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Bimolecular Reactions of Radical Generation Involving Nitrogen-Containing Compounds with Multiple Bonds

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Abstract—Retrodisproportionation reactions R'C=NR" + HY ⟶ R'C$^{\bullet}$NHR" + Y$^{\bullet}$, RC≡N + HY ⟶ RC$^{\bullet}$=NH + Y$^{\bullet}$, RN=NR + HY ⟶ RN$^{\bullet}$NHR + Y$^{\bullet}$, RNO + HY ⟶ RN$^{\bullet}$OH + Y$^{\bullet}$, and RNO_2 + HY ⟶ RN(O$^{\bullet}$)OH + Y$^{\bullet}$ (where HY represents hydrocarbons, alcohols, phenols, amines, thiophenols, etc.) are considered as sources of radical generation. The enthalpies of these reactions are calculated. The parabolic model is used to calculate the rate constants for 254 such reactions. Various HY compounds acting as hydrogen-atom donors are compared with nitrogen-containing compounds acting as hydrogen-atom acceptors. The PhN(O) and $PhNO_2$ compounds exhibit the highest activity among the studied acceptors.

INTRODUCTION

Radical disproportionation is a very rapid exothermic reaction [1]. Retrodisproportionation, for example,

$$PhCH{=}CH_2 + HR \longrightarrow PhC^{\bullet}HCH_3 + R^{\bullet}$$

is endothermic and characterized by a high activation energy. Ruchardt *et al.* [2] studied a number of such reactions of bimolecular radical generation. These reactions can involve various molecules with multiple bonds. In retrodisproportionation, one molecule (with a multiple bond) acts as a hydrogen-atom acceptor, and the other (RH) acts as a hydrogen-atom donor. To describe such reactions and to calculate their activation energies, one can use the parabolic model of a bimolecular radical reaction [3–5] as applied to very endothermic reactions [6]. We used this method earlier to calculate the activation energies of retrodisproportionation involving olefins [7], oxygen [8, 9], and quinones [7, 10, 11]. In this work, we studied retrodisproportionation involving nitrogen-containing compounds as hydrogen-atom acceptors, namely,

$$R'CH{=}NR" + HY \longrightarrow R'C^{\bullet}HNHR" + Y^{\bullet}$$

(imines),

$$RC{\equiv}N + HY \longrightarrow RC^{\bullet}{=}NH + Y^{\bullet}$$

(nitriles),

$$RN{=}NR + HY \longrightarrow RN^{\bullet}NHR + Y^{\bullet}$$

(azo compounds),

$$RNO_2 + HY \longrightarrow RN(O^{\bullet})OH + Y^{\bullet}$$

(nitro compounds), and

$$RNO + HY \longrightarrow RN^{\bullet}OH + Y^{\bullet}$$

(nitroso compounds).

The hydrogen-atom donors were hydrocarbons, alcohols, phenols, amines, etc.

CALCULATION PROCEDURE

Within the framework of the parabolic model, the reaction is characterized by the following parameters: the enthalpy ΔH_e, the activation energy E_e, the sum of the amplitudes of the stretching vibration of the reacting bonds r_e, and the dynamic parameters of these bonds corresponding to the initial (b) and forming (b_f) bonds ($\alpha = b/b_f$).

The enthalpy ΔH_e includes the difference in the zero-point vibration energies of the reacting bonds

$$\Delta H_e = D_i - D_f + 0.5hN_A(\nu_i - \nu_f), \qquad (1)$$

where D_i and D_f are the dissociation energies of the breaking and forming bonds, respectively; ν_i and ν_f are the frequencies of their stretching vibrations, respectively; and h and N_A are the Planck and Avogadro constants, respectively. The E_e also includes the energy of the stretching vibration of a breaking bond

$$E_e = E + 0.5hN_A\nu_i - 0.5RT, \qquad (2)$$

where E is the experimental activation energy.

The model postulates the existence of a threshold value $\Delta H_e = \Delta H_{e,\max}$. At $\Delta H_e < \Delta H_{e,\max}$, the activation energy is expressed as follows:

$$\sqrt{E_e} = \frac{br_e}{1-\alpha^2}\left[1 - \alpha\sqrt{1 - \frac{1-\alpha^2}{(br_e)^2}\Delta H_e}\right], \qquad (3)$$

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Table 1. Activation energies (E) and rate constants (k, 550 K) calculated in terms of the parabolic model (Eqs. (2) and (3), $\alpha = 1$, $br_e = 17.80$ (kJ/mol)$^{1/2}$, $A = 4 \times 10^9$ l mol^{-1} s^{-1}) and obtained in the experiments in [2] for the retrodisproportionation of olefins with 9,10-dihydroanthracene ($D_{C-H} = 322$ kJ/mol)

RCH=CH$_2$	ΔH, kJ/mol	E, kJ/mol	$k \times 10^5$, l mol^{-1} s^{-1}	ΔH^*, kJ/mol	$-\Delta S^*$, J mol^{-1} K^{-1}	$k \times 10^5$, l mol^{-1} s^{-1}
	calculation			experiment		
PhCH=CH$_2$	131.7	145.5	6.08	106.7	132.6	10.0
PhMeC=CH$_2$	131.2	145.2	6.49	133.0	90.0	5.35
PhEtC=CH$_2$	131.2	145.2	6.49	144.3	77.4	2.05
Ph(Me$_2$CH)C=CH$_2$	131.2	145.2	6.49	126.4	112.1	1.58
Ph(Me$_3$C)C=CH$_2$	131.2	145.2	6.49	143.5	99.6	1.70
E-PhCH=CHPh	159.0	165.2	0.16	157.3	72.8	0.21
Indene	145.0	155.0	0.76	151.0	73.2	0.79
1,2-Dihydronaphthalene	143.5	153.9	0.97	149.8	75.7	0.76

whereas at $\Delta H_e > \Delta H_{e,\max}$,

$$E = \Delta H + 0.5RT, \quad (4)$$

where $\Delta H = D_i - D_f$.

The threshold activation energy of the reaction ΔH_e depends on the br_e and α parameters [6]:

$$\Delta H_{e,\max} = (br_e)^2 - 2\alpha br_e(0.5hN_A\nu_f)^{1/2} + 0.5(\alpha^2 - 1)hN_A\nu_f. \quad (5)$$

At $\Delta H_e > \Delta H_{e,\max}$, the preexponential factor A depends on the ΔH_e parameter because of an increase in the amplitude of the reacting bond vibrations. This dependence is described by the equation [6]:

$$A = A_0\{1 + 1.3(\Delta H_e^{1/2} - \Delta H_{e,\max}^{1/2})\}^2, \quad (6)$$

where A_0 is the preexponential factor per one reacting bond typical of a certain reaction class. The rate constant for such bimolecular reaction was calculated by the Arrhenius equation:

$$k = A\exp(-E/RT). \quad (7)$$

This method of calculating the activation energy and the rate constant of retrodisproportionation was checked for the reactions

$$RH + CH_2{=}CR'Ph \longrightarrow R^{\cdot} + CH_3C^{\cdot}R'Ph,$$

the experimental data for which were reported in [2]. In these reactions, one C–H bond breaks down and another C–H bond is formed. Therefore, $\alpha = b_i/b_f = 1$ because $b_i = b_f$ and the energy of the zero-point bond vibration $0.5hN_A\nu_i$ is 17.4 kJ/mol [7]. Table 1 presents the calculation results for the reactions of 9,10-dihydroanthracene with olefins and compares them with the experimental data. The method of calculating the enthalpies of such reactions is described below. All the reactions listed in Table 1 are characterized by $\Delta H_e < \Delta H_{e,\max}$, the activation energy was calculated by Eqs. (2) and (3), and the preexponential factor $A = 4 \times 10^9$ l mol^{-1} s^{-1} [7]. The average discrepancy between the calculated and experimental $\log k$ values is 0.19 or $\Delta E = \pm 2.4$ kJ/mol. This discrepancy is insignificant because the error in the estimates of the reaction enthalpy is ± 5 kJ/mol.

In the H-atom abstraction reactions, unsaturated compounds are characterized by the same parameters (α, br_e, and the zero-point vibration energies) as structurally similar radicals [7–10]. In the attack of the Y–H bond, imines, nitriles, and azo compounds are characterized by the same parameters as the aminyl radicals, whereas the RNO and RNO$_2$ compounds are characterized by the same parameters as the nitroxyl radicals [4, 5]. Table 2 presents the α and $0.5hN_A\nu_i$ parameters, and Table 3 lists the br_e parameters for different reaction cases. The threshold reaction enthalpy $\Delta H_{e,\max}$ for different reaction classes was calculated by Eq. (6) (Table 4). Table 5 presents the A_0 values used in the calculations. For the reactions of imines, the A_0 values typical of the reactions of aminyl radicals [4] were used. Taking into account the electron structure of the multiple bonds in nitriles, we assumed for their reactions that A_0 (nitrile) = $2A_0$ (imine) because the triple bond in nitrile doubles the cross section of the attack. Taking into account that the reaction of azo compounds involves two nitrogen atoms, we set A_0(azo) = $2A_0$(imine), A_0(RNO) = A_0(nitroxyl), and A_0(RNO$_2$) = $2A_0$(RNO), because two oxygen atoms participate in the attack. Table 6 presents the Y–H bond dissociation energies and relevant references. The enthalpy of retrodisproportionation involving imines is

$$\Delta H = D_{Y-H} + \Delta H(R'CH{=}NR'' + H). \quad (8)$$

Table 2. The α, $0.5hN_A\nu_i$, and $0.5hN_A$ ($\nu_i - \nu_f$) parameters for retrodisproportionation involving imines, nirtriles, and azo, nitro, and nitroso compounds*

YH	α	$0.5hN_A\nu_i$, kJ/mol	$0.5hN_A(\nu_i - \nu_f)$, kJ/mol	α	$0.5hN_A\nu_i$, kJ/mol	$0.5hN_A(\nu_i - \nu_f)$, kJ/mol
	R'CH=NR", RN=NR, RC≡N			RNO, RNO_2		
RH	0.869	17.4	–2.6	0.802	17.4	–4.1
R_2NH	1.00	20.0	0.0	0.923	20.0	–1.5
ROOH	1.068	21.2	1.2	0.986	21.2	–0.3
ArOH	1.083	21.5	1.5	1.000	21.5	0.0
R_2NOH	1.083	21.5	1.5	1.000	21.5	0.0
RSH	0.703	13.8	–6.2	0.649	13.8	–7.7
R_3SiH	0.666	13.1	–6.9	0.615	13.1	–8.4
R_3GeH	0.649	12.6	–7.4	0.599	12.6	–8.9
R_3SnH	0.626	12.1	–7.9	0.578	12.1	–9.4

Table 3. The br_e parameter for retrodisproportionation involving nitrogen-containing compounds*

YH	br_e (kJ/mol)$^{1/2}$					
	RCH=NH	R'CH=NR"	RCH=NPh	RC≡N	RN=NR	RNO_x
R^1H	14.90	15.80	13.00	15.33	13.80	12.25
R^2H	16.21	17.10	14.30	16.64	15.10	13.68
R^3H	15.40	16.30	13.50	15.83	14.30	12.88
RNH_2	21.00	21.90	19.10	21.43	19.90	10.56
R'R"NH	21.90	22.80	20.00	22.33	20.80	11.50
AmH	19.10	20.00	17.20	19.53	18.00	11.93
ROOH	11.54	12.44	11.94	12.50	10.94	13.40
Ar^1OH	9.87	10.77	10.30	10.80	10.50	13.54
Ar^2OH	10.60	11.50	11.00	11.53	11.00	14.49
AmOH	10.88	11.78	11.30	11.81	11.30	13.53
RSH	9.75	10.65	7.85	10.18	8.65	10.80
R_3SiH	11.44	12.34	9.54	11.90	10.34	10.14
R_3GeH	12.26	13.16	10.36	12.70	11.16	11.05
R_3SnH	11.05	11.95	9.15	11.50	9.95	10.74

* R^1H, R^2H, and R^3H are aliphatic, unsaturated, and alkylaromatic hydrocarbons, respectively; Ar^1OH is phenol, Ar^2OH is sterically hindered phenol, and AmH is aromatic amine. The *x* value in RNO_x is 1 or 2.

The N–H bond dissociation energy in the resulting R'C$^\bullet$HNHR" radical was calculated using the following thermochemical equations:

$$\Delta H(\text{R'CH}_2\text{NHR"}) + D_{\text{C–H}} = \Delta H(\text{R'C}^\bullet\text{HNHR"}) + \Delta H(\text{H}),$$

$$\Delta H(\text{RC}^\bullet\text{HNHR"}) + D_{\text{N–H}} = \Delta H(\text{R'CH=NR"}) + \Delta H(\text{H}).$$

The enthalpies of amine and imine formation were taken from [19], the C–H bond dissociation energies in amines were taken from [13], and $\Delta H(H) = 218$ kJ/mol [16]. We obtained $D_{\text{N–H}} = 145.1$ kJ/mol for the C$^\bullet$H$_2$NH$_2$ radical, $D_{\text{N–H}} = 132.6$ kJ/mol for MeC$^\bullet$HNHMe, and $D_{\text{N–H}} = 173.8$ kJ/mol for C$^\bullet$H$_2$NHPh. Similarly, the enthalpy of the reactions involving the PhC≡N, RN=NR, PhNO, and $PhNO_2$ compounds were calculated. The enthalpies of the initial reactant formation were taken from [19] and [20]. The enthalpy of hydrogen-atom addition to PhC≡N was estimated by the thermochemical reactions

$$\text{PhC}{\equiv}\text{N} + \text{H} = \text{PhC}^\bullet{=}\text{NH},$$

$$\text{PhC}^\bullet{=}\text{NH} + \text{H} = \text{PhCH=NH},$$

$$\text{PhCH=NH} + \text{H}_2 = \text{PhCH}_2\text{NH}_2.$$

Table 4. The $\Delta H_{e,\,max}$ values for retrodisproportionation involving nitrogen-containing compounds calculated by Eq. (5)*

YH	$\Delta H_{e,\,max}$, kJ/mol					
	RCH=NH	R'CH=NR"	RCH=NPh	RC≡N	RN=NR	RNO_x
R^1H	101.3	121.9	63.1	111.0	78.3	51.3
R^2H	131.9	154.6	88.4	142.7	105.7	77.7
R^3H	112.5	134.1	72.4	122.6	88.4	62.4
RNH_2	253.2	283.7	194.0	267.6	218.0	17.9
R'R"NH	283.7	315.9	221.1	298.9	246.6	30.6
AmH	194.0	221.1	142.0	206.7	163.0	37.0
ROOH	25.7	38.7	31.3	39.6	18.0	56.4
Ar^1OH	5.3	15.1	9.8	15.5	12.0	57.7
Ar^2OH	13.1	24.3	17.9	24.7	17.9	75.6
AmOH	16.4	28.1	21.7	28.5	21.7	57.6
RSH	23.6	36.3	2.1	29.5	10.3	39.2
R_3SiH	53.6	67.6	23.0	59.6	34.2	33.2
R_3GeH	67.7	85.2	35.6	76.0	48.2	47.0
R_3SnH	57.8	63.7	20.3	55.7	31.1	52.6

* R^1H, R^2H, and R^3H are aliphatic, unsaturated, and alkylaromatic hydrocarbons, respectively; Ar^1OH is phenol, Ar^2OH is sterically hindered phenol, and AmH is aromatic amine. In RNO_x, x is 1 or 2.

Table 5. The preexponential factor A_0 for retrodisproportionation involving nitrogen-containing compounds with $\Delta H_e \le \Delta H^*_{e,\,max}$

YH	A_0, l mol^{-1} s^{-1}				
	R'CH=NR"	RC≡N	RN=NR	RNO_2	RNO
R^1H	1.5×10^8	3.0×10^8	3.0×10^8	2.0×10^9	1.0×10^9
R^2H	1.5×10^7	3.0×10^7	3.0×10^7	2.0×10^8	1.0×10^8
R^3H	1.5×10^7	3.0×10^7	3.0×10^7	2.0×10^8	1.0×10^8
RNH_2	4.0×10^8	8.0×10^8	8.0×10^8	4.0×10^8	2.0×10^8
R'R"NH	2.0×10^8	4.0×10^8	4.0×10^8	2.0×10^8	1.0×10^8
AmH	2.0×10^8	4.0×10^8	4.0×10^8	2.0×10^8	1.0×10^8
ROOH	2.0×10^7	4.0×10^7	4.0×10^7	6.4×10^7	3.2×10^7
Ar^1OH	2.0×10^7	4.0×10^7	4.0×10^7	2.0×10^9	1.0×10^9
Ar^2OH	2.0×10^7	4.0×10^7	4.0×10^7	2.0×10^9	1.0×10^9
AmOH	2.0×10^7	4.0×10^7	4.0×10^7	2.0×10^9	1.0×10^9
RSH	2.0×10^7	4.0×10^7	4.0×10^7	2.0×10^8	1.0×10^8
R_3SiH	1.5×10^8	3.0×10^8	3.0×10^8	2.0×10^9	1.0×10^9
R_3GeH	1.5×10^8	3.0×10^8	3.0×10^8	2.0×10^9	1.0×10^9
R_3SnH	1.5×10^8	3.0×10^8	3.0×10^8	2.0×10^9	1.0×10^9

* R^1H, R^2H, and R^3H are aliphatic, unsaturated, and alkylaromatic hydrocarbons, respectively; Ar^1OH is phenol, Ar^2OH is sterically hindered phenol, and AmH is aromatic amine.

The enthalpy of $PhCH_2NO_2$ formation is 83.7 kJ/mol [20]. The enthalpy of imine hydrogenation is –80.6 kJ/mol [19]. The C–H bond dissociation energy in imine was estimated as follows. The C–H bond in the α-position to the nitrogen atom in $MeCH{=}NH$ imine is stronger than that in $MeCH_2NH_2$ amine by 24 kJ/mol [13]. Assuming the same difference between $PhCH_2NH_2$ amine ($D_{\alpha\text{-C–H}}$ = 368 kJ/mol [13]) and PhCH=NH imine, we obtain for PhCH=NH imine that $D_{\alpha\text{-C–H}}$ = 368 + 24 = 392 kJ/mol. Therefore, the N–H bond dissociation energy in the $PhC^{\bullet}{=}N{-}H$ radical is $D_{N–H}$ = 97.3 kJ/mol.

Table 6. Enthalpies ΔH, preexponential factors A, and rate constants k for retrodisproportionation CH_2=NH + HY ⟶ $C^{\bullet}H_2NH_2 + Y^{\bullet}$ calculated by Eqs. (4)–(8)

No.	HY	D_{Y-H}, kJ/mol	n^*_{Y-H}	ΔH, kJ/mol	A, l mol^{-1} s^{-1}	k(500 K), l mol^{-1} s^{-1}	Reference
1	Norbornane	393.1	2	248.0	1.25×10^{10}	1.54×10^{-16}	[12]
2	CH_2=CHCH–H(Me)	349.4	2	204.3	3.73×10^{8}	1.70×10^{-13}	[12]
3	Me_2CH=CHCH–H(Me)	332.0	2	186.9	2.51×10^{8}	7.50×10^{-12}	[12]
4	1,4-Cyclohexadiene	312.6	4	167.5	2.78×10^{9}	8.81×10^{-9}	[12]
5	PhC–H(Me_2)	354.7	1	209.6	3.19×10^{8}	4.05×10^{-14}	[12]
6	Tetralin	345.6	4	200.5	1.10×10^{10}	1.25×10^{-11}	[12]
7	9,10-Dihydroanthracene	322.0	2	176.9	3.50×10^{9}	1.16×10^{-9}	[12]
8	$(Me_2C–H)_3N$	370.0	3	224.9	1.45×10^{10}	4.65×10^{-14}	[13]
9	$(CH_2$=CHCH–H$)_3N$	345.6	6	200.5	1.04×10^{9}	1.17×10^{-12}	[13]
10	PhCH–H(NH_2)	368.0	2	222.9	7.73×10^{8}	4.00×10^{-15}	[13]
11	Cyclohexanol	388.4	1	243.3	5.94×10^{9}	2.27×10^{-16}	[14]
12	CH_2=CHCH–H(OH)	360.0	2	214.9	4.57×10^{8}	1.62×10^{-14}	[14]
13	CH_2=CMeC–H(MeOH)	339.2	1	194.1	1.50×10^{8}	7.91×10^{-13}	[14]
14	PhMeC–H(OH)	356.0	1	210.9	3.26×10^{8}	3.02×10^{-14}	[14]
15	MeC–H(O)	373.8	1	228.7	5.06×10^{9}	6.50×10^{-15}	[14]
16	PhC–H(O)	348.0	1	202.9	2.87×10^{8}	1.83×10^{-13}	[14]
17	CH_2=CHCH–HC(O)Me	346.6	2	201.5	3.53×10^{8}	3.14×10^{-13}	[14]
18	$(PhCH–H)_2O$	359.0	4	213.9	1.36×10^{9}	6.14×10^{-14}	[14]
19	Ph_2N–H	364.7	1	219.6	4.23×10^{7}	4.85×10^{-16}	[15]
20	N,N'-Diphenyl-*p*-phenylenediamine	346.6	2	201.5	4.40×10^{8}	3.92×10^{-13}	[15]
21	*cyclo*-[$CMe_2(CH_2)_3CMe_2$NO–H]	297.7	1	152.6	1.71×10^{9}	1.95×10^{-7}	[15]
22	*cyclo*-[CMe_2CHMeNMeCMe_2NO–H]	290.8	2	145.7	3.21×10^{9}	1.93×10^{-6}	[15]
23	4-HOC_6H_4O–H	352.0	2	206.9	6.82×10^{9}	1.66×10^{-12}	[15]
24	α-Tocopherol	330.0	1	184.9	3.01×10^{9}	1.45×10^{-10}	[15]
25	2,6,7-Me_3C_6(O–H)-3,4-*cyclo*-[CH_2CMe_2O–]	326.0	1	180.9	2.94×10^{9}	3.71×10^{-10}	[15]
26	4-$MeOC_6H_4$O–H	345.8	1	200.7	3.30×10^{9}	3.56×10^{-12}	[15]
27	2,6-$(Me_3C)_2$-4-MeC_6H_2O–H	339.0	1	193.9	2.54×10^{9}	1.41×10^{-11}	[15]
28	2,6-$(Me_3C)_2$-4-$MeOC_6H_2$O–H	327.1	1	182.0	2.34×10^{9}	2.27×10^{-10}	[15]
29	MeSS–H	295.0	1	149.9	1.28×10^{9}	2.80×10^{-7}	[16]
30	PhS–H	338.1	1	193.0	1.88×10^{9}	1.29×10^{-11}	[15]
31	1-$C_{10}H_7$S–H	328.4	1	183.3	1.74×10^{9}	1.24×10^{-10}	[15]
32	Et_3Ge–H	343.1	1	198.0	6.19×10^{9}	1.28×10^{-11}	[17]
33	Bu_3Sn–H	309.6	1	164.5	4.96×10^{9}	3.24×10^{-8}	[17]
34	Me_3Si–H	362.3	1	217.2	9.71×10^{9}	1.98×10^{-13}	[18]
35	Ph_3Si–H	354.8	1	209.7	9.08×10^{9}	1.13×10^{-12}	[18]
36	$(Me_3Si)_3$Si–H	351.0	1	205.9	8.77×10^{9}	2.71×10^{-12}	[18]

* The number of the breaking C–H bonds in HY.

Similarly, we calculated the N–H bond dissociation energy in the $MeN^{\bullet}$N–HMe radical formed in the reaction of YH with *trans*-MeN=NMe using ΔH(*trans*-MeN=NMe) = 150.6 kJ/mol and ΔH(MeNHNHMe) = 92.0 kJ/mol [19]. The N–H bond dissociation energy in the $MeN^{\bullet}$N–HMe radical was calculated as follows. The difference in the N–H bond dissociation energies in $MeNH_2$ and Me_2NH is ΔD(N–H) = 35.8 kJ/mol. Assuming the same difference in the N–H bond strength for hydrazine and 1,2-dimethylhydrazine, we

Table 7. Enthalpies ΔH, preexponential factors A, and rate constants k for retrodisproportionation R'CH=NR" + HY ⟶ R'C$^{\bullet}$HNHR" + Y$^{\bullet}$ calculated by Eqs. (4)–(8)

HY*	ΔH, kJ/mol	A, l mol^{-1} s^{-1}	k(500 K), l mol^{-1} s^{-1}	ΔH, kJ/mol	A, l mol^{-1} s^{-1}	k(500 K), l mol^{-1} s^{-1}
	MeCH=NMe			CH_2=NPh		
1	260.5	1.03×10^{10}	6.29×10^{-18}	219.3	1.75×10^{10}	2.15×10^{-13}
2	216.8	2.71×10^{8}	6.09×10^{-15}	175.6	6.28×10^{8}	2.84×10^{-10}
3	199.4	1.72×10^{8}	2.53×10^{-13}	158.2	4.53×10^{8}	1.35×10^{-8}
4	180.0	1.68×10^{9}	2.64×10^{-10}	138.8	5.67×10^{9}	1.79×10^{-5}
5	222.1	2.46×10^{8}	1.55×10^{-15}	180.9	4.84×10^{8}	6.12×10^{-11}
6	213.0	8.39×10^{9}	4.70×10^{-13}	171.8	1.71×10^{10}	1.92×10^{-8}
7	189.4	2.51×10^{9}	4.10×10^{-11}	148.2	5.75×10^{9}	1.90×10^{-6}
8	237.4	1.18×10^{10}	1.86×10^{-15}	196.2	2.09×10^{10}	6.67×10^{-11}
9	213.0	7.44×10^{8}	4.17×10^{-14}	171.8	1.76×10^{9}	1.99×10^{-9}
10	235.4	6.08×10^{8}	1.56×10^{-16}	194.2	1.14×10^{9}	5.90×10^{-12}
11	255.8	4.89×10^{9}	9.25×10^{-18}	214.6	8.38×10^{9}	3.19×10^{-13}
12	227.4	3.40×10^{8}	5.97×10^{-16}	186.2	7.43×10^{8}	2.62×10^{-11}
13	206.6	1.05×10^{8}	2.75×10^{-14}	165.4	2.62×10^{8}	1.38×10^{-9}
14	223.4	2.52×10^{8}	1.16×10^{-15}	182.2	4.92×10^{8}	4.55×10^{-11}
15	241.2	4.11×10^{9}	2.61×10^{-16}	200.0	7.26×10^{9}	9.28×10^{-12}
16	215.4	2.19×10^{8}	6.89×10^{-15}	174.2	4.41×10^{8}	2.80×10^{-10}
17	214.0	2.54×10^{8}	1.12×10^{-14}	172.8	5.98×10^{8}	5.31×10^{-10}
18	226.4	1.06×10^{9}	2.36×10^{-15}	185.2	2.05×10^{9}	9.20×10^{-11}
19	232.1	1.98×10^{7}	1.12×10^{-17}	190.9	1.09×10^{8}	1.25×10^{-12}
20	214.0	1.14×10^{8}	5.04×10^{-15}	172.8	1.64×10^{9}	1.45×10^{-9}
21	165.1	1.44×10^{9}	8.12×10^{-9}	123.9	1.09×10^{9}	1.25×10^{-4}
22	158.2	2.69×10^{9}	8.00×10^{-8}	117.0	2.01×10^{9}	1.20×10^{-3}
23	219.4	5.65×10^{9}	6.79×10^{-14}	178.2	5.00×10^{9}	1.21×10^{-9}
24	197.4	2.47×10^{9}	5.90×10^{-12}	156.2	2.13×10^{9}	1.02×10^{-7}
25	193.4	2.41×10^{9}	1.51×10^{-11}	152.2	2.06×10^{9}	2.60×10^{-7}
26	213.2	2.73×10^{9}	1.46×10^{-13}	172.0	2.39×10^{9}	2.57×10^{-9}
27	206.4	2.16×10^{9}	5.91×10^{-13}	165.2	1.83×10^{9}	1.01×10^{-8}
28	194.5	1.98×10^{9}	9.51×10^{-12}	153.3	1.65×10^{9}	1.60×10^{-7}
29	162.4	1.07×10^{9}	1.16×10^{-8}	121.2	2.07×10^{9}	4.50×10^{-4}
30	205.5	1.61×10^{9}	5.47×10^{-13}	164.3	2.90×10^{9}	1.99×10^{-8}
31	195.8	1.48×10^{9}	5.21×10^{-12}	154.6	2.71×10^{9}	1.92×10^{-7}
32	210.5	5.15×10^{9}	5.26×10^{-13}	169.3	8.70×10^{9}	1.79×10^{-8}
33	177.0	5.15×10^{9}	1.66×10^{-9}	135.8	8.81×10^{9}	5.73×10^{-5}
34	229.7	8.58×10^{9}	8.65×10^{-15}	188.5	1.37×10^{10}	2.79×10^{-10}
35	222.2	8.01×10^{9}	4.91×10^{-14}	181.0	1.29×10^{10}	1.59×10^{-9}
36	218.4	7.72×10^{9}	1.18×10^{-13}	177.2	1.25×10^{10}	3.85×10^{-9}

* The HY numbers correspond to those given in Table 6.

Table 8. Enthalpies ΔH, preexponential factors A, and rate constants k for retrodisproportionation involving PhC≡N and *trans*-MeN=NMe calculated by Eqs. (4)–(8)

HY*	ΔH, kJ/mol	A, l mol^{-1} s^{-1}	k(500 K), l mol^{-1} s^{-1}	ΔH, kJ/mol	A, l mol^{-1} s^{-1}	k(500 K), l mol^{-1} s^{-1}
	PhC≡N			*trans*-MeN=NMe		
1	295.8	3.33×10^{10}	4.17×10^{-21}	228.8	2.98×10^{10}	3.73×10^{-14}
2	252.1	1.31×10^{9}	6.04×10^{-18}	185.1	9.82×10^{8}	4.52×10^{-11}
3	234.7	1.01×10^{9}	3.07×10^{-16}	167.7	6.84×10^{8}	2.07×10^{-9}
4	215.3	1.43×10^{10}	4.60×10^{-13}	148.3	8.05×10^{9}	2.59×10^{-6}
5	257.4	9.84×10^{8}	1.27×10^{-18}	190.4	7.90×10^{8}	1.02×10^{-11}
6	248.3	3.55×10^{10}	4.08×10^{-16}	181.3	2.76×10^{10}	3.16×10^{-9}
7	224.7	1.30×10^{10}	4.37×10^{-14}	157.7	8.97×10^{9}	3.01×10^{-7}
8	272.7	4.10×10^{10}	1.33×10^{-18}	205.7	3.51×10^{10}	1.14×10^{-11}
9	248.3	3.73×10^{9}	4.29×10^{-17}	181.3	2.74×10^{9}	3.15×10^{-10}
10	270.7	2.26×10^{9}	1.19×10^{-19}	203.7	1.89×10^{9}	9.92×10^{-13}
11	291.1	1.60×10^{10}	6.22×10^{-21}	224.1	1.42×10^{10}	5.52×10^{-14}
12	262.7	1.51×10^{9}	5.42×10^{-19}	195.7	1.18×10^{9}	4.25×10^{-12}
13	241.9	5.66×10^{8}	3.03×10^{-17}	174.9	4.01×10^{8}	2.15×10^{-10}
14	258.7	9.98×10^{8}	9.40×10^{-19}	191.7	8.05×10^{8}	7.57×10^{-12}
15	276.5	1.41×10^{10}	1.84×10^{-19}	209.5	1.22×10^{10}	1.59×10^{-12}
16	250.7	9.12×10^{8}	5.89×10^{-18}	183.7	7.15×10^{8}	4.61×10^{-11}
17	249.3	1.26×10^{9}	1.14×10^{-17}	182.3	9.31×10^{8}	8.41×10^{-11}
18	261.7	4.12×10^{9}	1.89×10^{-18}	194.7	3.36×10^{9}	1.54×10^{-11}
19	267.4	2.35×10^{8}	2.73×10^{-20}	200.4	1.43×10^{8}	1.66×10^{-13}
20	249.3	3.97×10^{9}	3.59×10^{-17}	182.3	1.85×10^{9}	1.67×10^{-10}
21	200.4	3.81×10^{9}	4.42×10^{-12}	133.4	2.44×10^{9}	2.83×10^{-5}
22	193.5	7.23×10^{9}	4.41×10^{-11}	126.5	4.52×10^{9}	2.75×10^{-4}
23	254.7	1.35×10^{10}	3.33×10^{-17}	187.7	1.00×10^{10}	2.47×10^{-10}
24	232.7	6.03×10^{9}	2.96×10^{-15}	165.7	4.29×10^{9}	2.10×10^{-8}
25	228.7	5.90×10^{9}	7.57×10^{-15}	161.7	4.16×10^{9}	5.33×10^{-8}
26	248.5	6.55×10^{9}	7.18×10^{-17}	181.5	4.81×10^{9}	5.26×10^{-10}
27	241.7	5.32×10^{9}	2.99×10^{-16}	174.7	3.94×10^{9}	2.22×10^{-9}
28	229.8	4.96×10^{9}	4.89×10^{-15}	162.8	3.59×10^{9}	3.53×10^{-8}
29	197.7	3.45×10^{9}	7.66×10^{-12}	130.7	3.11×10^{9}	6.91×10^{-5}
30	240.8	4.65×10^{9}	3.25×10^{-16}	173.8	4.52×10^{9}	3.15×10^{-9}
31	231.1	4.38×10^{9}	3.15×10^{-15}	164.1	4.20×10^{9}	3.02×10^{-8}
32	245.8	1.72×10^{10}	3.62×10^{-16}	178.8	1.47×10^{10}	3.08×10^{-9}
33	212.3	1.78×10^{10}	1.18×10^{-12}	145.3	1.47×10^{10}	9.72×10^{-6}
34	265.0	2.55×10^{10}	5.28×10^{-18}	198.0	2.35×10^{10}	4.86×10^{-11}
35	257.5	2.42×10^{10}	3.05×10^{-17}	190.5	2.20×10^{10}	2.77×10^{-10}
36	253.7	2.36×10^{10}	7.39×10^{-17}	186.7	2.13×10^{10}	6.68×10^{-10}

* The HY number corresponds to that in Table 6.

Table 9. Enthalpies ΔH, preexponential factors A, and rate constants k for retrodisproportionation involving nitrobenzene and nitrosobenzene calculated by Eqs. (4)–(8)

HY*	ΔH, kJ/mol	A, l mol^{-1} s^{-1}	k(500 K), l mol^{-1} s^{-1}	ΔH, kJ/mol	A, l mol^{-1} s^{-1}	k(500 K), l mol^{-1} s^{-1}
	$PhNO_2$			PhNO		
1	170.1	1.73×10^{11}	2.93×10^{-7}	160.1	7.61×10^{10}	1.43×10^{-6}
2	126.4	3.72×10^{9}	2.32×10^{-4}	116.4	1.33×10^{9}	9.22×10^{-4}
3	109.0	1.98×10^{9}	8.11×10^{-3}	99.0	5.89×10^{8}	2.68×10^{-2}
4	89.6	1.18×10^{10}	5.16	79.6	1.70×10^{9}	8.20
5	131.7	3.55×10^{9}	6.20×10^{-5}	121.7	1.41×10^{9}	2.73×10^{-4}
6	122.6	1.16×10^{11}	1.80×10^{-2}	112.6	4.42×10^{10}	7.63×10^{-2}
7	99.0	2.79×10^{10}	1.27	89.0	8.90×10^{9}	4.48
8	147.0	1.90×10^{11}	8.36×10^{-5}	137.0	8.10×10^{10}	3.95×10^{-4}
9	122.6	9.91×10^{9}	1.54×10^{-3}	112.6	3.45×10^{9}	5.96×10^{-3}
10	145.0	9.20×10^{9}	6.55×10^{-6}	135.0	3.81×10^{9}	3.00×10^{-5}
11	165.4	8.15×10^{10}	4.29×10^{-7}	155.4	3.57×10^{10}	2.08×10^{-6}
12	137.0	4.97×10^{9}	2.42×10^{-5}	127.0	1.89×10^{9}	1.02×10^{-4}
13	116.2	1.32×10^{9}	9.61×10^{-4}	106.2	4.34×10^{8}	3.49×10^{-3}
14	133.0	3.65×10^{9}	4.66×10^{-5}	123.0	1.46×10^{9}	2.06×10^{-4}
15	150.8	6.70×10^{10}	1.18×10^{-5}	140.8	2.88×10^{10}	5.62×10^{-5}
16	125.0	3.06×10^{9}	2.67×10^{-4}	115.0	1.18×10^{9}	1.15×10^{-3}
17	123.6	3.41×10^{9}	4.18×10^{-4}	113.6	1.20×10^{9}	1.63×10^{-3}
18	136.0	1.55×10^{11}	9.63×10^{-4}	126.0	6.27×10^{10}	4.31×10^{-3}
19	141.7	8.73×10^{9}	1.37×10^{-5}	131.7	3.81×10^{9}	6.64×10^{-5}
20	123.6	1.35×10^{11}	1.65×10^{-2}	113.6	5.70×10^{10}	7.73×10^{-2}
21	74.7	6.80×10^{9}	1.07×10^{2}	64.7	1.53×10^{9}	2.67×10^{2}
22	67.8	8.19×10^{9}	6.76×10^{2}	57.8	1.25×10^{9}	1.15×10^{2}
23	129.0	8.41×10^{10}	2.81×10^{-3}	119.0	3.41×10^{10}	1.26×10^{-2}
24	107.0	2.53×10^{10}	0.17	97.0	9.35×10^{9}	0.69
25	103.0	2.26×10^{10}	0.39	93.0	8.13×10^{9}	1.56
26	122.8	3.71×10^{10}	5.50×10^{-3}	112.8	1.47×10^{10}	2.42×10^{-2}
27	116.0	1.66×10^{10}	1.26×10^{-2}	106.0	5.75×10^{9}	4.86×10^{-2}
28	104.1	1.06×10^{10}	0.14	94.1	3.23×10^{9}	0.48
29	72.0	1.31×10^{9}	39.3	62.0	3.61×10^{8}	1.20×10^{2}
30	115.1	4.86×10^{9}	4.60×10^{-3}	105.1	1.96×10^{9}	2.06×10^{-2}
31	105.4	3.95×10^{9}	3.85×10^{-2}	95.4	1.54×10^{9}	0.17
32	120.1	4.07×10^{10}	1.16×10^{-2}	110.1	1.62×10^{10}	5.09×10^{-2}
33	86.6	1.09×10^{10}	9.75	76.6	3.01×10^{9}	29.9
34	139.3	8.52×10^{10}	2.39×10^{-4}	129.3	3.69×10^{10}	1.15×10^{-3}
35	131.8	7.66×10^{10}	1.30×10^{-3}	121.8	3.28×10^{10}	6.18×10^{-3}
36	128.0	7.24×10^{10}	3.07×10^{-3}	118.0	3.07×10^{10}	1.45×10^{-2}

* The HY number corresponds to that in Table 6.

obtain $D_{N–H}$ = 330.3 kJ/mol (in hydrazine, $D_{N–H}$ = 366.1 kJ/mol [16]). Then, we have ΔH(H + MeN=NMe) = –164.3 kJ/mol for H-atom addition to *trans*-MeN=NMe.

In the PhN($O^{\bullet}$)OH $D_{O–H}$ radical formed from nitrobenzene, PhN($O^{\bullet}$)OH $D_{O–H}$ is 223 kJ/mol [21]. Using ΔH(PhNO) = 200.8 kJ/mol, ΔH(PhNHOH) = 79.5 kJ/mol [19], and $D_{N–H}$ = 324.3 kJ/mol [22], we estimated the $D_{O–H}$ value for the $PhN^{\bullet}OH$ radical equal to 233 kJ/mol.

RESULTS AND DISCUSSION

Tables 6 and 7 summarize the results of our calculations of the enthalpies, the preexponential factors, and the rate constants for the retrodisproportionation of three imines with various hydrogen-atom donors (hydrocarbons, amines, alcohols, hydroxylamines, phenols, thiophenols, and R_3MH compounds (M = Si, Ge, Sn). Taking into account that all these reactions are endothermic and their enthalpy $\Delta H_e > \Delta H_{e,max}$, we obtained for them that $E = \Delta H + 0.5RT$ and calculated the rate constant by Eq. (7). The enthalpies of these reactions vary widely from 260 to 117 kJ/mol, and the k(500 K) value ranges from 6×10^{-18} to 1.2×10^{-3} l mol^{-1} s^{-1}. Tables 8 and 9 summarize the calculated ΔH, A, and k parameters for retrodisproportionation involving benzonitrile, azomethane, nitrobenzene, and nitrosobenzene. Comparison of our data suggests that the weaker the Y-H bond in a hydrogen-atom donor HY, the lower its activity. Cyclic hydroxylamines, methyl sulfide, phenols and thiophenols were the most active hydrogen-atom donors among the studied compounds. Hydrogen atom acceptors are arranged in the following activity series: MeCH=NMe < CH_2NH < *trans*-MeN=NMe < CH_2=NPh < $PhNO_2$ < PhNO. This pattern is related to the strength of the forming N–H or O–H bond. It sounds reasonable to compare the accepting ability of the nitrogen-containing compounds with multiple bonds with other compounds examined in [7]. Cumene was chosen as a reference hydrogen-atom donor. We obtained the following order series (the enthalpy in the reaction with cumene is given in brackets (kJ/mol)): PhNO (122) ≈ *p*-OC_6H_4O(122) > $PhNO_2$(132) > CH_2CHPh(154) > CH_2NPh(181) > MeN=NMe (190) > CH_2CH_2(196) > CH_2=NH(210) > PhCOPh (227). For these hydrogen-atom acceptors, the enthalpy of hydrogen-atom abstraction varies over a wide range (more than 100 kJ/mol).

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