Catalyzed Decomposition of Tetramethyl-1,2-dioxetane by Rhodium and Iridium Complexes

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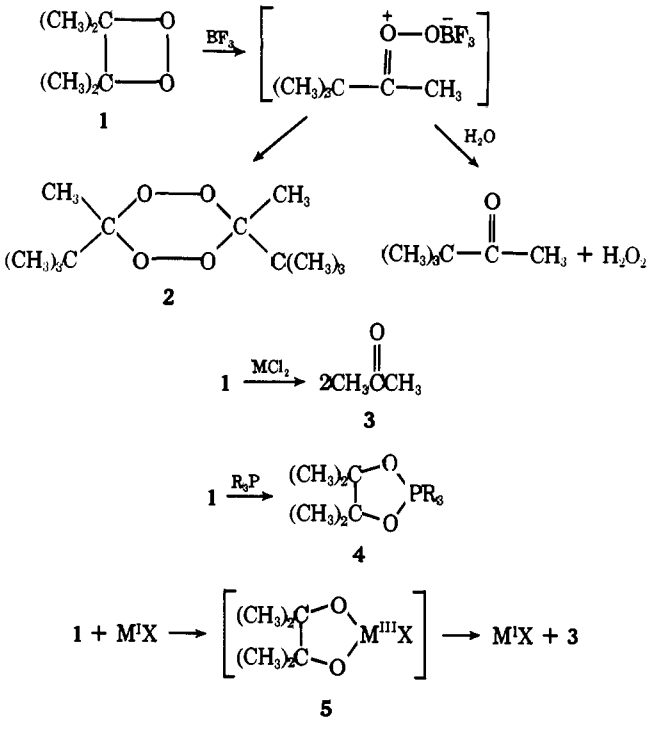
Abstract: Two iridium and 13 rhodium complexes of a type known to undergo oxidative addition have been found to catalyze the cleavage of tetramethyl-1,2-dioxetane to acetone and the rates are reported in Tables I and II. The rate is increased by electron release in substituted triphenylphosphines attached to the rhodium; the reaction therefore behaves like an oxidative addition and unlike the electrophilic cleavages by Lewis acids previously studied. Within the limited scope of the data, the rate appears to depend with unusual emphasis on the resonance effects of the substituents. This reaction represents the fourth distinct mode of attack by various reagents on the dioxetane ring to be studied.

Tetramethyl-1,2-dioxetane (TMD) (**1**) is attacked in several ways by different reagents. Boron fluoride, a strong Lewis acid with a single vacant coordination site, produces an apparent "peroxypinacol rearrangement" to the carbonyl oxide of pinacolone, its dimerization product (**2**) and products of hydrolysis.[2] A series of chlorides of divalent metals in methanol decompose tetramethyldioxetane cleanly to acetone (**3**) at rates parallel to their Lewis acidities.[3] Tertiary phosphines yield cyclic phosphoranes (**4**) by insertion of phosphorus between the oxygen atoms of the dioxetane.[4]



By analogy, a metal salt capable of a reversible valence increase by two units would seem to offer an especially easy path for the cleavage of a 1,2-dioxetane: first, insertion by oxidative addition between oxygen atoms, and then cleavage of the resulting metallocycle (**5**) in a symmetry-allowed fragmentation to the original catalyst and two carbonyl-containing molecules. That this is not the mechanism in the cases of copper, zinc, and nickel salts is indicated by the rates being independent of the nature of the higher valence states of the metals and parallel to their Lewis acidities.[3] In view of the demonstrated existence of a variety of mechanisms of attack on dioxetanes we have studied the reaction of tetramethyl-1,2-dioxetane with some complexes of univalent rhodium and iridium known to be capable of oxidative addition to H_2, O_2, alkyl, and hydrogen halides.[5]

Experimental Section

Tetramethyl-1,2-dioxetane was prepared by the method of Kopecky.[6] Norbornadiene rhodium chloride dimer (**1**) and rhodium dicarbonyl chloride dimer (**2**) were purchased from Strem Chemicals, Inc., Danvers, Mass. Rhodium carbonyl triphenylphosphine chloride dimer (**3**) was prepared according to Steele and Stephenson.[7]

Iridium carbonyl bis(triphenylphosphine) bromide (**4**) was prepared by the method of Chock and Halpern,[9] mp 253–255 °C (lit. 254–256,[10] 318–320 °C[11]). Iridium carbonyl bis(triphenylphosphine) chloride (**5**) was purchased from Ventron Corp., Alfa Products, Danvers, Mass. Rhodium carbonyl bis(triphenylphosphine) iodide (**6**) was prepared according to Vallarino,[12] cf. Collman,[10] mp 164–166 °C (lit. 165–167 °C[10]). Rhodium carbonyl bis(triphenylphosphine) bromide (**7**) was prepared by a modification of the method for the chloride (**8**), applied to rhodium tris(triphenylphosphine) bromide,[13] mp 177–181 °C (lit. 173–175 °C[10]). Rhodium carbonyl bis(triphenylphosphine) chloride (**8**) was prepared by the method of Evans, Osborn, and Wilkinson,[14] mp 195–202 °C (lit. 195–197 °C). Rhodium carbonyl bis(tri-*p*-anisylphosphine) chloride (**9**) was prepared by the generalized method of ref 14, mp 174–176 °C (lit. 193–195 °C[12]), IR (Nujol) ν_{CO} 1958 cm^{-1} (lit. 1958 cm^{-1} [15]). Anal. Calcd for $C_{43}H_{42}ClO_7P_2Rh$: C, 59.29; H, 4.86; P, 7.11. Found: C, 58.45; H, 4.82; P, 7.26. A sample prepared by the method of Vallarino[12] gave a high carbon analysis: C, 61.10; H, 5.11; P, 6.71. Neither sample could be brought to the reported[12] melting point of 193–195 °C. Rhodium carbonyl bis(tri-*p*-tolylphosphine) chloride (**10**) was prepared by the *Inorganic Syntheses* method,[14] mp 196–199 °C (lit. 190–195,[12] 195,[14] 260–263 °C[16]), IR ν_{CO} 1960–1965 cm^{-1} (Nujol) (lit. 1965 cm^{-1} [14]). Rhodium carbonyl bis(tri-*p*-chlorophenylphosphine) chloride (**11**) was prepared according to ref 12, mp 197–200 °C (lit. 190–195 °C[12]), IR ν_{CO} 1975 cm^{-1} (Nujol) (lit. 1985 cm^{-1} [17] ($CHCl_3$)). Rhodium carbonyl bis(triphenylarsine) chloride (**12**) was prepared according to ref 14, mp 243–245 °C (lit. 242–244 °C[12]). Rhodium carbonyl bis(triphenyl phosphite) chloride (**13**) was prepared according to ref 12, mp 154–157 °C (from chloroform–ethanol) (lit. 160–170 °C[12]). Rhodium tris(triphenylphosphine) chloride (**14**) was prepared according to Osborn and Wilkinson,[18] mp 138 °C[19] dec. Rhodium thiocarbonyl bis(triphenylphosphine) chloride (**15**) (red form) was prepared according to Baird, Hartwell, and Wilkinson,[20] mp 247–248 °C dec (lit. 250–252 °C[20]).

Rate Measurements. Solutions of the metal complexes in benzene were prepared immediately before addition to the solution containing TMD. The concentrations in the mixed solution follow: TMD, 4.4×10^{-2} M; metal complex, 1.3×10^{-3} M, or 3 mol % based on the dioxetane. Degassing of the solvent had no perceptible effect on the reaction rates. Controls showed no decomposition of TMD in benzene in 2 h in the absence of metal complexes.

Rates of reaction were determined by following the disappearance of TMD and appearance of acetone by ^1H NMR at 38 ± 2 °C. The half-lives determined under these conditions were reproducible within ±10% and ranged from 0.3 to 64 min for the complexes examined. In the late part of a run deviations from pseudo-first-order kinetics were noted.

Table I. Catalyzed Decomposition of TMD by Rhodium(I) and Iridium(I) Metal Complexes in Benzene

Metal complex	Rel rate[a]
(1) $[Rh(Nbd)Cl]_2$[b]	187
(2) $[Rh(CO)_2Cl]_2$	31
(3) $[Rh(CO)(Ph_3P)Cl]_2$	25
(4) $IrBr(CO)(Ph_3P)_2$	187
(5) $IrCl(CO)(Ph_3P)_2$	62
(6) $RhI(CO)(Ph_3P)_2$	2.9
(7) $RhBr(CO)(Ph_3P)_2$	2.2
(8) $RhCl(CO)(Ph_3P)_2$	1.5
(9) $RhCl(CO)[(p\text{-}CH_3OC_6H_4)_3P]_2$	3.5
(10) $RhCl(CO)[(p\text{-}CH_3C_6H_4)_3P]_2$	2.0
(11) $RhCl(CO)[(p\text{-}ClC_6H_4)_3P]_2$	1.7
(12) $RhCl(CO)(Ph_3As)_2$	6.2
(13) $RhCl(CO)[(PhO)_3P]_2$	0.88
(14) $RhCl(Ph_3P)_3$	1.0
(15) $RhCl(CS)(Ph_3P)_2$	2.1

[a] Relative rate 1.0 corresponds to $t_{1/2}$ = 56 min at 38 °C. [b] Nbd = norbornadiene.

A control experiment showed that the reaction product, acetone, was not responsible for the declining rate.

The change from the TMD NMR singlet to the acetone singlet was a clean one, with no other products being detectable.

Results and Discussion

The rhodium and iridium complexes of Table I cover a range of more than 200-fold in reactivity toward tetramethyldioxetane. In interpreting these data caution is required at a number of points.

Characterization of the complexes is not as precise as is generally expected of more stable organic compounds; many of them melt with decomposition, and there are large disparities in a few of the reported melting ranges in the literature. The CO frequencies in the infrared often reported in the literature cover too narrow a range to serve as definitive characterizations.

It is known that oxidative additions as similar as those of H_2 and of CH_3I proceed by mechanisms different enough to reverse the reaction rate order with the ligands Cl, Br, I.[9,5c] In many cases a dissociation must precede any addition step. Many oxidative additions of hydrogen are followed by a series of rapid steps resulting in catalytic hydrogenation of unsaturated substances that may be present.[13,21] There is no correlation between the rates of hydrogen uptake by a series of rhodium complexes and the identically constituted complexes of iridium,[22] although the latter are generally more reactive.

In interpreting these effects it is safest to begin with the same limitation as was used in the original study of linear free energy relations in organic reactions. It should be possible to observe the effect of pure intramolecular electron release and withdrawal in a series of catalysts where molecular shape, steric interactions, and through-space electrostatic and orbital effects are held constant, and the variations are those transmitted to the reaction center from the para positions of benzene rings. Such a series is presented by complexes **8–11**, wherein everything in the structure is held constant except the para substituents in the triarylphosphine ligands. Every feature of the environment through which the reactant passes in its approach to the reactive center of the catalyst remains constant except for the crucial electron availability at the metal atom where the reaction with the dioxetane is initiated.

The validity of this approach is indicated by the fact that the iridium complexes corresponding to **8–11**, in reaction with molecular oxygen, studied by Vaska and Chen,[23] yield both rate constants and equilibrium constants which fit the Hammett equation very well. The rates of oxygen uptake yield a value of ρ (based on a single para substitution in one of the six benzene rings) of −0.37. The hydrogen uptake, which has been measured for the iridium complex **5** and the corresponding tri-*p*-tolylphosphine complex,[22] shows an effect in the same direction, consistent with $\rho = -0.14$. These models support the concept that the valence increase implied in the name "oxidative addition" is favored by electron-releasing substituent effects identifiable in the ligands.[25] For the present purpose it is important that any *electrophilic* catalysis by the metallic center would have required a ρ value of the opposite sign, being enhanced by electron withdrawal, not electron release.

Table II. Effect of Ligands on Rate of Catalytic Cleavage of Tetramethyl-1,2-dioxetane

Metal complex	Rate rel to **14**	Rel rate within group
$RhCl(L)(Ph_3P)_2$		
L = Ph_3P	1.0	1.0
L = CO	1.5	1.5
L = CS	2.1	2.1
$RhCl(CO)[(p\text{-}XC_6H_4)_2P]_2$		
X = H	1.5	1.0
X = CH_3O	3.5	2.3
X = CH_3	2.0	1.3
X = Cl	1.7	1.13
$RhCl(CO)(L)_2$		
L = Ph_3P	1.5	1.7
L = Ph_3As	6.2	7.0
L = $(PhO)_3P$	0.88	1.0
$RhX(CO)(Ph_3P)_2$		
X = I	2.9	1.9
X = Br	2.2	1.5
X = Cl	1.5	1.0
$MCl(CO)(Ph_3P)_2$		
M = Ir	62	41
M = Rh	1.5	1.0
$[Rh(L)_2Cl]_2$		
$(L)_2$ = NBD	187	7.5
$(L)_2 = (CO)_2$	31	1.2
$(L)_2 = (CO)(Ph_3P)$	25	1.0

In the cleavage of tetramethyldioxetane by rhodium complexes, as seen from Tables I and II, the substituents H, CH_3, and CH_3O fall in the same order as in the oxidative additions by iridium complexes of the same constitution. The differences are large enough to place this reaction in the class of the oxidative additions, favored by electron release. The fit to the Hammett equation, however, is poor; the rates for these three substituents appear to follow σ^+ rather than σ. More confusing is the fact that the tri(*p*-chlorophenyl)phosphine derivative **11** reacts slightly *faster* than the unsubstituted **8**, although the difference between them is within the sum of the estimated experimental uncertainties of the two.

The definite conclusion from this work is that the catalytic cleavage of tetramethyldioxetane by the rhodium complexes falls in the class of the oxidative additions of which models exist and not of the electrophilic catalysis by divalent metal ions previously observed.[3] The behavior of dioxetanes is unique; the bond to be broken is neither like the strong, unstrained bond of molecular hydrogen nor is it like the triplet π structure of molecular oxygen, in which the σ bond remains intact during metal-complex formation. It is perhaps of some importance to speculate on the unusual features of the reactivity pattern, unexplained though they are.

We could not help noticing that the cup-shaped Hammett plot for the reaction of complexes **8–11** with TMD could be replaced by a straight line when the Yukawa-Tsuno equation[26] was fitted to the data by the method of least squares. The equation becomes

$$\log (k/k_0) = -0.094[\sigma + 7.1(\sigma^+ - \sigma)]$$

The Yukawa-Tsuno equation is usually a flexible expression of situations intermediate between dependence on σ and on σ^+, the latter case being represented by a value of unity for the coefficient R (which is here 7.1). Values of R greater than 1, which are rare, correspond to dominance not by σ^+, which is itself a blend, but by that component of σ^+ which depends on a noninductive electron release mechanism. The effect of dominance by $(\sigma^+ - \sigma)$ rather than by σ^+ is (a) to make CH_3O 3.6 times as electron releasing as CH_3 instead of only 2.5 times, and (b) to transfer Cl from the electron-withdrawing to the electron-releasing groups, falling now between H and CH_3. One of the unusual cases of R greater than 1[26] is the brominolysis of benzeneboronic acids,[27] where a value of $R = 2.29$ is assigned.

Until we have longer substituent series and greater total rate effects, we postpone further speculation about the meaning of the unusual form of the substituent effects on the opening of tetramethyldioxetane. The data are alternatively fitted by the Swain-Lupton equation,[28] with $f = 0.116$ and $r = 0.833$. The ratio $r/f = 7.18$ has a similar meaning to the $R = 7.1$ of the Yukawa-Tsuno equation. The sensitivity to a single substituent in the present reaction is much less than in the direct reaction of triarylphosphines with molecular sulfur, which follows the Hammett σ and produces triarylphosphine sulfide as the final product.[24] By way of direct rate comparison, there is a free-energy ratio, $\log (k/k_0)_S / \log (k/k_0)_{TMD}$, of 10.3 between the effect of a methyl group in the sulfur reaction and that in the opening of TMD. This is at least in part a measure of the attenuation resulting from the intervention of a rhodium ion between the phosphorus and the site of the chemical change.

Acknowledgment. We thank the Robert A. Welch Foundation for support of this research.

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(25) Hydrogen uptake by the rhodium complexes **8** and **10** has also been measured,[22] but the authors reporting this work remained unconvinced that the complexes themselves were adding hydrogen: no hydrogen-addition products could be isolated, a higher temperature was required to bring about the reaction than in the case of the iridium complexes, and the response to ligand change was small and irregular. Prior changes in the complexes may account for the fact that **8** and **10** fall in the opposite order from the corresponding iridium complexes toward hydrogen.
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Hydrolysis of 1-Benzyl-3-bromoacetylpyridinium Bromide. Evidence for Neighboring Group Participation

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Abstract: The unusual solvolytic reactivity of 3-bromoacetylpyridinium ions has been investigated in a kinetic study of the hydrolysis of 1-benzyl-3-bromoacetylpyridinium bromide (**5**). The α-hydroxy ketone product of the hydrolysis was quantitatively determined by a novel application of the 2,6-dichlorophenol indophenol reagent. The progress of the hydrolysis reaction was followed by continuous titration of the hydrobromic acid which was formed (pH stat method). In addition to a direct dependence of the rate on the hydroxide ion concentration in the vicinity of neutrality, a primary solvent deuterium isotope effect as well as an inhibitory effect of added halide ions ($I^- > Br^- > Cl^-$) were observed. These findings were not consistent with a direct displacement mechanism for the reaction. The spectroscopic properties of **5** revealed that the carbonyl group exists in the hydrated form in aqueous solution. A mechanism for the hydrolysis involving ionization and cyclization of the hydrate to give an epoxide intermediate is proposed. The formation of epoxide intermediates in the solvolysis was confirmed by isolation of the α-hydroxyl dimethyl ketal, **6**, when the reaction was carried out in methanol solution.

We have initiated studies on the conversion of moderate molecular weight enzymes which are hydrolytic catalysts into modified enzymes capable of catalyzing a wide variety of synthetically important reactions such as oxidation-reduction, transamination, and decarboxylation. In the course of our studies we have focused our efforts on the preparation of coenzyme analogues containing reactive functional groups, permitting them to be attached at or near the periphery of the active sites of hydrolytic enzymes which are very available, easily purified, stable, and readily immobilized on solid supports. If suitable coenzyme analogues can be covalently attached to such relatively simple enzymes in a manner which permits the binding sites of the enzymes to remain accessible to organic substrates, it may be possible to catalyze many new