Quantitative Relationship between Rate Constants of the Gas-Phase Homolysis of C−X Bonds and Molecular Descriptors

Rein Hiob and Mati Karelson*

Department of Chemistry, University of Tartu, 2 Jakobi Street, Tartu, 51014 Estonia

A quantitative structure−property relationship (QSPR) study on the kinetic parameters of the gas-phase homolysis for 287 different C−X bonds was carried out using the CODESSA program. Successful five-, four-, and three-parameter models were developed for the prediction of the log k (891 K) values. These respective multiple linear correlations were obtained by automatic selection of appropriate molecular descriptors for reagents and products, using only the information encoded in the chemical structure.

INTRODUCTION

The gas-phase homolysis, also known as simple bond fission

$$R_i R_j \rightarrow R_i^{\cdot} + R_j^{\cdot} \qquad (1)$$

belongs to a typical class of the unimolecular gas-phase reactions. The theory of these reactions has a long history, starting from the Lindemann two-stage scheme, Rice-Ramsperger-Kassel-Marcus (RRKM) theory (see books[1,2]) and can also be described by the generalization of the Slater's theory of unimolecular reactions.[3] However, there have been only a few attempts of a comprehensive direct comparison of theoretical and experimental values of kinetic parameters for the gas-phase homolysis. First, an approach by Benson and co-workers[4−8] has been based on the methodology known as thermochemical kinetics. It was used for the comparison of the kinetic parameters of a large number of unimolecular gas-phase reactions including the simple bond fission. Second, Tsang and others[9−19] have experimentally determined kinetic parameters for many bond fission reactions using mainly the comparative rate single pulse shock tube method. Additionally, predicted kinetic parameters have been evaluated using in principle the Benson's approach. The chemical compounds investigated include aliphatic hydrocarbons,[9] some alkenes,[10−11] alkynes,[12] alcohols,[13] primary amines,[14] halogen containing compounds,[15,16] nitroaromatic compounds,[17,18] and ethers.[19] In a previous study by one of us (see reference 20 and papers therein), all available experimental kinetic data on the gas-phase homolysis were treated using a formal correlational approach. As a result of this treatment, a computer program was developed that predicts the free energies and rate constants of the gas-phase homolysis and standard heats of formation for initial covalent compounds.[21] However, the reliability of predictions by this program was limited because of the lack of sufficient number of experimental data required. A general approach of the CODESSA (*Co*mprehensive *D*escriptors for *S*tatistical and *S*tructural *A*nalysis) methodology that is based on theoretical

molecular descriptors derived solely from the molecular structure of the individual compounds[22,23] should however enable to extend the correlations to the previously unknown compounds.

Therefore, the CODESSA program has been used in the present work for the calculation of descriptors and for the statistical analysis to obtain multiparameter QSPR (Quantitative Structure−Property Relationship) equations describing the logarithms of rate constants of the gas-phase C−X bond fission reactions.

DATA AND METHODOLOGY

At sufficiently high pressures, reaction 1 is unimolecular and thus characterized by the (temperature-dependent) first-order rate constant k. The temperature dependence of the reaction rate is usually described by the activation parameters of the respective Arrhenius equation. A data set of experimental kinetic parameters for reaction 1 was created including 287 different bond fission reactions. Many of those have alternative values of kinetic parameters, and thus, altogether 475 different pairs of log A and E values were collected (for the list, cf. references 20 and 24). The log A and E values given in Table 1 are estimates of the high-pressure limit values, denoted as log A_∞ and E_∞, respectively. The reactivity (property) characteristics in this QSPR study were defined as follows

$$\log k_{ijT} = \log A_{ij} - \log n_{ij} - E_{ij}/4.576T \qquad (2)$$

where k_{ijT} are rate constants (in s^{-1}) of reaction 1 at temperature T as estimates of high-pressure limit values k_∞, log A_{ij} (in s^{-1}), and E_{ij} (kcal/mol) are the parameters of the Arrhenius equation and n is a statistical coefficient denoting the number of equivalent dissociating homolytically bonds. The employment of rate constants restricted our statistical treatment to a single temperature. Thus, the value of temperature $T = 891$ K was selected as an arithmetic mean of all ranges of temperatures used to estimate the Arrhenius parameters log A and E. The mean values of log k for each separate reaction were calculated by excluding the deviating points according to the Student's criterion at the confidence level 0.95.

* Corresponding author phone: +37-27-375 255; fax: +37-27-375 264; e-mail: mati@chem.ut.ee.

Table 1. Structural Formulas of $R^1R^2R^3C$ and X, Statistical Factor n, Ranges of Experimental log A (s^{-1}) and E (kcal/mol) for Reaction 3 and Number of Different Sources for log A and E ns

no.	a	$R^1R^2R^3C$	X	n	range of log A	range of E	ns
1.	2	CH_3	H	4	14.1−16.45	101−107.6	11
2.	3	$CH_2CH=CH_2$	H	3	13.4	78	1
3.	4	$CH_2C(CH_3)=CH_3$	H	3	13.7	76	1
4.	5	CH_2CN	H	3	15.79	96.6	1
5.	6	$CH_2C_6H_5$	H	3	13.3−16.9	77.5−91.4	7
6.	7	$CH_2(2-CH_3C_6H_4)$	H	3	13.7−16.3	74.8−92.26	2
7.	8	$CH_2(3-CH_3C_6H_4)$	H	3	13.6−16.3	77.1−89.63	2
8.	9	$CH_2(4-CH_3C_6H_4)$	H	3	13.7−16.3	76−89.39	4
9.	10	$CH_2(1-C_{10}H_7)$	H	3	13.18	73.5	1
10.	11	$CH_2(2-C_{10}H_7)$	H	3	13.18	73.5	1
11.	12	$2-CH_2C_5H_4N$	H	3	13.3	75.5	1
12.	13	$3-CH_2C_5H_4N$	H	3	13.3	76.5	1
13.	14	$4-CH_2C_5H_4N$	H	1	13.3	77.5	1
14.	15	$CH(C_6H_5)_2$	H	2	15.3	81.4	1
15.	16	COC_6H_5	H	1	15.6	83.7	1
16.	17	$C(C_6H_5)_3$	H	1	16.45	83	1
17.	18	$CH(CH_3)C_6H_5$	H	2	17.1	81.3	1
18.	19	C_6H_5	H	6	15.2−17.3	102−118	3
19.	20	$CH_2(4-FC_6H_4)$	H	3	13.3	78	1
20.	21	$CH_2/3,5-(CH_3)_2C_6H_3/$	H	9	16.5	88.91	1
21.	22	$CH(C_6H_5)(4-C_5H_4N)$	H	2	15.3	82.3	1
22.	23	$2-C_5H_4N$	H	2	16.2	100.4	1
23.	24	$C\equiv CH$	H	2	15.42	124.1	1
24.	31	CH_3	Cl	1	12.67−15.52	71.2−91.54	3
25.	32	$CH_2CH=CH_2$	Cl	1	13.17	59.3	1
26.	33	CH_2OCH_3	Cl	1	18.63	69.3	1
27.	34	$CH_2C_6H_5$	Cl	1	15.36	70	1
28.	35	COC_6H_5	Cl	1	15.38	73.6	1
29.	36	CH_2CH_2Cl	Cl	2	13	70	1
30.	37	C_6H_5	Cl	1	15.15	96.9	1
31.	38	$CCl=CCl_2$	Cl	4	14.65	80	1
32.	39	CH_3	Br	1	13.3	67.5	1
33.	40	$CH_2CH=CH_2$	Br	1	12.7−15	47.5−54.7	2
34.	41	CH_2Cl	Br	1	13.3	61	1
35.	42	CH_2Br	Br	2	13.3	62.5	1
36.	43	$CH_2C_6H_5$	Br	1	13.3	50.5	1
37.	44	$CHCl_2$	Br	1	13.3	53.5	1
38.	45	$CHBr_2$	Br	3	13.08−13.3	51−55.5	2
39.	46	CF_3	Br	1	13.3	64.5	1
40.	47	CCl_3	Br	1	13.3	50	1
41.	48	CBr_3	Br	4	13.3	49	1
42.	49	COC_6H_5	Br	1	13.7	57	1
43.	50	C_6H_5	Br	1	13.3−14.63	70.9−81	5
44.	51	$1-C_{10}H_7$	Br	1	13.55	70.9	1
45.	52	$2-C_{10}H_7$	Br	1	13.18	70	1
46.	53	9-anthryl	Br	1	13.18	65.6	1
47.	54	9-phenanthryl	Br	1	13	67.7	1
48.	55	CH_2COCH_3	Br	1	16	62.5	1
49.	56	$CH_2C_6F_5$	Br	1	14.54	53.8	1
50.	57	CF_2CF_2Br	Br	2	15.2	64.5	1
51.	58	CH_3	I	1	13.42	54.7	1
52.	59	C_2H_5	I	1	13.65−14.33	50−51.6	2
53.	60	C_3H_7	I	1	15.5−16.5	54.9−55.7	2
54.	61	$CH_2CH=CH_2$	I	1	14.45	42.8	1
55.	62	CF_3	I	1	14.4−16.72	47.2−52.8	4
56.	63	$CH=CH_2$	I	1	15.62	66.5	1
57.	64	C_6H_5	I	1	14.93−15	64.4−65.2	2
58.	65	$2-CH_3C_6H_4$	I	1	15.15	66.3	1
59.	66	C_6F_5	I	1	15.4−15.9	67−69.2	2
60.	67	C_6F_{13}	I	1	14.3	48.2	1
61.	77	CH_3	OH	1	14.4−16.28	78.84−91.8	5
62.	87	CH_3	NH_2	1	10.84	48.15	1
63.	88	$C(CH_3)_2C_2H_5$	NH_2	1	15.9	78.9	1
64.	89	$CH_2C_6H_5$	NH_2	1	12.78−15.2	59−71.9	3
65.	91	CF_2NF_2	NF_2	2	15.75	53.6	1
66.	92	$CF(NF_2)_2$	NF_2	3	16.45	48.3	1
67.	93	$CCl(NF_2)_2$	NF_2	3	13.24	36.05	1
68.	94	$C(NF_2)_3$	NF_2	4	16.14	40.4	1
69.	103	$C(CH_3)_3$	NO	1	15.6	36	1
70.	104	CF_3	NO	1	15.6	41.5	1
71.	105	C_6H_5	NO	1	15.4	49	1

Table 1 (Continued)

no.	a	$R^1R^2R^3C$	X	n	range of log A	range of E	ns
72.	108	C_6F_5	NO	1	15.3	48	1
73.	119	CH_3	NO_2	1	13.43–16.25	49.2–58.5	7
74.	120	C_2H_5	NO_2	1	15.9	57	1
75.	121	C_3H_7	NO_2	1	15.36	55	1
76.	122	$CH(CH_3)_2$	NO_2	1	15.38	54	1
77.	123	$CHFNO_2$	NO_2	2	16.68	48.5	1
78.	124	$CH(NO_2)_2$	NO_2	3	15.94	42.4	1
79.	125	CCl_3	NO_2	1	15.35–15.69	37.47–37.67	2
80.	126	CF_2NO_2	NO_2	2	15.83	47.4	1
81.	127	$CFClNO_2$	NO_2	2	15.7	41.5	1
82.	128	$CFBrNO_2$	NO_2	2	15.3	39.5	1
83.	129	$CFINO_2$	NO_2	2	15.7	39.7	1
84.	130	$CF(NO_2)_2$	NO_2	3	15.4	41.9	1
85.	131	CCl_2NO_2	NO_2	2	15.26	34.37	1
86.	132	$CCl(NO_2)_2$	NO_2	3	15.75	36.4	1
87.	133	$CBr(NO_2)_2$	NO_2	3	16.1	36.2	1
88.	134	$CI(NO_2)_2$	NO_2	3	15.25	34.4	1
89.	135	$C(NO_2)_3$	NO_2	4	16.3–17.53	38.6–40.9	3
90.	136	$CH(CH_3)NO_2$	NO_2	2	16.74	47.1	1
91.	137	CCl_2CH_3	NO_2	1	15.22	42.6	1
92.	138	$C(NO_2)_2CH_3$	NO_2	3	17.18	43.2	1
93.	139	$CF(NO_2)CH_3$	NO_2	2	17	47.7	1
94.	140	$CCl(NO_2)CH_3$	NO_2	2	14.73	37.4	1
95.	141	$CBr(NO_2)CH_3$	NO_2	2	16.14	40.5	1
96.	142	$CF(NO_2)CF(NO_2)_2$	NO_2	4	18.03	42.2	1
97.	143	$C(NO_2)_2CF(NO_2)_2$	NO_2	3	17.3	36.5	1
98.	144	$C(NO_2)_2C(NO_2)_3$	NO_2	6	17.3	35.8	1
99.	145	$CH(C_2H_5)NO_2$	NO_2	2	16.91	48	1
100.	146	$C(CH_3)_2NO_2$	NO_2	2	18.5	50.5	1
101.	147	$CCl_2C_2H_5$	NO_2	1	15.15	42.7	1
102.	148	$C(NO_2)_2C_2H_5$	NO_2	3	16.86	42.3	1
103.	149	$CH(NO_2)C_3H_7$	NO_2	2	17	48.2	1
104.	150	$C(NO_2)_2C_3H_7$	NO_2	3	17.7	43.6	1
105.	151	C_6H_5	NO_2	1	12.65–17.32	53.4–69.7	5
106.	152	$2\text{-}ClC_6H_4$	NO_2	1	12.83–17	51.1–67.3	2
107.	153	$3\text{-}ClC_6H_4$	NO_2	1	12.22–17.4	49.8–70.2	2
108.	154	$4\text{-}ClC_6H_4$	NO_2	1	13.73–17.4	54.4–71.7	2
109.	155	$2\text{-}NO_2C_6H_4$	NO_2	2	12.3–14.6	48.9–55.1	2
110.	156	$3\text{-}NO_2C_6H_4$	NO_2	2	13–16.9	52.9–70	3
111.	157	$4\text{-}NO_2C_6H_4$	NO_2	2	13.5–17.1	53.7–68.6	2
112.	158	$2\text{-}CH_3C_6H_4$	NO_2	1	14.81–16.4	61.4–67	2
113.	159	$3\text{-}CH_3C_6H_4$	NO_2	1	16.9–17.88	65–68	2
114.	160	$4\text{-}CH_3C_6H_4$	NO_2	1	14.89–16.73	61.5–68.2	5
115.	161	$2,5\text{-}(NO_2)_2C_6H_3$	NO_2	1	12.3	46.2	1
116.	162	$3,5\text{-}(NO_2)_2C_6H_3$	NO_2	3	13.6–17.2	51.9–67.3	2
117.	163	$2\text{-}CH_3\text{-}5\text{-}NO_2C_6H_3$	NO_2	1	13.35–15.3	49.1–67.4	2
118.	164	$3\text{-}CH_3\text{-}5\text{-}NO_2C_6H_3$	NO_2	2	12.4	48.2	1
119.	165	$4\text{-}NH_2\text{-}3,5\text{-}(NO_2)_2C_6H_2$	NO_2	1	12.6	49.4	1
120.	166	$4\text{-}CH_3\text{-}3,5\text{-}(NO_2)_2C_6H_2$	NO_2	1	12.4	46.9	1
121.	167	$C(NO_2)_2SCH_3$	NO_2	3	16.2	30.8	1
122.	168	$C(NO_2)_2SC_6H_5$	NO_2	3	16	31.5	1
123.	169	$C(NO_2)_2S/2,4\text{-}(NO_2)_2C_6H_3/$	NO_2	3	16.2	31.2	1
124.	170	$C(CH_3)(NO_2)SCH_3$	NO_2	3	18	38.2	1
125.	171	$C(CH_3)(NO_2)SC_6H_5$	NO_2	3	17.75	38.5	1
126.	172	$C(CH_3)(NO_2)S/2,4\text{-}(NO_2)_2C_6H_3/$	NO_2	3	17.55	37.5	1
127.	173	$3\text{-}BrC_6H_4$	NO_2	1	17.4	71	1
128.	174	$4\text{-}BrC_6H_4$	NO_2	1	17.5	72.3	1
129.	175	$4\text{-}IC_6H_4$	NO_2	1	17.5	71.6	1
130.	176	$2\text{-}OHC_6H_4$	NO_2	1	12.6	52.4	1
131.	177	$3\text{-}OHC_6H_4$	NO_2	1	17.4	71.2	1
132.	178	$2\text{-}NH_2C_6H_4$	NO_2	1	13.5–16.9	57.5–63.4	2
133.	179	$3\text{-}NH_2C_6H_4$	NO_2	1	10.55–17.5	43–72	2
134.	180	$4\text{-}NH_2C_6H_4$	NO_2	1	12.36–17.5	47.9–79.7	2
135.	181	$2\text{-}C_6H_5C_6H_4$	NO_2	1	16	62.9	1
136.	185	$C(NO_2)_2CH_2CH_2NO_2$	NO_2	3	16.92	42.1	1
137.	186	$CFNO_2CH_2CH_2CF(NO_2)_2$	NO_2	4	16.46	46.1	1
138.	187	$C(NO_2)_2CH_2CHNO_2CH_2C(NO_2)_3$	NO_2	6	15.86	35.5	1
139.	188	$C(NO_2)_2CH_2CFNO_2CH_2C(NO_2)_3$	NO_2	6	16.2	35.2	1
140.	189	$C(NO_2)_2CH_2CClNO_2CH_2C(NO_2)_3$	NO_2	6	16.21	34.9	1
141.	190	$C(NO_2)_2CH_2CBrNO_2CH_2C(NO_2)_3$	NO_2	6	15.93	34.2	1
142.	191	$CFNO_2CH_2CHNO_2CH_2CF(NO_2)_2$	NO_2	4	15.62	41.3	1
143.	192	$CFNO_2CH_2CFNO_2CH_2CF(NO_2)_2$	NO_2	4	15.37	39.6	1
144.	193	$CFNO_2CH_2CClNO_2CH_2CF(NO_2)_2$	NO_2	4	16.06	38.8	1

Table 1 (Continued)

no.	*a*	R^{1}R^{2}R^{3}C	X	*n*	range of log A	E	ns
145.	194	CFNO$_2$CH$_2$CBrNO$_2$CH$_2$CF(NO$_2$)$_2$	NO$_2$	4	15.72	38.8	1
146.	195	C(NO$_2$)/CH$_2$CF(NO$_2$)$_2$/$_2$	NO$_2$	2	16	36.4	1
147.	212	CH$_3$	SH	1	13.48	67	1
148.	213	C$_2$H$_5$	SH	1	13.48	63	1
149.	214	C(CH$_3$)$_3$	SH	1	17.34	57.9	1
150.	215	CH$_2$C$_6$H$_5$	SH	1	13.48	53	1
151.	218	CH$_3$	OCH$_3$	2	15−17.5	76−83.7	8
152.	219	CH$_2$C$_6$H$_5$	OCH$_3$	1	14.5	65.2	1
153.	225	C$_2$H$_5$	OC$_2$H$_5$	1	14−17.2	76.8−82.4	5
154.	230	C$_2$H$_5$	OCH=CH$_2$	1	15.9	70	1
155.	231	CH$_2$C$_6$H$_5$	OCH=CH$_2$	1	16.63	53.74	1
156.	233	CH$_2$C$_6$H$_5$	OCOCH$_3$	1	14.5	67	1
157.	236	CH$_2$C$_6$H$_5$	OCOC$_6$H$_5$	1	15.3	69	1
158.	237	CH$_3$	OC$_6$H$_5$	1	13.7−16.08	58−65.8	5
159.	238	C$_2$H$_5$	OC$_6$H$_5$	1	15.3−15.5	60.4−61.9	2
160.	239	C$_4$H$_9$	OC$_6$H$_5$	1	16	65.6	1
161.	240	CH$_2$CH=CH$_2$	OC$_6$H$_5$	1	14.6	48.5	1
162.	241	CH$_2$C$_6$H$_5$	NHCH$_3$	1	12.86−15.1	57.7−68.7	2
163.	242	CH$_3$	NHC$_6$H$_5$	1	13.4−15.1	60−66.7	2
164.	245	CH$_2$C$_6$H$_5$	N(CH$_3$)$_2$	1	15.2	60.9	1
165.	247	CH$_3$	N(CH$_3$)C$_6$H$_5$	2	12.9−15.1	57−64.7	2
166.	248	CH$_2$CH=CH$_2$	N(CH$_3$)C$_6$H$_5$	1	13.75	48.5	1
167.	249	CH$_3$	NNCH$_3$	2	13.9−17.3	46−55.4	10
168.	250	CH$_2$CH=CH$_2$	NNCH$_3$	1	14.51	35.4	1
169.	252	CF$_3$	NNCF$_3$	2	13.96−16.2	48.5−55.2	5
170.	253	C$_2$H$_5$	NNC$_2$H$_5$	2	14.2−16.4	44.5−49.7	9
171.	254	C$_3$H$_7$	NNC$_3$H$_7$	2	14.6	45.7	1
172.	255	C$_2$H$_5$	NNCH(CH$_3$)$_2$	1	16.5	49.2	1
173.	256	CH(CH$_3$)$_2$	NNCH(CH$_3$)$_2$	2	13.68−18.1	40.75−51.8	10
174.	257	C$_4$H$_9$	NNC$_4$H$_9$	2	17.71	53.2	1
175.	258	CH(CH$_3$)C$_2$H$_5$	NNCH(CH$_3$)C$_2$H$_5$	2	17.28	48.4	1
176.	259	C(CH$_3$)$_3$	NNC(CH$_3$)$_3$	2	15.94−17.15	41.9−43	4
177.	262	CH$_3$	SCH$_3$	2	16.7	74	1
178.	263	CH$_2$C$_6$H$_5$	SCH$_3$	1	13.48−14.7	51.5−56	2
179.	264	CH$_3$	SC$_6$H$_5$	1	14.48−15.3	60−63.6	2
180.	265	CH$_2$COOH	SC$_6$H$_5$	1	15	58	1
181.	266	CH$_3$	SO$_2$CH$_3$	2	14.33	60.6	1
182.	267	CH$_2$CH=CH$_2$	SO$_2$CH$_3$	1	14.1	47.7	1
183.	268	CH$_2$C$_6$H$_5$	SO$_2$CH$_3$	1	14.52	51.2	1
184.	270	CH$_3$	Si(CH$_3$)$_3$	4	14.1−17.6	67.6−84.9	4
185.	282	CH$_3$	SnCl$_2$CH$_3$	2	13.52	56.1	1
186.	283	CH$_3$	Sn(CH$_3$)$_3$	4	13.9−15.7	55.4−64.5	2
187.	284	CH$_3$	Pb(CH$_3$)$_3$	4	13.25−14.7	41.2−49.4	2
188.	285	C$_2$H$_5$	Pb(C$_2$H$_5$)$_3$	4	12.08−18	36.9−53.6	6
189.	318	CH$_3$	OC(CH$_3$)=CH$_2$	1	15.8	66.3	1
190.	340	CH$_3$	2-FC$_6$H$_4$O	1	15.5	61.6	1
191.	341	CH$_3$	3-FC$_6$H$_4$O	1	15.5	64.4	1
192.	342	CH$_3$	4-FC$_6$H$_4$O	1	15.5	62.4	1
193.	343	CH$_3$	2-ClC$_6$H$_4$O	1	15.5	61.3	1
194.	344	CH$_3$	3-ClC$_6$H$_4$O	1	15.5	63.7	1
195.	345	CH$_3$	4-ClC$_6$H$_4$O	1	15.5	62.4	1
196.	346	CH$_3$	2-BrC$_6$H$_4$O	1	15.5	61.8	1
197.	347	CH$_3$	2-OHC$_6$H$_4$O	1	15.5	56.3	1
198.	348	CH$_3$	3-OHC$_6$H$_4$O	1	15.5	63.8	1
199.	349	CH$_3$	4-OHC$_6$H$_4$O	1	15.5	61	1
200.	350	CH$_3$	2-NH$_2$C$_6$H$_4$O	1	15.5	56.1	1
201.	351	CH$_3$	3-NH$_2$C$_6$H$_4$O	1	15.5	63.1	1
202.	352	CH$_3$	4-NH$_2$C$_6$H$_4$O	1	15.5	60.5	1
203.	353	CH$_3$	2-NO$_2$C$_6$H$_4$O	1	15.5	62.1	1
204.	354	CH$_3$	3-NO$_2$C$_6$H$_4$O	1	15.5	63	1
205.	355	CH$_3$	4-NO$_2$C$_6$H$_4$O	1	15.5	64.6	1
206.	356	CH$_3$	2-OCH$_3$C$_6$H$_4$O	1	15.5	59.3	1
207.	357	CH$_3$	3-OCH$_3$C$_6$H$_4$O	1	15.5	62.5	1
208.	358	CH$_3$	4-OCH$_3$C$_6$H$_4$O	1	15.5	59.6	1
209.	359	CH$_3$	2-CH$_3$C$_6$H$_4$O	1	15.5	60.9	1
210.	360	CH$_3$	3-CH$_3$C$_6$H$_4$O	1	15.5	63	1
211.	361	CH$_3$	4-CH$_3$C$_6$H$_4$O	1	15.5	61.6	1
212.	362	CH$_3$	2-CH$_2$OHC$_6$H$_4$O	1	15.5	61	1
213.	363	CH$_3$	2-COCH$_3$C$_6$H$_4$O	1	15.5	62	1
214.	364	CH$_3$	3-COCH$_3$C$_6$H$_4$O	1	15.5	63.7	1
215.	365	CH$_3$	4-COCH$_3$C$_6$H$_4$O	1	15.5	64.1	1
216.	366	CH$_3$	2-CH=CH$_2$C$_6$H$_4$O	1	15.5	61	1
217.	367	CH$_3$	2-CNC$_6$H$_4$O	1	15.5	63.4	1

Table 1 (Continued)

no.	a	$R^1R^2R^3C$	X	n	range of log A	range of E	ns
218.	368	CH_3	$3\text{-}CNC_6H_4O$	1	15.5	64.6	1
219.	369	CH_3	$4\text{-}CNC_6H_4O$	1	15.5	63.8	1
220.	370	CH_3	C_6F_5O	1	15.5	60.8	1
221.	371	CH_3	$1\text{-}C_{10}H_7O$	1	15.5	57.5	1
222.	372	CH_3	$2\text{-}C_{10}H_7O$	1	15.5	61	1
223.	383	C_2H_5	C_2H_5	1	15.3−16.8	77.2−82.5	6
224.	384	$C(CH_3)_2C_2H_5$	C_2H_5	2	16.57	77.1	1
225.	385	$CH_2CH=CH_2$	C_2H_5	1	16	70.7−71.3	2
226.	386	CH_2CN	C_2H_5	1	15.4	76.7	1
227.	387	$CH_2C_6H_5$	C_2H_5	1	12.48−15.6	57.5−71.5	4
228.	388	$1\text{-}C_{10}H_7$	C_2H_5	1	13.9	64.8	1
229.	389	C_2H_5	$NNCH_2C_6H_5$	1	15.72	51	1
230.	391	C_2H_5	$Sn(C_2H_5)_3$	4	16	59.3	1
231.	392	$C(CH_3)_2NH_2$	C_2H_5	1	16.5	76.5	1
232.	394	C_2H_5	$P(C_2H_5)_2$	3	16−17.5	63−67	4
233.	397	C_2H_5	$2\text{-}OHC_6H_4O$	1	15.5	55.2	1
234.	398	$CH_2CH=CH_2$	C_3H_7	1	15.9	70.7−70.8	2
235.	399	$CH_2C\equiv CH$	C_3H_7	1	15.9	72.1	1
236.	400	$CH_2C_6H_5$	C_3H_7	1	14.48−14.5	65−67.2	2
237.	402	$CH(CH_3)_2$	$CH(CH_3)_2$	1	16.1−17.9	74.6−80.3	7
238.	403	$C(CH_3)_3$	$CH(CH_3)_2$	1	16.2−16.46	72.9−73	2
239.	404	$C(CH_3)_2C_2H_5$	$CH(CH_3)_2$	1	16.15	71.3	1
240.	405	$CH(CH_3)CH=CH_2$	$CH(CH_3)_2$	1	15.7	64.6	1
241.	406	$CH_2C\equiv CH$	$CH(CH_3)_2$	1	15.56	69.4	1
242.	407	CH_2CN	$CH(CH_3)_2$	1	15.4	73.1	1
243.	408	$CH_2C_6H_5$	$CH(CH_3)_2$	1	15.23−15.6	67.8−69.1	2
244.	409	$C(CH_3)_2OH$	$CH(CH_3)_2$	1	16.24	74.3	1
245.	410	$CH_2C_6H_5$	C_4H_9	1	16	70.7	1
246.	411	$CH(CH_3)C_2H_5$	$CH(CH_3)C_2H_5$	1	16.34	75.3	1
247.	412	$C(CH_3)_3$	$CH(CH_3)C_2H_5$	1	16.3	72.3	1
248.	413	$CH_2C(CH_3)=CH_2$	$CH(CH_3)C_2H_5$	1	15.63−15.9	66−67.4	2
249.	414	$CH_2C\equiv CH$	$CH(CH_3)C_2H_5$	1	15.9	69.5	1
250.	415	$C(CH_3)_3$	$C(CH_3)_3$	1	10.7−17.4	42.4−72.1	15
251.	416	$CH_2CH=CH_2$	$C(CH_3)_3$	1	15.78	65.53	1
252.	417	$CH_2C_6H_5$	$C(CH_3)_3$	1	15.5	64.3	1
253.	418	$CH(CH_3)OH$	$C(CH_3)_3$	1	16.33	74.5	1
254.	419	C_6H_{11}	$C(CH_3)_3$	1	16.31	74.1	1
255.	420	$SC(CH_3)_3$	$C(CH_3)_3$	2	15.1−16.7	54.7−59.8	3
256.	421	$CH_2CH=CH_2$	$CH_2CH=CH_2$	1	13.3−16.3	45.6−58	4
257.	422	$CH_2SiH(CH_3)_2$	$CH_2CH=CH_2$	1	15.5	68.4	1
258.	423	$CH_2Si(CH_3)_3$	$CH_2CH=CH_2$	1	14.6	68.6	1
259.	424	$CH_2CH_2SiH(CH_3)_2$	$CH_2CH=CH_2$	1	15.4	67.6	1
260.	425	$CH_2CH_2Si(CH_3)_3$	$CH_2CH=CH_2$	1	15.3	67.4	1
261.	426	$CH_2C_6H_5$	$CH_2C\equiv CH$	1	14.6	60.3	1
262.	427	$CH_2CH(CH_3)_2$	$CH_2C\equiv CH$	1	16.1	72.9	1
263.	428	CH_2OCH_3	CH_2OCH_3	1	15.36	71.3	1
264.	429	$CH_2C_6H_5$	$CH_2C_6H_5$	1	14.8	60.4	1
265.	430	$COOH$	$CH_2C_6H_5$	1	12.9−14.3	55−66.3	2
266.	431	$COCH_3$	$CH_2C_6H_5$	1	16	68.2	1
267.	432	C_6H_5	$CH_2C_6H_5$	2	15.3−16.6	82.3−84	2
268.	433	CH_2NH_2	$CH_2C_6H_5$	1	14.7	60.9−63.9	1
269.	434	$CH_2N(CH_3)_2$	$CH_2C_6H_5$	1	14.8	58.7	1
270.	435	$4\text{-}C_5H_4N$	$CH_2C_6H_5$	1	15.3	82.3	1
271.	436	$COOH$	$CH(C_6H_5)_2$	1	12.9	52	1
272.	437	CF_3	CF_3	1	17.63	94.4	1
273.	438	$C(CF_3)=CF_2$	CF_3	2	14.04	82.7	1
274.	439	C_6H_5	CF_3	1	17.9	98.7	1
275.	440	CH_2F	CF_3	1	16.9	92.3	1
276.	441	CHF_2	CF_3	1	16.6	93.5	1
277.	442	CHO	CF_3	1	16.63−17	80−83	2
278.	443	CCl_3	CCl_3	1	17.75	68	1
279.	444	$COCH_3$	$COCH_3$	1	15.7−16.5	66−67.7	4
280.	445	C_6H_5	COC_6H_5	2	16.2	87.5	1
281.	446	$CH=CH_2$	$CH=CH_2$	1	16.61	93.4	1
282.	447	C_6H_5	NNC_6H_5	2	12.61−16.6	53.4−66.4	2
283.	449	CHF_2	CHF_2	1	17.4	91.4	1
284.	451	$CH_2CH(CH_3)_2$	$NNCH_2CH(CH_3)_2$	2	15.6	40.6	1
285.	452	$CH_2C\equiv CCH_3$	$CH_2CH(CH_3)_2$	1	16.2	73.1	1
286.	453	CH_2NH_2	CH_2NH_2	1	15.5	65.1	1
287.	454	$CH_2N(CH_3)_2$	$CH_2N(CH_3)_2$	1	15.6	63.2	1

^{a} The number in the second column is the number of order of the whole data set of the gas-phase homolysis used in the treatment.

The molecular structures were generated using the PC-MODEL program.[25] The three-dimensional optimization of molecules was carried out for 287 compounds involving the cleavage of C−X bonds using the semiempirical MNDO parametrization.[26] The respective output files of MOPAC[27] or AMPAC[28] calculations were treated using the CODESSA program to derive a large variety of molecular descriptors including the constitutional, topological, geometric, electrostatic, quantum-chemical, and thermodynamic descriptors.[23]

Finally, the log k (891) values for 287 structures corresponding to the formal $R^1R^2R^3CX$ type (see Table 1) and dissociating homolytically according to the following scheme

$$R^1R^2R^3CX \rightarrow R^1R^2R^3C^{\bullet} + {}^{\bullet}X \qquad (3)$$

were selected for the subsequent QSPR treatment. The molecular descriptors were calculated separately for the reagents $R^1R^2R^3CX$, the products $R^1R^2R^3C^{\bullet}$, the free radicals ${}^{\bullet}X$, and for the C−X bonds. The overall number of calculated molecular descriptors exceeded 2000 different descriptors. Two strategies were employed to develop the best multiparameter QSPR models: the heuristic[22,29] and the best multilinear regression (BMLR)[22,29] schemes, both based on the scales forward selection methodology.[30]

The CODESSA calculations were carried out on PC in the Microsoft Windows 95 environment.[22,31]

RESULTS AND DISCUSSION

The 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 any of those two procedures for the development of a QSPR multilinear equation for all 287 reagents reveals that the accuracy of the best models up to those including five parameters ($R^2 = 0.7963$, $s^2 = 3.15$, see Table 2) is not sufficient. This result shows that the rate constant of the gas-phase homolysis of C−X bonds is a difficult chemical property to be described by an uniform QSPR model. Therefore, we proceeded with the partitioning of the compounds $R^1R^2R^3CX$ into several groups according to the type of atoms X involved. By treating the respective separate sets of the data, good individual three- to five-parameter correlations were obtained for the log k (891) of compounds involving C−H, C−Cl, C−Br, C−I, C−O, C−S, C−NO$_2$, C−NNR, and C−N (except C−NO$_2$ and C−NNR) bond fissions, respectively. The corresponding correlation coefficients squared R^2 were spanning from 0.9650 to 0.9996, and the standard deviations squared s^2 from 0.0080 to 0.2818 (Table 3). The best five-parameter model of log k (891) for the C−C bond (except C−CH$_3$) homolysis is, however, rather poor ($R^2 = 0.7971$, $s^2 = 0.7411$, see Table 3). Obviously, in the case of small sets (8−12 compounds for C−Cl, C−I, C−S, and C−NNR) the use of five parameters leaves too small a number of statistical degrees of freedom and probably gives overfitted results. Therefore, in Table 3 we have given also the best two- to four-parameter models as developed using the heuristic procedure and BMLR. In all cases, the three- or even two-parameter correlations give satisfactory fit of experimental data.

For two larger sets, the C−NO$_2$ and C−H bond fission reactions, the most important descriptors are the minimum

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

notation	descriptor	ref
d1	vibrational entropy (300 K) divided by number of atoms	22
d2	rotational entropy (300 K)	22
d3	relative number of C atoms	22
d4	maximum $\sigma-\pi$ bond order	32
d5	HOMO-1 energy−highest occupied molecular orbital energy	22
d6	relative number of I atoms	22
d7	minimum nuclear−nuclear repulsion for a C−H bond	33
d8	maximum Coulombic interaction for a C−H bond	22
d9	average bonding information content (order 2)	34, 35
d10	maximum $\pi-\pi$ bond order for $R^1R^2R^3C^{\bullet}$	32
d11	HACA-1−hydrogen bonding specific charged surface area for $R^1R^2R^3C$	29
d12	(C) valency	32
d13	average one-electron reaction index for a C atom for $R^1R^2R^3C^{\bullet}$	29
d14	ZX shadow divided by ZX rectangle	38
d15	RPCG−relative positive charge for $R^1R^2R^3C^{\bullet}$	36, 37
d16	total molecular two-center exchange energy divided by number of atoms	22
d17	molecular volume divided by XYZ box	22
d18	maximum atomic state energy for a Br atom	22
d19	DPSA-3−difference in charged partial surface area (PPSA3-PNSA3)	36, 37
d20	relative number of F atoms	22
d21	minimum electron−electron repulsion for a Br−C bond	22
d22	maximum atomic orbital electronic population	22
d23	minimum resonance energy for a C−I bond	22
d24	total hybridization component of the molecular dipole	22
d25	(C) WPSA−weighted partial surface area for C atom	36. 37
d26	average bonding information content (order 1) for $R^1R^2R^3C^{\bullet}$	34, 35
d27	RNCS−relative negative charged surface area	39, 40
d28	Wiener index	41
d29	HOMO−LUMO energy gap	22
d30	minimum (>0.1) bond order of a C atom for $R^1R^2R^3C^{\bullet}$	32
d31	β polarizability	27
d32	average complementary information content (order 1) for $R^1R^2R^3C^{\bullet}$	34, 35
d33	relative number of single bonds	22
d34	Kier shape index (order 3)	42
d35	lowest normal mode vibrational frequency	22
d36	YZ shadow	38
d37	minimum partial charge for a C atom	39, 40
d38	relative molecular weight	22
d39	minimum total interaction for a C−S bond	22
d40	maximum partial charge for a H atom	39, 40
d41	minimum nuclear−nuclear repulsion for a C−N bond	33
d42	minimum (>0.1) bond order of a N atom	32
d43	maximum atomic state energy for a C atom	22
d44	maximum electron−nuclear attraction for a N−O bond	33
d45	relative number of S atoms	22
d46	RPCG−relative positive charge	36, 37
d47	maximum $\pi-\pi$ bond order	32
d48	relative number of single bonds	22
d49	absolute value of average one-electron reaction index for a C atom	22
d50	Kier and Hall index (order 2)	43
d51	highest normal mode vibrational transition dipole	22
d52	HA dependent HDSA-2−surface area of hydrogens which can be donated	29
d53	maximum atomic force constant	22
d54	number of N atoms	22
d55	minimum number of hydrogen acceptor and donor atoms	22
d56	minimum Coulombic interaction for a C−N bond	22
d57	minimum atomic state energy for a C atom	22
d58	number of F atoms	22
d59	YZ shadow divided by YZ rectangle	38
d60	minimum resonance energy for a C−C bond	22
d61	LUMO energy−lowest unoccupied molecular orbital energy	22
d62	relative number of rings	22

Table 3. Best One- to Five-Parameter Correlation Equations between log k (891) Values and Descriptors (Table 2) for Reaction 3 Derived by the Heuristic and BMLR Procedures[a]

reaction	N	n	intercept	error	eq descriptor	coeff	error	R^2	F	s^2	R^2_{CV}
C−X bond	287	1	−6.23	0.41	d1	4.20	0.26	0.4696	252.3	8.09	0.4522
		2	−12.73	0.94	d2	0.71	0.04	0.6470	260.2	5.40	0.6089
					d3	−21.77	1.26				
		5	−1.62	1.87	d2	0.55	0.03	0.7963	219.7	3.15	0.7601
					d3	−23.7	1.54				
					d4	130.1	10.4				
					d5	0.73	0.11				
					d6	22.3	3.8				
C−H bond	23	1	269.4	45.6	d7	−6.85	1.13	0.6370	36.9	2.90	0.6888
		2	281.9	17.0	d7	−8.72	0.45	0.9572	199.1	0.401	0.9173
					d8	13.99	1.22				
		5	293.1	14.6	d9	5.36	0.81	0.9815	180.8	0.1845	0.9681
					d7	−7.55	0.36				
					d10	2.40	0.42				
					d11	−0.247	0.054				
					d12	−0.324	0.082				
C−Cl bond	8	1	−5.16	0.72	d13	−0.00183	0.050	0.6897	13.3	3.78	0.4691
		2	9.54	3.26	d14	−26.8	4.3	0.9525	50.2	0.7239	0.8996
					d15	16.2	1.9				
		3	7.58	0.35	d14	−29.6	0.5	0.9996	3181.8	0.0080	0.9974
					d15	16.8	0.2				
					d16	−0.71	0.03				
C−Br bond	19	1	13.6	1.9	d17	−35.6	4.5	0.7828	61.3	1.0200	0.6586
		2	−45.6	152	d17	−34.2	3.7	0.8639	50.8	0.6791	0.7343
					d18	1.36	0.44				
		5	−33.9	83	d17	−36.7	2.2	0.9662	74.3	0.1860	0.9115
					d19	0.088	0.014				
					d20	−6.91	0.76				
					d21	−0.013	0.002				
					d22	178	42				
C−I bond	10	1	23.2	3.2	d23	−2.33	0.34	0.8573	48.1	0.5580	0.6946
		2	33.1	2.8	d23	−1.90	0.21	0.9624	89.5	0.1681	0.8829
					d14	−18.4	4.2				
		3	20.8	0.6	d24	−14.9	0.4	0.9951	405.4	0.0271	0.9855
					d25	−12.2	0.9				
					d26	6.74	0.45				
C−O bond	40	1	1.28	0.12	d27	−0.196	0.010	0.9070	370.6	0.2897	0.6882
		2	2.35	0.21	d27	−0.181	0.009	0.9282	239.3	0.2296	0.7251
					d28	−0.0065	0.0013				
		5	6.00	1.14	d29	−0.519	0.114	0.9650	187.3	0.1220	0.8212
					d27	−0.189	0.029				
					d30	1.18	0.23				
					d31	−0.0028	0.0005				
					d32	−0.403	0.126				
C−O bond	39	1	1.22	0.10	d27	−0.193	0.009	0.9272	470.9	0.2183	0.7045
		2	8.14	0.34	d29	−0.889	0.035	0.9478	326.9	0.1607	0.8186
					d31	−0.0051	0.0012				
		5	8.95	0.34	d29	−1.35	0.08	0.9831	382.9	0.0569	0.8880
					d31	−0.0036	0.0007				
					d33	7.47	1.02				
					d34	−0.566	0.094				
					d35	−0.0047	0.0011				
C−S bond	12	1	−6.36	1.29	d36	0.265	0.049	0.7446	29.2	0.8100	0.6915
		2	−8.49	1.30	d36	0.298	0.042	0.8513	25.8	0.6430	0.7059
					d37	−68.8	29.8				
		4	33.3	1.2	d38	−1.43	0.08	0.9922	222.2	0.0434	0.9666
					d17	−31.4	1.67				
					d39	−0.970	0.086				
					d40	33.3	3.64				
C−NO$_2$ bond	74	1	139.8	7.4	d41	−0.871	0.047	0.8256	340.9	1.6574	0.7979
		2	−120.3	14.8	d42	−48.4	2.1	0.9243	433.4	0.7297	0.9072
					d43	1.58	0.14				
		5	587.2	61.3	d41	−1.22	0.051	0.9720	472.1	0.2818	0.9635
					d43	−0.0188	0.1698				
					d44	−0.739	0.076				
					d45	44.0	6.0				
					d20	−16.1	2.9				
C−NNR bond	12	1	13.7	2.0	d17	−25.6	5.0	0.7246	26.3	0.5661	0.7076
		2	−52.4	5.4	d46	−14.3	1.3	0.9405	71.2	0.1359	0.7177
					d47	59.0	5.6				
		4	−4.09	0.78	d48	7.61	0.76	0.9867	129.6	0.0600	0.9499
					d49	4591	348				
					d50	0.584	0.068				
					d51	−1.95	0.37				

Table 3 (Continued)

reaction	N	n	intercept	error	eq descriptor	coeff	error	R^2	F	s^2	R^2_{CV}
C–N (except C–NO$_2$	16	1	4.37	0.50	d52	−1.19	0.14	0.8394	73.2	1.6385	0.7548
and C–NNR) bond		2	−15.8	1.7	d53	1.52	0.17	0.8989	57.8	1.1111	0.8320
					d54	1.62	0.31				
		5	−27.0	7.4	d55	−3.23	0.19	0.9946	366.8	0.0799	0.9883
					d47	4.44	0.25				
					d56	−3.57	0.24				
					d49	338.8	33.8				
					d57	0.455	0.072				
C–C bond	58	1	−1.46	0.20	d58	0.79	0.15	0.3355	28.3	2.2538	0.3885
(except C–CH$_3$)		2	−106.0	14.8	d57	1.14	0.15	0.5679	36.1	1.4921	0.4929
					d59	−15.1	2.7				
		5	34.8	3.6	d20	−10.6	1.6	0.7971	40.9	0.7411	0.7236
					d60	−2.00	0.22				
					d61	0.900	0.129				
					d62	45.1	6.0				
					d5	0.6765	0.1670				

[a] N is a number of compounds, n is a number of parameters of the correlation equation, R^2 is a squared correlation coefficient, F is Fischer's criterion, s^2 is a squared standard deviation, and R^2_{CV} is the square of the cross validated correlation coefficient, see reference 29.

nuclear–nuclear repulsion energy for the C–N and C–H bonds,[33] respectively. Other descriptors for the C–NO$_2$ bond fission include the relative numbers of S and F atoms,[22] maximum atomic state energy for a C atom,[22] and maximum electron–nuclear attraction energy for a N–O bond.[33] Clearly, all these theoretical characteristics can be directly related to the reactivity as representing different partitionings of the bond energy. The same conclusion can be drawn about the remaining four descriptors in the case of C–H bond homolysis data.

The log k (891) of 40 C–O bond fission reactions were used to develop a QSPR model for this subset. The most important descriptor, the relative negative charged surface area (RNCS)[39,40] (see Table 2), had already given a very significant one-parameter correlation with high R^2 and F values ($R^2 = 0.9070$, $F = 370.6$). The best five-parameter model involved additionally the HOMO–LUMO energy gap[22] and three more descriptors ($R^2 = 0.9650$, $F = 187.3$, $s^2 = 0.1220$, see Table 3). However, there is an obvious outlier from the last correlation (vinyl phenyl ether, no. 161-(240) in Table 1). Without this structure, R^2 for the five-parameter model increases to 0.9831 ($F = 382.9$, $s^2 = 0.0569$, see Table 3). The descriptors involved in the last correlation were the HOMO–LUMO energy gap, the β-polarizability,[27] the relative number of single bonds,[22] the Kier shape index (order 3),[42] and the lowest normal mode vibrational frequency.[22] Again, most of those descriptors are directly related to the dissociating bond strength.

In the case of carbon–halogen bond fission reactions, the five-parameter models for C–Cl and C–I are obviously overfitted. For the C–Cl bond homolysis, however, the most important descriptor is the relative positive charge (RPCG)[36,37] for the fragment R^{1}R^{2}R^{3}C$^•$. Together with two other descriptors involved in the three-parameter correlation, the ZX shadow of the molecule divided by ZX rectangle defined by the longest and the shortest principal axes of the molecules[38] and the total molecular two-center exchange energy divided by number of atoms,[22] the model obtained provides an excellent fit of the data ($R^2 = 0.9996$, $F = 3181.8$, $s^2 = 0.0080$, see Table 3). Another good three-parameter model was derived for the set of data on the C–I bond fission reactions involving 10 compounds ($R^2 = 0.9951$, $F = 405.4$, $s^2 = 0.0271$, see Table 3). The descriptors included were
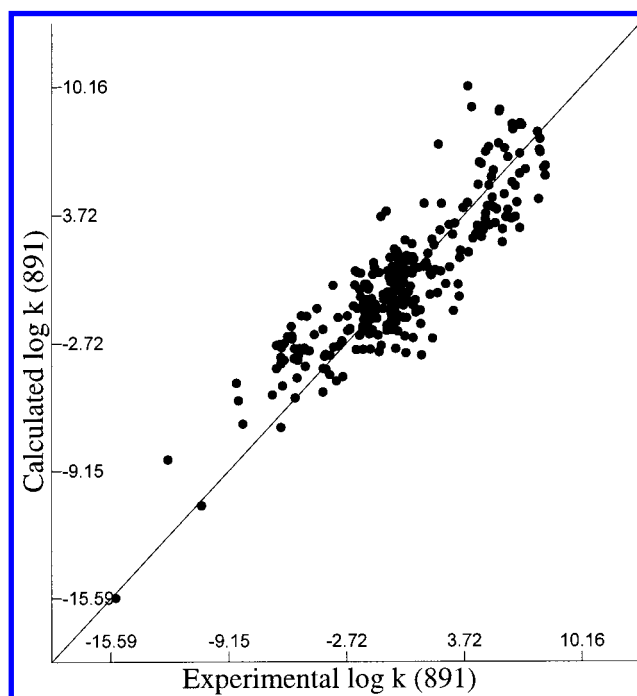

Figure 1. Correlation of the experimental and calculated log k (891) for 287 R^{1}R^{2}R^{3}C–X bond fission reactions using the five-parameter equation in Table 3.

the total hybridization component of the molecular dipole,[22] the surface weighted charged partial surface area for C atom,[36,37] and the average bonding information content (order 1) for R^{1}R^{2}R^{3}C$^•$.[34,35]

The data of log k (891) of 19 compounds for C–Br fission reactions are obviously less reliable, because even the best five-parameter model ($R^2 = 0.9662$, $F = 74.3$, $s^2 = 0.1860$) is poorer as compared to the results of C–Cl and C–I bond fissions. The main descriptor is the factorized molecular volume calculated as the ratio of the molecular volume to the volume of a box defined by X_{max}, Y_{max}, and Z_{max} (the maximum dimensions of the molecule).[22] The same descriptor is also the most important in correlating the data for the set of the C–S bond fission reactions. The latter data set involving 12 compounds was well-described by a four-parameter model ($R^2 = 0.9922$, $F = 222.2$, $s^2 = 0.0434$, see Table 3), involving the relative molecular weight,[22] the
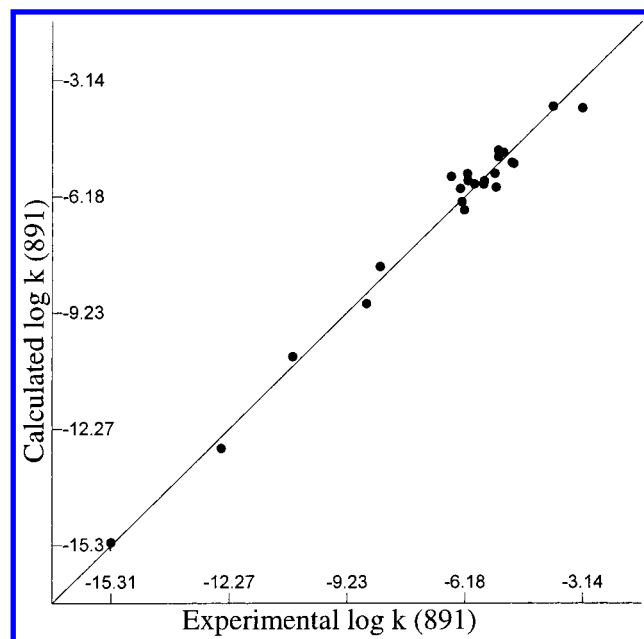
Figure 2. Correlation of the experimental and calculated log *k* (891) for C$-$H bond fission reactions using the five-parameter equation in Table 3.
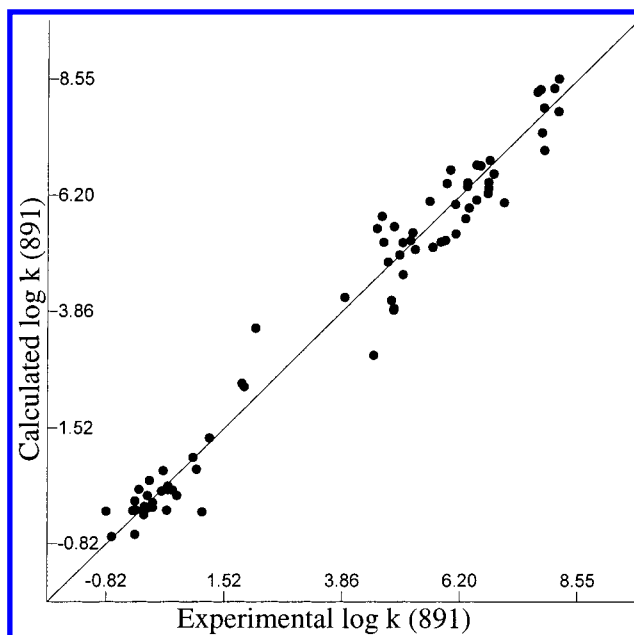

Figure 4. Correlation of the experimental and calculated log *k* (891) for C$-$NO$_2$ bond fission reactions using the five-parameter equation in Table 3.
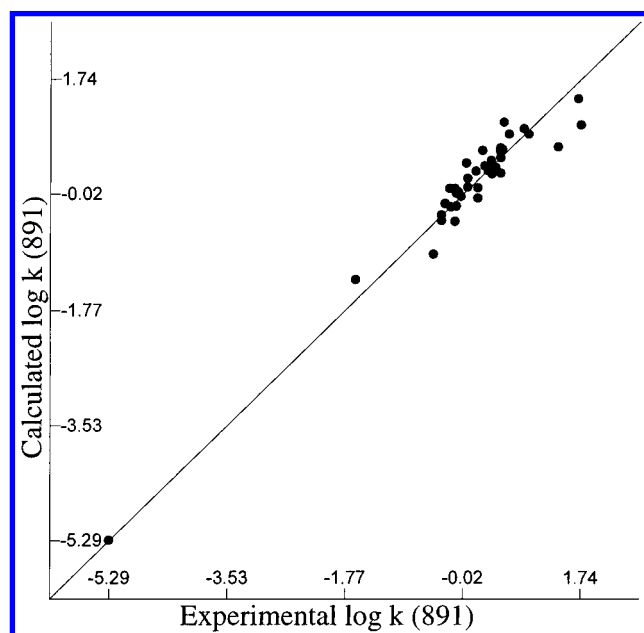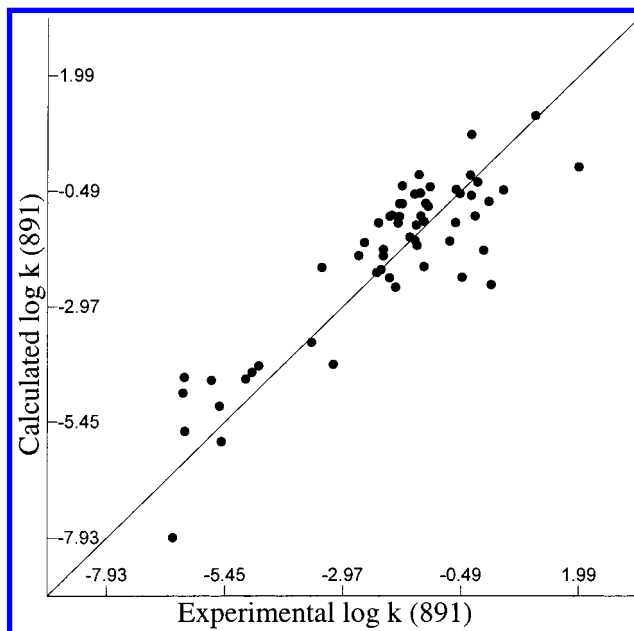

Figure 3. Correlation of the experimental and calculated log *k* (891) for C$-$O bond fission reactions (39 compounds) using the five-parameter equation in Table 3.

Figure 5. Correlation of the experimental and calculated log *k* (891) for C$-$C (except C$-$CH$_3$) bond fission reactions using the five-parameter equation in Table 3.

minimum total interaction for a C$-$S bond[22] and the maximum partial charge for a H atom[39,40] as descriptors.

The best correlations with log *k* (891) for C$-$NNR and C$-$N (except C$-$NO$_2$ and C$-$NNR) data sets were obtained using the four- and five-parameter models, respectively. The definition of the most important descriptors is more vague for these two data sets, because the list of descriptors changed depending on the search algorithms (BMLR or heuristic) and the number of parameters used.

A comparison of the experimental (observed) log *k* (891) values with the values predicted by QSPR models is depicted in Figures 1$-$5. It should be noted that the absolute accuracy of the experimental rate constants used can be estimated only

approximately. A subjective assumption about the uncertainty factor being approximately equal to three leads to the error of the rate constant in the logarithmic units as 0.48. Among 23 structures having C$-$H bond fissions, the values for four compounds (nos. 5(6), 7(8), 8(9), and 17(18) in Table 1) exceed this criterion. Taking into account excellent three-parameter correlations for C$-$Cl and C$-$I bond fissions, it is not surprising that the maximum differences are only -0.10 and -0.22, respectively. The maximum differences of calculated and experimental log *k* (891) values are also below 0.48 for C$-$S, C$-$NNR, and C$-$N (except C$-$NO$_2$ and C$-$NNR) bond fissions. The comparison of the calculated by the best model and experimental values for the C$-$O

bond fission shows that only for four compounds the prediction error exceeds the arbitrary value 0.48. For the largest subset, C—NO$_2$ bond fissions, a number of compounds exhibit errors exceeding the value 0.48 both in the case of the best five-parameter model (26 outlying structures) and in the case of the best seven-parameter model (18 outlying compounds).

CONCLUSIONS

The application of the CODESSA approach enables to obtain correlations between the characteristics of chemical reactivity and theoretical molecular descriptors, generated using semiempirical MNDO calculations. The statistically good correlations were obtained for the log k (891) values for different classes of homolysis reaction with the precision of the predictions comparable with the precision of the experimental values.

ACKNOWLEDGMENT

REFERENCES AND NOTES

(1) Robinson, P. J.; Holbrook, A. *Unimolecular Reactions*; Wiley-Interscience: London, New York, Sydney, Toronto, 1972.

(2) Forst, W. *Theory of Unimolecular Reactions*; Academic Press: New York, 1973.

(3) Doll, J. D. A Unified Theory of Dissociation. *J. Chem. Phys.* **1980**, *73*, 2760−2762.

(4) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas-Phase Unimolecular Reactions*; Wiley Interscience National Bureau of Standards: Washington, 1970.

(5) O'Neal, H. E.; Benson, S. W. Thermochemistry of Free Radicals. In *Free Radicals*; Kochi, J. K., Ed.; Wiley and Sons: New York, 1973; Chapter 17, pp 275−359.

(6) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(7) Benson, S. W. Future Perspectives in Physical Chemistry. The Prediction of Chemical Reactivity. *J. Chim. Phys. Phys.-Chim. Biol.* **1979**, *76*, 791−796.

(8) Benson, S. W. The Prediction of Thermochemical and Kinetic Data for Gas-Phase Reactions. Current Status. *Pure Appl. Chem.* **1980**, *52*, 1767−1771.

(9) Tsang, W. Thermal Decomposition of 3,4-Dimethylhexane, 2,2,3-Trimethylpentane, *tert*-Butylcyclohexane, and Relatrd Hydrocarbons. *J. Phys. Chem.* **1972**, *76*, 143−156.

(10) Tsang, W. Thermal Decomposition of Cyclopentane and Related Compounds. *Int. J. Chem. Kinet.* **1978**, *10*, 599−617.

(11) Tsang, W. Thermal Stability of Cyclohexane and 1-Hexene. *Int. J. Chem. Kinet.* **1978**, *10*, 1119−1138.

(12) Tsang, W. Thermal Stability of Intermediate Sized Acetylenic Compounds and the Heats of Formation of Propargyl Radicals. *Int. J. Chem. Kinet.* **1978**, *10*, 687−711.

(13) Tsang, W. Thermal Stability of Alcohols. *Int. J. Chem. Kinet.* **1976**, *8*, 173−192.

(14) Tsang, W. Thermal Stability of Primary Amines. *Int. J. Chem. Kinet.* **1978**, *10*, 41−46

(15) Tsang, W. Single-Pulse Shock-Tube Studies on the Decompositions of 1,2-Dibromoperfluoroethane and Allyl Bromide. *J. Phys. Chem.* **1984**, *88*, 2812−2817

(16) Robaugh, D.; Tsang, W. Thermal Decomposition of Phenyl Iodide and *o*-Iodotoluene. *J. Phys. Chem.* **1986**, *90*, 5363−5367.

(17) Tsang, W.; Robaugh; D., Mallard, W. G. Single-Pulse Shock-Tube Studies on C—NO$_2$ Bond Cleavage during the Decomposition of Some Nitro Aromatic Compounds. *J. Phys. Chem.* **1986**, *90*, 5968−5973.

(18) He, Y. Z.; Cui, J. P.; Mallard; W. G., Tsang, W. Homogeneous Gas-Phase Formation and Destruction of Anthranil from *o*-Nitrotoluene Decomposition. *J. Am. Chem. Soc.* **1988**, *110*, 3754−3759.

(19) Walker, J. A.; Tsang, W. Single-Pulse Shock Tube Studies on the Thermal Decomposition of *n*-Butyl Phenyl Ether, *n*-Pentylbenzene, and Phenotole and the Heat of Formation of Phenoxy and Benzyl Radicals. *J. Phys. Chem.* **1990**, *94*, 3324−3327.

(20) Hiob, R. J. Quantitative Statistical Interpretation of Kinetic Data in the Gas-Phase Homolysis. 7. Recalculation of Conventional Heats of Formation and Entropies of Free Radicals in Transition State. *Org. React.* **1986**, *23*, 144−208.

(21) Palm, V. A.; Hiob R. J. Quantitative Statistical Interpretation of Kinetic Data in the Gas-Phase Homolysis. 8. Program for Automatic Computational Estimation of Rate Constants of Gas-Phase Homolysis and Heats of Formation of Covalent Compounds. *Org. React.* **1986**, *23*, 412−439.

(22) Katritzky, A. R.; Lobanov, V. S.; Karelson, M. *CODESSA: Reference Manual*; University of Florida, 1994.

(23) Karelson, M.; Maran; U.; Wang, Y.; Katritzky, A. R. QSPR and QSAR Models Derived Using Large Molecular Descriptor Spaces. A Review of CODESSA Applications. *Collect. Czech Chem. Commun.* **1999**, *64*, 1551−1557.

(24) Hiob, R. J.; Palm, V. A. Quantitative Statistical Interpretation of Kinetic Data in the Gas-Phase Homolysis. 3. Calculation of Conventional Formation Enthalpies of Free Radicals in the Approximation of Constant Effective Mean Value of log A$_0$ = 14.64. *Org React.* **1983**, *20*, 151−202.

(25) *PCMODEL*, *Molecular Modeling Software*; Serena software: Bloomington, IN, 1992.

(26) Dewar, M. J. S.; Thiel, W. Grand States of Molecules. 38. The MNDO Methodol. Approximations and Parameters. *J. Am. Chem. Soc.* **1977**, *99*, 4899−4907.

(27) Stewart, J. J. P. *MOPAC Program Package 6.0;* QCPE, No. 445, 1990.

(28) *AMPAC 5.0*; Semichem: Shawnee, 1994.

(29) Katritzky, A. R.; Lobanov, V. S.; Karelson, M.; Murugan, R.; Grendze, M. P.; Toomey, J. E., Jr. Comprehensive Descriptors for Structural and Statistical Analysis. 1. Correlation Between Structure and Physical Properties of Substituted Pyridines. *Rev. Roum. Chim.* **1996**, *41*, 851−867.

(30) Draper, N. R.; Smith, H. *Applied Regression Analysis*; Wiley: New York, 1966.

(31) Katritzky, A. R.; Lobanov, V. S.; Karelson, M. *CODESSA: Training Manual;* University of Florida: Gainsville, 1995.

(32) Sannigrahi, A. B. Ab initio Molecular Orbital Calculations of Bond Index and Valency. *Adv. Quantum Chem.* **1992**, *23*, 301−351.

(33) Strouf, O. *Chemical Pattern Recognition*; Wiley: New York, 1986.

(34) Kier, L. B. Use of Molecular Negentropy to Encode Structure Governing Biological Activity. *J. Pharm. Sci.* **1980**, *69*, 807−810.

(35) Bonchev, D. *Information Theoretic Indices for Characterization of Chemical Structure;* Wiley-Interscience: New York, 1983.

(36) Stanton, D. T.; Jurs, P. C. Development and Use of Charged Partial Surface Area Structural Descriptors in Computer-Assisted Quantitative Structure−Property Relationship Studies. *Anal. Chem.* **1990**, *62*, 2323−2329.

(37) Stanton, D. T.; Egolf, L. M.; Jurs, P. C.; Hicks, M. G. Computer-Assisted Prediction of Normal Boiling Points of Pyrans Pyrroles. *J. Chem. Inf. Comput. Sci.* **1992**, *32*, 306−316.

(38) Rohrbaugh, R. H.; Jurs, P. C. Descriptions of Molecular Shape Applied in Studies of Structure−Activity and Structure−Property Relationships. *Anal. Chim. Acta* **1987**, *199*, 99−109.

(39) Zefirov, N. S.; Kirpichenok, M. A.; Izmailov, F. F.; Trofimov, M. I. Scheme for the Calculation of the Electronegativities of Atoms in a Molecule in the Framework of Sanderson's Principle. *Dokl. Akad. Nauk SSSR* **1987**, *296*, 883−887.

(40) Kirpichenok, M. A.; Zefirov, N. S. Electronegativity and molecular geometry. I. General Principles of the Method and Analysis of the Effect of Short-Range Electrostatic Interactions on Bond Lengths in Organic Molecules. *Zh. Org. Khim.* **1987**, *23*, 673−691.

(41) Wiener, H. Structural Determination of Paraffin Boiling Points. *J. Am. Chem. Soc.* **1947**, *69*, 17−20

(42) Kier, L. B. In *Computational Chemical Graph Theory;* Rouvray, D. H., Ed.; Nova Science Publishers: New York, 1990; pp 151−174.

(43) Kier, L. B.; Hall, L. H. In *Molecular Connectivity in Chemistry and Drug Research*; Academic Press: New York, 1976; pp 27−39.