

Kinetic Parameters for Direct Atomic Substitution Reactions

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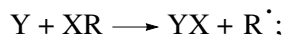
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Abstract—Experimental data (the rate constants and activation energies) for seven reactions of direct substitution of one atom for another $D + CH_3R \longrightarrow CH_2DR + H$, $D + NH_3 \longrightarrow DNH_2 + H$, $D + H_2O \longrightarrow HOD + H$, $F + CH_3X \longrightarrow CH_3F + X$ ($X = F, Cl, Br$, and I) involving atoms D and F and molecules C_2H_6 , H_2O , NH_3 , CH_3F , CH_3Cl , CH_3Br , and CH_3I are analyzed using the parabolic model of a bimolecular radical reaction. The activation energies for the thermally neutral analogs of these substitution reactions are calculated. Atomic substitution involving deuterium atoms has a lower activation energy of a thermally neutral reaction than radical abstraction or substitution.

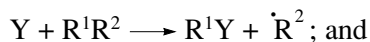
INTRODUCTION

Until very recently, the gas-phase homolytic reactions of thermally equilibrated free atoms with polyatomic closed-shell molecules have been identified with one of the following three types of radical reactions [1–11]:

(1) X atom abstraction from the molecule and its addition to the attacking atom



(2) Radical abstraction to form another radical R_2^{\cdot} and a closed-shell molecule

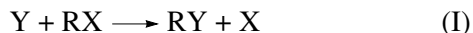


(3) Atom addition to a multiple bond, for example,



In these reactions, X and Y are atoms, R represent polyatomic radicals, RX and R^1R^2 stand for closed-shell molecules, and $CH_2=CHR$ is a molecule with a multiple bond.

Earlier (see, for instance, [1, 2, 5]), the reactions of direct X atom substitution in the polyatomic molecule by the atomic reactant



were assumed to have very high activation energies, which was tantamount to denying them (see, for instance, [1, 2, 5]). Several researchers [4, 12, 13] speculated that these reactions practically do not occur. The reactions of type (I) are not even considered in chemical kinetics and physical chemistry [1, 8, 9, 14].

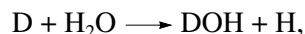
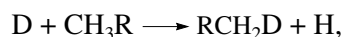
However, more recently [15–21], the gas-phase reactions of direct atomic substitution (I) were directly identified by kinetic methods combined with ESR spec-

troscopy when studying the reactions of thermal equilibrium deuterium and oxygen atoms with different polyatomic molecules. Most of these reactions occurred much more rapidly than atom abstraction reactions. The detection of fast reactions of direct substitution of one atom for another in polyatomic molecules poses new problems concerning the dynamics of an elementary chemical act and the specific features of the activated complexes that ensure their high rates. The high rate of atomic substitution also suggests that these reactions can play a significant role in complex chemical processes involving free atoms, for example, in combustion and pyrolysis [21]. These reactions should be considered when interpreting the results of mechanistic studies of complex processes involving isotopes.

Atomic substitution reactions are fundamentally different from abstraction and substitution reactions and are new interesting objects for analyzing the reactivity of molecules and radicals by the method of intersecting parabolas [22–24]. In this work, we used this method to investigate a number of atomic substitution reactions that had already been studied experimentally. These reactions are compared with other radical reactions involving free deuterium and fluorine atoms.

CALCULATION PROCEDURE

Within the framework of the parabolic model, the reaction of direct substitution of the hydrogen (deuterium) atom bound to a carbon or oxygen atom,



occurring in a single act can be considered as a result of the intersection of two parabolic potential curves in the coordinates amplitude of the stretching vibration of

Table 1. Kinetic parameters for atomic substitution reactions involving H and D atoms [21, 24]

Reaction	$b \times 10^{-11}$, (kJ/mol) ^{-1/2} m ⁻¹	α	$0.5hN_A\nu_i$, kJ/mol	$0.5hN_A(\nu_i - \nu_f)$, kJ/mol	A , l mol ⁻¹ s ⁻¹
D + CH ₃ R → DCH ₂ R + H	3.743	1.019	17.4	4.2	3.6×10^{10}
D + NH ₃ → NH ₂ D + H	4.306	1.000	20.0	-2.8	1.9×10^{10}
D + H ₂ O → HOD + H	4.733	1.000	21.8	-5.8	5.0×10^9
H + H ₂ O ₂ → H ₂ O + HO [•]	3.238	0.684	5.1	-17.1	1.0×10^{10}
F + CH ₃ F → F + CH ₃ F	3.790	1.000	6.3	0	6.8×10^{10}
F + CH ₃ Cl → Cl + CH ₃ F	3.288	0.867	4.9	-1.4	7.9×10^{10}
F + CH ₃ Br → Br + CH ₃ F	2.364	0.624	3.3	-3.0	1.3×10^{11}
F + CH ₃ I → I + CH ₃ F	1.542	0.407	2.1	-4.2	1.6×10^{11}

atoms forming the bond vs. potential energy. This substitution reaction can be characterized by the following parameters [22]:

1. The reaction enthalpy, ΔH_e , including the difference in the zero-point energies of the reacting bonds,

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

Table 2. Rate constants for atom substitution reactions and parameters br_e calculated from them for atom substitution reactions

$-\Delta H$, kJ/mol	T , K	k , l mol ⁻¹ s ⁻¹	E , kJ/mol	br_e , (kJ/mol) ^{1/2}	Reference
D + CH ₃ CH ₃ → CH ₂ DCH ₃ + H					
-4.2	395	8.47×10^6	27.4	13.27	[21]
D + NH ₃ → NH ₂ D + H					
-2.8	555	2.03×10^6	42.2	15.50	[17]
D + H ₂ O → DOH + H					
5.8	298	5.0×10^3	34.2	14.81	[21]
H + H ₂ O ₂ → H ₂ O + HO [•]					
285	300	3.07×10^7	14.4	16.53	[26]
285	300	2.45×10^7	15.0	16.60	[27]
285	300	2.53×10^7	14.9	16.59	[28]
F + CH ₃ F → F + CH ₃ F					
0	283	3.61×10^6	23.2	10.64	[29]
F + CH ₃ Cl → Cl + CH ₃ F					
110	283	2.23×10^7	19.2	14.69	[29]
F + CH ₃ Br → Br + CH ₃ F					
168	283	1.02×10^8	16.8	12.81	[29]
F + CH ₃ I → I + CH ₃ F					
224	283	4.82×10^8	13.7	10.05	[29]

where D_i and D_f are the energies of the breaking and forming bonds, respectively; ν_i and ν_f are the frequencies of the stretching vibrations of these bonds, respectively; h is the Planck constant; and N_A is the Avogadro constant;

2. The activation energy, E_e , including the zero-point vibration energy of the bond being attacked, which is related to the experimental activation energy E by the equation

$$E_e = E + 0.5(hN_A\nu_i - RT). \quad (2)$$

3. The distance r_e equal to the sum of the amplitudes of the vibration of reacting bonds in the transition state;

4. The parameters b and b_f , which are the dynamic characteristics of the breaking and forming bonds ($2b^2$ is the force constant of the bond, $b = \pi\nu_i(2\mu_i)^{1/2}$, $b_f = \pi\nu_f(2\mu_f)^{1/2}$, and μ_i and μ_f are the reduced weights of atoms forming the corresponding bond).

The above five parameters are related to each other by the following equation [22]:

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}, \quad (3)$$

where $\alpha = b/b_f$.

Using the parameter br_e , one can calculate the activation energy of a thermally neutral reaction $E_{e,0}$ that characterizes all reactions with $br_e = \text{const}$:

$$\sqrt{E_{e,0}} = \frac{br_e}{1 + \alpha}. \quad (4)$$

All reactions of the same group are usually characterized by the constant preexponential factor A (per one reacting bond), which allows one to calculate the value of E from the rate constant k using the Arrhenius equation

$$E = RT \ln(A/k). \quad (5)$$

Table 1 presents the parameters α , b , and the zero-point vibration energies of the relevant bonds for six classes of atomic substitution reactions. The values of ν_i and ν_f

Table 3. Kinetic parameters for atomic substitution reactions

Reaction	br_e , (kJ/mol) ^{1/2}	$E_{e,0}$, kJ/mol	$r_e \times 10^{11}$, m
$D + CH_3R \longrightarrow CH_2DR + H$	13.27	43.2	3.54
$D + NH_3 \longrightarrow DNH_2 + H$	15.50	60.0	4.14
$D + H_2O \longrightarrow HOD + H$	14.81	54.8	3.13
$H + H_2O_2 \longrightarrow H_2O + HO^\bullet$	16.56	96.7	5.11
$F + CH_3F \longrightarrow F + CH_3F$	10.64	28.3	2.81
$F + CH_3Cl \longrightarrow Cl + CH_3F$	14.69	61.1	4.47
$F + CH_3Br \longrightarrow Br + CH_3F$	12.81	62.2	5.42
$F + CH_3I \longrightarrow I + CH_3F$	10.05	51.0	6.52

Table 4. Comparison of the kinetic parameters (br_e , $E_{e,0}$, and r_e) for the reactions of direct atomic substitution, abstraction, and addition [22, 23]

Reaction	br_e , (kJ/mol) ^{1/2}	$E_{e,0}$, kJ/mol	$r_e \times 10^{11}$, m
Reaction involving a C atom			
$D + CH_3R \longrightarrow CH_2DR + H$	13.27	43.2	3.54
$H + RH \longrightarrow H_2 + R^\bullet$	14.50	58.2	3.66
$H + CH_2=CHR \longrightarrow CH_3\dot{C}HR$	24.59	101.6	4.56
Reaction involving a N atom			
$D + NH_3 \longrightarrow DNH_2 + H$	15.50	60.0	4.14
$H + NH_3 \longrightarrow H_2 + \dot{N}H_2$	17.55	74.2	4.69
$H + NH=CHR \longrightarrow NH_2\dot{C}HR$	25.63	124.3	4.54
Reaction involving an O atom			
$D + H_2O \longrightarrow DOH + H$	14.81	54.8	3.13
$H + H_2O \longrightarrow H_2 + HO^\bullet$	16.17	56.7	3.34
$H + O=CR^1R^2 \longrightarrow HO\dot{C}R^1R^2$	26.37	102.9	4.40

of the bond stretching vibrations were taken from handbook [25].

CALCULATION OF KINETIC PARAMETERS OF ATOMIC SUBSTITUTION REACTIONS

Table 2 presents the starting experimental data and the calculated parameters br_e . The values of this param-

eter determined by different measurements coincide for the reaction of a hydrogen atom with hydrogen peroxide, which is characterized by the average value $br_e = 16.56 \pm 0.03$ (kJ/mol)^{1/2}. The activation energies for thermally neutral substitution reactions br_e calculated from the parameter $E_{e,0}$ and the values of r_e are given in Table 3.

According to the $E_{e,0}$ values, the reactions of direct atomic substitution involving deuterium atoms are arranged in the following series: $E_{e,0}(D + CH_3R) < E_{e,0}(D + H_2O) < E_{e,0}(D + NH_3)$ and cover the range from 43 to 60 kJ/mol. The substitution of the H atom for the $\cdot OH$ radical in hydrogen peroxide occurs with a high activation energy $E_{e,0} = 97$ kJ/mol. The substitution of the fluorine atom for the halogen atoms in metal halides are characterized by the activation energy of 28–62 kJ/mol.

It is interesting to compare the parameters $E_{e,0}$ and r_e for the reactions of direct atomic substitution, abstraction, and addition with structurally similar transition states. The abstraction of the H atom from a hydrocarbon occurs via the reaction center of the linear transition state $H\cdots H\cdots C$. This configuration of the transition state ensures the minimal repulsion of the atoms involved. Most likely, the substitution reaction $D + C_2H_6$ also occurs via the formation of the linear reaction center $D\cdots C\cdots H$, thus favoring a relatively low activation energy. On the other hand, direct atomic substitution can formally be considered as the addition of an atom to the molecule with the simultaneous abstraction of the other atom. Table 4 presents the parameters for the reactions of direct atomic substitution, abstraction (taken from [22]), and addition (taken from [23]).

For all the three groups of reactions under consideration, we have $E_{e,0}$ (addition) $> E_{e,0}$ (abstraction) $> E_{e,0}$ (atom substitution) and r_e (addition) $> r_e$ (abstraction) $> r_e$ (atomic substitution).

Thus, the experimental data suggest that direct atomic substitution occurs very rapidly with a low activation energy. Comparison with radical abstraction and substitution reactions within the framework of the method of intersecting parabolas showed that the activation energies of thermally neutral abstraction and addition reactions are higher than those of direct atomic substitution.

REFERENCES

1. Glesston, S., Leidler, K., and Eiring, G., *The Theory of Rate Processes*, New York: Princeton University, 1941.
2. Waters, W.A., *The Chemistry of Free Radicals*, London: Oxford University Press, 1948.
3. Steacie, E.W.R., *Atomic and Free Radical Reactions*, New York: Reinhold, 1954, vol. 2.
4. Semenov, N.N., *O nekotorykh problemakh khimicheskoi kinetiki i reaktivnoi sposobnosti* (On Some Problems of Chemical Kinetics and Reactivity), Moscow: Akad. Nauk SSSR, 1958.

5. Kondrat'ev, V.N., *Kinetika khimicheskikh gazovykh reaktsii* (Kinetics of Chemical Gaseous Reactions), Moscow: USSR Academy of Sciences, 1958.
6. Melander, L., *Isotope Effects on Reaction Rates*, New York: Ronald, 1959.
7. Kondrat'ev, V.N., Nikitin, E.E., Reznikov, A.I., and Umanskii, S.Ya., *Termicheskie bimolekulyarnye reaktsii v gazakh* (Thermal Bimolecular Reactions in Gases), Moscow: Nauka, 1976.
8. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1984.
9. Eyring, H., Lin, S.H., and Lin, S.M., *Basic Chemical Kinetics*, New York: Wiley, 1980.
10. Fujisaki, N., Gaumann, T., and Ruf, A., *Ber. Bunsen-Ges. Phys. Chem.*, 1986, vol. 90, no. 2, p. 375.
11. Baulch, D.L., Cobos, C.J., Cox, R.A., *et al.*, *Combust. Flame*, 1994, vol. 98, no. 11, p. 59.
12. Geib, K.H. and Steacie, E.W.R., *Trans. Roy. Soc. Canada*, 1935, vol. 3, no. 1, p. 91.
13. Geib, K.H. and Steacie, E.W.R., *Z. Phys. Chem.*, 1935, vol. 29, no. 1, p. 215.
14. Semiokhin, I.A., Strakhov, B.V., and Osipov, A.I., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Mosk. Gos. Univ., 1995.
15. Azatyan, V.V. and Filippov, S.B., *Dokl. Akad. Nauk SSSR*, 1969, vol. 184, no. 3, p. 625.
16. Azatyan, V.V. and Filippov, S.B., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, no. 5, p. 1186.
17. Kurilo, M.J., Holinden, G.A., Le Fevre, H.F., and Timmons, R.B., *J. Chem. Phys.*, 1969, vol. 51, p. 4497.
18. Azatyan, V.V., Filippov, S.B., and Khachatryan, M.S., *Kinet. Katal.*, 1971, vol. 12, no. 1, p. 17.
19. Azatyan, V.V., *Doctoral (Chem.) Dissertation*, Moscow: Inst. of Chemical Physics, 1978.
20. Azatyan, V.V., Gazaryan, K.G., and Garobyan, T.A., *Kinet. Katal.*, 1987, vol. 29, no. 1, p. 38.
21. Azatyan, V.V., *Kinet. Katal.*, 2002, vol. 43, no. 2, p. 165.
22. Denisov, E.T., *Usp. Khim.*, 1997, vol. 66, no. 10, p. 953.
23. Denisov, E.T., *Usp. Khim.*, 2000, vol. 69, no. 2, p. 166.
24. Denisov, E.T., *General Aspects of the Chemistry of Radicals*, Alfassi, Z.B., Ed., New York: Wiley, 1999, p. 79.
25. *Handbook of Chemistry and Physics*, Lide, D.R., Ed., CRC, 1992.
26. Tsang, W. and Hampson, R.F.H., *J. Phys. Chem. Ref. Data*, 1986, vol. 15, p. 1087.
27. Warnatz, J., *Combustion Chemistry*, Gardines, W., Ed., New York: Springer, 1984, p. 197.
28. Baulch, D.L., Cobos, C.J., Cox, R.A., *et al.*, *J. Phys. Chem. Ref. Data*, 1992, vol. 21, p. 411.
29. Iyer, R.S. and Rowland, F.S., *J. Phys. Chem.*, 1981, vol. 85, no. 17, p. 2488.