tonate (**5**) with OH^- as the nucleophile.[7,8] The rates of CH_3O^- appearance are comparable for **1** ($k = 3.2 \pm 0.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and **2** ($k = 1.8 \pm 0.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), while for **3**, **4**, and **5**, alkoxide appearance was too slow for us to measure[9] ($k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}).

Under the conditions of our experiments, only products of exocyclic cleavage of the esters are observable. Ring opening would lead to a vibrationally excited ion-molecule adduct which would probably not live long enough to be collisionally stabilized at these low pressures (10^{-6} Torr). It is significant that both the cyclic and acyclic rates are low (by about an order of magnitude) compared with collision rates. This suggests the existence of a barrier somewhere along the potential surface.[10]

Alkaline hydrolysis of cyclic phosphinate esters is slow in solution, and, similarly, the rate of reaction of OH^- with **4** is too slow for us to measure in the gas phase. Here the pentacoordinate intermediate required for exocyclic cleavage is energetically unfavorable because it places an alkyl group in an apical position. Reaction of **3** in solution leads to fast ring opening but slow exocyclic cleavage. In agreement with solution work, the rate of reaction of **3** to give exocyclic product is also slow in the gas phase. In this case, although the initial pentacoordinate intermediate should be formed easily, pseudorotation to the intermediate in which CH_3O is in an apical position is energetically unfavorable because it simultaneously places an alkyl group in an apical position.[11,12] Alkaline hydrolysis of **2** in solution gives very fast ring opening and moderately fast exocyclic cleavage. In agreement with these results, **2** is the only one of the cyclic esters investigated whose exocyclic cleavage is fast enough for us to measure. Here, both the initial pentacoordinate intermediate and that formed after pseudorotation have oxygen atoms in apical positions, thus making the necessary intermediates (and transition states) readily accessible.

Interestingly, alkaline solution hydrolysis of **1** is much slower than exocyclic cleavage of **2**, whereas in the gas phase the rates are comparable. In both gas phase and solution, relief of strain in **2** should accelerate reaction. In solution ring opening is much faster than pseudorotation, indicating a measurable barrier to pseudorotation. In the gas phase, the intermediates are energetically activated,[10] and return to reactants (loss of OH^-) with its large A factor is faster than pseudorotation. Apparently the pseudorotation barrier superimposed upon the strain relief acceleration results in a rate comparable with that in the acyclic system.

In conclusion, we believe that the general picture proposed to explain solution hydrolysis rates in phosphorus esters[5] is applicable to the gas phase as well. The remarkable agreement suggests that differential behavior of the potential surface after nucleophilic addition has occurred is not dramatically affected by solvation.

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(7) Commercial $(CH_3O)_3PO$ (Aldrich) was purified by distillation. Compounds **2** and **5** were kindly provided by Professor Westheimer. **3** and **4** were prepared according to A. Eberhard. Ph.D. Thesis. Harvard University, 1965. OH^- was formed from H_2O at 5.2 eV (electron energy minus trapping voltage). After complete formation of OH^-, its decay and the growth of the corresponding alkoxide ions were monitored as a function of time. Neutral pressures were measured on an ionization gauge calibrated against an MKS Baratron capacitance manometer for each neutral sample.
(8) Rate constants are uncorrected for ion loss. Errors are standard deviations for 10 experiments. The absolute accuracy is not better than a factor of 2.
(9) This is the lower limit for reactions which we are normally able to observe. In the reaction with **5**, $C_2H_5O^-$ and $C_2H_3O^-$ were sometimes observed, but we could not obtain any consistent data on the rates. These ions may arise from reactions of neutrals produced from pyrolysis on the filament.
(10) For examples of other classes of ion-molecule reactions where barriers have been found and a general description of these phenomena, see W. E. Farneth and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 7891 (1976); W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 4219 (1977).
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(12) Endocyclic cleavage followed by reclosure could result in an appropriate intermediate for loss of CH_3O, but this apparently does not occur.
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Sulfur 2p Photoelectron Spectrum of Blue Copper Proteins. Comment on Papers by Solomon et al. and Peeling et al.

Sir:

The sulfur 2p region in x-ray photoelectron spectra of plastocyanin and some other blue copper proteins has a strong component at 5-eV higher binding energy (HBE) than the main line.[1-3] The apoplastocyanin does not show a similar HBE line and Solomon et al. therefore suggested that one of the sulfurs (the cysteine sulfur) was bonded to a copper(II) ion.[1] Peeling et al. pointed out that a 5-eV shift is too large to be caused by coordination to a transition metal ion[2] and suggested that the HBE line was due to oxidized sulfur present in the preparations, a conclusion also reached by Rupp and Weser.[4] Peeling et al. also argued that the integrated sulfur 2p intensity had a correct magnitude compared to the nitrogen 1s line only if the S 2p HBE line was omitted in the integration. In a reply, Solomon et al. rejected, however, the possibility of sulfates or other impurities.[3]

Since it is quite unreasonable to expect a 5-eV chemical shift, I would like to suggest as another possible source for the HBE line a charge-transfer satellite which appears because of the bonding to a transition metal ion. The conclusions made by Solomon et al.[1,3] would then be correct although based on a less probable interpretation of the spectrum.

Let us write the valence hole orbital as

$$\varphi = \sin \eta \, u_{Cu} + \cos \eta \, u_S \qquad (1)$$

where u_{Cu} and u_S are Cu 3d and S 3p orbitals and $\sin \eta$ and $\cos \eta$ coefficients. We disregard for simplicity the overlap between u_{Cu} and u_S. $\eta = 90°$ corresponds to the completely ionic case $Cu^{2+}S^{2-}$ and $\eta = 0°$ to $Cu^{+}S^{-}$. After ionization from S 2p the valence electrons flow toward S which means that the valence hole is now more localized on copper than before ionization. Thus if

$$\varphi' = \sin \zeta u_{Cu} + \cos \zeta u_S \quad (2)$$

is the new valence hole we should have $\zeta > \eta$. The orthogonal complement to φ' is φ'':

$$\varphi'' = -\cos \zeta u_{Cu} + \sin \zeta u_S \quad (3)$$

Using eq 2 and 3 we may write eq 1 as

$$\varphi = \cos (\zeta - \eta) \varphi' + \sin (\zeta - \eta) \varphi'' \quad (4)$$

According to the sudden approximation[5] a satellite appears corresponding to φ'' with an intensity proportional to $\sin^2 (\zeta - \eta)$.

Let us compare to the case when the ligands are O^{2-} or F^-. η should here be close to 90° since the bonding is fairly ionic. ζ should be even closer to 90° and therefore $\zeta - \eta$ will be very small. Thus, if the ionization is done in O 1s or F 1s, it is not likely that any satellite will appear. If the ionization is done in Cu 2p on the other hand, the valence electrons will be attracted to the Cu 3d orbital and the hole to S 3p. Thus $\zeta \ll \eta < 90°$, and a satellite appears.[6] It is likely that the satellite will be smaller the smaller η and that is the more covalent the bond between Cu and the ligand. This is in agreement with experiments.[4,7,8] In particular, complexes with sulfur ligands have very weak Cu 2p satellites[8] which thus may be explained by the large covalency of the Cu-S bond, known in a number of Cu-S complexes.[9]

In a covalent case with η much smaller than 90° it may be possible to have a satellite also to the anion inner-shell lines, since it is possible to have $\zeta - \eta$ significantly different from zero. An S 2p satellite is thus possible. Such a satellite has been found for the diethyl dithiocarbamate complex with Cu(II) although of weak intensity.[8] In many other cases with Cu-S bonds it is apparently very hard to decide whether Cu(II) has been reduced to Cu(I). In the latter case the hole orbital φ is filled and no strong satellites will appear either at Cu 2p or S 2p.

In any case, satellites are theoretically possible for inner-shell ionization from S^{2-} contrary to the case for F^- or O^{2-}. One may certainly not exclude the possibility that the HBE line in Cu and Co plastocyanin is a satellite and therefore indicative of Cu-S bonding. It is hard to decide from the XPS spectrum whether methionine or cysteine sulfur is involved.

The model with a delocalized hole ($\sin \eta \ll 90°$) has earlier been suggested by Blumberg and Peisach[10] and by Sugiura et al.[9] to explain ESR data. It is also in substantial agreement with calculations on $MeS_4{}^{6-}$ clusters with Me = Cu, Ni, Co, and Fe.[11] The latter calculations also suggest that an allowed charge-transfer transition ($1t_1 \rightarrow 5t_2$) should appear in the visible region when S is a ligand to Cu. The transition energy for the corresponding Co-S complex should be larger by a factor of 2-3. This gives some support to the current interpretation of the strong absorption line in the blue copper proteins.[12]

The absence of a satellite to Cu 2p in a compound which has proven to correspond to Cu^{2+} by EPR may be regarded as an anomaly. According to the model presented above a satellite should be weak only when the hole φ is considerably delocalized to the ligand already before Cu 2p ionization. This can happen only if at least one of the ligands has a large donating power. Absence of a Cu 2p satellite may thus be regarded as strong support for a Cu-S bond.

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Kinetic Evidence for the Template Effect of Added Cations on the Rate of Formation of Benzo-18-crown-6 in Water Solution

Sir:

The possibility that certain cations facilitate the formation of many-membered rings has been ascribed to a template effect,[1] which presumably operates by complexing the open-chain precursor(s) prior to ring formation and organizing the latter in a conformation close enough to the ring being formed. Convincing evidence of the operation of the template effect in crown ether syntheses has been presented,[2] as based on sets of comparative yields. However, any kinetic information on these reactions is missing, as is any quantitative estimate of the energetic factors involved in this most interesting type of catalysis, implying a crucial interaction of the host-guest type.[3]

Being currently engaged in a systematic study of the energetics of ring-closure reactions,[4] we have undertaken a kinetic investigation on the effect of added cations on the rate of formation of benzo-18-crown-6 (**4**). To isolate the cation effect in the cyclization step, and to avoid any kinetic interference from the intermolecular nucleophilic substitution leading to the crown's precursor (**1**), we have not followed the "shotgun" approach in the construction of **4**, i.e., the reaction of catechol with the proper α,ω-dihalopolyoxa compound in the presence of base. Rather, o-hydroxyphenyl-3,6,9,12-tetraoxa-14-bromotetradecyl ether (**1**) was synthesized first,[5] and then subjected to base-promoted cyclization to **4** in the presence of a variety of added alkali and alkali-earth metal cations in water solution at 50 °C. In view of its far too large size for a good fit into the cavity of **4** (or of its ring-shaped precursor), Et_4N^+ cation was used as a reference. In the runs with the monovalent cations 0.022 M $Et_4N^+OH^-$ was present, and the cation was added as the bromide. The divalent cations were added as the hydroxides up to concentrations close to saturation. The concentration of the substrate was in the order of 2×10^{-4} M, i.e., sufficiently low as to let any contribution of the second-order dimerization be negligible.[6] In all experiments the conversion of **1** to **2** was complete, so that corrections for incomplete dissociation were unnecessary. The kinetics were followed spec-