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ONE-ELECTRON OXIDATION OF ANISPINACOLONE WITH DIAROYL PEROXIDES: MECHANISTIC CHANGEOVER OF THE PEROXIDE FUNCTION FROM RADICAL TO MOLECULAR OXIDATION[1]

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Abstract. Oxidative cleavage of anispinacolone ($An_3C\cdot CO\cdot An$, An=p-methoxyphenyl) with diaroyl peroxides proceeds by electron-transfer mechanism, which starts with rate-determining decomposition of the peroxide, unimolecular for dibenzoyl and bimolecular for bis(3,5-dinitrobenzoyl) peroxide.

It has been difficult to distinguish electron-transfer (ET) from ionic pathways in the nucleophile/diaroyl peroxide reaction in the light of products or kinetics, except a few reactions. Pryor and his collaborators have demonstrated that accelerated decomposition of dibenzoyl peroxide (2) by N,N-diphenylhydroxylamine[2] and dibenzenesulfenimide[3] proceeds by ET mechanism. Schuster and his coworkers have recently presented some concrete examples for the ET mechanism on the reactions of diphenoyl and phthaloyl peroxides with electron donors such as aromatic amines, pyrene, anthracene, and some of their analogues; they discussed the details of the bimolecular rate-determining step.[4] More recently, Walling has also discussed on the other formulations of these relatively slow rate-determining steps.[5] Such renewed interest in the ET pathway on the peroxide transformation prompted us to report on our recent findings which clearly indicate the ET mechanism of a peroxide oxidation and in particular the dichotomy of the pathway, which includes unimolecular and bimolecular decomposition of the diaroyl peroxide, bringing on radical and molecular one-electron oxidation of a donor molecule, respectively.

It has been demonstrated that the Ce(IV) oxidation of anispinacolone [tetrakis(p-methoxyphenyl)ethanone] (1) proceeds by ET mechanism in acetic acid to give tris(p-methoxyphenyl)-methanol (4) and anisic acid after work-up of the reaction mixture with water; it has been concluded that the reaction proceeds via a radical cation of anispinacolone $[\text{Anisp.}]^{\ddagger}$, which subsequently is cleaved into the tris(p-methoxyphenyl)methyl cation and the anisoyl radical.[1b] Meantime, investigations in these laboratories have revealed that anispinacolone is cleaved as well to give the same oxidation products, 4 (20% yield) and anisic acid (24% yield), when treated with bis(3,5-dinitrobenzoyl) peroxide (3) in 1,2-dichloroethane at 50.0°C for 24 h, and then worked up with water.

The low nucleophilicity of the pinacolone 1 and the steric congestion on its carbonyl group seemed to be inconsistent with the notion of the operation of a simple nucleophile/electrophile displacement pathway. Instead, the identity of the products with the Ce(IV) oxidation suggested the ET pathway. To gain more insights into the mechanism we followed the reaction between 1 and 3 by ^{13}C NMR analysis of the reaction mixture, using $An_3{}^{13}C\cdot{}^{13}CO\cdot An$ (1a). As recorded in Fig. 1, the ^{13}C absorption peak for the ester $An_3{}^{13}C \cdot O \cdot COAr$ (Ar=3,5-dinitrophenyl) (6a)[6] was observed at the initial stage of the reaction at 73°C. Besides, the emission peak for the polarized anhydride $An^{13}CO \cdot O \cdot COAr$ (5a) was distinctly observed. According to Kaptein rule[7] this anhydride emission should result from the free anisoyl radical $An^{13}CO\cdot$ by the attack on the peroxide 3. Furthermore, in another run carried out in the presence of nitrosodurene, labelled with ^2H on the four methyls, the anisoyl radical was trapped at 50°C, affording the ESR signal of the corresponding nitroxide radical, as shown in Fig. 2.

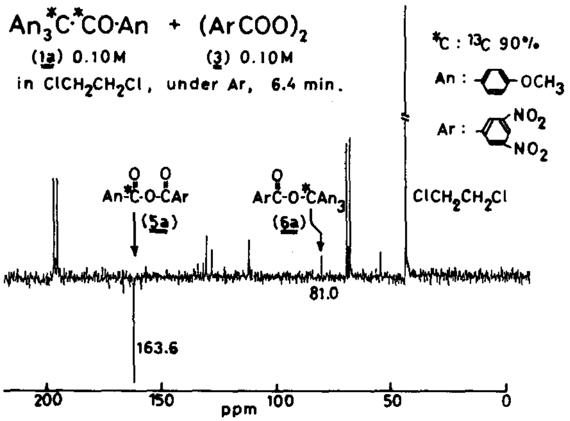

Fig. 1. ^{13}C NMR spectrum of the reaction mixture for the reaction of 1a and 3 at 73°C.

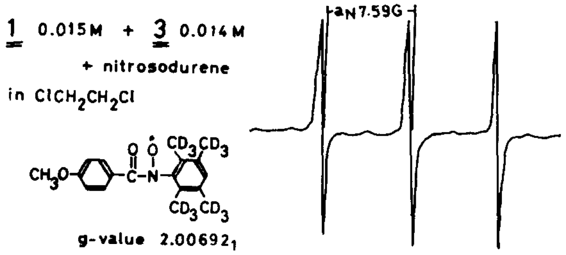

Fig. 2. ESR spectrum for the anisoyl radical trapped by nitrosodurene at 50°C.

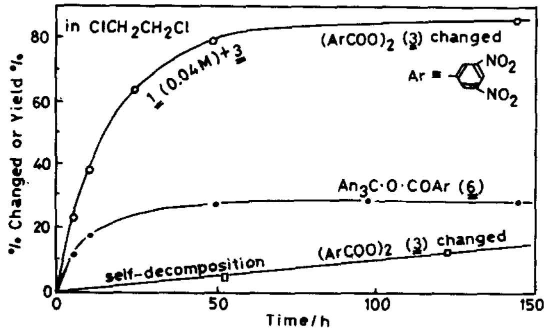

Fig. 3. Decomposition of 3, $[\,3\,]_0$ = 0.04 M, and formation of 6 at 50.0°C.

Finally, the decomposition of the peroxide 3, determined titrimetrically, in the presence of the pinacolone 1 was dramatically accelerated at 50.0°C, when compared with the self-decomposition rate (Fig. 3). Hence, the reaction possibly starts by a bimolecular mechanism.[8] In fact, the decrease in the peroxide concentration and that in the pinacolone 1, estimated by the ^{13}C NMR analysis, coincide with each other at the initial stage of the reaction.

With these results it is evident that the cleavage reaction actually starts with a bimolecular redox step,[9] and presumably through a radical-ion, although a direct proof of the transient formation of the radical-ion has not been given at the present stage of the study.[10] A plausible major reaction sequence would be represented as follows:

$$\underset{(1)}{\text{Anisp.}} + \underset{(3)}{(\text{ArCOO})_2} \xrightarrow{\text{r.d.}}$$

$$[\text{Anisp.}]^{+\cdot} + \text{ArCOO}^- + \text{ArCOO}\cdot \quad \text{(cf. ref. 5)}$$

$$[\text{Anisp.}]^{+\cdot} \longrightarrow \text{An}_3\text{C}^+ + \text{AnCO}\cdot$$

$$\text{AnCO}\cdot + \underset{(3)}{(\text{ArCOO})_2} \longrightarrow \underset{(5)}{\text{AnCO}\cdot\text{O}\cdot\text{COAr}} + \text{ArCOO}\cdot$$

$$\text{An}_3\text{C}^+ + \text{ArCOO}^- \longrightarrow \underset{(6)}{\text{An}_3\text{C}\cdot\text{O}\cdot\text{COAr}}$$

r.d. = rate-determining; Anisp. = 1.

The fate of the 3,5-dinitrobenzoyloxy radical $ArCOO\cdot$ was not quantitatively estimated.

However, in view of the detection of ArCOOH, CO_2, and ArH in the reaction mixture, hydrogen abstraction from the solvent $ClCH_2CH_2Cl$ and thermal decomposition of ArCOO· into Ar· and CO_2 seem to be the dominant pathways.[11]

The gap between the two curves (Fig. 3) for the peroxide 3 and for the ester 6,[12] is attributed to further oxidation of the ester 6 with the peroxide 3 to afford 4,4'-dimethoxybenzophenone, which was proved by the product analysis and by the ^{13}C NMR analysis of the reaction mixture. It also is partly attributed to the concurrent bimolecular reaction of 1 and 3, which does not give the ester 6.[8]

Similarly to the reaction of the peroxide 3, dibenzoyl peroxide 2 cleaved the pinacolone 1 to give the carbinol 4 and anisic acid albeit in low yield (13 and 10%, respectively), when the reaction was carried out in 1,2-dichloroethane for 60 h at 50.0°C and the reaction mixture was worked up with water. In addition, when the reaction was followed by ^{13}C NMR measurement by use of $An_3{}^{13}C{\cdot}{}^{13}CO{\cdot}An$ (1a) and $(Ph^{13}COO)_2$ (2a), the formation of the ester $An_3{}^{13}C{\cdot}O{\cdot}{}^{13}COPh$ (7a) and of benzoic anhydride was clearly observed as shown in Fig. 4. If the reaction proceeds via the radical cation $[Anisp.]^{+\cdot}$, the expected anhydride should be a mixed anhydride. However, it is conceivable that a large amount of benzoic acid formed in the reaction mixture can easily convert the mixed anhydride to benzoic anhydride and anisic acid under the reaction conditions.

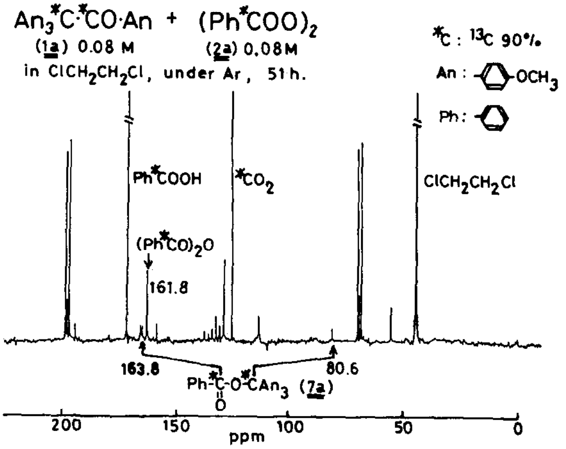

Fig. 4. ^{13}C NMR spectrum of the reaction mixture for the reaction of 1a and 2a at 75°C.

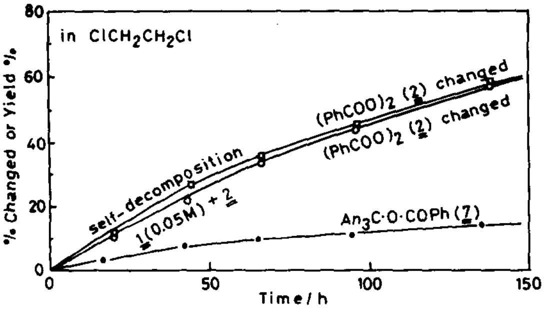

Fig. 5. Decomposition of 2, [2]₀ = 0.05 M, and formation of 7 at 50.0°C.

The salient feature of the reaction of dibenzoyl peroxide 2 is that the rate of decomposition was not affected by added pinacolone 1, as illustrated in Fig. 5. This is in marked contrast to the decomposition of the peroxide 3, and clearly indicates that the reaction with 1 actually starts with thermal decomposition of the peroxide 2 and that the electron abstraction by the benzoyloxy radical PhCOO· from the pinacolone 1 subsequently occurs.[13] The concurrent reactions of PhCOO·, such as hydrogen abstraction and decomposition, also were observed to give PhCOOH and CO_2. Furthermore, added 3,4-dichlorostyrene much diminished the yield of the cleavage products by scavenging the benzoyloxy radical and affording polymers, but it gave no effect on the decomposition rate of the peroxide 2.

Thus a possible oxidation sequence for the peroxide 2 may be represented as follows:

$(PhCOO)_2$ (2) $\xrightarrow{r.d.}$ 2 $PhCOO\cdot$; $PhCOO\cdot$ + Anisp. (1) $\longrightarrow$ $PhCOO^-$ + $[Anisp.]^{+\cdot}$

$[Anisp.]^{+\cdot}$ $\longrightarrow$ An_3C^+ + $AnCO\cdot$

An_3C^+ + $PhCOO^-$ $\longrightarrow$ $An_3C{\cdot}O{\cdot}COPh$ (7); $AnCO\cdot$ + $(PhCOO)_2$ $\longrightarrow$ $AnCO{\cdot}O{\cdot}COPh$ + $PhCOO\cdot$

In conclusion, the identification of the anisoyl radical and of the esters strongly suggests transient formation of the radical cation $[Anisp.]^{+\cdot}$ as the precursor of $AnCO\cdot$ and An_3C^+.[14] In turn it clearly indicates the ET nature of these oxidative cleavage reactions. Furthermore, the examination of the oxidation rate reveals the dichotomy of the oxidation mechanism: unimolecular and bimolecular rate-determining steps of the peroxide decomposition, depending on the nature of the substituent of the diaroyl peroxide; each pathway brings on radical and molecular ET oxidation, respectively for 2 and 3. Hence, as far as the molecularity of the peroxide is concerned, the dichotomy in these ET reactions can be considered a counterpart to the S_N1-S_N2 dichotomy in the nucleophilic substitution.

References and Notes

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2. W. A. Pryor and W. H. Hendrickson, Jr., J. Amer. Chem. Soc., 1975, 97, 1582.
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4. a) K. A. Horn and G. B. Schuster, J. Amer. Chem. Soc., 1979, 101, 7097; b) J. J. Zupancic, K. A. Horn, and G. B. Schuster, ibid., 1980, 102, 5279; c) G. B. Schuster, Acc. Chem. Res., 1979, 12, 366.
5. C. Walling, J. Amer. Chem. Soc., 1980, 102, 6854.
6. The esters 6 and 7 are readily hydrolyzed into the carbinol 4 in the course of the work-up.
7. R. Kaptein, Chem. Commun., 1971, 732.
8. Although the detailed product analysis revealed that another bimolecular reaction between 1 and 3 concurrently proceeds to give an anispinacolone derivative, which is 3,5-dinitrobenzoyloxylated at the position ortho to one of the methoxy groups of the tris(p-methoxyphenyl)methyl group, this does not make the conclusion unsound.
9. E. S. Huyser, 'Free Radicals,' in 'Organic Reactive Intermediates,' S. P. McManus, ed., Academic Press, New York, 1973, p. 16.
10. An alternative pathway might start with formation of a charge-transfer complex. However, we were not able to detect evidence of any charge-transfer complex in the electronic absorption spectra of the peroxide 3 and the pinacolone 1.
11. In view of the reaction of 2, it can not be ruled out that a very minor part of $ArCOO\cdot$ might act as an electron acceptor to oxidize another molecule of the pinacolone 1 to afford the radical cation $[Anisp.]^{+\cdot}$.
12. The ester was determined by UV after converted into the tris(p-methoxyphenyl)methyl cation An_3C^+ in an aliquot acidified with CF_3COOH.
13. The radicals derived from 1,2-dichloroethane, such as $ClCH_2CHCl\cdot$, seem to have no oxidizing ability, and we were not able to detect the products expected from the carbanion $ClCH_2CHCl^-$.
14. Radical dissociation of the pinacolone 1 into $An_3C\cdot$ and $AnCO\cdot$ was not observed under the reaction conditions (cf. Ref. 1b).

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