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Ab Initio Calculations of Group IVA Tetrachloride Complexes: V.[1] Dynamics of the Formation of the Complex of $SiCl_4$ with Tetramethylurea

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Abstract — Quantum-chemical calculations of the system $SiCl_4 \leftarrow OC[N(CH_3)_2]_2$ were fulfilled by the RHF/6-31G(d) method with full geometry optimization and at varied Si←O distances. The calculation with full geometry optimization does not lead to the unusual trigonalbipyramidal structure of the complex, found experimentally, and this structure is reproduced when the right angles between axial Si–Cl bonds and the coordination Si←O bond were set. Complex formation results in electron density transfer from the carbonyl C atom and from the H atoms of the electron donor, as well as from the Si atom is transferred mainly on axial Cl atoms [basically, on their p_z (p_σ) orbitals]. The total energy of such complex is higher by 0.936 eV than that of the most energetically favorable form of the studied system.
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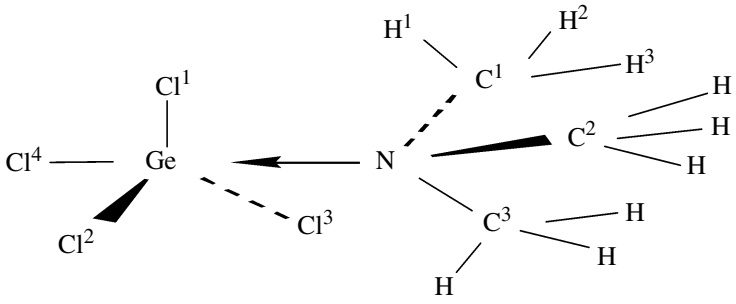
Usually in trigonal-bipyramidal complexes of Group IVA tetrachlorides the ligand occupies an axial position of the bipyramid (see, for example, [2–6]). The ^{35}Cl NQR spectrum of the $SiCl_4$ complex with tetramethylurea [2, 4, 5] points to its unusual trigonal-bipyramidal structure: The ligand occupies an equatorial position of the bipyramid, two Cl atoms occupy the other equatorial positions, and the other two Cl atoms occupy axial positions. This spectrum consists of two doublets rather distant from each other. The high-frequency doublet (21.653 and 21.155 MHz) is in a higher frequency region as compared to the ^{35}Cl NQR spectrum of individual $SiCl_4$ (20.464, 20.415, 20.408, and 20.273 MHz [7]), and the low-frequency doublet (18.448 and 17.343 MHz), in a lower frequency region. The first doublet belongs to equatorial, and the second, to axial Cl atoms [2]. The asymmetry parameters of the electric field gradient at ^{35}Cl nuclei, too, agree with such structure of the $SiCl_4 \cdot OC[N(CH_3)_2]_2$ complex: larger asymmetry parameters (43.1 ± 4.1 and $38.8 \pm 2.6\%$) characteristic of equatorial Cl atoms correspond to the high-frequency doublet and small parameters (7.5 ± 2.0 and $1.7 \pm 0.5\%$), to the low-frequency doublet [4, 5]. Usually the asymmetry parameters for axial Cl atoms of trigonal-bipyramidal compounds are close to zero (see, for example, [4–6]). Judging from the essential splitting of the low-frequency doublet in the NQR spectrum and from the difference in the corresponding asymmetry parameters, the $SiCl_4 \cdot OC[N(CH_3)_2]_2$ complex has the structure of a rather distorted trigonal bipyramid, which is probably caused by the crystal effect.

The results of semiempirical MNDO quantum-chemical calculations of the $SiCl_4 \cdot OC[N(CH_3)_2]_2$ complex with the ligand in axial (**I**) and equatorial (**II**) positions of the trigonal bipyramid show [8] that the formation heat of complex **I** (–183.0 kcal mol^{-1}) is more negative than that of complex **II** (–181.5 kcal mol^{-1}), which agrees with the ^{35}Cl NQR data. The variations of charges on atoms and populations of their valence *p* orbitals on variation of the Si←O distance allowed us to conclude [8] that, as the components of the complex come together, they are mutually polarized, and at a sufficiently short distance between them the electron density is also transferred from the donor onto the Cl atoms of the acceptor. The Si and O atoms serve only as conductors.

In the present work we studied the structure of the complex $SiCl_4 \cdot OC[N(CH_3)_2]_2$ and the dynamics of its formation using the higher level Hartree–Fock quantum-chemical method with split-valence and polarized 6-31G(d) basis set. Structures **I** and **II** were calculated using the GAUSSIAN 94W program [9] with full geometry optimization and with fixed Si←O distances. Both with structure **I** and structure **II**, the

[1] For communication IV, see [1].



I

coordinate origin was placed on Cl^1. To estimate populations of valence *p* orbitals of the Cl atoms in other positions of the bipyramid, the calculations were repeated. In these cases, the coordinate origin was placed on these atoms.

The full geometry optimization of the $SiCl_4 \leftarrow O \cdot C[N(CH_3)_2]_2$ system gave structure **I** with the Si←O distance of 3.555 Å (Table 1), which is far from an ideal trigonal-bipyramidal structure. A similar structure with an unreally long Si←N distance was also obtained for the $SiCl_4 \leftarrow N(CH_3)_3$ system by RHF/6-31G(d) (3.95 Å) and B3LYP/6-311G(d) (3.67 Å) calculations with full geometry optimization [1]. The calculated populations of valence *p* orbitals of Cl atoms in the $SiCl_4 \leftarrow OC[N(CH_3)_2]_2$ system were used to calculate, by Eqs. (1) and (2) [10], ^{35}Cl NQR frequencies (ν) and asymmetry parameters (η) of the electric field gradient at ^{35}Cl nuclei (Table 2).

$$\nu = (e^2Qq_{at}/2h[-N_z + (N_x + Ny)/2](1 + \eta^2/3)^{1/2}, \quad (1)$$

$$\eta = |3(Np_x - Np_y)/(2Np_z - Np_x - Np_y)|. \quad (2)$$

Here e^2Qq_{at} is the atomic quadrupole coupling constant; *h*, Planck's constant; and N_x, N_y, and N_z, populations of the p_x, p_y, and p_z valence orbitals of an indicator atom, respectively. The e^2Qq_{at} value was found from the experimental NQR frequency of Cl_2 and from the calculated valence 3*p* orbital populations of the Cl atoms of this molecule.

The calculated NQR frequency of the axial Cl atom is much higher than the experimental value, and the asymmetry parameter, as would be expected, is equal to zero. The calculated NQR frequency of equatorial Cl atoms practically coincides with the experimental value, but their asymmetry parameter is much lower than experimental, and it is uncharacteristic of such atoms. A satisfactory fit of calculated to experimental NQR characteristics for the $SiCl_4$ complex with trimethylamine [1] could be obtained by using the populations of the 3p components of valence *p* orbitals of Cl atoms, found from the calculation of this complex by the RHF/6-31G(d) method with a fixed Si←N distance (2.14 Å). This distance was determined with account for X-ray diffraction data for the $GeCl_4$ complex with trimethylamine and the covalent radii of the Si and Ge atoms [11]. Taking into consideration the smaller (by 0.4 Å) [12]) covalent radius of O compared to N, we suggest that the Si←O distance in the $SiCl_4 \cdot OC[N(CH_3)_2]_2$ complex is 2.1 Å. At such a fixed Si←O distance and optimized remaining geometric parameters, we calculated system **I**. In this case, the structure of the coordination polyhedron of the Si atom becomes close to trigonal-bipyramidal (Table 1), and the total energy of the system is higher by 0.653 eV than in its most energetically favorable form.

The calculated ^{35}Cl NQR frequency of the axial Cl atom is slightly reduced, but still remains essentially

Table 1. Bond lengths (*d*)[a] and valence angles in structure **I**, calculated by the RHF/6-31G(d) method with varied Si←O distances

d, Å					Angle, deg							
Si←N	$Si–Cl^1$	$Si–Cl^2$	$O=C^1$	$C^1–N^1$	Cl^1SiCl^2	Cl^2SiCl^3	Cl^2SiCl^4	Cl^2SiO	Cl^1SiO	OCl^1N^1	OC^1N^2	$N^1C^1N^2$
3.555	2.041	2.027	1.205	1.377	107.91	110.91	111.08	71.53	178.81	121.95	121.80	116.25
2.1	2.119	2.057	1.232	1.352	96.92	117.97	116.31	86.97	176.09	120.17	122.52	117.31
2.0	2.132	2.065	1.237	1.347	95.73	118.23	116.15	88.55	175.69	119.89	122.36	117.75
1.707	2.164	2.088	1.255	1.332	93.57	116.50	113.61	94.05	172.37	118.93	121.52	119.55

[a] The $Si–Cl^3$ and $Si–Cl^4$ bond lengths are 2.069, 2.079, and 2.127 Å at Si←O distances of 2.1, 2.0, and 1.707 Å, respectively.

Table 2. Populations (N) of the 3p components of valence p orbitals of the Cl^1 and Cl^2 atoms in structure **I** at various Si←O distances and the ^{35}Cl NQR frequencies (ν) and asymmetry parameters of the electric field gradient at ^{35}Cl nuclei (η), calculated from these populations

Si–O, Å	Cl^1					Cl^2				
Si←N	$N3p_x$, e	$N3p_y$, e	$N3p_z$, e	ν, MHz	η, %	$N3p_x$, e	$N3p_y$, e	$N3p_z$, e	ν, MHz	η, %
3.555	1.279	1.279	1.056	20.765	0.0	1.288	1.276	1.050	21.687	7.64
2.1	1.271	1.274	1.060	19.796	2.62	1.306	1.262	1.049	22.163	28.09
2.0	1.269	1.274	1.060	19.723	3.34	1.306	1.260	1.051	21.892	29.38
1.707	1.264	1.276	1.056	19.925	8.71	1.300	1.256	1.063	20.311	30.46

Table 3. Bond lengths (d)[a] and valence angles in structure **II** calculated by the RHF/6-31G(d) method with varied Si←O distances

d, Å							Angle, deg				
Si←O	Si–Cl^1	Si–Cl^4	O=C^1	C^1–N^1	N^1–C^2	N^1–C^3	Cl^1SiCl^2	Cl^1SiO	Cl^2SiO	OC^1N^1	OC^1N^2
7.0	2.091	2.093	1.203	1.379	1.451	1.454	141.06	109.45	109.49	121.95	120.83
5.0	2.093	2.093	1.204	1.378	1.451	1.454	139.82	110.14	110.04	121.88	121.88
3.0	2.097	2.098	1.215	1.366	1.453	1.455	136.74	111.55	111.71	121.29	121.97
2.0	2.099	2.148	1.243	1.340	1.460	1.458	131.13	114.41	114.46	119.63	119.64
1.707	2.094	2.199	1.258	1.329	1.465	1.460	126.79	116.60	116.61	118.72	118.74

[a] The Si–Cl^1 and Si–Cl^2 bond lengths at this Si←O distance are practically equal. The same relates to the Si–Cl^3 and Si–Cl^4, C^1–N^1 and C^1–N^2, N^1–C^2 and N^2–C^5, and N^1–C^3 and N^2–C^4 bond lengths.

higher than the experimental value, and the frequency of the equatorial Cl atoms slightly increases. The calculated asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei of the axial Cl atom (Table 2) is close to and that of the equatorial atoms is noticeably lower than the experimental value (see above). At the Si←O distance of 2.0 Å, the geometric parameters of structure **I** are even closer to those characteristic of the trigonal-bipyramidal structure, and its ^{35}Cl NQR frequencies and asymmetry parameters become closer to experiment. However, the NQR frequency of the axial Cl atom and the asymmetry parameter for equatorial Cl atoms remain far from the corresponding experimental values. At the Si←O distance of 2.0 Å, the total energy of the system is higher by 0.706 eV than in the most energetically favorable form.

Structure **II** found by the ^{35}Cl NQR method can be obtained by RHF/6-31G(d) calculations, provided the Cl^3SiO and Cl^4SiO angles are set equal to 90° and the $SiOC^1$ angle, to 180°. Optimizing the remaining geometric parameters of system **II** we obtained a structure in which the coordination polyhedron of the Si atom is close to trigonal bipyramid (Table 3) and the Si←O distance (1.707 Å) is even shorter than the sum of the covalent radii of the Si and O atoms (1.83 Å) [12]. The Cl^1SiCl^3 and Cl^2SiCl^3 angles are practically equal to 90° (90.02° and 89.95°, respectively). Therewith, the ^{35}Cl NQR frequency of the axial Cl atoms, calculated from the 3p-component populations of their valence p orbitals (Table 4), is close to the experimental frequency, and that of the equatorial Cl atoms is only slightly higher than it. The calculated asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei of the axial and equatorial Cl atoms are close to the experimental values (see above). In this case, the total energy of system **II** is higher by 0.936 eV than that structure **I** calculated with full geometry optimization. The calculation of system **I** with the Si←O distance fixed at 1.707 Å and optimization of its other geometric parameters (Table 1) practically does not make them closer to values characteristic of the trigonal-bipyramidal structure, and the ^{35}Cl NQR parameters calculated with the calculated populations (Table 2) do not become closer to the experimental values than those obtained calculations with the Si←O distance fixed at 2.0 Å.

The fact that the experimental ^{35}Cl NQR parameters of the $SiCl_4 \cdot OC[N(CH_3)_2]_2$ complex fit the respective parameters calculated from the 3p-com-

Table 4. Populations of the 3*p* components of valence *p* orbitals of the Cl atoms in structure **II**, calculated by the RHF/6-31G(d) with varied Si←O distances and the ^{35}Cl NQR frequencies (ν) and asymmetry parameters of the electric field gradient at ^{35}Cl nuclei (η), calculated from these populations

Si–O, Å	Cl^1					Cl^4				
Si←N	$N3p_x$, e	$N3p_y$, e	$N3p_z$, e	ν, MHz	η, %	$N3p_x$, e	$N3p_y$, e	$N3p_z$, e	ν, MHz	η, %
7.0	1.323	1.228	1.042	23.073	60.91	1.312	1.240	1.026	24.012	42.93
5.0	1.322	1.229	1.042	23.001	59.87	1.311	1.242	1.025	24.043	40.80
3.0	1.319	1.232	1.043	22.692	56.82	1.304	1.253	1.026	23.876	30.41
2.0	1.314	1.241	1.045	22.446	46.79	1.281	1.265	1.052	20.640	10.66
1.707	1.311	1.246	1.046	22.293	41.87	1.266	1.259	1.072	17.730	5.49

Table 5. Atomic charges (*q*) in system **II**[a] at various Si←O distances, calculated by the RHF/6-31G(d) method, and their changes $|\Delta q| = q(1.707\ Å) - q(7.0\ Å)$

Si←O, Å	*q*, e													
	Cl^1	Cl^4	Si	O	C^1	N^1	C^2	C^3	H^1	H^2	H^3	H^4	H^5	H^6
7.0	–0.271	–0.252	1.048	–0.633	0.986	–0.667	–0.277	–0.304	0.164	0.163	0.202	0.203	0.173	0.170
5.0	–0.276	–0.256	1.064	–0.645	0.992	–0.668	–0.278	–0.305	0.164	0.165	0.201	0.202	0.174	0.171
3.0	–0.295	–0.291	1.112	–0.690	1.034	–0.669	–0.289	–0.307	0.174	0.172	0.213	0.203	0.178	0.182
2.0	–0.318	–0.416	1.258	–0.781	1.124	–0.671	–0.313	–0.312	0.202	0.189	0.237	0.207	0.190	0.204
1.707	–0.321	–0.491	1.275	–0.735	1.140	–0.670	–0.327	–0.315	0.216	0.197	0.250	0.209	0.197	0.214
Δ*q*, e	0.050	0.239	0.227	0.102	0.154	0.003	0.050	0.011	0.052	0.034	0.048	0.006	0.024	0.044

[a] The Cl ^{1} and Cl^2 atomic charges are equal to each other at this Si←O distance. The same relates to the charges on Cl^3 and Cl^4, N^1 and N^2, C^2 and C^5, and C^3 and C^4. The charges on methyl H atoms are also equal in pairs.

ponent populations of valence *p* orbitals of the axial and equatorial Cl atoms in structure **II** points to correctness of our quantumchemical calculations and allows us to examine variations in the electronic and steric structure of this complex on variation of the Si←O distance and, therefore, the dynamics of complex formation. When the components of structure **II** approach each other at a distance of 7.0–1.707 Å, the Si–Cl^1 and Si–Cl^2 bond lengths practically do not vary, the Si–Cl^3, Si–Cl^4, and O=C^1 bond lengths increase, and the C^1–N^1 and C^1–N^2 bond lengths decrease, starting from the Si←O distance of about 3.0 Å (Table 3). Starting from approximately the same Si←O distance, the valence angles presented in Table 3 also essentially vary.

According to the RHF/6-31G(d) calculation, the Si–Cl bond lengths in individual $SiCl_4$ are 2.029 Å, and the ClSiCl valence angles are 109.45–109.49°. The NQR frequency of individual $SiCl_4$, estimated from the populations of the 3*p* components of valence *p* orbitals of the Cl atoms, is 21.117 MHz, and the asymmetry parameter of the electric field gradient on ^{35}Cl nuclei is 0.23%. Comparison of these parameters with those calculated for system **II** with a fixed long Si←O distance to exclude direct interaction of its components shows that calculation conditions (right Cl^3SiO and Cl^4SiO angles) affect the resulting characteristics. However, as the components of system **II** come closer together, the values of these angles get closer to those expected for a real trigonal-bipyramidal complex. The ^{35}Cl NQR frequencies and asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei of the axial and equatorial Cl atoms, calculated from the populations of the 3*p* components of their valence *p* orbitals, have unreally high values at long Si←O distances (Table 4), and get closer to the experimental values at shorter Si←O distances (see above).

As the Si←O distance decreases, the partial negative charges of all Cl atoms and the partial positive charge of the Si atom of the electron acceptor increase (Table 5). Therewith, the partial negative charges on O, N^1, N^2, C^2, and C^3 and the positive charges C^1 of all hydrogen atoms of the electron donor also increase.

Table 6. Populations of valence *p* orbital of the Cl atoms in system **II**, calculated by the RHF/6-31G(d) method at varied Si←O distances

d, Å	Cl^1			Cl^4		
Si←O	Np_x, e	Np_y, e	Np_z, e	Np_x, e	Np_y, e	Np_z, e
7.0	1.975	1.892	1.440	1.963	1.904	1.415
5.0	1.976	1.893	1.443	1.963	1.906	1.416
3.0	1.977	1.899	1.453	1.965	1.923	1.430
2.0	1.973	1.908	1.468	1.970	1.959	1.511
1.707	1.969	1.911	1.470	1.971	1.968	1.575

At the Si←O distance of 7.0 Å, the electron acceptor and donor remain practically neutral. When this distance decreases, the electron donor acquires a partial positive charge, and the acceptor, a negative charge. For example, at the distance of 1.707 Å, the electron acceptor has a charge of –0.349 e, and the donor, practically the same positive charge (0.347 e). Such charge has been transferred from the electron donor onto acceptor. When complex **II** is formed, the strongest increase of electron density takes place on Cl atoms which become axial on complex formation (Table 5), which agrees with the low NQR frequency of these atoms. This increase occurs mainly due to increase in the population of their p_z (p_σ) orbitals (Table 6). The increase in the electron density of Cl atoms which become equatorial on complex formation, is rather insignificant (Table 5), and their NQR frequencies, too, change only slightly (Table 4). This increase, too, results mainly from increased populations of their p_z (p_σ) orbitals (Table 6). The increase of the electron density of Cl atoms, induced by complex formation, results not only from its transfer from the electron donor, but also from polarization of Si–Cl bonds. In this case, the partial positive charge of the silicon atom essentially increases (Table 5). The carbonyl group is strongly polarized on complex **II** formation. The charges on its atoms in the donor fragment vary to the greatest extent. The electron density from the C^1 and hydrogen atoms passes onto the O and Cl atoms of the acceptor. The N^1, N^2, C^2, and C^3 atomic charges (Table 5) practically do not vary as the components of system **II** come closer together. Apparently, the N, O, and methyl C atoms do not participate in the electron density transfer on the electron acceptor and act only as conductors.

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