

Intrinsic Barriers in Identity SN2 Reactions and the Periodic Table

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According to the Marcus theory,¹ two factors contribute to the height of the activation barrier (ΔG^\ddagger) in a chemical reaction: the intrinsic barrier ($\Delta G_{\text{int}}^\ddagger$) and the exo-/endothermicity of the reaction (ΔG°). Equation 1, the Marcus equation, shows how the activation barrier is related to these two quantities (work terms omitted).

$$\Delta G^\ddagger = \Delta G_{\text{int}}^\ddagger + \frac{1}{2} \Delta G^\circ + (\Delta G^\circ)^2 / 16 \Delta G_{\text{int}}^\ddagger \quad (1)$$

The intrinsic barrier $\Delta G_{\text{int}}^\ddagger$ is the barrier in the absence of a thermodynamic bias; $\Delta G^\circ = 0$. This condition is obtained automatically in an identity SN2 reaction (eq 2).



In an exothermic reaction, a thermodynamic driving force will lower the transition-state energy (within a structurally close family of reactions), whereas in endothermic reactions the thermodynamics will induce a higher activation energy (Figure 1), all relative to the $\Delta G^\circ = 0$ situation. Thus, given the values of its two constituents, the Marcus equation enables the determination of the actual barrier in a chemical reaction. Over the years, chemists have developed reasonably good intuition for the thermodynamics (ΔG°) of reactions, being able to estimate the relative stabilities of the reactants and products by using models such as resonance, bond energies, charge delocalization, etc. However, we have not yet acquired any feeling for the factors determining the height of the intrinsic barrier $\Delta G_{\text{int}}^\ddagger$. In the course of our attempt to evaluate the strain contribution in various strain releasing reactions,² we calculated the identity reactions of some SN2 reactions as strain-free reference reactions. The surprising preliminary results³ for the barrier heights prompted us to significantly widen the scope of this study. Our more extensive results are reported here.

The geometries and energies of the reactant (ion-dipole) complexes and transition states were obtained by a modified form of G2 theory, outlined by Glukhovtsev et al.,^{4,5} called G2(+), which was adapted from G2 to treat anions better by adding diffuse functions and to calculate heavy-atom systems by using the Wadt-Hay⁶ effective core potentials (ECPs). All electron basis sets were used for all first- and second-row atoms, and the appropriately modified ECP basis sets⁶ were used for the third- and fourth-row atoms. All calculations were carried out using the GAUSSIAN94^{7a} and GAUSSIAN98^{7b} sets of programs. Previous results by GPSBR⁸ for reaction 2, using X = halogens, showed that the calculated energy differences were relatively insensitive to minor specific details of the G2(+) procedure.⁹

(1) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(2) Sella, A.; Basch, H.; Hoz, S. *J. Am. Chem. Soc.* **1996**, *118*, 416. Sella, A.; Basch, H.; Hoz, S. *Tetrahedron Lett.* **1996**, *31*, 5573.

(3) The preliminary results for the intrinsic barrier height were obtained for a smaller set of reactions at the RHF/6-31+G* theory level. They showed the same column dependence described in this paper for the G2(+) level reaction barriers but with higher values, as is to be expected.

(4) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024.

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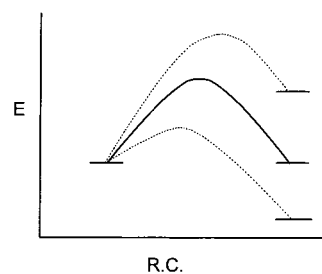


Figure 1. Schematic presentation of the effect of ΔG° on ΔG^\ddagger .

Table 1. G2(+) Energies and MP2-Optimized Structural Parameters for the Reactant Complex^a

X	G2(+), au	Bond lengths (Å)				Angles (°)	
		a	b	c	d	α	β
C	-197.810 64	1.525	1.527	1.529	4.379	112.4	61.0
N	-229.909 62	1.475	1.456	1.449	3.110	111.4	109.5
O	-269.680 55	1.448	1.409	1.363	2.810	110.5	169.6
F	-239.333 87	1.454			2.627		
Si	-699.947 31	1.865	1.888	1.967	3.857	111.7	149.4
P	-802.447 11	1.845	1.856	1.900	3.973	99.7	72.7
S	-914.954 99	1.811	1.806	1.831	3.448	98.1	151.0
Cl	-959.376 95	1.809			3.266		
Ge	-129.364 29	1.951	1.974	2.063	3.857	111.3	151.0
As	-132.871 05	1.969	1.983	2.031	4.182	97.4	62.1
Se	-137.921 06	1.962	1.960	1.992	3.569	95.8	155.9
Br	-66.210 13	1.983			3.394		
Sn	-128.549 44	2.128	2.155	2.248	3.976	111.2	146.2
Sb	-131.412 53	2.160	2.177	2.233	4.377	95.1	58.4
Te	-135.553 38	2.153	2.153	2.198	3.898	93.2	68.7
I	-62.631 60	2.173			3.662		

^a Bond lengths are given in angstroms, angle in degrees.

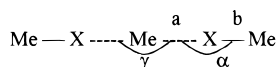
For nucleophiles (X of eq 2), the following anions were chosen (charges omitted): MeCH₂⁻, MeNH⁻, MeO⁻, F⁻, MeSiH₂⁻, MePH⁻, MeS⁻, Cl⁻, MeGeH₂⁻, MeAsH⁻, MeSe⁻, Br⁻, MeSnH₂⁻, MeSbH⁻, MeTe⁻, and I⁻. In most cases, the geometry of the ion-dipole reactant complexes (product complexes) had to be restricted to linearity; namely, the angle X--C-X (where X in this case represents only the nucleophilic atom) was constrained to 180°. This procedure, which is rather common for SN2 reactions, is adopted be-

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(9) In these G2(+) calculations, unscaled MP2 frequencies were used (instead of RHF). For the ECP basis sets, the smaller splitting factors were used to obtain the multiple sets of d-type polarization functions, the single d- and f-type polarization functions were obtained for the neutral heavy-atom halides at the QCISD(T) level, and the s- and p-type diffuse functions were optimized for the anions also using QCISD(T).^{4,5,8}

Table 2. G2(+) Energies and MP2-Optimized Structural Parameters for the Transition States^a

X	G2(+), au	a	b	α	γ
C	-197.739 40	1.934	1.506	106.7	179.0
N	-229.862 87	1.935	1.449	106.2	179.7
O	-269.649 43	1.864	1.383	107.8	178.8
F	-239.315 42	1.836			180.0
Si	-699.874 33	2.476	1.931	95.9	161.7
P	-802.399 59	2.463	1.877	88.9	173.7
S	-914.920 08	2.363	1.816	91.5	177.1
Cl	-959.355 91	2.316			180.0
Ge	-129.303 49	2.541	2.022	95.8	163.9
As	-132.831 96	2.575	2.007	86.0	173.7
Se	-137.892 76	2.511	1.977	87.9	176.0
Br	-66.192 72	2.476			180.0
Sn	-128.500 60	2.680	2.204	95.0	164.4
Sb	-131.381 12	2.752	2.206	82.2	173.2
Te	-135.528 98	2.704	2.176	83.4	174.4
I	-62.616 27	2.674			180.0

^a Bond lengths are given in angstroms, angle in degrees.

Table 3. G2(+) Intrinsic Barrier Heights (kcal) Listed According to the Location of the Nucleophilic Atom in the Periodic Table

C	N	O	F
44.7	29.3	19.5	11.6
Si	P	S	Cl
45.8	29.8	21.9	13.2
Ge	As	Se	Br
38.1	24.5	17.8	10.8
Sn	Sb	Te	I
30.6	19.7	15.3	9.6

cause the ion-dipole complex is very often more stabilized when the negatively charged nucleophile is directed toward a methyl hydrogen rather than toward the target carbon atom of the methyl group.

The energies and structural parameters for the reactant complexes and the transition states are given in Tables 1 and 2, respectively. In Table 3, the activation energies are given according to the location of the nucleophilic atoms in the Periodic Table. In this arrangement, the regularity immediately becomes obvious. The intrinsic barrier is largely determined by valence, i.e., by the column of the nucleophilic atom in X. Thus, for the tetravalent atoms (C, Si, and Ge) the G2(+) intrinsic barrier is 42.0 ± 3.9 kcal. For the trivalent atoms (N, P, and As) the intrinsic barrier is 27.2 ± 2.7 kcal, for the divalent atoms (O, S, and Se) it is 19.6 ± 1.8 kcal, and for the halogens it is 11.4 ± 1.8 .

The borderline between the metallic and nonmetallic elements clearly reflects the results presented in Table 3. Although the consistency is kept within a column without having E_a values overlapping between two columns, the quality of adherence to a single value is eroded the closer the nucleophilic atom is to the diagonal line separating the metallic and nonmetallic groups of elements.

Supportive evidence for the column dependence effect comes from the G2(+) calculations reported by Glukhovtsev, Pross, Schlegel, Bach, and Radom (GPSBR).^{8,9} They calculated the intrinsic barrier for the identity reaction of halides with the corresponding methyl halides ($X = F, Cl, Br, \text{ and } I$). Their results (11.6 ± 1.1) support those reported here, since they also clearly show that the barrier height down the column of halogens is, indeed, nearly constant.

The question can be raised as to why this phenomenon has not been observed earlier. The largest compilation of computa-

tional data for SN2 reactions can be found in the book by Shaik, Schlegel, and Wolfe.^{10a} The most comprehensive data sets are available for the RRKM and for the HF/4-31G calculations combined with the Shaik-Pross SCD model. Although a lot of sorting has to be done, the RRKM results show that the E_a for Cl and Br is 10.2 and 11.2 kcal, respectively. The average E_a for oxygen nucleophiles is 24.3 kcal, for the sulfur nucleophiles it is 24.5 kcal, and for carbon nucleophiles it is 37 kcal. The 4-31G-SCD results show that the E_a for F and Cl is 11.7 and 5.5 kcal, respectively. The average E_a for oxygen nucleophiles is 20.5 kcal, for the sulfur nucleophile (single value) it is 15.6 kcal, and for carbon nucleophiles it is 47.1 kcal. Both the RRKM and the 4-31G-SCD results are clearly in line with our more accurate results, although they are not as consistent.

We believe that the pattern observed in Table 3 was not realized before because of the large scatter of data. Thus, for example, in the RRKM computations, although the average for oxygen nucleophiles is 24.3 kcal, the individual results span the range from 13.2 to 30.6 kcal. At the 4-31G-SCD level, the datum for the sulfur nucleophile (15.6 kcal) falls between the lower limit of the oxygen nucleophiles (18.5 kcal) and the upper limit (11.7 kcal) of the halogen nucleophiles. However, despite the scatter, it was noticed that the intrinsic barrier decreases in the order nitrogen nucleophiles > oxygen nucleophiles > F, which is in line with our observation^{10b} in Table 3.

At the moment, however, we are unable to offer any explanation for the trends in E_a , based on current models in the field. The curve-crossing diagram developed by Shaik and Pross¹¹ for prediction of the barrier height, in its simplistic form, fails to yield the observed results. In a more sophisticated treatment, a resonance term (B) has to be added to the model. The magnitude by which this resonance term reduces the energy of the transition state is difficult to estimate. Recently, Shaik and Shurki¹² were successful in reproducing the intrinsic barriers of the halide series calculated by GPSBR.⁸ For this purpose, they assumed that the resonance term depends on the HOMO-LUMO orbital splitting and the charge distribution at the transition state. However, the remarkable success of the surface-crossing diagram in predicting correctly the barriers in the halide-methyl halide SN2 identity reaction cannot be, at the moment, reduced to a simple, easy-to-use model or explanation.

To the best of our knowledge, this is the first time ever that any study has shown a direct quantitative correlation between the position of an element in the Periodic Table and a reaction parameter such as the intrinsic barrier. The importance of this observation is not only in its novelty, its predictive capability, or the power of the Periodic Table. Its importance is in the questions that up to now could not have been asked: What is the complementary reaction which "fits" the metallic elements in the Periodic Table on the other side of the diagonal line? (Is it an electrophilic reaction?) Are there any other reactions, besides SN2, which "fit" the Periodic Table? Are there any other basic properties of nature, besides the intrinsic barrier, which "fit" the Periodic Table? The answers to these and similar questions may result in the addition of another and hitherto unknown dimension to the Periodic Table.

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Supporting Information Available: Listing of archive files for the MP2-optimized reactant complexes and transition states (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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