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Metal-Rare Gas Interaction. A New Bond?

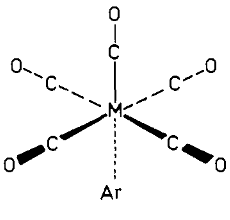
J. Demuynck,* E. Kochanski, and A. Veillard

Contribution from the E. R. No. 139 du CNRS, Université L. Pasteur, 67000 Strasbourg, France. *Received December 14, 1978*

Abstract: The interaction between the pentacarbonyls $M(CO)_5$ (M = Cr and Mo) and a rare-gas atom X (X = Ar, Kr, Xe) has been studied through ab initio calculations both at the SCF level and at the level of the dispersion energy. The SCF calculations were carried out with two different basis sets, the largest one being of double-ζ quality. The interaction at the SCF level was attractive with the small basis set but repulsive with the large one. This repulsive character of the interaction at the SCF level has been discussed in terms of (1) the donor ability of the rare gas; (2) the existence of a destabilizing π interaction together with a stabilizing σ interaction; (3) the steric requirements of the rare gas. The dispersion energy in $Mo(CO)_5Kr$ has been estimated on the basis of a perturbation treatment for MoKr. This produces for the stabilization energy of $Mo(CO)_5Kr$ a value of 2.5 kcal/mol; however, this result is certainly underestimated and the exact value may be as high as 8-10 kcal/mol.

Introduction

Turner and his collaborators have reported that, in the UV-visible spectra of the matrix-generated pentacarbonyls $M(CO)_5$ (M = Cr, Mo, and W), the position of the visible band is extraordinarily sensitive to the matrix material used.[1] This band, which corresponds to the symmetry-allowed $^1A_1 \rightarrow {}^1E$ ($d_{xy}{}^2d_{xz}{}^2d_{yz}{}^2 \rightarrow d_{xy}{}^2d_{xz}{}^{3/2}d_{yz}{}^{3/2}d_{z^2}{}^1$) transition is shifted from 624 nm in a Ne matrix to 490 nm in a Xe matrix. This observation together with the spectra in a mixed matrix and the dependence of the IR spectra with the matrix was interpreted by assuming that $Cr(CO)_5$, a square pyramid,[2-6] forms a weak bond with a rare-gas atom.[1] This weak bond corresponds to a stereospecific interaction via the vacant coordination site as shown in **1**. Perutz and Turner stated that the interaction energy between $Cr(CO)_5$ and a Xe atom occupying its vacant site might be comparable in energy to a weak chemical bond, namely, in the range 1-5 kcal/mol. Two possible explanations (or a combination of both) were given for the shift in the visible spectrum: (1) The rare-gas atom behaves as a weak σ donor through a σ lone pair (the np_z orbital of the rare gas if z is the rare gas-metal axis) which interacts with the a_1 orbital (mostly a metal $3d_{z^2}$ orbital). This raises the a_1 orbital in energy (Figure 1), thus increasing the $e \rightarrow a_1$ transition energy. (2) Small changes in the axial-radial bond angle α of $M(CO)_5$ (**2**) are induced by the rare-gas atom in the vacant coordination site with the energy of the orbital a_1 falling rapidly when α increases. Thus a small increase in α can generate a large decrease in the $e \rightarrow a_1$ energy. Subsequently Turner and his collaborators have reported that "$Fe(CO)_4$ reacts with the matrix to form $Fe(CO)_4Xe$";[7] their statement implies the formation of a new species with a rare gas-metal bond (both $Cr(CO)_5$ and $Fe(CO)_4$ are 16-electron species).



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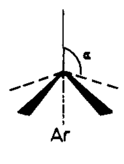

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The ability of the rare gases to enter into chemical combination with other atoms is very limited and so far compounds of Kr and Xe have been reported only with the most electronegative elements.[8] For this reason, we considered it worthwhile to investigate, through ab initio calculations, the nature of the interaction between $M(CO)_5$ and a rare gas. Through these ab initio calculations we have sought some answers to the following questions: (1) Is the interaction of the donor-acceptor type, namely, is it a dative bond involving a lone pair of the rare-gas atom and the vacancy on $M(CO)_5$, as postulated initially by Turner,[1] or is the interaction of the van der Waals type with the dispersion energy representing the predominant contribution? (2) Is the interaction energy large enough that one can speak of a metal-rare gas bond or is it merely a weak interaction of the type found in many van der Waals complexes? The borderline between the chemical bond and molecular interactions is a loose one. Rather arbitrarily we would put the border between a "weak interaction" and a "chemical bond" at 5 kcal/mol; however, we agree that the distinction is rather arbitrary.[9]

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Table I. Basis Sets Used

	basis set I			basis set II		
	Gaussian basis	contracted basis	ref	Gaussian basis	contracted basis	ref
C, O	(8,4)	[3,2]	23	(9,5)	[4,2]	28
Cr	(11,7,5)	[4,3,2]	24,25			
Mo	(13,9,7)	[5,4,3]	26	(15,10,8,1)	[10,7,5,1]	26
Ar	(10,6)	[4,3]	27			
Kr	(12,8,4)	[5,4,1]	26	(13,9,5)	[8,6,2]	29
Xe	(14,10,6)	[6,5,2]	26	(15,11,7)	[10,8,4]	30

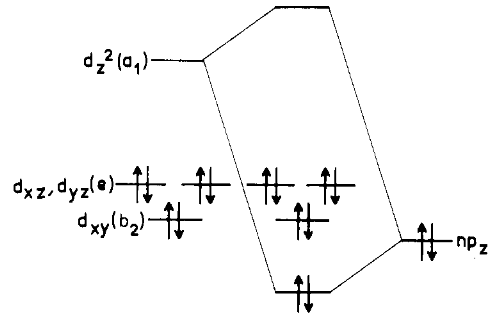


Figure 1. A simplified metal-rare gas interaction diagram according to ref 1.

A number of data may be related to the possible existence of a metal-rare gas interaction of the donor-acceptor type. Klemperer has extended the idea of a HOMO-LUMO interaction to the "van der Waals" complexes such as ArHCl, ArClF, and KrClF.[10] Under his description Ar or Kr would act as an electron-donor species, namely, a Lewis base, in its binding with the acceptors (weak Lewis acids) HCl or ClF. This model implies a very weak charge-transfer interaction. Hartree-Fock calculations have been used to predict the formation of hydrogen bonds between neon and water or hydrogen fluoride.[11,12] This hydrogen bonding could not be explained in simple electrostatic terms and some degree of covalency was postulated in the formation of the hydrogen bonds. However, the hydrogen-bond energy was very weak, 0.17 kcal/mol for neon-water and 0.23 kcal/mol for neon-hydrogen fluoride. Finally Fischer and his collaborators have reported the preparation, at low temperatures, of the pentacarbonyl (hydrogen halide) tungsten complexes $(CO)_5WXH$ (X = Cl, Br, I)[13] which are isoelectronic to the $W(CO)_5$-rare gas systems. The W-IH bond was best represented as a dative bond: $(CO)_5W^-$-I^+-H. Since the donor ability increases with decreasing ionization potential[14] and the ionization potentials of the hydrogen halides are lower than those of the rare gas (respectively 12.7, 11.6, and 10.4 eV for HCl, HBr, and HI vs. 15.8, 14.0, and 12.1 eV for Ar, Kr, and Xe[15]), the dative bond between $M(CO)_5$ and a donor should be stronger for the hydrogen halides than for the rare gas. However, Xe has an ionization potential which is intermediate between those of HCl and HBr. It is also intermediate between the ionization potentials of ammonia (10.2 eV) and water (12.6 eV). The existence of neutral molecular complexes between ammonia or water and a metal atom has been predicted recently.[16]

We report here ab initio calculations for the systems $Cr(CO)_5Ar$, $Cr(CO)_5Kr$, $Mo(CO)_5Kr$, and $Mo(CO)_5Xe$. The calculations were carried out first at the SCF level, since the SCF-MO method has been very successful in predicting both the equilibrium geometry and stabilization energy of hydrogen-bonded and electron donor-acceptor complexes.[17,18] The effect of the basis set was investigated at the SCF level in order to assess a possible basis set superposition error[19] (Klemperer has emphasized the need for extended basis set calculations if the nature of weak bonding is to be understood[10]). However, the SCF calculations cannot account for the dispersion energy which is essentially due to the intermolecular electron correlation. The dispersion energy is responsible for most of the stabilization of van der Waals molecules[20] and can also make an important contribution to the stabilization of electron donor-acceptor complexes.[21] In a next step, we have attempted to estimate the contribution of the dispersion forces through a perturbation method.[22] The results reported here not only provide an analysis of the metal-rare gas interaction but serve also to illustrate the difficulties associated with the calculation of weak interactions for large systems.

SCF Calculations

Two sets of calculations were carried out at the SCF level. The first set, for the systems $Cr(CO)_5Ar$, $Cr(CO)_5Kr$, $Mo(CO)_5Kr$, and $Mo(CO)_5Xe$, was carried out with basis set I (Table I), which is a minimal basis set for the inner shells and a double-ζ set for the valence shells (the $(n+1)$s and $(n+1)$p shells of the transition metals are described with only one function and the *n*d shell of a rare gas is treated as an inner shell). The Gaussian basis sets used throughout these calculations (Table I) are comparable to the (8,4) set for the first-row atoms. With this basis set, a limited geometry optimization was carried out for (1) the angle α between the apical bond and a basal bond in $Cr(CO)_5$ and $Mo(CO)_5$; (2) the distance between the metal and the rare gas for each of the above systems. The Cr-C and Mo-C bond lengths were set to 1.92 and 2.06 Å, namely, the corresponding values in $Cr(CO)_6$[31] and $Mo(CO)_6$[32] (the C-O bond length was set equal to 1.147 Å). Optimization of the angle α (Table II) yielded values of 92° for $Cr(CO)_5$ and 91° for $Mo(CO)_5$; the value $\alpha = 91°$ has been retained for all the calculations on the $M(CO)_5$-rare gas systems.[33] The SCF energies for $Cr(CO)_5Ar$, $Cr(CO)_5Kr$, $Mo(CO)_5Kr$, and $Mo(CO)_5Xe$ as a function of the metal-rare gas distance are reported in Table III.

It is well-known that the binding energies calculated for most intermolecular interactions tend to be overestimated as a consequence of the basis set superposition error (in fact, it turned out, cf. below, that the binding energies calculated with basis set I represent an artifact of the calculations). For this reason, a limited number of calculations were carried out for $Mo(CO)_5Kr$ and $Mo(CO)_5Xe$ with a larger basis set (called basis set II) which is of double-ζ quality (Table I) (in fact, the 4d shell of Mo was represented by three contracted functions). Furthermore, this basis set has one set of f-type polarization functions on Mo.[34] The Mo-Kr distance was varied with basis set II since the basis set superposition error leads usually to donor-acceptor separations which are underestimated. However, for economy reasons, the calculation for $Mo(CO)_5Xe$ was carried out with the Mo-Xe separation optimized with basis set I. The corresponding SCF energies are reported in Table IV.

The SCF calculations were carried out with the system of programs ASTERIX.[35] All one- and two-electron integrals were computed with single-word accuracy on the Univac 1110 (word of 36 bits); the SCF iterations were carried out with double-word accuracy.

Table II. SCF Energies (au) of $Cr(CO)_5$ and $Mo(CO)_5$ for the Two Structures of Square Pyramid and Trigonal Bipyramid (with Basis Set I)

$Cr(CO)_5$	C_{4v}	$\alpha = 85°$	−1603.9801
		$\alpha = 91°$	−1603.9963
		$\alpha = 95°$	−1603.9953
	D_{3h}		−1603.980
$Mo(CO)_5$	C_{4v}	$\alpha = 85°$	−4529.588
		$\alpha = 91°$	−4529.600
		$\alpha = 95°$	−4529.595
	D_{3h}		−4529.564

Table III. SCF Energies for the $M(CO)_5$-Rare Gas Systems, as a Function of the Metal-Rare Gas Distance (with Basis Set I)

	metal-rare gas distance, Å	SCF energy (au)	ΔH, kcal/mol
$Cr(CO)_5Ar$	2.68	−2129.87164	0.28
	2.94	−2129.87398	1.74
	3.06	−2129.8742[a]	1.90
	3.20	−2129.87385	1.66
	3.47	−2129.87306	1.17
	3.74	−2129.87225	0.66
	4.00	−2129.87174	0.34
	∞	−2129.87120	0.
$Cr(CO)_5Kr$	2.68	−4349.4453	1.57
	2.94	−4349.4489	3.82
	3.03	−4349.4491[a]	3.96
	3.20	−4349.4482	3.39
	3.47	−4349.4466	2.38
	3.74	−4349.4451	1.44
	∞	−4349.4428	0.
$Mo(CO)_5Kr$	2.63	−7275.0526	3.57
	2.79	−7275.0589	7.52
	2.90	−7275.0602[a]	8.32
	3.20	−7275.0577	6.77
	3.47	−7275.0541	4.52
	∞	−7275.0469	0.
$Mo(CO)_5Xe$	2.84	−11 745.2415	3.14
	3.11	−11 745.2465	6.26
	3.18	−11 745.2467[a]	6.28
	3.32	−11 745.2459	5.64
	∞	−11 745.2366	0.

[a] Interpolated value.

Table IV. SCF Energies for $Mo(CO)_5Kr$ and $Mo(CO)_5Xe$ with Basis Set II

	metal-rare gas distance, Å	SCF energy, au	ΔH, kcal/mol
$Mo(CO)_5Kr$	2.95	−7290.3516	−1.76
	3.05	−7290.3535	−0.56
	3.16	−7290.3542	−0.12
	∞	−7290.3544	0.
$Mo(CO)_5Xe$	3.16	−11 769.986	−3.
	∞	−11 769.991	0.

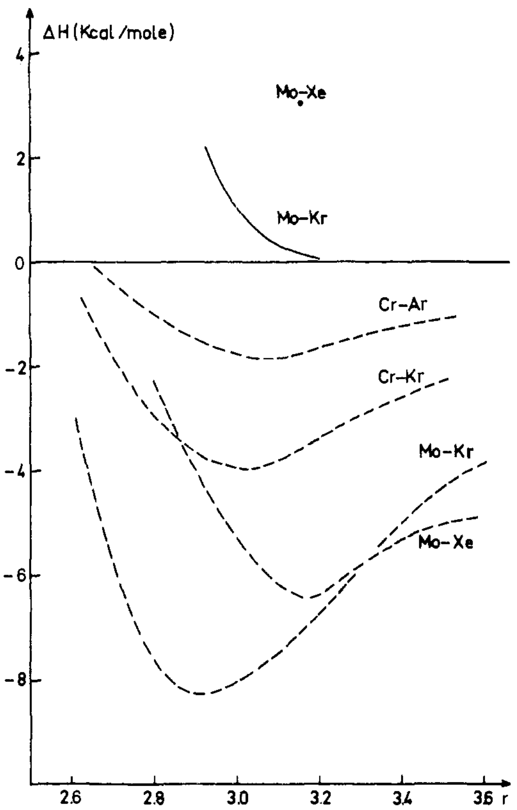


Figure 2. The potential energy curves for $Cr(CO)_5Ar$, $Cr(CO)_5Kr$, $Mo(CO)_5Kr$, and $Mo(CO)_5Xe$ as a function of the metal-rare gas distance (with basis set I and basis set II).

Discussion

SCF Results. The results for $Cr(CO)_5$ are similar to the ones which we have reported previously.[5] The square pyramid structure is found more stable than the trigonal bipyramid, with a lower limit of 10 kcal/mol for the stabilization of the square pyramid (this lower limit is obtained as the difference of the energies for two states with different spin multiplicity, the error at the SCF level due to the correlation energy being larger for the singlet state $^1A_1\ (b_2)^2(e)^4$ of the square pyramid than for the triplet state $^3A_2'\ (e'')^4(e')^2$ of the trigonal bipyramid).[36] This lower limit for the stabilization of the square pyramid increases to 22 kcal/mol for $Mo(CO)_5$.

The potential energy curves obtained with the basis set I for $Cr(CO)_5Ar$, $Cr(CO)_5Kr$, $Mo(CO)_5Kr$, and $Mo(CO)_5Xe$ as a function of the metal-rare gas distance are shown in Figure 2. The curves are attractive and the calculated binding energies increase from 1.9 kcal/mol for $Cr(CO)_5Ar$ to 4.0 kcal/mol for $Cr(CO)_5Kr$, 8.3 kcal/mol for $Mo(CO)_5Kr$, and 6.3 kcal/mol for $Mo(CO)_5Xe$. The increase in the binding energy from $Cr(CO)_5Ar$ to $Cr(CO)_5Kr$ is expected since Kr should be a better donor than Ar. However, the decrease in the binding energy from $Mo(CO)_5Kr$ to $Mo(CO)_5Xe$ was rather unexpected, since one would expect the same trend which we find from $Cr(CO)_5Ar$ to $Cr(CO)_5Kr$. This decrease might be interpreted as a consequence of the balance between two different metal-rare gas interactions. The first one, of symmetry σ, namely, between the orbital np_z of the rare gas and the orbital $a_1(d_{z^2})$ of the complex, is a two-electron stabilizing interaction (Figures 1 and 3). The second one, of symmetry π, namely, between the orbitals np_x and np_y of the rare gas and the orbitals e (d_{xz} and d_{yz}) of the complex, is a four-electron destabilizing interaction (Figure 3). When going from Kr to Xe, the change in the binding energy might be dominated by the repulsive π interaction as a consequence of the fact that the 5p level of Xe is well above the 4p level of Kr and is closer to the e (d_{xz}, d_{yz}) level of $Mo(CO)_5$ (Figure 3), thus decreasing the energy denominator in the interaction term (the energy denominator will also decrease for the σ interaction term, but comparatively less since the a_1 (d_{z^2}) level is well above the e (d_{xz}, d_{yz}) level).

The question which we have to answer now is whether the attractive curves of Figure 2 (and the corresponding binding energies) correspond to the reality or to an artifact of the calculations? One possible way to answer this question without extending the basis set is to use the counterpoise method.[37] The

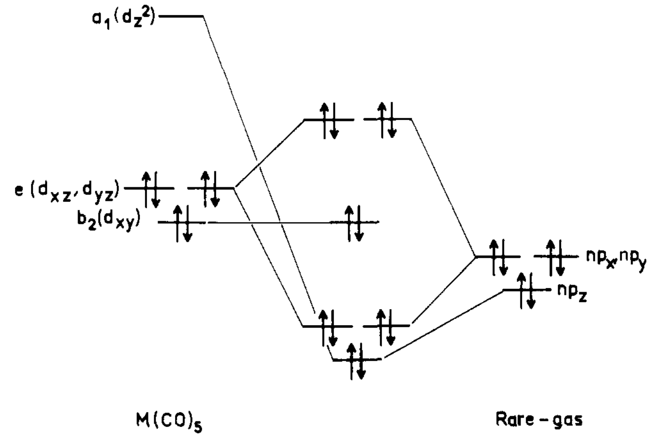


Figure 3. The metal-rare gas interaction diagram.

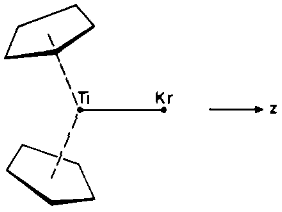
method consists of calculating the energy of a supermolecule AB as well as the energies of the constituents A and B with the basis set of the supermolecule AB (namely, the energy of A is calculated with the electrons and nuclei of B removed, while retaining the basis set centered on B). It has been claimed that this technique gives a considerably better description of the intermolecular interactions than the normal supermolecule calculations.[38] When applied to the system Mo(CO)$_5$Kr with a Mo-Kr distance of 2.90 Å, the method yields a small repulsive interaction (with a destabilization of about 2 kcal/mol; see Table V) instead of the binding energy of 8 kcal/mol calculated by the supermolecule approach. This raises some doubt about the validity of the binding energies calculated with basis set I.

This conclusion, regarding the repulsive character of the metal-rare gas interaction *at the SCF level,* is substantiated by the calculations for Mo(CO)$_5$Kr and Mo(CO)$_5$Xe with basis set II. In both cases, the metal-rare gas interaction appears repulsive (Table IV and Figure 2) (one cannot exclude that the curve of Figure 2 for Mo(CO)$_5$Kr, with basis set II, becomes slightly attractive for Mo-Kr distances larger than 3.3 Å; however, the binding energy will certainly not exceed 0.5 kcal/mol). One result which is probably significant is that, for a metal-rare gas separation of 3.16 Å, the interaction is much more repulsive for Xe than for Kr. This parallels the results obtained with the small basis set and indicates that the potential ability of Kr to bind to a M(CO)$_5$ unit should be greater at the SCF level, probably as a consequence of the electronic factors mentioned above (see also below). Finally the fact that the potential energy curve for Mo(CO)$_5$Kr changed from attractive with a medium-size basis set to repulsive with a large basis set is not unprecedented; a similar basis set extension effect has been reported for He$_2$.[38]

On the basis of the results with the large basis set, one is led to the conclusion that the metal-rare gas interaction is probably repulsive *at the SCF level* (or only weakly attractive, by 1 kcal/mol or less). Different explanations can be put forward for this inability of the rare gas to form a dative bond with the M(CO)$_5$ complexes (at least for M = Cr and Mo). The first one, that the ionization potential of the rare gas is too high, would be acceptable for argon and krypton but probably does not hold for xenon. Another explanation would be based on the fact that the σ interaction, which is stabilizing, may be counterbalanced by a π destabilizing interaction. Some support for this explanation comes from the fact that, with the large basis set, the interaction is much more repulsive for Xe than for Kr. To check this hypothesis, we have looked for a complex-rare gas system where a stabilizing interaction σ would not be opposed by a π destabilizing interaction. Preliminary extended Hückel calculations showed that this condition was met by the system TiCp$_2$Kr (**3**); the d^2 system TiCp$_2$ has one low-lying vacant orbital 2a$_1$ which overlaps well with the Kr 4p$_z$ orbital while the orbitals of TiCp$_2$ which would overlap with the 4p$_\pi$ orbitals of Kr are empty (for a discussion of the bonding ability of the fragment MCp$_2$, see ref 39). But again this interaction turned out to be repulsive at the SCF level.[40] This seems to rule out our hypothesis that the repulsive character of the interaction in the systems M(CO)$_5$-rare gas is due to the π interactions.

Table V. SCF Energies of Mo(CO)$_5$Kr and of the Fragments Mo(CO)$_5$ and Kr by the Counterpoise Method (with a Distance Mo-Kr of 2.90 Å and Basis Set I)

	energy, au
Kr	−2745.4565
Mo(CO)$_5$	−4529.6069
Mo(CO)$_5$ + Kr	−7275.0634
Mo(CO)$_5$Kr	−7275.0602



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Finally, another explanation for the repulsive character of the metal-rare gas interaction at the SCF level may be found in the steric constraints, namely, the fact that the rare-gas atom is too bulky to get in close contact with the metal atom (to ensure a suitable overlap of the orbitals). Mulliken stressed that a good donor should have a good approachability, which is synonymous with small size for an atom.[14] This condition is probably not satisfied for the xenon atom with a van der Waals radius of 2.18 Å.[41] A donor-acceptor bond would probably correspond to a metal-rare gas separation less than 3.0 Å. For a Mo-Xe separation of 3.16 Å in Mo(CO)$_5$Xe, the distance between the Xe atom and a cis carbon atom is 3.74 Å, i.e., less than the sum of the corresponding van der Waals radii of 3.88 Å. Thus part of the destabilization of the system Mo(CO)$_5$Xe probably arises from these steric interactions between the rare gas and the cis ligands (a similar explanation holds for TiCp$_2$Kr). Thus the dilemma about this type of donor-acceptor bond is that the light rare gases have too high a ionization potential, whereas the heavier ones are too bulky.

Dispersion Contribution. The above metal-rare gas complexes are probably not bound (or only very weakly) at the SCF level. However, this does not mean that they are unstable, since the dispersion energy (which is not included in the SCF calculation) can make a significant contribution (by several kilocalories per mole) to the binding energy. Among the various theoretical ab initio methods which account for the dispersion energy,[42,43] a perturbation treatment based on the SCF calculations for the fragments[22] is particularly suitable for relatively large systems.[44,45] However, with the present computational limitations, the method cannot be applied to a system such as Mo(CO)$_5$Kr. We have attempted to *estimate* the dispersion contribution in Mo(CO)$_5$Kr by calculating the dispersion energy for the model system MoKr (fortunately, cf. below, this estimate yields probably a lower bound to the dispersion energy in Mo(CO)$_5$Kr).

The dispersion energy for MoKr has been calculated according to formula (2) of ref 22. The electronic configuration of the Mo atom was set as $d_{xy}{}^2 d_{xz}{}^2 d_{yz}{}^2$. The basis set used was derived from the Gaussian basis of basis set II in the following way. One s function and one set of p functions of the Mo atom (the ones with the lowest exponent in basis set II) were deleted.

Then diffuse functions were added, namely, one set of d functions for Kr and one set of s, p, and d functions for Mo (the corresponding exponents were optimized in order to give the largest polarizability[46] for each atom). Owing to the practical limitations, no f function was included in this basis set, although f functions on the Mo atom may contribute significantly to the dispersion energy (cf. below). The contracted basis set was [6,4,4] for Mo and [5,4,2] for Kr, namely, minimal basis set for the inner shells and double-ζ for the shells 4s and 4p of Kr and 4d of Mo plus the diffuse functions which were left uncontracted. The calculated dispersion energy amounts to 5.3, 3.3, and 3.0 kcal/mol for a Mo-Kr separation of 2.735, 3.00, and 3.052 Å, respectively.

If we assume that the dispersion energy is not too different in $Mo(CO)_5Kr$ and MoKr, adding the above values to the SCF energies obtained with the large basis set gives a stabilization energy of about 2.5 kcal/mol for $Mo(CO)_5Kr$ with a Mo-Kr separation of 3.05 Å.[47] In fact, these values of the dispersion energy in MoKr are probably seriously underestimated owing to the lack of f functions in the basis set. Since the dispersion energy between two systems is directly related to the polarizabilities of each system,[20,48] this is a consequence of the fact that the polarizability calculated for the Mo atom is 4.68 or 2.71 $Å^3$ depending whether the basis set includes or not a set of f functions (the polarizability of Mo was calculated according to formula (4) of ref 46). Including an appropriate f function in the calculation of the dispersion energy for MoKr may yield a stabilization energy as large as 4.0-4.5 kcal/mol. Furthermore, it seems that MoKr is not a very good model for estimating the dispersion energy in $Mo(CO)_5Kr$, which is almost certainly underestimated, since the polarizability of the Mo atom represents only a lower limit of the polarizability of $Mo(CO)_5$. Practical limitations in our programs have prevented us from evaluating the polarizability of $Mo(CO)_5$ but we have been able to calculate that of $Mo(CO)_2$ (the two carbonyl ligands being respectively along the x and y axis). Using the method of ref 46, we have obtained for $Mo(CO)_2$ $\alpha_x = \alpha_y = 11.9$ $Å^3$ and $\alpha_z = 5.7$ $Å^3$, to be compared to the corresponding values for Mo and CO:[49] $\alpha_{\|}(CO) = 2.0$ $Å^3$, $\alpha_{\perp}(CO) = 1.3$ $Å^3$, and $\alpha(Mo\ d^6) = 4.7$ $Å^3$. Thus it is clear that $Mo(CO)_2$ is much more polarizable than Mo or CO. It is expected that the components of the polarizability of $Mo(CO)_5$ will be at least as large as α_x or α_y for $Mo(CO)_2$. If we assume a rough proportionality between the dispersion energy of two interacting systems and the polarizabilities of the components, then the stabilization energy of $Mo(CO)_5Kr$ may be as large as 8-10 kcal/mol. Such an estimate is necessarily approximate, but points to a significant stabilization energy of $Mo(CO)_5Kr$ due to the dispersion energy.[51] One will notice that our conclusion regarding the dominant role of the dispersion term in the stabilization energy of $Mo(CO)_5Kr$ is in agreement with the fact that $M(CO)_5$ forms a weak bond not only with the rare gas but also with methane (which lacks a lone pair).[1]

Conclusion

The results of the present study may be summarized as follows.

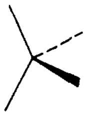
(1) The calculation of the interaction energy at the SCF level between systems with a relatively large number of electrons, such as the present ones, requires a basis set which is at least of the (9,5) quality for first-row atoms with a double-ζ contraction.

(2) The metal-rare gas interaction in the systems $M(CO)_5X$ (M = Cr, Mo; X = rare gas) or $TiCp_2X$ is repulsive at the SCF level. This may be a consequence of the fact that the rare-gas atom is too bulky, leading to steric interactions with the other ligands.

(3) An estimate of the dispersion energy in $Mo(CO)_5Kr$, based on a model calculation for MoKr and on the relationship between the dispersion energy and the polarizabilities of the interacting systems, yields a lower limit of 2.5 kcal/mol for the stabilization energy, but the exact value might be as high as 8-10 kcal/mol.[57] Thus it would be highly desirable to perform a calculation of the dispersion energy for $Mo(CO)_5Kr$.

We have mentioned in the Introduction the existence of the pentacarbonyl (hydrogen halide) tungsten complexes $W(CO)_5XH$ (X = Cl, Br, I)[13] which are isoelectronic to the $W(CO)_5$-rare gas systems. One may ask whether some specific feature accounts for the stability of $W(CO)_5XH$ when compared, for instance, to $Mo(CO)_5Kr$ or $Mo(CO)_5Xe$. Since the ionization potential of HCl is intermediate between those of Kr and Xe, the most significant difference is probably the existence of a relatively large dipole moment for the hydrogen halides, leading to a dipole-induced dipole term which can contribute significantly to the stabilization energy of $W(CO)_5XH$. This will be reinforced by the fact that the polarizability of the hydrogen halide is somewhat higher than the value for the corresponding rare gas (5.4 $Å^3$ for IH[50] *vs.* 4.0 $Å^3$ for Xe[59]).

Finally, one may look for a transition-metal complex with a Lewis acid behavior but less steric requirements than $M(CO)_5$ (M = Cr, Mo) or $TiCp_2$. This might result in a stabilization of the metal complex-rare gas system at the SCF level.[60] For instance, a system like $Fe(CO)_4$ might be a better candidate with this respect than $M(CO)_5$ or $TiCp_2$, since $Fe(CO)_4$ has a C_{2v} structure **4** with bond angles of ~145 and ~120° [61] which probably could be distorted relatively easily to a structure such as **5** or even **6** upon the approach of the rare gas (however, $Fe(CO)_4$ is paramagnetic and, although a 16e system, has no empty d orbital[7]).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Reactions of Methyl Cations with Methylsilanes[1]

G. W. Goodloe, E. R. Austin, and F. W. Lampe*

Contribution from the Davey Laboratory, Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received October 23, 1978*

Abstract: The gas-phase reactions of CH$_3^+$ with (CH$_3$)$_{4-n}$SiH$_n$ (n = 0, 1, 2, 3) have been studied in a tandem mass spectrometric apparatus. Reaction cross sections at 1-eV kinetic energy in the laboratory system have been determined by direct comparison with the known cross section for hydride ion transfer from SiH$_4$ to CH$_3^+$. Relative cross sections have been determined as a function of kinetic energy in the range of 1–10 eV in order to determine whether reactions were endothermic or exothermic. The major reactions are hydride and methide (CH$_3^-$) transfer from the silane to CH$_3^+$, with methide transfer becoming dominant for (CH$_3$)$_3$SiH and (CH$_3$)$_4$Si. Isotopic studies show only very minor incorporation of ^{13}C atoms and D atoms in the ionic products when CH$_3^+$ reactant ions are replaced by ^{13}CH$_3$ and CD$_3^+$. This is interpreted as indicating that the reactions do not proceed through pentavalent collision complexes but rather are of the direct type.

Introduction

Standard enthalpies of formation of gaseous ions,[2-4] determined for the most part from electron-impact appearance potentials, indicate that siliconium ions are thermodynamically more stable with respect to their constitutive elements than are the corresponding carbonium ions. Thus, for example, the standard enthalpy changes for hydride ion transfer from silane and the methylsilanes to methyl-substituted carbonium ions, i.e.

$$(CH_3)_nCH_{3-n}^+ + (CH_3)_mSiH_{4-m} \rightarrow (CH_3)_nCH_{4-n} + (CH_3)_mSiH_{3-m}^+ \quad (1)$$

are as shown in Figure 1 for m, n = 0, 1, 2, 3. As seen in this figure, all reactions are exothermic, i.e., energetically feasible, with the exception of (CH$_3$)$_2$CH$^+$ and (CH$_3$)$_3$C$^+$ reacting with SiH$_4$ and CH$_3$SiH$_3$. It is to be expected, therefore, that gaseous carbonium ions will usually react rapidly with silanes that contain a silicon–hydrogen bond to produce siliconium ions. Moreover, the simplicity of hydride transfer suggests that it should be a major pathway for the reaction to take. However, with the exception of the reactions of gaseous CH$_3^+$ ions with SiH$_4$,[5,6] there do not seem to have been any investigations of the reactions of alkyl ions with alkylsilanes.

Studies of organosilicon chemistry in solution[7,8] have not detected the presence of siliconium ions, i.e., $>$Si$^+$ of sp^2 hybridization, in systems in which they had been expected on the basis of analogy with carbonium ion chemistry. Instead, it appears that in solution most reactions at silicon centers involve pentavalent silicon intermediates of sp^{3}d hybridization. This tendency of silicon to use the accessible 3d orbitals to expand its valence shell, at least in solution, suggests that ion–molecule

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