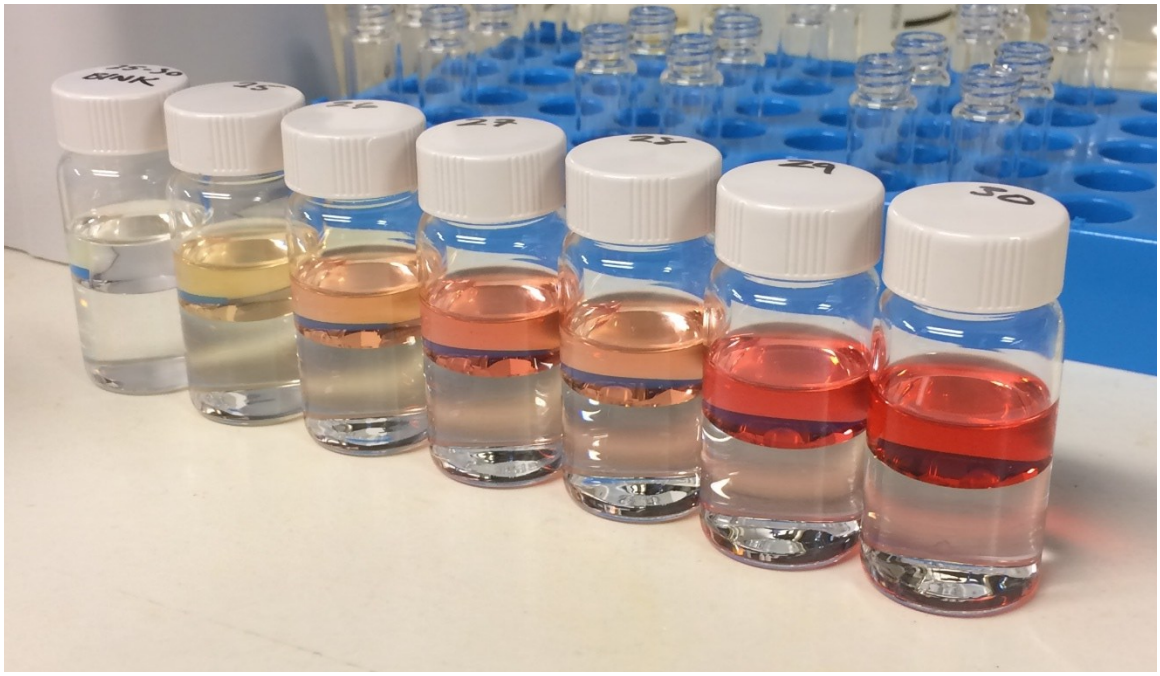

Fig. S14 Colour change of gamma irradiated organic-only 1.0 M DEHBA *n*-dodecane solution following contact with 4.0 M HNO_3 (extraction conditions). *From left to right:* 0, 81, 163, 214, 292, 405, and 639 kGy.