Selected parameters mentioned in the text

Percentage of negative charge transferred from the HO^-, and degree of evolution for selected bonds at RICs and TSs, using the microsolvated model. Atom labels are the same as in Fig. 2.

	Hofmann Elim.		Zaitsev Elim.		Bimol. Fragm.		Intram. Elim.	
	RIC	**TS**	**RIC**	**TS**	**RIC**	**TS**	**RIC**	**TS**
% $q_{transferred}$	21.2	44.1	62.4	70.9	15.1	62.4	18.1	64.3
				% Evolution[a]				
O_{OH}-H_T (f)	3.1	34.8	1.4	58.5	-	-	-	-
O_{OH}-H_O (f)	-	-	-	-	19.8	74.3	23.3	75.0
O-H_O (b)	-	-	-	-	27.6	82.8	30.8	83.3
O-C_3 (f)	-	-	-	-	4.0	29.5	-	-
C_3-C_2 (b)	-	-	-	-	2.3	33.5	-	-
O-H_T (f)	-	-	-	-	-	-	1.4	28.2
C_1-H_T (b)	7.4	42.4	-	-	-	-	4.1	38.5
C_2-H_T (b)	-	-	4.5	66.7	-	-	-	-
C_1-N (f)	-1.7	8.8	-	-	-	-	-0.8	17.0
C_2-N (f)	-	-	-2.2	0.8	-2.2	23.2	-	-
N-Cl (b)	0.7	15.9	0.1	7.1	0.4	37.5	0.7	29.4
S_y		0.68		0.43		0.74		0.68

[a] Bonds being formed and broken are labelled **f** and **b**, respectively.

Mulliken atomic charges and dipole moments obtained by using MP2=full/6-31++G(d,p) level. Atom labels are the same as in Fig. 2.

	C_1	N	Cl	C_2	C_3	O	H_T	H_O	O_{OH}	H_{OH}	O_{WO}	H_{WO}	O_{WN}	H_{WN}	μ[a]
							Hofmann Elimination								
R	-0.15	-0.31	-0.11	-0.09	0.02	-0.59	0.14	0.39	-1.21	0.21	-0.72	0.36	-0.72	0.36	-
RIC	-0.20	-0.43	-0.14	0.04	-0.09	-0.64	0.21	0.41	-1.17	0.31	-0.93	0.55	-0.84	0.52	10.60
TS	-0.42	-0.33	-0.31	-0.02	-0.05	-0.64	0.41	0.43	-1.03	0.31	-0.86	0.52	-0.88	0.54	6.16
PIC	-0.07	-0.36	-0.80	-0.04	-0.08	-0.64	0.36	0.43	-0.78	0.40	-0.78	0.36	-0.86	0.51	8.37
P	-0.04	-0.27	-1.00	-0.19	0.07	-0.58	0.36	0.38	-0.72	0.36	-0.72	0.36	-0.72	0.36	-
							Zaitsev Elimination								
R	-0.15	-0.31	-0.11	-0.09	0.02	-0.59	0.13	0.39	-1.21	0.21	-0.72	0.36	-0.72	0.36	-
RIC	-0.25	-0.42	-0.10	0.07	-0.08	-0.64	0.10	0.40	-1.18	0.31	-0.91	0.55	-0.82	0.52	10.43
TS	-0.21	-0.32	-0.23	-0.55	-0.03	-0.65	0.50	0.40	-0.86	0.32	-0.80	0.48	-0.83	0.52	9.80
PIC	-0.21	-0.43	-0.82	0.00	-0.04	-0.65	0.36	0.47	-0.80	0.38	-0.83	0.42	-0.79	0.46	11.64
P	-0.24	-0.26	-1.00	-0.07	0.01	-0.57	0.36	0.36	-0.72	0.36	-0.72	0.36	-0.72	0.36	-
							Bimolecular Fragmentation								
R	-0.15	-0.31	-0.11	-0.09	0.02	-0.59	-	0.39	-1.21	0.21	-0.72	0.36	-0.72	0.36	-
RIC	-0.21	-0.38	-0.13	-0.15	0.15	-0.73	-	0.55	-1.21	0.31	-0.89	0.54	-0.79	0.49	15.73
TS	-0.19	-0.21	-0.48	-0.20	0.18	-0.80	-	0.53	-0.95	0.35	-0.80	0.48	-0.79	0.48	15.41
PIC	-0.23	-0.36	-0.82	-0.03	0.34	-0.52	-	0.44	-0.90	0.47	-0.80	0.47	-0.75	0.36	9.50
P	-0.25	-0.24	-1.00	-0.04	0.27	-0.44	-	0.36	-0.72	0.36	-0.72	0.36	-0.72	0.36	-
							Intramolecular Elimination								
R	-0.15	-0.31	-0.11	-0.09	0.02	-0.59	0.14	0.39	-1.21	0.21	-0.72	0.36	-0.72	0.36	-
RIC	-0.21	-0.39	-0.14	0.08	-0.13	-0.72	0.16	0.57	-1.21	0.33	-0.84	0.52	-0.79	0.51	11.78
TS	-0.34	-0.18	-0.44	-0.08	0.04	-0.83	0.30	0.56	-0.93	0.35	-0.79	0.47	-0.80	0.49	7.54
PIC	0.00	-0.33	-0.85	-0.22	0.07	-0.68	0.41	0.51	-0.87	0.36	-0.79	0.45	-0.77	0.34	12.34
P	-0.04	-0.27	-1.00	-0.19	0.07	-0.58	0.38	0.36	-0.72	0.36	-0.72	0.36	-0.72	0.36	-

[a] Debyes

Relevant geometrical parameters of the stationary points (distances in Å and angles in degrees) for the HO^--promoted decomposition of (*N*-Cl),*N*-methylethanolamine. Atom labels are the same as in Fig. 2. Superscripts to values refer to the respective parameters, as indicated in left column.

	Hofmann Elim.	**Zaitsev Elim.**	**Bimol. Fragm.**	**Intram. Elim.**
		R		
H_T-C_1[c]/C_2[d]/O[e]	1.095[c]	1.097[d]	-	1.095[c]/4.783[e]
C_1-N		1.465		
N-Cl		1.761		
N-C_2		1.469		
C_2-C_3		1.516		
C_3-O		1.423		
O-H_O		0.970		
		RIC		
O_{OH}-H_T[a]/H_O[b]	1.978[a]	2.302[a]	1.511[b]	1.465[b]
H_T-C_1[c]/C_2[d]/O[e]	1.095[c]	1.092[d]	-	1.087[c]/2.218[e]
C_1-N	1.473	1.478	1.476	1.472
N-Cl	1.778	1.773	1.778	1.782
N-C_2	1.486	1.482	1.480	1.480
C_2-C_3	1.520	1.517	1.530	1.530
C_3-O	1.437	1.437	1.408	1.404
O-H_O	0.970	0.970	1.036	1.051
H_{WO}-O_{OH}	1.452	1.063	1.518	1.599
H_{WN}-N	1.772	1.770	1.864	1.877
H_O-O_{WN}	2.058	2.122	-	-
O_{OH}-H_T[a]/H_O[b]-C_1[c]/C_2[d]/O[e]	152.31[ac]	166.07[ad]	168.51[be]	169.62[be]
		TS		
O_{OH}-H_T[a]/H_O[b]	1.316[a]	1.108[a]	1.019[b]	1.021[b]
H_T-C_1[c]/C_2[d]/O[e]	1.296[c]	1.569[d]	-	1.264[c]/1.377[e]
C_1-N	1.415	1.470	1.455	1.390
N-Cl	1.967	1.866	2.126	2.048
N-C_2	1.477	1.455	1.362	1.441
C_2-C_3	1.525	1.492	1.804	1.561
C_3-O	1.427	1.470	1.302	1.390
O-H_O	0.976	0.971	1.560	1.549
H_{WO}-O_{OH}	1.625	1.754	1.804	1.816
H_{WN}-N	1.680	1.736	1.877	1.890
H_O-O_{WN}	1.928	2.255	-	-
O_{OH}-H_T[a]/H_O[b]-C_1[c]/C_2[d]/O[e]	170.29[ac]	174.15[ad]	175.92[be]	176.91[be]
		PIC		
O_{OH}-H_T[a]/H_O[b]	0.974[a]	0.967[a]	0.972[b]	0.985[b]
H_T-C_1[c]/C_2[d]/O[e]	3.303[c]	2.511[d]	-	3.328[c]/0.974[e]
C_1-N	1.285	1.466	1.464	1.285
N-Cl	4.256	3.965	4.169	4.193
N-C_2	1.466	1.287	1.285	1.468
C_2-C_3	1.519	1.507	3.650	1.516
C_3-O	1.427	1.420	1.232	1.449
O-H_O	0.974	0.981	1.995	1.736
H_{WO}-O_{OH}	2.850	2.319	1.827	1.882
H_{WN}-N	1.757	1.963	5.137	3.716
H_O-O_{WN}	1.969	6.012	-	-
O_{OH}-H_T[a]/H_O[b]-C_1[c]/C_2[d]/O[e]	88.37[ac]	144.49[ad]	168.69[be]	174.59[be]
		P		
O_{OH}-H_T[a]/H_O[b]	0.963[a]	0.963[a]	0.963[b]	0.963[b]
H_T-C_1[c]/C_2[d]/O[e]	-	-	-	3.570[c]/0.969[e]
C_1-N	1.280	1.462	1.456	1.280
N-C_2	1.458	1.283	1.279	1.458
C_2-C_3	1.519	1.513	-	1.519
C_3-O	1.422	1.425	1.223	1.422
O-H_O	0.969	0.965	-	-

Optimized geometries of all structures used in the paper

All the structures obtained following full geometry optimization (without any geometrical restriction) at MP2=full/6-31++G** computational level, as were used along the paper are appended here. The geometries are specified by Cartesian coordinates, gas phase computed total energies in hartrees (atomic units) are also indicated.

Common species

(*N*-Cl),*N*-methylethanolamine

C	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.46490
C	1.36422	0.00000	2.01028
C	1.32499	-0.32634	3.49053
O	0.64800	-1.55828	3.71107
Cl	-0.83190	1.45367	2.01017
H	0.46161	-0.93345	-0.31553
H	0.55175	0.84579	-0.42259
H	-1.02615	0.02713	-0.35389
H	1.88124	-0.80555	1.48739
H	1.88761	0.94517	1.81959
H	2.33794	-0.45231	3.86767
H	0.84943	0.48611	4.04491
H	-0.15680	-1.51617	3.17160

E -707.9818753

Water

O	0.00000	0.00000	0.00000
H	0.00000	0.00000	0.96279
H	0.92826	0.00000	-0.25553

E -76.2362086

Hydroxyl ion

O	0.00000	0.00000	0.00000
H	0.00000	0.00000	0.97044

E -75.6053027

Chloride ion

E -459.6814648

Hofmann Elimination

RIC

C	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.47260
C	1.38540	0.00000	2.01020
C	1.90630	1.42563	2.09217
O	1.30782	2.16379	3.17000
Cl	-0.81783	-1.48090	2.02027
H	0.61018	0.84131	-0.34550
H	-1.02703	0.09632	-0.34780
H	0.44467	-0.91599	-0.39569
H	1.35176	-0.40851	3.01863
H	2.04778	-0.59556	1.37535
H	2.96997	1.36769	2.31874
H	1.80815	1.92776	1.12858
H	0.39984	2.39126	2.91426
O	2.26850	1.60672	-1.10539
H	2.73537	2.36991	-1.47058
H	3.14958	0.54109	-0.66181
O	3.70070	-0.29280	-0.30216
H	3.85010	-0.82941	-1.08804
H	-1.07065	1.28759	2.05198
O	-1.57203	2.05986	2.42691
H	-2.03323	1.69968	3.19239

E -936.1588039

TS

C	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.41507
C	1.37390	0.00000	1.95818
C	1.88981	1.43160	2.05056
O	1.34641	2.16919	3.14473
Cl	-0.76275	-1.67374	2.11247
H	0.09864	-1.20399	-0.46887
H	0.93655	0.40120	-0.38467
H	-0.87551	0.52092	-0.38677
H	1.35691	-0.40700	2.96687
H	2.03714	-0.60872	1.33541
H	2.96459	1.39105	2.22875
H	1.72198	1.95566	1.10550
H	0.37456	2.18640	3.05908
O	0.40919	-2.41781	-0.87200
H	-0.08430	-3.01424	-0.29062
H	1.98872	-2.33111	-0.50044
O	2.97083	-2.18256	-0.31629
H	3.39046	-2.33551	-1.16901
H	-1.04176	1.06265	2.19522
O	-1.48364	1.79252	2.73136
H	-1.96308	1.32291	3.42314

E -936.1315274

PIC

C	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.28509
C	1.31282	0.00000	1.93753
C	1.34664	1.02483	3.05822
O	0.57444	0.66088	4.20172
Cl	3.30567	-0.55023	-1.33836
H	1.48728	-1.67584	-2.42654
H	-0.95417	-0.00607	-0.51552
H	0.91493	-0.01368	-0.58846
H	1.47239	-0.99330	2.35877
H	2.10919	0.19913	1.21444
H	2.37146	1.12128	3.41553
H	1.03059	1.99941	2.66966
H	-0.35972	0.58190	3.93818
O	0.71105	-2.26310	-2.45891
H	0.80090	-2.74386	-1.62273
H	2.59916	-3.55923	0.24483
O	1.93919	-2.85877	0.19895
H	2.43307	-2.09844	-0.19349
H	-1.42557	0.04146	2.31065
O	-2.07008	0.15185	3.06353
H	-2.38849	-0.73602	3.25921

E -936.2588305

Imine

C	-0.04943	0.00240	0.09230
N	0.03762	-0.04190	1.36837
C	1.37501	-0.00371	1.94751
C	1.37886	1.03395	3.05742
O	0.43437	0.70367	4.06835
H	-1.02908	-0.01230	-0.36945
H	0.82239	0.05120	-0.56499
H	1.57608	-0.98173	2.38712
H	2.14863	0.22209	1.20220
H	2.35217	1.06722	3.54316
H	1.16884	2.02147	2.63387
H	-0.39690	0.51201	3.60932

E -247.7870989

Zaitsev Elimination

RIC

C	-0.81164	0.27228	-1.46714
N	-0.89926	0.21420	0.00686
C	0.43266	0.07129	0.64149
C	1.36763	1.18408	0.20541
O	0.80971	2.50451	0.29904
Cl	-1.83572	-1.22070	0.46083
H	-0.11181	-0.46356	-1.87469
H	-0.44836	1.27282	-1.69646
H	-1.81738	0.16414	-1.86682
H	0.26219	0.11484	1.72061
H	0.91079	-0.87931	0.39571
H	2.26227	1.10136	0.83024
H	1.66828	1.01564	-0.82524
H	0.17024	2.53659	1.02724
O	2.38732	-2.58702	-0.05469
H	1.90241	-3.39376	-0.25972
H	2.23474	-1.97192	-0.90825
O	1.88744	-1.09060	-2.00616
H	2.53019	-1.19341	-2.72106
H	-1.64372	1.52399	0.93655
O	-1.84951	2.23525	1.60301
H	-2.22935	1.76203	2.35149

E -936.1542446

TS

C	0.00155	0.00837	-0.00044
N	-0.00018	0.00106	1.46972
C	1.34113	0.00344	2.03248
C	2.22641	1.01689	1.38787
O	1.72170	2.39455	1.29862
Cl	-0.84658	-1.59607	1.93465
H	0.66599	-0.75183	-0.42029
H	0.32592	1.00177	-0.30630
H	-1.01366	-0.15948	-0.35092
H	1.23686	0.22001	3.10279
H	2.02621	-1.38453	1.77722
H	3.15722	1.03609	1.96154
H	2.47996	0.76289	0.35722
H	0.99917	2.47554	1.94200
O	2.45494	-2.36724	1.49823
H	1.69995	-2.96835	1.55568
H	3.23948	-2.25549	-0.06613
O	3.66768	-2.07545	-0.94075
H	3.70946	-1.11426	-0.97626
H	-0.84465	1.31787	2.22255
O	-1.10865	2.16571	2.68170
H	-1.24217	1.90482	3.59951

E -936.1290373

PIC

C	-0.07544	0.62747	-0.23350
N	0.31773	0.70623	1.17674
C	1.57148	0.83501	1.43559
C	2.71067	0.91216	0.45140
O	3.96109	0.76658	1.10789
Cl	1.58273	-2.60364	-0.60181
H	0.37659	1.42757	-0.82376
H	-1.15676	0.71665	-0.29382
H	0.23383	-0.33696	-0.64226
H	1.86102	0.87107	2.48533
H	0.40067	-1.25340	2.19388
H	2.56731	0.15099	-0.32065
H	2.71720	1.89235	-0.03353
H	3.99077	-0.16857	1.40398
O	0.50758	-2.19993	2.35817
H	0.68972	-2.53802	1.45549
H	2.82185	-2.05928	2.40955
O	3.51473	-1.90822	1.74918
H	3.07353	-2.20963	0.92171
H	-1.09126	0.41526	2.51189
O	-1.75281	0.10237	3.16116
H	-1.60122	-0.85001	3.20237

E -936.2665011

Imine

C	-0.08654	0.63623	-0.23321
N	0.31226	0.63169	1.17345
C	1.56259	0.75271	1.43264
C	2.70204	0.89955	0.44882
O	3.97028	0.86522	1.09864
H	0.51788	1.29394	-0.86129
H	-1.12255	0.95556	-0.29519
H	-0.02669	-0.37810	-0.63176
H	1.85445	0.75532	2.48179
H	2.63533	0.13276	-0.32913
H	2.65658	1.87091	-0.04418
H	4.09989	-0.01525	1.47284

E -247.7688985

Bimolecular Fragmentation

RIC

C	0.83982	0.50719	-0.28913
N	0.49289	0.03229	1.06464
C	1.67962	0.02184	1.94883
C	2.12231	1.43998	2.31645
O	3.24471	1.36212	3.16296
Cl	-0.06065	-1.64905	0.89856
H	1.72375	0.00430	-0.68668
H	1.04117	1.57230	-0.20011
H	-0.02385	0.37044	-0.93537
H	1.40369	-0.49084	2.86860
H	2.51300	-0.49970	1.47403
H	1.31061	1.95172	2.84043
H	2.36404	2.00608	1.41200
H	4.01866	1.10674	2.52266
O	4.92601	0.69859	1.38563
H	5.62484	1.34133	1.21019
H	4.40226	0.03500	0.12454
O	4.00130	-0.47216	-0.68496
H	4.47318	-1.31169	-0.68712
H	-1.06388	0.88894	1.62634
O	-1.95799	1.23929	1.84960
H	-2.46605	0.44780	2.05616

E -936.1737779

TS

C	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.45537
C	1.25325	0.00000	1.98847
C	1.99394	1.61296	1.66465
O	3.06967	1.70224	2.39214
Cl	-0.99685	-1.83414	1.85878
H	0.69292	-0.73344	-0.42508
H	0.30234	1.00235	-0.31895
H	-1.00498	-0.19138	-0.36284
H	1.26572	-0.00516	3.07220
H	1.99973	-0.66070	1.53924
H	1.16219	2.28850	1.91114
H	2.13150	1.52507	0.57312
H	4.27692	0.99065	1.70770
O	5.02015	0.47325	1.23955
H	5.18957	-0.28783	1.80394
H	6.38822	1.13474	0.26796
O	7.06281	1.41902	-0.38521
H	6.57379	1.44944	-1.21310
H	-1.45088	0.97867	2.13259
O	-2.31648	1.34755	2.41966
H	-2.80747	0.54987	2.64698

E -936.1472443

PIC

C	1.08577	-0.48921	-0.67121
N	1.93779	-0.66758	0.50561
C	1.33120	-0.97288	1.59643
C	0.79363	2.62648	1.87936
O	1.96966	2.99049	1.84471
Cl	-2.02178	0.40848	1.24400
H	0.02226	-0.53315	-0.43169
H	1.34651	-1.25313	-1.40369
H	1.31442	0.48010	-1.11314
H	1.91983	-1.09337	2.49835
H	0.24960	-1.07253	1.66320
H	0.03560	3.22129	2.39877
H	0.43667	1.71818	1.39219
H	3.45564	1.89927	1.08317
O	4.04047	1.24398	0.66683
H	3.47608	0.44502	0.59094
H	5.85712	1.20295	0.86018
O	6.83080	1.24541	0.76736
H	6.95163	1.57149	-0.12966
H	-0.89757	0.80354	4.52918
O	-0.31485	0.74597	3.76502
H	-0.92742	0.60917	3.00032

E -936.2314099

Imine

C	-0.11543	-0.21895	-0.14125
N	0.80971	0.41803	0.78456
C	1.40830	-0.35265	1.61126
H	-0.18120	-1.30434	-0.00793
H	0.20386	-0.00019	-1.15819
H	-1.10160	0.22047	-0.00568
H	2.10577	0.07648	2.31992
H	1.25381	-1.43511	1.64348

E -133.5421987

Formaldehyde

C	2.37917	2.80292	1.70206
O	3.22790	2.23608	2.37579
H	1.43750	3.15947	2.13973
H	2.52174	2.98695	0.62963

E -114.2008827

Intramolecular Elimination

RIC

C	-0.12219	0.45150	-0.27082
N	0.35517	-0.04416	1.02988
C	1.82859	0.03343	1.14399
C	2.29617	1.48241	1.29613
O	2.19842	2.26415	0.13364
Cl	-0.09287	-1.76643	1.12998
H	0.35034	-0.07320	-1.10398
H	0.16524	1.49857	-0.31540
H	-1.20402	0.34038	-0.30751
H	2.10019	-0.50828	2.05085
H	2.31953	-0.42818	0.28379
H	1.71360	1.96338	2.08793
H	3.33614	1.41203	1.64945
H	2.68110	1.72029	-0.62532
O	3.29721	0.75044	-1.53441
H	3.57278	1.11689	-2.38428
H	-0.61819	0.64813	2.47772
O	-1.19042	0.85175	3.25355
H	-1.46751	-0.01817	3.56008
H	4.48019	-0.09402	-0.86799
O	5.21810	-0.57083	-0.35550
H	5.59423	0.13032	0.18672

E -936.1743736

TS

C	-0.03397	0.17140	-0.15337
N	0.25790	-0.05759	1.18581
C	1.68536	-0.06739	1.38505
C	2.19318	1.39313	1.16954
O	1.87476	1.90416	-0.08343
Cl	-0.37197	-1.90490	1.80568
H	0.39494	-0.54188	-0.86708
H	0.72589	1.17228	-0.28650
H	-1.08926	0.35810	-0.33541
H	1.91572	-0.37503	2.40389
H	2.19564	-0.73227	0.67524
H	1.77904	2.00642	1.98167
H	3.28187	1.33182	1.31313
H	3.03008	1.74343	-1.10232
O	3.82702	1.63693	-1.73170
H	4.23309	2.50933	-1.76349
H	-0.77836	0.81533	2.50351
O	-1.36200	1.07814	3.25058
H	-1.67921	0.22370	3.56413
H	4.87148	0.25215	-1.19425
O	5.37426	-0.51969	-0.85490
H	4.70857	-1.05283	-0.40814

E -936.1562176

PIC

C	-1.01268	-0.31945	0.02768
N	0.06972	0.25577	-0.35887
C	1.27039	-0.07038	0.41946
C	1.86226	1.24558	0.88487
O	2.04298	2.12747	-0.25014
Cl	-0.37353	-2.11057	3.07410
H	-1.05066	-1.01224	0.86838
H	1.25181	1.97580	-0.79719
H	-1.92800	-0.08689	-0.50905
H	1.05856	-0.72720	1.26692
H	1.97366	-0.56106	-0.25850
H	1.20183	1.70923	1.61553
H	2.84684	1.10435	1.32846
H	3.59850	2.05941	-1.01702
O	4.51876	2.02505	-1.36722
H	4.95269	2.80252	-1.00056
H	-1.09047	1.13275	3.83370
O	-0.24346	0.97044	3.40543
H	-0.21399	-0.01432	3.33683
H	5.40988	0.40128	-1.03317
O	5.87825	-0.42330	-0.80603
H	5.25505	-0.92003	-0.26590

E -936.2477836

Imine

Same species as for Hofmann Elimination