

DONOR–ACCEPTOR OXO BONDS TO N, P, As AND Sb STATES OF III–V SEMICONDUCTORS

Roger CHANG and William A. GODDARD III

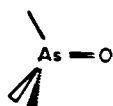
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA*

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As a model for a proposed phosphine oxide-type initial state in the oxidation of III–V semiconductors, we have examined the structure and bonding of the phosphine oxide-type bond in $Cl_3Y = O$ where $Y = N, P, As,$ and Sb . We calculate an $Y = O$ bond energy of 114 kcal for $P = O$, in reasonable agreement with experiment, 123 kcal/mol. The other calculated bond energies (kcal/mol) are 47 (N), 82 (As), and 63 (Sb). Based on these results, we conclude that such bonds should play an important role in phosphides and are likely to be important in arsenides but not in nitrides or antimonides.

1. Introduction

It has been suggested [1,2] that group V donor–acceptor bonds to oxygen, e.g.,

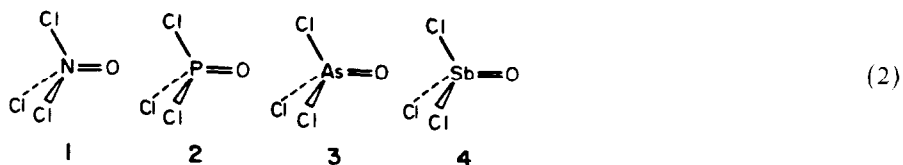


(1)

might play a role in the initial steps of oxidation of III–V semiconductor surfaces. Surface EXAFS studied by Stöhr et al. [3] have provided some confirmation of these ideas. For \sim monolayer coverages of oxygen, EXAFS indicated only As bonds to oxygen and an As–O bond length of 1.5 ± 0.05 Å calibrated against the O–Fe phase shift and 1.70 ± 0.05 Å calibrated against the O–Ni phase shift [3]. These values are in reasonable agreement with the predictions of Barton et al. [1] who obtained an As–O distance of 1.63 Å for H_3AsO from ab initio calculations. In order to provide information that could

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be useful in assessing the plausibility of such a species and to obtain data that would provide a spectroscopic signature useful for experimental probes, we have carried out calculations on



One reason for using Cl is that one system, 2, has already been characterized experimentally.

2. Results

The GVB orbitals for 2 are shown in fig. 1, where (a) is the P–O sigma bond and (b) and (c) are, respectively, the oxygen $2p_x$ and $2s$ bonds. The bonding can be visualized in terms of PCl_3 bonded to an oxygen atom



or as PCl_3^+ bonded to O^-



The results of our calculations are summarized in tables 1 and 2. From these tables we see that the P = O bond length is 0.02 Å longer and the ClPCl angle is 0.6° smaller than experiment. The calculated P = O bond energy of 114 kcal/mol compares reasonably well with the experimental value of 123 kcal/mol. The Y = O stretching vibrational frequencies from our calculations are also in good agreement (4% low) with the reported experimental values [4,5]. There seem to be no other experimental data for comparison with the other quantities in these tables.

For P = O, As = O, and Sb = O, the calculated bond energies (see table 1) are 114.4, 81.5, and 62.5 kcal/mol, and the bond distances are 1.47, 1.58, and 1.77 Å, respectively. As expected, the Y = O bond energies decrease and the Y = O bond distances increase as we proceed from P to As to Sb. The

exception to this trend occurs for the N = O bond (bond energy 47 kcal/mol, bond distance 1.26 Å).

One criterion as to where species such as (1) would play a role in oxidation is whether the process

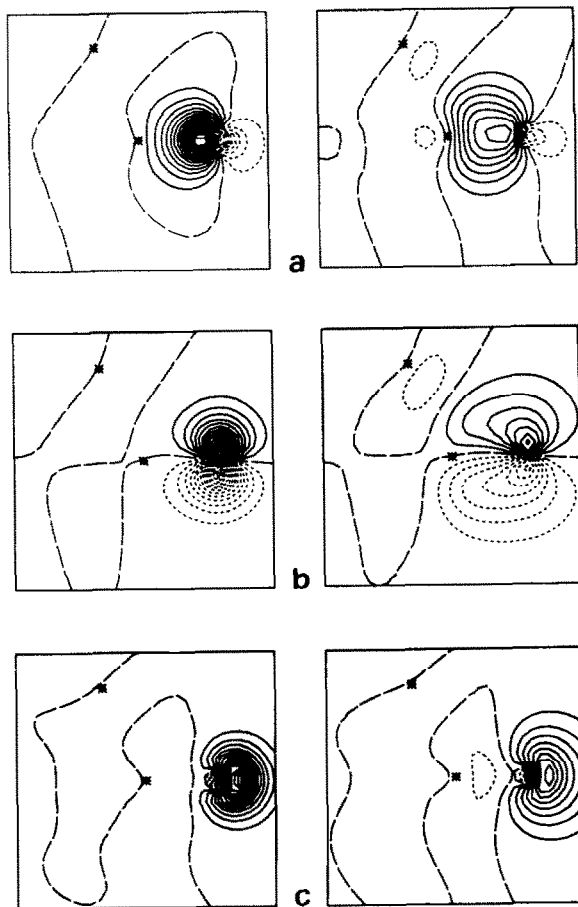


Fig. 1 Probability amplitudes for the GVB(4/8) orbitals of the P = O bond (Cl_3PO molecule); (a) P = O sigma bond pair; (b) O $2p_x$ bond pair; (c) O $2s$ bond pair. The plot plane is defined by one of the Cl atoms, the P atom and the O atom. The O $2p_y$ bond pair is omitted since it is similar to the O $2p_x$ bond pair. Contour increments are 0.05 a.u., positive contours are solid lines, and negative contours are short dashed lines. Long dashed lines indicate zero amplitude.

Table 1
Comparison of calculated and experimental molecular parameters for Cl_3YO and Cl_3Y ($\text{Y} = \text{N, P, As, Sb}$)

	$\text{Cl}_3\text{N} = \text{O}$		$\text{Cl}_3\text{P} = \text{O}$		$\text{Cl}_3\text{As} = \text{O}$		$\text{Cl}_3\text{Sb} = \text{O}$	
	Theory	Exper. ^{a)}	Theory	Exper. ^{a)}	Theory	Exper. ^{a)}	Theory	Exper. ^{a)}
Geometry ($\text{Cl}_3\text{Y} = \text{O}$)								
$R_{\text{YO}}(\text{\AA})$	1.258	(b)	1.471	1.45	1.578	(a)	1.773	(a)
$\angle\text{ClYCl}$ (deg)	105.7	(b)	102.8	103.4	101.7	(a)	100.4	(a)
$R_{\text{ClY}}(\text{\AA})$	1.834	(b)	2.052	2.00	2.166	(a)	2.342	(a)
Energies								
Bond energy (kcal/mol)	47.3	(b)	114.4	123.2	81.5	(80.5) ^{c)}	62.5	(a)
ΔH ($\text{YCl}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{OYCl}_3$)	+13	(b)	-55	-63	-20	-20	-3	(a)
YO vibrational frequency (cm^{-1}) ^{d)}	1518	(1530) ^{c)}	1259	1290 1322	940	970	920	(a)
Geometry (Cl_3Y)								
$R_{\text{YCl}}(\text{\AA})$	1.777	1.759	2.098	2.039	2.208	2.1655	(2.333) ^{c)}	2.3328
$\angle\text{ClYCl}$ (deg)	(107.1) ^{e)}	107.1	(100.3) ^{c)}	100.3	(98.6) ^{c)}	98.6	(97.2) ^{c)}	97.2

^{a)} Refs. [4,5].

^{b)} Not available.

^{c)} Extrapolated from related molecules from ref. [5].

^{d)} The calculated frequencies were based on a cubic spline fit to four or more data points.

^{e)} Not calculated; used experimental data from ref. [4].

is exothermic. The results are (per O atom)

$$\Delta H = 13 \text{ kcal/mol for N, } \quad \Delta H = -55 \text{ kcal/mol for P,}$$

$$\Delta H = -20 \text{ kcal/mol for As, } \quad \Delta H = -3 \text{ kcal/mol for Sb,}$$

suggesting that *phosphine oxide surface bonds* (as in (4)) are *quite likely* for such systems as InP or GaP, *arsine oxide surface bonds* are *permissible* for systems such as InAs or GaAs, but that *antimonine oxide* and *nitroxide surface bonds* are *highly unlikely* for systems such as InSb or InN. Lucovsky and Bauer [6] also have concluded from molecular symmetry comparisons of the constituent atoms Ga, In, P, As, and Sb, that oxides of the phosphide materials, GaP and InP, are likely to be more stable than those of the arsenides and antimonides

Table 2

Calculated total energies (h) and bond energies ^{a)} D_e (kcal) for Cl_3YO ($Y = \text{N, P, As, Sb}$) at HF, GVB, and GVB-CI levels

		HF	GVB-PP(4/8)	GVB-CI
$\text{Cl}_3\text{N} = \text{O}$	Total	-1507.444976	-1507.521541	-1507.592965
	D_e	-10.6 ^{b)}	6.6	47.3
$\text{Cl}_3\text{P} = \text{O}$ ^{c)}	Total	-1794.020392	-1794.072499	-1794.151848
	D_e	53.2	67.2	113.5
$\text{Cl}_3\text{As} = \text{O}$	Total	(d)	-1459.315869	-1459.399311
	D_e	(d)	33.3	81.5
$\text{Cl}_3\text{Sb} = \text{O}$	Total	(d)	-1458.564588	-1458.647449
	D_e	(d)	14.7	62.5

^{a)} Obtained as the difference in total energy between $\text{Cl}_3\text{Y} = \text{O}$ and $(\text{Cl}_3\text{Y} + \text{O } ^1\text{D})$, all carried out at a consistent level of calculation, then corrected by an experimental energy term (45.3 kcal) corresponding to the oxygen $^1\text{D} \rightarrow ^3\text{P}$ separation.

^{b)} Negative bond energy (unstable).

^{c)} Using experimental geometry.

^{d)} Not calculated.

Table 3

Comparison of the calculated bond lengths $\text{Y} = \text{O}$ for $\text{Cl}_3\text{Y} = \text{O}$ with the corresponding $\text{Y}-\text{O}$ single bond lengths (\AA)

Y	Y = O		Y-O Exper.	Change
	Theory	Exper.		
N	1.258	-	1.36, 1.41 ^{a)}	-0.10, -0.15
P	1.471	1.45 ^{b)}	1.64 ^{b)}	-0.17
As	1.576 ^{c)}	-	1.80 ^{a)}	-0.22
Sb	1.773	-	2.00 ^{b)}	-0.23

^{a)} Ref. [7].

^{b)} Ref. [4].

^{c)} This compares with the calculated $\text{As} = \text{O}$ bond distance of 1.63 \AA from ab initio calculations of the molecule H_3AsO ; see ref. [1].

Table 4
Mulliken populations for the σ and π states of Y and O atoms of the Cl_3YO molecules (z -direction parallel to the direction of the Y = O bond)

Y	Total charge		Y atom				O atom				Total π charge
	Y	O	σ charge		π charge		σ charge		π charge		
			s	p_z	s + p_z	$p_x + p_y$	s	p_z	s + p_z	$p_x + p_y$	
N	5.44 ^{a)}	8.19	1.72	1.12	2.84	2.44	1.84	1.00	2.84	3.32	5.76
P	4.35	8.52	1.24	0.76	2.00	1.62	1.83	1.40	3.23	3.26	4.88
As	3.96	8.62	1.30	0.73	2.03	1.46	1.89	1.30	3.19	3.41	4.87
Sb	3.40	8.78	1.21	0.19	1.40	1.74	1.92	0.97	2.89	3.87	5.61

^{a)} Since an ab initio potential was used for N, the two electrons of the 1s orbital have been subtracted for ease of comparison with other atoms.

and that the element of stability is a terminal O atom that participates in a donor-acceptor pair bond.

A comparison of the Y = O bonds lengths from our calculation with Y-O single bond lengths reported in the literature [4,7] is given in table 3. Generally the double bond leads to a decrease of 0.2 Å in the bond length. Our calculated value of 1.58 Å for Cl₃As = O compares with 1.63 Å for H₃As = O obtained by Barton et al. [1]. This difference is partially due to the greater electronegativity of Cl which favors π back-bonding from the oxygen.

The Mulliken populations for the Y and O atoms in both the σ (parallel to the Y = O direction) and the π (perpendicular to the Y = O direction) states of the Cl₃YO molecules are summarized in table 4. For the sequence P, As and Sb, we see a decreasing charge transfer to the oxygen, as expected from the electronegativities. However, somewhat surprising is the partition of this charge in terms of σ and π character with decreasing σ and increasing π charges on O from P, As to Sb. There is a distinct difference in the Mulliken populations for the N and O atoms pertaining to the N = O bond in comparison with those for the P = O, As = O, and Sb = O bonds. Both the σ and π states of the N atom have considerably greater population than the corresponding states of the P, As, and Sb atoms. In other words, the N atom donates considerably less charge than P, As, or Sb to the O atom, suggesting that the N = O donor-acceptor bond is considerably weaker than the P = O, As = O, and Sb = O bonds. This is consistent with the particularly weak nature of the N = O bond.

3. Computational details

The Y = O bond energy evaluation requires total energy calculations of molecules Cl₃YO, Cl₃Y (Y = P, As, Sb, and N) and the oxygen atom (¹D and ³P states). All electrons were included for N and O, while the SHC ab initio effective potentials of Rappé and co-workers [8] were used for As, Cl, and P, and the Wadt-Hay effective potential [9] was used for Sb. Normal double zeta basis sets were used for As, Cl, P, and Sb, while the Dunning-Huzinaga VDZ basis (9s5p/3s2p) sets were used for O and N. D polarization functions were used for all atoms except Cl ($\alpha_N = 0.76$, $\alpha_O = 0.95$, $\alpha_P = 0.37$, $\alpha_{As} = 0.39$, $\alpha_{Sb} = 0.27$). The polarization exponents for As and Sb were optimized with HF calculations on AsH₃ and SbH₃ for the atoms As and Sb using the effective potentials.

The bond energies of table 2 were calculated as follows. On Cl₃YO, all four valence pairs associated with the Y-O bond were correlated [GVB-PP(4/8)] and a full CI was carried out in this space (1107 spatial configurations or 1764 spin eigenfunctions). For Cl₃Y, the analogous calculation is GVB-PP(1/2). For O atom the analogous calculation is GVB-PP(2/4) on the open-shell singlet

configuration followed by a GVB-CI among the six open-shell and correlated orbitals (141 spatial configurations or 175 spin eigenfunctions). These calculations lead directly to the spin-allowed dissociation limit. This was converted to the adiabatic dissociated limit involving ground state $O(^3P)$ by using the experimental $O(^1D)-O(^3P)$ separation of 45.3 kcal/mol.

Acknowledgements

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References

- [1] J.J. Barton, W.A. Goddard III and T.C. McGill, *J. Vacuum Sci. Technol.* 16 (1979) 1178.
- [2] W.A. Goddard III, J.J. Barton, A. Redondo and T.C. McGill, *J. Vacuum Sci. Technol.* 15 (1978) 1274.
- [3] J. Stöhr, R.S. Bauer, J.C. McMenamin, L.I. Johansson and S. Brennan, *J. Vacuum Sci. Technol.* 16 (1979) 1195.
- [4] *Structural Data for Polyatomic Molecules*, Landolt-Börnstein, Vol. 7 (Springer, Berlin, 1976).
- [5] JANAF Thermochemical Tables, 2nd ed. (NSRDS-NBS-37) (National Bureau of Standards, US Government Printing Office, Washington, DC, 1971).
- [6] G. Lucovsky and R.S. Bauer, *J. Vacuum Sci. Technol.* 17 (1980) 946.
- [7] A.F. Well, *Inorganic Chemistry* (Clarendon, Oxford, 1975).
- [8] A.K. Rappé, T.A. Smedley and W.A. Goddard III, *J. Phys. Chem.* 85 (1981) 1662.
- [9] W.R. Wadt and P.J. Hay, unpublished results.