Supporting Information for

Temperature and Pressure Dependences of the Reactions of Fe^+ with Methyl Halides CH_3X (X = Cl, Br, I): Experiments and Kinetic Modeling Results

Shaun G. Ard,[1] Nicholas S. Shuman,[1] Nicholas R. Keyes[2], Albert A. Viggiano,[1*] Hua Guo,[2] and Jürgen Troe[3]

[1]*Air Force Research Laboratory, Space Vehicle Directorate, Kirtland AFB, Albuquerque, NM 87117, USA*

[2]*Department of Chemistry and Chemical Biology, University of New Mexico,Albuquerque, NM 87131, USA*

[3]*Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany and Max-Planck-Institut für Biophysikalische Chemie, D-37077 Göttingen, Germany*

(S1) Vibrational frequencies and rotational constants of stationary points on the potential energy surfaces

$Fe^+ + CH_3I$

	RCi (cm^{-1})	*TSi (cm^{-1})*	*IMi (cm^{-1})*	*RCs (cm^{-1})*	*TSs (cm^{-1})*	*IMs (cm^{-1})*
Quartet	70.12	-187.29	109.36	97.81	-198.05	36.99
	96.62	165.10	126.13	122.68	56.15	44.30
	187.39	195.06	280.94	162.08	95.87	68.32
	459.98	449.72	404.55	603.06	391.32	503.76
	884.59	855.39	591.64	961.16	726.13	610.26
	898.97	967.81	626.14	985.70	733.62	612.40
	1260.76	1333.90	1123.19	1188.94	756.25	1104.57
	1426.02	1341.44	1327.15	1395.70	1346.26	1369.23
	1429.65	1496.21	1407.11	1405.91	1356.00	1374.39
	3082.10	2566.52	2911.61	2826.90	2989.13	3020.12
	3223.81	3128.89	3135.49	2957.65	3159.76	3154.84
	3235.98	3223.70	3217.22	2966.45	3163.38	3156.44
A	0.05	0.05	0.05	0.02	0.02	0.01
B	0.06	0.06	0.06	0.02	0.02	0.01
C	0.28	0.31	0.39	4.79	4.70	4.65
Sextet	51.67	-407.62	74.60	65.08	-396.65	33.40
	76.04	92.15	86.01	77.96	91.90	36.56
	140.44	125.71	256.62	108.16	101.91	41.64
	476.45	257.25	467.50	515.85	163.70	507.46
	894.87	469.99	494.12	923.68	752.15	563.27
	902.77	600.07	533.59	945.25	770.93	594.08
	1267.99	1007.08	1046.60	1121.59	799.50	1104.68
	1425.76	1305.16	1350.16	1413.23	1353.96	1187.28
	1432.10	1401.12	1370.27	1421.63	1355.36	1373.43
	3083.13	2845.53	3003.77	2958.40	3027.64	3019.66
	3224.22	3160.57	3138.25	3073.23	3215.79	3152.86
	3234.60	3270.28	3148.80	3098.99	3221.46	3154.28
A	0.04	0.05	0.04	0.02	0.02	0.01
B	0.05	0.07	0.04	0.02	0.02	0.01
C	0.27	0.20	0.68	4.93	4.66	4.67

$Fe^+ + CH_3Br$

	RCi (cm^{-1})	*TSi (cm^{-1})*	*IMi (cm^{-1})*	*RCs (cm^{-1})*	*TSs (cm^{-1})*	*IMs (cm^{-1})*
Quartet	89.76	-288.23	117.73	85.92	-227.16	18.75
	106.56	156.04	118.63	113.63	61.41	39.15
	174.04	193.53	330.91	172.20	115.56	41.43
	513.61	312.26	394.90	681.49	382.00	509.45
	956.02	746.48	583.13	1046.51	743.27	618.57
	973.10	811.81	624.86	1069.21	745.81	625.07
	1316.80	1192.22	1134.69	1300.85	806.15	1134.13
	1439.16	1394.87	1339.70	1428.30	1358.33	1380.26
	1443.87	1452.11	1417.76	1434.49	1368.33	1383.68
	3079.62	3049.25	2914.50	2800.20	2989.35	3007.34
	3214.80	3187.43	3124.77	2907.88	3140.57	3131.01
	3225.45	3217.56	3200.16	2916.81	3147.11	3133.19
A	0.06	0.07	0.07	0.03	0.02	0.02
B	0.07	0.10	0.08	0.03	0.02	0.02
C	0.37	0.27	0.40	4.79	4.68	4.44
Sextet	70.02	-398.32	67.50	33.69	-446.76	27.21
	87.50	64.60	91.74	44.03	117.64	41.32
	159.57	79.20	324.62	97.24	119.46	44.64
	526.89	288.71	442.73	617.33	178.59	511.56
	960.40	591.91	488.62	1004.95	818.71	600.55
	970.14	646.51	548.31	1007.65	829.25	602.47
	1319.33	1024.66	1049.93	1238.43	834.62	1112.11
	1438.76	1374.66	1355.95	1440.75	1364.96	1368.69
	1445.07	1417.51	1378.34	1442.23	1369.09	1372.66
	3078.04	3090.06	2992.71	2941.07	3026.91	3019.43
	3212.63	3260.72	3121.69	3042.13	3197.59	3153.57
	3220.23	3278.62	3133.19	3046.50	3203.30	3156.21
A	0.05	0.06	0.06	0.03	0.02	0.02
B	0.06	0.09	0.06	0.03	0.02	0.02
C	0.38	0.20	0.68	4.94	4.66	5.01

$Fe^+ + CH_3Cl$

	RCi (cm^{-1})	*TSi (cm^{-1})*	*IMi (cm^{-1})*	*RCs (cm^{-1})*	*TSs (cm^{-1})*	*IMs (cm^{-1})*
Quartet	97.46	-309.6	118.97	82.47	-286.65	23.81
	107.1	223.55	125.41	101.5	42.63	24.97

	265.04	323.16	359.36	202.74	57.88	62.89
	604.24	423.61	470.91	802.12	387.4	512.85
	1006.95	867.86	580.41	1096.6	722.92	614.21
	1022.79	983.9	617.54	1123.3	725.77	615.09
	1356.76	1307.48	1132.37	1379.97	831.01	1132.98
	1442.77	1361.46	1338.78	1436.24	1351.6	1379.56
	1450.5	1502.07	1416.18	1440.66	1363.71	1382.45
	3079.96	2276.17	2922.68	2766.89	2989.84	3008.78
	3213.78	3125.79	3126.99	2860.04	3138.01	3131.91
	3221.63	3221.26	3201.74	2869.4	3147.11	3134.32
A	0.08	0.11	0.10	0.07	0.05	0.09
B	0.09	0.15	0.13	0.07	0.07	0.10
C	0.60	0.39	0.42	0.61	0.25	0.73
Sextet	80.67	-65.33	52.72	28.32	-509.59	20.02
	99.65	42.99	99.47	35.59	98.01	32.02
	210.37	56.3	402.28	83.88	102.39	61.35
	609.31	159.66	461.99	754.92	212.58	514.54
	1008.09	171.84	466.03	1049.05	775.78	592.75
	1018.07	447.39	549.15	1050.67	781.84	595.47
	1354.51	772.97	1039.46	1324.26	842.25	1112.54
	1443.36	1390.93	1352.38	1448.57	1360.96	1367.5
	1450.59	1394	1375.86	1449.69	1363.42	1371.25
	3077.26	3098.28	2992.63	2933.37	3025.2	3020.23
	3211	3282.27	3124.52	3017.92	3193.92	3153.92
	3216.07	3286.84	3136.33	3019.97	3196.02	3156.54
A	0.05	0.04	0.03	0.04	0.04	0.03
B	0.05	0.04	0.03	0.04	0.04	0.03
C	4.81	4.68	5.00	5.02	4.66	5.01

(S2) Simplified decoupling of chemical activation and adduct stabilization

A crucial quantity in the kinetic modeling is the limiting high pressure rate constant $k_{Ass,\infty}$ of the association process, to be obtained either by extrapolation of k_{tot} to its high pressure limit or to be estimated by theoretical means. All rate constants are expressed as yields Y relative to $k_{Ass,\infty}$. The simplified approach of ref. 12 then "decouples" association from chemical activation (here leading to FeX^+ and/or $FeCH_3^+$ products), i.e. it considers association in the absence of chemical activation steps and chemical activation in the absence of association steps. The corresponding yields Y^* differ from the yields Y in the presence of coupling. The rationale for the decoupling is the fact that the yields Y^*can be interpreted in a much simpler way by statistical unimolecular rate theory than the yields Y. In the simplified approach of ref. 12, the Y and Y^* are related to each other in a number of approximate relationships. The most important ones are

$$Y_{CA}/(1 - Y_{Ass}) \approx k_{CA,0} / k_{Ass,\infty} \quad \text{(SI1)}$$

$$Y_{Ass}^* \approx Y_{Ass}/(1 - Y_{CA}) \quad \text{(SI2)}$$

$$Y_{CA}^* \approx Y_{CA}/(Y_{Ass} + Y_{CA}) \quad \text{(SI3)}$$

Once Y_{Ass}^* and Y_{CA}^* are optimized with eqs. (SI1) – (SI3), the inverse operation from Y_{Ass}^* and Y_{CA}^* leads to Y_{Ass} and Y_{CA} by the relationships

$$Y_{Ass} \approx Y_{Ass}^*(1 - Y_{CA}^*)/(1 - Y_{CA}^*/(1 - Y_{Ass}^*)) \quad \text{(SI4)}$$

$$Y_{CA} \approx Y_{CA}^* Y_{Ass}^*/(1 - Y_{CA}^*/(1 - Y_{Ass}^*)) \quad \text{(SI5)}$$

The modeling of the decoupled Y_{Ass}^* and Y_{CA}^* in terms of standard unimolecular rate theory requires the calculated molecular parameters of section S1 and needs only few other parameters to be adjusted (if necessary) such that the experimental Y_{Ass} and Y_{CA} are reproduced. On the one hand, this allows one to identify the most important parameters of the analysis and/or to validate the intrinsic mechanism of the reaction. On the other hand, extrapolations of Y_{Ass} and Y_{CA} into experimentally inaccessible ranges of conditions become possible.

Falloff curves for association in the form of $Y_{Ass}^*([M])$ are represented in the form given in of refs. 27 and 31 while modified Stern-Volmer plots of $Y_{CA}^*([M]^{-1})$ are approximated in the form of ref. 33, i.e. of eq. (17) of the main text,

$$Y_{CA}^* \approx [\, 1 + \gamma_c(E,J)\, Z\, [He] / \langle k(E,J) \rangle\,]^{-1} \quad \text{(SI6)}$$

where the collision efficiency $\gamma_c(E,J)$ is related to the average energy transferred per collision $\langle \Delta E \rangle$ by

$$\gamma_c(E,J)/(1 - \gamma_c(E,J)^2) \approx - \langle \Delta E \rangle\, s^*/(\langle E \rangle - E_0) \quad \text{(SI7)}$$

In this relationship it is assumed that $k(E,J)$ can be approximated by $k(E,J) \propto (E - E_0)^{s^*-1}$, while $\langle E \rangle$ is the average energy of the dissociating species directly after its formation. One should note that these representations of falloff curves and Stern-Volmer plots have been extracted from master equation simulations, e.g. in refs. 33 and 36. Nevertheless, a full master

equation simulation would appear desirable when the required detailed knowledge of intra- and intermolecular parameters is available. Unfortunately, this generally is not the case, in particular when rovibrational collisional transfer plays an important role such as this is the case in the present reactions.

The references for this section correspond to those given in the main text.

(S3) Modeled parameters for decoupled chemical activation and adduct stabilization

$Fe^+ + CH_3Cl \rightarrow FeCl^+ + CH_3$

$k_{Ass,0}^*/[He] \approx 2.0 \times 10^{-26} (T/300\ K)^{-3.0}\ cm^6\ s^{-1}$

$k_{cap,SuCh} \approx 2.08 \times 10^{-9} (T/300\ K)^{-0.33}\ cm^3\ s^{-1}$

$k_{Ass,\infty} \approx 0.8\ k_{cap,SuCh}$

$F_{cent}^* = 0.49\ (T/300\ K)^{-0.68}$

$k_{CA,\infty}^* \approx 5.0 \times 10^7 (T/300\ K)^1\ s^{-1}$

$k_{CA,0} \approx 1.9 \times 10^{-10} (T/300\ K)^{-0.8}\ cm^3\ s^{-1}$

$Fe^+ + CH_3Br \rightarrow FeBr^+ + CH_3$

$k_{Ass,0}^*/[He] \approx 5.2 \times 10^{-26} (T/300\ K)^{-3.0}\ cm^6\ s^{-1}$ (fine-tuned by multiplying with a factor 1.4)

$k_{cap,SuCh} \approx 1.78 \times 10^{-9} (T/300\ K)^{-0.32}\ cm^3\ s^{-1}$

$k_{Ass,\infty} \approx 0.8\ k_{cap,SuCh}$

$F_{cent}^{*} = 0.43\ (T/\ 300\ K)^{-0.73}$

$k_{CA,\infty}^{*} \approx 5.5 \times 10^{7}\ (T/300\ K)^{2}\ s^{-1}$

$k_{CA,0} \approx 4.2 \times 10^{-10}\ (T/300\ K)^{-0.2}\ cm^{3}\ s^{-1}$