Another criterion which must be satisfied before the catalytic cycle can be closed is that both k_2 and k_3 must be large compared to the rate at which the metal ion M may be reduced to metal by the strongly reducing ligands.

The unusual reaction which allyl chloride and allyl acetate undergo, reduction to propylene, has been the subject of some speculation. Eaborn has suggested that the catalyst may promote the normal ability of silicon hydrides to reduce organic halides.[18] Speier has suggested that reduction results from an unusual addition to the double bond to give β-acetoxyalkylsilanes which yield propylene by β-elimination.[4a] While silane addition in this sense is unusual, it is evident from the above mechanism that hydride addition must occur in this less favored manner to give a secondary carbanion in order to give rise to isomerization in terminal olefins. Following hydride addition to allyl chloride or acetate to give a secondary carbanion, it is only necessary to eliminate chloride or acetate ion to give propylene. Thus propylene and the silyl chloride or acetate could result without the necessity of ever forming β-acetoxyalkylsilanes. That it is the addition to the double bond of allyl chloride in the less-favored sense which leads to the formation of propylene may be inferred from recent work by Speier.[4d] Thus, trichlorosilane-d gave 3-chloropropyl-2-d_1-trichlorosilane, but also propylene-3-d_1, on treatment with allyl chloride.

The mechanism proposed in eq. 4 requires that a catalyst be capable of the following.

(a) Activation of the silane (Si–H bond cleavage). This is probably the least critical requirement since a large number of transition metal ions react readily with silanes,[19] a larger number, for example, than those which activate hydrogen.

(b) Activation of the olefin. By this we imply the weakening of the C=C bond resulting from coordination. This is particularly marked for Pt(II).[20] Phosphine complexes of Pt(II) and Ir(I) which satisfy requirements (a) and (c) are ineffective as catalysts, presumably because of the inability of the olefin to coordinate.

(c) Resistance to destructive reduction of the metal ion. Palladium complexes are in general readily reduced to the metal by silicon hydrides even in the presence of excess olefin. This is at least one cause of their inability to catalyze homogeneous hydrosilation reactions. The dark color of reaction mixtures and the decline in catalyst activity observed with the platinum(II)–trialkylsilane system are also presumably due to irreversible reduction of the catalyst.

The square-planar to octahedral transformation required by the proposed mechanism is particularly satisfied by the d^8 ions of group VIII, and the exceptional activity of platinum and rhodium ions may be in part due to this effect.

Finally, it should be pointed out that the mechanism proposed for this reaction is of the same general type as that proposed for Ziegler catalysis, the "Oxo" reaction, and many other reactions of unsaturated compounds catalyzed by transition metal ions. The similarities in the mechanisms of these reactions were clearly recognized at the Symposium on Homogeneous Catalysis at the 139th National Meeting of the American Chemical Society.[21]

(18) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 53.

(19) H. H. Anderson, *J. Am. Chem. Soc.*, **80**, 5083 (1958).
(20) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); J. Chatt, L. A. Duncanson, and R. G. Guy, *Chem. Ind.* (London), 430 (1959).
(21) *Chem. Eng. News*, **39**, 43 (1961).

Chelate Chemistry. II.[1] Hydrolysis of Metal Tropolonates

E. L. Muetterties and C. M. Wright

Contribution No. 1011 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware. Received August 31, 1964

Tracer studies with O^{18}-enriched water have shown in the base hydrolysis of metal tropolonates that (1) initial attack occurs primarily on the chelate ligand rather than on the central metal atom for four- and six-coordinate cationic chelates, i.e., T_2B^+, T_3Si^+, T_3Ge^+, and T_3P^{2+}; (2) no significant attack of ligand takes place in neutral metal chelates; and (3) more than one mechanism is operative for the eight-coordinate cations T_4Nb^+ and T_4Ta^+. Chelates derived from β-diketones seem to behave analogously to those derived from tropolone.

Introduction

In the first paper of this series,[1] a number of chelates

derived from the tropolone anion, T, were described. These chelates exhibited coordination numbers of four
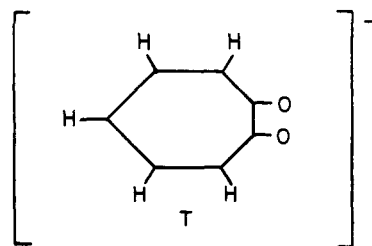
(T_2B^+), six $(T_3La$ and $T_3Si^+)$, and eight (T_4Zr). More recently we have prepared[2] eight-coordinate cations, T_4Nb^+ and T_4Ta^+, as well as new octahedral chelates,[2]

(1) Paper I: E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 5132 (1964).

(2) Paper III: E. L. Muetterties and C. M. Wright, to be published.

e.g., $(CH_3)_2SiT_2$. Most of these chelates are resistant to hydrolysis in acidic or neutral solution and are not subject to rapid (10^3 sec.$^{-1}$) ligand exchange in solution (n.m.r. criterion). In basic solution, all of the tropolone chelates are rapidly and completely hydrolyzed.

Because of the wide range of chelate structures, the absence of rapid ligand exchange, and the fast, clean hydrolysis in aqueous base, the metal tropolonates constitute ideal subjects for hydrolysis studies. In our initial attempts to characterize these hydrolyses, the possibility of ligand attack has been explored by tracer studies with O^{18}-enriched water.

Results

Hydrolysis of the metal chelates was effected in basic solution with O^{18}-enriched water. Under these conditions, tropolone undergoes no detectable oxygen exchange even at 100°. Tropolone evolved in the basic hydrolysis of all the neutral chelates was not enriched in O^{18}. Enrichment of tropolone was detected in the hydrolysis of all the cationic species even under neutral conditions. Mass spectroscopic assay of the enriched tropolone showed that one O^{18} atom was introduced. The enrichment corresponded to about

Table I. Hydrolysis Data for O^{18} Enrichment in Tropolone

Compound	Observed O^{18} introduction, %	Maximum possible O^{18} introduction, %	Enrichment, %	Hydrolysis method
Tropolone	−0.02	11.1	∼0	1
Tropolone	−0.03	11.1	∼0	2
$T_3Si^+Cl^-$	2.93	10.8	27.1	1
$T_3Si^+I^-$	2.99	10.9	27.4	1
$T_3Si^+I^-$	2.83	10.2	27.8	1[a]
$T_3Si^+I^-$	2.82	10.8	26.1	1[b]
$T_3Si^+PF_6^-$	2.82	10.1	27.9	1
$T_3Si^+T^-$	2.72	10.9	25.0	1[a]
$T_3Ge^+Cl^-$	3.57	10.9	32.8	2
$T_3Ge^+I^-$	3.41	11.1	30.7	2
$T_3Ge^+T^-$	2.75	11.0	25.0	2[a]
$T_3P^{2+}2I^-$	5.86	11.1	52.8	2[a]
$T_2B^+I^-$	5.33	11.1	48.0	2
$T_4Ta^+Cl^-$	0.32	11.1	2.8	3
$T_4Ta^+Cl^-$	0.28	10.0	2.8	3
$T_4Ta^+PF_6^-$	0.71	11.1	6.4	3
$T_4Ta^+PF_6^-$	0.75	10.9	6.9	3
$T_4Ta^+PF_6^-$	0.60	10.9	5.5	3
$T_4Nb^+Cl^-$	1.61	11.1	14.5	3
$T_4Nb^+Cl^-$	1.94	10.3	18.8	3
$T_4Nb^+Cl^-$ (49°)	0.15	10.4	1.4	4
T_3In	0.07	10.8	∼0	3
T_3Al	0.03	11.1	∼0	3
T_3Ga	0.10	11.0	1.	3
T_3Tl	0.05	11.1	∼0	3
T_3Fe	−0.03	11.0	∼0	3
T_2SnCl_2	0.04	11.1	∼0	3
T_3SnCl	0.05	11.1	∼0	3
T_4Sn	0.10	10.8	∼1	3
T_4Ce	0.13	11.0	∼1	3
T_4Zr	0.00	10.9	0	3
$T_2Si(CH_3)_2$	0.01	11.1	∼0	1
T_2SbCl	0.05	10.9	∼0	3
T_2BiCl	0.01	11.1	∼0	3
$D_3Si^+Cl^-$ [c]	3.22	11.0	29.3	1

[a] No methanol was present. [b] The OH$^-$ concentration was reduced by a factor of three and no methanol was present. [c] D = dibenzoylmethane ion; the enrichment is based on the measured increase of the 226 mass number. Observed O^{18} introduction is $I_{m/e122}$ (cor.)/[$I_{m/e122}$ + $I_{m/e124}$ (cor.)].

one-half of the maximum possible for T_2B^+, one-third for T_3Si^+ and T_3Ge^+, one-fourth for $T_3Si^+T^-$ and $T_3Ge^+T^-$, and two-thirds for T_3P^{2+}. Similarly, for the dibenzoylmethane derivative of silicon [$(C_6H_5)_2C_3HO_2]_3Si^+$, hydrolysis yields dibenzoylmethane enriched to about one-third of the maximum possible value.

In the hydrolysis of the eight-coordinate cations, T_4Nb^+ and T_4Ta^+, enrichment occurs but is low. Degree of enrichment for the tantalum cation is reproducibly a function of the associated anion, low for the chloride and high for the hexafluorophosphate. Hydrolysis of T_4Nb^+ to T_3NbO proceeds rapidly in neutral solution, and there is no enrichment of the tropolone under these conditions.

Data from these tracer studies are summarized in Table I.

Discussion

Absence of tropolone enrichment in the hydrolysis of the neutral chelates demonstrates unequivocally that there is no significant attack of the chelate ligand by hydroxyl ion. We have no data yet on the molecularity of these hydrolyses; therefore, nothing substantive can be said about the hydrolysis mechanism. These results with the neutral chelates, however, bear importantly on the conclusions regarding the hydrolysis of the cationic chelates.

Enrichment of tropolone in O^{18} in the hydrolysis of the cationic chelates rigorously establishes attack on the chelate ligand by hydroxyl ion. The only plausible site of attack in the ligand is the carbon atom adjacent to the oxygen atom. Models of the chelates show that this is a sterically unencumbered path.

In the case of the four- and six-coordinate cationic species (T_2B^+, T_3Si^+, [$(C_6H_5)_2C_3HO_2]_3Si^+$, and T_3Ge^+) the fraction of ligand enriched is close to the ratio of cation charge to number of ligands in the chelate. Thus, enrichment, *i.e.*, attack on ligand, takes place only when there is a *formal* positive charge on the metal chelate. For example, hydrolysis of T_3Si^+ may be envisioned as
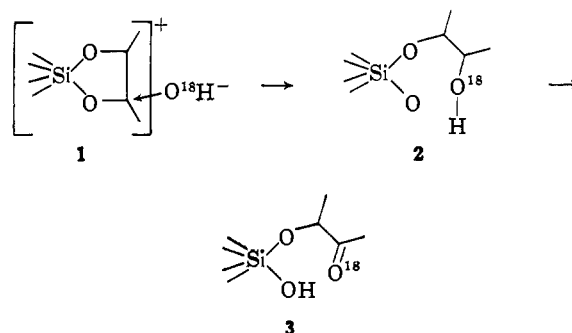
From stage **3** on, the silicon chelate species has lost the *formal* positive charge. The remaining two-thirds of the tropolone ligands should not be O^{18} enriched on hydrolysis since the studies of the neutral chelates give no evidence of enrichment ($(CH_3)_2SiT_2$ is especially relevant). Observed enrichment values are ∼27% *vs.* 33.3% theory. Similar reasoning applied to T_3P^{2+} leads to an expected 66.7% enrichment, and the observed enrichment was 53%. The closest experimental check was with germanium, 31–33% *vs.* 33.3% theory, and with boron, 48% *vs.* 50% theory.

The tropolone enrichment in the hydrolysis of the tropolonosilicon cation is reproducible and is independent of the associated anion for the simple chloride, iodide, and hexafluorophosphate salts. The discrepancy (5–6%) between the observed enrichment and that expected for initial attack at a ligand site exceeds experimental error. Therefore, it would appear necessary to invoke a secondary competing process that could either be dissociative or S_N2 with attack on the silicon atom by hydroxide ion. If the latter were the competing process, it would seem most reasonable to expect a more dominant role for this process in the hydrolysis of the analogous germanium chelate since the steric factor is more favorable and the energy of the d-orbitals is lower. However, the fit for the observed and expected enrichments in T_3Ge^+ hydrolysis is excellent. On the other hand, we would expect a dissociative process to be more favorable for silicon. Hydrolysis of the black $T_3Si^+T^-$ salt showed a tropolone enrichment that agrees with the expected value within experimental error. This result might be taken as evidence of a competing dissociative hydrolysis since the presence of the tropolone ion should inhibit a dissociative step.

Degree of O^{18} enrichment in T_3Si^+ hydrolysis was not significantly affected by changes in OH^- concentration, although in all instances excess hydroxide ion was present to ensure complete hydrolysis. In one experiment, $T_3Si^+Cl^-$ and H_2O^{18} were heated at 80° in a sealed tube for 20 hr. Under these experimental conditions, there is an equilibrium between cation and hydrolysis products; the equilibrium is such that relatively little tropolone is present. Enrichment under these reversible conditions was about 30% complete. Hydrolysis of T_3P^{2+} is irreversible and the observed enrichment for the neutral hydrolysis was 57.9%.

The hydrolysis of the trisacetylacetone derivative of silicon, $(C_5H_7O_2)_3Si^+$, has been shown to be first order in base and in silicon cation.[3] This hydrolysis was characterized as an example of an S_N2 octahedral reaction with a seven-coordinate silicon intermediate.[3] Our results with the tropolone chelates and with the dibenzoylmethane analog of $(C_5H_7O_2)_3Si^+$ establish, without question, that initial attack is primarily on the ligand rather than the central atom. Our data are not, however, sufficiently precise to rule out a minor competing attack on the central atom.

Ligand attack in the basic hydrolysis of the eight-coordinate niobium cation is the dominant process since the observed O^{18} enrichments were 15–19% compared to the 25% expected. The degree of enrichment is very sensitive to the hydrolysis temperature; with increase of initial hydrolysis temperature to 49°, the enrichment dropped nearly to zero. This competing hydrolysis mechanism is believed to be a dissociative hydrolysis because (1) the niobium chelate is rather unstable and degrades rapidly even in neutral solution with precipitation of T_3NbO (eq. 1); (2) the

$$T_4Nb^+ + H_2O \longrightarrow T_3NbO + TH + H^+ \qquad (1)$$
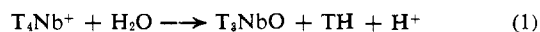
neutral hydrolysis of T_4Nb^+ in H_2O^{18} produces tropolone *unenriched* in O^{18}; and (3) the rate of neutral hydrolysis is markedly temperature dependent.[2]

(3) R. G. Pearson, D. N. Edington, and F. Basolo, *J. Am. Chem. Soc.*, 84, 3233 (1962).

Tropolone enrichment in T_4Ta^+ basic hydrolysis is low (3–7%) and is dependent upon the nature of the associated anion. Preliminary studies of the electronic spectra of T_4Ta^+ salts in various media suggest that ion pairing occurs. It is conceivable that the enrichment studies reflect variations in ion-pair tendencies of the salts. The geometry of the ion pair may be such to hinder or promote attack at some particular position. Also, in an ion pair, the positive charge at the carbon atoms of the ligand may be reduced to the point that attack on these positions by hydroxide ion is unfavorable. We hope to evaluate this anion effect through conductivity, tracer hydrolysis, and electronic spectral studies. Tropolone enrichment was independent of the initial hydrolysis temperature (20–50° range) for the T_4Ta^+ cation, unlike the niobium analog.

The major hydrolysis mechanism for T_4Ta^+, competitive with ligand attack, cannot be a dissociative one because the tantalum chelate is much more stable hydrolytically than T_4Nb^+. For example, there is no evidence in the proton n.m.r. spectrum of T_4Ta^+ of hydrolysis at temperatures up to 140° (acidic aqueous solutions of the chelate). We suggest attack on the tantalum atom by hydroxide ion as the major hydrolysis process. A nine-coordinate intermediate or transition state seems a reasonable postulate since isolable nine-coordinate derivatives of third-row transition elements are well established.

General Conclusion

The results of this investigation clearly show that ligand attack can be an important step in reactions of cationic complexes. Since ligand sites are generally less sterically hindered than the central metal atom and since significant positive charge may reside at ligand positions, *it is important to consider the possibility of initial attack on a ligand site for any reaction of a nucleophile and a cationic complex.*

Experimental

Reagents and Procedure. Preparation of most of the chelates was described in an earlier paper.[1] Synthesis details for the remaining chelates will be reported in paper III.[2] The water enriched in O^{18} was purchased from Yeda Research and Development Co., Ltd.

Hydrolysis of the tropolone chelates was effected in a strongly basic medium enriched in O^{18}. Four different hydrolysis procedures were utilized because of differences in solubilities of the chelates and interferences arising from the metal ion in the neutralization step. These procedures are described below. For all chelates, it was established by ultraviolet analysis that hydrolysis to the tropolone anion was complete under the given experimental conditions. Standard runs were made in each case with tropolone itself; there was no evidence of oxygen exchange in tropolone in basic or acidic media.

Enrichment of the tropolone was followed by mass spectral analysis. The spectrometer used was a Consolidated Engineering Corporation Model 103-C. Samples of tropolone were introduced into the spectrometer from an inlet heated to 150°. The $m/e = 122$ species is the parent ion of tropolone and was the most abundant in the cracking pattern of tropolone. The increase in the $m/e = 124$ ion represents the increase in

the O^{18} content of the tropolone. The corrected values reported were obtained by subtracting the normal abundance of the $m/e = 124$ isotope of natural tropolone from the observed $m/e = 124$ isotope of the samples. Two mass spectrometric determinations were made on each sample with a precision of 0.1%. The average value is given. Isotopic fractionation was not taken into consideration in the calculation of maximum enrichments. If there was an isotope effect in the hydrolysis, the values would not change by more than one to three parts in a hundred. Results are given in Table 1, and the hydrolysis procedure for each chelate is identified. Accuracy of the determinations was not established. The reproducibility was excellent as shown by the data in Table I.

Hydrolysis Method 1 ($T_3Si^+Cl^-$). Sodium hydroxide (0.18 g., 0.005 mole) was dissolved in water (1.148 g., 0.063 mole) containing 11.75 atom % O^{18} and methanol (2 ml.). Solid $T_3Si^+Cl^-$ (0.100 g., 0.00024 mole) was added to the solution. After stirring for 9 min., the solution was cooled in an ice bath and neutralized with concentrated sulfuric acid to pH 7. The mixture was then stirred at room temperature for 15 min. with benzene to extract the tropolone. The benzene layer was separated and evaporated to dryness under reduced pressure. Sublimation at 40° (1 μ) gave tropolone in 72% yield. The tropolone was resublimed prior to analysis.

Three additional runs were made on $T_3Si^+I^-$ and two runs on tropolone using method 1 and replacing the O^{18}-enriched water with O^{18}-enriched deuterium oxide. The reactions were also carried out with the chelate and with tropolone in D_2O^{16} to correct for deuterium–hydrogen exchange. The D_2O^{18} results were in agreement with those for the H_2O^{18} work.

Hydrolysis Method 2 ($T_3Ge^+Cl^-$). Addition of $T_3Ge^+Cl^-$ (0.100 g., 0.00021 mole) to a solution of sodium hydroxide (0.20 g., 0.005 mole) in water (1.161 g., 0.060 mole) containing 11.75 atom % O^{18} and methanol (2 ml.) gave a yellow slurry. Heating the mixture for 9 min. on a steam bath gave a clear solution, which was then cooled in ice to give a yellow crystalline solid. The solid was isolated by filtration and dissolved in 7 ml. of water. The solution was neutralized to pH 7 with concentrated sulfuric acid, then evaporated to dryness under reduced pressure. Tropolone sublimed from the residue at 40° (1 μ) and was resublimed prior to analysis.

The hydrolysis of $T_3P^{2+}2I^-$ (Table I) was carried out in the absence of methanol.

Hydrolysis Method 3 (T_3In). Sodium hydroxide (0.20 g., 0.005 mole) was dissolved in 12.0 atom % O^{18}-enriched water (1.134 g., 0.062 mole) and 2 ml. of methanol; T_3In (0.090 g., 0.00019 mole) was added. The mixture was heated for 9 min. on a steam bath during which time an additional 1 ml. of methanol was

added. The indium oxide was isolated by filtering the hot solution. The filtrate was then neutralized with concentrated sulfuric acid and evaporated to dryness under reduced pressure. Tropolone was sublimed from the residue at 40° (1 μ) and then resublimed prior to analysis.

Hydrolysis Method 4 ($T_4Nb^+Cl^-$). A solution of sodium hydroxide (0.17 g., 0.004 mole) in water (1.152 g., 0.063 mole) containing 10.95 atom % O^{18} and methanol (2 ml.) was thermostated at 49° in a water bath. The chelate $T_4Nb^+Cl^-$ (0.150 g., 0.00024 mole) was added and the mixture agitated. The total time, from addition of the chelate until removal of the flask from the bath, was 1 min. Hydrolysis appeared to be complete, based on the disappearance of the orange color. The flask was then heated for 8 min. over a steam bath and then filtered hot. The solution was neutralized with concentrated sulfuric acid and extracted with 15 ml. of benzene. After evaporation of the benzene layer, tropolone was sublimed from the residue.

Hydrolysis of $T_4Nb^+Cl^-$ to T_3NbO. $T_4Nb^+Cl^-$ (0.150 g.) was added to a solution of 11.75 atom % O^{18} water (1.074 g.) and 2 ml. of methanol. The mixture was stirred 10 min., during which time the orange solid was converted to a cream solid. The mixture was filtered, and the solid was identified as T_3NbO by infrared comparison with a known sample. The filtrate was concentrated to one-fourth its volume under reduced pressure, and 5 ml. of benzene was added. After stirring 15 min., the benzene layer was extracted and evaporated to dryness. Tropolone was sublimed from the residue, 40.9% yield. Mass spectroscopic analysis showed no enrichment.

Neutral Hydrolysis of $T_3Si^+I^-$. A 0.100-g. sample of the chelate and 1 ml. of 10.95 atom % O^{18} were placed in an ampoule, which was sealed and heated to 85° for 20 hr. Unhydrolyzed $T_3Si^+I^-$ still remained in the ampoule. The mixture was filtered and 1 ml. of dried benzene was added to the filtrate. After stirring 15 min., the benzene layer was removed and evaporated to dryness. Tropolone was sublimed from the residue. The O^{18} introduction was about 6.8%.

Neutral Hydrolysis of $T_3P^{2+}2I^-$. The chelate (0.150 g.) and 1 ml. of 10.95 atom % O^{18} were heated in a sealed tube at 85° for 2 hr. which is time for complete hydrolysis based on n.m.r. and ultraviolet data. Sodium hydroxide was added to the solution to pH ~14, and then the solution was neutralized with concentrated sulfuric acid. The solution was stirred for 15 min. with 1 ml. of benzene. The benzene layer was extracted and evaporated to dryness; tropolone was sublimed from the residue. The enrichment was 57.9% of the maximum value.