Supporting Information

Kinetic Study of the Gas-Phase Reactions of Nitrate Radicals with Methoxyphenol Compounds: Experimental and Theoretical Approaches

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Numbers of Figures: 10

Figure S1. Kinetic data plot for the reaction of 3-methoxyphenol (3-MP) with nitrate radicals at (294 ± 3) K using *m*-cresol (▪) and *o*-cresol (■) as reference compounds. For clarity, data obtained with *m*-cresol have been vertically shifted by 0.5 units. The organic compound concentrations were monitored with PTR-ToF-MS.

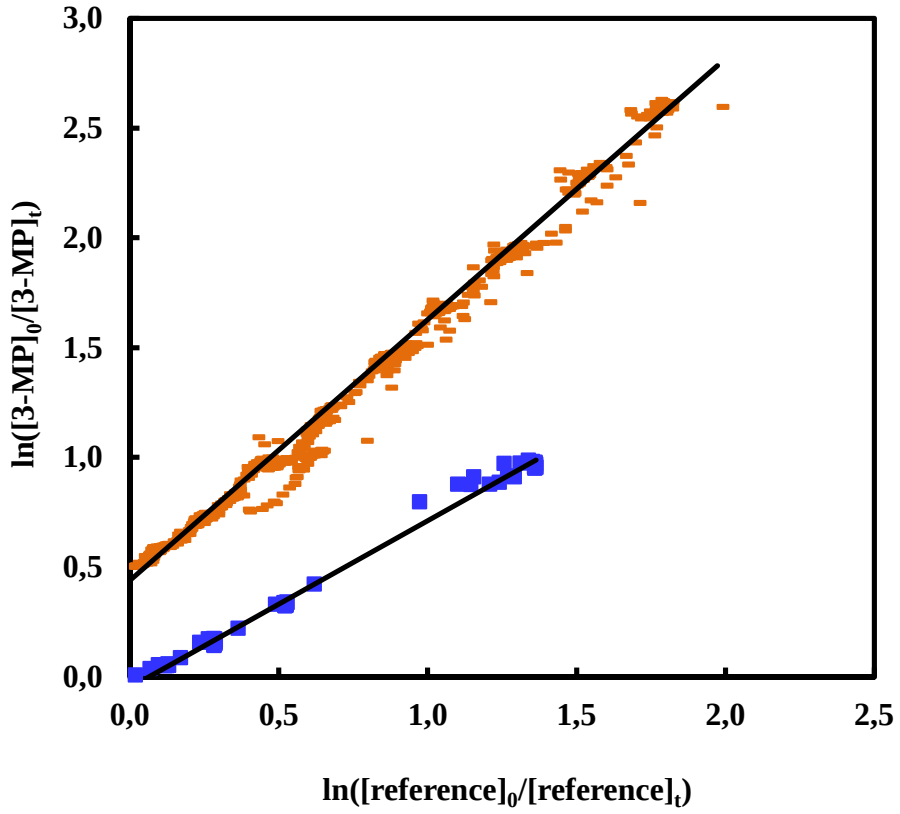


Figure S2. Kinetic data plot for the reaction of 4-methoxyphenol (4-MP) with nitrate radicals at (294 ± 3) K using α-phellandrene (◆) and catechol (●) as reference compounds. For clarity, data obtained with α-phellandrene have been vertically shifted by 0.5 units. The organic compound concentrations were monitored with PTR-ToF-MS.

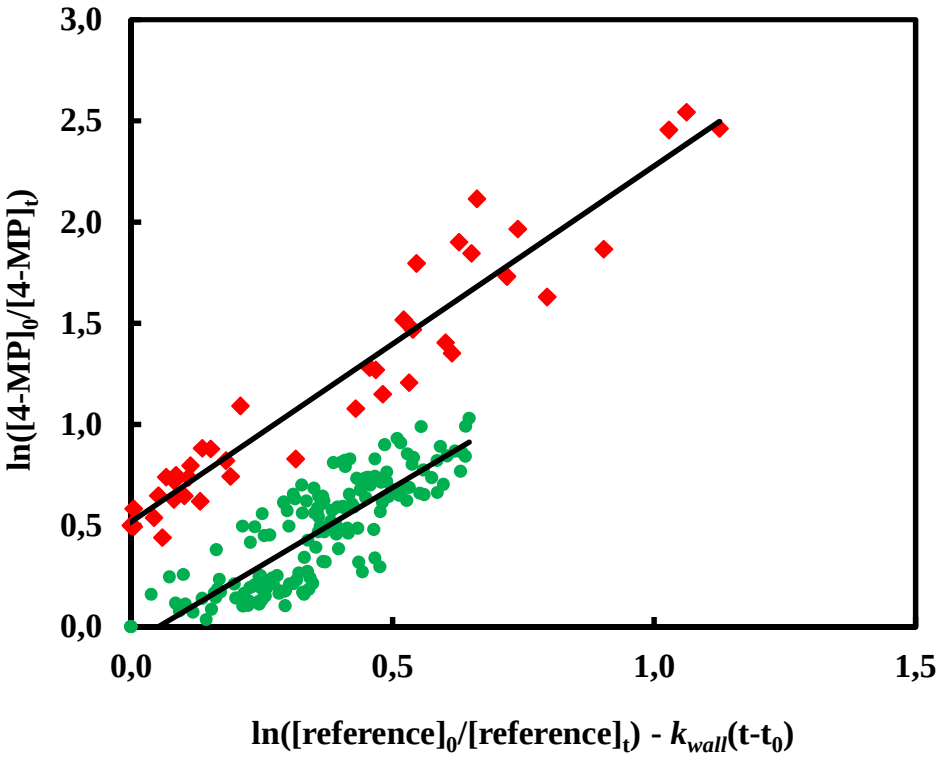


Figure S3. Kinetic data plot for the reaction of 2-methoxy-4-methylphenol (2-M-4-MeP) with nitrate radicals at (294 ± 3) K using α-phellandrene (◆) and catechol (●) as reference compounds. For clarity, data obtained with α-phellandrene have been vertically shifted by 0.5 units. The organic compound concentrations were monitored with PTR-ToF-MS.

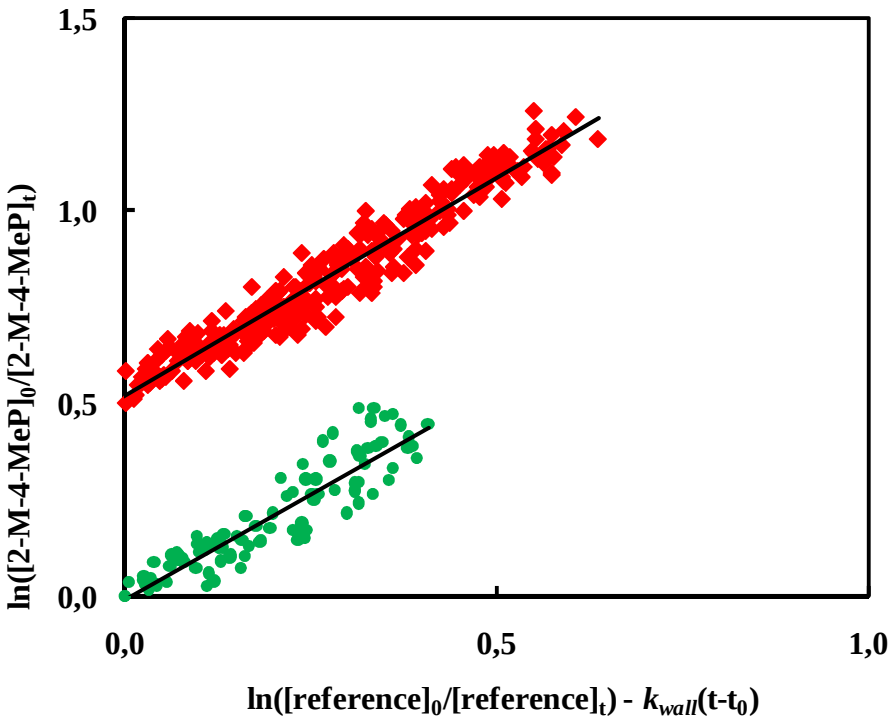


Figure S4. Kinetic data plot for the reaction of syringol (2,6-DMP) with nitrate radicals at (294 ± 3) K using catechol (●) and 3-methylcatechol (▲) as reference compounds. For clarity, data obtained with catechol have been vertically shifted by 0.5 units. The organic compound concentrations were monitored with PTR-ToF-MS.

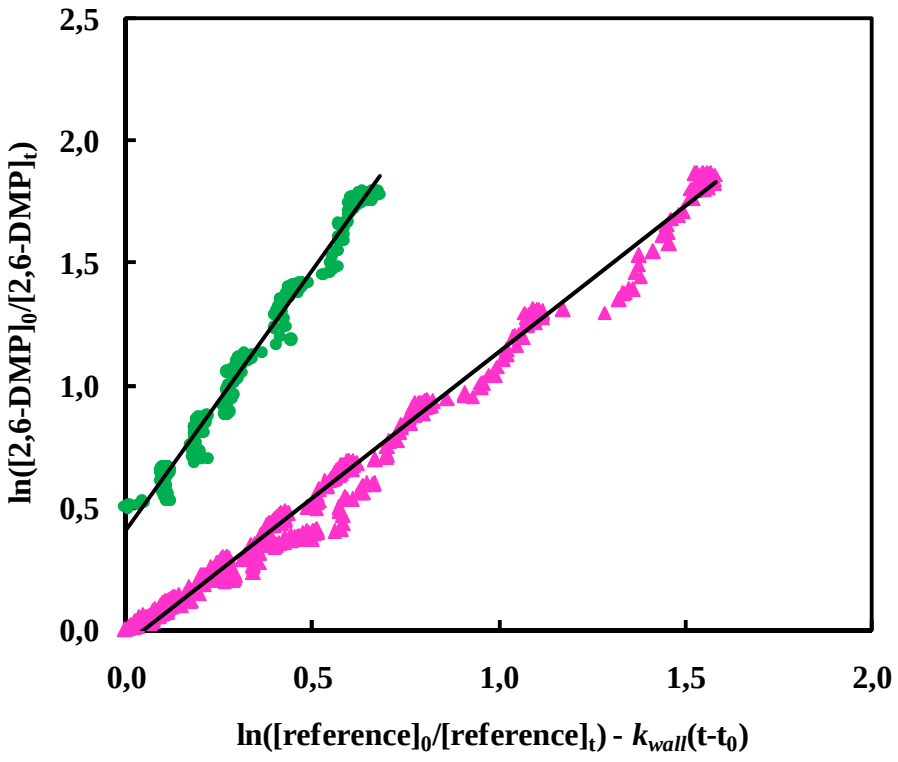


Figure S5. Relative stability, ΔE_0, of the adducts formed from the reaction of 2-MP with nitrate radicals (calculation performed using DFT: UM06-2X/6-31G(d,p)).

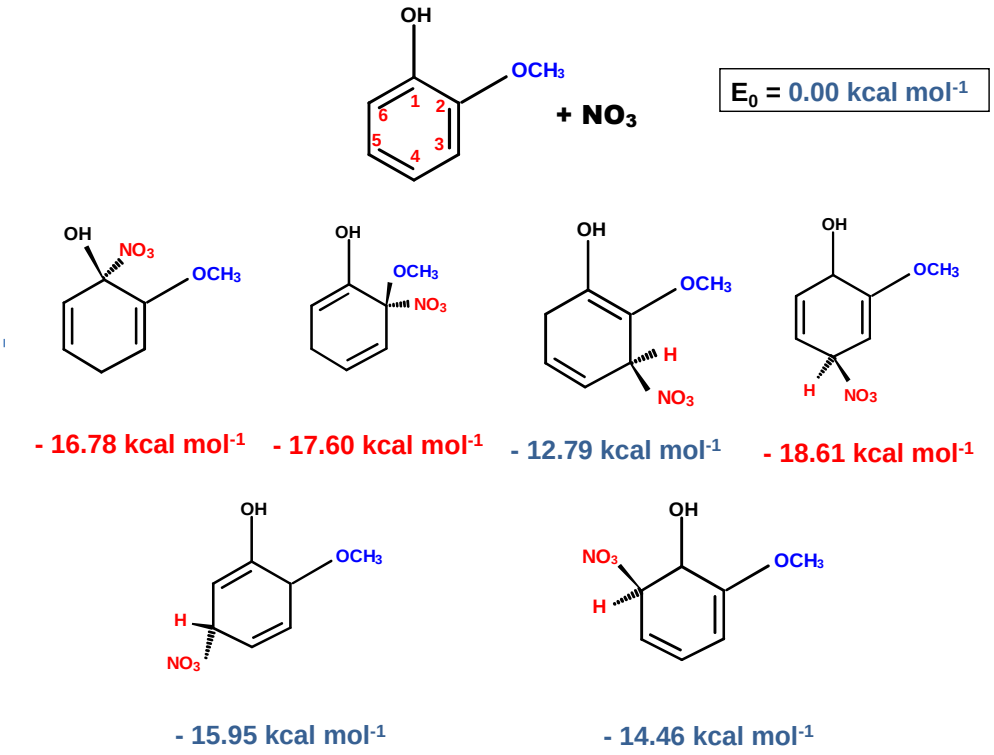


Figure S6. Relative stability, ΔE_0, of the adducts formed from the reaction of 3-MP with nitrate radicals (calculation done using DFT: UM06-2X/6-31G(d,p)).

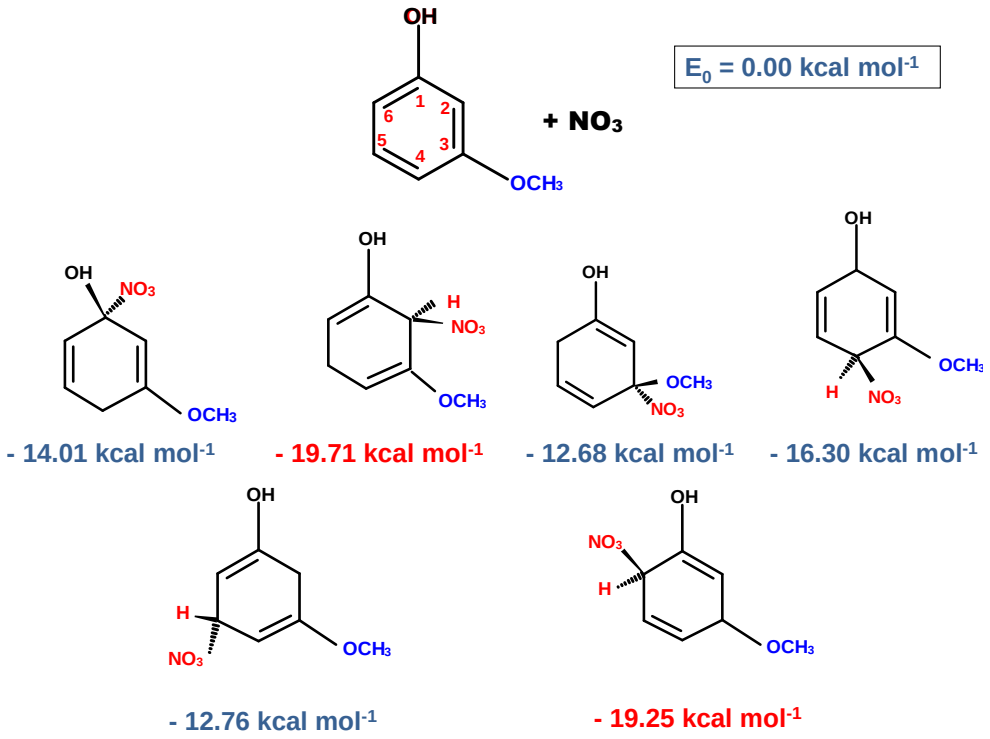


Figure S7. Relative stability, ΔE_0, of the adducts formed from the reaction of 4-MP with nitrate radicals (calculation done using DFT: UM06-2X/6-31G(d,p)).

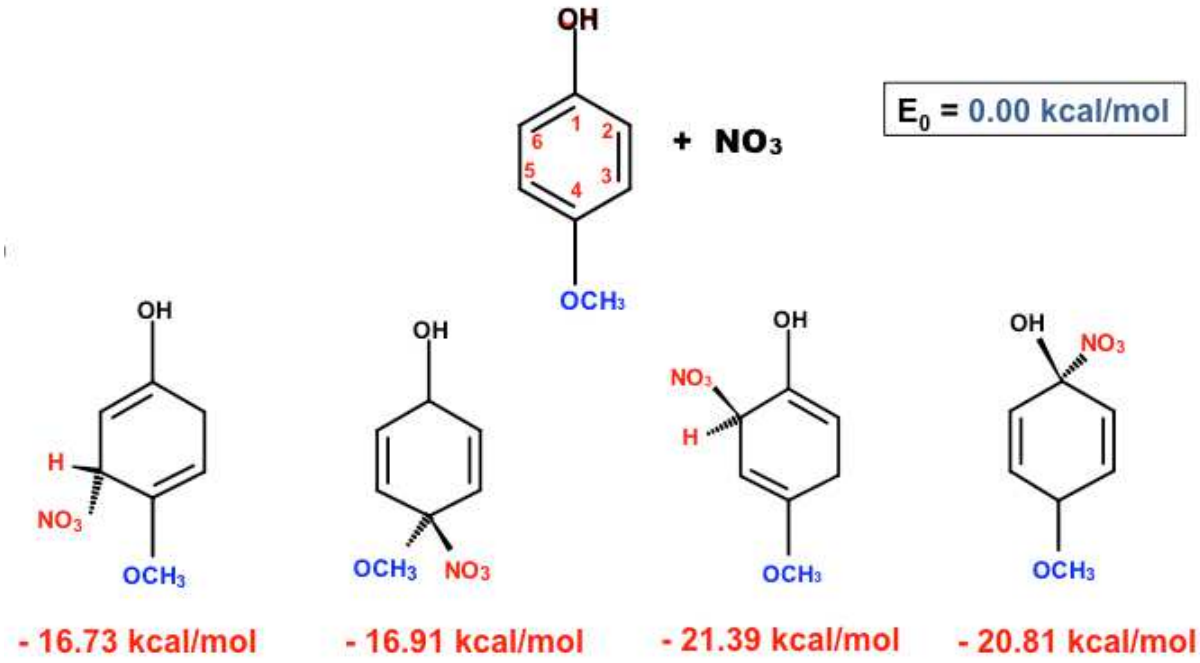


Figure S8. Relative stability, ΔE_0, of the adducts formed from the reaction of 2-M-4-MeP with nitrate radicals (calculation done using DFT: UM06-2X/6-31G(d,p)).

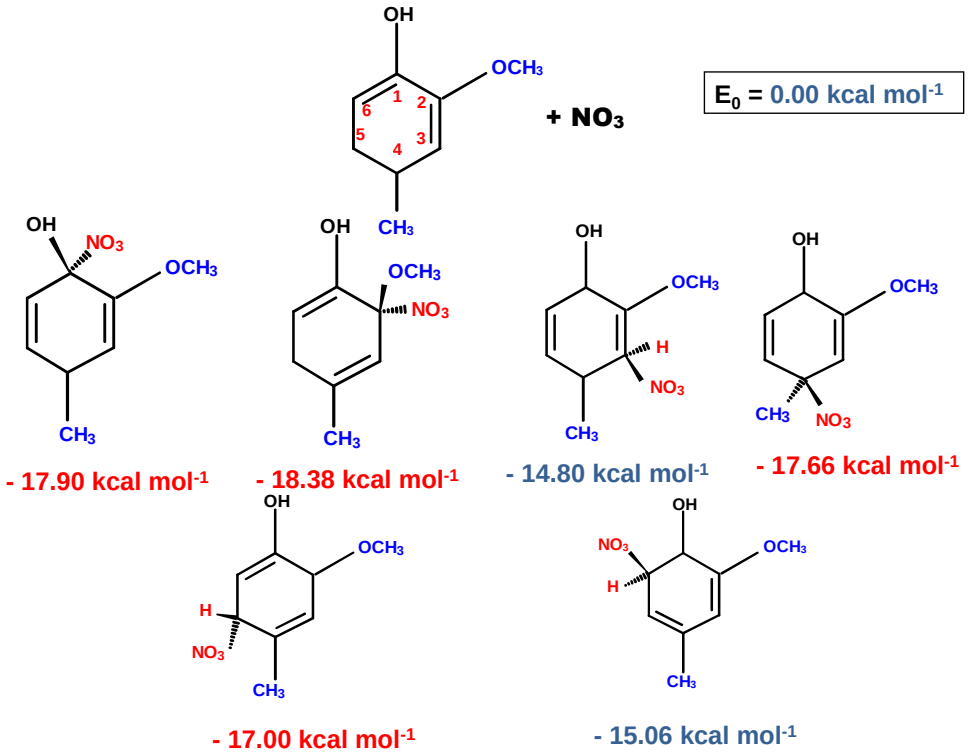
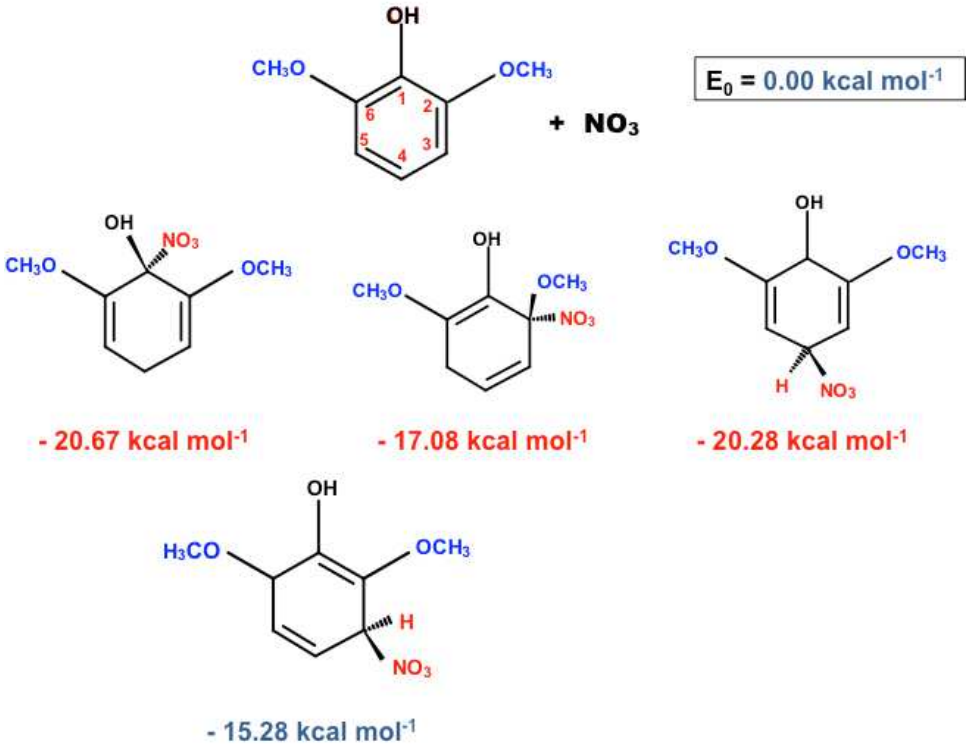


Figure S9. Relative stability, ΔE_0, of the adducts formed from the reaction of 2,6-DMP with nitrate radicals (UM06-2X/6-31G(d,p) calculations).



S10. Theoretical NO_3 rate constants calculated if NO_3 is considered as a D_{3h} symmetry system

If NO_3 is considered as a D_{3h} symmetry system, then $d_{NO3} = 0$. Consequently, we have to consider an interaction dipole-quadrupole and the long-range rate constant k takes now the following form (T independent):

$k = 0.8568 \times \pi \, (d_A.Q_B/\mu)^{1/2}$ (*)

The calculated value of the quadrupole moment of NO_3 is: $Q_{NO3} = 21.5$ Buckingham $= 21.5\ 10^{-26}$ esu CGS. Using this formula, we get the following values for the NO_3 rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}): $k_{2\text{-MP(theoretical)}} = 23 \times 10^{-11}$, $k_{3\text{-MP(theoretical)}} = 20 \times 10^{-11}$, $k_{4\text{-MP(theoretical)}} = 11 \times 10^{-11}$, $k_{2M\text{-}4\text{-MeP(theoretical)}} = 20 \times 10^{-11}$ and $k_{2\text{-}6\ DMP(theoretical)} = 21 \times 10^{-11}$. These values are in the same range of magnitude and in the same order than those calculated using the value 0.71D for the dipole moment of NO_3. So, the theoretical calculations lead to similar NO_3 rate coefficients for the methoxyphenols if NO_3 is considered with a C_{2v} (interaction dipole-dipole) or D_{3h} symmetry (interaction dipole-quadrupole).

(*) Stoecklin, T.; C.E. Dateo, C. E.; Clary, D. C. Rate Constant Calculations on fast Diatom-Diatom Reactions *J. Chem. Soc. Faraday Trans.*, **1991,** *87*, 1667-1679.