161. Stability of Charge-Transfer Complexes of CS_2 with PH_3 and Its Derivatives: *Ab initio* MRSDCI/CASSCF Study

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Dedicated to Prof. *Jan Linderberg*, an excellent theoretician and marvelous friend, on the occasion of his 60th birthday

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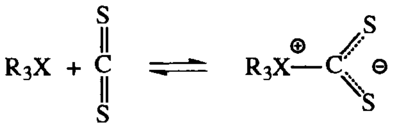
While trialkylamines and dialkyl(phenyl)amines do not react with CS_2 in the sense of an addition reaction, the analogous phosphines react smoothly. Attempts to interpret the reaction course on the basis of semiempirical, HF, MP2, and MP4 calculations of energy changes failed completely. To understand why Me_3P or Me_2PhP react so vigorously (liquid phase, 300 K) with CS_2, CASSCF and MRSDCI calculations must be carried out.

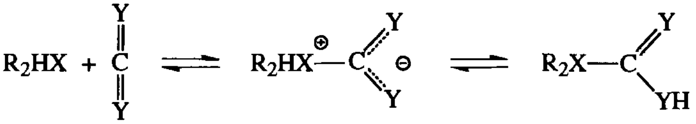
1. Introduction. – While numerous differences in the properties and reactivity between the first- and second-row elements are understood, reactivity difference between tertiary amines and phosphines towards CS_2 is still puzzling. Addition reaction (*Scheme 1*) leading to a dipolar product takes smoothly place with some tertiary phosphines (X = P) but not with tertiary amines.

Scheme 1



For a better understanding, it is desirable to consider this process in the broader context as shown in *Scheme 2*.

Scheme 2

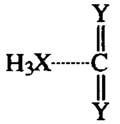


So far, the interest has been limited to species containing N or P, and O or S atoms. Years ago, one of us (*R.Z.*) studied carbamic, monothiocarbamic, and dithiocarbamic acids (or rather their salts) [1] [2], derived from primary and secondary amines. Intention to fix the dipolar form in *Scheme 2* led to attempts to prepare adducts of $R_3N^{\oplus}CS_2^{\ominus}$

(R = alkyl or aryl) type but all the effort failed. However, it has been known for a long time that some tertiary phosphines do react with CS_2, and that their reactivity could be enhanced by proper substituents [3–6]. While a vigorous reaction takes place between CS_2 and Me_3P or aryl(dimethyl or diethyl)phosphine, $MePh_2P$ and Ph_3P do not react. Reactivity of Me_2PhP can be modified by substitution in the *para*-position of the benzene ring [6].

It is the purpose of this study to obtain a deeper insight into the interaction between tertiary phosphines and CS_2 leading to a zwitterionic structure. It was the size of the systems under study which originally prevented a quantum-chemical study. Only recently have we realized that the object of this study is only seemingly very simple: to obtain a reliable piece of theoretical information on the electronic structure of the products and on the energetics of the process, sophisticated (multireference) quantum-chemical methods are required.

Finally, simpler-level calculations have been used for qualitative or semiquantitative estimates of the stability of *van der Waals* systems **I** and **II**.



$$H_3X\cdots\cdots\underset{\underset{Y}{\|}}{\overset{\overset{Y}{\|}}{C}}$$

I

$$H_2X{-}H\cdots\cdots Y{=}C{=}Y$$

II

In connection with the above complexes, an *ab initio* study of noncatalytic and H_2O-catalyzed decarboxylation of carbamic acid, $HN_2{-}COOH$, should be mentioned [7]. It is mainly the reverse reaction that is related to the processes under study.

2. Computational Method. – Reaction profiles of association of CS_2 to PH_3, Me_3P, or Me_2PhP were first pre-investigated at the HF/6-31G* level. A fully optimized reaction coordinate was constructed for the first reaction, while only the geometries of the reactants (*i.e.*, isolated CS_2 and substituted phosphine) and product (*i.e.*, charge-transfer complex) were optimized for the other two reactions at the above mentioned level. For stationary points, single-point MP2/6-31G* and MP4(SDTQ)6-31G* energies were evaluated.

As we found that a single-determinant description of the charge-transfer complexes under study is not quantitatively correct, and that a second, 'covalent' state mixes slightly with the ground state (for further discussion, see the following section), we repeated our calculations using the CASSCF method with the same basis set. The active space consisted to two electrons in the two frontier molecular orbitals, as we found by larger test calculations (up to 8 electrons in 8 frontier molecular orbitals) that the only configuration, besides the HF ground state, which contributes more than 1% to the CASSCF wavefunction, is that resulting from a double-excitation from HOMO to LUMO. Finally, for the first reaction, single-point MRSDCI calculations based on the CASSCF wavefunction were performed. More precisely, we performed a two reference CI based on the two leading configurations, *i.e.*, the HF ground state and the above described doubly excited configuration.

All the localized stationary points were classified *via* vibrational frequencies analysis at the CASSCF/6-31G* level for the first reaction, and at the HF/6-31G* level for the other two reactions. The relative energies with respect to the dissociated species were corrected for the zero-point energy (ZPE). The basis set superposition error (BSSE) was estimated using the standard *Boys-Bernardi* scheme [8], and all the relative energies were corrected to it.

The stability of *van der Waals* complexes **I** and **II** (X = N or P, and Y = O or S) was investigated at the MP2/6-31G* level, corrected for the ZPE and BSSE. All the calculations were carried out using the GAMESS [9] and GAUSSIAN 90 [10] program packages.

3. Results and Discussion. – The fully optimized HF/6-31G* and CASSCF/6-31G* reaction coordinate of association of CS_2 to PH_3 is depicted in *Fig. 1*. The *Table* summarizes the absolute and relative (to the products) energies of the products and the transition state at the HF, MP2, MP4(SDTQ), CASSCF, and MRSDCI/6-31G* levels. Finally, *Fig. 2* shows the principal geometrical parameters of the above structures.

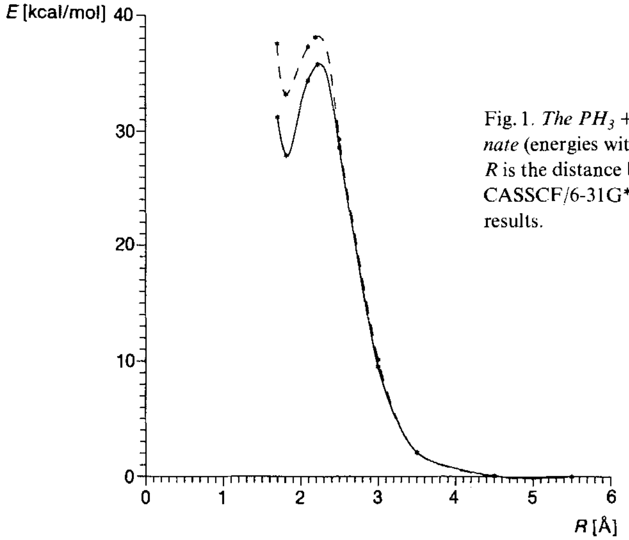


Fig. 1. *The PH_3 + CS_2 fully optimized reaction coordinate* (energies without ZPE and BSSE corrections). *R* is the distance between the C- and P-atoms. *Full line*: CASSCF/6-31G* results, *dashed line*: HF/6-31G* results.

Table. *HF, CASSCF, MP2, MP4(SDTQ), and MRSDCl Energies for the Complexes under Study.* Total energies in a.u. Values in brackets represent energies in kcal/mol relative to the dissociated species, corrected for the ZPE and BSSE.

	HF/6-31G*	CASSCF/6-31G*	MP2/6-31G*	MP4(SDTQ)/6-31G*	MRSDCl/6-31G*	MRSDCl/6-31G* (*Davidson* corr.)
H_3P-CS_2	−1175.279879 (+38.56)[a])	−1175.299896 (+33.75)[b])	−1175.76360 (+44.49)[a])	−1175.82874 (+48.47)[a])	−1175.58799 (+16.55)[b])	−1175.62187 (+12.19)[b])
H_3P-CS_2 (saddle)	−1175.271335 (+41.13)[a])	−1175.287381 (+38.79)[b])	– –	– –	−1175.575871 (+21.16)[b])	−1175.61042 (+15.38)[b])
Me_3P-CS_2	−1292.4395.60 (+10.97)[a])	−1292.457748 (+0.15)[a])	–	–	–	–
$Me_2PhP-CS_2$	−1482.940126 (+12.35)[a])	−1482.958992 (+0.51)[a])	–	–	–	–

[a]) Energies calculated for HF-optimized structures.

[b]) Energies calculated for CASSCF-optimized structures.

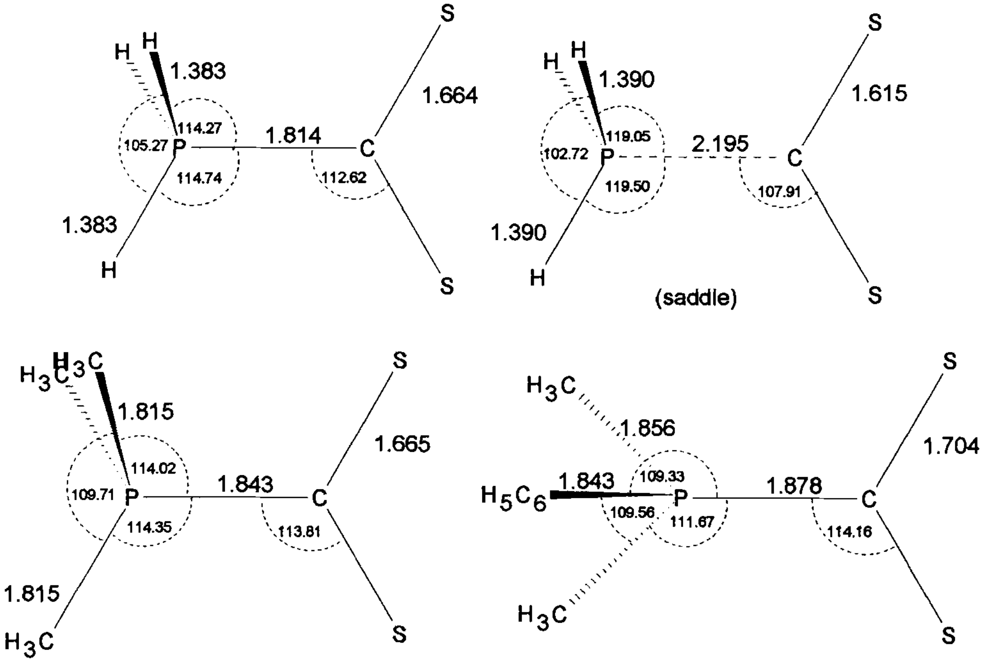


Fig. 2. *Geometries of the three charge-transfer complexes under study optimized at the CASSCF/6-31G* level* (PH$_3$CS$_2$ *and HF/6-21G* level* (Me$_3$P)CS$_2$ and Me$_2$PhPCS$_2$). Distances are in Å, angles in degrees.

Association of CS$_2$ with PH$_3$ (the complex being a C_s-symmetric species) is an endothermic process with the product lying, at the HF level, 38.56 kcal/mol above the reactants, from which it is separated by a barrier of 2.57 kcal/mol. Inclusion of dynamic correlation slightly increases the endothermicity of the process to 44.49 kcal/mol at MP2 level and to 48.47 kcal/mol at MP4(SDTQ) level.

At the CASSCF level, the endothermicity of the association is reduced to 33.75 kcal/mol, and the barrier height is 5.04 kcal/mol. The lowering of the energy of the products is a result of the fact that an exited 'covalent' state mixes slightly with the ground 'charge-transfer' state. The highest occupied orbitals of the two single-determinant states that contribute 94% ('charge-transfer' state) and 6% ('covalent' state) to the CASSCF wavefunction are depicted in *Fig. 3*.

Thus, the small contribution of the 'covalent' state has a non-negligible influence on the calculated endothermicity; however, it practically does not affect the geometry of the product. The only exception is the length of the C–P bond, which is shortened by 0.03 Å by inclusion of the non-dynamic correlation *via* CASSCF.

At the MRSDCI level, the PH$_3$CS$_2$ complex is further stabilized, so that the endothermicity of the process is reduced to +16.55 kcal/mol (+12.19 after *Davidson* size-consistency correction [11]). The barrier height separating the complex from the dissociated species is now 4.61 kcal/mol (3.19 after *Davidson* correction [11]). We can conclude that correlation energy recovered *via* the MRSDCI method acts significantly (~ 20 kcal/mol) in favor of stabilization of the complex.

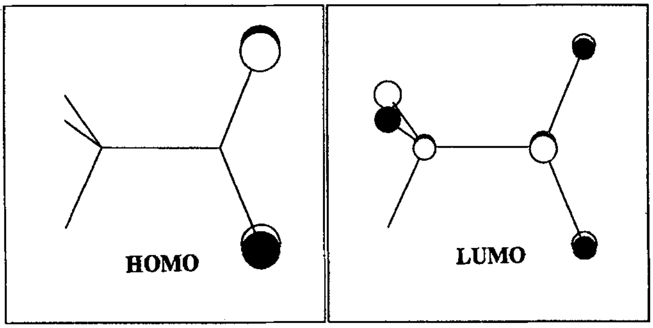


Fig. 3. *The shape of the frontier orbitals* (HOMO and LUMO) *included in the multiconfigurational active space*

The effect of substituents on the investigated association reaction was studied by replacing PH_3 by Me_3P, and Me_2PhP, which are the only two substituents known experimentally to form a stable charge-transfer complex with CS_2. Both C_s-symmetric complexes were optimized at the HF/6-31G* level, and single-point CASSCF/6-31G* calculations with the same active space as above followed (see the *Table* and *Fig. 2*). Although the effect of substituents works strongly (~ 20 kcal/mol at the HF level) in favor of the complex (which is not true for the analogous reaction of NH_3 with CS_2 where we found a marginal increase of endothermicity, at the HF level, from 27.10 to 27.97 kcal/mol upon trimethylation of ammonia), at the HF level both reactions are endothermic, in clear disagreement with experiment. Let us close this paragraph by a brief qualitative remark on the solvent effect. The two reactions proceed smothly in pure CS_2, as well as in non-polar (*e.g.* benzene) and polar (*e.g.* dimethyl sulfoxide) solvents. This is in agreement with our understanding of solvent effects on such a type of reactions.

CASSCF Calculations reveal that the 'covalent' state contributes 5% in both substituted phosphine-CS_2 adducts which causes an additional stabilization of the complex. As a result, both reactions are found to be practically thermoneutral at the CASSCF level (see the *Table*).

The CASSCF method predicts the two complexes to be significantly less stable than the experiment reveals. In fact, from our calorimetric measurements it follows that both reactions are exothermic with reaction heats of 20.6 ± 3.1 kcal/mol for Me_3P and 17.0 ± 2.7 kcal/mol (for details see *Exper. Part*). Given our experience from the first reaction, we can assign this discrepancy to the lack of dynamic correlation stabilization of the complexes, as recovered by the MRSDCI method.

Unfortunately, the two complexes are prohibitively large for performing post-CASSCF calculations with a reasonably saturated basis set, so we can only estimate the effect of dynamic correlation on further stabilization of the complex using the results for the $PH_3 + CS_2$ reaction. Provided that this stabilization of *ca.* 20 kcal/mol is roughly transferable to reactions of CS_2 with the PH_3 derivatives under study, the agreement with experiment becomes reasonably good.

It is interesting to see whether a *van der Waals* complex is formed upon approaching XH_3 (X = N or P) to CY_2 (Y = O or S). Therefore, we investigated complexes **I** and **II** (see *Sect. 1*) at the MP2/6-31G* level. Surprisingly, we found only one complex of the type **I**, which is stabilized by more than 1 kcal/mol (after correction for ZPE and BSSE), namely the $H_3N\cdots CO_2$ complex. We found that this complex with the $N\cdots C$ distance of 2.949 Å lies 1.94 kcal/mol below the free components. Our result is an improvement on that of *Ruelle et al.* [7], who, at the HF/3-21G level without any corrections, found a significantly more stable complex (stability of of 7.1 kcal/mol). Our calculations also clearly indicate that no other stable complex of type **I** and no stable complex of type **II** is formed.

4. Conclusions. – *1*) The energy of association between PH_3 and CS_2 decreases from 39 to 34 kcal/mol when passing from *Hartree-Fock* to CASSCF, and further to 12 kcal/mol at the MRSDCI (*Davidson* correction included) level. On the other hand, inclusion of dynamic correlation by single-reference methods (MP2 and MP4(SDTQ)) does not result in stabilization of the complex.

2) Trimethyl and dimethyl(phenyl)substitution of PH_3 is connected with an association energy decrease of *ca.* 34 kcal/mol (at the CASSCF level). From the above results, we can estimate that the exoergicity of the addition of the substituted species to CS_2 amounts to some −20 kcal/mol, in good correlation with the results of our calorimetric measurements described in the *Exper. Part.*

3) Lack of reactivity between Me_3N and CS_2 can be traced to the fact that, unlike the phospine analogue, methylation of ammonia does not result in stabilization of the charge-transfer complex. Also, steric hindrance plays a much more significant role in methylated ammonia than in methylated phosphine, due to the fact that the C–N bond is by 0.28 Å shorter than the C–P bond (at the HF/6-31G* level).

4) Except for the $NH_3\cdots CO_2$ pair, there is no significant tendency to form stable *van der Waals* or H-bonded complexes in the systems under study.

Our thanks are due to Dr. *Z. Havlas* from the Institute of Organic Chemistry and Biochemistry for his valuable comments.

Experimental Part

1. *General.* The adducts were prepared in benzene soln. at r.t. analogously as in [6]. CS_2 was used in three times the molar amount of proper phosphine. Under these conditions, PH_3, $MePh_2P$, and Ph_3P do not react. Ph_3P can be recrystallized from CS_2. Only Me_3P and Me_2PhP give the red-brown crystalline adducts in an exothermic reaction. These adducts can be also prepared in EtOH as well as in CS_2, MeCN, and DMSO.

2. *Calorimetry.* Calorimetric measurements on a *Calvet SETARAM C-80D* calorimeter in DMSO, where the complexes do not crystallize, give the following reaction heats at 297.5 K: 20.6 ± 3.1 kcal/mol for Me_3P and 17.0 ± 2.7 kcal/mol for Me_2PhP.

3. *NMR and UV Spectra.* NMR Spectra were obtained with a *Varian Unity-200* instrument in (D_6)DMSO. The chemical shifts are given in the δ scale. TMS was used as internal standard for the ^{1}H-NMR spectra, the ^{13}C-NMR spectra were referenced to the (D_6)DMSO signal (39.7) and, for the ^{31}P-NMR spectra, 85% H_3PO_4 was used as the external standard (−112.5). UV Spectra were recorded in MeCN solns. with a *Hewlett-Packard 8452A* instrument (λ_{max} in nm (logε)).

Me_2PCS_2: b.p. 113–114°. UV: 250 (2.90), 354 (3.02). ^{1}H-NMR: 1.94 (*d*, J(H,P) = 13.7, 9 H). ^{13}C-NMR: 11.1 (*q*, J(C,P) = 54.8).

Me_2PhP: b.p. 100–102°. UV: 250 (3.09), 346 (2.42). ^{1}H-NMR: 2.34 (*d*, J(H,P) = 13.4, 2 Me); 7.60 (*m*, 2 H_m, 1 H_p); 7.90 (*dd*, J(H,P) = 11.2, J(H,H) = 7.6, 2 H_o). ^{13}C-NMR: 10.9 (*q*, J(C,P) = 56.3, Me); 124.5 (*s*, J(C,P) = 78.6, C(1)); 129.2 (*d*, J(C,P) = 11.1, C(3)); 131.2 (*d*, J(C,P) = 8.8, C(2)); 133.3 (*d*, J = C,P) = 56.3, C(4)).

For the nonreactive phosphines, the UV and NMR spectra of the parent compounds (phosphines and CS_2) and the mixture show no difference. For the reactive species, the ^{31}P chemical shifts (δ (P′), $\Delta\delta$ (P)) are: Me_3P: (−173.4,–), Me_3PCS_2: (−129.7, 43.7), (−157.4,–), and Me_2PhPCS_2: (123.8, 33.6). The larger relative shift $\Delta\delta$ (P) for the trimethylated species indicates also greater exoergicity of the complex formation, in agreement with the calorimetric data.

REFERENCES

[1] R. Zahradník, *Collect. Czech. Chem. Commun.* **1956,** *21,* 447, 1111.
[2] R. Zahradník, *Chem. Techn.* **1959,** *11,* 546.
[3] A. W. Hofmann, *Ann. Chim. Phys.* **1861,** *62,* 413.
[4] L. Czismatis, *Ber. Dtsch. Chem. Ges.* **1882,** *15,* 2014, 2018.
[5] W. C. Davies, C. J. O. R. Morris, *Bull. Soc. Chim. Fr.* **1933,** *53,* 980.
[6] W. C. Davies, W. P. Walters, *J. Chem. Soc.* **1935,** 1786.
[7] P. Ruelle, U. W. Kesselring, H. Nam-Tran, *J. Mol. Struct. (Theochem)* **1985,** *124,* 41.
[8] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970,** *19,* 553.
[9] GAMESS, M. T. Guest, SERC Daresbury Laboratory, 1990.
[10] Gaussian 90, M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzales, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Steward, S. Topiol, J. A. Pople, *Gaussian, Inc.,* Pittsburgh PA, 1990.
[11] A. Szabo, N. S. Ostlund, 'Modern Quantum Chemistry', Mc Graw Hill, New York, 1989, p. 267.