Figure 1. Upper portion of SCF-XαSW valence energy-level diagram for Pt(PH₃)₂(O₂). The highest occupied level is 7a₂.

were calculated explicitly in full self-consistent-field manner. The upper portion of the resulting valence energy-level diagram appears in Figure 1. The omitted lower portion contains only essentially unperturbed O_2 $2\sigma_g$ and $2\sigma_u$ and P 3s orbitals in the range -0.65 to -0.95 hartrees. Analysis of the character of each one-electron level yields the following conclusions.

(1) There are no levels involving significant mixing between Pt 5d and O_2 $1\pi_g$ orbitals. Of the three levels with appreciable $1\pi_g$ character, 18b₂ (an occupied level) is about 50% $1\pi_g$, 30% P 3p, and 15% Pt $6p_y$; 7a₂ (the highest occupied level) is 100% $1\pi_g$, and 19b₂ (the lowest unoccupied level) is 50% $1\pi_g$ and 50% Pt $6p_y$. There are thus the equivalent of about three $1\pi_g$ electrons in the molecule, but the only Pt orbital involved with the $1\pi_g$ orbitals is $6p_y$, empty in free Pt, and its involvement is large scale only in the lowest unoccupied molecular level. The Pt d orbitals of proper symmetry to overlap with $1\pi_g$ are $5d_{xy}$ in a₂ and $5d_{yz}$ in b₂ symmetry. They are found instead to interact with P $3p_z$ (in 5a₂ and 6a₂) and 3s orbitals (16b₂) to form major components of the Pt–P bond.

(2) Pt–O_2 bonding is accomplished through extensive mixing of O_2 $1\pi_u$ and $3\sigma_g$ orbitals with Pt mainly $5d_{z^2}$ and $5d_{z^2-y^2}$ orbitals in levels 23a₁, 24a₁, 25a₁, and 28a₁ and mixing of an O_2 $1\pi_u$ with the Pt $5d_{zz}$ orbital in levels 10b₁ and 12b₁. The $3\sigma_g$ appears comparable, not secondary, in importance to the $1\pi_u$ orbital in the a₁ levels.

(3) Phosphorus 3d orbitals make up more than 6% of total phosphorus character only in 6a₂, where the figure is 17%. As a whole this level is 50% Pt $5d_{xy}$, 30% P $3p_z$, $3d_{zz}$, and $3d_{yz}$, and 20% H 1s. The 3d orbitals thus appear to hybridize with 3s and 3p functions in small amounts to promote better overlap, rather than serving in themselves as acceptor orbitals for "back-donation."

(4) Of the levels not mentioned above, all (26a₁, 11b₁, and 17b₂) have chiefly P–H character except 27a₁, mainly Pt 6s, and unoccupied 20b₂, mainly O_2 $3\sigma_u$.

The quantitative calculations thus appear to roughly

confirm Mason's picture of a shift in O–O bonding electrons toward the metal, through mixing of O_2 $1\pi_u$ and $3\sigma_g$ with Pt orbitals, and a buildup of extra anti-bonding electron density in the $1\pi_g$ orbitals. However, the latter phenomenon apparently arises *not* through direct Pt $d\pi \rightarrow O_2$ $1\pi_g$ back-donation but in some more subtle reorganization of electrons throughout the Pt, PH_3, and O_2 components as the molecule is formed. The exact nature of such reorganization should be sensitive to the particular ligand–metal combination bound to dioxygen, and indeed O–O distances in known complexes vary from 1.30 to 1.63 Å[3]—though I am not suggesting without further study that the picture developed here applies to all such complexes. It is not necessary to invoke $d\pi \rightarrow \pi_g$ back-donation to explain the observed diamagnetism of Pt(PPh₃)(O₂), as compared to two unpaired electrons in free O_2. The presence of the platinum atom lifts the degeneracy of the O_2 $1\pi_g$ orbitals, and distributes $1\pi_g$ character among two fully occupied (18b₂ and 7a₂) levels and one unoccupied level (19b₂).

No experimental data are available for Pt(PPh₃)₂(O₂) to confirm these results. There is no reason to believe that the excellent agreement between experimental and XαSW-calculated one-electron energies observed in other cases, notably $PtCl_4^{2-}$,[8] $PtCl_3(C_2H_4)^-$,[9] and $(C_5H_5)_2Fe$,[10] should not also be found here. Further calculations on metal–dioxygen complexes are planned, in particular on Pt(PF₃)₂(O₂). The present results will be presented in more detail when contour maps of electron density in important levels have been generated.

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Molecular Beam Chemistry. Facile Six-Center Reactions of Dimeric Chlorine with Bromine and with Hydrogen Iodide

Sir:

The formation of interhalogens by exchange reactions of diatomic molecules is known to proceed rapidly in both the gas phase and in solution.[1-4] Until recently, these processes were assumed to be elementary bimolecular reactions of the "four-center" type, AB + CD → AD + BC. According to orbital symmetry arguments, such a reaction (nominally a 4n process) is

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forbidden.[5-7] Renewed experimental scrutiny has now cast doubt on the four-center mechanism for inter-halogen reactions. Schweitzer and Noyes[4] conclude that catalysis by surfaces or moisture occurs in some cases but also find evidence for a third-order reaction, $Br_2 + 2I_2 \rightarrow 2IBr + I_2$. According to orbital symmetry, this reaction (a $4n + 2$ process) is allowed as an elementary termolecular six-center reaction.

In cross-beam studies of $Cl_2 + Br_2$ and $Cl_2 + HI$ under single-collision conditions, we found no BrCl or ICl attributable to the bimolecular exchange reactions.[7] These experiments employed a supersonic "nozzle-beam" technique[8] to obtain collision energies up to $\sim$25 kcal/mol. Here we report further experiments in which large yields of interhalogens are obtained at thermal collision energies from processes that are tantamount to termolecular reactions (eq R1 and R2). The dimeric chlorine reactant is a weakly bound

$$(Cl_2)_2 + Br_2 \longrightarrow Cl_2 + 2BrCl \qquad (R1)$$

$$(Cl_2)_2 + HI \longrightarrow Cl_2 + HCl + ICl \qquad (R2)$$
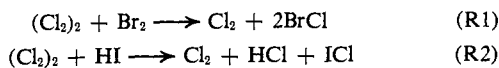
"van der Waals molecule." From gas viscosity data[9] and halogen crystal structures,[10] we estimate the dissociation energy to form $2Cl_2$ is roughly 1 kcal/mol and the equilibrium distance between centroids of the Cl_2 molecules is roughly 4.3 Å. The $(Cl_2)_2$ is generated as an "impurity" (up to $\sim$10%) in the chlorine beam by operating the nozzle source at high pressure (typically $\sim$500 Torr) and relatively low temperature ($\sim$290°K). The Br_2 or HI beam also comes from a nozzle source but in these experiments it is heated (typically to $\sim$425°K) to prevent condensation and dimer formation. The parent beams are monitored and the reaction products detected by a mass spectrometer equipped with a time-of-flight velocity analyzer.[11]

The distributions in angle and velocity of the reactive and nonreactive scattering were measured at various collision energies and compared with scattering obtained with Br_2 or HI replaced by a Xe beam. The yields of BrCl or ICl were found to be proportional to the $(Cl_2)_2$ intensity, which was varied over a 20-fold range by adjusting the nozzle operating conditions.[12] Precise estimates of the reaction cross sections are not feasible because $(Cl_2)_2$ fragments extensively in the mass spectrometer, but the cross sections are very large, probably larger than 50 Å^2.

Figure 1 shows contour maps of the reactive scattering. The BrCl from (R1) peaks sharply forwards and backwards along the initial relative velocity vector of the reactants whereas the ICl from (R2) peaks backwards with respect to the incident HI direction.[13] The Cl_2 product distribution is broad for both reactions but for (R1) it again displays forward-backward sym-
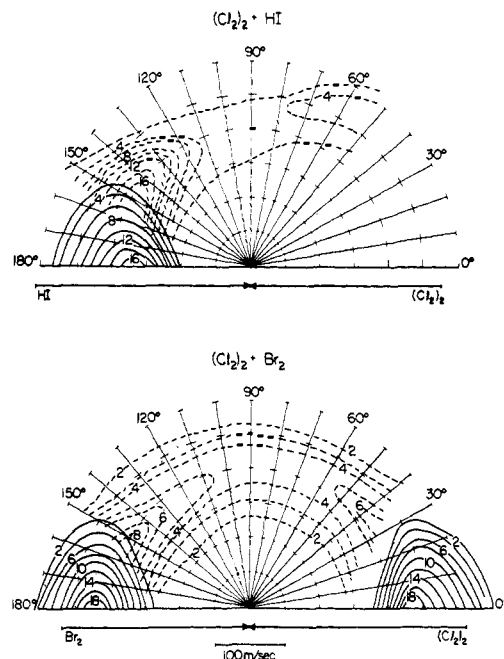

Figure 1. Polar contour maps of angle–velocity product flux distributions from reactions of $(Cl_2)_2$ with Br_2 and HI. Collision energies arc 3.0 and 2.7 kcal/mol, respectively. The coordinate system has the center-of-mass as origin; direction of incident Br_2 or HI is designated 0°, that of incident $(Cl_2)_2$ as 180°. Map has cylindrical symmetry about 0–180° axis. Solid contours pertain to BrCl or ICl and dashed contours to Cl_2 product.
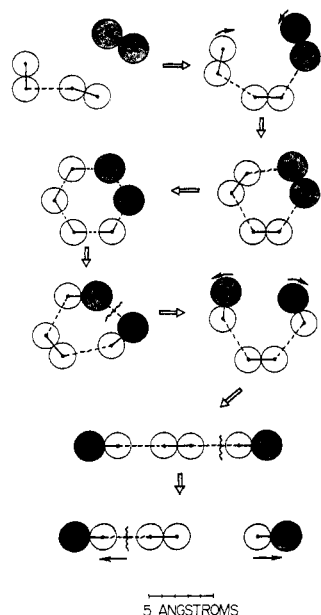
metry and for (R2) predominantly backward scattering. These Cl_2 data had to be derived indirectly. The velocity spectra of Cl_2 scattering shows prominent angle-dependent structure which appears to contain three components: (i) a high velocity peak from elastic scattering of the parent beam; (ii) a low velocity peak from collisional dissociation of $(Cl_2)_2$ or its fragmentation in the detector; and (iii) an intermediate peak which probably comes mostly from the Cl_2 released in the reaction. Components (i) and (ii) appear to be nearly unchanged but (iii) disappears when the surrogate Xe beam is used. Thus we evaluated the Cl_2 reactive scattering by deducting the Xe data. Regions where (i) becomes too large (gaps in Figure 1) are inaccessible to this method, but elsewhere the results show good internal consistency for numerous runs.

The forward–backward symmetry of the reactive scattering for (R1) might be attributed either to statistical dissociation of the collision complex[14] or to recoil of the two BrCl molecules in opposite directions. The latter appears more likely, in view of the marked asymmetry found for (R2). Experiments at higher collision energy give further evidence for the nonstatistical character of these reactions. The total kinetic energy (relative to the center-of-mass) of the three product molecules from (R1) and the two detected products from (R2) is found to be comparable to the reactant collision energy throughout the range studied, from $\sim$2 to 12 kcal/mol.[15]

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(11) J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.*, **56**, 769 (1972).
(12) The dimer content varies drastically with nozzle temperature. Small amounts of trimer (roughly tenfold less than dimer) were also observed but show markedly different dependence on nozzle temperature and pressure than the product yields.
(13) The HCl product was not detectable because the feasible mass resolution was inadequate to distinguish HCl$^+$ from a large Cl$^+$ background. Also, the HCl is likely to have high velocity (*cf.* ref 15), which weakens the signal.

(14) W. B. Miller, S. A. Safron, and D. R. Herschbach, *J. Chem. Phys.*, **56**, 3581 (1972).
(15) The kinetic energy thus accounts for most of the available energy for reaction R1, which is almost thermoneutral. However, reaction R2 is exoergic by $\sim$20 kcal/mol and hence energy balance requires that most of the exoergicity goes into internal excitation of the products or kinetic energy of the undetected HCl product.

Figure 2. Schematic reaction sequence for $(Cl_2)_2 + Br_2$, illustrating the formation of van der Waals bonds (shown dashed), six-center exchange, and three successive bond scissions.

Figure 2 outlines the reaction sequence we infer from the scattering data. The sharp peaking of the BrCl and ICl angular distributions shows these molecules are emitted with very high centrifugal angular momentum; the broader distribution of Cl_2 shows it emerges with lower centrifugal momentum.[14] These properties indicate a chain structure for dissociative configurations of the reaction complex, $X-Cl \cdots Cl-Cl \cdots Cl-Y$. This presumably results from quick scission of the $X \cdots Y$ bond as the complex traverses a cyclic configuration.[16] The nonstatistical character of the reactive scattering indicates that at least one of the two weak $Cl \cdots Cl$ bonds also breaks quickly (within $\gtrsim 10^{-12}$ sec). The comparable velocities found for the Cl_2 and the $X-Cl$ products suggest that the second $Cl \cdots Cl$ bond persists longer, at least until $X-Cl \cdots Cl-Cl$ and $Cl-Y$ separate sufficiently to approach their asymptotic exit translational momenta (equal and opposite). For (R1) the first $Cl \cdots Cl$ bond to break might be either one. For (R2) the asymmetry of the Cl_2 distribution indicates it is usually the bond which releases HCl and $ICl \cdots Cl_2$. There is some Cl_2 corresponding to the opposite case, however, and this portion (at right in Figure 1) shows higher velocities consistent with the different mass distribution of the initial fragments (ICl and $HCl \cdots Cl_2$). Several aspects of the data thus offer evidence that three sequential bond scissions can be resolved in these single-collision experiments.

Few reaction mechanisms have postulated termolecular processes involving molecules rather than atoms, radicals, or ions. Apparently only two such examples are known with near-zero activation energies, reactions involving two nitric oxide molecules with oxygen and with halogens, and participation of van der Waals mole-

(16) Velocity spectra of $(Cl_2)_2$ scattered by Br_2 or HI without reaction show a very large inelastic component. Much of this may come from break-up of the six-atom complex to re-form the reactants, as an initial $Cl-Cl \cdots Cl-Cl \cdots X-Y$ chain complex probably often fails to attain the cyclic configuration.

cules is suspected.[17] Potential surface calculations show a termolecular hydrogen reaction *via* H_6 is possible and indicate it would involve coupling H_2 to an H_4 chain.[18] Our results suggest that many analogous six-center reactions may be found by exploiting the nozzle-beam technique.

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Oxidation of Diazo Compounds with Singlet Oxygen. Formation of Ozonides

Sir:

As part of our continuing studies of the mechanism of ozonolysis[1] we earlier reported[2,3] that ozonides can be prepared by photooxidizing diazo compounds in the presence of aldehydes. The formation of ozonides in such cases was interpreted as involving the reaction of a carbonyl oxide, or Criegee[4] zwitterion, with the excess aldehyde present. The zwitterion was seen as arising from the reaction of a methylene with ground state oxygen.[2,3] This method has also been extended to cases where either the aldehyde or the oxygen is enriched with ^{18}O and has provided[5] information which is extremely valuable to the problem of the mechanism of ozonolysis. The method used in these earlier reports was successful only for diaryl-substituted diazo compounds, and thus the usefulness of this approach to our ozonolysis mechanism studies was somewhat limited.

We now wish to report that diazo compounds can be converted to ozonides by allowing them to react with singlet oxygen in the presence of aldehydes. The reaction is observed with both aryl and alkyl diazo compounds and can be used to produce ozonides capable of existing as stereoisomers.

In a typical reaction 5.0 mmol of diphenyldiazomethane in acetonitrile solution containing 4 ml of a Methylene Blue stock solution[6] and 20 mmol of benzaldehyde were photolyzed using a General Electric DWY 650-W lamp operated at 50 V. The reaction mixture was worked up by removing solvent, washing with sodium bisulfite to remove excess benzaldehyde, and analyzing the residue by thin-layer chromatography. The major products were triphenylethylene ozonide (26% yield) and benzophenone (67% yield). Using a similar procedure the photosensitized oxidation of isopropyldiazomethane in the presence of isobutyraldehyde and of phenyldiazomethane in the presence of

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(5) R. W. Murray and D. P. Higley, *J. Amer. Chem. Soc.*, **95**, 7886 (1973).
(6) The stock solution of Methylene Blue was prepared by dissolving 10 mg of Methylene Blue in 10 ml of methylene chloride.