initiate chemical reactions in solution.[18] While the present studies do not overlap with these experiments, they complement them in a wider frame of microelectrode chemistry in solution.

Colloidal metals are known to catalyze the reduction of various organic compounds by molecular hydrogen.[19] The present studies may contribute to a more detailed knowledge of the mechanism of such reduction processes. In our experiments, electrons are transferred from a donor to the colloid, transformed into adsorbed hydrogen atoms (eq 3), molecular hydrogen being the final product. A catalyzed reduction by hydrogen may proceed via the same elementary reactions in the opposite direction. H_2 is adsorbed at the colloid, dissociated into adsorbed atoms, which are in equilibrium with electrons on the colloid. The electrons are finally transferred to the substrate.

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(17) Koryakin, B. V.; Dzhabiev, T. S.; Shilov, A. E. *Dokl. Phys. Chem. (Engl. Transl.)* **1977**, *233*, 359-361. Lehn, J. M.; Sauvage, J. P. *Nouv. J. Chim.* **1977**, *1*, 449-451. Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Ibid.* **1978**, *2*, 547-549. Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214-7217. Grätzel, C. K.; Grätzel, M. *Ibid.* **1979**, *101*, 7741-7743.

(18) Bard, A. J. *Science (Washington, D.C.)* **1980**, *207*, 139-144.

(19) Dunworth, W. P.; Nord, F. F. *Adv. Catal.* **1954**, *6*, 125-141.

The Conformations and Energetics of Simple Ylids

Robert A. Eades, Paul G. Gassman,* and David A. Dixon*[1]

Contribution from the Chemistry Department, University of Minnesota, Minneapolis, Minnesota 55455. *Received July 11, 1980*

Abstract: The electronic structures of the simplest ylids of nitrogen, oxygen, phosphorus, and sulfur have been determined from ab initio molecular orbital theory at the Hartree-Fock-SCF level. The calculations were carried out by using basis sets of double-ζ quality with polarization functions added to the heavy atoms and s and p diffuse functions added to carbon. Full-geometry optimization was performed by using both point-wise searches and gradient methods. Rotation barriers about the X-S bond were determined to be 2.3, 5.6, 0.2, and 21.2 kcal/mol for X = N, O, P, and S, respectively. Energies for the internal proton-transfer reaction to form the ylid from its most stable isomer were determined to be 68.7, 86.5, 57.8, and 81.7 kcal/mol for X = N, O, P, and S, respectively. Simple physical arguments for these values are presented. The charge distributions of the ylids are also discussed.

Introduction

Ylids are extremely useful synthetic intermediates.[2] Although much is known about the details of the chemistry of these species, little is known about their electronic[3] and molecular[4] structure and thermodynamic properties. For the simplest ylids, with only hydrogens as substituents, an unequivocal molecular structure is available only for the phosphorus ylid.[3b,d,e] In order to provide quantitative information about the molecular structure, relative energetics, and conformational preferences of the simplest ylids of N, O, P, and S (**1**-**4**), we have examined the electronic structure of these compounds by using ab initio molecular orbital theory.

All calculations were done by using the program HONDO (version 5) with contracted Gaussian orbitals.[5] The basis sets were of double-ζ quality with polarization functions added to the heavy atoms.[6] Since the methylene group is nominally a carbanion, an additional set of diffuse s and p functions were added to the carbon basis set to allow for a proper description of anionic character at this center.[7] Geometry optimization was carried out for two conformations of each of the four ylids studied by using both point-wise searches and gradient methods.[8] Both types of

Table I. Dipole Moments and Ionization Potentials for Nonzwitterionic Isomers

molecule	μ^a	$\mu(\text{exptl})^{a,b}$	IP^c	$\text{IP}(\text{exptl})^{c,d}$
CH_3NH_2	1.63	1.31	10.53	8.97
CH_3OH	2.01	1.69	12.22	10.83
CH_3PH_2	1.16	1.10	9.81	9.72
CH_3SH	1.79	1.53	9.64	9.44

[a] Dipole moment in Debye. [b] Experimental value.[11] [c] Ionization potential in eV. [d] Experimental value.[12]

Table II. Geometry-Optimized Parameters for the Ylids **1a**-**4a**

parameter^a	N	O	P	S
$r(\text{C-S})^{b,c}$	1.591 (1.538)	1.870 (1.587)	1.668 (1.762)	1.646 (1.801)
θ(HCH)	106.6 (103.6)	106.2 (96.7)	120.4 (109.2)	121.8 (117.7)
θ(HCX)	101.0	95.1	119.2	119.2
θ(HXH)	107.5 $(109.5)^d$	110.2 (120.0)	99.8 $(109.5)^d$	93.9 (105.4)

[a] Bond lengths in Å and bond angles in deg. [b] Values in parentheses are the values taken from ref 14. [c] The C-X bond lengths for the nonzwitterionic isomers are, X = N, 1.474; O, 1.427; P, 1.863; and S, 1.819. [d] Constrained values in parentheses from ref 14.

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(1) (a) A. P. Sloan Fellow, 1977-1979. (b) Camille and Henry Dreyfus Teacher-Scholar, 1978-1983, (c) Du Pont Young Faculty Grantee, 1978.

(2) A. W. Johnson, "Ylid Chemistry"; Academic Press: New York, 1966.

(3) (a) K. A. O. Starzewski, H. T. Dieck, and H. Bock, *J. Organomet. Chem.*, **65**, 311 (1974); (b) G. Trinquier and J.-P. Malrieu, *J. Am. Chem. Soc.*, **101**, 7169 (1979); (c) I. Absar and J. F. van Wazer, *ibid.*, **94**, 2382 (1972); (d) H. Lischka, *ibid.*, **99**, 5633 (1977); (e) H. Strich, *Nouv. J. Chem.*, 3, 105 (1979); (f) R. Hoffman, D. B. Boyd, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **92**, 3929 (1970); (g) S. L. Graham and C. H. Heathcock, *ibid.*, **102**, 3713 (1980); (h) V. Král and A. Arnold, *Collect. Czech. Chem. Commun.* **45**, 80, 92 (1980).

(4) (a) E. A. V. Ebsworth, T. E. Fraser, and D. W. H. Rankin, *Chem. Ber.*, **110**, 3494 (1977); (b) J. C. J. Bart, *J. Chem. Soc.*, **13**, 350 (1969); (c) A. T. Christensen and W. G. Witmore, *Acta. Crystallogr., Sect. B*, **25**, 73 (1969); (d) W. Sawodny, *Z. Anorg. Allg. Chem.*, **368**, 284 (1969).

(5) (a) M. Dupuis, J. Rys, and H. F. King, Jr., *J. Chem. Phys.* **65**, 111 (1976). (b) M. Dupuis, private communication.

(6) (a) T. H. Dunning, Jr., and P. J. Hay in "Methods of Electronic Structure Theory", Vol. 3, H. F. Schaeffer, III, Ed.; Plenum Press, New York, 1977 Chapter 1. (b) ζ_d for P and S are 0.5 and 0.6, respectively. T. H. Dunning, Jr., private communication.

(7) The diffuse carbon functions are ζ_s : 0.04548 and $\zeta_p = 0.034$[5a] The basis sets are summarized as follows: H, (4)/[2]; C, (10,6,1)/[4,3,1]; N and O, (9,5,1)/[3,2,1]; P and S, (11,7,1)/[6,4,1].

(8) P. Pulay in "Applications of Electronic Structure Theory", Vol. 4, H. F. Schaeffer, III, Ed., Plenum Press, New York, 1977, Chapter 4.

0002-7863/81/1503-1066$01.25/0

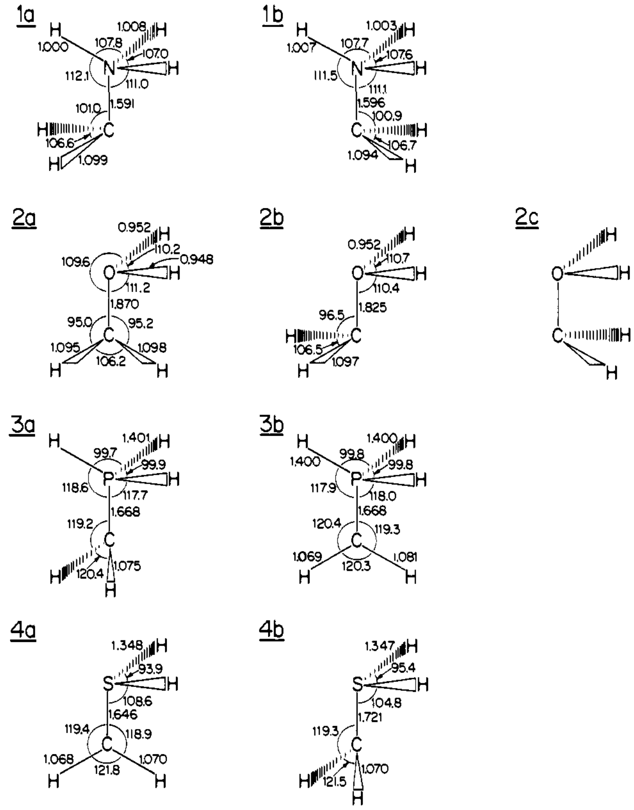

Figure 1. Conformations of the simple ylids. The **a** conformations are the most stable. For structure **2**, **2c** represents the eclipsed conformation, **2b** represents a 180° rotation about the C–O bond of **2c**, and **2a** results from a 90° rotation about the C–O bond of **2c**.

optimization proved to be useful, especially for the oxonium ylid **2**, which shows a large coupling between certain bond angles and the C–O distance. The geometries for the nonzwitterionic isomers CH_3NH_2, CH_3OH, and CH_3PH_2 were taken from experiment[9a–e] while the structure of CH_3SH was taken from the calculations of Collins et al.[9f]

Results and Discussion

The dipole moments and ionization potentials (IP) determined from Koopmans' theorem[10] for the nonzwitterionic isomers are shown in Table I, where they are compared with the experimental values.[11,12] The values for the dipole moments are larger than experimental values by 5–25% which is typical for such calculations. The IP's for CH_3NH_2 and CH_3OH are too high while the IP's for CH_3PH_2 and CH_3SH are in excellent agreement with the experimental IP's.

The conformation of the ylids studied in this work are shown in Figure 1 together with the relevant geometry parameters. Optimizations of the geometry as described above were carried out for the **a** and **b** conformations of the ylids **1** and **4**. For the oxonium ylid, **2**, the geometry of a third conformation, **2c**, was obtained by using the geometry of conformation **2b** and rotating about the C–O bond. The important geometric parameters of the most stable confirmation of each of the ylids are summarized in Table II. In each instance, this refers to conformation **a** of Figure 1. The C–N and C–O bond lengths in the ammonium and oxonium ylids are longer than the corresponding distances in the nonzwitterionic isomers methylamine and methanol by approximately 0.1 and 0.4 Å, respectively. The C–S and C–P distances, however, are shorter than their nonzwitterionic counterparts by approximately 0.2 Å. The most suprising value is the 0.4-Å lengthening of the C–O bond in **2** when compared to the C–O bond in methanol. The C–P and C–S bond lengths in **3** and **4**, respectively, and their optimum conformations are in good agreement with experimental values determined from the crystal structures of $(Ph)_3PCH_2$[3c] and $(CH_3)_2SC(CN)_2$.[4b] The HCH angles in the oxygen and nitrogen ylids are close to tetrahedral, but the CH_2 group is strongly bent away from the C–X axis. In fact, the plane of the CH_2 group is almost perpendicular to the C–X bond, especially for the oxonium ylid, **2**. In contrast, the HXH bond angles in the phosphonium and sulfonium ylids are far less than tetrahedral. The CH_2 groups in the sulfur and phosphorus ylids have angles near 120°, and C–X and C–H bonds essentially lie on one plane.[13] *Thus, there are significant geometry differences between ylids formed from first- and second-row atoms.* Our geometry for $H_3P^+{-}CH_2^-$ is in good agreement with the calculated results of Lischka[3d] and Strich.[3c,14] In contrast, the partially optimized geometries determined by Wolfe et al.[14] using the 4-31G basis set[15] differ significantly from our geometries as shown in Table II. There are significant discrepancies in the bond distances and in a number of the bond angles. These differences could be due to the geometric constraints placed on the optimizations by the calculations of Wolfe et al., e.g., the HPH angle, or to deficiencies in the 4-31G basis set. As Wolfe et al.[14] discuss, it is well-known that double-ζ basis sets do not properly treat angles at pyramidal centers since these basis sets always overestimate the stability of the planar species relative to the pyramidal form. This could result in an incorrect description of the interaction of the CH_2^- moiety with other fragment leading to a distorted bond length. Our basis set, which involves the use of heavy-atom polarization functions, avoids this problem with pyramidal centers which was inherent in the earlier calculations.[14]

Table III. Rotation Barriers in the Ylids

X	barrier[a]	X	barrier[a]
N	2.3	P	0.2
O	5.6[b]	S	21.2

[a] Barrier to internal rotation in kcal/mol. More accurate values for the ammonium and phosphonium ylids are 2.26 and 0.24 kcal/mol, respectively. [b] Energy difference between conformations 2a and 2c. The energy difference between 2a and 2b is 1.0 kcal/mol.

Table IV. Internal Proton-Transfer Energies for Formation of the Ylids 1a–4a[a]

X	proton-transfer energy[b]	X	proton-transfer energy[b]
P	57.5	S	81.7
N	68.7	O	86.5

[a] $\Delta E°$ for the reactions $XH_2CH_3 \rightarrow XH_3^+{-}CH_2^-$ and $XHCH_3 \rightarrow XH_2^+{-}CH_2^-$. [b] In kcal/mol.

The barriers to internal rotation are shown in Table III. As illustrated in the conformations shown in Figure 1, we find that the oxonium and sulfonium ylids have different conformations than the phosphonium and ammonium ylids. These latter species have low barriers to rotation while the sulfonium and oxonium ylids have higher barriers. Considering the short P–C bond distance in **3**, the barrier to rotation in the phosphonium ylid is extremely low. The higher barrier and the preferred conformations in the oxonium and sulfonium ylids can be attributed to lone-pair repulsions. The preferred conformation places the lone pair on

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(9) (a) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2276 (1967); (b) T. Nishikawa, *J. Phys. Soc. Jpn.*, **12**, 668 (1957); (c) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967); (d) T. Nishikawa, *J. Phys. Soc. Jpn.*, **11**, 781 (1956); (e) T. Kojima, E. L. Breig, and C. C. Lin, *J. Chem. Phys.*, **35**, 2139 (1961); (f) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *ibid.*, **64**, 5142 (1976).

(10) T. Koopmans, *Physica (Amsterdam)*, **1**, 104 (1933).

(11) R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* NSRDS-NBS 10 (1967).

(12) H. M Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **1** (1977).

(13) The CH_2 group and the P–C bond are close to being copolanar with an angle of 169.2° between the P–C bond and the bisector of the angle HCH.

(14) F. Bernardi, H. B. Schlegel, M. -H. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, **99**, 5633 (1977).

(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

Table V. Charge Distributions for the Ylids and Their Nonzwitterionic Isomers[a]

charge	N	O	P	S
group charge[b] (ylid) = A	0.43	0.16	0.53	0.44
group charge[b] (isomer) = B	0.09	0.20	0.14	0.01
$\Delta_{\text{charge}} = A - B$	0.34	−0.04	0.39	0.43
d orbital (ylid) = C	0.12	0.08	0.37	0.23
d orbital (isomer) = D	0.09	0.06	0.19	0.07
$\Delta_d = C - D$	0.03	0.02	0.18	0.13

[a] All charges in units of electrons. [b] The group charge is defined as the sum of the charge on the heavy atom plus the charges on the directly bonded hydrogens.

S and O and the lone pair on the CH_2 group perpendicular to each other. This alleviates lone-pair repulsions. The barrier in the sulfonium ylid is larger than that of the oxonium ylid because the lone pairs can interact more strongly due to both the shorter bond length and the conformation of the CH_2 group.

The energy required for internal proton transfer from the nonzwitterionic isomer to form the ylid is given in Table IV at the SCF level.[16] These energy values provide a quantization of the stability of the ylids in the gas phase relative to their stable nonzwitterionic isomers. The lowest energy required to transfer a proton is that for formation of the phosphonium ylid while the largest amount of energy is required for formation of the oxonium ylid. Nominally, the energetics can be visualized as breaking a C–H bond to form C^- and H^+ and subsequent protonation of the atom X to form XH^+. Since the energy required for breaking the C–H bond should be approximately constant, the energetics would be dominated by the ability of X to accept a proton, i.e., the proton affinity, PA(X). The experimentally determined ordering of proton affinities in the gas phase is $NH_3 > PH_3 > H_2S \approx H_2O$ with values relative to NH_3 of 15.9, 29.7, and 33.5 kcal/mol,[17] respectively. On the basis of these values the ammonium ylid should require the lowest amount of energy for formation of the ylid by internal proton transfer since nitrogen is the best proton acceptor. It should be noted that we have ignored hypervalent effects which would lower the energy of both of the ylids which contain second-row atoms relative to those containing first-row atoms. Hypervalent effects for these compounds can be considered as the ability of the heteroatom to employ d orbitals for back-bonding of the lone pair on the CH_2^- group to the heteroatom. In the limit, this would form a pentavalent heteroatom, for example, $H_3P{=}CH_2$. For phosphorus, hypervalent character is important and the internal proton-transfer energy is lowered significantly for the formation of **3** (until it lies below that obtained for **1**). The ylids with only one lone pair (**1** and **3**) require less energy for their formation than do the O and S ylids, which have two repulsive lone pairs. The presence of hypervalent character can also be noted since **4** is more stable than **2** and more stable relative to **1** than predicted by the simple proton affinity arguments. The energy for formation of **4** is only 13.0 kcal/mol above that required for formation of **1** vs. a 29.7-kcal/mol difference expected from proton affinity arguments.

The oxonium ylid is quite different in character from the other ylids. This ylid closely resembles a dative bonding between water and methylene rather than a classically bonded zwitterion. In fact, generalized valence bond calculations and orbital contour plots suggest that the system resembles H_2O solvating the $^1A_1$ state of CH_2.[18] A lone pair from H_2O forms a weak dative bond with the vacant orbital of the CH_2 moiety. The lone pair on carbon then corresponds to the doubly occupied orbital present in the $^1A_1$ methylene. This description accounts for the long C–O bond and the spatial relationship of the H_2O and CH_2 fragments.

In order to examine the hypervalent character in these systems, we have reported in Table V group charges for the heteroatom and the sum of the charge in the d orbitals on the heteroatoms for both the ylids and their nonzwitterionic isomers. The group charge on carbon is simply the negative of the value reported in Table V for the heteroatom. We report group charges because this eliminates some of the arbitrary nature inherent in the Mulliken charge analysis.[19,20] Comparison of the charge distributions shows that for the heteroatoms N, P, and S, there is a charge separation with a positive charge of approximately 0.5 e on each heteroatom. For the oxonium ylid, a positive charge of only 0.16 is found on the heteroatom. In fact, there is less positive charge on the oxygen in the ylid than in methanol which supports the model of dative bonding between water and methylene for the ylid given above. Although the phosphonium ylid has the largest charge separation, comparison of the values of Δ_{charge} (which represents the difference in group charges between the ylid and its isomer) shows that the largest amount of charge transfer is actually observed for the sulfonium ylid. A more precise measurement of the hypervalent character on each heteroatom is given by the amount of d character present on this atom in excess of the value found for its nonzwitterionic isomer, i.e., for the value of Δ_d given in Table V. The values of Δ_d for the ammonium and oxonium ylids is very small, showing essentially no hypervalent character for these ylids. The values of Δ_d for the phosphonium and sulfonium ylids, in contrast, show the presence of significant d character on the heteroatom in excess of the amount found for the nonzwitterionic isomer. This further reinforces our conclusions about the presence of hypervalent effects in the second-row ylids and the lack of such effects in the first-row ylids.

We have also examined the ylids and their nonzwitterionic forms by using generalized valence bond wave functions[21] and configuration interaction calculations. Complete results on these calculations including plots of the important orbitals will be presented in a subsequent paper.

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(16) Generalized valence bond and POL–CI calculations show that a description of the energetics at the SCF level provides reasonable results.

(17) (a) D. H. Aue and M. T. Bowers in "Gas Phase Ion Chemistry", Vol. 2, M. T. Bowers, Ed., Academic Press, New York, 1979, Chapter 9; (b) S. G. Lias, D. M. Shold, and P. Ausloos, *J. Am. Chem. Soc.*, **102**, 2540 (1980).

(18) L. B. Harding and J. A. Pople in studies on the H_4CO surface have obtained similar results for this compound (private communication).

(19) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(20) (a) J. H. Hall, Jr., D. A. Dixon, D. A. Kleier, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **97**, 4202 (1975); (b) D. A. Dixon, D. A. Kleier, T. A. Halgren, and W. N. Lipscomb, *ibid.*, **98**, 2086 (1976).

(21) W. A. Goddard, III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).