The crystals are cubic with one molecule per unit cell, a = 12.22 A, and of space group symmetry $P\bar{4}3m$. Three-dimensional X-ray data were collected with a precession camera using Mo Kα radiation. A Patterson synthesis provided coordinates for all atoms of the asymmetric unit ($CuOClOPC_6H_5$) except the atoms of the phenyl group; an electron density synthesis then revealed the carbon atom positions, some of which were disordered. Subsequent least-squares refinement yielded a final discrepancy factor, R, of 10%. Details of the structure determination will be published elsewhere.

The structure of the cluster is shown in Figure 1; triphenylphosphine oxide is represented by L in the figure. The central oxygen is at the center of a tetrahedron of copper atoms with a Cu–O distance of 1.90 A. Between each pair of copper atoms, there is a bridging chlorine atom with a Cu–Cl distance of 2.38 A; the six chlorine atoms form an octahedron around the central oxygen. Attached to each copper and completing a slightly distorted trigonal bipyramid around the copper is the oxygen of a triphenylphosphine oxide with a Cu–O distance of 1.89 A; the Cl–Cu–O(P) angle is 95°, indicating that the copper is displaced slightly from the trigonal plane of chlorine atoms. The space group symmetry requires a linear arrangement of the O, Cu, O(P), and P, and the bond angle at the oxygen of the phosphine oxide is, thus, 180°. The Cu–Cu distance of 3.11 A is too large for direct metal–metal bonding.

Although some interaction through the oxygen was expected, the magnetic moment of 2.21 BM is normal[2] and no interaction is apparent.

The spectrum in the visible and near-infrared region was obtained for a mull and for an acetone solution; there was little difference in the two, suggesting that the cluster also exists in acetone solution. The spectrum shows a broad absorption band at *ca.* 11,000 cm^{-1}. This is shifted slightly from the position found for the trigonal bipyramidal $CuCl_5{}^{3-}$ ion[3,4] (*ca.* 10,000 cm^{-1}); the direction of the shift is consistent with the stronger ligand field effect of oxygen as compared to chlorine.

The P–O stretching frequency (1194 cm^{-1}) is considerably higher than that found for other complexes of triphenylphosphine oxide.[5] The linear P–O–Cu arrangement found for this compound results in better overlap of the phosphorus and copper d_{xz}, d_{yz} orbitals with the p_x, p_y orbitals of oxygen and, thus, allows more transfer of electron density to phosphorus than is possible when the P–O–M arrangement is bent, as in $[(CH_3)_3PO]_2Co(NO_3)_2$.[6]

The source of the central oxygen in the preparation of the compound has not been established, but it probably comes from small amounts of water present in the system. The compound can also be prepared from $CuCl_2$, CuO, and triphenylphosphine oxide in either methanol or nitromethane. A stoichiometric amount of CuO was added, but in all preparations some solid CuO remained unreacted.

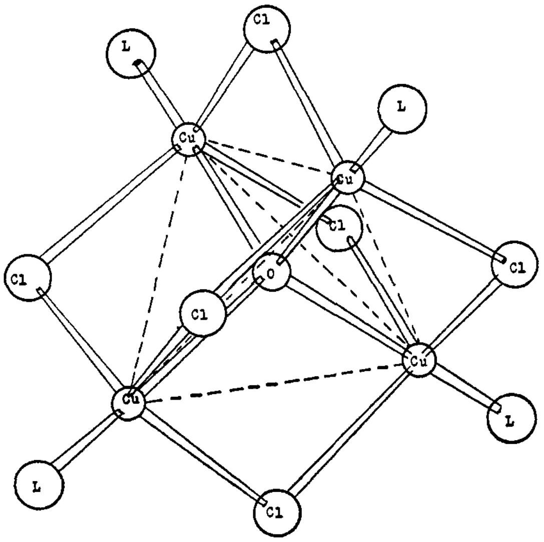

Figure 1. Perspective drawing of the structure of μ_4-oxo-hexa-μ-chloro-tetrakis[(triphenylphosphine oxide)copper(II)]. L represents a triphenylphosphine oxide group.

To investigate the possibility of forming related complexes with the formula $Cu_4OCl_6L_4$ (where L represents a monodentate ligand), $(CH_3)_4NCl$ was added to a methanol solution of $CuCl_2$ which had been refluxed with CuO for 24 hr; deep red crystals of $[(CH_3)_4N]_4Cu_4OCl_{10}$ were obtained. *Anal.* Calcd for $Cu_4Cl_{10}ON_4C_{16}H_{48}$: Cu, 27.58; Cl, 38.48; C, 20.85; H, 5.26. Found: Cu, 27.77; Cl, 38.10; C, 21.00; H, 5.22.

The spectral and magnetic properties of this compound are very similar to those of the triphenylphosphine oxide complex, and a similar cluster, with chlorides replacing the triphenylphosphine oxide groups, is probably present. The crystals are also cubic, but a much larger unit cell was found (a = 19.04 A). The structure of this compound is presently being investigated.

Investigations of related copper compounds are in progress; attempts to prepare similar compounds of other transition metals have been unsuccessful but are also continuing.[6a]

Acknowledgment. This work was supported by the National Science Foundation under Grant No. GP 3826. The help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is gratefully acknowledged.

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(2) E. A. Boudreaux, *Trans. Faraday Soc.*, **59**, 1055 (1963).

(3) P. Day, *Proc. Chem. Soc.*, 18 (1964).

(4) W. E. Hatfield, H. D. Bedon, and S. M. Horner, *Inorg. Chem.*, **4**, 1181 (1965).

(5) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

(6) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

(6a) NOTE ADDED IN PROOF. The structure of a magnesium compound, $Mg_4OBr_6(C_4H_{10}O)_4$, with a similar cluster has been reported by G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4821 (1964).

(7) Alfred P. Sloan Research Fellow, 1966–1968.

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Concerning Structural Limitations in the Relationship between Trityl Cation Stability and Reactivity[1]

Sir:

The very rapid reaction rates of unstable carbonium ions with nucleophiles has limited our knowledge of their reactivities to (1) relative rates or (2) solvolysis

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(1) This research has been supported in part by the National Science Foundation.

Table I. Activation Parameters for the Reaction of *para*-Substituted Trityl Cations with Water

Trityl cation	log k_f, sec^{-1}	pK_{R^+}	ΔH^*, kcal ±0.5	ΔS^* ±2, eu	Temp, °C
Tris-p-N(CH$_3$)$_2$	−4.32 ± 0.10	+9.36	. . .	. . .	. . .
Bis-p-N(CH$_3$)$_2$	−3.48 ± 0.05	+6.92	15.6	−23	0–55
p-N(CH$_3$)$_2$	−2.02 ± 0.07	+3.88	13.4	−24	0–32
Tris-2,4-di-OCH$_3$	+0.31 ± 0.03	+3.28	. . .	. . .	. . .
Tris-p-OCH$_3$	+1.11 ± 0.03	+0.82	8.1	−27	1–33
Bis-p-OCH$_3$	+1.98 ± 0.07	−1.14	5.4	−30	1–30
p-OCH$_3$	+3.0 ± 0.3	−3.4	. . .	. . .	. . .

rates, generally of halides or sulfonate esters, in which the carbonium ion is presumed to be formed in a rate-determining step.[2] Implicit in many discussions of these latter reactivities has been the notion that the solvolysis rates are close measures of the stabilities of the cations.

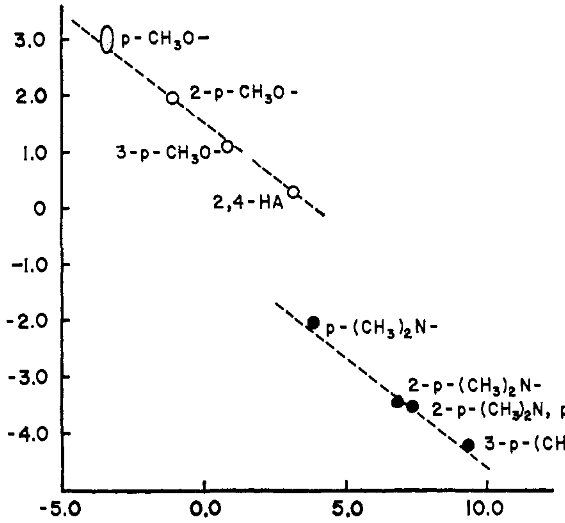

Figure 1. Rate *vs.* equilibrium for the reaction of *para*-substituted trityl cations with water. Numbers preceding the designated *para* substituent indicate the number of rings substituted; 2,4-HA = tris-2,4-dimethoxy. Ordinate, log k_f, H$_2$O, 25°; abscissa, pK_{R^+}, H$_2$O, 25°.

We wish to report the results of measurement of the rate constants for the reaction with water of a series of *para*-substituted triphenylmethyl (trityl) cations of widely varying stability. In Figure 1 the logarithm of the pseudo-first-order rate constant for the cation reacting with water is plotted *vs.* the corresponding pK_{R^+} value.[3] The results in Figure 1 show that *there are important and severe structural limitations in linear relationships between cation stabilities* (*equilibria*) *and their reactivities* (*rates*). It is probable from the structures involved that the dispersion may not be attributed to differing steric requirements at the central carbon atom.

The reaction rates for the slower reacting ions have been obtained by the conventional ultraviolet spectrophotometric method, and agreement with previous results (where comparison is possible) is satisfactory.[4] The rate constants for the rapidly reacting cations have been obtained by the use of a stop-flow reactor of the Hartridge–Roughton type.[5] Aqueous solutions of acid and carbinol (or trityl fluoroborate) were flowed together and the pseudo-first-order rate constant, k_f, was obtained from the rate of reestablishment of the carbinol–carbonium ion equilibrium.[3]

$$R^+ + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ROH + H^+$$

$$\ln\left(\frac{X_e}{X_e - X_t}\right) = k_{obsd}t$$

where X = concentration of R$^+$ reacted and $k_f = k_{obsd}/(1 + h_R/K_{R^+})$. The rate constant k_f is strongly medium sensitive, being sharply reduced by the presence of either electrolytes or nonelectrolytes. The values of k_f given in Figure 1 have been obtained by extrapolation to zero acid concentration. The acid dependence of the rate constant will be the subject of a subsequent full report of this work.

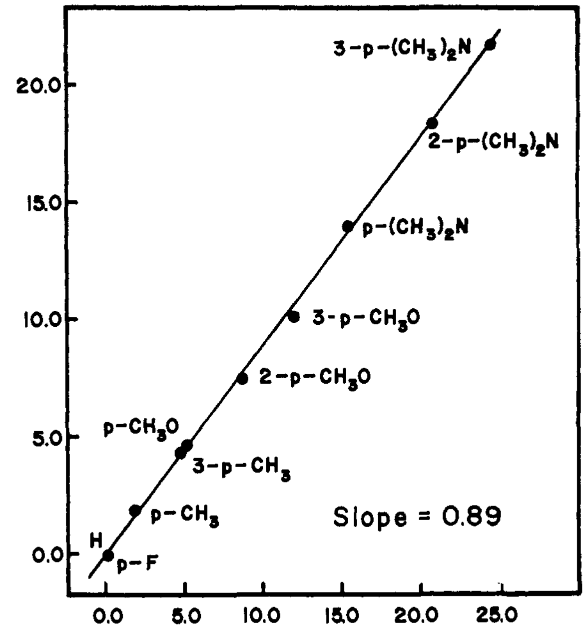

Figure 2. Equilibrium linear free energy relationship for *para*-substituted trityl cations. Ordinate, $f_R\Delta F°$, H$_2$O, 25°, for carbinol ionization; abscissa, $f_R\Delta F°$, CH$_3$CN, 25°, for ethane oxidation.

Ranges of 10 kcal in the free energy of activation and 18 kcal in the standard free energy of ionization are encompassed by the data of Figure 1. It is abundantly clear that no single (even crude) linear free energy relationship between rate and equilibrium (for the same reaction) prevails. In Table I are listed activation parameters which have also been obtained. The near-

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(2) *Cf.* A. Streitwieser, Jr., *Chem. Rev.* **56**, 571 (1956).

(3) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955).

(4) E. F. J. Duynstee and E. Grunwald, *ibid.*, 81, 4542 (1959).

(5) *Cf.* G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

constancy of the entropies of activation for rate constants differing by about five orders of magnitude is suggestive (but certainly not conclusive) that a single mechanism, presumably the direct bimolecular attack of water at the central carbon atom, is involved.

The results of Figure 1 are the more remarkable in light of the relatively precise (equilibrium) linear free energy relationship which has been obtained for these *para*-substituted trityl cations between $\mathrm{p}K_{\mathrm{R}^+}$ values and corresponding log $K_{\mathrm{R\text{-}R}}$ values for the reaction

$$\mathrm{R^+ + 0.5(R_0\text{-}R_0) \rightleftharpoons R_0^+ + 0.5(R\text{-}R)}$$

The log $K_{\mathrm{R\text{-}R}}$ values have been obtained from emf cell measurements in acetonitrile solution.[6] Figure 2 illustrates this linear free energy relationship. Linear free energy relationships between rate and equilibria for analogous reactions (rather than for the same reaction as in Figure 1) have also been previously reported, but the ranges of cation structures have been limited.[7]

It is apparent from the dashed lines (slope 0.5) drawn in Figure 1, for example, that structurally limited linear free energy relationships may exist (the lines shown are not the only existing possibilities).[8] Further work is in progress to define the structural considerations relevant to rate *vs.* equilibrium in this reaction. However, the results in Figure 1 do suffice to support the general conclusion that, in the absence of collaborating evidence, arguments regarding cation stability based upon solvolysis rates (k_{r} corresponds to such a process) should be regarded as tenuous.

Acknowledgment. The authors wish to acknowledge the helpful assistance of Dr. N. Sutin of the Brookhaven National Laboratory in the use of his stop-flow reactor for conducting preliminary rate measurements.

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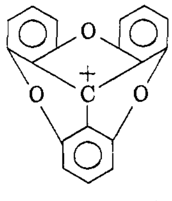
(6) (a) E. D. Jenson and R. W. Taft, *J. Am. Chem. Soc.*, **86**, 116 (1964); (b) R. W. Taft and L. D. McKeever, *ibid.*, 87, 2489 (1965); (c) Ph.D. Thesis of L.D. McKeever, University of California, Irvine, Sept 1966.

(7) (a) N. C. Deno, G. Sains, and M. Spangler, *J. Am. Chem. Soc.*, **84**, 3295 (1962); (b) N. Lichten, *Progr. Phys. Org. Chem.*, 1, 75 (1963); (c) R. Ginter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 882 889 (1964); (d) H. Dauben Jr., private communication.

(8) As drawn in Figure 1, the cations with only oxygen substituents react about *two powers* of ten faster than nitrogen-substituted cations of equal $\mathrm{p}K_{\mathrm{R}^+}$. We have also noted that the Martin cation



(J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, **84**, 2252 (1964)), of very similar $\mathrm{p}K_{\mathrm{R}^+}$ (+9.05) to that of crystal violet, reacts with water 4.3 log units faster.

(9) Taken in part from the Ph.D. Thesis of R. A. Diffenbach, The Pennsylvania State University, Sept 1966.

(10) Grateful acknowledgment is made to the Fuji Photo Film Co., Ltd., Kanagawa, Japan, for support of K. S. during the period of this research at The Pennsylvania State University.

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The Mechanism of the Chromic Acid Oxidation of Ketones. Kinetic Proof for an Enol Intermediate

Sir:

Several groups of investigators have suggested that the chromic acid oxidation of a ketone proceeds *via* an enol intermediate.[1-3] However, until now no conclusive experimental evidence for this view has been offered. Mechanism 1

$$\text{ketone} \underset{k_{\mathrm{K}}}{\overset{k_{\mathrm{E}}}{\rightleftharpoons}} \text{enol} \xrightarrow[k]{\mathrm{CrO_3}} \text{product} \tag{1}$$

leads to the rate expression 2

$$\frac{-\mathrm{d}[\mathrm{CrO_3}]}{\mathrm{d}t} = \frac{k_{\mathrm{E}}k[\text{ketone}][\mathrm{CrO_3}]}{k_{\mathrm{K}} + k[\mathrm{CrO_3}]} \tag{2}$$

where k_{E}, k_{K}, and k are the rate constants for enolization, ketonization, and oxidation, and [ketone] and $[\mathrm{CrO_3}]$ denote the total analytical concentrations of the ketone and of hexavalent chromium, respectively.

Rate eq 2 predicts a change from rate-limiting oxidation to rate-limiting enolization when $k[\mathrm{CrO_3}]$ becomes much larger than k_{K} and, consequently, a change from first- to zero-order dependence in hexavalent chromium. Furthermore, the limiting oxidation rate should be of the same order and very approximately of the same magnitude as the rate of enolization.[4] However, none of the previously investigated chromic acid oxidations of ketones exhibited zero-order kinetics. In the case where enolization and oxidation rates were compared,[3] the enolization was found to be considerably faster.

We found now two ketones, isobutyrophenone and 2-chlorocyclohexanone, in which the relative rate of oxidation to enolization is favorable enough to allow the observation of the predicted change in the rate-limiting step. Figure 1 shows the dependence of the initial oxidations rates[5] (corrected for unit ketone concentration) as a function of the analytical concentration of chromic acid. Both curves demonstrate clearly the change from first- to zero-order dependence as required by the above mechanism. Furthermore, the oxidation rates reach a value of about 0.67 of the enolization rate for isobutyrophenone[6] and of approximately 2.2 for 2-chlorocyclohexanone. Both of these findings are fully in accord with the kinetic consequences of eq 2

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(1) E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, **80**, 211 (1958).

(2) K. Umeda and K. Tarama, *Nippon Kagaku Zasshi*, **83**, 1216 (1962).

(3) P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 822 (1962).

(4) The reason why only a similarity and not an exact identity of enolization and oxidation rates can be expected lies in the different units used to measure the rate of the two reactions. While enolization rates are expressed in changes of the concentration of the ketone in a unit of time, oxidation rates use out of necessity changes in the concentration of the oxidant. The two scales can be interconverted only if the exact stoichiometry of the oxidation reaction is known. The oxidation rate will be two-thirds of the enolization rate if only one oxygen atom is consumed for each molecule of ketone which has reacted; it will be 1.3, 2.0, 2.7, etc., times higher than the rate of enolization if an average of two, three, four, etc., oxygen atoms is used to oxidize the ketone to stable oxidation products.

(5) The rates were measured spectrophotometrically in a thermostated cell holder of a Carl Zeiss PMQ II spectrophotometer at 350 mμ.

(6) Enolization rates were determined from bromination studies under the assumption that only the monobromo derivative is formed in the presence of excess ketone. Bromination rates were measured spectrophotometrically; very good zero-order plots were generally obtained.