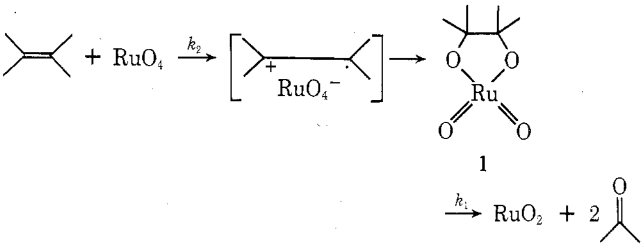
Communications

The Oxidation of Methyl Cinnamate by Ruthenium Tetroxide

Summary. A kinetic study of the oxidation of methyl cinnamate by ruthenium tetroxide indicates that the reaction proceeds via a cyclic ruthenium(VI) diester intermediate.

Sir: We wish to report evidence which indicates that the oxidative cleavage of carbon–carbon double bonds by ruthenium tetroxide proceeds by a mechanism similar to that outlined in Scheme I. The reaction is of both practical and theoretical importance; its practical value is illustrated by its use in a variety of synthetic sequences,[1] while theoretically it represents another example of a transition metal oxide that can participate in multielectron transfer reactions.[2]

Scheme I



A series of substituted methyl cinnamates was chosen as model compounds for a kinetic study of this reaction. These compounds are soluble in carbon tetrachloride (the solvent most commonly used for ruthenium tetroxide oxidations), and they readily permit a study of both substituent and isotope effects on the rate of reaction. Furthermore, their use allows for a direct comparison with the rates of oxidation of substituted cinnamate ions (in aqueous base) by MnO_4^-, RuO_4^- and RuO_4^{2-}.[3,4]

When the course of the reaction was monitored at 385 nm using a Perkin-Elmer 356 double wavelength spectrophotometer equipped with a thermostated cell compartment and a rapid mixing device, it was observed that the reaction proceeded in two distinct steps. The first exhibited good second-order kinetics and resulted in the formation of a detectable intermediate while the second was slower and first order. The rate constants obtained are summarized in Table I.

Examination of the spectral properties of the intermediate indicated that it was likely a ruthenium(VI) moiety, but with somewhat broader bands than those observed for the ruthenate ion.[5] A likely structure for such an intermediate (as suggested by analogy with osmium tetroxide oxidations[6]) would be the cyclic ruthenate diester **1**. However, a comparison with permanganate oxidations[3] indicates that formation of such an intermediate directly from the reactants should result in an inverse secondary isotope effect. The observation of a normal secondary isotope effect for the first step of the reaction suggests that the transition state must be one which can be stabilized by hyperconjugation.[7] Two possibilities could therefore be considered: electrophilic addition (in analogy with aromatic oxidations[8]) or ion radical formation. While both of these possibilities are in agreement with the effect of substituents ($\rho = -0.99$) the former can be disregarded because it predicts, in contradiction with the experimental evidence, that an inverse secondary isotope effect should be observed when the hydrogen on the α carbon is replaced by deuterium.[9] Consequently, it would appear that the transition state of the first step resembles a radical cation–perruthenate complex which would give **1**, as outlined in Scheme I.

Table I. Rate Constants for the Oxidation of Unsaturated Esters by Ruthenium Tetroxide [a]

Substrate	k_2 (×10^{-3}),[b] M^{-1} s^{-1}	k_1 (×10^3),[c] s^{-1}
Methyl cinnamate	10.7 ± 0.5	1.72 ± 0.26
Methyl cinnamate-α-d	8.9 ± 0.2	1.18 ± 0.18
Methyl cinnamate-β-d	8.3 ± 0.5	1.13 ± 0.20
Methyl p-chlorocinnamate	10.0 ± 1.0	1.79 ± 0.27
Methyl p-nitrocinnamate	1.84 ± 0.04	0.74 ± 0.11
Methyl m-nitrocinnamate	2.32 ± 0.04	0.59 ± 0.09
Methyl p-methoxycinnamate	18.1 ± 0.4	3.23 ± 0.48
Methyl m-methoxycinnamate	8.0 ± 0.6	1.76 ± 0.26
Methyl m-chlorocinnamate	5.0 ± 0.1	1.23 ± 0.18
Methyl p-methylcinnamate	22.8 ± 1.1	2.07 ± 0.31
Dimethyl fumarate	1.95 ± 0.08	0.134 ± 0.020
Dimethyl fumarate-α-β-d_2	1.51 ± 0.05	

[a] k_2 and k_1 are defined in Scheme I. [b] $[RuO_4] = 5 \times 10^{-5}$ M, [substrate] = 1×10^{-4} M, T = 25.0 °C. [c] $[RuO_4] = 1.5 \times 10^{-4}$ M, [substrate] = 5×10^{-4} M, T = 25.0 °C.

The isotope and substituent effects ($\rho = -0.61$) on the second step of the reaction are entirely consistent with it being an oxidative decomposition of **1** to carbonyl compounds. Confirmation of these products was obtained by the observation that good yields of benzoic acid and oxalate were obtained when methyl cinnamate was oxidized under similar conditions by an excess of ruthenium tetroxide.

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Kinetics of the Oxidation of Some Unsaturated Compounds by Sodium Perruthenate

Summary. The results obtained from a kinetic study of the oxidation of unsaturated compounds by sodium perruthenate ($NaRuO_4$) are reminiscent of those previously reported for the oxidation of the same compounds by potassium permanganate.

Sir: The rates of reaction of perruthenate ion with a number of unsaturated carboxylic acid anions were followed spectrophotometrically by monitoring the disappearance of an absorbance band at 385 nm[1] using a Durrum Model D-110 stopped-flow spectrophotometer. When an excess of substrate was used, good pseudo-first-order plots were obtained, with the product being ruthenate ion (RuO_4^{2-}). The rate of reaction was also found to be first order with respect to reductant concentration but independent of the concentration of base between 0.04 and 0.5 M NaOH. Because perruthenate ion is stable only under basic conditions, it was convenient to use unsaturated carboxylic acids as substrates. The rate constants obtained are summarized in Table I.

The similarities between the results in Table I and those which have previously been reported for permanganate oxidations are remarkable. Similar isotope effects are observed with both oxidants when deuterated compounds are used as substrates.[2] Ring substitution has little effect on the rate of oxidation by both reagents.[5] The rates of both reactions are independent of base concentration.[5] The relative rates of oxidation of fumaric and maleic acid are similar for both oxidants[6] as are the relative rates for crotonic and cinnamic acid.[5] Methyl substitution at the double bond decreases the rate of oxidation by both permanganate[5,7] and perruthenate ions, and the activation parameters for both reactions are characterized by large negative entropies and low enthalpies of activation (Table II).

Table I. Rate Constants for the Oxidation of Unsaturated Carboxylate Ions by Sodium Perruthenate [a]

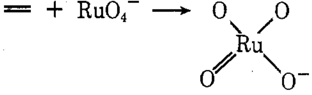
Carboxylate ion	Concn, M	[NaOH], M	k_2, $M^{-1}\,s^{-1}$
Crotonate	5.25×10^{-3}	0.041	56.6 ± 3.0
Crotonate	5.25×10^{-3}	0.124	54.4 ± 2.3
Crotonate	5.25×10^{-3}	0.207	56.1 ± 0.3
Crotonate	4.13×10^{-3}	0.310	56.3 ± 0.8
Crotonate	5.25×10^{-3}	0.414	56.1 ± 0.2
Crotonate-α-*d*	4.13×10^{-3}	0.310	58.6 ± 1.1
Crotonate-β-*d*	4.13×10^{-3}	0.310	58.7 ± 1.4
Acrylate	5.25×10^{-3}	0.207	83.9 ± 3.6
Methacrylate	5.25×10^{-3}	0.207	66.3 ± 0.6
α-Methylcrotonate	5.25×10^{-3}	0.310	11.7 ± 0.8
β-Methylcrotonate	5.25×10^{-3}	0.310	11.7 ± 0.2
Fumarate	3.50×10^{-3}	0.140	137 ± 5
Fumarate	3.50×10^{-3}	0.193	140 ± 4
Fumarate	3.50×10^{-3}	0.350	135 ± 3
Fumarate	3.50×10^{-3}	0.451	142 ± 3
Maleate	3.50×10^{-3}	0.350	8.7 ± 0.09
Mesaconate	3.50×10^{-3}	0.350	14.3 ± 0.2
Citraconate	3.50×10^{-3}	0.350	0.6 ± 0.02
Cinnamate	3.40×10^{-2}	0.282	133 ± 2
Cinnamate-β-*d*	3.40×10^{-2}	0.282	138 ± 2
p-Methoxycinnamate	5.60×10^{-2}	0.388	113 ± 3
p-Methylcinnamate	5.60×10^{-2}	0.388	121 ± 4
m-Methoxycinnamate	5.60×10^{-2}	0.388	136 ± 7
p-Chlorocinnamate	5.60×10^{-2}	0.388	119 ± 3
m-Chlorocinnamate	5.60×10^{-2}	0.388	123 ± 5
m-Bromocinnamate	5.60×10^{-2}	0.388	119 ± 1

[a] Temperature 21 °C; ionic strength was maintained at 0.500 M by use of sodium perchlorate. Initial perruthenate concentration was about 1.5×10^{-4} M.

Table II. A Comparison of the Activation Parameters for the Oxidation of Unsaturated Carboxylate Ions by Permanganate and Perruthenate Ions in Aqueous Base

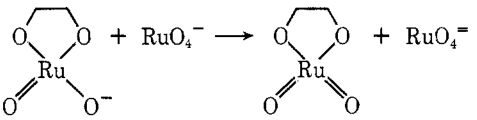
Carboxylate ion	Oxidant	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
Crotonate	RuO_4^-	6.0	−31	14
Crotonate[2]	MnO_4^-	4.8	−32	14
Cinnamate	RuO_4^-	5.0	−32	14
Cinnamate[2]	MnO_4^-	3.3	−36	14
Fumarate	RuO_4^-	3.6	−37	15
Fumarate[4]	MnO_4^-	3.1	−34	13

Because of the many similarities with the reactions of permanganate ion, it seems reasonable to assume that perruthenate ion reacts with carbon–carbon double bonds in an analogous way. Thus it appears that the initial step is quite probably formation of a cyclic ruthenium(V) diester (eq 1).[3]



(1)

1



(2)

2

However, since the first detectable product was observed to be ruthenate ion, the initial step must be followed by a fast reaction of **1** with perruthenate ion as in eq 2. A comparison with the rates of transfer of electrons between other transition metal oxy anions suggests it is not unreasonable to expect that this step would be fast,[8] and from a study of the reactions of unsaturated compounds with sodium ruthenate it is known that the decomposition of **2** would be slow at this temperature.[9] Although it might be expected that a ruthenium(V) compound would have some stability under these conditions,[10] no evidence for the presence of an intermediate could be found by monitoring the reaction at several wavelengths between 300 and 650 nm.

When the reaction was carried out on a larger scale (more appropriate for product isolation), it was found that benzoic acid and oxalic acid could be obtained in yields of 99 and 91% from the oxidation of cinnamic and fumaric acids, respectively, if the process was allowed to proceed until the oxidant had been completely reduced to ruthenium dioxide. When attempts were made to intercept the intermediate by quenching the reaction with an excess of sodium arsenite, the expected diol was not detected, but benzaldehyde was then found among the products obtained from the oxidation of cinnamic acid. This suggests that the quenching was effective only at some later step in the reaction.

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Kinetics of the Oxidation of Some Unsaturated Compounds by Sodium Ruthenate

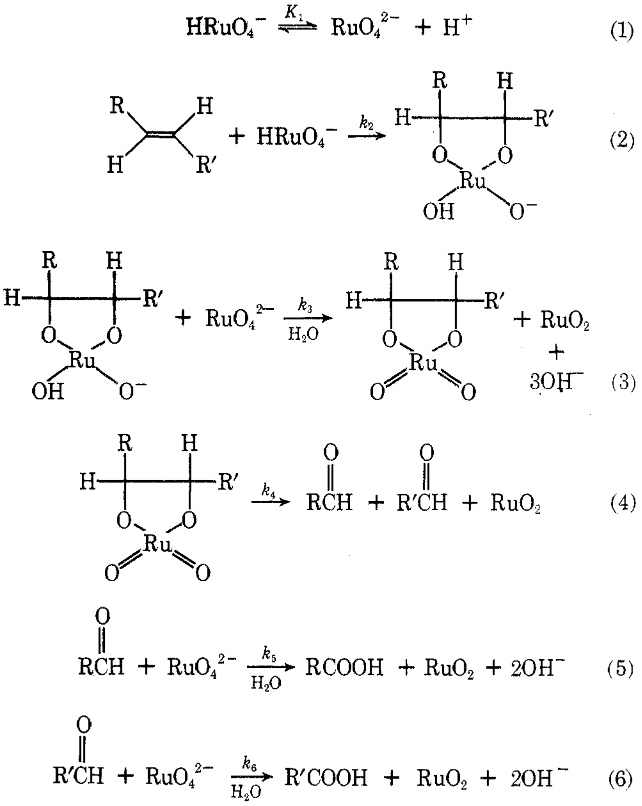
Summary. A kinetic study of the oxidation of a number of unsaturated carboxylic acids by sodium ruthenate suggests that the reaction proceeds by way of a complex mechanism which involves both ruthenium(IV) and ruthenium(VI) diesters as intermediates.

Sir: An investigation of the oxidative cleavage of carbon–carbon double bonds by sodium ruthenate (Na_2RuO_4) is of interest because ruthenium(VI) oxides may be involved as intermediates in ruthenium tetroxide oxidations.[1] We have found that the results obtained from a kinetic study of the oxidation of a large number of unsaturated carboxylate ions by sodium ruthenate can all be accommodated by the reaction mechanism outlined in Scheme I. Aqueous sodium hydroxide was used as the solvent for these experiments because ruthenate ion is not stable in neutral or acidic solutions.[2]

Sodium ruthenate[3] was found to react at easily measurable rates with unsaturated carboxylate ions in aqueous base at 85 °C. The rates were determined by removing aliquots at appropriate intervals and estimating the concentration of ruthenate ion using a Perkin-Elmer 356 dual wavelength, double beam spectrophotometer which has previously been described.[4] The absorbance at 460 nm (maximum) was compared with that at 570 nm (minimum) and the concentration of ruthenate ion obtained from a previously prepared calibration curve.

Initial rate studies indicated that the reaction was first order in both ruthenate and carboxylate ions. However, good second-order kinetics were not maintained throughout the entire course of the reaction, and subsequent studies revealed that the experimental data could not be satisfactorily fitted to any integral rate expression. Consequently, a computer program which simulates reaction kinetics by numerical integration was used to define the rate law.[5] The program generates data for a particular scheme starting from an initial set of rate constants, compares the generated data with the experimental data, adjusts the rate constants, and repeats the process until the differences between calculated and experimental absorbance values have been minimized. When approximately 30 different possible reaction schemes were investigated in this way, Scheme I was found to give the best agreement with all of the available data.

Scheme I



The approximate values for k_2 were first obtained from initial reaction rates, and k_3, k_5, and k_6 were assumed to be large relative to k_2 and k_4. Since step 3 involves the transfer of electrons between two oxy anions, it is not unlikely that k_3 would be relatively large.[6] Test tube experiments indicated

Table I. Rate Constants for the Oxidation of Unsaturated Carboxylic Acids by Sodium Ruthenate in Aqueous Sodium Hydroxide[a]

Carboxylate ion	Concn, M	[NaOH], M	$k_2 \times 10^3$, M^{-1} s^{-1} [b]	$k_4 \times 10^5$, M^{-1} s^{-1} [b]
Acrylate	0.00820	0.717	25.1 ± 1.2	23.0 ± 7
Crotonate	0.00780	0.717	11.9 ± 0.6	3.3 ± 0.9
Crotonate	0.00798	0.628	16.8 ± 0.1	3.6 ± 1.1
Crotonate-*β*-*d*	0.00798	0.628	28.4 ± 0.7	5.5 ± 1.6
Methacrylate	0.00796	0.717	9.1 ± 0.2	1.7 ± 0.5
α-Methylcrotonate	0.0177	0.717	8.8 ± 0.1	4.7 ± 1.4
β-Methylcrotonate	0.00795	0.717	3.4 ± 0.1	0.76 ± 0.23
Cinnamate	0.00121	0.532	59.2 ± 1.5	1.9 ± 0.6
Cinnamate-*α*-*d*	0.00121	0.532	73.3 ± 0.9	1.4 ± 0.4
Cinnamate-*β*-*d*	0.00121	0.532	70.2 ± 2.0	1.7 ± 0.5
p-Methylcinnamate	0.00462	0.516	48.6 ± 0.4	7.2 ± 2.2
m-Methoxycinnamate	0.00462	0.516	45.5 ± 0.7	5.2 ± 1.6
m-Nitrocinnamate	0.00462	0.516	42.4 ± 0.4	4.8 ± 1.4

[a] Temperature 85.0 ± 0.1 °C. Initial ruthenate concentration was 4.3 × 10^{-4} to 5.0 × 10^{-4} M. [b] k_2 and k_4 are defined in Scheme I.