Supplementary Material

The 1,2-hydrogen shift reaction for monohalogenophosphanes PH_2X and HPX ($\text{X}=\text{F}, \text{Cl}$)

Rommel B. Viana ^{1*}, Jaldyr J.G. Varela Jr. ², Ana C.M. Tello ¹, Ranylson M.L. Savedra ³,
Albérico B.F. Da Silva ¹

1. Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo (USP), São Carlos-SP, Brazil.

2. Laboratório de Química Quântica Computacional, Centro Tecnológico, Universidade Federal do Maranhão (UFMA), São Luís-MA, Brazil.

3. Departamento de Química, Universidade de Lavras (UFLA), Lavras-MG, Brazil.

*Corresponding author:

Email: rommelbv@yahoo.com.br

Av. Trabalhador São Carlense, 400 (caixa-postal: 780). Bairro: Centro. CEP: 13560970 - São Carlos, SP – Brasil.

=====

Table S1. Vibrational frequencies (in cm^{-1}) and the mean absolute error (MAE, in cm^{-1}) calculated for each method in the prediction of the experimental vibrational frequencies of HPCl .

Table S2. Vibrational frequencies (in cm^{-1}) and the mean absolute error (MAE, in cm^{-1}) calculated for each method in the prediction of the experimental vibrational frequencies of PH_2F .

Table S3. Vibrational frequencies (in cm^{-1}) and the mean absolute error (MAE, in cm^{-1}) calculated for each method in the prediction of the experimental vibrational frequencies of PH_2Cl .

Table S4. Equilibrium constants (K^{eq}) for each reaction ($T = 298.15 \text{ K}$ and 1 atm pressure)

Table S5. Phosphorous [$q(\text{P})$] and halogen charges [$q(\text{F})$ and $q(\text{Cl})$] with different population methodologies for each monohalogenophosphane.

=====

Table S1. Vibrational frequencies (in cm^{-1}) and the mean absolute error (MAE, in cm^{-1}) calculated for each method in the prediction of the experimental vibrational frequencies of HPCI.

HPCI	ν_1	ν_2	ν_3	MAE
Experimental	529.9	879.2	2277.3	-
MP2/cc-pVQZ	547.4	905.7	2444.1	64
QCISD/6-311G(2df,2pd)	533.5	901.4	2415.1	56
W1BD	512.6	881.5	2338.9	31
G4MP2	517.8	880.4	2337.9	29
CBS-QB3	501.5	883.6	2351.3	38
TPSSh/cc-pVQZ	522.2	880.6	2361.0	39
O3LYP/cc-pVQZ	524.2	873.1	2336.6	29
tHCTHhyb/cc-pVQZ	519.1	877.5	2329.4	26
B3PW91/cc-pVQZ	529.0	879.9	2351.9	33
B3LYP/cc-pVQZ	510.4	877.9	2340.7	33
B3P86/cc-pVQZ	530.9	881.8	2359.8	36
B97-1/cc-pVQZ	521.9	880.8	2343.0	31
B97-2/cc-pVQZ	532.7	886.6	2368.8	38
B98/cc-pVQZ	512.6	879.8	2345.6	34
PBE1PBE/cc-pVQZ	519.3	883.1	2344.9	32
X3LYP/cc-pVQZ	538.6	884.0	2366.7	37
M06/cc-pVQZ	535.0	883.1	2380.1	44
M05/cc-pVQZ	546.6	873.8	2382.4	44
BMK/cc-pVQZ	539.7	905.4	2399.5	46
M06-2X/cc-pVQZ	540.7	895.6	2425.1	60
M05-2X/cc-pVQZ	530.4	895.5	2400.6	51
BHandH/cc-pVQZ	562.9	911.1	2428.6	53
BhandHLYP/cc-pVQZ	536.5	918.7	2441.2	63
M06-HF/cc-pVQZ	535.2	906.7	2498.6	91
wB97/cc-pVQZ	565.4	910.3	2432.0	54
wB97X/cc-pVQZ	553.8	903.6	2410.0	48
wB97XD/cc-pVQZ	543.5	894.4	2376.5	38
CAM-B3LYP/cc-pVQZ	531.9	897.5	2391.5	46
LC-wPBE/cc-pVQZ	562.9	910.9	2446.8	61
B97D/cc-pVQZ	494.8	872.4	2281.6	15
M06L/cc-pVQZ	547.3	897.0	2389.0	42
BP86/cc-pVQZ	506.1	846.1	2266.6	8
BPW91/cc-pVQZ	508.8	849.4	2275.6	11
B2P-LYP/cc-pVQZ	525.5	894.4	2388.9	47
B2P-LYP-D/cc-pVQZ	525.2	899.7	2387.4	45
mPW2P-LYP/cc-pVQZ	529.2	899.6	2401.8	51
mPW2P-LYP-D/cc-pVQZ	528.9	903.2	2400.6	50

Table S2. Vibrational frequencies (in cm^{-1}) and the mean absolute error (MAE, in cm^{-1}) calculated for each method in the prediction of the experimental vibrational frequencies of PH_2F .

PH_2F	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	MAE
Experimental	807.36		976.50	1109.20	2283.12	2286.97	
MP2/cc-pVQZ	825.35	947.22	996.41	1153.89	2446.46	2453.97	66
QCISD/6-311G(2df,2pd)	839.03	956.12	1011.04	1152.30	2402.75	2408.36	40
W1BD	802.54	921.88	976.81	1132.70	2340.94	2347.50	25
G4MP2	825.11	929.18	990.35	1133.28	2330.63	2339.18	15
CBS-QB3	745.81	920.14	978.99	1128.72	2345.37	2351.34	38
TPSSH/cc-pVQZ	801.62	921.82	973.62	1135.40	2357.24	2363.25	33
O3LYP/cc-pVQZ	798.58	912.09	961.11	1110.07	2326.71	2338.46	27
tHCTHhyb/cc-pVQZ	795.30	919.19	969.04	1122.19	2325.46	2335.87	23
B3PW91/cc-pVQZ	808.16	921.84	969.86	1118.28	2345.17	2355.07	31
B3LYP/cc-pVQZ	794.91	921.01	973.52	1128.44	2335.89	2343.51	26
B3P86/cc-pVQZ	812.80	923.81	971.88	1120.57	2353.32	2363.05	33
B97-1/cc-pVQZ	803.27	923.14	973.34	1126.45	2340.37	2350.36	27
B97-2/cc-pVQZ	812.49	926.75	975.69	1125.03	2361.42	2370.96	36
B98/cc-pVQZ	799.27	922.82	975.18	1129.59	2341.03	2348.46	27
PBE1PBE/cc-pVQZ	807.88	927.15	978.04	1131.16	2342.53	2352.13	26
X3LYP/cc-pVQZ	820.32	924.89	971.49	1117.63	2359.78	2369.88	36
M06/cc-pVQZ	825.86	931.59	979.62	1123.44	2365.47	2370.41	34
M05/cc-pVQZ	819.72	920.43	965.13	1110.08	2371.43	2382.78	44
BMK/cc-pVQZ	819.46	953.62	1003.35	1166.54	2418.06	2428.38	51
M06-2X/cc-pVQZ	831.33	947.76	996.38	1150.52	2423.35	2428.68	54
M05-2X/cc-pVQZ	834.07	941.40	991.91	1148.77	2405.49	2411.19	46
BHandH/cc-pVQZ	877.84	954.60	999.95	1140.53	2425.36	2432.81	49
BhandHLYP/cc-pVQZ	847.62	962.56	1017.19	1173.99	2440.40	2444.05	52
M06-HF/cc-pVQZ	842.93	948.04	1002.80	1178.92	2504.59	2505.77	85
wB97/cc-pVQZ	810.41	931.13	980.67	1141.21	2424.81	2432.13	63
wB97X/cc-pVQZ	818.45	934.70	984.14	1139.54	2404.22	2411.34	51
wB97XD/cc-pVQZ	818.58	935.52	984.74	1137.54	2372.72	2381.34	37
CAM-B3LYP/cc-pVQZ	819.62	933.11	985.20	1139.87	2385.50	2391.19	41
LC-wPBE/cc-pVQZ	831.37	936.04	984.05	1138.13	2435.04	2442.57	64
B97D/cc-pVQZ	768.46	915.79	967.13	1135.21	2279.70	2289.38	16
M06L/cc-pVQZ	800.17	939.11	984.20	1137.13	2380.39	2392.02	44
BP86/cc-pVQZ	766.76	886.86	934.01	1082.58	2254.89	2267.29	8
BPW91/cc-pVQZ	767.01	889.72	936.95	1086.08	2264.55	2277.08	11
B2P-LYP/cc-pVQZ	807.60	933.86	985.89	1143.33	2387.74	2394.32	44
B2P-LYP-D/cc-pVQZ	807.28	940.24	992.59	1158.11	2393.57	2395.57	42
mPW2P-LYP/cc-pVQZ	816.57	939.44	991.72	1148.97	2400.68	2406.76	47
mPW2P-LYP-D/cc-pVQZ	816.33	943.89	996.43	1159.69	2405.94	2406.06	45

Table S3. Vibrational frequencies (in cm^{-1}) and the mean absolute error (MAE, in cm^{-1}) calculated for each method in the prediction of the experimental vibrational frequencies of PH_2Cl .

PH_2Cl	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	MAE
Experimental	511.23		861.05	1095.74	2303.44	2309.68	
MP2/cc-pVQZ	531.35	863.12	883.19	1138.02	2464.74	2474.12	65
QCISD/6-311G(2df,2pd)	519.98	862.17	889.37	1139.39	2435.62	2440.33	50
W1BD	490.72	836.43	867.56	1125.14	2375.92	2383.60	33
G4MP2	496.46	833.48	866.88	1124.27	2372.60	2383.37	31
CBS-QB3	482.87	838.00	870.17	1126.42	2383.68	2390.65	37
TPSSh/cc-pVQZ	501.92	837.81	865.49	1127.42	2387.67	2394.86	36
O3LYP/cc-pVQZ	502.91	831.71	856.60	1102.52	2359.62	2371.80	29
tHCTHhyb/cc-pVQZ	497.03	834.51	861.53	1114.20	2356.83	2367.99	26
B3PW91/cc-pVQZ	507.95	837.91	862.03	1109.63	2375.28	2385.84	34
B3LYP/cc-pVQZ	488.81	833.56	863.74	1120.89	2366.72	2375.31	30
B3P86/cc-pVQZ	509.54	839.28	863.51	1111.91	2383.10	2393.49	37
B97-1/cc-pVQZ	501.04	837.54	864.57	1118.58	2370.43	2381.34	31
B97-2/cc-pVQZ	510.59	843.44	868.30	1116.24	2391.68	2402.00	39
B98/cc-pVQZ	491.27	835.32	865.19	1122.04	2371.78	2380.22	32
PBE1PBE/cc-pVQZ	498.68	839.30	867.44	1123.53	2372.91	2383.55	31
X3LYP/cc-pVQZ	518.48	842.38	864.10	1108.78	2389.48	2400.25	39
M06/cc-pVQZ	514.18	836.62	863.97	1115.80	2396.01	2401.50	40
M05/cc-pVQZ	524.81	832.27	850.03	1098.52	2395.22	2407.27	45
BMK/cc-pVQZ	518.24	865.70	891.20	1155.25	2461.20	2472.18	61
M06-2X/cc-pVQZ	521.63	855.02	878.74	1137.23	2445.00	2451.78	57
M05-2X/cc-pVQZ	506.41	846.09	868.68	1133.67	2426.42	2433.90	53
BHandH/cc-pVQZ	544.50	867.33	886.39	1131.45	2453.65	2462.19	58
BhandHLYP/cc-pVQZ	519.62	872.40	903.51	1165.17	2468.64	2474.12	60
M06-HF/cc-pVQZ	516.69	846.95	870.88	1162.83	2520.68	2523.23	90
wB97/cc-pVQZ	546.02	870.58	890.57	1131.94	2455.78	2463.93	58
wB97X/cc-pVQZ	534.10	863.68	885.87	1130.72	2433.03	2441.19	49
wB97XD/cc-pVQZ	523.57	856.26	880.64	1129.01	2398.44	2408.10	36
CAM-B3LYP/cc-pVQZ	512.26	852.45	879.56	1132.51	2417.85	2424.67	46
LC-wPBE/cc-pVQZ	545.96	868.38	886.28	1130.00	2467.91	2476.35	64
B97D/cc-pVQZ	471.17	832.61	862.44	1128.74	2313.26	2322.03	18
M06L/cc-pVQZ	522.90	862.03	884.84	1129.52	2409.92	2421.18	41
BP86/cc-pVQZ	482.08	805.42	830.20	1075.33	2288.40	2300.95	7
BPW91/cc-pVQZ	485.35	809.16	833.66	1078.51	2297.66	2310.31	10
B2P-LYP/cc-pVQZ	506.04	848.30	875.59	1132.89	2413.63	2421.62	46
B2P-LYP-D/cc-pVQZ	506.02	855.71	883.26	1147.92	2420.25	2420.78	44
mPW2P-LYP/cc-pVQZ	510.25	853.35	880.84	1138.70	2426.68	2434.25	50
mPW2P-LYP-D/cc-pVQZ	510.20	858.56	886.27	1149.58	2431.77	2433.18	48

Table S4. Equilibrium constants (K^{eq}) for each reaction ($T = 298.15$ K and 1 atm pressure)

Reaction	K^{eq}
$PH_2F \rightarrow HPFH$	6.96×10^{-54}
$PH_2Cl \rightarrow HPCIH$	9.27×10^{-49}
$HPF \rightarrow PFH$	5.17×10^{-55}
$HPCl \rightarrow PClH$	3.10×10^{-51}
$PFH \rightarrow PF + H$	9.03
$PClH \rightarrow PCl + H$	7.05×10^{-3}

Table S5. Phosphorous [$q(P)$] and halogen charges [$q(F)$ and $q(Cl)$] with different population methodologies for each monohalogenophosphane.

Radical	Charge	NPA	QTAIM	Chelp	ChelpG	MK	GAPT	Mulliken	Lowdin
PH_2F	$q(P)$	0.73	1.84	0.09	0.03	0.01	0.81	0.31	0.25
	$q(F)$	-0.57	-0.80	-0.17	-0.15	-0.15	-0.54	-0.31	-0.03
$HPFH$	$q(P)$	-0.02	0.48	-0.08	-0.19	-0.21	0.11	-0.14	0.01
	$q(F)$	-0.48	-0.72	-0.14	-0.14	-0.15	-0.45	-0.22	0.36
PH_2Cl	$q(P)$	0.36	1.53	0.02	0.01	-0.02	0.64	0.14	0.21
	$q(Cl)$	-0.30	-0.53	-0.09	-0.15	-0.14	-0.41	-0.23	-0.01
$HPCIH$	$q(P)$	-0.17	0.46	-0.25	-0.26	-0.28	0.02	-0.24	-0.21
	$q(Cl)$	-0.01	-0.20	0.13	0.01	0.01	0.09	0.06	0.49
HPF	$q(P)$	0.69	1.32	0.10	0.08	0.06	0.61	0.29	0.15
	$q(F)$	-0.56	-0.79	-0.14	-0.14	-0.13	-0.50	-0.29	-0.02
PFH	$q(P)$	-0.08	-0.02	-0.07	-0.13	-0.14	0.03	-0.11	-0.11
	$q(F)$	-0.49	-0.72	-0.13	-0.13	-0.14	-0.45	-0.22	0.35
$HPCl$	$q(P)$	0.36	1.03	0.01	0.04	0.02	0.49	0.15	0.10
	$q(Cl)$	-0.28	-0.52	-0.04	-0.11	-0.10	-0.40	-0.18	0.03
$PClH$	$q(P)$	-0.20	-0.04	-0.21	-0.22	-0.23	-0.10	-0.23	-0.36
	$q(Cl)$	-0.03	-0.21	0.04	0.01	0.01	0.15	0.07	0.48