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Oxidation of hydrocarbons. 17. Solvent and substituent effects on the oxidation of styrene derivatives by quaternary ammonium permanganates

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This paper is dedicated to Professor Arthur N. Bourns

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When alkenes are oxidized by quaternary ammonium or phosphonium permanganates in polar organic solvents, such as acetone, the structures of the cations have little or no effect on the rates of reaction. In less polar solvents, such as methylene chloride or toluene, the rates of reaction are, however, dependent on the identity of the quaternary ammonium or phosphonium ions. It thus appears as if the reacting species may exist as solvent-separated ion pairs in polar solvents and as intimate ion pairs in nonpolar solvents. The rates of reaction are also very sensitive to substituent effects, a nonlinear (concave upward) Hammett plot being obtained for the oxidation of substituted β -bromo and β -methoxystyrenes. The mechanism is best visualized as proceeding by way of a continuum of transition states that can vary from electron rich to electron poor depending on the capacity of the substrate structures to accommodate either negative or positive charges.

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Lorsque des alcènes sont oxydés par des permanganates d'ammonium ou de phosphonium quaternaires, dans des solvants organiques polaires comme l'acétone, les structures des cations n'ont pas ou peu d'effet sur les vitesses des réactions. Dans des solvants moins polaires, comme le chlorure de méthylène ou le toluène, les vitesses dépendent toutefois de l'identité des ions quaternaires. Il semble donc que les entités qui réagissent peuvent exister sous la forme de paires d'ions solvatés dans les solvants polaires et de paires d'ions intimes dans les solvants non-polaires. Les vitesses de réaction sont aussi très sensibles aux effets de substituants: on obtient une courbe de Hammett qui n'est pas linéaire (concave vers le haut) lors de l'oxydation de β -bromo et de β -méthoxystyrènes substitués. La meilleure représentation du mécanisme de la réaction implique des états de transition continus qui varient suivant leur nature riche ou pauvre en électrons, qui dépend elle-même de la capacité des structures des substrats d'accommoder soit des charges positives ou négatives.

[Traduit par la revue]

Introduction

Recent studies have shown that a wide variety of organic functional groups may be oxidized by quaternary ammonium and phosphonium permanganates under mild, nonpolar conditions (1). For example, this reaction has been used for the oxidation of aliphatic hydrocarbons (2), arenes (2, 3), alcohols (4, 5), aldehydes (5, 6), ethers (7), sulfides (8), amines (9), and alkenes (10).

Because these reactions appear to have considerable synthetic potential and because they present an interesting example of electron transfer processes under nonaqueous conditions, we have undertaken a study of the oxidation of a number of styrene derivatives in three solvents, methylene chloride, toluene, and acetone. Our purpose was to investigate the reaction mechanism and to achieve a better understanding of the role that solvents play in these reactions.

Experimental

Reactants and solvents

The quaternary ammonium and phosphonium permanganates were prepared as previously described (11). The substituted methyl cinnamates were prepared by methylation of the corresponding cinnamic acids and purified by distillation or recrystallization (12). The physical properties of the esters corresponded well with those reported in the literature (Table 1). The substituted β -bromostyrenes were prepared, as described in the literature (12), by treating the corresponding cinnamic acids with bromine in hot chloroform, isolating the product (a substituted 2,3-dibromo-3-phenylpropanoic acid), and refluxing it in aqueous sodium bicarbonate. β -Bromostyrene was isolated by vacuum distillation and purified by prepartive glc using a 7-ft 15% Apiezon L on Chromosorb P column. The other substituted β -bromostyrenes, being volatile solids, were purified by vacuum sublimation. The physical properties of these compounds are summarized in Table 1. The substituted β -methoxystyrenes were prepared, as described in the literature (13), by treatment of the corresponding phenylacetylenes with potassium hydroxide in absolute methanol. The products were isolated from the reaction mixture by vacuum distillation and purified by radial chromatography, using a Harrison Research model 7924 chromatotron. The physical properties of these compounds are summarized in Table 1.

Proton magnetic spectra were recorded using a Perkin-Elmer 60-MHz R12B spectrophotometer.

The solvents (methylene chloride, toluene, and acetone) were purified by treatment with tetrabutylammonium permanganate for several hours, followed by fractional distillation from the solution.

Kinetics

Solutions of the substrate (0.8 M) and quaternary ammonium permanganate $(4 \times 10^{-4} M)$ were prepared in a particular solvent and thermostated for 15 min. Then an aliquot (3.0 mL) of the oxidant solution was transferred to a 10-mm cuvette in the thermostated cell compartment of a Hewlett-Packard 8450A spectrophotometer. A small portion of the reductant solution was injected from a syringe, and the absorbance was recorded at intervals. Plots of $\ln (A - A_{\infty})$ against time were linear (10), thus indicating that the reaction is first order in permanganate. The pseudo-first-order rate constants, obtained from the slopes of these plots, were found to be directly proportional to the concentration of the reductant, thereby confirming that the reaction is also first order in reductant concentration (10).

Stoichiometry

The stoichiometry of the reaction was determined by adding small portions of a reductant solution to a standardized solution of permanganate and recording the spectrum of the product. A calculation of the number of moles of permanganate reduced, per mole of reductant added, indicated a 1:1 stoichiometry.

Products

The brown-yellow solution remaining after all of the permanganate had been reduced in methylene chloride by a typical alkene, 1-phenyl-1-

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TABLE 1. Properties of substituted styrenes

| Substituted styrene | Melting or boiling point (°C) (lit. value) | Nuclear magnetic resonance (δ ppm) | | |
|--------------------------------------|---|--|--|--|
| Methyl (E)-cinnamate | mp = 34 - 36 (36.5(14)) | 3.73(s, 3H), 6.53(d, 1H, J = 2.8) 7.48(m, 5H), 7.73(d, 1H, J = 2.8) | | |
| Methyl (E)-p-methyl- cinnamate | mp = 56–57.4 (57–58(15)) | 2.34(s, 3H), 3.78(s, 3H), 6.50(3, 1H, $J = 2.8$), 7.40(m, 4H), 7.75(d, 1H, $J = 2.8$) | | |
| Methyl (E)-m-methyl- cinnamate | bp = 78-79/0.2 Torr | 2.29(s, 3H), 3.73(s, 3H), 6.33(d, 1H, $J = 2.7$), 7.22(s, 4H), 7.64(d, 1H, $J = 2.7$) | | |
| Methyl (E)-p-methoxy- cinnamate | mp = 89–91.5 (94–95(15)) | 3.77(s, 3H), 3.86(s, 3H), 6.43(d, 1H, J = 2.8), 7.35(m, 4H), 7.73(d, 1H, J = 2.8) | | |
| Methyl (E)-m-methoxy- cinnamate | $bp = 107 - 109/0.36 \text{ Torr} \\ (162/13 \text{ Torr}(15))$ | 3.71(s, 6H), 6.37(d, 1H, J = 2.8), 7.05(br, 4H), 7.63(d, 1H, J = 2.8) | | |
| Methyl (E)-p-chloro- cinnamate | mp = 74.5 - 76.5(76 - 76.5(16)) | 3.79(s, 3H), 6.59(d, 1H, J = 2.8), 7.57(m, 4H), 7.72(d, 1H, J = 2.8) | | |
| Methyl (E)-m-chloro- cinnamate | mp = 46-47.5 | 3.83(s, 3H), 6.60(d, 1H, J = 2.8), 7.59(m, 4H), 7.72(d, 1H, J = 2.8) | | |
| Methyl (E)-p-isopropyl- cinnamate | bp = 109–112/0.2 Torr | 1.18(d, 6H), 2.85(m, 1H), 3.71(s, 3H), $6.37(d, 1H, J = 2.8)$, 7.32(m, 4H), 7.69(d, 1H, $J = 2.8$) | | |
| Methyl (E)-m-fluoro- cinnamate | bp = 91-92/0.7 Torr | 3.78(s, 3H), 6.44(d, 1H, J = 2.8), 7.34(br, 4H), 7.67(d, 1H, $J = 2.8$) | | |
| (E)-β-Bromostyrene | bp = 80-83/5 Torr (108/20 Torr (14)) | 6.90(m, 2H), 7.28(s, 5H) | | |
| (E)-p-Methyl-β-bromo- styrene | mp = 46-46.5 | 2.34(s, 3H), 6.90(m, 2H), 7.18(s, 4H) | | |
| (E)-p-Methoxy-β-bromo- styrene | mp = 54.5 - 56 (55 - 55.5(17)) | 3.76(s, 3H), 6.90(m, 6H) | | |
| (E)-p-Chloro-β-bromo- styrene | mp = 47-49 | 6.94(m, 2H), 7.31(s, 4H) | | |
| (Z) - β -Methoxystyrene | bp = 70–72/3 Torr (44/0.3 Torr (15)) | 3.60(s, 3H), 5.15(d, 1H, J = 1.2), 5.99(d, 1H, J = 1.2), 7.19(br, 5H) | | |
| (Z)-p-chloro-β-methoxy- styrene | bp = 57-59/0.03 Torr | 3.67(s, 3H), 5.07(d, 1H, J = 1.1), 6.03(d, 1H, J = 1.1), 7.33(m, 4H) | | |
| (Z)-p-Methoxy-β-methoxy- styrene | bp = 51-52/0.05 Torr | 3.77(s, 3H), 3.75(s, 3H), 5.13(d, 1H, J = 1.1), 5.99(d, 1H, J = 1.1), 7.11(m, 4H) | | |

pentene, was found by iodometric analysis (18) to contain manganese in the +4 oxidation state. Although no organic products could be detected in this solution when it was analyzed by glc, the corresponding diol, 1-phenyl-1,2-dihydroxypentane, could be isolated after treatment with base. On the other hand, when the yellow-brown methylene chloride solution was treated with aqueous acid, benzaldehyde was found to be a major product. similar results for other compounds have previously been reported (19).

The oxidation state of the manganese remained at +4 after treatment with aqueous base, but decreased to about +3 after treatment with aqueous acid. Thus, it appears that the organic product (diol) may be complexed to a manganese(IV) compound (MnO₂?) in organic solvents, and released only by hydrolysis. Under basic conditions no further redox reactions occur during hydrolysis, but under acidic conditions the diol is oxidatively cleaved with concurrent reduction of the manganese, as in eq. [1].

[1] Alkene + MnO₄⁻
$$\xrightarrow{CH_2Cl_2}$$
 Manganese(IV) complex
 OH^-/H_2O $\downarrow H^+/H_2O$
Diol + MnO₂ cleavage + Mn(III)
products + Mn(III)

Results and discussion

Although most salts exist as discrete ions in aqueous solutions, quaternary ammonium compounds when dissolved in organic solvents are more likely to form ion pairs (11). Brandstrom has shown that the probability of salts existing as ion pairs is inversely dependent on the distance between the centres of the two ions and the dielectric constants of the solvents (20). Using his method of calculation, we have previously shown that most quaternary ammonium permanganates would be expected to exist as ion pairs in all solvents except water (1). This can be demonstrated by examining the 1 H nmr spectrum of tetraethylammonium permanganate in three solvents, D_2O , acetone- d_6 , and methylene chloride- d_2 (Fig. 1). In water a distinct triplet and quartet is apparent, while in acetone and methylene chloride the resolution is dramatically reduced, with the spectrum becoming two broad multiplets in the latter solvent. Assuming that the lack of resolution in the organic solvents is due to close association of the quaternary ammonium ion with the permanganate ion (11), it would appear that $Et_4N^+MnO_4^-$ exists as separate ions in water, as a loose ion pair in acetone, and as a tight ion pair in methylene chloride.

The data sumarized in Table 2 are also in agreement with this

| TABLE 2. | Second-order | rate constan | ts for th | e oxidation | of methyl | cinnamate | by Q ⁺ MnO ₄ ⁻ | in |
|-----------------------------|--------------|--------------|-----------|-------------|-----------|-----------|---|----|
| three solvents ^a | | | | | | | | |

| Q ⁺ | Acetone | Methylene chloride | Toluene ^b |
|------------------------------------|-----------------|-----------------------|----------------------|
| Tetra- <i>n</i> -butylammonium | 0.32±0.01 | 1.15±0.02 | |
| Tetra-n-octylammonium | 0.31 ± 0.01 | 0.91 ± 0.02 | 1.31 ± 0.05 |
| Methyltri- <i>n</i> -octylammonium | 0.33 ± 0.01 | 1.54 ± 0.05 | 2.17 ± 0.04 |
| Methyltri-n-butylammonium | | 1.54 ± 0.02 | |
| Methyltriphenylphosphonium | 0.34 ± 0.02 | 1.35 ± 0.02 | |
| n-Butyltriphenylphosphonium | 0.27 ± 0.01 | 0.99 ± 0.02 | |
| Benzyltriphenylphosphonium | 0.30 ± 0.01 | 1.53 ± 0.04 | |
| 8-Crown-6-K ⁺ | 0.27 ± 0.01 | 1.64 ± 0.01 | |
| | | | |

^aTemperature = 22.0°C. $[Q^+MnO_4] = 4 \times 10^{-4} M$. [Methyl cinnamate] = $8 \times 10^{-3} M$. Units are $M^{-1} s^{-1}$. ^bStudies in toluene were limited by the insolubility of most quaternary ammonium and phosphonium salts in solvents of low polarity (11).



FIG. 1. Proton magnetic resonance spectra of tetraethylammonium permanganate in water- d_2 , acetone- d_6 , and methylene chloride- d_2 .

interpretation; the rate constants for the oxidation of methyl cinnamate in acetone are not dependent on the nature of the quaternary ammonium ion, whereas substantial variations in rates are found in the less polar solvents, methylene chloride and toluene. It thus appears as if the ion pairing in acetone is sufficiently loose to not affect the relative energies of the ground and transition states. However, in less polar solvents, where theory predicts tighter ion pairs (20), the ions must be intimately associated in either (or both) the ground state and the transition state. Furthermore, close contact within the ion pair seems to increase the rate of reaction. For example, the rate constants for oxidation of methyl cinnamate by methyltri-*n*-octylammonium permanganate are greater (in toluene and methylene chloride)



FIG. 2. Hammett plot for the oxidation of substituted methyl cinnamates by tetrabutylammonium permanganate in methylene chloride and acetone. [QMnO₄] = $3.7 \times 10^{-4} M$. [Methyl cinnamates] = $7.5 \times 10^{-3} M$. Temperature = $20.0 \pm 0.1^{\circ}$ C. For upper plot, slope = 0.95 ± 0.12 , r = 0.989. For lower plot, slope = 1.43 ± 0.18 , r = 0.99.

than for tetra-*n*-octylammonium permanganate, presumably because the former allows for greater penetration of the anion into the structure of the cation (11, 21). Hence it appears as if quaternary ammonium permanganates may exist as solventseparated ion pairs in acetone, but as intimate ion pairs in toluene and methylene chloride (22).

Additional evidence in support of this conclusion is obtained from a consideration of the effect of substituents on the rates of reaction. The Hammett ρ value for the oxidation of substituted methyl cinnamates by tetrabutylammonium permanganate is greater in acetone ($\rho = 1.43$) than it is in methylene chloride ($\rho = 0.95$). See Fig. 2. Since the ρ values are positive in both solvents, it is apparent that the transition state bears a greater

TABLE 3. Activation parameters for the oxidation of methyl cinnamate by methyltri-n-octylammonium permanganate^a

| Solvent | ΔH^{\pm} (kcal/mol) | ΔS^{\pm} (eu) | $\Delta G^{\ddagger} (\text{kcal/mol})^{b}$ |
|-------------------------------|------------------------------------|----------------------------|---|
| Acetone | 8.06±0.50 | -33.3±1.8 | 18.0±1.0 |
| Methylene chloride Toluene | 5.34 ± 0.28 3.69 ± 0.74 | -39.2 ± 1.0 -44.1±0.3 | 17.0 ± 0.6 16.8±0.8 |

"Temperature range from 0 to 30°C.

^bAt 25°C.

electron density than the ground state. However, the lower sensitivity of the reaction to substituent effects in methylene chloride suggests that, in this solvent, some of the increased negative charge is shared by the quaternary ammonium ions. In acetone, where the ion pair is much looser, the effect of substituents is greater because of a greater net charge developed in the transition state.

The thermodynamic parameters observed when different solvents are used could also be a consequence of ion pairing (Table 3). Since these reactions are clearly second order in all three solvents, the values of ΔH^{\pm} must reflect the differences in potential energies between the ground and transition states, while the relative magnitudes of ΔS^{+} must be associated with the different amounts of structure (or organization) in the ground and transition states. On this basis, the increase in organization on going from ground state to transition state is least in acetone ($\Delta S^{\pm} = -33.3 \pm 1.8$ eu) and greatest in toluene ($\Delta S^{\pm} = -44.1 \pm 0.3$ eu), with the value in methylene chloride being intermediate ($\Delta S^{\pm} = -39.2 \pm 1.0 \text{ eu}$). Despite the fact that the reaction in toluene exhibits the least favorable entropy of activation, its rate of reaction is greatest because of the relatively low enthalpy of activation ($\Delta H^{\pm} = 3.69 \pm 0.74$ kcal/mol), the converse observation being true for the reaction in acetone ($\Delta H^{\pm} = 8.06 \pm 0.50$ kcal/mol). It therefore appears as if the formation of an intimate ion pair provides relatively greater organization and stability to the transition state than to the ground state during the oxidation of methyl cinnamate.

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Current theory (23, 24) suggests that these reactions are initiated by formation of a π -complex between the alkene and manganese, as in eq. [2]. It is believed that this complex, 1, can rapidly transform into a metallocyclooxetane, 2, which then rearranges into a cyclic manganese(V) diester, 3, long known to be an intermediate in these reactions (25). The latter is an example of a well-known group of reactions in which carbon migrates from metal to oxygen (23).



3

It is not possible to specify where, in this reaction sequence, the transition state is located. However, it may be noted that the formation of both 1 and 2 involves bond making, whereas conversion of 2 into 3 requires cleavage of the C—Mn bond. Hence it is not unreasonable, to assume, in the absence of other compelling evidence, that the last step in eq. [2] is likely to be rate limiting.

Since the effect of substituents indicates an electron-rich transition state when methyl cinnamate is oxidized, it seems reasonable to suggest that this rate-limiting step may involve heterolytic cleavage of the carbon-manganese bond to give an enolate-like transition state, as in eq. [3].



In this picture of the reaction, it is assumed that the proximity of the quaternary ammonium ion would increase the stability of the transition state in nonpolar solvents, but that this effect would be less in more polar solvents (such as acetone) where the cation could be surrounded by a sheath of solvent molecules.

Although the Hammett ρ value is observed to be positive for the oxidation of methyl cinnamates, previous work has shown that this observation is not universally true. For example, Toyoshima et al. (26) have reported that the oxidation of vinyl ethers by potassium permanganate in aqueous THF exhibited a negative ρ value (10), while Brownridge found that the ρ value for the oxidation of substituted cinnamic acids in aqueous acetic acid/HClO₄ solutions is essentially zero (27). Since some substituted alkenes (such as methyl cinnamates) that are capable of delocalizing negative charges exhibit positive p values, while other alkenes (such as vinyl ethers) that are able to stabilize positive charges exhibit negative p values, it is not surprising that for certain reactions, the sign of p actually changes when different substituents are present. The oxidation of substituted stilbenes, which has been studied by Henbest et al. (28), is one example of this phenomenon; the rate of reaction is accelerated by both electron-donating and electron-withdrawing substituents (10). The oxidation of substituted β -methoxy and β-bromostyrenes also gives Hammett plots with a distinctive



FIG. 3. Hammett plot for the oxidation of substituted β -bromostyrenes and β -methoxystyrenes by tetrabutylammonium permanganate in methylene chloride at 20.0°C.

upward curvature, as demonstrated in Fig. 3. Concave upward plots of this type are obtained only when the variation in substituents causes a change in mechanism (29). In other words, when substituents that are capable of stabilizing a positive charge are present, the reaction must be capable of selecting a pathway in which the transition state is electron deficient (eq. [3]), while the converse must be true when substituents that could stabilize a negative charge are present (eq. [4]).



Since the mechanism chosen by the reaction can be altered from an electron-rich to an electron-deficient path merely by a change in substituents, it follows that the two transition states must be of similar energy and suggests that the reaction could best be visualized by use of a potential energy surface diagram (Fig. 4). According to transition state theory (30), the reaction would select the lowest energy pathway from 2 to 3. When the substrate is capable of accommodating a negative charge, the reaction pathway would be shifted toward the lower right hand side of the surface, whereas the use of substrates capable of bearing positive charges would shift the reaction pathway toward the upper left hand corner of the diagram.

Although there is an overwhelming amount of evidence that **3** is an intermediate in these reactions, the yellow-brown product solution contains manganese in the +4 not the +5 oxidation state. Hence, it appears as if **3** may be a very reactive compound that rapidly undergoes a one-electron reduction, possibly by abstraction of a hydrogen atom from a molecule of solvent, as in [5].





FIG. 4. Potential energy surface diagram for the rearrangement of structure 2 into structure 3.

The product of this reaction would be a manganese(IV) cyclic diester, 4, which could decompose to a diol anion, 5, and manganese dioxide (31). Treatment of this product with aqueous base would release diol plus MnO_2 , while addition of aqueous acid causes a further redox reaction in which the diol is oxidatively cleaved and manganese reduced to a lower oxidation state. The latter reaction is consistent with the higher reduction potential of manganese dioxide under acidic conditions (32).

Summary

1. A study of the effect of solvents on the rate of oxidation of methyl cinnamate by quaternary ammonium and phosphonium permanganates indicates that the cations are intimately associated with the transition state in nonpolar solvents, such as methylene chloride and toluene. In more polar solvents, such as acetone, the structure of the quaternary ammonium and phosphonium ions has no observable effect on the rate of reaction, presumably because they form solvent-separated ion pairs in both the ground state and the transition state.

2. A study of substituent effects on the rates of these reactions leads to the conclusion that they can proceed by way of continuum of transition states ranging from electron rich to electron poor. Although the mechanism is best visualized by use of a potential energy surface diagram (Fig. 4), the two extremes may be summarized as in Scheme 1.

3. The initial product of this reaction, 3, is very reactive and rapidly undergoes a one-electron reduction to a manganese(IV) compound (or complex) that can be hydrolyzed under basic conditions to liberate a diol, or under acid conditions to produce cleavage products.



SCHEME 1. The reaction mechanism.

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