

Duality of Mechanism in the Oxidation of Alkenylbenzenes by Cerium(IV) Ammonium Nitrate

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The oxidation of styrenes and other alkenylbenzenes by cerium(IV) ammonium nitrate takes place either by an electron-transfer mechanism or by a free-radical addition depending on the structure of the substrate.

Considerable information is available concerning the oxidation of alcohols and alkylbenzenes by cerium(IV) ammonium nitrate (CAN),¹ but relatively little is known regarding the reaction of this oxidant with olefins.²⁻⁶ It has been suggested

that this reaction, which leads to products of addition^{4,5} or allylic substitution,⁶ is initiated by the attack of NO₂⁺ (either free⁶ or bonded to the metal⁴) at the double bond.

We herein provide evidence that two mechanisms are

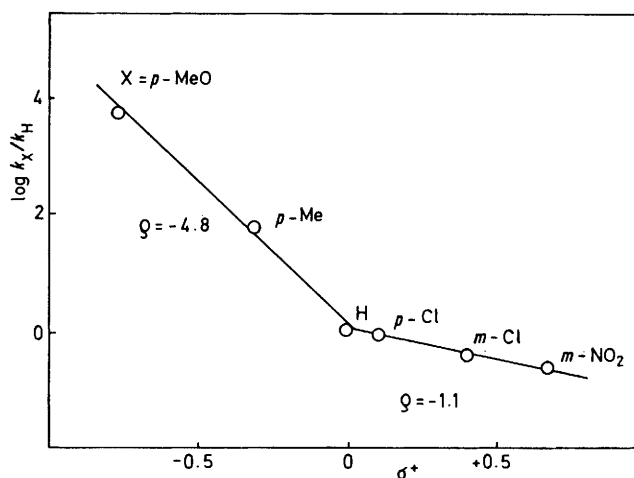


Figure 1. Correlation between relative reactivities ($\log k_x/k_H$) of substituted styrenes $X.C_6H_4.CH=CH_2$ and the substituent constant (σ^+) in the oxidation with CAN in MeCN at 30 °C.

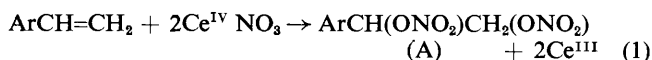
Table 1. Second-order rate constants (k) for CAN^a oxidations of some alkenylbenzenes in MeCN at 30 °C.

Substrate	$k^b/dm^3 mol^{-1} s^{-1}$
<i>p</i> -Methoxystyrene (1)	2.5×10^{-1}
Indene (2)	1.9×10^{-2}
<i>trans</i> - β -Methylstyrene (3)	5.5×10^{-3}
<i>p</i> -Methylstyrene (4)	2.6×10^{-3}
α -Methylstyrene (5)	2.7×10^{-4}
Styrene (6)	4.2×10^{-5}
<i>p</i> -Chlorostyrene (7)	3.7×10^{-5}
<i>m</i> -Chlorostyrene (8)	1.5×10^{-5}
<i>m</i> -Nitrostyrene (9)	1.0×10^{-5}

^a $[Ce^{IV}]_0 = 6.17 \times 10^{-3} mol dm^{-3}$. ^b The average error is $\pm 2\%$.

operating in the oxidation of alkenylbenzenes by CAN in MeCN. With substrates more reactive than styrene the reaction is initiated by an electron-transfer process, however with less reactive substrates a free-radical addition appears to be much more likely.

The oxidation of styrene and other alkenylbenzenes by CAN in MeCN leads to the quantitative formation of the addition compounds (A) as shown in equation (1).



Neither allylic substitution (with α -methylstyrene, *trans*- β -methylstyrene, and indene), nor side-chain substitution (with *p*-methylstyrene) appear to compete significantly with the formation of addition products.

Reaction (1) follows regular second-order kinetics (first-order in CAN and in substrate)[†] and the rate is accelerated by electron-releasing substituents, as shown by the data in Table 1. A Hammett plot for a series of *para*- and *meta*-substituted styrenes (Figure 1) gives a value for the reaction constant ρ of -4.8 with electron-releasing substituents and -1.1 with electron-withdrawing substituents, thus suggesting that two mechanisms are operating in the oxidation of these substrates.

[†] The rates were followed spectrophotometrically by determination of the rate of disappearance of CAN at 504 nm. The products were characterized spectroscopically by comparison with literature data.⁵

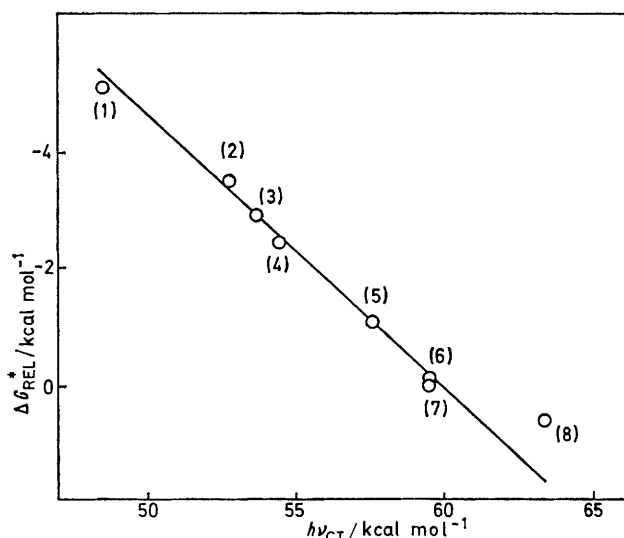
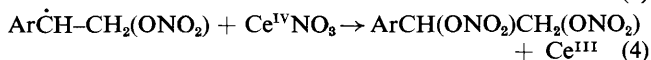
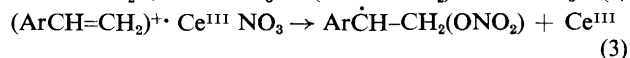
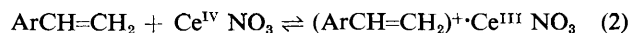


Figure 2. Correlation between the relative activation free energies (ΔG_{rel}^\ddagger) for the oxidation with CAN (in MeCN at 30 °C) of alkenylbenzenes, and charge-transfer transition energies ($h\nu_{CT}$) of the corresponding complexes with TCNE. 1 kcal = 4.184 kJ. For the numbering see Table 1.

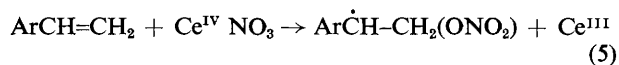
The very high negative ρ value for the activated styrenes and the additional observation that a very good linear relationship exists between the oxidation rates and the ionization potentials (Figure 2)[‡] strongly suggest that the reaction of these substrates with CAN takes place by an electron-transfer mechanism leading to the formation of a radical cation intermediate, probably in the rate-determining step. The radical cation may remain associated with the reduced form of cerium (equation 2) and be converted into the final products according to the sequence in equations (3) and (4).



Further evidence strongly supporting the initial formation of a radical cation intermediate is the observation that *trans*- β -methylstyrene is oxidized much more rapidly than α -methylstyrene (Table 1), in agreement with the lower ionization potential of the former substrate (Figure 2). In contrast, in addition reactions where initial attack leads directly either to a free radical⁸ or to a carbocation⁹ the reverse situation holds: α -methylstyrene is more reactive than *trans*- β -methylstyrene. We suggest that the relative reactivity of α -methylstyrene and *trans*- β -methylstyrene may represent a mechanistic criterion allowing discrimination between rate-determining electron transfer and direct attack on the double bond.

With alkenylbenzenes less reactive than styrene the low value of ρ (-1.1) is in agreement with a free-radical mechanism,^{4,6} probably involving the direct formation of the benzylic free radical in a ligand-transfer process (equation 5) as suggested by others.⁴ The possibility that these substrates

[‡] The correlation is actually between the oxidation rates and the $h\nu$ values for the charge-transfer complexes of alkenylbenzenes with tetracyanoethylene (TCNE). However, it is well known that these latter values can be correlated with the ionization potentials.⁷



react by a fast and reversible electron-transfer process, followed by slow formation of the benzylic free radical, appears unlikely since a significantly higher ρ value would then have been expected.¹⁰ Moreover, it would be somewhat surprising that in a series of styrenes the formation of the radical cation becomes faster as the stability of the radical cation decreases.

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