Internet Electronic Journal of Molecular Design **2002**, *1*, 193–202 ISSN 1538–6414
BioChem Press http://www.biochempress.com

Internet Electronic Journal of
Molecular Design

April 2002, Volume 1, Number 4, Pages 193–202

Editor: Ovidiu Ivanciuc

Special issue dedicated to Professor Alexandru T. Balaban on the occasion of the 70th birthday
Part 4

Guest Editor: Mircea V. Diudea

Quantitative Relationship between Rate Constants of the Gas–Phase Homolysis of N–N, O–O and N–O Bonds and Molecular Descriptors

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Received: April 1, 2002; Revised: April 17, 2002; Accepted: April 22, 2002; Published: April 30, 2002

Citation of the article:

R. Hiob and M. Karelson, Quantitative Relationship between Rate Constants of the Gas–Phase Homolysis of N–N, O–O and N–O Bonds and Molecular Descriptors, *Internet Electron. J. Mol. Des.* **2002**, *1*, 193–202, http://www.biochempress.com.

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Quantitative Relationship between Rate Constants of the Gas–Phase Homolysis of N–N, O–O and N–O Bonds and Molecular Descriptors[#]

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Internet Electron. J. Mol. Des. **2002**, *1* (4), 193–202

Abstract

Motivation. Quantitative structure–property relationships (QSPR) for kinetic parameters of the gas–phase homolysis for N–N, O–O, and N–O bonds can be used to predict rate constants by using theoretical descriptors computed from the chemical structure.

Method. QSPR models were obtained using the CODESSA program. The molecular structures were generated using the PCMODEL program and the three–dimensional optimization of molecules was carried out using the semi–empirical MNDO parameterization. The property characteristics log k (552) were computed according to the Arrhenius equation using literature values of log A and E at T = 552 K.

Results. Good individual five–parameter correlations were obtained for the log k (552) of compounds involving N–N and N–O, and three–parameter correlation for O–O bond fission, respectively. The corresponding correlation coefficients squared R^2 were spanning from 0.9774 to 0.9969 and the standard deviations s from 0.19 to 0.47.

Conclusions. The application of the CODESSA approach allows confident prediction of the kinetic parameters log k (552) of the gas–phase homolysis of three different types of the homolyzing bonds using the molecular descriptors derived from the structure. Statistically good correlations are obtained for N–N, O–O and N–O bonds with uncertainties in the predictions comparable to the uncertainties in the values for the experimental estimates.

Keywords. QSPR; CODESSA; gas–phase homolysis; rate constants.

Abbreviations and notations

BMLR, best multi–linear regression
CODESSA, Comprehensive Descriptors for Statistical and Structural Analysis
MNDO, modified neglect of diatomic overlap
MOPAC, molecular orbital package
QSPR, quantitative structure–property relationships

1 INTRODUCTION

The quantitative structure–property relationship (QSPR) approach has been beneficial for correlation and prediction of unimolecular rate constants of the gas–phase homolysis for carbon–X bonds [1]. The application of the CODESSA approach enables searching correlations between chemical reactivity and fundamental structural parameters derived from large databases of

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[#] Dedicated on the occasion of the 70th birthday to Professor Alexandru T. Balaban.

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molecular descriptors. The reactivity (property) characteristics were defined as follows

$$\log k = \log A - \log n - E/4.576\ T \tag{1}$$

where k are rate constants (in s^{-1}) of the gas–phase homolysis at temperature T = 891 K as estimates of high pressure limit values k_∞, log A (in s^{-1}) and E (kcal/mol) are the parameters of the Arrhenius equation and n is a statistical coefficient denoting the number of equivalent homolyzing bonds.

Table 1. Structural Formulas of X and Y, Statistical Factor n, Ranges of Experimental log A (s^{-1}) and E (kcal/mol) for Reaction (2), Number of Different Literature Sources for log A and E (ns), log k (552) Calculated with Three– (O–O Bonds) or Five–parameter Correlations, Experimental log k (552) and Residuals Δ.

No	X	Y	Bond type	n	log A	E	ns	References	log k (552)		
									Calc	Exp	Δ
1	NH_2	H	N–H	3	12.82…15.74	98…107.8	2	2, 3	–25.73	–26.88	1.15
2	ONO_2	F	O–F	1	14.96…15.39	31.75…32.3	2	4, p. 537	3.04	2.51	0.53
3	SF_5	F	S–F	6	12.95	75.92	1	5, p. 104	–16.21	–17.85	1.64
4	SO_3F	F	O–F	2	15.13	33	1	5, p. 104	–4.40	1.78	–6.18
5	OCF_3	F	O–F	1	14.33…14.9	43.3…45	2	6, 7	0.12	–2.84	2.96
6	NO_2	Cl	N–Cl	1	12.36	27	1	4, p. 536	–0.39	1.68	–2.07
7	ClOF	O	O–Cl	2	13.4	45	1	5, p. 104	–3.33	–4.69	1.36
8	ClO_2F	O	O–Cl	3	13.59	58.4	1	5, p. 104	–2.63	–9.98	7.35
9	NO_2	OH	N–O	1	15.1…15.3	47.7…49	2	8	–3.68	–3.92	0.24
10	OCH_3	OH	O–O	1	11	32	1	5, p. 94	–1.63	–1.65	0.02
11	OC_2H_5	OH	O–O	1	13.4	37.7	1	5, p. 94	–1.41	–1.51	0.10
12	$OCH(CH_3)_2$	OH	O–O	1	15.2	40	1	5, p. 94	–1.00	–0.62	–0.38
13	$OC(CH_3)_3$	OH	O–O	1	13.7	37.8	1	5, p. 94	–0.66	–1.25	0.59
14	$OCOCH_3$	OH	O–O	1	14	32	1	5, p. 96	1.04	1.35	–0.31
15	$N{=}CHCH_3$	OH	N–O	1	12.83	47	1	5, p. 98	–5.80	–5.75	–0.05
16	OC_7H_{15}	OH	O–O	1	15.85	41.5	1	9	–0.87	–0.56	–0.31
17	$OCH(CH_3)C_5H_{11}$	OH	O–O	1	16.04	43.5	1	9	–0.83	–1.16	0.33
18	NO_2	OF	N–O	1	14.96…15.39	31.75…32.3	2	5, p. 103	2.65	2.51	0.14
19	NO_2	Ocl	N–O	1	14.18	30	1	5, p. 104	2.77	2.32	0.45
20	NH_2	NH_2	N–N	1	13…13.9	53…55	3	5, p. 98; 10; 11	–7.50	–7.85	0.35
21	$NHCH_3$	NH_2	N–N	1	13.19	51.9	1	5, p. 98	–7.91	–7.33	–0.58
22	NHC_6H_5	NH_2	N–N	1	11.8	40	1	5, p. 98	–4.09	–4.02	–0.07
23	$N(CH_3)_2$	NH_2	N–N	1	13.22…17.6	49.6…63	2	5, p. 98; 12	–6.68	–6.85	0.17
24	NF_2	NF_2	N–N	1	14.98…15.37	19.4…19.8	2	5, p. 98; 13	7.26	7.43	–0.17
25	OCH_3	NO	N–O	1	12.9…16.01	34…41.2	6	5, p. 96–97; 14	–1.32	–0.53	–0.79
26	OC_2H_5	NO	N–O	1	13.66…16	36.69…41.8	5	5, p. 97; 15	–0.54	–0.76	0.22
27	OC_3H_7	NO	N–O	1	13.2…16.5	34.7…40	5	5, p. 97	–0.25	–0.34	0.09
28	$OCH(CH_3)_2$	NO	N–O	1	14.1…16.2	37…41	3	5, p. 97; 16	–0.08	–0.33	0.25
29	OC_4H_9	NO	N–O	1	13.66…16.5	36.2…41	3	5, p. 97; 17	0.16	–0.17	0.33
30	$OC(CH_3)_3$	NO	N–O	1	15.8…16.4	39.3…42.8	3	18; 19; 20	0.37	0.33	0.04
31	$OC(CH_3)_2C_2H_5$	NO	N–O	1	16.3	40.3	1	21	0.22	0.37	–0.15
32	$N(CH_3)_2$	NO	N–N	1	15.3	50.2	1	5, p. 99	–3.36	–4.55	1.19
33	$OCH(CH_3)C_2H_5$	NO	N–O	1	16.2	40.9	1	22	0.03	0.03	0.00
34	$OCOCF_3$	NO	N–O	1	14.26	33.8	1	23	0.89	0.90	–0.01
35	4–Morpholinyl	NO	N–N	1	12.2	40.9	1	24	–3.97	–3.97	0.00
36	NO_2	NO_2	N–N	1	16	13.1	1	5, p. 103	10.74	10.82	–0.08
37	ONO_2	NO_2	N–O	2	13.1…14.98	20…22	4	5, p. 103; 25	5.52	5.57	–0.05
38	OCH_3	NO_2	N–O	1	14.4…16.3	39.5…41	2	5, p. 97; 26	–1.13	–0.56	–0.57
39	OC_2H_5	NO_2	N–O	1	14.74…16.85	38…41.23	4	5, p. 98; 26	0.36	0.09	0.27
40	$OCH(CH_3)_2$	NO_2	N–O	1	16.3	41	1	26	0.01	0.09	–0.08
41	$OCH(CH_2ONO_2)_2$	NO_2	N–O	1	15.5	36	1	27	1.30	1.27	0.03
42	$NHCH_3$	NO_2	N–N	1	13.65	41	1	28	–2.58	–2.56	–0.02
43	$N(CH_3)_2$	NO_2	N–N	1	13.7	38.9	1	29	–1.71	–1.68	–0.03
44	$N(C_2H_5)_2$	NO_2	N–N	1	15.1	41.6	1	29	–1.75	–1.35	–0.40
45	1–Piperidyl	NO_2	N–N	1	14.8	42.1	1	29	–1.62	–1.85	0.23
46	4–Morpholinyl	NO_2	N–N	1	13.6…14.9	38.9…41.6	2	24;29	–2.43	–1.66	–0.77

Table 1. (Continued)

No	X	Y	Bond type	*n*	log A	E	ns	References	log *k* (552) Calc	Exp	Δ
47	Perhydro–1,3,5–triazin–1–yl	NO_2	N–N	1	15.58	40.4	1	30	–0.74	–0.39	–0.35
48	$N(NO_2)CH_3$	NO_2	N–N	2	14.6	28.3	1	31	3.98	3.11	0.87
49	$N(NO_2)C_2H_5$	NO_2	N–N	2	15.6	29.7	1	31	3.66	3.56	0.10
50	$N(NO_2)C_3H_7$	NO_2	N–N	2	16.4	31	1	31	3.75	3.84	–0.09
51	$N(NO_2)C_4H_9$	NO_2	N–N	2	15.5	29.6	1	31	3.89	3.50	0.39
52	NHC_2H_5	NO_2	N–N	1	13.69	41.8	1	28	–3.01	–2.84	–0.17
53	NHC_3H_7	NO_2	N–N	1	14.89	45.2	1	28	–2.91	–2.98	0.07
54	$NHCH(CH_3)_2$	NO_2	N–N	1	13.55	41.3	1	28	–2.55	–2.78	0.23
55	NHC_4H_9	NO_2	N–N	1	15.34	45.8	1	28	–2.74	–2.77	0.03
56	$NHCH_2CH(CH_3)_2$	NO_2	N–N	1	14.61	43.7	1	28	–2.29	–2.67	0.38
57	$OOCH_3$	NO_2	N–O	1	16.04	21	1	32	7.17	7.74	–0.57
58	OOC_2H_5	NO_2	N–O	1	15.94	20.75	1	32	8.02	7.74	0.28
59	$OOCCl_3$	NO_2	N–O	1	16.68	23.5	1	33	7.39	7.39	0.00
60	$OOCF_2Cl$	NO_2	N–O	1	16.2	23.8	1	33	6.72	6.79	–0.07
61	$OOCFCl_2$	NO_2	N–O	1	16.82	24.3	1	33	6.98	7.21	–0.23
62	$OOCOCH_3$	NO_2	N–O	1	16.4	27	1	34	5.96	5.72	0.24
63	CO_2	CO	C–O	1	14.1	54	1	5, p. 104	2.89	–7.25	10.14
64	OCH_3	OCH_3	O–O	1	15.2…15.7	35.3…37.1	4	5, p. 95; 35; 36	0.96	1.04	–0.08
65	$N=N(O)CH_3$	OCH_3	X–Y	1	14.5	48.6	1	37	0.80	–4.72	5.52
66	$N=N(O)CH_2C(CH_3)_3$	OCH_3	X–Y	1	14.6	49.2	1	37	0.19	–4.85	5.04
67	OCF_3	OCF_3	O–O	1	15.2…15.94	46.2	2	38, 39	–2.72	–2.70	–0.02
68	OC_2H_5	OC_2H_5	O–O	1	12.04...16.1	29.9...37.3	5	5, p. 95	0.97	0.75	0.22
69	$OC(CH_3)_3$	OC_2H_5	O–O	1	14.4	34.5	1	5, p. 95	0.86	0.76	0.10
70	OC_3H_7	OC_3H_7	O–O	1	14.96…15.3	35…36.5	2	5, p. 95	1.01	0.99	0.02
71	$OCH(CH_3)_2$	$OCH(CH_3)_2$	O–O	1	15.15...15.4	36.8...37.1	2	5, p. 95	0.87	0.67	0.20
72	$OC(CH_3)_3$	$OC(CH_3)_3$	O–O	1	13.3…16.6	34…39.1	23	5, p. 95–96	0.86	0.90	–0.04
73	$OC(CH_3)_2C_2H_5$	$OC(CH_3)_2C_2H_5$	O–O	1	15.8…16.72	36.4…38.7	2	5, p. 96	1.15	1.41	–0.26
74	$OCOCH_3$	$OCOCH_3$	O–O	1	14.25	29.5	1	5, p. 96	2.55	2.59	–0.04
75	$OCOC_2H_5$	$OCOC_2H_5$	O–O	1	14.4	30	1	5, p. 96	2.55	2.54	0.01
76	$OCOC_3H_7$	$OCOC_3H_7$	O–O	1	14.28	29.6	1	5, p. 96	2.80	2.58	0.22
77	$N(CH_3)_2$	$N(CH_3)_2$	N–N	1	17.7	54	1	12	–4.10	–3.65	–0.45
78	$NNN(CH_3)_2$	$N(CH_3)_2$	N–N	2	11.4…13.83	31.9…34.59	3	5, p. 98–99	–0.11	–0.16	0.05
79	$NNN(C_2H_5)_2$	$N(C_2H_5)_2$	N–N	2	13.7	33	1	5, p. 99	0.43	0.35	0.08
80	$N(O)CH_3$	$N(O)CH_3$	N–N	1	11.8…13.4	21.7…23	2	5, p. 99	3.05	3.76	–0.71
81	$N(O)CH_2H(CH_3)_2$	$N(O)CH_2CH(CH_3)_2$	N–N	1	14.4	25.6	1	5, p. 99	4.04	4.28	0.24
82	$Si(CH_3)_3$	$Si(CH_3)_3$	Si–Si	1	13.51…17.2	67.3…80.5	2	5, p. 94; 40	–13.17	–13.86	0.69
83	$OC(CF_3)_3$	$OC(CF_3)_3$	O–O	1	16.2	35.5	1	41	2.25	2.16	0.09

It was demonstrated that the kinetic parameters log *k* (891) of the gas–phase homolysis correlate with the molecular descriptors derived from the structure for each type of the homolyzing bonds. Statistically good correlations were obtained with uncertainties in the predictions comparable with the uncertainties in the values of the experimental rate constants.

However, the attempt to develop a successful QSPR multi–linear equation simultaneously for all C–X bond data revealed that the accuracy of the best models up to that including five parameters is not sufficient. Therefore, it was concluded that the rate constant of the gas–phase homolysis of C–X bonds is a difficult chemical property to be described by a uniform QSPR model.

The goal of the present work is to introduce new QSPR models developed with CODESSA for rate constants of the gas–phase homolysis of N–N, O–O and N–O bonds.

2 MATERIALS AND METHODS

A large majority of the kinetic data on the gas–phase homolysis reactions, proceeding according to the scheme

$$XY \rightarrow X^{\cdot} + Y^{\cdot} \quad (2)$$

fall into the classes of C–X (including the case when X is C) bond fission reactions [1]. The next larger sets of kinetic data on the reaction (2) involve the N–N, O–O and N–O bond fission. The respective log A and E values listed in Table 1 are estimates of the high–pressure limit values, *i.e.* log A_∞ and E_∞. The ninth column in Table 1 shows the literature sources [2–41] of the listed kinetic parameters for 83 compounds. The value of T = 552 K has been selected as an arithmetic mean of all ranges of temperatures used to estimate the Arrhenius parameters log A and E for all compounds in the entire set of Table 1. If intervals of alternative log A and E values are listed in Table 1, the mean values of log *k* (552) for each separate reaction were calculated. For example, if five pairs of log A and E are available, five log *k* (552) values were calculated and thereafter mean value. Obvious outliers were excluded according to the Student's criterion at the confidence level 0.95.

Table 2. List of Molecular Descriptors Used in the Best One– to Five–Parameter QSPR Models from Table 3.

Notation	Descriptor	References
d1	Principal moment of inertia A divided by the number of atoms	[50]
d2	Total molecular electrostatic interaction divided by the number of atoms	[44]
d3	Maximum net atomic charge	[44]
d4	Maximum atomic orbital electronic population	[44]
d5	Vibrational entropy (300K) divided by the number of atoms	[47]
d6	Internal heat (300K) divided by the number of atoms	[44]
d7	Total heat capacity (300K) divided by the number of atoms	[44]
d8	Total molecular electrostatic interaction	[44]
d9	Total molecular 1–center electron–nuclear attraction	[51]
d10	Total enthalpy (300 K) divided by the number of atoms	[44]
d11	FNSA–3 – Fractional charged partial surface area divided by the total molecular surface area where partial charges are computed with electronegativity	[52,53]
d12	Minimum valence of an N atom	[54]
d13	Kier flexibility index	[55]
d14	Bonding Information content (order 0)	[47]
d15	Maximum atomic force constant	[47]
d16	HACA–2/SQRT(TMSA) – Hydrogen bonding specific charged surface area computed with quantum charges	[48]
d17	σ–π bond order for an O–O bond	[54]
d18	Minimum total interaction for an N–O bond	[47]
d19	RNCS – Relative negative charged surface area where partial charges are computed with electronegativity	[56,57]
d20	Minimum 1–electron reaction index for an O atom	[47]
d21	Minimum resonance energy for an N–O bond	[47]
d22	Average bonding information content (order 1)	[47]
d23	DPSA–2 – Difference in charged partial surface area (PPSA2–PNSA2) computed with quantum charges	[52,53]
d24	Minimum valence of an O atom	[54]

The molecular structures were generated using the PCMODEL program [42]. The three–dimensional optimization of molecules was carried using the semi–empirical MNDO parameterization [43]. The respective output files of MOPAC [44] or AMPAC [45] calculations were treated by the CODESSA program to derive a large variety of molecular descriptors including the constitutional, topological, geometric, electrostatic, quantum–chemical and thermodynamic descriptors [46]. The molecular descriptors were calculated separately for the reagents XY, the fragments X and Y and for the X–Y bond.

Two strategies were employed to develop the best multi–parameter QSPR models: the heuristic [47,48] and the best multi–linear regression (BMLR) [47,48] approaches, both based on the forward selection of scales methodology [49].

Table 3. The Best One to Five–Parameter Correlation Equations Derived by the Heuristic and BMLR Procedures between log *k* (552) Values and Theoretical Descriptors (Table 2) for Reaction (2).[a]

Reaction	N	n	c_0	e_0	D	c_i	e_i	R^2	F	s	R^2_{CV}	IC
X–Y bond	79	1	0.34	0.44	d1	–10.67	1.34	0.4513	63.3	3.72	0.3337	
		2	–9.75	1.73	d2	1.47	0.25	0.5508	46.59	3.64	0.5091	0.0903
					d1	–9.99	1.40					
		5	–32.7	4.50	d2	1.16	0.17	0.8155	64.55	2.22	0.6932	–0.4143
					d1	–7.73	0.96					
					d3	–6.94	1.00					
					d4	12.78	2.44					
					d5	2.28	0.59					
N–N bond	28	1	–22.55	1.38	d6	13.97	0.87	0.9077	255.6	1.46	0.8740	
		2	–31.45	1.09	d7	12.18	0.45	0.9701	405.6	0.85	0.9515	–0.2224
					d8	0.073	0.005					
		5	–29.28	2.18	d9	–0.005	0.0002	0.9908	473.6	0.47	0.9759	0.7528
					d10	0.0335	0.0016					
					d11	231.0	18.7					
					d12	3.22	0.785					
					d13	–0.640	0.112					
O–O bond	19	1	–2.35	0.61	d14	0.48	0.09	0.6086	26.4	0.74	0.6003	
		2	–2.86	0.21	d15	0.46	0.02	0.9684	245.2	0.22	0.9513	–0.1809
					d16	–33.9	2.4					
		3	–2.72	0.19	d15	0.47	0.02	0.9774	216.0	0.19	0.9652	–0.2783
					d16	–35.6	2.2					
					d17	–9.19	3.77					
N–O bond	24	1	29.9	3.6	d18	–2.02	0.25	0.7448	64.2	1.60	0.7250	
		2	32.7	2.5	d19	–0.17	0.035	0.8965	91.0	1.26	0.8640	–0.1469
					d18	–2.11	0.18					
		5	69.0	2.3	d20	148.5	9.0	0.9935	551.2	0.34	0.9889	0.6672
					d21	–2.23	0.07					
					d22	–7.02	0.45					
					d23	–0.0065	0.0005					
					d24	–10.2	1.2					

[a] *N* is the number of compounds, *n* is the number of descriptors in the QSPR, R^2 is the squared correlation coefficient, F is the Fischer's criterion, *s* is the standard deviation, R^2_{CV} is the square of the cross validated correlation coefficient, see [48], IC is the maximum intercorrelation coefficient between pairs of descriptors [47].

3 RESULTS AND DISCUSSION

A list of the molecular descriptors selected by the heuristic and BMLR procedures for the best one– to five–parameter correlation equations is presented in Table 2. The application of the two above–mentioned methods for the development of the QSPR multi–linear equation for 79 reagents reveals that the accuracy of the best models up to that including five parameters (R^2 = 0.8155, s = 2.22, see Table 3) is not sufficiently high. This result is not surprising, because the entire set is characterized by a high degree of structural variety. Therefore, we have proceeded with the partitioning of the initial data set into three groups according to the type of atoms X and Y involved. By treating the respective separate sets of the data, good individual five–parameter correlations were obtained for the log k (552) of compounds involving N–N and N–O, and three–parameter correlation for O–O bond fission, respectively. The corresponding squared correlation coefficients R^2 were spanning from 0.9774 to 0.9969 and the standard deviations s from 0.19 to 0.47 (Table 3).

The most important descriptors of the five–parameter model for the N–N bond fission reactions are total molecular 1–center electron–nuclear attraction [51], total enthalpy (300 K) divided by the number of atoms [44] and fractional charged partial surface area divided by the total molecular surface area where partial charges are computed with electronegativity [52,53]. Other descriptors are minimum valence of an N atom [54] and Kier flexibility index [55].

For 19 peroxides in which O–O bonds are homolyzed, already the two–parameter model is satisfactory, including the maximum atomic force constant [47] and hydrogen bonding specific charged surface area computed with quantum charges [48]. This correlation has a very low value of s = 0.22 (see Table 3) compared to the respective values for N–N and N–O bond fission reactions. One additional descriptor included in the three–parameter correlation is the σ–π bond order for the O–O bond [54] (Table 3).

For N–O bond fission reactions, the best five–parameter model includes the following descriptors: minimum 1–electron reaction index for an O atom [47], minimum resonance energy for an N–O bond [47], average bonding information content (order 1) [47], DPSA–2 – difference in charged partial surface area (PPSA2–PNSA2) computed with quantum charges [52,53] and minimum valence of an O atom [54]. The value of s = 0.34 is between the corresponding values of s for N–N and O–O bond fission reactions.

Clearly, almost all of these theoretical descriptors are directly related to the reactivity in the three types of bond fission reactions considered.

It has been shown that the five– or the three–parameter equations in the three cases of different X–Y bonds, namely the log k (552) values of the gas–phase homolysis can now be predicted with a considerable degree of confidence. A comparison of the experimental (observed) log k (552) values with the recalculated by QSPR models values is presented in Figures 1–4. As usually it is hard to give an estimate of the absolute accuracy of the used experimental rate constants. Assuming that the uncertainty factor is approximately three, the value in the logarithmic units is 0.48. Among the 28 structures of the N–N bond fission, the prediction errors for five compounds (No. 21, 32, 46, 48 and 80 in Table 1) exceed this criterion. Taking into account good two–parameter correlation for O–O bond fission, it is not surprising that only three compounds have maximum deviations spanning from –0.48 to –0.52. For the three–parameter model of the same bond–type the maximum difference for one compound is 0.59 and the next one is –0.38 (Table 1). The comparison of the experimental values for the N–O bond fission with those calculated using the best five–parameter model shows that only three compounds have prediction error exceeding the value 0.48 (the structures No. 25, 38 and 57 (see Table 1).

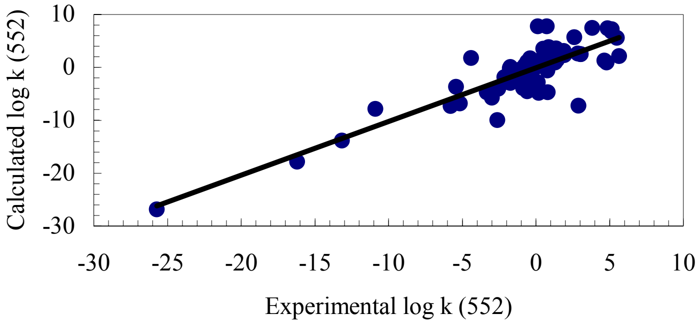

Figure 1. Correlation of the experimental and calculated log *k* (552) for 79 X–Y bond fission reactions using the five–parameter equation in Table 3.

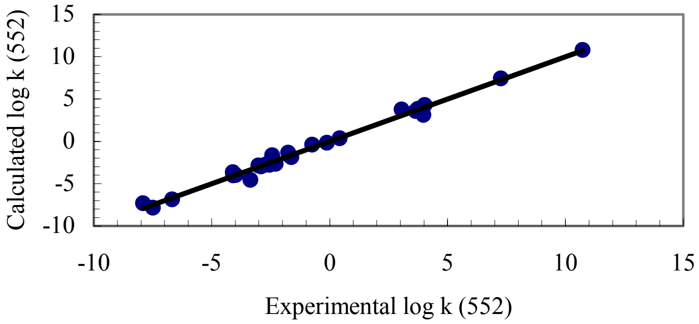

Figure 2. Correlation of the experimental and calculated log *k* (552) for 28 N–N bond fission reactions using the five–parameter equation in Table 3.

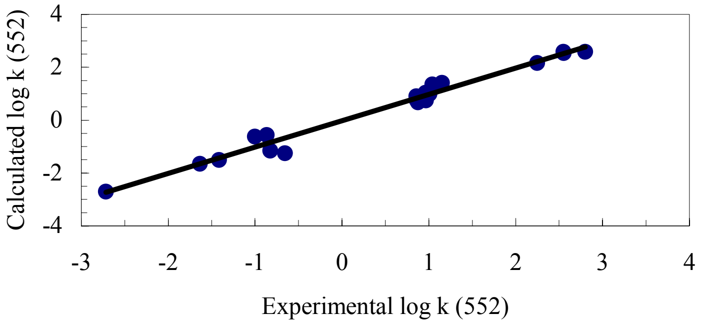

Figure 3. Correlation of the experimental and calculated log *k* (552) for 19 O–O bond fission reactions using the three–parameter equation in Table 3.

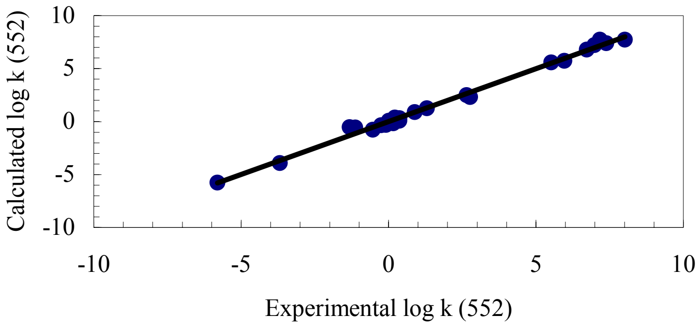

Figure 4. Correlation of the experimental and calculated log *k* (552) for 24 N–O bond fission reactions using the five–parameter equation in Table 3.

4 CONCLUSIONS

The application of the CODESSA approach allows confident prediction of the kinetic parameters log *k* (552) of the gas–phase homolysis of three different types of the homolyzing bonds using the theoretical descriptors derived from the molecular structure. Statistically good correlations are obtained for N–N, O–O and N–O bonds with uncertainties in the predictions comparable to the uncertainties in the values for the experimental estimates.

Acknowledgment

The authors gratefully acknowledge the financial support of this research by the Estonian Science Foundation (Grants No. ESF–4548 and No. ESF–2438).

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