8 QSPR

Given in the table are the experimental rate constants for the atmospheric oxidation (by the OH radical) of several hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) which are proposed as alternatives for chlorofluorocarbons (CFCs). In this exercise we will determine if the rate constant is related to selected molecular parameters (Heat of Formation, HOMO Energy, Dipole Moment, and the Number of H Atoms in the Molecule) as calculated using PM3 and predict the rate constant for two compounds based on this relationship. We will use a spreadsheet analysis. Please note that the data set is rather small for highly accurate calculations, but accuracy of a factor of 2-3 in the "lifetime" is acceptable.

Chemical Sample	Experimental Reaction Rate ($year^{-1}$)	Heat of Formation (kcal/mol)	HOMO Energy (eV)	Dipole Moment (D)	Number of H atoms
CF3CF2CH2F	6.31	-308.782	-13.613	1.928	2
CF3CH2CF3	0.44	-326.455	-14.776	2.466	2
CF3CH2OCH3	620	-205.089	-11.449	3.417	5
CF3CH2OCF2H	13	-308.679	-12.635	3.646	3
CF3CHFCF3	1.6	-365.5	-14.356	1.853	1
CF3CHO	550	-190.489	-11.87	2.228	1
CH2F2	11	-103.761	-12.855	1.812	2
CH2FCF3	4.9	-211.763	-13.849	2.2	2
CH2FCH2F	110	-152.023	-12.893	1.696	3
CH2FOCHFCF2CF3	73	-405.001	-12.41	3.531	3
CH3CF3	1.3	-172.274	-14.376	2.402	3
CH3CH2F	230	-60.221	-12.067	1.577	5
CH3CHF2	36	-111.923	-12.818	2.119	4
CH3F	17	-53.804	-12.919	1.436	3
CH3OCF3	21	-216.189	-12.402	2.061	3
CHF2CF2CF2CHF2	4.2	-397.276	-13.174	0.046	2
CHF2CF3	1.9	-261.057	-13.71	1.833	1
CHF2CHF2	5.7	-203.119	-13.055	2.679	2
CHF2OCF3	3.4	-319.994	-13.993	2.078	1
CHF2OCHF2	25	-258.292	-13.3	3.854	2
CHF3	0.24	-161.971	-14.364	1.885	1
CF3CHFCHFCF2CF3	??	-509.816	-13.756	2.256	2
CH2FCHF2	??	-152.013	-12.898	1.668	3

[Note: If using Microsoft Excel, be sure that the Data Analysis Tools are "activated".]

Change the values of k to log(k) using =log(xx) for each compound.

We will begin by considering each molecular parameter individually.

In cell A28 type "log(rate) vs heat of formation". In cell A29 perform choose Data Analysis / Regression with the y range C2:C22, x range D2:D22, and output range A29. Record the value of R Square _____. Usually, values less than 0.1 indicate no correlation between y and x.

In cell A51 type "log(rate) vs HOMO energy". In cell A52 perform the regression analysis using the x range E2:E22 and record the value of R Square _____.

In cell A74 type "log(rate) vs dipole moment". In cell A75 perform the regression analysis using the x range F2:F22 and record the value of R Square _____.

In cell A97 type "log(rate) vs # of H Atoms". In cell A98 perform the regression analysis using the x range G2:G22 and record the value of R Square _____.

Which parameters are important? _____

If two or more parameters are important, we can do a multivariable analysis.

In cell A120 type "log(rate) vs ... and copy the respective molecular property data columns (including heading) to cells B121, C121, etc. In cell A144 perform the regression analysis using the x range D122:E142 for two variables, D122:F142 for three variables, etc. Record the value of R Square _____.

Write the equation for the final relationship:

y = (Intercept) + (X Variable 1)[molecular parameter 1] + (X Variable 2)[molecular parameter 2] + ...

Substitute the values of the respective molecular parameters given in rows 25 and 26 for the two "unknown" compounds and calculate log(rate) for each. Record the results _____ and _____ (literature are 0.591 and 1.255).

If the "lifetime" is given by $63.42/10^{\log(k)}$, calculate and record the respective lifetime values _____ and _____. If the lifetime is greater than 2 yr, a substantial amount of the compound will reach the stratospheric ozone layer. Will either of these compounds present environmental concerns?