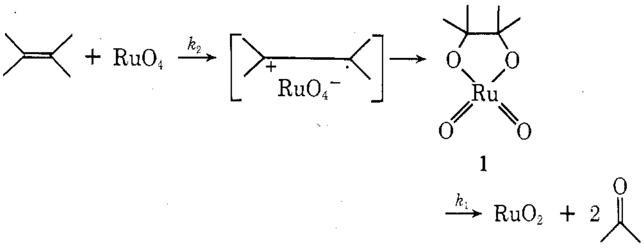
Communications

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 ($\times 10^{-3}$),[b] $M^{-1}\,s^{-1}$	k_1 ($\times 10^{3}$),[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] $= 1 \times 10^{-4}$ M, $T = 25.0$ °C. [c] $[RuO_4] = 1.5 \times 10^{-4}$ M, [substrate] $= 5 \times 10^{-4}$ 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.

Acknowledgments. The authors gratefully acknowledge the financial assistance of the National Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

(1) D. G. Lee and M. van den Engh in "Oxidation in Organic Chemistry", Part B, W. S. Trahanovsky, Ed., Academic Press, New York, N.Y., 1973, pp 177–227.
(2) J. S. Littler, *Tetrahedron,* **27,** 81 (1971); K. B. Sharpless and D. R. Williams, *Tetrahedron Lett.,* 3045 (1975).
(3) D. G. Lee and J. R. Brownridge, *J. Am. Chem. Soc.,* **96,** 5517 (1974).
(4) Accompanying manuscripts.
(5) R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.,* **74,** 5012 (1952).
(6) R. Stewart, "Oxidation Mechanisms: Applications to Organic Chemistry", W. A. Benjamin, New York, N.Y., 1964, p 84.
(7) E. A. Halevi, *Progr. Phys. Org. Chem.,* **1,** 109 (1963).
(8) U. A. Spitzer and D. G. Lee, *Can. J. Chem.,* **53,** 2865 (1975).
(9) F. Freeman and N. J. Yamachika, *J. Am. Chem. Soc.,* **94,** 1214 (1972).

Donald G. Lee,* Udo A. Spitzer
Department of Chemistry, The University of Regina
Regina, Canada S4S 0A2

Received March 29, 1976

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.