Physical Chemistry

Ab initio quantum-chemical calculations of interactions of ions and hydrides of alkali metals with C_3H_6 and C_4H_8 molecules

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Calculations of the $C_3H_6 \cdot LiH$, $C_4H_8 \cdot M^+$, and $C_4H_8 \cdot MH$ systems and of $C_2H_2 \cdot MH$ complexes (M = Li or Na) were carried out by the unrestricted Hartree—Fock—Roothaan (UHF) method with partial optimization of the geometry using fixed geometric parameters of the C_3H_6 and C_4H_8 molecules. The standard 3-21G and 6-31G* basis sets were used. Unlike the $C_3H_6 \cdot LiH$ structure, the $C_4H_8 \cdot M^+$ and $C_4H_8 \cdot MH$ systems are typical complexes. It was found that the $C_4H_8 \cdot M^+$, $C_4H_8 \cdot MH$, and $C_2H_2 \cdot MH$ complexes are similar in coordination of M^+ ions and MH molecules by carbon atoms in spite of considerable differences in the interatomic distances (~1 Å) between these atoms in the C_4H_8 and C_2H_2 molecules. The heats of formation (Q), which were calculated in the UHF/6-31G* approximation and using second- and fourth-order Möller—Plesset perturbation theory taking into account the electron correlation energy in the MP2/6-31G*, MP4(SDQ)/6-31G*, and MP4(SDTQ)/6-31G* approximations, satisfy the following relationships: $Q(C_2H_2 \cdot MH) < Q(C_4H_8 \cdot MH) < Q(C_4H_8 \cdot M^+)$. It was observed that in going from Li to Na the corresponding values of Q tend to decrease.

Key words: Hartree—Fock—Roothaan method, Möller—Plesset perturbation theory, polyradicals, geometric structure, heats of formation, hydrides of alkali metals.

Studies of the formation of complexes of ions and hydrides of alkali metals with polyradicals are of interest in connection with the problem of the absorption of radio waves by the products of the pyrolysis of organic materials. It has been suggested[1,2] that the crystal phase of carbon, which exhibits ferromagnetic ordering and which is called ferrocarbon, may occur. This phase, which contains the maximum possible number of radical centers per unit of volume, can be considered to be a polyradical absorber and, therefore, it was of interest to study the interaction of this structure with ions and hydrides of Li, Na, and K, *i.e.*, to demonstrate that complexes of the above-mentioned ions and hydrides with fragments of this phase can form and occur.

Because nonequivalent exchange interactions caused by different spatial arrangements of radical centers in ferrocarbon are modeled using C_3H_6 and C_4H_8 molecules,* [3,4] in this work, we have studied the geometric

* Two conformations of C_3H_6 model the exchange interactions of radicals within one quasi-graphite plane of ferrocarbon, and four conformations of C_4H_8 model the exchange interactions between the radicals in adjacent quasi-graphite planes.[4]

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structures and the "thermodynamic" stability of the complexes formed by Li^+ and Na^+ cations and LiH and NaH hydrides with C_3H_6 and C_4H_8 molecules adopting certain conformations.

Calculation procedure

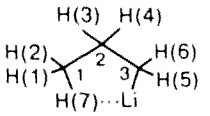
We carried out *ab initio* calculations of the systems formed by the reaction of LiH with C_3H_6 in the C_1-conformation and by the reactions of Li^+, Na^+, LiH, and NaH with C_4H_8 in the *cis*-(104.0, 104.0, 0.0)-conformation (see ref. 4). In our opinion, the conformations chosen are the most probable conformations (among those occurring in ferrocarbon) that may form complexes with the above-mentioned cations and hydrides. All calculations were carried out on a CONVEX-C210 minisupercomputer using the GAUSSIAN-82 program by the unrestricted Hartree—Fock—Roothaan (UHF) method and by second- and fourth-order Möller—Plesset perturbation theory taking into account the electron correlation energy with double, triple, and quadruple excitations (MP2, MP4(SDQ), and MP4(SDTQ)).

The standard valence-split 3-21G and 6-31G* basis sets were used. Calculations of the $C_3H_6 \cdot LiH$, $C_4H_8 \cdot Li^+$, $C_4H_8 \cdot LiH$, $C_4H_8 \cdot Na^+$, and $C_4H_8 \cdot NaH$ systems were carried out with partial optimization of their geometric parameters allowing for fixed geometry for the C_3H_6 and C_4H_8 fragments in the UHF/3-21G and UHF/6-31G* approximations. In addition, the LiH molecule and the $C_3H_6 \cdot LiH$ system were calculated with the 6-31G* basis set using geometric parameters that were optimized in a similar manner in the UHF/3-21G approximation (the UHF/6-31G*/3-21G scheme).

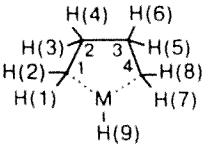
In our calculations, the C_3H_6 fragment has the triplet ground state because this fragment has the triplet ground state in the crystal of ferrocarbon. All other systems were calculated in the singlet ground state. Then calculations were carried out taking into account the electron correlation energy with the use of the geometry determined as described above.

With the aim of comparing the complexes calculated and the complexes formed by hydrides LiH and NaH with common molecules in the same approximation, we performed calculations of the $C_2H_2 \cdot LiH$ and $C_2H_2 \cdot NaH$ compounds with full optimization of the geometry in the UHF/6-31G* approximation; the correlation energy was then included in calculations. This makes it possible to compare the geometric parameters and heats of formation of the complexes of Li and Na hydrides with acetylene,[5] in which carbon atoms are linked by a short (triple) bond, with the corresponding values obtained in the case in which the analogous carbon atoms coordinated to the LiH or NaH molecules are radical centers, which are separated by ~2—3 Å and which are not linked even by a single chemical bond. This comparison may be useful in the chemistry of acetylene compounds.

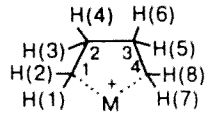
The results of calculations of the geometric parameters are given in Tables 1 and 2; the heats of formation are listed in Table 3. The geometric structures of the compounds studied are shown below.



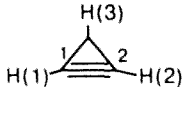
$C_3H_6 \cdot LiH$



$C_4H_8 \cdot MH$



$C_4H_8 \cdot M^+$



$C_2H_2 \cdot MH$

Table 1. Geometric parameters of the C_2H_2, LiH and $C_3H_6 \cdot LiH$ molecules and the $C_4H_8 \cdot LiH$, $C_4H_8 \cdot Li^+$, and $C_2H_2 \cdot LiH$ complexes optimized in the UHF/3-21G and UHF/6-31G*[a] approximations

System	Distance	*R*/Å		Angle	φ/deg	
		UHF/3-21G	UHF/6-31G*		UHF/3-21G	UHF/6-31G*
$C_3H_6 \cdot LiH$	Li—C(3)	2.078	2.087	Li—C(3)—C(2)	94.3	98.2
	H(7)—C(1)	1.137	1.122	H(7)—C(1)—C(2)	98.1	98.2
	Li—H(7)	2.012	2.080	Li—C(3)—C(2)—C(1)	64.5	63.5
				H(7)—C(1)—C(2)—C(3)	29.4	29.6
$C_4H_8 \cdot LiH$	Li—C(1)	2.511	2.528	Li—C(1)—C(4)	62.9	63.1
	Li—H(9)	1.651	1.652	H(9)—Li—C(1, 4)	151.0	152.9
				Li—C(1)—C(4)—C(3)	125.8	131.0
				H(9)—Li—C(1)—C(4)	186.6	176.1
$C_4H_8 \cdot Li^+$	Li—C(1)	2.441	2.442	Li—C(1)—C(4)	62.0	62.1
				Li—C(1)—C(4)—C(3)	126.7	130.9
$C_2H_2 \cdot LiH$	Li—H(3)		1.647	H(3)—Li—C(1, 2)		166.5
	Li—C(1, 2)		2.472	Li—C(1)—C(2)		76.0
	C(1)—C(2)		1.189	Li—C(1)—H(1)		105.6
	C(1)—H(1, 2)		1.060			
C_2H_2	C—C		1.186			
	C—H		1.057			
LiH	Li—H		1.636			

[a] Internuclear *R*(M—X) distances are given in Å, angles are given in deg.

Table 2. Geometric parameters of the NaH molecule and the $C_4H_8 \cdot NaH$, $C_4H_8 \cdot Na^+$, and $C_2H_2 \cdot NaH$ complexes optimized in the UHF/3-21G and UHF/6-31G* [a] approximations

System	Distance	R/Å		Angle	φ/deg	
		UHF/3-21G	UHF/6-31G*		UHF/3-21G	UHF/6-31G*
$C_4H_8 \cdot NaH$	Na—C(1)	2.992	3.023	Na—C(1)—C(4)	67.6	67.8
	Na—H(9)	1.951	1.939	H(9)—Na—C(1,4)	158.2	158.0
				Na—C(1)—C(4)—C(3)	129.3	130.1
				H(9)—Na—C(1)—C(4)	177.9	178.1
$C_4H_8 \cdot Na^+$	Na—C(1)	2.872	2.866	Na—C(1)—C(4)	67.6	67.8
				Na—C(1)—C(4)—C(3)	127.2	131.6
$C_2H_2 \cdot NaH$	Na—H(3)		1.931	H(3)—Na—C(1, 2)		166.6
	Na—C(1, 2)		2.986	Na—C(1)—C(2)		77.6
	C(1)—C(2)		1.188	Na—C(1)—H(1)		103.6
	C(1)—H(1, 2)		1.060			
NaH	Na—H		1.915			

[a] Internuclear R(M—X) distances are given in Å, angles are given in deg.

Table 3. Heats of formation (kcal mol^{-1}) of the $C_3H_6 \cdot LiH$ system and the $C_4H_8 \cdot LiH$, $C_4H_8 \cdot Li^+$, $C_4H_8 \cdot NaH$, $C_4H_8 \cdot Na^+$, $C_2H_2 \cdot LiH$, and $C_2H_2 \cdot NaH$ complexes obtained in different approximations

System	Basis set	Method			
		UHF	MP2	MP4(SDQ)	MP4(SDTQ)
$C_3H_6 \cdot LiH$	3-21G	4.2	34.4	30.9	33.3
	6-31G*/3-21G	3.5	44.5	38.9	41.4
	6-31G*	3.6	44.6	38.0	41.5
$C_4H_8 \cdot LiH$	3-21G	17.3	17.4	16.1	16.3
	6-31G*	15.5	16.4	15.6	15.7
$C_4H_8 \cdot Li^+$	3-21G	32.1	30.3	29.7	28.8
	6-31G*	31.4	30.3	29.4	29.4
$C_2H_2 \cdot LiH$	6-31G*	11.0	12.8	12.5	12.8
$C_4H_8 \cdot NaH$	6-31G*	9.5	9.4	8.6	8.8
$C_4H_8 \cdot Na^+$	6-31G*	20.7	19.7	18.8	18.9
$C_2H_2 \cdot NaH$	6-31G*	7.0	7.8	7.5	7.7

Results and Discussion

Let us analyze the arrangement of the Li and H atoms of the LiH molecule and the Li^+ cation in the $C_3H_6 \cdot LiH$, $C_4H_8 \cdot Li^+$, and $C_4H_8 \cdot LiH$ systems determined in the UHF/3-21G and UHF/6-31G* approximations. As can be seen from Table 1, the R(M—X) distances between these atoms determined in these approximations differ by no more than ~0.070 Å. Changes in the dihedral angles for the $C_4H_8 \cdot Li^+$ and $C_4H_8 \cdot LiH$ complexes in going from the UHF/3-21G to UHF/6-31G* approximation are ~4.2° and ~10.5°, respectively, which is substantially larger than their differences for the $C_3H_6 \cdot LiH$ system, in which they are no more than ~1°. In the case of $C_3H_6 \cdot LiH$, the maximum difference in the bond angles calculated in these approximations is somewhat larger (~3.9°) than those for the $C_4H_8 \cdot LiH$ and $C_4H_8 \cdot Li^+$ systems (~1.9°).

The difference in the sensitivity of the bond angles and torsion angles to the sizes of the basis sets in these three systems is, apparently, associated with the fact that, unlike $C_4H_8 \cdot LiH$ (and, conventionally, $C_4H_8 \cdot Li^+$), the $C_3H_6 \cdot LiH$ system is not a molecular complex. Actually, R(Li—H) in $C_3H_6 \cdot LiH$ is 2.080 Å, which is ~0.444 Å larger than R(Li—H) in the isolated LiH molecule. In terms of Mulliken population analysis, the overlap Q(M—X) between the Li and H atoms of the formal LiH fragment in the $C_3H_6 \cdot LiH$ system is 0.036 e, whereas the overlap between the Li and H atoms and the radical centers of the C_3H_6 molecule are as follows: Q(Li—C(3)) = 0.336 e and Q(H(7)—C(1)) = 0.366 e. In spite of the fact that R(H(7)—C(1)) is ~0.04—0.06 Å larger than the C—H bond lengths in C_3H_6, the bond in the LiH subsystem is actually broken. However, R(Li—H) in $C_4H_8 \cdot LiH$ virtually coincides with the distance in the isolated LiH molecule (the difference is

only ~0.016 Å), *i. e.*, this system is an ordinary molecular complex formed by the LiH and C_4H_8 molecules.

Note that the differences in the geometric parameters of the LiH fragment in the $C_2H_2 \cdot LiH$ and $C_4H_8 \cdot LiH$ complexes considered are quite small. Thus, the distance from the Li atom to each of the carbon atoms in the first complex (2.472 Å) is only 0.056 Å shorter than that between Li and the radical centers in the second complex (2.528 Å), which is only ~2 % of the values of these distances. The differences in R(Li—H) are even smaller. Thus, R(Li—H) in $C_4H_8 \cdot LiH$ is only 0.005 Å larger than in $C_2H_2 \cdot LiH$.

These small differences in the geometric parameters of the LiH fragment in these complexes deserve attention because the distances between the carbon atoms in acetylene (1.185 Å) and the radical centers in C_4H_8 (2.288 Å) differ by more than ~1 Å. Therefore, it can be expected that when the LiH molecule forms complexes with carbon compounds in which the carbon atoms that are coordinated to LiH are separated by ~1.2—~2.2 Å, the position of the LiH fragment with respect to these atoms will be the same as in the $C_2H_2 \cdot LiH$ and $C_4H_8 \cdot LiH$ complexes. Evidently, no significant error is introduced by considering the geometry of C_4H_8 in the $C_4H_8 \cdot LiH$ complex to be fixed because when the geometry of the $C_2H_2 \cdot LiH$ complex, which is chemically related to $C_4H_8 \cdot LiH$, is fully optimized, the R(C(1)—C(2)) distance increases by only 0.003 Å over that in the isolated molecule of acetylene. In the $C_4H_8 \cdot Li^+$ complex, the distances between the Li^+ cation and the radical centers are ~0.086 and ~0.030 Å smaller than those in the $C_4H_8 \cdot LiH$ and $C_2H_2 \cdot LiH$ complexes, respectively; these differences are substantially smaller than the distances themselves, *i. e.*, this complex is close to the $C_4H_8 \cdot LiH$ and $C_2H_2 \cdot LiH$ systems in its geometric parameters.

Let us consider the changes in the positions of the Na and H atoms of the NaH molecule and the Na^+ cation in the $C_4H_8 \cdot NaH$ and $C_4H_8 \cdot Na^+$ complexes in going from the UHF/3-21G to the UHF/6-31G* approximation. As can be seen from Table 2, the R(M—X) distances between these atoms and the bond angles change by no more than ~0.031 Å and ~0.2°, respectively. The differences in the dihedral angles are somewhat larger and are as much as ~4.4°, *i. e.*, the changes in the geometric parameters with this extension of the basis set are somewhat smaller than those in the case of the Li complexes considered. Both systems containing Na atoms are ordinary complexes. Thus, the R(Na—H) distance in $C_4H_8 \cdot NaH$ virtually coincides with that in the isolated NaH molecule (the difference is only ~0.024 Å).

Similarly, the geometric parameters of the NaH fragment in the $C_2H_2 \cdot NaH$ and $C_4H_8 \cdot NaH$ complexes differ only slightly. Thus, the distance between the Na atom and each of the carbon atoms in the first complex (2.986 Å) is only ~0.037 Å shorter than that between the Na atom and the radical centers in the second complex (3.023 Å), which is only ~1.3 % of the values of these distances. Therefore, the suggestion that the geometric parameters of the LiH molecule change only slightly when it forms complexes with carbon compounds, in which the carbon atoms coordinated to LiH are at distances from ~1.2 to ~2.2 Å, can be extended to the NaH molecule. In the $C_4H_8 \cdot Na^+$ complex, the distances between the Na^+ cation and the radical centers are shorter than those in $C_4H_8 \cdot NaH$ and $C_2H_2 \cdot NaH$ by ~0.157 Å and ~0.120 Å, respectively, *i.e.*, this complex is close to the $C_4H_8 \cdot NaH$ and $C_2H_2 \cdot NaH$ structures in its geometric parameters.

Now let us analyze the heats of formation (Q) calculated in the different approximations. As can be seen from Table 3, the dependence of the heat of formation of the $C_3H_6 \cdot LiH$ system on the approximation differs substantially from the corresponding dependences for the $C_2H_2 \cdot LiH$, $C_4H_8 \cdot LiH$, $C_4H_8 \cdot Li^+$, $C_4H_8 \cdot NaH$, and $C_4H_8 \cdot Na^+$ complexes. In the case of $C_3H_6 \cdot LiH$ calculated by the UHF method, the value of Q is equal to ~4 kcal mol^{-1} regardless of the basis set. When the correlation energy is taken into account, this value increases to ~30—34 kcal mol^{-1} with the use of the 3-21G basis set and to ~37—45 kcal mol^{-1} with the use of the 6-31G*/3-21G and 6-31G* basis sets. For this system, the heats of formation calculated with the 3-21G basis set taking into account the correlation energy are ~8—10 kcal mol^{-1} smaller than the corresponding values obtained by calculations with the 6-31G* basis set. The differences in the geometric parameters optimized with the use of the 3-21G and 6-31G* basis sets cause no significant differences in the heats of formation of $C_3H_6 \cdot LiH$. Thus, the differences in the heats of formation of this system calculated taking into account the correlation energy with the 6-31G*/3-21G and 6-31G* basis sets are no more than ~1 kcal mol^{-1} for each approximation.

Unlike $C_3H_6 \cdot LiH$, the changes in the values of Q for the $C_4H_8 \cdot LiH$ and $C_4H_8 \cdot Li^+$ complexes are no more than ~2.0 kcal mol^{-1} in going from the UHF method to the MP2, MP4(SDQ), and MP4(SDTQ) methods with any one of the basis sets (3-21G and 6-31G*). In the case of the $C_4H_8 \cdot NaH$ and $C_4H_8 \cdot Na^+$ complexes, these changes are also small and are no more than ~1.9 kcal mol^{-1}. As exemplified by the $C_4H_8 \cdot LiH$ and $C_4H_8 \cdot Li^+$ complexes, the heats of formation Q calculated with the 3-21G basis set are overestimated by no more than ~2 kcal mol^{-1} as compared to the corresponding values of Q calculated with the 6-31G* basis set by the UHF method as well as taking into account the correlation energy. Therefore, the sizes of the basis sets are much less significant in calculations of Q for these complexes than for the $C_3H_6 \cdot LiH$ system, which is not a molecular complex.

This difference in behavior of the heat of formation of the $C_3H_6 \cdot LiH$ system from those of all the complexes considered is, apparently, attributable to the fact that when the $C_3H_6 \cdot LiH$ system forms from C_3H_6 and

LiH, the bond in the LiH molecule breaks and two new bonds (Li—C and H—C) form, *i.e.*, the number of coupled electrons changes, whereas when complexes form, this change does not occur. This results in an increase in the significance of the electron correlation energy and the necessity to include it in the calculations of the heats of formation of the $C_3H_6 \cdot LiH$ compound from the C_3H_6 and LiH molecules.

Because a substantial extension of the basis set (from 3-21G to 6-31G*) has such a slight effect on the heats of formation of these complexes, it can be expected that a further increase in the size of the basis set will not cause a substantial change in the heats of formation. Therefore, in the subsequent discussion of the peculiarities of the behavior of Q, we shall use the results obtained by calculations with the 6-31G* basis set. Note that the values of Q for the $C_4H_8 \cdot Li^+$, $C_4H_8 \cdot NaH$, and $C_4H_8 \cdot Na^+$ complexes decrease slightly (~1—2 kcal mol^{-1}) in going from the UHF to the MP4(SDTQ) method, except for the $C_4H_8 \cdot LiH$ complex, for which the value of Q remains virtually unchanged (~0.02 kcal mol^{-1}). However, when passing from the UHF to the MP4(SDTQ) method, the values of Q for the $C_2H_2 \cdot LiH$ and $C_2H_2 \cdot NaH$ complexes increase slightly (~1.8 and ~0.70 kcal mol^{-1}, respectively), *i.e.*, the UHF method slightly underestimates the values of Q for the complex of LiH with acetylene and slightly overestimates these values in the case of polyradicals containing radical centers, which are separated by a significant distance and which coordinate the NaH molecule and the Li^+ and Na^+ cations.

Let us consider the changes in the values of Q in going from Li to Na in the complexes formed by LiH, NaH, Li^+, and Na^+ with the C_4H_8 fragments calculated in the MP4(SDTQ)/6-31G* approximation, which is the most precise of those used in this work. As can be seen from Table 3, $Q(C_4H_8 \cdot Li^+) - Q(C_4H_8 \cdot Na^+) \approx 10.5$ kcal mol^{-1} and $Q(C_4H_8 \cdot LiH) - Q(C_4H_8 \cdot NaH) \approx 6.9$ kcal mol^{-1}. Apparently, the replacement of Na by K may result in even smaller heats of formation, *i.e.*, when going from the top down along Group IA of the Periodic system, the possibility of the formation of thermodynamically stable complexes of this type decreases.

Let us compare the values of Q for all three complexes with LiH and Li^+ calculated in the same MP4(SDTQ)/6-31G* approximation. As can be seen from Table 2, the following relationships are fulfilled: $Q(C_2H_2 \cdot LiH) < Q(C_4H_8 \cdot LiH) < Q(C_4H_8 \cdot Li^+)$. $Q(C_2H_2 \cdot LiH) - Q(C_4H_8 \cdot LiH) \approx 3$ kcal mol^{-1}, whereas $Q(C_4H_8 \cdot Li^+)$ is ~17 kcal mol^{-1} larger than $Q(C_2H_2 \cdot LiH)$ and ~14 kcal mol^{-1} larger than $Q(C_4H_8 \cdot LiH)$. However, the $C_4H_8 \cdot Li^+$ complex, unlike the two other complexes, can exist only in the absence of the H^- anion because the associated form $C_4H_8 \cdot LiH$ is energetically much more favorable than the dissociated form $C_4H_8 \cdot Li^+ + H^-$. This is attributable to the fact that the bond between the Li and H atoms in $C_4H_8 \cdot LiH$ is stronger than the bond between C_4H_8 and Li^+ in $C_4H_8 \cdot Li^+$.

As can be seen from Table 3, analogous relationships occur for the complexes with NaH and Na^+: $Q(C_2H_2 \cdot NaH) < Q(C_4H_8 \cdot NaH) < Q(C_4H_8 \cdot Na^+)$. The values of Q are as follows: $Q(C_4H_8 \cdot NaH) - Q(C_2H_2 \cdot NaH) \approx 1$, $Q(C_4H_8 \cdot Na^+) - Q(C_2H_2 \cdot NaH) \approx 11.2$, and $Q(C_4H_8 \cdot Na^+) - Q(C_4H_8 \cdot NaH) \approx 10.1$ kcal mol^{-1}. Similarly, the $C_4H_8 \cdot Na^+$ complex can occur only in the absence of the H^- anion for analogous reasons as in the case of $C_4H_8 \cdot Li^+$. It can be seen from Table 3 that the relationships $Q(C_2H_2 \cdot MH) < Q(C_4H_8 \cdot MH) < Q(C_4H_8 \cdot M^+)$ are fulfilled in the UHF/6-31G*, MP2/6-31G*, and MP4(SDQ)/6-31G* approximations as well.

Therefore, our calculations demonstrated that complexes of LiH and NaH with C_4H_8 molecules can form; the mode of coordination of LiH and NaH in these complexes is almost the same as in the $C_2H_2 \cdot LiH$ and $C_2H_2 \cdot NaH$ complexes. When H^- anion are absent, rather stable $C_4H_8 \cdot Li^+$ and $C_4H_8 \cdot Na^+$ complexes may occur. It was also demonstrated that complexes of LiH and NaH with molecules possessing a triple bond are less favorable than those with polyradicals that have radical centers separated by rather large distances. Finally, there is a tendency for the heats of formation of complexes with cations and hydrides of alkali metals to decrease as the light alkali metals are replaced by heavier elements.

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