Electron-transfer Oxidation of Organic Compounds. Part 5.[1] Oxidation of Cyclohexanone by the Tris-2,2'-bipyridylruthenium(III) Cation

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Evidence is presented, from kinetic and product studies, that the rate-determining step in the oxidation of cyclohexanone by the trisbipyridylruthenium(III) cation is a non-bonded electron-transfer process from the enol form of the substrate. This gives rise to a free radical and a ruthenium(II) species. The subsequent fate of the radical has been investigated.

TRIS-2,2'-BIPYRIDYLRUTHENIUM(III) PERCHLORATE is an obvious candidate for study as a potential oxidant of organic compounds by a non-bonded electron-transfer mechanism. It has a redox potential[2] of 1.2—1.3 V in 1.0M-acid, which is higher than that of the analogous tris-o-phenanthrolineiron(III) complex (ferriin) studied previously,[3] yet the Ru^{III} complex is more inert than the iron(III) one in racemisation[4] or acid decomposition[5] processes. It is known to undergo inorganic non-bonded redox processes,[6] in particular with the iron(II) analogue and with hexachloroiridium(III).[7] The resistance of the ruthenium(III) complex to two-equivalent redox processes is demonstrated by the two-stage reaction of $[Ru^{II}(bipy)_3]^{2+}$ with Tl^{3+}.[8] It therefore seemed that a study of the reaction of $[Ru^{III}(bipy)_3]^{3+}$ with cyclohexanone might extend some of the conclusions reached earlier in this series, and clarify some of the problems raised. A few measurements on the reaction were reported by Ng and Henry[9] while this work was in progress, but no detailed study of the kinetics or products has been made.

EXPERIMENTAL

Materials.—Trisbipyridylruthenium(II) perchlorate was prepared from potassium aquopentachlororuthenate (Johnson, Matthey and Co.) by reduction with tartaric acid.[10] The spectrum of the product agreed with literature values to within 5%.[2,8] The ruthenium(III) species was formed by oxidation of the Ru^{II} solution with MnO_2 or PbO_2 until no further change occurred. The observed spectra were as follows: Ru^{II} $\lambda_{max.}$ 244 (ε 2.56 × 10^4), 254 (2.24 × 10^4), 286.5 (ε 8.01 × 10^4), 314 (1.18 × 10^4), and 454 (1.41 × 10^4); Ru^{III} $\lambda_{max.}$ 286.5 (ε 2.24 × 10^4), 304 (4.39 × 10^4), 314 (4.36 × 10^4), 418 (1.5 × 10^3), 454 (250), and 678 nm (400). Other materials were obtained and purified as described in Part 4.[1]

Kinetics.—The reactions were followed by spectrophotometry at the following wavelengths: 286.5 and 454 nm (Ru^{II} appearance), and 314 nm (Ru^{III} disappearance) using both Cary 14 and Unicam SP 800 instruments. The former was more suitable at low optical densities, but it could not be thermostatted so accurately. In all other respects kinetics were carried out as described in Part 3.[11] The reaction is found to be insensitive to the light being used for observation, and the reduction of the oxidant by water was found to be negligible during the period of a kinetic run. It was, however, necessary to use the Ru^{III} solution within 12 h of its preparation. The Ru^{II} complex produced is rather insoluble in perchloric acid and is observed to precipitate slowly after the completion of an oxidation.

Inorganic Products.—During reduction of the Ru^{III} complex by cyclohexanone, successive spectra showed isosbestic points at 298 and 329 nm, and the final spectrum was identical to that of the original Ru^{II} solution from which the oxidant had been prepared. At the concentrations used in the kinetic studies the quantity of organic products was necessarily very small, so a catalytic system in which Ru^{III} was regenerated by MnO_2 was set up for product studies. Typically 2 × 10^{-2}M-cyclohexanone in 1M-HClO$_4$ (100 ml) was stirred under nitrogen with MnO_2 (10 g) or PbO_2 (5 g) for 20 min in the presence of 10^{-4}M-trisbipyridylruthenium-(II) as catalyst. After filtration, the mixture was extracted continuously with ether. Under these conditions some ruthenium(II) complex passed into the ether layer, although pure trisbipyridylruthenium(II) is not extracted. The extracted Ru^{II} complex showed a new peak at 500 nm, while the remaining aqueous Ru^{II} also showed a bathochromic shift, with a broad peak at 475 nm, and the 286.5-nm peak shifted to 288 or 289 nm. The ether-soluble Ru^{II} product precipitated, and after being washed with chloroform, showed absorptions at 3 600, 2 910, and 1 700 cm^{-1} (hexachlorobutadiene mull) in addition to the normal i.r. peaks of the pure trisbipyridylruthenium(II) perchlorate.

Organic Products.—The ether extract was examined and the following compounds among others were detected: cyclohexanone-1,2-dione (nickel dioxime test and g.l.c.), 2-hydroxycyclohexanone (t.l.c. and g.l.c. of trimethylsilyl derivative), cyclopentanecarboxylic acid (g.l.c. of methyl ester); adipic acid (i.r., g.l.c., and m.s. of methyl ester) cyclohexenone (g.l.c.–m.s.). The silylation reagent was bistrimethylsilylacetamide; methylation was by BF$_3$–MeOH; no 2,2'-bipyridyl was detected (g.l.c.). If air was present during the oxidation less 2-hydroxycyclohexanone was observed, and cyclopentanecarboxylic acid was not detected, but peroxide materials were present which could oxidise iodide solution. Blank runs with MnO_2 alone gave negligible quantities of products. T.l.c. was carried out using ethyl acetate–light petroleum (b.p. 40—60°) (1 : 1) as solvent on Kieselgel G (Merck), and developed with Brady's reagent; the g.l.c. was performed at 160° using a 1-m column packed with 25% Embaphase silicone oil (May and Baker) on F and M 60—80 mesh Diatoport S at 8 lb in^{-2}, using flame-ionisation detection; g.l.c.–m.s. used the same column at 100 °C with an MS30 spectrometer.

RESULTS AND DISCUSSION

Oxidation of Cyclohexanone in the Absence of Air (Table 1).—The inorganic product studies show that trisbipyridylruthenium(III) is quantitatively reduced to trisbipyridylruthenium(II) under kinetic conditions, and the absence of bipyridyl from the organic products con-

firms this, since the acidity of the solution is such that had dissociation occurred bipyridyl would not be free to recombine with a ruthenium species. The reaction is of first order in ketone, and individual runs at low initial Ru^{III} concentrations give good first order plots for at least three half-lives. Under the same conditions the reaction appears to be insensitive to the acidity of the solution. However, at higher Ru^{III} concentrations two effects can be observed. First the logarithmic (first

TABLE 1

The reaction of cyclohexanone with trisbipyridyl-ruthenium(III) perchlorate, under nitrogen

(i) Dependence on [Ru^{III}]

(a) [$HClO_4$] 0.95M; [ketone] 2.7×10^{-4}M; temperature 23 °C

$10^5[Ru^{III}]$/M	1.17	0.896	0.448	0.111
$10^2k'$/s^{-1}	1.42	1.41	1.40	1.43
k''/l mol^{-1} s^{-1}	52.6	52.3	51.8	53.0

Second-order rate constant k'' 52.4 $\pm$ 0.4 l mol^{-1} s^{-1}

(b) [H^+] 0.488M; [ClO_4^-] 0.95M; [ketone] 6.93×10^{-4}M; temperature 20 °C

$10^5[Ru^{III}]$/M	1.63	1.25	0.55	0.15	0.08
10^8Initial rate (l^{-1} mol s^{-1})	15.6	14.0	9.35	3.3	1.85
Initial rate/[Ru^{III}]-[ketone] (l mol^{-1} s^{-1})	13.9	16.1	24.6	31.8	33.2
10^4Rate/2[H^+][ketone] (l mol^{-1} s^{-1})	2.31	2.08	1.39	0.49	0.27

(ii) Dependence on [ketone]

[$HClO_4$] 0.95M; [Ru^{III}] 1.17×10^5M; temperature 23 °C

10^4[ketone]/M	6.75	3.38	2.70	2.02	1.35	1.08
$10^3k'$/s^{-1}	35.6	18.1	14.1	11.0	7.15	5.75
k''/l mol^{-1} s^{-1}	52.7	53.6	52.2	54.5	53.0	53.2

Second-order rate constant k'' 53.2 $\pm$ 0.6 l mol^{-1} s^{-1}

(iii) The effect of acid strength

(a) [ClO_4^-] 0.95M; [Ru^{III}] 1.17×10^{-5}M; [ketone] 2.7×10^{-4}M; temperature 23 °C

[H^+]/M	0.95	0.712	0.475	0.238
$10^3k'$/s^{-1}	14.4	13.5	13.8	14.6
k''/l mol^{-1} s^{-1}	53.2	50.0	51.0	54.0

Second-order rate constant 52.3 $\pm$ 1.6 l mol^{-1} s^{-1}

(b) [ClO_4^-] 0.95M; [Ru^{III}] 7.5×10^{-5}M; [ketone] 6.92×10^{-4}M; temperature 20 °C

[H^+]/M	0.95	0.712	0.475	0.238
10^8Initial rate (l^{-1} mol s^{-1})	31.0	22.0	14.9	8.10
10^4Rate/2[H^+][ketone] (l mol^{-1} s^{-1})	2.36	2.24	2.28	2.46

(iv) Activation parameters

[$HClO_4$] 0.95M; [ketone] 1.35×10^{-4}M; [Ru^{III}] 1.17×10^{-5}M

k''/l mol^{-1} s^{-1}	28.2	42.0	44.1	52.0	66.0	75.5
Temperature (°C)	15.1	18.7	20.3	23.0	26.1	28.2

Activation energy E_a 12.9 $\pm$ 0.7 kcal mol^{-1}
Activation enthalpy $\Delta H^{\ddagger}$ 12.4 $\pm$ 0.7 kcal mol^{-1}
Free-energy of activation $\Delta G^{\ddagger}$ 15.0 $\pm$ 1.4 kcal mol^{-1}
Activation entropy ΔS_a -8.9 $\pm$ 2.4 cal mol^{-1} K^{-1}

order) plot does not achieve linearity until some time after the beginning of the reaction, the initial rate of reduction of Ru^{III} being slower than expected for a pure first-order reaction, and secondly the initial rates measured become dependent on the acidity. The dependence of initial rates on initial concentration of Ru^{III} for a number of runs shows that the reaction is becoming zero-order in Ru^{III} at the higher Ru^{III} concentrations, and reciprocal plots between instantaneous rate and

Ru^{III} concentration were well fitted by lines calculated on the assumption that the enolisation of the ketone is becoming rate-limiting and that the overall stoicheiometry of the reaction involves the reduction of two Ru^{III} ions per molecule of enol (Figure). The observed rate under acid dependent conditions is also consistent with the known enolisation rate derived from bromination experiments.[12] These observations are closely similar to those found in oxidation by hexachloroiridium(IV).[11] The organic products observed are consistent with the first oxidation step giving the 2-oxocyclohexyl radical, which is then further oxidised to the unstable 2-oxocyclohexyl carbonium ion. This may be solvated to give 2-hydroxycyclohexanone or it may rearrange to give cyclopentanecarboxylic acid or other products.[13] The
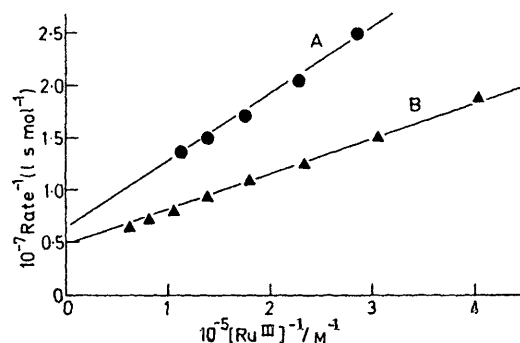
Plot of $10^7/k$ against $10^5/[Ru^{III}]$ at 25° where k = rate of removal of Ru^{III} under oxygen-free conditions: A, [$HClO_4$] 0.488M, [$NaClO_4$] 0.46M, [ketone] 6.9×10^{-4}M; B, [$HClO_4$] 0.95M, [ketone] 2.7×10^{-4}M. The superimposed lines have intercepts of $1'2k$[ketone] where 2 is the stoicheiometry factor and k_1 is taken as 3.0×10^{-4} l mol^{-1} s^{-1} at [H^+] 1M, and is the rate constant for acid-catalysed enolisation at 25°. The lines have slopes of $1/k''$[ketone] where k'' is the experimental second-order rate constant for the removal of Ru^{III} by reaction with ketone

more highly oxidised materials found in the product study throw no further light on the initial attack since they must arise by subsequent oxidation of the initial products either by Ru^{III} or MnO_2, but the predominance of adipic acid supports the hypothesis that attack is primarily at the α-position. The mechanism may then be written as in the Scheme.

The electron-transfer step is therefore represented by the bimolecular constant k_1, which is related to our observed rate constant by the equilibrium constant K, which is small. Using a recent value of K,[14] 2.3×10^{-7}, k_1 is found to be ca. 1×10^8 l mol^{-1} s^{-1}, which is clearly too fast to be anything other than a non-bonded electron transfer at a rate approaching the diffusion limit. Similarly $\Delta G^{\ddagger}$ is ca. 8.5 kcal mol^{-1} which must be much lower than the activation energies necessary to accomplish ligand displacement.

The only evidence for any bonded or inner-sphere process is that under catalytic conditions the ruthenium complex is degraded, and the changes in u.v. spectrum observed are in the direction expected if the ligands had become alkylated. Similarly the i.r. spectrum shows the

probable presence of aliphatic C–H and C=O groups. A similar phenomenon was observed in oxidations by ferriin,[3] and a similar explanation can be proposed. Evidently to a small extent the second electron-transfer step can take place by attack of the 2-oxocyclohexyl radical on the ligand, with concomitant reduction of the Ru^{III} centre and subsequent loss of a proton.

Removal of oxygen from Ru^{III} solutions is difficult, because to reach a level of oxygen concentration comparable with the Ru^{III} concentration requires considerable care, and the slow decomposition of Ru^{III} is liable to reintroduce oxygen. The above results were obtained

those briefly reported by Ng and Henry,[15] who used a higher concentration of ketone, a sulphuric acid medium, and the chloride salt of the oxidant. Furthermore (iii)(b) demonstrates the acid-independence of the electron transfer step while (vi) illustrates that under the alternative enolisation-limited condition, the enolisation rate is of the expected magnitude. It is evident that the presence of oxygen has no effect on the form of the kinetics, so any influence must be due to its intervention at a later stage, for example, by the capture of the 2-oxocyclohexyl radical to give peroxide materials.

Activation Parameters.—The activation enthalpy under
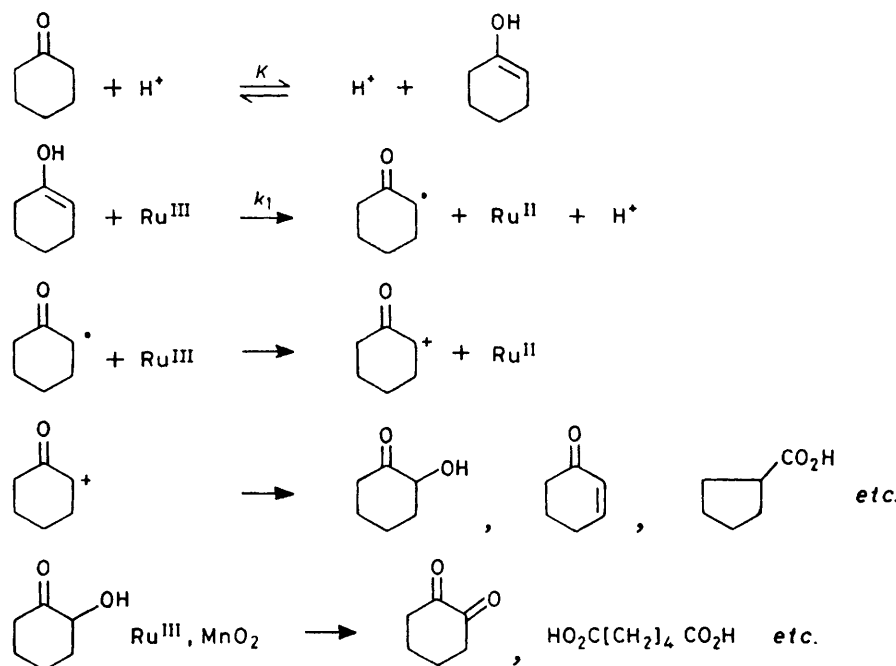
SCHEME

by careful freeze–thaw degassing of the individual components of reaction mixtures after they had been introduced into a compartmentalised mixing vessel, but the change of rate caused by this procedure was never more than a factor of 2, and often much less. Alternative techniques tried (bulk degassing of stocks of reagent solutions either by freeze–thaw or by blowing oxygen-free nitrogen through) had no reproducible effect on the rate, so there are considerable doubts whether the small apparent oxygen effect is significant. The reaction was therefore also studied in detail using normal air-saturated solutions, to avoid any errors which might inadvertently be introduced by the degassing procedures.

Oxidation of Cyclohexanone in the Presence of Oxygen (*Table* 2).—Section (i)(a) of Table 2 shows that the reaction is still first-order in Ru^{III} at low oxidant concentrations, while (i)(b) shows the tendency towards zero-order dependency which demonstrates attack on the enol. Section (ii) shows that the reaction is first-order in ketone concentration; the values obtained are similar to

oxygen is identical within experimental error with that under nitrogen, and is almost the same as that in the reaction with ferriin. The oxidation by [IrCl$_6$]$^{2-}$ has a somewhat higher value (16 kcal mol^{-1}). The greater ease of the present reaction, compared with that of ferriin, arising from the more negative standard free-energy (the Ru^{III} potential is *ca.* 0.3 more positive than the ferriin potential) is apparent in its less negative entropy of activation. This comparison is of interest because the two oxidants are of very similar size and charge type, but it assumes that the organic molecule is in the same form in both reactions. A Marcus free-energy plot[16] of the non-bonded electron-transfer oxidations of cyclohexanone, with rates referred to cyclohexanone concentration in each case, also shows that the point for ferriin falls on the same line as tris-bipyridylruthenium(III) and other Fe^{III} and Ru^{III} complexes with heterocyclic ligands, though the rates are faster than those observed for halogenoiridium(IV) complexes. This may be due to their different charge-types,

TABLE 2

The reaction of cyclohexanone with trisbipyridyl-ruthenium(III) perchlorate in air

(i) Dependence on [Ru^{III}]

(a) [$HClO_4$] 0.95M; Ru^{III} prepared by oxidation by Ce^{IV}; [ketone] 1.41×10^{-4}M; temperature 25 °C

10^6[Ru^{III}]/M	8.96	6.72	4.48	2.22	1.11
$10^3k'$/s^{-1}	4.08	4.04	3.96	4.17	4.21
k''/l mol^{-1} s^{-1}	29.0	28.7	28.1	29.6	29.9

Second-order rate constant $k'' = 29.1 \pm 0.5$ l mol^{-1} s^{-1}

(b) [$HClO_4$] 0.95M; Ru^{III} prepared by oxidation by PbO_2; [ketone] 2.7×10^{-4}M; temperature 24 °C

10^5[Ru^{III}]/M	1.59	1.25	0.88	0.62	0.50	0.39
10^8 Initial rate (mol l^{-1} s^{-1})	4.87	4.35	3.76	2.95	2.48	2.04
Rate/[Ru^{III}][ketone] (l mol^{-1} s^{-1})	11.3	12.9	15.8	17.6	18.4	19.5
10^4Rate/[H^+][ketone] (l mol^{-1} s^{-1})	1.91	1.70	1.47	1.15	0.96	0.80

(ii) Dependence on [ketone]

[$HClO_4$] 0.95M; temperature 25 °C; [Ru^{III}] 2.4×10^{-6}M

10^4[ketone]/M	6.7	3.3	1.3	0.67	0.35
$10^3k'$/s^{-1}	26.1	13.2	5.33	2.68	1.4
k''/l mol^{-1} s^{-1}	39	40	41	40	40

[Ru^{III}] 4.9×10^{-6}M

10^4[ketone]/M	4.8	3.8	2.9	1.9	1.0
$10^3k'$/s^{-1}	20.4	15.1	12.3	7.32	4.02
k''/l mol^{-1} s^{-1}	42.3	39.8	42.5	38.5	40.2

Second-order rate constant $k'' = 40.2 \pm 1.2$ l mol^{-1} s^{-1}

(iii) Dependence on [H^+]

(a) [ClO_4^-] 1.43M; [Ru^{III}] 7.0×10^{-6}M; [ketone] 2.7×10^{-4}M; temperature 25 °C

[H^+]/M	1.43	1.19	0.95	0.715	0.48
$10^3k'$/s^{-1}	8.00	7.53	7.50	7.85	7.97
k''/l mol^{-1} s^{-1}	29.6	27.9	27.8	29.1	29.5

Second-order rate constant $k'' = 28.8 \pm 0.8$ l mol^{-1} s^{-1}

(b) [ClO_4^-] 0.95M; [Ru^{II}] 7.5×10^{-5}M; [ketone] 1.35×10^{-3}M; temperature 20 °C

[H^+]/M	0.95	0.712	0.475	0.238
10^8 Initial rate (l^{-1} mol s^{-1})	33.8	24.4	15.9	8.35
10^4Rate/[H^+][ketone] (l mol^{-1} s^{-1})	2.48	2.53	2.64	2.60

(iv) Activation parameters

[$HClO_4$] 0.95M; [ketone] 2.7×10^{-4}M; [Ru^{III}] 1.17×10^{-5}M

Temperature (°C)	14.4	16.1	19.5	22.8	24.1	26.0
k''/l mol^{-1} s^{-1}	13.3	15.6	20.6	23.5	27.5	31.1
Temperature (°C)	27.1	29.2				
k''/l mol^{-1} s^{-1}	34.4	38.6				

Activation energy E_a 12.3 ± 0.4 kcal mol^{-1}
Activation enthalpy $\Delta H^{\ddagger}$ 11.7 ± 0.4 kcal mol^{-1}
Free energy of activation $\Delta G^{\ddagger}$ 15.5 ± 0.8 kcal mol^{-1}
Activation entropy $\Delta S^{\ddagger}$ -12.7 ± 1.4 cal mol^{-1} K^{-1}

(v) The effect of changes of ionic strength

[H^+] 0.95M; [Ru^{III}] 3.5×10^{-6}M; [ketone] 2.7×10^{-4}M; temperature 27 °C

[ClO_4^-]/M	0.95	1.58	2.20
k''/l mol^{-1} s^{-1}	32.9	30.1	22.5

(vi) The apparent rate of enolisation

[Ru^{III}] $\geqslant 10^{-5}$M

[ketone]/M	[H^+]/M	Temp. (°C)	Initial rate (mol l^{-1} s^{-1})	10^4k_2/l mol^{-1} s^{-1} = rate/ [H^+][ketone]
1.14×10^{-3}	1.0	25	2.4×10^{-7}	2.1
5.70×10^{-4}	1.0	25	1.3×10^{-7}	2.3
7.6×10^{-4}	0.1	28	2.95×10^{-8}	3.9
7.6×10^{-3}	0.1	28	2.30×10^{-7}	3.0

but it must also be expected from their known greater self-exchange rates, which are at least 10^2 faster.[17]

If this correlation is validly extended to the oxidation of cyclohexanone by ferriin, it implies that the suggestion made in Part 1 that ferriin attacks the unenolised ketone directly is not correct. This was based essentially on two observations, first a low CH/CD isotope effect, in the oxidation of 2,2,6,6-tetradeuteriocyclohexanone, and secondly that the observed rate was too fast by a factor of *ca.* 2 to be possible without the enolisation step becoming rate-limiting. In view of the difficulties found in the earlier work in getting good kinetics under oxygen-free conditions, we now have doubts whether the oxygen was completely removed. This would result in the data for the oxygen-free reactions, by means of the distinctions between enol and keto routes were made, being less reliable. Ng and Henry[9] also found that ferriin and related systems were ill behaved kinetically under oxygen-free conditions, and they were able to find evidence for the enolisation process being rate limiting in air-saturated solutions.[15] Although the explanation of the peculiar behaviour and variable effects of oxygen is not at all clear it seems unlikely that oxygen would affect the relative ease of electron removal from the keto or the enol form, so we can conclude that ferriin and trisbipyridylruthenium(III) attack ketones *via* essentially the same mechanisn, non-bonded electron transfer from the neutral enol molecule.

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