

Relative energy of organic compounds IV. Radicals, carbocations, and carbanions

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Abstract The structure-dependent energies of organic radicals, cations, and anions are deduced from their calculated relative enthalpies and are compared to the relative enthalpies of their parent compounds. The use of relative enthalpies to express the relative energies of organic radicals, cations, and anions proved to be as fruitful as in the case of their parent organic compounds. The same energy-determining structural factors may have stronger, weaker, or even opposite effects in the radicals, cations, or anions than those in their parent molecules.

Keywords Heat of formation · Relative energy · Relative enthalpy · Radicals · Carbocations · Carbanions · Education

Abbreviations

SDE Structure-dependent energy
RSDE Structure-dependent energy of radicals, cations, and anions relative to those of their parent compounds

Introduction

In the previous papers of this series [1–3], the structure-dependent energies of different types of organic compounds were demonstrated using their calculated relative

enthalpies. The relative enthalpies are quantities that replace enthalpies of formation in a new thermochemical reference system [4, 5] because the traditionally used enthalpies of formation depend on composition and only the energies of isomers can be compared. The relative enthalpies are calculated from the heats of formation by correcting them with the relative enthalpies of their component elements.

C : −22.85 H : 21.73 O : 125.83 N : −89.31
S : −41.62
F : 198.06 Cl : 47.11 Br : 4.08 I : −53.82

The relative enthalpy of ethane (0.0 kJ/mol), for example, is calculated by adding to its heat of formation (−84.7 kJ/mol) twice the relative enthalpy of carbon ($2 \times (-22.85 \text{ kJ/mol})$) and six times the heat of formation of hydrogen ($6 \times 21.73 \text{ kJ/mol}$). By correcting the heats of formation of other gas-phase organic compounds by the above values, the relative enthalpies of the following compounds become zero or very close to zero, where R means a linear alkyl group and X any of the halogen atoms.

$R-CH_3$ $R-CH_2-O-CH_2-R$ $R-CH_2-S-CH_2-R$
 $N(CH_2-CH_3)_3$ $R-CH_2-X$

As a consequence, instead of the elements, the above compounds are considered as reference substances. Unlike the heats of formation, the relative enthalpies do not depend on composition and can be compared to each other without restriction.

The relative enthalpies of compounds throughout the paper are taken from the previous publications of the series [1–3], those of the radicals, cations, and anions are calculated from their enthalpies of formation [6, 7].

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Radicals, cations, and anions

The relative enthalpies (H_{rel}° -s) of radicals, cations, and anions can be used to characterize their energy. The H_{rel}° -s do not depend on composition and, as a consequence, can be compared to each other or to the H_{rel}° -s of their parent compounds without any restriction. As mentioned, the H_{rel}° -s of the parent compounds of radicals, cations, and anions directly show the effect of structures on energy. This is not true for radicals, cations, and anions since their relative enthalpy (H_{rel}°), in addition to the effects on energy of the structural varieties, is influenced by the energy needed for dissociation, too. This effect of dissociation needs to be removed. In order to do this, the H_{rel}° of methyl radical, methyl cation, or methyl anion is subtracted from the H_{rel}° -s of radicals, cations, and anions, respectively. The methyl radical, cation, and anion in this respect can be regarded structureless entities since they have no functional groups that could have influence on energy. The quantity that reflects the effect of structure on energy is the remainder of the above subtractions; it is called structure-dependent energy and is abbreviated as SDE.

It is a question whether the same structural elements in radicals, carbocations, or carbanions or those in the parent compounds have a stronger or weaker influence on energy. This is revealed by comparing SDEs to the H_{rel}° -s of the parent compounds. The relative structure-dependent energies (RSDEs) are deduced by subtracting the SDE values

of radicals, cations, or anions from the H_{rel}° -s of their parent compounds. A negative RSDE value means, for example, that the same structural element brings about either a larger energy decrease or a smaller energy increase in a radical than it causes in the parent compound.

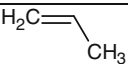
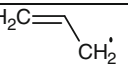
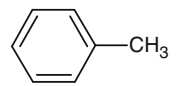
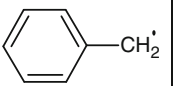
Radicals

Radicals that can be deduced from the methyl radical by substituting one hydrogen atom with different functional groups, as well as their parent compounds, are summarized in Table 1. The heats of formation of radicals from which their relative enthalpies are calculated are found in the fourth column.

The SDE of the ethyl radical is -5.9 kJ/mol. Since the H_{rel}° of ethane is 0.0 kJ/mol, the energy of the ethyl radical looks more favorable, but the RSDE value is very low (RSDE: -6 kJ/mol).

Substitutions by vinyl or phenyl groups bring about larger effects. As reflected by H_{rel}° -s, the presence of the double bond in propene and the benzene ring in toluene increases considerably the energy (by 82.3 and 64 kJ/mol, respectively). The same structural elements in the radicals, however, cause only 22.4 and 10.6 kJ/mol increase, demonstrating that considering energy, the double bond or the benzene ring is less unfavorable in the radicals than in the parent compounds (RSDEs are -60 and -53 kJ/mol, respectively).

Table 1 Effect of substituents replacing one hydrogen atom in the methyl radical

Compound	H_{rel}° (kJ/mol)	Radical	$\Delta H_{\text{f}}^{\circ}$ (kJ/mol)	H_{rel}° (kJ/mol)	SDE (kJ/mol)	RSDE (kJ/mol)
		CH_3^{\bullet}	144.5	188.9	0.0	
$\text{CH}_3\text{-CH}_3$	0.0	$\text{H}_3\text{C-CH}_2^{\bullet}$	119.9	183.0	-5.9	-5.9
	82.3		171.0	211.3	22.4	-59.9
	64.0		207.0	199.5	10.6	-53.4
$\text{HC}\equiv\text{-CH}_3$	203.8	$\text{HC}\equiv\text{-CH}_2^{\bullet}$	351.5	348.3	159.4	-44.4
$\text{CH}_3\text{-OH}$	-11.3	HO-CH_2^{\bullet}	-16.1	152.1	-36.8	-25.5
$\text{CH}_3\text{-NH}_2$	-26.5	$\text{H}_2\text{N-CH}_2^{\bullet}$	148.7	123.5	-65.4	-38.9

Substitution by ethynyl group also increases the energy in both the parent compound (H_{rel}° : 204 kJ/mol) and in the radical (SDE: 159 kJ/mol). The energy increase, however, is smaller in the case of the radical (RSDE: -44 kJ/mol).

By substitution with hydroxyl or amino group, the energies are reduced in both the parent compounds (H_{rel}° : -11 and

-27 kJ/mol) and the radicals (SDE: -37 and -65 kJ/mol). The RSDE values (-26 and -39 kJ/mol) show that the presence of hydroxyl and amino group in the radicals is more favorable than that in the parent compound.

Radicals deduced by replacing two hydrogen atoms in the methyl radical are listed in Table 2. The SDE of the

Table 2 Effect of substituents replacing two hydrogen atoms in the methyl radical

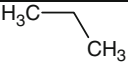
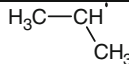
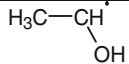













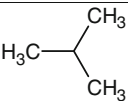
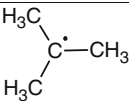



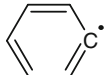
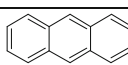
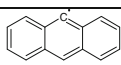
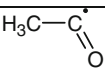

Compound	H_{rel}° (kJ/mol)	Radical	ΔH_f° (kJ/mol)	H_{rel}° (kJ/mol)	SDE (kJ/mol)	RSDE (kJ/mol)
	1.5		74.5	158.1	-30.8	-32.3
$\text{CH}_3\text{-CH}_2\text{-OH}$	-24.3		-55.3	133.6	-55.3	-31.0
CH_2F_2	-35.1	$\cdot\text{CHF}_2$	-238.9	156.1	-32.8	2.3
CH_2ClF	-25.0	$\cdot\text{CHClF}$	-83.5	160.6	-28.3	-3.2
CH_2Br_2	24.6	$\cdot\text{CHBr}_2$	198.5	205.6	16.7	-7.9
	115.2		280.0	320.2	131.4	16.1
	109.1		230.3	291.2	102.3	-6.8
	0.6		75.8	178.1	-10.8	-11.4
	25.0		77.7	200.6	11.7	-11.4
	294.6		486.8	483.6	294.7	0.1
	150.1		263.3	257.9	69.0	-81.1
$\text{H}_2\text{C}=\text{CH}_2$	93.6	$\text{H}_2\text{C}=\text{CH}\cdot$	297.3	316.9	128.0	34.6
$\text{CH}_2=\text{C}=\text{O}$	62.6	$\text{O}=\text{C}=\text{CH}\cdot$	178.0	280.0	91.1	28.5
$\text{H}_2\text{C}=\text{CH}_2$	93.6	$\text{H}_2\text{C}=\text{CH}\cdot$	297.3	316.9	128.0	34.6
$\text{CH}_2=\text{C}=\text{CH}_2$	210.5	$\text{CH}_2=\text{C}=\text{CH}\cdot$	348.4	345.2	156.3	-54.2
HCHO	30.5		41.83	166.6	-22.3	-52.8

Table 3 Effect of replacing three hydrogen atoms in the methyl radical

Compound	H_{rel}° (kJ/mol)	Radical	$\Delta H_{\text{f}}^{\circ}$ (kJ/mol)	H_{rel}° (kJ/mol)	SDE (kJ/mol)	RSDE (kJ/mol)
	-8.6		31.4	135.6	-53.3	-44.7
CHF ₃	-104.4	F ₃ C [•]	-468.2	103.2	-85.7	18.7
CHI ₃	48.3	I ₃ C [•]	406.0	221.7	32.8	-15.5
	294.6		524.0	520.8	331.9	37.3
	76.3		337.3	309.1	120.2	43.9
	128.5		488.0	364.4	175.5	47.0
HC≡CH	224.5	HC≡C [•]	567.9	544.0	355.1	130.6
H ₃ C—C≡CH	203.8	H ₃ C—C≡C [•]	528.4	525.2	336.3	132.5
N≡CH	40.1	N≡C [•]	440.0	327.9	139.0	98.9
CH ₃ CHO	0.7		-9.7	135.7	-53.2	-53.9
FCHO	-53.7		-176.3	124.8	-64.1	-10.4

isopropyl radical shows a significant energy reduction relative to the H_{rel}° of the parent propane (RSDE: -32 kJ/mol). The energy reduction effect is about the same (RSDE: -31 kJ/mol) if the methyl radical is substituted by one methyl and one hydroxyl group. Although the SDE of 1-hydroxy-ethyl radical is much lower (-55 kJ/mol) than that of the isopropyl radical, the RSDE values are almost the same. The reason is that the energy-reducing effect of the hydroxyl group in the radical and in the parent compound is about the same.

Relative to their parents, substitution by two fluorine atoms, one fluorine and one chlorine atom, or two bromine atoms brings about only small changes in the radicals.

Inclusion of the radical carbon atom into cyclohexane and cycloheptane rings also causes only small relative changes (RSDEs are -11 kJ/mol). The ring strain in cyclopropyl and cyclobutyl radicals are considerable (SDE: 131 and

102 kJ/mol) but are close to those appearing in their parent compounds (H_{rel}° : 115 and 109 kJ/mol). The situation looks similar if cyclopropenyl radical is compared to cyclopropene (RSDE: 0.1 kJ/mol). The cyclopentadienyl radical is different. The appearance of the two double bonds in the ring causes a 69 kJ/mol SDE. The H_{rel}° of cyclopentadiene, however, is much higher, 150 kJ/mol. The negative RSDE value (-81 kJ/mol) shows that the two double bonds are "feeling better" in the radical than in the parent molecule.

Comparing the vinyl radical to ethylene shows that the presence of the double bond in the radical causes a somewhat larger energy increase than that in the parent compound (RSDE: 35 kJ/mol). The situation looks similar when the radicals deduced from butadiene (RSDE 42 kJ/mol) and ketene (RSDE: 29 kJ/mol) are considered, showing that the double-bonded radical carbon atom is also more unfavorable in these radicals.

Table 4 Substituents replacing one or more hydrogen atoms in the methyl cation

Compound	H_{rel}° (kJ/mol)	Cation	ΔH_f° (kJ/mol)	H_{rel}° (kJ/mol)	SDE (kJ/mol)	RSDE (kJ/mol)
		CH_3^+	1095.5	1137.9	0	
$\text{CH}_3\text{-CH}_3$	0.0	$\text{CH}_3\text{-CH}_2^+$	902.9	966.0	-171.9	-171.9
CF_3H	-104.4	CF_3^+	405.7	977.1	-160.8	-56.4
$\text{HC}\equiv\text{CH-CH}_3$	203.8	$\text{HC}\equiv\text{CH-CH}_2^+$	1188.1	1184.9	47.0	-156.8
CH_3OH	-11.3	HOCH_2^+	710.1	878.3	-259.6	-248.3
$\text{H}_2\text{N-CH}_3$	-26.5	$\text{H}_2\text{N-CH}_2^+$	752.1	726.9	-411.0	-384.5

The opposite is observed if the propadienyl and the formyl radical are compared to their parent compounds, allene and formaldehyde. The SDEs are in both cases significantly smaller than the H_{rel}° -s (RSDEs are -54 and -53 kJ/mol).

Table 3 summarizes the radicals arising by replacing three hydrogen atoms of methyl radical by three substituents or by replacing one sp^2 or one sp carbon atom in different compounds by a radical carbon atom.

It can be seen that the SDE of *tert*-butyl radical is significantly lower than the H_{rel}° of isobutane (RSDE: -45 kJ/mol). The SDE of trifluoromethyl radical is a large negative value (-86 kJ/mol) while the H_{rel}° of trifluoromethane is somewhat even smaller (-104 kJ/mol) showing that considering the energy, the three fluorine atoms in the radical are somewhat less favorable than in trifluoromethane (RSDE: 19 kJ/mol). The presence of the three iodine atoms in both triiodomethane and the triiodomethyl radical is unfavorable. In the latter case, however, the energy increase is somewhat smaller (RSDE: -16 kJ/mol).

A radical carbon atom replacing one sp^2 atom in cyclopropene, benzene, or anthracene rings is unfavorable (RSDEs are about 40 kJ/mol) if compared to the parent compounds. A radical carbon atom replacing one sp carbon atom in acetylene, propyne, or hydrogen cyanide is even more unfavorable (RSDEs are 131, 133, and 99 kJ/mol, respectively). In contrast, if the SDE of the acetyl radical (-53 kJ/mol) is compared to the H_{rel}° of acetaldehyde (0.7 kJ/mol), it shows that the C-O double bond is more favorable in the radical than in the parent compound. The situation is similar if the fluoroformyl radical is compared to its parent compound, but the RSDE is a smaller negative value (-10 kJ/mol).

Carbocations

The relative enthalpies of carbocations for obvious reasons are much larger than those of the radicals. The structure-dependent energies are calculated by subtracting the H_{rel}° of methyl cation (1137.9 kJ/mol) from the H_{rel}° -s carbocations. The carbocations deduced from the methyl cation by substituting one of its hydrogen atoms by different functional groups are found in Table 4.

Comparing the SDE of the ethyl cation (-172 kJ/mol) to the H_{rel}° of its parent ethane (0.0 kJ/mol) shows large RSDE (-172 kJ/mol). This value demonstrates that the effect of a methyl group on the energy of the cation is much larger than that on the energy of the ethyl radical. The presence of three fluorine atoms in both the trifluoromethyl radical and its parent trifluoromethane brings about large energy reductions (SDE: -161 kJ/mol and H_{rel}° : -104 kJ/mol) showing at the same time that the fluorine atoms are more favorable in the radical than in the parent compound.

The presence of the C-C triple bond in propyne as well as in the propargyl cation increases the energy (H_{rel}° : 204 kJ/mol, SDE: 47 kJ/mol). The -157 kJ/mol value of RSDE indicates the triple bond being much less unfavorable in the cation than in the parent compound.

The H_{rel}° of methanol is a small negative value (-11 kJ/mol). The effect of the hydroxyl group on the SDE of the hydroxymethyl cation (-260 kJ/mol) looks huge relative to H_{rel}° value of the parent compound demonstrating the much larger effect of the hydroxyl group in the cation than in the parent compound. The effect of the amino group in the aminomethyl cation is even larger (RSDE: -385 kJ/mol).

Table 5 Carbocations with charged sp^2 and sp carbon atoms



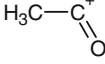



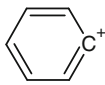
Compound	H_{rel}° (kJ/mol)	Cation	$\Delta H_{\text{f}}^{\circ}$ (kJ/mol)	H_{rel}° (kJ/mol)	SDE (kJ/mol)	RSDE (kJ/mol)
$\text{CH}_2=\text{CH}_2$	93.6	$\text{CH}_2=\text{CH}^+$	1115.8	1135.4	-2.5	-96.1
	30.5		827.2	952.0	-185.9	-216.1
CH_3-CHO	0.7		659.6	805.0	-332.9	-333.6
	-56.1		723.9	1025.0	-112.9	-56.8
	76.3		1136.8	1108.7	-29.2	-105.5
$\text{HC}\equiv\text{CH}$	224.5	$\text{HC}\equiv\text{C}^+$	1697.1	1673.2	537.8	313.3
$\text{HC}\equiv\text{C}-\text{CH}_3$	203.8	$\text{H}_3\text{C}-\text{C}\equiv\text{C}^+$	1536.0	1555.6	417.7	213.9
$\text{N}\equiv\text{CH}$	40.1	$\text{N}\equiv\text{C}^+$	1782.7	1669.9	534.5	494.4

Table 6 Effect of substituents replacing one or more hydrogen atoms in the methyl anion

Compound	H_{rel}° kJ/mol	Anion	$\Delta H_{\text{f}}^{\circ}$ kJ/mol	H_{rel}° kJ/mol	SDE kJ/mol	RSDE kJ/mol
		CH_3^-	144.4	186.8	0	
CH_3-CH_3	0.0	$\text{CH}_3-\text{CH}_2^-$	144.6	207.7	20.9	20.9
$\text{H}_2\text{N}-\text{CH}_3$	-26.5	$\text{H}_2\text{N}-\text{CH}_2^-$	201.1	175.9	-10.9	15.6
CHF_3	-104.4	F_3C^-	-640.5	-69.1	-255.9	-151.5

Carbocations in which the positively charged atom is sp^2 - or sp -type carbon atom are listed in Table 5. When the energies of the vinyl, formyl, acetyl, or fluoroformyl cations are compared to those of their parent compounds, large energy reductions are observed. The largest reduction (RSDE: -334 kJ/mol) belongs to the acetyl cation, the second largest (RSDE: -216 kJ/mol) to the formyl cation. RSDE -96 kJ/mol belongs to the vinyl cation and RSDE -57 kJ/mol to the fluoroformyl cation. The phenyl cation also shows a significant energy reduction in comparison with benzene (RSDE: -106 kJ/mol). All these data demonstrate that considering the energy, the positive charge on sp^2 carbon atom is particularly favorable.

In contrast, the ethynyl, 1-propynyl, and cyanide cations all show large energy increase if their SDEs are compared to the H_{rel}° -s of their parent compounds (RSDE: 409, 214, and 493 kJ/mol, respectively). This indicates that the triple C-C bond formed by the positively charged carbon atom is much more unfavorable than the presence of the triple bond in the parent compounds.

Carbanions

The structure-dependent energies of carbanions are calculated by subtracting the H_{rel}° of the methyl anion (186.8 kJ/mol) from the H_{rel}° -s of the other carbanions. The

Table 7 Carbanions with charged sp^2 and sp carbon atoms

Compound	H_{rel}° (kJ/mol)	Anion	$\Delta H_{\text{f}}^{\circ}$ (kJ/mol)	H_{rel}° (kJ/mol)	SDE (kJ/mol)	RSDE (kJ/mol)
$\text{H}_2\text{C}=\text{CH}_2$	93.6	$\text{H}_2=\text{CH}^-$	233.2	252.8	66.0	-27.6
HCHO	30.5	$\text{H}-\overset{\ominus}{\text{C}}=\text{O}$	12.0	136.8	-50.0	-81.1
	0.7	$\text{H}_3\text{C}-\overset{\ominus}{\text{C}}=\text{O}$	-49.4	96.0	-90.8	-91.5
$\text{HC}\equiv\text{CH}$	224.5	$\text{HC}\equiv\text{C}^-$	280.9	257.0	70.2	-154.3
$\text{H}_3\text{C}-\text{C}\equiv\text{CH}$	203.8	$\text{H}_3\text{C}-\text{C}\equiv\text{C}^-$	257.8	277.4	90.6	-113.2
$\text{N}\equiv\text{CH}$	40.1	$\text{N}\equiv\text{C}^-$	67.3	-44.8	-231.6	-271.7

Table 8 Dissociation energies and relative stability of alkyl radicals

Compound	H_{rel}° (kJ/mol)	$D_{298}(\text{H})$ (kJ/mol)	Radical	H_{rel}° (kJ/mol)	SDE	Compound	H_{rel}° (kJ/mol)	$D_{298}(\text{Br})$ (kJ/mol)
CH_4	-10.8	439.2	CH_3^{\bullet}	188.9	0.0	CH_3Br	6.7	301.9
CH_3-CH_3	0.0	423.3	$\text{CH}_3-\text{CH}_2^{\bullet}$	183.0	-5.9	$\text{CH}_3\text{CH}_2\text{Br}$	3.0	303.1
$\text{CH}_3-\text{CH}_2-\text{CH}_3$	1.5	412.8	$\text{H}_3\text{C}-\overset{\bullet}{\text{C}}\text{H}-\text{CH}_3$	158.1	-30.8	$(\text{CH}_3)_2\text{CHBr}$	-9.4	309.4
	-8.6	404.0	$\text{H}_3\text{C}-\overset{\bullet}{\text{C}}(\text{CH}_3)_2$	135.6	-53.3	$(\text{CH}_3)_3\text{CBr}$	-25.6	304.0

anions deduced from the methyl anion by substitution one of its hydrogen atom by different functional groups are listed in Table 6. The carbanions, except the trifluoromethyl anion, show small energy increases when compared to their parent compounds (RSDE: 21, 16 kJ/mol). In this respect, they differ from both radicals and carbocations. The presence of three fluorine atoms in both trifluoromethane and trifluoromethyl anion brings about a large

energy reduction. This reduction is much larger in the anion (RSDE: -152 kJ/mol), indicating that the presence of the fluorine atoms in the anion is greatly preferred.

Those carbanions in which the charged atom is sp^2 or sp carbon atom appear in Table 7. The H_{rel}° of ethylene is 94 kJ/mol, and the SDE of the vinyl anion is only 66 kJ/mol demonstrating that the presence of the double bond in the anion is less unfavorable than that in ethylene.

This tendency is even more emphasized in the case of formyl and acetyl anions by their negative RSDE values (−81 and −92 kJ/mol).

The triple bonds in the ethynyl and 1-propynyl anion increase the energy in both cases (SDE: 70 and 91 kJ/mol, respectively), but the energy increase is much larger in the parent acetylene (H_{rel}° : 225 kJ/mol) and propyne (H_{rel}° : 204 kJ/mol). As a result, they show very large negative RSDE values (−154 and −113 kJ/mol) that are in accordance with the acidity of these compounds. An even larger negative RSDE value comes out (−272 kJ/mol) when the cyanide ion is compared to hydrogen cyanide. This indicates the acidity of hydrogen cyanide.

Homolytic dissociation energies and relative enthalpies

The homolytic dissociation energies can be used to deduce from them the heats of formation of alkyl radicals and may also demonstrate their relative stability.

The data of the third column of Table 8 show that the homolytic dissociation energies of the listed alkanes are decreasing with the increasing order of the radical carbon atom. The data of the last column, however, where the dissociation energies of alkyl bromides are summarized do not support this trend. The reason is found in the eighth column of the table which shows that the relative energies of alkyl bromides themselves are also decreasing with their increasing order. This decrease (from 6.7 to −25.6 kJ/mol) is larger than the decrease in the H_{rel}° -s of alkanes listed in the first column (from −10.8 through 0.0 to −8.6 kJ/mol). These differences in the energies of the parent compounds

(that do not appear if their heats of formation are compared) influence the dissociation energies and provide the reason of the mentioned discrepancy. The use of either H_{rel}° -s or SDEs offers a possibility to solve the problem. Going downwards in the columns 5 and 6, the data show that the increasing relative stabilities of the radicals are properly reflected by the values of both their H_{rel}° -s and SDEs.

Conclusions

All the examples mentioned above show that the use of relative enthalpies to express the relative energies of organic radicals, cations, and anions is as fruitful as in the case of their parent organic compounds. The same energy-determining structural factors may have stronger, weaker, or even opposite effects in radicals, cations, or anions than those in the parent molecules.

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