

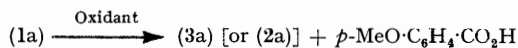
One-electron Oxidation of Closed-shell Molecules. Part 1. Oxidative Cleavage of *para*-Substituted Benzpinacolones by Cerium(IV) Ammonium Nitrate

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The stoichiometry and kinetics of the Ce^{IV} oxidation of 1,2,2,2-tetrakis-(*p*-methoxyphenyl)ethanone (1a) have been investigated at 25.0 °C in acetic acid as solvent by the use of cerium(IV) ammonium nitrate as oxidant. The reaction occurs with the stoichiometry $2 \text{Ce}^{\text{IV}} + \text{An}_3\text{C}\cdot\text{CO}\cdot\text{An} \longrightarrow 2 \text{Ce}^{\text{III}} + \text{An}_3\text{C}^+ + \text{An}\cdot\text{CO}^+$ ($\text{An} = p$ -methoxyphenyl), affording tris-(*p*-methoxyphenyl)methanol and anisic acid after work-up. The kinetics were monitored by u.v.-visible spectrophotometry of the tris-(*p*-methoxyphenyl)methyl cation, showing that the rate-determining step is first order in each reactant. Evidence was found for the formation of *p*-methoxybenzoyl radical by means of spin-trapping with 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene. The rate constants at 25.0 °C, the oxidation potential, as measured by cyclic voltammetry, and the charge transfer energy with tetracyanoethylene have been measured for five *para*-substituted benzpinacolones (substituents MeO, Me, and Cl) including (1a). A good correlation of the logarithms of the rates with the oxidation potentials or with the charge transfer energies was found, indicating that a single electron-transfer step between the substrate and Ce^{IV} is rate determining. The formation of a radical cation of the benzpinacolone in the rate-determining step and subsequent rapid cleavage into the triarylmethyl cation and the aroyl radical are proposed as a possible mechanism.

In 1960 Buckles and his co-workers¹ reported the spectrophotometric observation that 1,2,2,2-tetrakis-(*p*-methoxyphenyl)ethanone (anispinacolone) (1a) (*ca.* $1 \times 10^{-5}\text{M}$) gave rise to tris-(*p*-methoxyphenyl)methyl cation (2a) in 1,2-dichloroethane at room temperature in the presence of such electron acceptors as iodine, bromine, iodine chloride, trifluoroacetic acid,[†] and trichloroacetic acid.[†] Although enough evidence to establish the mechanism was not available, they tentatively suggested that anispinacolone (1a) interacts with an electron acceptor at the carbonyl group and then dissociates to give (2a).

With our interest in the one-electron oxidation by an electron acceptor of closed-shell molecules, we reinvestigated² the cleavage of anispinacolone (1a) at higher concentrations (*ca.* 0.1M) in the presence of trifluoroacetic acid (*ca.* 2.0M) and unexpectedly found that cleavage was inhibited under vacuum or in nitrogen even in the presence of acid, but on exposure to air or oxygen it proceeded with rapid absorption of oxygen to give rise to cation (2a). Subsequent work-up with water afforded tris-(*p*-methoxyphenyl)methanol (3a) and anisic acid (Scheme 1).^{2,‡}

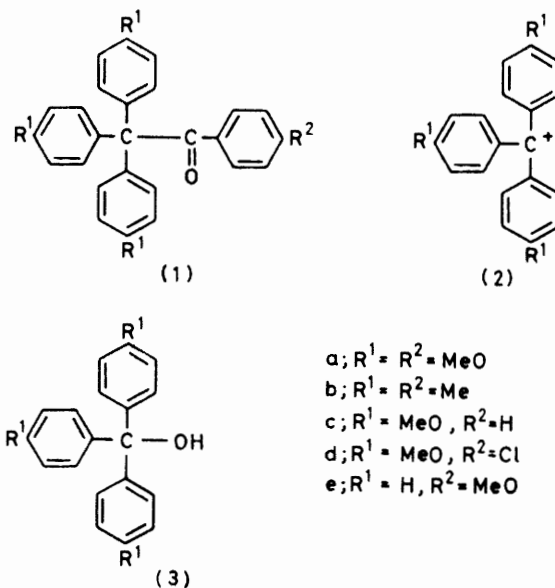


SCHEME 1 Oxidants: $\text{O}_2 + \text{H}^+$,² diaroyl peroxide,³ or nitrobenzene + H^+ .⁵ Solvent: $\text{ClCH}_2\text{CH}_2\text{Cl}$

Following the clarification of the mechanism of this cleavage of anispinacolone (1a), it was demonstrated that bis-3,5-dinitrobenzoyl peroxide also cleaves (1a) in 1,2-dichloroethane, giving the carbinol (3a) and anisic acid at 50 °C,^{3a} and that oxidative cleavage with less reactive diaroyl peroxides readily proceeds in the presence of added trifluoroacetic acid.^{3b} It has also been found that in acidic nitrobenzene, which is known to be an electron acceptor,⁴ anispinacolone (1a) is smoothly oxidized in similar fashion even upon exclusion of oxygen.⁵

† In the light of later studies,² it was demonstrated that these halogenoacetic acids do not play a role as electron acceptor.

The ready cleavage of anispinacolone (1a) with these oxidants^{1-3,5} (Scheme 1) consequently suggests that cleavage can be initiated by a one-electron oxidation step, presumably giving rise to the corresponding radical cation.



As a starting point for confirmation of the mechanism of these cleavages, it is of interest to seek a system wherein the benzpinacolone would be unambiguously oxidized by a single-electron transfer, because product analysis and mechanistic examination of such an oxidation would be indispensable for the consideration of the mechanism of seemingly more complicated oxidations with oxygen² or diaroyl peroxides.³

‡ At higher temperature (50 °C) under nitrogen or in a vacuum another reaction, *i.e.*, aromatic protidealkylation of anispinacolone (1a) with trifluoroacetic acid, becomes predominant affording anisole and 2,3-bis-(*p*-methoxyphenyl)-6-methoxybenzofuran (*ca.* 90%), although the oxidation product (3a) (5%) was still isolated even upon careful exclusion of oxygen.²

Oxidation with cerium(IV) ammonium nitrate (CAN) was chosen as a prototype reaction, since it is generally recognized as a typical one-electron oxidation of various closed shell molecules.⁶ Product and kinetic studies were carried out on the CAN oxidation of the *para*-substituted benzpinacolones (1a–e) in acetic acid and the mechanistic implications are discussed.

RESULTS

Reaction Products and Stoichiometry.—All oxidations were carried out in the dark and under nitrogen. Owing to the low solubilities of CAN and anispinacolone (1a) in acetic acid at room temperature, an initial concentration of $1.4 \times 10^{-3} \text{M}$ for the substrate and a *ca.* 2.5-fold greater concentration for CAN were employed for product analysis. The oxidation proceeded smoothly at 25 °C and after 2 h work-up with water gave the expected cleavage products,

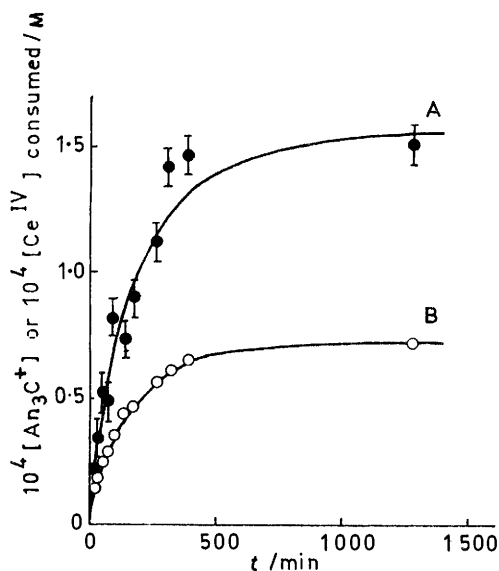


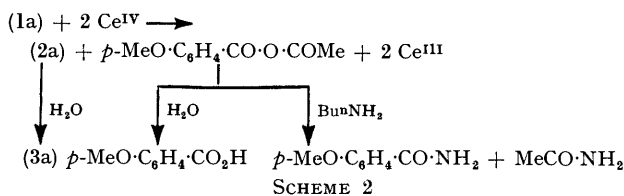
FIGURE 1 Ce^{IV} oxidation of anispinacolone (1a) in acetic acid at 25.0 °C: A, $[\text{Ce}^{\text{IV}}]$ consumed; B, $[\text{An}_3\text{C}^+]$, $[(1a)]_0 = 0.905 \times 10^{-4} \text{M}$, $[\text{Ce}^{\text{IV}}]_0 = 3.61 \times 10^{-4} \text{M}$

carbinol (3a) (90%) and anisic acid (91%), along with *p,p'*-dimethoxybenzophenone (*ca.* 3%) and a mixture (*ca.* 12 wt %) of other unidentified carbonyl compounds.

In a run at lower concentrations (*ca.* 10^{-4}M) of the reactants the increase in concentration of cation (2a) was followed by an aliquot method. After washing aliquot portions of the reaction mixture with water they were acidified with trifluoroacetic acid and the amount of cation (2a) liberated was spectrophotometrically assayed. The decrease in CAN concentration was followed titrimetrically. The results are illustrated as a function of the reaction time in Figure 1. Since under the reaction conditions cation (2a) is stable but CAN is consumed in an amount far from negligible even in the absence of the substrate, the curve for the consumption of CAN has been calibrated for this extra decrease in CAN concentration. It is clear from Figure 1 that 2 equivalents of CAN oxidize 1 equivalent of anispinacolone (1a).

When the reaction mixture was treated with butylamine, the formation of *N*-butylanisamide and *N*-butylacetamide was revealed by g.l.c. analysis. This indicates

that there existed an acid anhydride, presumably *p*- $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{COMe}$, which was produced from *p*-methoxybenzoyl cation (a primary oxidation product) and the solvent acetic acid. Accordingly the stoichiometry of the oxidation and the results of work-up can be described as in Scheme 2.

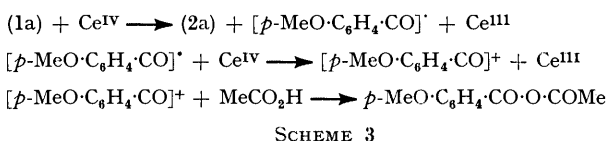


Detection of the *p*-Methoxybenzoyl Radical.—Although the direct observation of a radical cation in acetic acid was not accomplished, evidence was found for the formation of *p*-methoxybenzoyl radical as an intermediate.

When the oxidation was carried out in the presence of 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene as a spin trapping reagent⁷ the e.s.r. spectrum of *p*-methoxybenzoyl-2,3,5,6-tetrakis(trideuteriomethyl)phenyl nitroxide radical was observed as a triplet with nitrogen splittings of 7.56 G.*

Furthermore, when the oxidation was carried out in the presence of 0.598M-acrylonitrile in acetic acid in the dark at 25 °C, a precipitate (1 wt %) was produced which was identified as polyacrylonitrile, ν_{max} 2250 cm^{-1} . Control experiments confirmed that no polymerization of acrylonitrile proceeded in the presence of CAN or anispinacolone (1a) alone. This indicates that during the oxidation a radical, most probably *p*-methoxybenzoyl radical, was produced to start the polymerization. It is known that benzoyl radical can initiate the polymerization of acrylonitrile.⁸

The data appear consistent, to a first approximation, with a three-step pathway for the oxidation (Scheme 3). First, the reaction of anispinacolone (1a) with 1 equivalent of CAN gives rise to the cation (2a) and *p*-methoxybenzoyl radical. In the succeeding step another equivalent of CAN oxidizes the radical, affording *p*-methoxybenzoyl cation. Finally, a mixed anhydride is formed from *p*-methoxybenzoyl cation and acetic acid.



The relatively low yield of the polymer may be ascribed to the much better radical trapping power of Ce^{IV} than acrylonitrile.⁸

Rate Studies of the Oxidation of Anispinacolone (1a).—In order to determine the kinetic order in anispinacolone (1a) the conversion rates, *i.e.* $d[(2a)]/dt$ at 12–15% conversion, at various initial concentrations of (1a) were calculated from the formation curve of cation (2a), which was followed

* Authentic *p*-methoxybenzoyl 2,3,5,6-tetrakis(trideuteriomethyl)phenyl nitroxide radical was prepared from *p*-methoxybenzoyl radical and the 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene. The *p*-methoxybenzoyl radical was produced *in situ* by irradiating a mixture of *p*-methoxybenzaldehyde and di-*t*-butyl peroxide in acetic acid. The spectrum of the radical observed in the spin-trapping experiment exhibited a *g* value (2.00685) and a coupling constant identical with those of the authentic nitroxide.

spectrophotometrically, λ_{\max} 484 nm (ϵ 78 000), in a 10 mm cell under nitrogen at 25.0 °C.* The results are illustrated in Figure 2, and the excellent linear plot through the origin clearly indicates that the oxidation is first order in anis-pinacolone (1a).

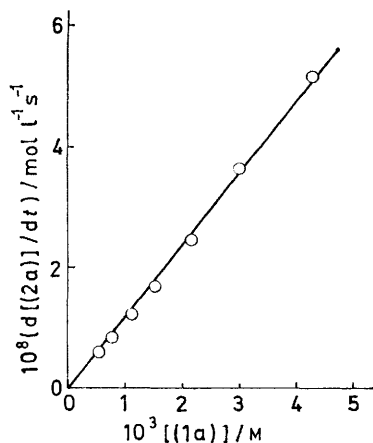


FIGURE 2 Plot of the rate of formation of tris-(*p*-methoxyphenyl)methyl cation (2a) against the concentration of anis-pinacolone (1a) for the Ce^{IV} oxidation of (1a) in acetic acid at 25.0 °C: $[\text{Ce}^{\text{IV}}] = 1.03 \times 10^{-4}\text{M}$

In addition, when the percentage conversion of anis-pinacolone (1a) was plotted against the reaction time, no induction period was detected (Figure 1). This may indicate that an intermediate complex of the Michaelis–Menten type, which usually gives a downward concavity instead of the straight line in Figure 2, is not involved in this reaction, although it is impossible to rule out completely the formation of such an intermediate.

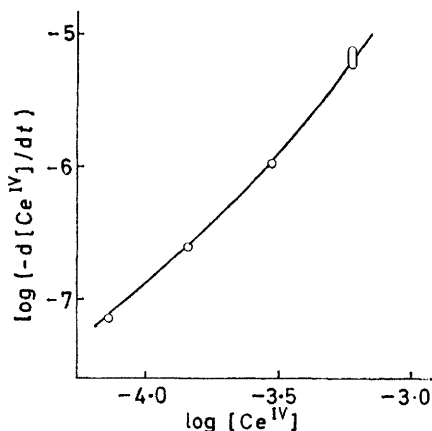


FIGURE 3 Logarithmic plot of the rate of Ce^{IV} consumption against Ce^{IV} concentration for the Ce^{IV} oxidation of anis-pinacolone (1a) in acetic acid at 25.0 °C: $[(1a)] = 3.06 \times 10^{-3}\text{M}$

For the determination of the kinetic order in Ce^{IV} the rates of conversion, *i.e.* the $-\text{d}[\text{Ce}^{\text{IV}}]/\text{d}t$ values, which were estimated to be twice $\text{d}[(2a)]/\text{d}t$ on the basis of the stoichiometry, were plotted against various initial concentrations of Ce^{IV} . No linear plot was observed, and the points showed a tendency to curve upward. Since this can be

* A rate study under vacuum gave identical results within experimental error.

† A large ionic strength effect was observed on addition of lithium nitrate.

ascribed to the ionic strength effect † of CAN, the kinetic order at zero concentration of Ce^{IV} was determined as follows. First, logarithms of $-\text{d}[\text{Ce}^{\text{IV}}]/\text{d}t$ were plotted against logarithms of the initial concentrations of Ce^{IV} , giving a curved line (Figure 3). Secondly, the apparent kinetic orders calculated from the tangents of the curved line (Figure 3) were plotted against the concentrations of Ce^{IV} (Figure 4). Graphic extrapolation to zero concentration of Ce^{IV} clearly indicates that the reaction is first order in Ce^{IV} at infinite dilution.

Thus, as is known for many Ce^{IV} oxidations,^{6a} this reaction also obeys second-order kinetics, being first order in each component. Further experimentation is needed for the identification of the reactive species of Ce^{IV} in acetic acid, ‡ and this might give another explanation for the curved plot in Figure 3.

Oxidation Rates of para-Substituted Benzpinacolones.—The initial rates were measured on *para*-substituted benzpinacolones (1a–e) with an excess of Ce^{IV} by following

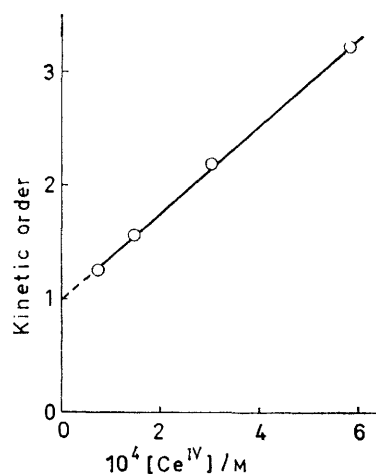


FIGURE 4 Plot of the kinetic order against Ce^{IV} concentration for the Ce^{IV} oxidation of anis-pinacolone (1a) in acetic acid at 25.0 °C

the rate of formation of the triarylmethyl cation at 25.0 °C. The pseudo-first-order rate constant (at 2–5% conversion) was calculated by dividing $\text{d}[\text{triarylmethyl cation}]/\text{d}t$ by the initial concentration of the benzpinacolone. The results are in Table 1 along with the relative rates. It is

TABLE 1

Pseudo-first-order rate constants (k') for the Ce^{IV} oxidation of substituted benzpinacolones in acetic acid at 25.0 °C^a

| Benzpinacolone | k'/s^{-1} ^b | Relative k' |
|----------------|-----------------------------------|-------------------|
| (1a) | 1.8×10^{-1} ^c | 2.3×10^6 |
| (1c) | 1.1×10^{-1} ^c | 1.4×10^6 |
| (1d) | 5.5×10^{-2} ^c | 7.1×10^5 |
| (1b) | 1.5×10^{-6} | 1.9×10 |
| (1e) | 7.8×10^{-8} | 1.0 |

^a $[\text{Ce}^{\text{IV}}] = 4.25 \times 10^{-3}\text{M}$. ^b $\text{d}[\text{Ar}_3\text{C}^+]/\text{d}t$ /[substrate]. ^c Estimated by extrapolation from data at lower Ce^{IV} concentrations; see Experimental section.

clear that *para*-substituents on the triarylmethyl function accelerate the oxidation when they are electron releasing. However, the substituents on aryl moiety do not have much effect even if they are electron releasing.

‡ For a recent elucidation of the reactive species of Ce^{IV} in acidic aqueous solution see ref. 9.

Cyclic Voltammetry of para-Substituted Benzpinacolones.—Oxidation potentials of the benzpinacolones (1a—e) were measured by cyclic voltammetry in 1,2-dichloroethane. The compounds exhibited an irreversible one-wave pattern at a scan rate of 0.1 V s⁻¹. The results are in Table 2.

TABLE 2

Oxidation peak potentials of substituted benzpinacolones ^a

| Benzpinacolone | <i>E</i> vs. s.c.e./V |
|----------------|-----------------------|
| (1a) | 1.65 ^b |
| (1c) | 1.68 ^c |
| (1d) | 1.67 ^c |
| (1b) | 1.99 ^c |
| (1e) | 2.02 ^d |

^a Measured in 1,2-dichloroethane; [benzpinacolone] = 3 × 10⁻³M; [Bu⁺₄NClO₄] = 0.1M; scan rate 0.1 V s⁻¹. ^b Accurate to ±0.01 V. ^c Accurate to ±0.02 V. ^d Accurate to ±0.05 V.

When the red solution around the anode, which appeared in the case of anispinacolone (1a) at a scan rate of 0.1 V s⁻¹, was examined spectrophotometrically, the existence of the tris-(*p*-methoxyphenyl)methyl cation (2a) was verified. However, when the scan rate was increased to 100—500 V s⁻¹, the oxidation wave shifted to higher voltage and the colour disappeared. This indicated that at low scan rates the initial oxidation product is cleaved to form cation (2a) but at higher rates the intermediate promptly returns to anispinacolone (1a), not giving the cation (2a). The probable intermediate is a radical cation of the benzpinacolone.

When the logarithms of the relative oxidation rates for the benzpinacolones (1a—e) were plotted against the corresponding oxidation potentials, a linear correlation was observed, indicating that both Ce^{IV} oxidation and anodic oxidation are controlled by the same rate-limiting step, *i.e.* a single electron-transfer process (Figure 5).

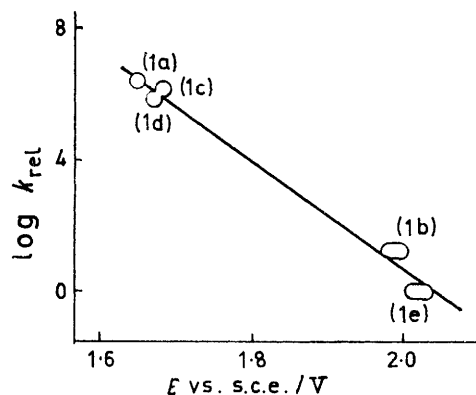


FIGURE 5 Plot of $\log k_{rel}$ of the Ce^{IV} oxidation in acetic acid at 25.0 °C against oxidation peak potentials as measured by cyclic voltammetry for substituted benzpinacolones: for (1a—e) see text; cyclic voltammetry in 0.1M-Bu⁺₄NClO₄ in dry ClCH₂·CH₂Cl at a scan rate of 0.1 V s⁻¹

Charge Transfer Spectra of para-Substituted Benzpinacolones.—When the u.v. spectra of the benzpinacolones (1a—e) were measured in the presence of tetracyanoethylene, as an electron acceptor, in carbon tetrachloride, the charge transfer bands for the respective pinacolones were observed. The results are summarized in Table 3.

A linear relation was observed between the logarithms of the relative rates for Ce^{IV} oxidation and the charge transfer energy (Figure 6). This indicates that oxidation

with Ce^{IV} is controlled by a one-electron transfer process similar to the charge transfer between the benzpinacolones (1a—e) and tetracyanoethylene.

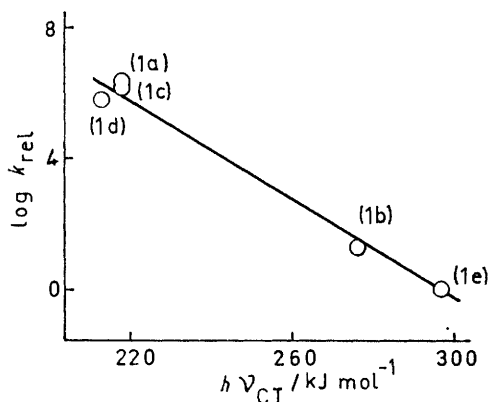


FIGURE 6 Plot of $\log k_{rel}$ of the Ce^{IV} oxidation in acetic acid at 25.0 °C against transition energies of charge transfer band with tetracyanoethylene in CCl₄ for substituted benzpinacolones: for (1a—e) see text

DISCUSSION

Oxidative Fission of Carbonyl Compounds with Ce^{IV}.—It has been reported that cyclopentanone, cyclohexanone, norbornanone, and adamantanone are cleaved with CAN initially to afford an acyl cation and an alkyl radical.^{6b} It is also known that substituted phenylacetic acids are oxidized by CAN to give substituted benzyl radicals, carbon dioxide, and a proton.¹⁰ These α -cleavages of carbonyl compounds can formally be expressed by an α -fission of a radical cation (or its complex with the oxidant) into an acyl cation and an alkyl radical.

TABLE 3

Transition energies of charge transfer band for substituted benzpinacolones with tetracyanoethylene ^a

| Benzpinacolone | $h\nu_{CT}/\text{kJ mol}^{-1}$ |
|----------------|--------------------------------|
| (1a) | 218 |
| (1c) | 218 |
| (1d) | 213 |
| (1b) | 276 |
| (1e) | 297 |

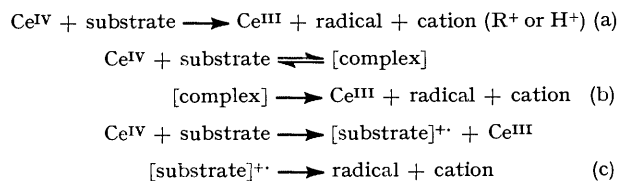
^a Measured in CCl₄ as solvent.

Compared with this mode of fission, cleavage of the benzpinacolones (1) is notable in that it proceeds to give an acyl radical and a carbenium ion. It is analogous to the Ce^{IV} oxidation of benzaldehyde which proceeds through formation of benzoyl radical and a proton.⁸

A few examples of the α -fission of ketones or aldehydes to give acyl radicals and alkyl cations have been found for anodic oxidation of 3,3-dimethylbutan-2-one¹¹ and of several benzylic aldehydes and ketones.¹² The ease of this type of fission for these systems may be ascribed to the stability of the alkyl cation or triarylmethyl cations.

Rate-limiting Step in Ce^{IV} Oxidation.—Much work has been devoted to the elucidation of the kinetic features of the oxidative cleavage with Ce^{IV}. These are classified,

at least formally, into three categories: (a) a simple bimolecular reaction between Ce^{IV} and the substrate to form a radical, a cationic species (a carbenium ion or proton), and Ce^{III} ; (b) a pathway which initially proceeds through an equilibrium step, *i.e.* the formation of a complex between the substrate and Ce^{IV} ; (c) a mechanism in which the one-electron oxidation by Ce^{IV} precedes to give a radical cation of the substrate and is followed by fission of the radical cation (Scheme 4).



SCHEME 4

Mechanism (a) has been proposed for the oxidation of 2,3-dimethylbutane-2,3-diol¹³ or formaldehyde.¹⁴ Pathway (b) has been suggested for several ketones,^{6a} alcohols,^{6a} glycols,^{6a} phenyl-substituted primary alcohols,¹⁵ tertiary alkanols,¹⁶ hydrobenzoin,¹⁷ phenylacetic acid,¹⁰ and benzylic acids.⁹ Path (c) has been suggested for the oxidation of polymethylbenzenes,¹⁸ *m*- and *p*-methoxyphenylacetic acid,¹⁰ and 1,2-diphenylethanes.¹⁹

In the case of CAN oxidation of polymethylbenzenes,¹⁸ it has been reported that a good linear relationship is found when $-RT \ln k_{\text{rel}}$ (k_{rel} = rate relative to that of 1,2,4,5-tetramethylbenzene) is plotted against the charge-transfer transition energies of the corresponding tetracyanoethylene-polymethylbenzene complexes. On the basis of the linear relationship, the radical cation formation pathway (c) in Scheme 4 has been proposed for these CAN oxidations.

Similarly, a good correlation of the logarithms of the rates with the oxidation potentials (Figure 5) and with the charge transfer energies (Figure 6) may indicate that the oxidation of these benzpinacolones (1a–e) proceeds through pathway (c) involving a radical cation of the benzpinacolone, although it remains to confirm directly the formation of the radical cation.

Possibility of Homolytic Cleavage of Anispinacolone (1a).—Since the tris(*p*-methoxyphenyl)methyl radical is rather stable, thermal homolytic dissociation of anispinacolone (1a) may occur prior to oxidation with CAN. However, this mechanism can be ruled out from the fact that in the trapping experiment with 2,3,5,6-tetrakis-(trideuteriomethyl)nitrosobenzene neither an e.s.r. signal for the trapped *p*-methoxybenzoyl radical nor that of the tris(*p*-methoxyphenyl)methyl radical itself was observed, unless the reaction was carried out in the presence of CAN. This could also be ruled out by the observed kinetics, *i.e.* first order in each of (1a) and Ce^{IV} . This is in conflict with a mechanism involving rate-limiting homolytic cleavage of (1a) followed by the rapid capture of the radicals formed by the Ce^{IV} ion.

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. Elemental analyses were performed at the Microanalytical Center, Kyoto University, Kyoto. I.r. and u.v. spectra were measured with Hitachi 215 and 200-10 spectrophotometers, respectively. N.m.r. and e.s.r. spectra were taken with Hitachi R-24 (60 MHz) and JEOL PE-2X spectrometers, respectively. Cyclic voltammetry was conducted with a Hokuto Denko potentiogalvanostat HA-104 and function generator HB-107A.

Materials.—All reagents were of reagent-grade quality except when otherwise noted. Acetic acid was refluxed over KMnO_4 for 4 h, distilled, and again distilled from triacetyl borate.²⁰ Cerium(IV) ammonium nitrate (CAN) containing water of crystallization was dehydrated at 20–25 °C and 10^{-3} mmHg for 2.5 h. 1,2-Dichloroethane was refluxed over P_2O_5 and distilled. Anispinacolone (1a) was prepared from *p,p'*-dimethoxybenzophenone following the procedure of Miller and Neidig,²¹ m.p. 138.2–141° (lit.,¹ 136–137°). 1,2,2,2-Tetrakis(*p*-methylphenyl)ethanone (1b) was prepared from *p,p'*-dimethylbenzophenone following the procedure of Weiler,²² m.p. 92.5–94.5° (lit.,²² 95°). 1-(*p*-Methoxyphenyl)-2,2,2-triphenylethanone (1c) was prepared from trityl sodium and *p*-methoxybenzoyl chloride following the procedure of Fuson and Wiegert,²³ m.p. 183.5–185.0° (lit.,²³ 184–185°). Tris(*p*-methoxyphenyl)methyl chloride was prepared by treating tris(*p*-methoxyphenyl)methanol (3a) with dry HCl in benzene, m.p. 145.8–146.6° (lit.,²⁴ 158°).

1-Phenyl-2,2,2-tris(*p*-methoxyphenyl)ethanone (1c).—To lithium (0.090 g, 13 mmol) in THF (1.75 ml) was added a solution of tris(*p*-methoxyphenyl)methyl chloride (1.62 g, 4.39 mmol) in THF (15 ml) over 40 min under nitrogen at 20–25 °C to afford a dark red solution. This was further stirred for 2 h at 20–25 °C and then transferred to another flask by means of a syringe in order to remove unchanged lithium. The solution was cooled to 0 °C and to this was added benzoyl chloride (0.628 g, 4.46 mmol) dissolved in THF (1 ml) to give a brown solution. The mixture was stirred at 20–25 °C for 1 h, refluxed for 3 h, and then kept at room temperature overnight. Work-up afforded a viscous liquid (1.89 g), from which compound (1c) (0.515 g, 27%) was separated by means of preparative t.l.c. (R_F 0.6; SiO_2 ; benzene-ether 93:7), m.p. 165.2–167.5°, ν_{max} (CHCl_3) 2 840, 1 670, 1 600, 1 580, 1 500, 1 460, 1 250, 1 180, and 1 030 cm^{-1} ; $\delta(\text{CDCl}_3)$ 3.70 (9 H, s) and 6.5–7.7 (17 H, m) (Found: C, 79.7; H, 6.1. $\text{C}_{29}\text{H}_{26}\text{O}_4$ requires C, 79.45; H, 6.0%).

1-(*p*-Chlorophenyl)-2,2,2-tris(*p*-methoxyphenyl)ethanone (1d).—*p,p'*-Dimethoxybenzophenone (10.0 g, 4.13 mmol) and *p*-chloro-*p'*-methoxybenzophenone (10.0 g, 4.05 mmol),²⁵ m.p. 123.0–124.5°, were dissolved in hot isopropyl alcohol (1 l) containing acetic acid (1 ml) in a flask. The flask was closed with a cork and exposed to direct sunlight for 5 days. The solvent was distilled off to afford pale yellow crystals (20 g), which were then dissolved in acetic acid (100 ml) containing iodine (0.1 g). After the solution had been refluxed for 10 min, acetic acid was distilled off and the resulting crude crystals (20 g) were washed with methanol and then purified with preparative t.l.c. (SiO_2 ; benzene-hexane 3:1) to give crystals (2.6 g) (R_F 0.82), which afforded compound (1d) (1.6 g, 3.4 mmol, 8%) after three recrystallizations from benzene-ethanol (1:5), m.p. 139.0–140.5°, ν_{max} (CCl_4) 2 830, 1 675, 1 600, 1 580, 1 500, 1 250, 1 175, and 1 030 cm^{-1} ; $\delta(\text{CCl}_4)$ 3.72 (9 H, s), 6.67

(6 H, d, J 9.0 Hz), 7.03 (6 H, d, J 9.0 Hz), 7.13 (2 H, d, J 9.0 Hz), and 7.63 (2 H, d, J 9.0 Hz) (Found: C, 73.9; H, 5.6. $C_{20}H_{25}ClO_4$ requires C, 73.65; H, 5.55%).

Stoichiometry of the Ce^{IV} Oxidation of Anispinacolone (1a).—To a solution of CAN ($4.33 \times 10^{-4}M$; 150 ml) in acetic acid was added a solution of (1a) ($5.43 \times 10^{-4}M$; 30.0 ml) in acetic acid under nitrogen at 25 °C. Portions (10.00 ml) were pipetted out at intervals and poured into an aqueous solution (17 ml) containing iron(II) ammonium sulphate (0.01 mmol). The solution was extracted with ether and the aqueous layer was titrated with 0.004N cerium(IV) sulphate using *N*-phenylanthranilic acid as indicator. The ether layer was washed with aqueous sodium hydrogencarbonate and 10% sodium chloride, and then dried ($MgSO_4$). After ether had been evaporated, the residue was dissolved in 1,2-dichloroethane (10.00 ml). 1 ml of the solution was diluted to 10.00 ml with 1,2-dichloroethane containing 2% (v/v) trifluoroacetic acid and the amount of (2a) was determined by measuring its absorbance at λ_{max} 487 nm (ϵ 118 000). Control experiments showed that iron(II) ammonium sulphate and (2a) were recovered in 90 and 84%, respectively, after this work-up procedure.

Products of the Ce^{IV} Oxidation of Anispinacolone (1a).—To a solution of CAN ($4.63 \times 10^{-3}M$; 270 ml) in acetic acid was added a solution of (1a) ($6.14 \times 10^{-3}M$; 80 ml) in acetic acid under nitrogen at 25 °C. After 2.25 h at this temperature in the dark, the mixture was poured into water (1 l) containing iron(II) ammonium sulphate (0.14 mol) and then extracted with benzene. The benzene solution was neutralized with saturated aqueous sodium hydrogencarbonate, washed with 10% sodium chloride, and dried ($MgSO_4$). Evaporation of the solvent followed by separation with preparative t.l.c. (SiO_2 ; benzene-ether 93:7) afforded (3a) (154 mg, 0.439 mmol), *p,p'*-dimethoxybenzophenone (3.6 mg, 0.015 mmol), and unidentified products (27 mg, 12 wt %). The aqueous layer was acidified with concentrated HCl and extracted with ether to give anisic acid (67 mg, 0.442 mmol). Each product exhibited i.r. and n.m.r. spectra identical with those of the respective authentic sample.

Treatment of the Reaction Mixture from (1a) and CAN with Butylamine.—To a solution of CAN ($5.96 \times 10^{-3}M$; 10 ml) in acetic acid was added a solution of (1a) ($5.89 \times 10^{-3}M$; 4 ml) in acetic acid under nitrogen at 25 °C. After the mixture had been kept at 25 °C for 3 h in the dark, a portion (2 ml) was transferred into anhydrous ether (5 ml) and treated with butylamine (6.77 ml, 0.068 mol). The mixture was refluxed for 1 h, washed with water, saturated aqueous sodium hydrogencarbonate, 10% hydrochloric acid, and finally with 10% sodium chloride, and dried ($MgSO_4$). After evaporation of the ether, the residue was treated with t.l.c. (SiO_2 ; benzene-ether 85:15) to remove (3a) and unchanged (1a). The fractions for $R_F < 0.5$ were collected and analysed for *N*-butylanisamide (14%) and *N*-butylacetamide (28%) by means of temperature-programmed (120–200 °C) g.l.c. on a PEG 20M column using biphenyl as internal standard.

Spin Trapping of *p*-Methoxybenzoyl Radical in the Ce^{IV} Oxidation of (1a).—In a quartz sample cell of inside diameter 2 mm was placed the spin trap, 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene (2–3 mg), a solution of (1a) ($2.4 \times 10^{-3}M$; 0.1 ml) in acetic acid, and a solution of CAN ($2.2 \times 10^{-3}M$; 0.1 ml) in acetic acid under nitrogen. After outgassing with high purity nitrogen for 5 min the cell was sealed with Parafilm, and the first e.s.r. scan was taken ca.

20 min after mixing or sooner. The nitrogen hyperfine splitting for the *p*-methoxybenzoyl spin adduct was accurate to ± 0.04 – 0.05 G. The g value was determined with an accuracy of ± 0.00005 by utilizing that of the perylene radical cation in concentrated sulphuric acid as a standard (g 2.002 583).²⁶

Spin Trapping of *p*-Methoxybenzoyl Radical from Anisaldehyde.—In a quartz sample cell were placed di-*t*-butyl peroxide (2–3 mg) and 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene (2–3 mg) and a solution of anisaldehyde ($2 \times 10^{-3}M$; 0.2 ml) in acetic acid. The resulting solution was outgassed with nitrogen and irradiated with a Phillips super-high-pressure mercury lamp. The *p*-methoxybenzoyl spin adduct showed an e.s.r. spectrum (triplet) with nitrogen splittings of 7.54 G and a g value of 2.006 92.

Examination of Homolytic Cleavage of Anispinacolone (1a) by Means of E.s.r.—A solution of (1a) (0.02M) in 1,2-dichloroethane was placed in a Pyrex sample cell, degassed by a repeated freezing, evacuation, and thawing cycle, and sealed. During the experiment the cell was covered with aluminium foil. No e.s.r. signal was observed either at ambient temperature or at 80 °C. The solution containing 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene as a spin trap showed no e.s.r. signal at an ambient temperature; however, at 80 °C an unidentified spectrum was observed. Although characterization of the species formed was not carried out, it was concluded that the signal was not due to the *p*-methoxybenzoyl spin trap.

Polymerization of Acrylonitrile initiated by the Reaction of (1a) and CAN.—An outgassed solution (30 ml) of CAN ($1.31 \times 10^{-4}M$) in acetic acid was mixed with a solution (10 ml) containing acrylonitrile (2.39M) and (1a) ($4.05 \times 10^{-3}M$) in acetic acid under nitrogen at 25 °C. After 3 h in the dark, gelation was observed. After a total reaction time of 19 h the polymer formed was separated by means of centrifuging, washed with ether and then with water, and dried *in vacuo*, to give material (13 mg; 1 wt % on acrylonitrile), ν_{max} (KBr) 2 250 cm^{-1} . The polymerization of acrylonitrile did not occur in the presence of either CAN or (1a) alone.

Kinetic Studies.—Rates of reaction of (1a, c, and d). A typical procedure is described for (1a) as an example. In a 10 mm u.v. quartz cell purged of air with nitrogen was placed a solution of CAN (3.000 ml) in acetic acid, and the cell was placed in the light path of a spectrometer. The light passed through a small water thermostat so that the solution was maintained at 25.0 °C. After equilibration, a solution of (1a) (0.500 ml) in acetic acid was added under nitrogen. The cell was stoppered and immediately shaken for a few seconds. The reaction was followed by recording the absorbance of the (2a) formed at 484 nm (ϵ 78 000). The rates of (1a, c, and d) at 25.0 °C at a Ce^{IV} concentration of $4.25 \times 10^{-3}M$ as given in Table 1 were too fast to measure. Therefore k' for (1a) at this Ce^{IV} concentration was estimated by extrapolation of the plot of the log k' values versus the logarithms of the Ce^{IV} concentrations ranging from 1.96×10^{-4} to $1.52 \times 10^{-3}M$, with constant concentration of (1a) ($1.76 \times 10^{-5}M$). The rates for (1c and d) were determined for a Ce^{IV} concentration of $1.4 \times 10^{-3}M$ and a substrate concentration of $2.2 \times 10^{-5}M$ and then extrapolated to a Ce^{IV} concentration of $4.25 \times 10^{-3}M$ by assuming that the reactions were accelerated by the same factor as in (1a) upon increasing the Ce^{IV} concentration.

Rates of reaction of (1b and e). These were determined by the aliquot method. The reaction was carried out in the

dark under nitrogen at 25.0 °C. Portions (2.000 ml) were pipetted out at intervals, quenched with iron(II) ammonium sulphate solution, and extracted with ether. Ether was evaporated off and the residue diluted with 2% (v/v) trifluoroacetic acid [5% in the case of (1e)] in 1,2-dichloroethane and examined spectrophotometrically. The cations ($p\text{-R}^1\text{C}_6\text{H}_4$)₃C⁺ from (1b and e) exhibited the following respective λ_{max} and ϵ values: 454 (ϵ 85 500) and 435 nm (41 200).

Determination of Molar Absorptivity (ϵ) of (2a) in Acetic Acid.—The ϵ value of (2a) formed from (3a) in 2% (v/v) trifluoroacetic acid in acetic acid was determined as 108 000. On the other hand, the ϵ value of (2a) in acetic acid was found to be 0.723 times as large as that in 2% (v/v) trifluoroacetic acid in acetic acid, *i.e.* 78 000 ($=108\,000 \times 0.723$).

Measurement of Charge Transfer Spectra.—The benzpinacolone (20–40 mg) was mixed with a saturated solution (5 ml) of tetracyanoethylene in CCl₄. In most cases the solution turned pale yellow or reddish purple. The u.v.-visible region spectra were measured using a 10 mm quartz cell.

Cyclic Voltammetry.—The oxidation peak potentials were measured for 0.003M-substrate in 0.1M-Buⁿ₄ClO₄ in ClCH₂·CH₂Cl using a three-electrode cell with platinum wire and auxiliary electrodes and a saturated calomel reference electrode. Scanning was conducted from 0.0 to 3.0 V at a rate of 0.1 V s⁻¹ under irreversible conditions. Cyclic voltammetry of anispinacolone (1a) at high scan rates was carried out for solutions of similar concentrations.

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