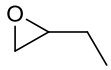
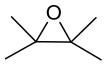
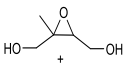
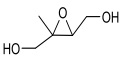
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for the article "A Kinetic Study of the Hydrolysis of Epoxides Initiated by Inorganic Ammonium Salts in Water: Evidence for Hydrogen Bond Catalysis"

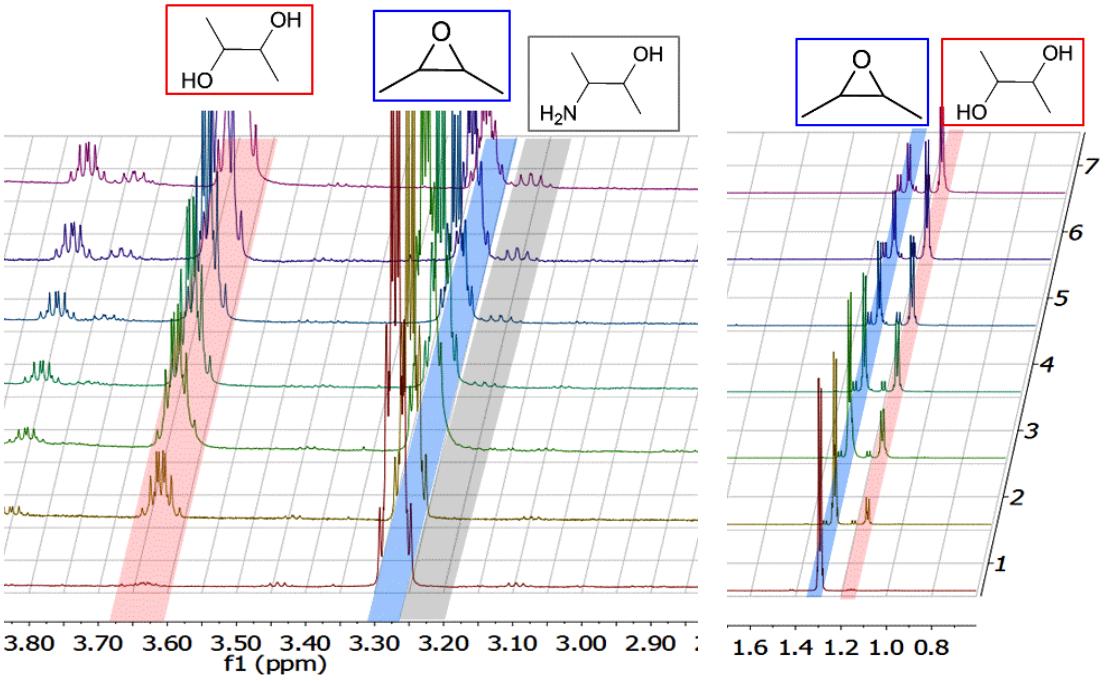
Table S1. List of experiments performed in this work.

Epoxide	Experiment #	$[Epoxide]_o$ ($\times 10^{-3}$ M)	Catalyst precursor and concentration (M)	pH	a_{NH4+} or a_{H+} (M)		Yield Diol/tetrol	k^I (s^{-1})
1,2-EB 	L1646	58	H_2O	7.0	/	NMR	/	6.4×10^{-07}
	L1645	48	NaCl 0.5 M	6.0	0	NMR	/	5.8×10^{-07}
	L1652	48	NaCl 1 M	6.0	0	NMR	/	9.6×10^{-07}
	L1644	60	Na_2SO_4 0.5 M	6.5	0	NMR	/	6.5×10^{-07}
	L1649	60	$MgSO_4$ 0.5 M	6.5	0	NMR	/	8.3×10^{-07}
	L1650	60	$MgSO_4$ 1 M	6.5	0	NMR	/	7.2×10^{-07}
	L1651	60	$MgSO_4$ 0.5 M	6.5	0	NMR	/	6.5×10^{-07}
	L1647	58	1amino2butanol 60mM /H_2O	7.0	0	NMR		9.6×10^{-06}
	L1657	58	1amino2butanol 60 mM /H_2O	7.0	0	NMR		9.6×10^{-06}
	L1658	58	1amino 2 butanol 30 mM /H_2O	7.0	0	NMR		3.2×10^{-06}
	L1665	60	HFIP 60 mM	7.0	0	NMR		3.6×10^{-06}
	L1666	60	TFE 60 mM	7.0	0	NMR		4.9×10^{-06}
	L1667	60	HFIP 60 mM	7.0	0	NMR		4.6×10^{-06}
	L1668	60	TFE 60 mM	7.0	0	NMR		3.5×10^{-06}
	L1643	48	NH_4F 0.5 M	6.5	0.29	NMR	0.70	1.2×10^{-06}
	L1648	58	NH_4F 1 M	7.0	0.61	NMR	/	2.2×10^{-06}
	L1659	58	NH_4F 1 M	7.0	0.61	NMR	/	2.0×10^{-06}
	L1660	58	NH_4F 1.5 M	7.0	0.98	NMR	0.49	4.0×10^{-06}
	L1177	51.2	$(NH_4)_2SO_4$, 0.1 M	5.7	0.12	GC	1.00	7.9×10^{-07}
	L1137	40	$(NH_4)_2SO_4$, 0.1 M	5.7	0.12	GC	0.84	8.5×10^{-07}
	L1138	40	$(NH_4)_2SO_4$, 0.1 M	8.0	0.12	GC	0.70	7.5×10^{-07}
	L1619	47	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	NMR	/	1.9×10^{-06}
	L1630	48	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	NMR	0.52	1.8×10^{-06}
	L1178	40	$(NH_4)_2SO_4$, 0.5 M	5.7	0.51	GC	0.55	1.7×10^{-06}
	L1139	51.2	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	GC	0.51	1.7×10^{-06}
	L1140	40	$(NH_4)_2SO_4$ 0.5 M	8.0	0.51	GC	0.44	1.9×10^{-06}
	L1620	47	$(NH_4)_2SO_4$ 0.5 M	10.0	0.51	NMR	/	1.7×10^{-06}
	L1631	48	$(NH_4)_2SO_4$ 0.5 M	10.0	0.51	NMR	0.49	1.8×10^{-06}
	L1179	40	$(NH_4)_2SO_4$ 1 M	5.7	1.0	GC	0.45	3.2×10^{-06}
	L1195	51.2	$(NH_4)_2SO_4$ 1 M	5.7	1.0	GC	0.41	3.4×10^{-06}
	L1242	40	$(NH_4)_2SO_4$ 1 M	7.0	1.0	GC	/	3.1×10^{-06}
	L1240	40	$(NH_4)_2SO_4$ 1.5 M	5.7	1.5	GC	0.32	5.4×10^{-06}
	L1241	40	$(NH_4)_2SO_4$ 1.5 M	8.0	1.5	GC	0.14	5.8×10^{-06}
	L1188	51.2	H_2SO_4 0.03 M	1.2	0.06	GC	1.01	4.2×10^{-03}
	L1187	53	H_2SO_4 0.05 M	2.0	0.01	GC	1.04	5.2×10^{-04}
	L1191	53	H_2SO_4 0.001 M,	2.7	0.002	GC	1.02	7.3×10^{-05}
2,3-EB 	L1641	48	H_2O	7.0	/	NMR	/	1.3×10^{-06}
	L1653	60	NaCl 1M	6.5	/	NMR	/	4.0×10^{-07}
	L1654	60	$MgSO_4$ 0.5 M	6.5	/	NMR	/	7.7×10^{-07}
	L1655	60	$MgSO_4$ 1 M	6.5	/	NMR	/	1.0×10^{-06}
	L1642	48	1amino2butanol 60 mM /H_2O	7.0	/	NMR		2.9×10^{-06}
	L1663	48	1amino2butanol 30 mM /H_2O	7.0	/	NMR		1.7×10^{-06}

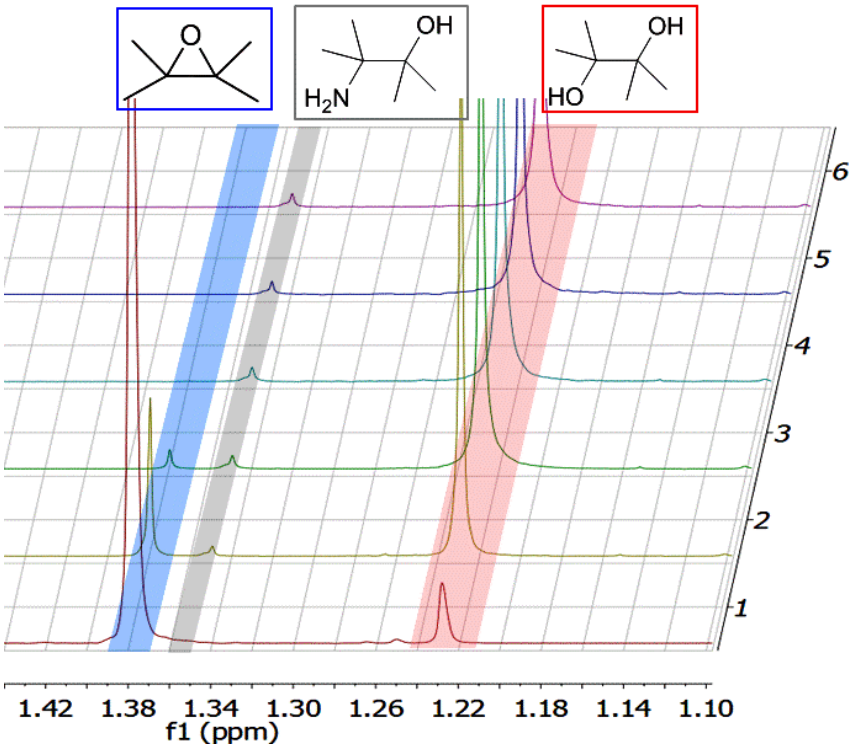
	L1656	60	NH_4F 0.5 M	6.5	0.29	NMR	0.93	2.1×10^{-06}
	L1661	60	NH_4F 1 M	6.5	0.61	NMR	0.70	3.4×10^{-06}
	L1662	60	NH_4F 1.5 M	6.5	0.98	NMR	/	4.1×10^{-06}
	L1176	52.1	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.93	1.4×10^{-06}
	L1153	40	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.75	1.6×10^{-06}
	L1152	25	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.74	1.4×10^{-06}
	L1164	26	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.66	1.7×10^{-06}
	L1621	47	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	NMR	0.75	3.0×10^{-06}
	L1632	48	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	NMR	0.88	2.9×10^{-06}
	L1154	40	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	GC	0.77	2.5×10^{-06}
	L1165	25	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	GC	0.88	2.7×10^{-06}
	L1622	47	$(NH_4)_2SO_4$ 0.5 M	10.0	0.51	NMR	/	2.8×10^{-06}
	L1633	48	$(NH_4)_2SO_4$ 0.5 M	10.0	0.51	NMR	0.96	3.3×10^{-06}
	L1193	40	$(NH_4)_2SO_4$ 1 M	5.7	1.0		0.65	4.0×10^{-06}
	L1194	51.2	$(NH_4)_2SO_4$ 1 M	5.7	1.0	GC	0.88	4.8×10^{-06}
	L1250	40	$(NH_4)_2SO_4$ 1 M	7.0	1.0	GC	0.61	4.6×10^{-06}
	L1251	40	$(NH_4)_2SO_4$ 1.5 M	5.7	1.5	GC	0.73	7.7×10^{-06}
	L1252	40	$(NH_4)_2SO_4$ 1.5 M	8.0	1.5	GC	0.64	8.4×10^{-06}
	L1190	40	H_2SO_4 0.005 M	2.0	0.01	GC	1.00	5.4×10^{-03}
	L1172	40	H_2SO_4 0.001 M	2.7	0.002	GC	1.02	5.8×10^{-04}
	L1170	40	H_2SO_4 0.00001 M	4.7	0.00002	GC	0.98	1.5×10^{-06}
	L1171	40	H_2SO_4 0.00001 M	4.7	0.00002	GC	0.96	1.3×10^{-06}
DM-2,3-EB 	L1133	51.2	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.98	2.6×10^{-05}
	L1155	40	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.92	2.5×10^{-05}
	L1181	40	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.98	2.6×10^{-05}
	L1182	25	$(NH_4)_2SO_4$ 0.1 M	5.7	0.12	GC	0.93	2.8×10^{-05}
	L1134	51.2	$(NH_4)_2SO_4$ 0.1 M	8.0	0.12	GC	1.00	2.1×10^{-05}
	L1634	49	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	NMR	0.99	3.0×10^{-05}
	L1183	51.2	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	GC	0.99	4.0×10^{-05}
	L1156	40	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	GC	0.86	2.9×10^{-05}
	L1184	40	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	GC	1.00	3.7×10^{-05}
	L1185	25	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	GC	1.03	3.2×10^{-05}
	L1136	51.2	$(NH_4)_2SO_4$ 0.5 M	8.0	0.51	GC	0.67	2.7×10^{-05}
	L1635	49	$(NH_4)_2SO_4$ 0.5 M	10.0	0.51	NMR	/	3.3×10^{-05}
	L1186	51.2	$(NH_4)_2SO_4$ 1 M	5.7	1.0	GC	1.01	4.4×10^{-05}
	L1192	51.2	$(NH_4)_2SO_4$ 1 M	5.7	1.0	GC	1.00	4.8×10^{-05}
	L1246	40	$(NH_4)_2SO_4$ 1.5 M	5.7	1.5	GC	0.79	5.8×10^{-05}
	L1157	40	H_2SO_4 0.005 M	2.0	0.01	GC	1.08	2.4×10^{-02}
	L1162	40	H_2SO_4 0.001 M	2.7	0.002	GC	1.03	1.6×10^{-02}
	L1166	40	H_2SO_4 0.001 M	2.7	0.002	GC	0.88	3.7×10^{-02}
	L1168	40	H_2SO_4 0.00001 M	4.7	0.00002	GC	1.03	1.2×10^{-04}
	L1169	40	H_2SO_4 0.00001 M	4.7	0.00002	GC	1.03	1.0×10^{-04}
IEPOX3  IEPOX4 	L1197	64	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	NMR	0.52	1.0×10^{-07}
	L1205	43	$(NH_4)_2SO_4$ 0.5 M	8.8	0.51	NMR	0.72	9.8×10^{-08}
	L1200	20.1	$(NH_4)_2SO_4$ 0.5 M	5.7	0.51	NMR	0.73	7.6×10^{-08}
	L1201	21.5	$(NH_4)_2SO_4$ 1 M	5.7	1.0	NMR	0.60	1.5×10^{-07}
	L1206	17.2	$(NH_4)_2SO_4$ 1 M	8.8	1.0	NMR	/	2.3×10^{-07}
	L1173	132	H_2SO_4 0.1 M	0.7	0.2	NMR	0.91	3.9×10^{-03}
	L1174	37	H_2SO_4 0.1 M	0.7	0.2	NMR	0.93	5.4×10^{-03}
	L1199	19.7	H_2SO_4 0.001 M	2.7	0.002	NMR	0.90	1.3×10^{-07}
	L1198	30.5	H_2SO_4 0.001 M	2.7	0.002	NMR	1.00	1.3×10^{-07}
	L1175	36.7	H_2SO_4 0.00001 M	5.0	0.00002	NMR	0.16	4.7×10^{-07}

S2. NMR spectra for the reaction mixtures and comparisons with reference compounds.

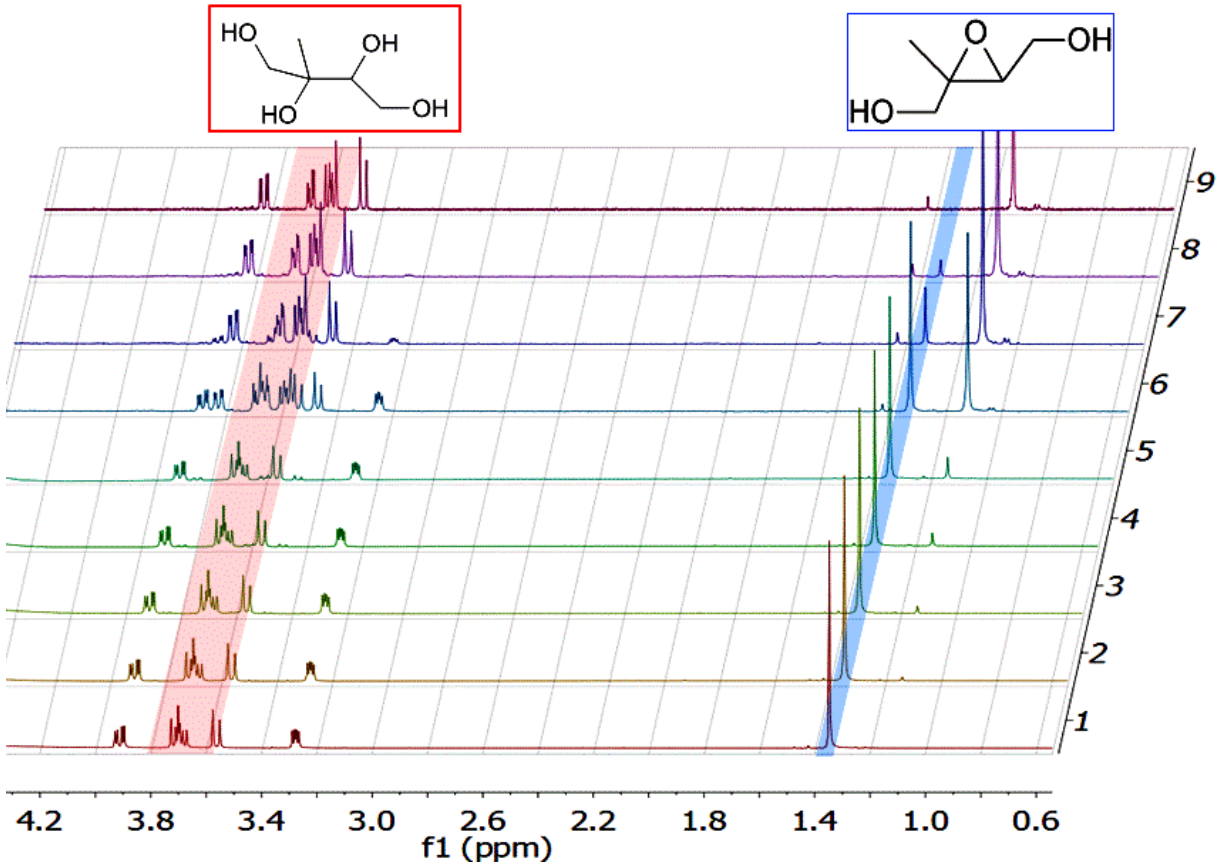
A) Evolution of the ^{1}H-NMR spectrum during the reaction of cis-2,3-EB in solution $(NH_4)_2SO_4$ 0.5 M showing the formation of 2,3-butanediol and 2-amino-3-butanol.



B) Evolution of the ^{1}H-NMR spectrum during the reaction of DM-2,3-EB in solution $(NH_4)_2SO_4$ 0.5 M showing the formation of 2,3-dimethyl-2,3-butanediol and 2,3-dimethyl-2-amino-3-butanol.

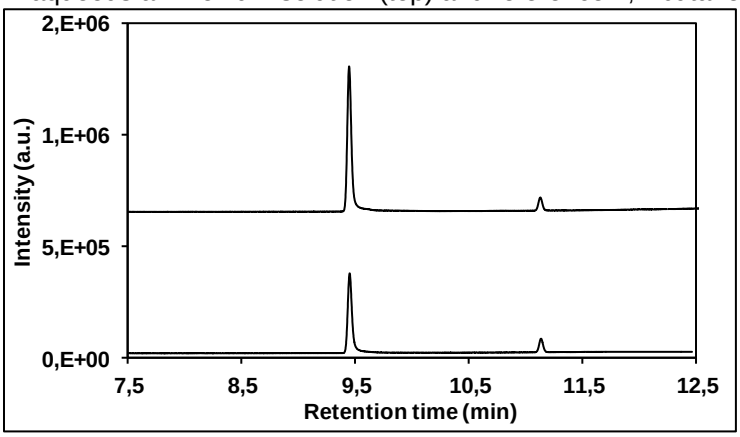


C) Evolution of the ^{1}H-NMR spectrum during the reaction of IEPOX 4 in solution $(NH_4)_2SO_4$ 0.5 M showing the formation of 2-methylbutane-1,2,3,4-tetraol (2-methylerythritol and 2-methylthreitol).

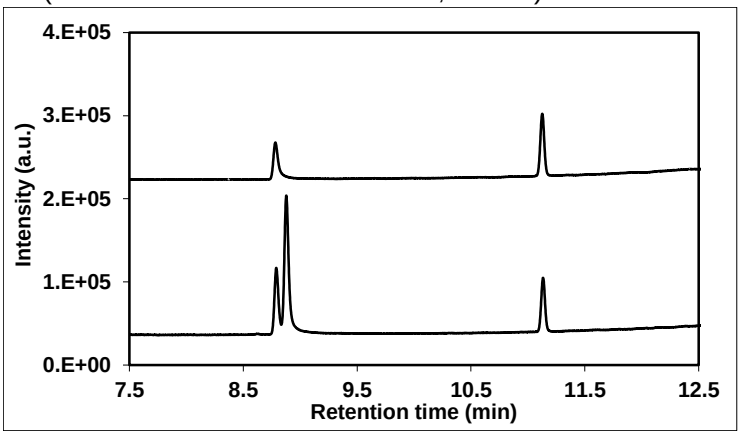


S3. Chromatograms for the reaction mixtures and comparisons with reference compounds.

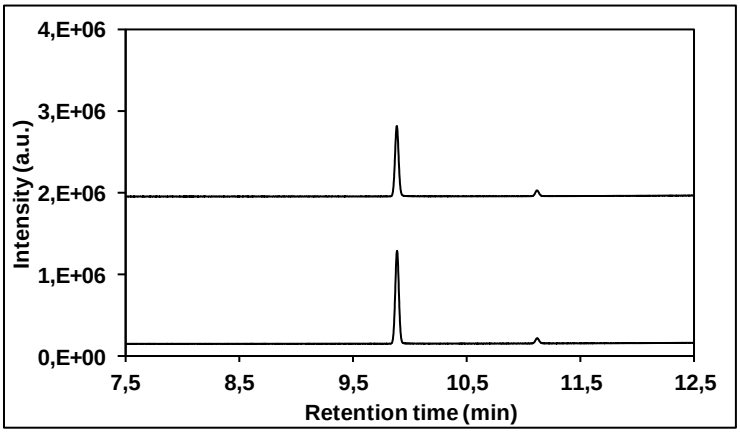
A) Reaction of 1,2EB in aqueous ammonium solution (top) and reference 1,2-butanediol (bottom)



B) Reaction of cis-2,3EB in aqueous ammonium solution (producing cis-2,3-butanediol only, top) and reference 2,3-butanediol (mixture of cis- and trans isomers, bottom)

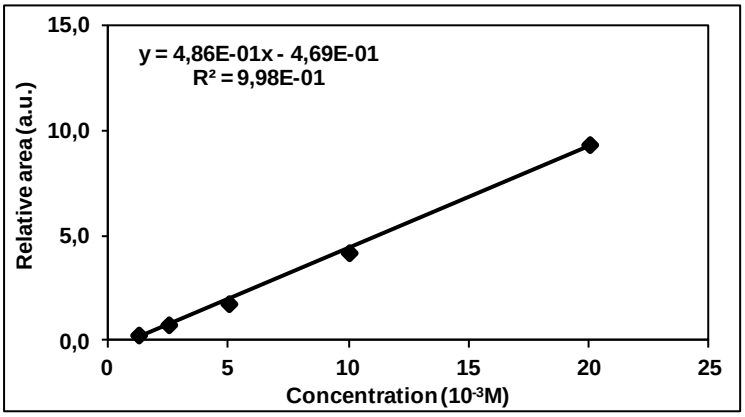


C) Reaction of DM-2,3-EB in aqueous ammonium solution (top) and reference 2,3-dimethyl-2,3-butanediol (bottom)

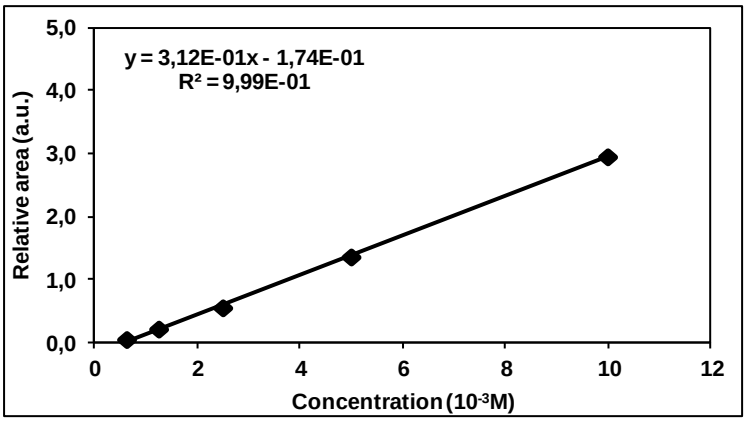


S4. Calibration curves used in GC/FID to quantify the hydrolysis products

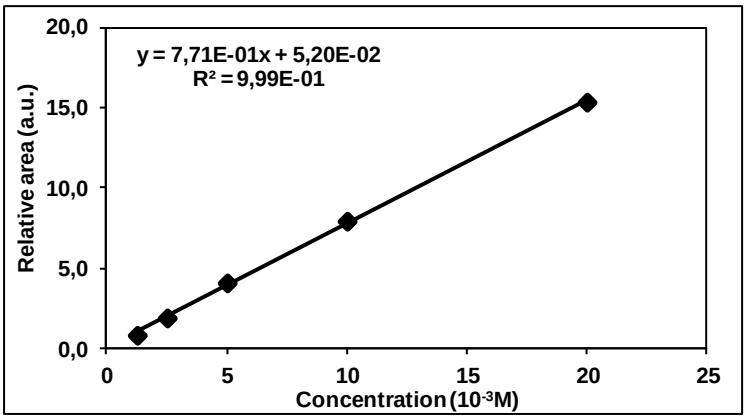
A) 1,2-butanediol



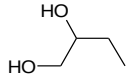
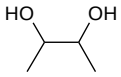
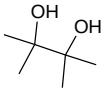
B) Cis-2,3-butanediol



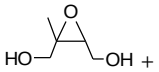
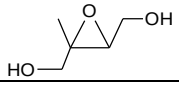
D) 2,3-dimethyl-2,3-butanediol



S5. Extraction efficiencies at 298 K for the different reactions and solutions studied by GC/FID

Precursor	Compound extracted	Solution	Extraction efficiencies
1,2-EB 	1,2-butanediol 	H_2O	0.27
		$(NH_4)_2SO_4$ 0.1 M, pH = 5.6	0.26
		$(NH_4)_2SO_4$ 0.1 M, pH = 8.0	0.26
		$(NH_4)_2SO_4$ 0.5 M, pH = 5.7	0.34
		$(NH_4)_2SO_4$ 0.5 M, pH = 8.0	0.34
		$(NH_4)_2SO_4$ 1 M, pH = 5.8	0.4
		$(NH_4)_2SO_4$ 1.5 M, pH = 5.8	0.47
		$(NH_4)_2SO_4$ 1.5 M, pH = 8	0.47
		H_2SO_4 0.03 M, pH = 1.2	0.28
		H_2SO_4 0.05 M, pH = 2.0	0.28
		H_2SO_4 0.001 M, pH = 2.7	0.27
2,3-EB 	2,3-butanediol 	H_2O	0.21
		$(NH_4)_2SO_4$ 0.1 M, pH = 5.6	0.27
		$(NH_4)_2SO_4$ 0.1 M, pH = 8.0	0.27
		$(NH_4)_2SO_4$ 0.5 M, pH = 5.7	0.31
		$(NH_4)_2SO_4$ 0.5 M, pH = 8.0	0.3
		$(NH_4)_2SO_4$ 1 M, pH = 5.8	0.36
		$(NH_4)_2SO_4$ 1.5 M, pH = 5.8	0.42
		H_2SO_4 0.05 M, pH = 2.0	0.50
		H_2SO_4 0.001 M, pH = 2.7	0.50
		H_2SO_4 0.00001 M, pH = 4.7	0.49
DM-2,3-EB 	2,3-dimethyl-2,3-butanediol 	H_2O	0.43
		$(NH_4)_2SO_4$ 0.1 M, pH = 5.6	0.55
		$(NH_4)_2SO_4$ 0.1 M, pH = 8.0	0.56
		$(NH_4)_2SO_4$ 0.5 M, pH = 5.7	0.60
		$(NH_4)_2SO_4$ 0.5 M, pH = 8.0	0.58
		$(NH_4)_2SO_4$ 1 M, pH = 5.8	0.65
		$(NH_4)_2SO_4$ 1.5 M, pH = 5.8	0.71
		H_2SO_4 0.001 M, pH = 2.7	0.51
		H_2SO_4 0.00001 M, pH = 4.7	0.53

S6. Relative contributions of acid (k^{I}_{H+}), base (k^{I}_{OH}) to the corrected hydrolysis rates, k'^{I}, in aqueous ammonium solutions as function of ammonium concentration.

Epoxide	a_{NH4+} (M)	k'^{I} (s^{-1})	Acid catalysis, Assuming pH = 5.7		Base catalysis Assuming pH = 8	
			k^{I}_{H+} (s^{-1})	%	k^{I}_{OH-} (s^{-1})	%
1,2-EB 	0.12	2.5×10^{-7}	1.0×10^{-7}	40	1.0×10^{-10}	0
	0.51	1.3×10^{-6}	1.0×10^{-7}	8	1.0×10^{-10}	0
	1.00	2.6×10^{-6}	1.0×10^{-7}	4	1.0×10^{-10}	0
	1.50	5.0×10^{-6}	1.0×10^{-7}	2	1.0×10^{-10}	0
2,3-EB 	0.12	5.3×10^{-7}	3.0×10^{-8}	6	1.0×10^{-10}	0
	0.51	1.9×10^{-6}	3.0×10^{-8}	2	1.0×10^{-10}	0
	1.00	3.5×10^{-6}	3.0×10^{-8}	1	1.0×10^{-10}	0
	1.50	7.1×10^{-6}	3.0×10^{-8}	0	1.0×10^{-10}	0
DM-2,3-EB 	0.12	2.1×10^{-5}	3.0×10^{-6}	14	1.0×10^{-10}	0
	0.51	2.8×10^{-5}	3.0×10^{-6}	11	1.0×10^{-10}	0
	1.00	4.1×10^{-5}	3.0×10^{-6}	7	1.0×10^{-10}	0
	1.50	5.3×10^{-5}	3.0×10^{-6}	4	1.0×10^{-10}	0
IEPOX3 	0.51	8.2×10^{-08}	2.0×10^{-8}	22	1.0×10^{-10}	0
IEPOX4 	1.00	1.8×10^{-07}	2.0×10^{-8}	9	1.0×10^{-10}	0