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

Supplementary Information

Ion chemistry at elevated ion-molecule interaction energies in a selected ion flow-drift tube: reactions of H_3O^+, NO^+ and O_2^+ with saturated aliphatic ketones

Anatolii Spesyvyi, David Smith and Patrik Španěl

J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, 18223 Prague 8, Czech Republic.

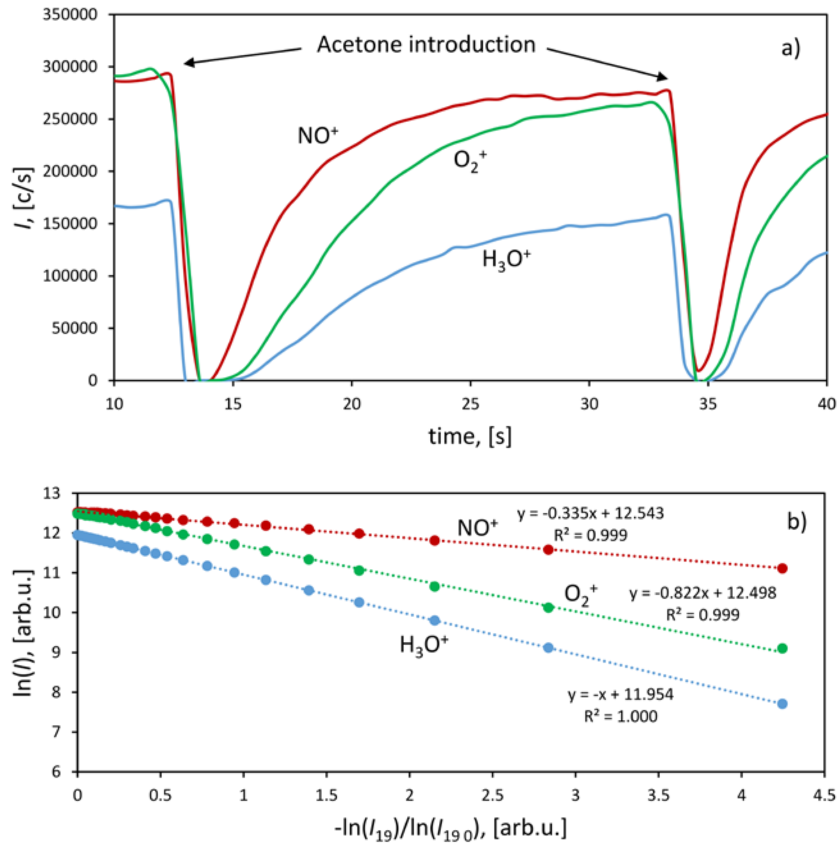

Fig. S1. Method of measurement of the rate coefficients for the NO^+ and O_2^+ acetone reactions relatively to the H_3O^+ reaction at *E/N* of 14.3 Td and drift tube pressure of 2 mbar. A Multi Ion Monitoring time profile of three reagent ion count rates obtained whilst introducing a variable acetone concentration into the inlet system is shown in a) and the corresponding ion signal decay plots are shown in b), where dotted lines represent linear regression fits. The slopes of these lines define relative reaction rate coefficients as $k\{NO^+\}=0.335k\{H_3O^+\}$ and $k\{O_2^+\}=0.822k\{H_3O^+\}$.

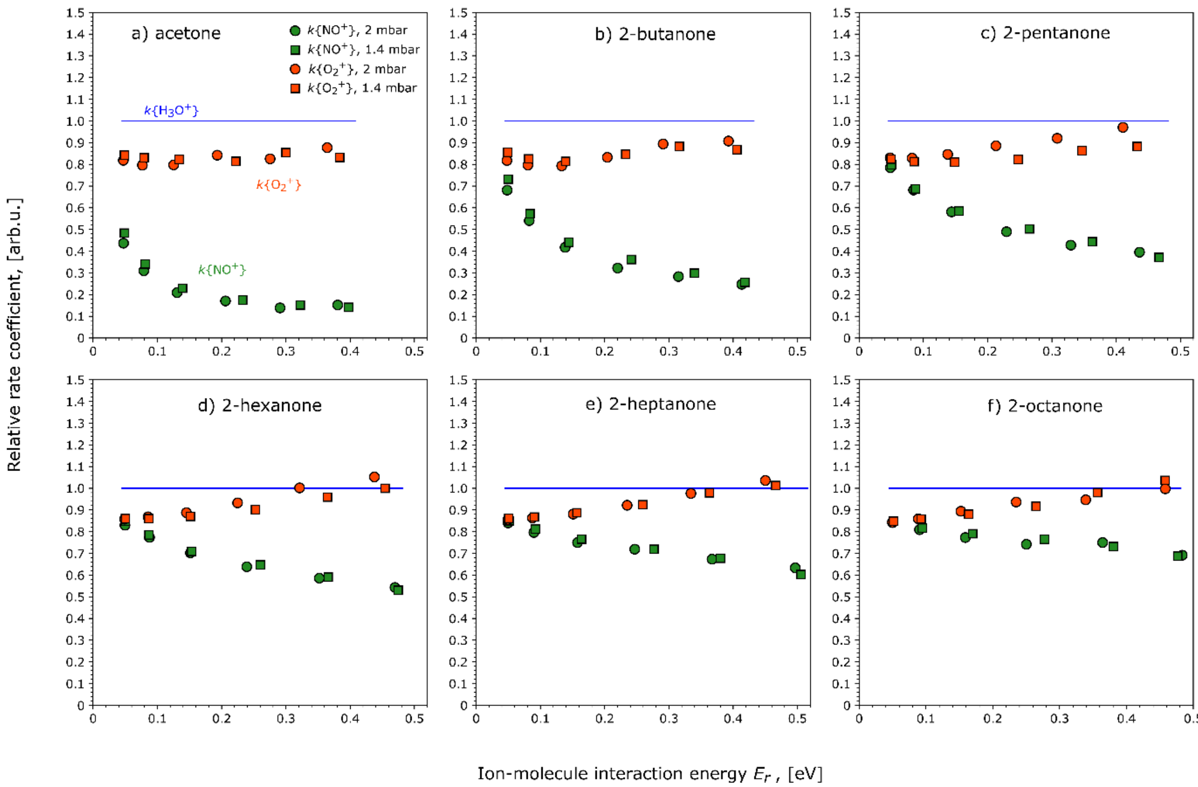

Fig. S2. Plots of the dependence of the experimentally derived relative reaction rate coefficients, *k*, for the NO^+ and O_2^+ ketone reactions with respect to the H_3O^+ rate coefficients as functions of the ion-molecule interaction energy E_r obtained at a flow-drift tube pressure of 1.4 (filled squares) and 2 mbar (filled circles).

Table S1. Rate coefficients for the NO^+ and O_2^+ reactions with the ketones indicated as determined experimentally relatively to H_3O^+ rate coefficients at the six *E/N* values indicated for drift tube pressures of 1.4 and 2 mbar. Note that relative values are shown in Italic.

1.4 mbar, 45 mL/min, 1.5 mL/min							2 mbar, 75mL/min, 3mL/min						
E/N, Td	E_r, eV	$k\{NO^+\}$, 10^{-9} cm^3s^{-1}		E_r, eV	$k\{O_2^+\}$, 10^{-9} cm^3s^{-1}		*E/N*, Td	E_r, eV	$k\{NO^+\}$, 10^{-9} cm^3s^{-1}		E_r, eV	$k\{O_2^+\}$, 10^{-9} cm^3s^{-1}	
Acetone													
6.5	0.05	**1.74**	*0.48*	0.05	**3.27**	*0.84*	7.2	0.05	**1.93**	*0.44*	0.05	**3.36**	*0.82*
13.3	0.08	**1.15**	*0.34*	0.08	**2.97**	*0.83*	14.3	0.08	**1.27**	*0.31*	0.08	**3.09**	*0.80*
20.5	0.14	**0.73**	*0.23*	0.13	**2.78**	*0.82*	21.4	0.13	**0.80**	*0.21*	0.13	**2.87**	*0.80*
28.6	0.23	**0.56**	*0.17*	0.22	**2.78**	*0.81*	28.4	0.21	**0.58**	*0.17*	0.19	**2.69**	*0.84*
35.0	0.32	**0.43**	*0.15*	0.30	**2.59**	*0.85*	35.4	0.29	**0.48**	*0.14*	0.28	**2.68**	*0.83*
40.6	0.40	**0.45**	*0.14*	0.38	**2.61**	*0.83*	42.3	0.38	**0.42**	*0.15*	0.36	**2.47**	*0.88*
2-butanone													
6.5	0.05	**2.80**	*0.73*	0.05	**3.36**	*0.86*	7.2	0.05	**3.01**	*0.68*	0.05	**3.51**	*0.82*
13.3	0.08	**2.08**	*0.57*	0.08	**3.06**	*0.83*	14.3	0.08	**2.20**	*0.54*	0.08	**3.17**	*0.80*
20.5	0.14	**1.51**	*0.44*	0.14	**2.87**	*0.81*	21.4	0.14	**1.59**	*0.42*	0.13	**2.94**	*0.79*
28.6	0.24	**1.11**	*0.36*	0.23	**2.86**	*0.85*	28.4	0.22	**1.24**	*0.32*	0.20	**2.90**	*0.83*
35.0	0.34	**0.92**	*0.30*	0.32	**2.89**	*0.88*	35.4	0.31	**0.97**	*0.28*	0.29	**2.86**	*0.89*
40.6	0.42	**0.75**	*0.26*	0.41	**2.76**	*0.87*	42.3	0.41	**0.78**	*0.25*	0.39	**2.64**	*0.91*
2-pentanone													
6.5	0.05	**3.17**	*0.80*	0.05	**3.35**	*0.82*	7.2	0.05	**3.22**	*0.78*	0.05	**3.33**	*0.83*
13.3	0.09	**2.59**	*0.69*	0.09	**3.15**	*0.81*	14.3	0.08	**2.61**	*0.68*	0.08	**3.09**	*0.83*
20.5	0.16	**2.10**	*0.59*	0.15	**3.06**	*0.81*	21.4	0.14	**2.11**	*0.58*	0.14	**2.93**	*0.85*
28.6	0.27	**1.67**	*0.50*	0.25	**3.03**	*0.82*	28.4	0.23	**1.72**	*0.49*	0.21	**2.81**	*0.89*
35.0	0.36	**1.35**	*0.44*	0.35	**2.91**	*0.86*	35.4	0.33	**1.40**	*0.43*	0.31	**2.73**	*0.92*
40.5	0.47	**1.15**	*0.37*	0.43	**2.81**	*0.88*	42.3	0.44	**1.07**	*0.40*	0.41	**2.56**	*0.97*
2-hexanone													
6.5	0.05	**3.44**	*0.85*	0.05	**3.55**	*0.86*	7.2	0.05	**3.51**	*0.83*	0.05	**3.56**	*0.86*
13.3	0.09	**3.04**	*0.78*	0.09	**3.41**	*0.86*	14.3	0.09	**3.08**	*0.77*	0.09	**3.37**	*0.87*
20.5	0.15	**2.62**	*0.71*	0.15	**3.31**	*0.87*	21.4	0.15	**2.64**	*0.70*	0.15	**3.24**	*0.89*
28.6	0.26	**2.24**	*0.65*	0.25	**3.27**	*0.90*	28.4	0.24	**2.27**	*0.64*	0.22	**3.16**	*0.93*
35.0	0.37	**1.87**	*0.59*	0.36	**3.19**	*0.96*	35.4	0.35	**1.88**	*0.59*	0.32	**3.06**	*1.00*
40.6	0.47	**1.56**	*0.53*	0.45	**3.03**	*1.00*	42.3	0.47	**1.53**	*0.54*	0.44	**2.88**	*1.05*

1.4 mbar, 45 mL/min, 1.5 mL/min							2 mbar, 75mL/min, 3mL/min						
E/N, Td	E_r, eV	*k*{NO^+}, 10^{-9} cm^3s^{-1}		E_r, eV	*k*{O_2^+}, 10^{-9} cm^3s^{-1}		*E/N*, Td	E_r, eV	*k*{NO^+}, 10^{-9} cm^3s^{-1}		E_r, eV	*k*{O_2^+}, 10^{-9} cm^3s^{-1}	
						2-heptanone							
6.5	0.05	**3.45**	*0.85*	0.05	**3.52**	*0.86*	7.2	0.05	**3.49**	*0.84*	0.05	**3.54**	*0.86*
13.3	0.09	**3.12**	*0.81*	0.09	**3.39**	*0.87*	14.3	0.09	**3.19**	*0.80*	0.09	**3.40**	*0.86*
20.5	0.16	**2.79**	*0.77*	0.16	**3.28**	*0.89*	21.4	0.16	**2.85**	*0.75*	0.15	**3.30**	*0.88*
28.5	0.28	**2.48**	*0.72*	0.26	**3.18**	*0.92*	28.4	0.25	**2.48**	*0.72*	0.23	**3.19**	*0.92*
35.0	0.38	**2.07**	*0.68*	0.36	**3.00**	*0.98*	35.3	0.37	**2.08**	*0.67*	0.33	**3.01**	*0.98*
40.5	0.51	**1.79**	*0.60*	0.47	**2.93**	*1.01*	42.3	0.50	**1.70**	*0.63*	0.45	**2.86**	*1.04*
						2-octanone							
6.5	0.05	**3.61**	*0.85*	0.05	**3.62**	*0.85*	7.1	0.05	**3.64**	*0.84*	0.05	**3.64**	*0.84*
13.3	0.09	**3.32**	*0.82*	0.09	**3.53**	*0.86*	14.3	0.09	**3.35**	*0.81*	0.09	**3.52**	*0.86*
20.4	0.17	**3.01**	*0.79*	0.16	**3.48**	*0.88*	21.4	0.16	**3.08**	*0.77*	0.15	**3.43**	*0.89*
28.5	0.28	**2.66**	*0.76*	0.26	**3.36**	*0.92*	28.4	0.25	**2.74**	*0.74*	0.23	**3.29**	*0.94*
34.9	0.38	**2.41**	*0.73*	0.36	**3.04**	*0.98*	35.3	0.36	**2.35**	*0.75*	0.34	**3.15**	*0.95*
40.4	0.48	**2.05**	*0.69*	0.46	**2.96**	*1.04*	42.2	0.48	**2.04**	*0.69*	0.46	**3.08**	*1.00*

Table S2. Product ion distributions for the NO^+ and O_2^+ reactions with the ketones indicated at six reduced electric field strengths *E/N* in the range of 7-44 Td, drift tube pressure of 2 mbar and corresponding reagent ion-neutral ketone interaction energies E_r.

Acetone

NO^+

E/N, Td	E_r, eV	m/z 43	m/z 58	m/z 88
7.2	0.05	1%	4%	95%
14.5	0.09	5%	11%	84%
21.7	0.15	5%	15%	79%
28.8	0.23	14%	23%	63%
35.9	0.33	35%	23%	42%
42.9	0.47	68%	8%	23%

O_2^+

E/N, Td	E_r, eV	m/z 43	m/z 58
7.3	0.05	27%	73%
14.7	0.08	28%	72%
21.8	0.13	31%	69%
29.0	0.20	41%	59%
36.0	0.28	65%	35%
43.1	0.38	87%	13%

2-butanone

NO^+

E/N, Td	E_r, eV	m/z 43	m/z 57	m/z72	m/z102
7.2	0.05	1%	1%	1%	97%
14.5	0.09	2%	2%	5%	92%
21.7	0.16	1%	2%	7%	90%
28.8	0.25	3%	7%	12%	77%
35.8	0.34	6%	16%	17%	61%
42.9	0.49	8%	26%	19%	47%

O_2^+

E/N, Td	E_r, eV	m/z 43	m/z 57	m/z 72
7.3	0.05	17%	22%	61%
14.6	0.08	19%	23%	58%
21.9	0.14	20%	24%	56%
29.1	0.22	22%	29%	49%
36.1	0.30	24%	36%	40%
43.1	0.40	25%	41%	34%

2-pentanone

NO^+

E/N, Td	E_r, eV	m/z 58	m/z 71	m/z 86	m/z 116
7.3	0.05	0%	1%	1%	98%
14.6	0.09	1%	1%	4%	93%
21.8	0.16	2%	1%	8%	89%
28.9	0.26	3%	2%	15%	80%
36.1	0.35	6%	3%	20%	71%
43.1	0.49	9%	4%	26%	60%

O_2^+

E/N, Td	E_r, eV	m/z 43	m/z 58	m/z 71	m/z 86
7.3	0.05	16%	21%	19%	44%
14.6	0.09	17%	24%	19%	41%
21.7	0.15	18%	24%	19%	39%
28.9	0.24	19%	24%	19%	38%
36.1	0.35	21%	24%	20%	35%
43.1	0.43	23%	25%	20%	31%

2-hexanone

NO^+

E/N, Td	E_r, eV	m/z 58	m/z 85	m/z 100	m/z 130
7.4	0.05	1%	0%	2%	97%
14.8	0.10	4%	1%	7%	88%
22.0	0.17	4%	1%	11%	84%
29.2	0.28	7%	1%	17%	75%
36.4	0.43	13%	2%	27%	58%
43.5	0.55	21%	5%	37%	37%

O_2^+

E/N, Td	E_r, eV	m/z 43	m/z 58	m/z 71	m/z 99	m/z 114
7.3	0.05	9%	46%	7%	8%	30%
14.6	0.09	7%	49%	6%	8%	31%
21.9	0.15	6%	49%	7%	7%	31%
29.0	0.24	5%	48%	7%	8%	33%
36.1	0.33	6%	49%	8%	8%	29%
43.1	0.45	6%	51%	9%	8%	27%

				NO+							O2+				
							2-heptanone								
E/N, Td	*E*$_r$, eV	m/z 58	m/z 72	m/z 85	m/z 99	m/z 114	m/z 144	*E/N*, Td	*E*$_r$, eV	m/z 43	m/z 58	m/z 71	m/z 99	m/z 114	
7.4	0.05	2%	0%	0%	1%	4%	93%	7.3	0.05	9%	46%	7%	8%	30%	
14.9	0.09	10%	1%	1%	1%	12%	75%	14.6	0.09	7%	49%	6%	8%	31%	
22.2	0.17	7%	2%	2%	1%	21%	67%	21.9	0.15	6%	49%	7%	7%	31%	
29.5	0.27	10%	1%	2%	1%	31%	55%	29.0	0.24	5%	48%	7%	8%	33%	
36.6	0.37	13%	3%	2%	3%	35%	44%	36.1	0.33	6%	49%	8%	8%	29%	
43.9	0.53	18%	4%	3%	2%	41%	31%	43.1	0.45	6%	51%	9%	8%	27%	
							2-octanone								
E/N, Td	*E*$_r$, eV	m/z 58	m/z 85	m/z 98	m/z 113	m/z 128	m/z 158	*E/N*, Td	*E*$_r$, eV	m/z 43	m/z 58	m/z 71	m/z 85	m/z 113	m/z 128
7.4	0.05	1%	0%	0%	1%	0%	98%	7.3	0.05	7%	48%	8%	4%	5%	28%
14.9	0.10	5%	0%	1%	1%	9%	83%	14.7	0.09	5%	48%	7%	5%	5%	30%
22.2	0.18	6%	1%	2%	2%	17%	72%	21.8	0.15	4%	49%	7%	5%	6%	30%
29.5	0.29	7%	1%	3%	3%	24%	61%	29.0	0.25	3%	46%	7%	6%	6%	32%
36.8	0.41	11%	2%	3%	4%	31%	48%	36.1	0.34	4%	47%	7%	5%	7%	30%
44.0	0.55	13%	3%	4%	6%	33%	42%	43.1	0.46	4%	48%	8%	6%	8%	26%