2f, 98269-48-8; **3a**, 98269-34-2; **3b**, 98269-37-5; **3c**, 98269-42-2; **3e**, 98269-47-7; **3f**, 98269-49-9; **4b**, 98269-38-6; **5a**, 98269-35-3; **5b**, 98269-39-7; **5c**, 98269-43-3; **5d**, 98269-45-5; **5f**, 98269-50-2; **7a**, 50745-74-9; **7b**, 98269-51-3; (E)-PhCH=CHC(O)CH$_3$, 1896-62-4; CH$_2$=CHCHO, 107-02-8; CH$_2$=CHC(O)CH$_3$, 78-94-4; CH$_3$CH=CHC(O)OEt, 10544-63-5; ethyl 4-bromocrotonate, 6065-32-3; 4,4-dimethylcyclopent-2-en-1-one, 22748-16-9; cyclohex-2-en-1-one, 930-68-7; cyclopent-2-en-1-one, 930-30-3.

Oxidation of Hydrocarbons. 16. Mechanism of the Reaction between Alkynes and Permanganate Ion

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The kinetics and mechanism of the oxidation of alkynes by tetrabutylammonium permanganate in methylene chloride have been studied. Second-order rate constants have been determined for several different alkynes in an attempt to evaluate the extent of electronic and steric effects on the reaction. The rates are found to be very sensitive to electronic effects, but much less dependent on steric effects. A concave plot is obtained when the logarithms of the rate constants are plotted against Taft's σ^* substituent constants. This result is explained in terms of a reaction that can proceed via two pathways of almost equal activation energy. The transition state in one pathway has a positively charged carbon and is thus favored when the alkyne bears electron-donating substituents, while the other pathway has a carbanion-like transition state that is stabilized by substituents which are able to delocalize a negative charge. As a consequence the rate of reaction is greatly accelerated for α-oxoalkynes.

Permanganate is one of the most versatile oxidants available[1] with applications ranging from its use in the elegant stereospecific syntheses of substituted tetrahydrofuran derivatives[2] to its much less esoteric, but nevertheless very necessary, use in the fumigation of chicken coops.[3] In recent years the scope of its reactions has been increased by the discovery that it can be used, with the assistance of phase-transfer agents, in nonaqueous solvents[4] or as a heterogeneous oxidant under a variety of nonpolar organic solvents.[5]

Because of its wide use in organic synthesis the reactions of permanganate have been the subject of mechanistic speculations for almost a century.[6] Most recently, an improved understanding of the reactions between high valent transition metal oxidants, such as permanganate, and unsaturated compounds has come from several theoretical studies, the most important of which were made by Sharpless[7] (who first suggested that organometallic intermediates might be involved) and Goddard[8] (who drew attention to factors which would lead to stabilization of the intermediates). Although the results of these studies have been applied primarily to an understanding of the reactions of alkenes,[9,10] we wish, in this paper, to show that they can also be used, in conjunction with certain experimental results, to develop a reasonable mechanism for the oxidation of alkynes by permanganate.

Table I. Rate Constants for the Oxidation of Ethyl 2-Butynate by Tetrabutylammonium Permanganate[a]

[alkyne], M × 10^2	[QMnO$_4$]$_i$, M × 10^4	initial slope,[b] M s^{-1} × 10^7	k_1,[c] s^{-1} × 10^3	k_2, M^{-1} s^{-1} [d]
1.52	1.67	−5.27	3.16	0.208
1.52	1.92	−6.05	3.15	0.207
1.52	2.51	−7.63	3.04	0.200
1.52	3.63	−11.2	3.09	0.203
1.06	3.51	−8.20	2.34	0.221
0.608	3.42	−4.37	1.28	0.211

[a] Temperature 22.0 °C in methylene chloride. [b] Initial slope = d[QMnO$_4$]$_i$/dt. [c] k_1 = −initial slope/[QMnO$_4$]$_i$. [d] k_2 = k_1/[ethyl 2-butynate].

Table II. Rate Constants for the Oxidation of Substituted Alkynes by Tetrabutylammonium Permantanage[a]

alkyne	[alkyne], M × 10^3	k_1, s^{-1} × 10^3	k_2, M^{-1} s^{-1} × 10^3
4-phenyl-3-butyn-2-one	12.7	12.0 ± 0.1	945 ± 8
ethyl 2-butynate	15.2	3.10 ± 0.05	204 ± 3
ethyl 1-propynyl ether[b]	16.4	0.18 ± 0.03	11 ± 2
1-phenyl-1-butyne	12.4	0.037 ± 0.006	3.0 ± 0.5
2-heptyne	14.0	0.046 ± 0.001	3.3 ± 0.1

[a] In methylene chloride at 22.0 °C. Symbols defined in Table I. [b] Unstable compound. Kinetics were determined by using a freshly distilled sample.

Experimental Section

Materials. Tetrabutylammonium permanganate was prepared and handled as previously described.[11] The alkynes were obtained

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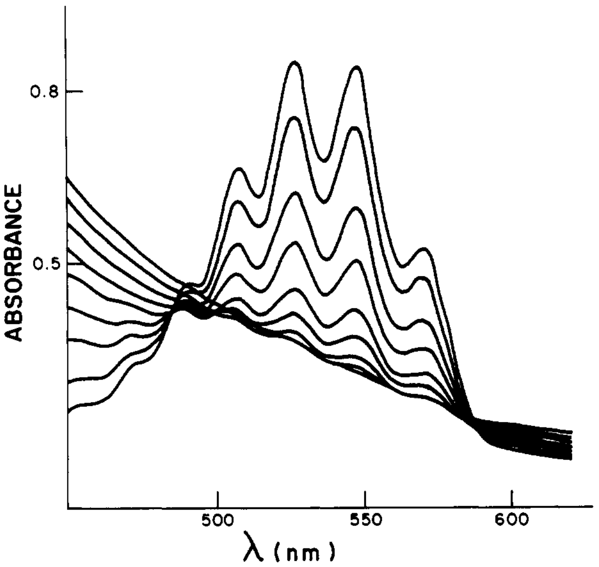

Figure 1. Successive scans obtained during the oxidation of ethyl 2-butynate (1.52×10^{-2} M) by tetrabutylammonium permanganate (3.52×10^{-4} M) in methylene chloride at 22.0 °C.

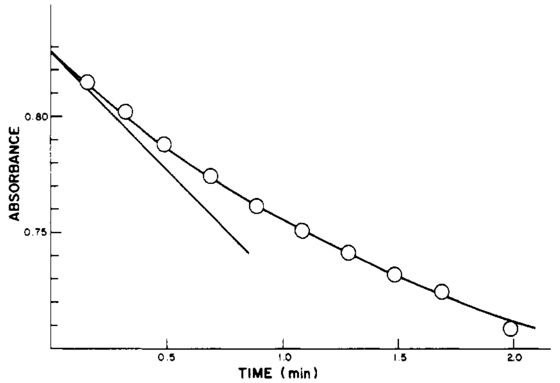

Figure 2. Typical rate plot. $[QMnO_4] = 3.48 \times 10^{-4}$ M, [5-methyl-2-hexyne] = 1.37×10^{-2} M, t = 22.0 °C. The open circles are experimental absorbance/time readings. The curve is the theoretical fit to the equation $A = 0.8276 - (9.066 \times 10^{-3})t + (2.282 \times 10^{-4})t^2 - (3.595 \times 10^{-6})t^3 + (2.925 \times 10^{-8})t^4 - (9.483 \times 10^{-11})t^5$. The straight line is the calculated tangent to the curve at $t = 0$.

from Farchan Labs[12] and carefully distilled before use. The purity in each case was confirmed by use of GLC and the identities were verified by use of mass spectrometry.

Kinetic Methods. In a typical experiment, tetrabutylammonium permanganate was dissolved in purified methylene chloride[9] and centifuged to remove any traces of MnO_2. A portion of this solution (2.0 mL) was transferred to a 1.0-cm cuvette and thermostated in the cell compartment of a Hewlett Packard 8450A spectrophotometer. A known excess of alkyne was then added by using a microliter syringe and absorbance measurements were made at 526 nm as the reaction progressed.

When successive scans were recorded, good isosbestic points were *not* obtained (Figure 1), presumably because one of the products of the reaction, MnO_2, slowly flocculates as the reaction proceeds.[13] This makes it impossible to obtain an accurate value for the final absorbance and thus eliminates the possibility of using an integrated form of the rate equation. Instead, a differential method was used to obtain initial reaction rates from time vs. absorbance plots. This was done by first making a computed fit of the data using a fifth-order expansion series of the type given in eq 1.

$$A = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5 \qquad (1)$$

Table III. Rate Constants for the Oxidation of Dialkylacetylenes (RC≡CR′) by Tetrabutylammonium Permanganate[a]

R	R'	k_2, $M^{-1}\,s^{-1} \times 10^4$	$\sum\nu$[b]
n-butyl	*n*-butyl	7.3 ± 0.7	1.36
isobutyl	isobutyl	18 ± 7	1.96
ethyl	phenyl	30 ± 5	2.22
methyl	*n*-butyl	33 ± 7	1.20
methyl	*tert*-butyl	60 ± 5	1.76
methyl	isobutyl	129 ± 9	1.50

[a] In methylene chloride at 22.0 °C. [b] Sum of Charton's steric parameter. See ref 33.

The slope (dA/dt) was then obtained by differentiation with respect to t, and initial rates, measured under pseudo-first-order conditions, were found by setting $t = 0$. A typical example of the experimental data and calculated curve is shown in Figure 2.

Results

The rate constants obtained have been summarized in Tables I, II, and III. The data in Table I indicate that the reaction is second order under these conditions. The first four entries illustrate the first-order dependence on oxidant and the last three confirm that the reaction is also first order in alkyne.

Table II contains a summary of the second-order rate constants obtained for several alkynes bearing a variety of polar and nonpolar substituents. These results, which were used to investigate electrical effects on the rate constants, indicate that the rates of reaction are greatly accelerated by electron-withdrawing substituents.

Table III contains data that was used in an attempt to evaluate the sensitivity of the rates of reaction to steric effects.

Discussion

The oxidation of alkynes by potassium permanganate in aqueous solutions usually results in cleavage of the carbon–carbon triple bond to give two carboxylic acids if the alkyne is nonterminal or a carboxylic acid plus 1 mol of CO_2 if the alkyne is terminal.[14] Although this reaction may be used for structure elucidation,[15] it serves little synthetic purpose since the alkynes are often more difficult to prepare than the corresponding carboxylic acids. However, if the reaction is carried out under carefully controlled conditions, α-diones, which are also believed to be intermediates in the cleavage reactions,[14] can be isolated in good yields.[16] The evidence for the supposition that α-diones are intermediates in the cleavage reactions comes mainly from a study of the products obtained when they are subjected to conditions under which the alkynes are cleaved.[17] For example, 8,9-hexadecanedione, when oxidized under a variety of conditions, gives approximately the same array of products as is obtained from the oxidation of 8-hexadecyne under the same conditions.[17]

The conditions under which good yields of α-diketones can be prepared have been defined in the literature. Thus when propiolic acid or phenylpropiolic acid was oxidized under acidic conditions with 1 molar equiv of permanganate the corresponding α-dione products were obtained in over 90% yield.[18] (However, if the inorganic

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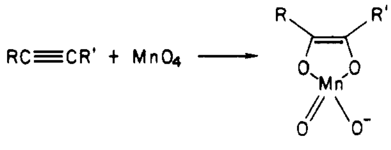
product, Mn^{3+}, remains unquenched it can participate in a cleavage reaction and thus lower the overall yield.) Under neutral aqueous conditions[16] (where Mn^{3+} would be expected to rapidly disproportionate) and in anhydrous organic solvents, α-diones (and manganese dioxide) were obtained in excellent yields.[17,19]

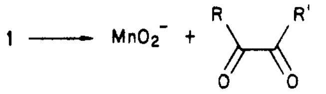
There is general agreement[17-20] that these reactions would likely be initiated by formation of a cyclic unsaturated manganate(V) diester, **1**, which is analogous to the intermediate formed during the oxidation of alkenes by permanganate (eq 2).



(2)

1

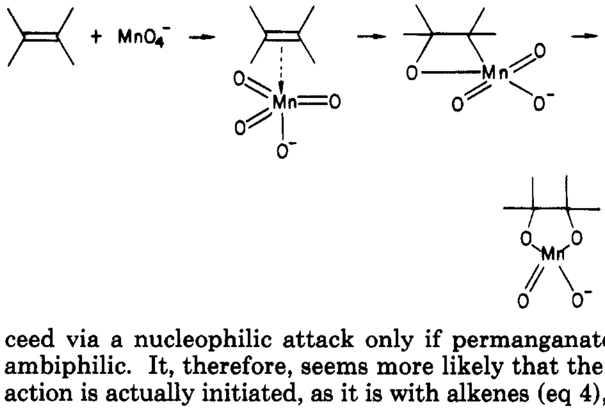
Oxidative decomposition of **1** with release of manganese(III) could then occur as in eq 3.



(3)

It has been suggested by Simandi and Jaky[18,20] that the oxidation of alkynes may be initiated by nucleophilic attack of permanganate on the triple bond. Such a possibility is consistent with the known susceptibility of triple bonds to nucleophilic attack[21] and with the observation that the rate of reaction is accelerated by the presence of oxo groups adjacent to the triple bond.

However, there are also a number of difficulties with a nucleophilic mechanism. First of all, since the charge is very diffuse in permanganate[7,22] it would not likely be a very good nucleophile. Secondly, if permanganate reactions were initiated by nucleophilic attack at a point of unsaturation, it is to be expected that alkynes would react more readily than alkenes.[21] However, the exactly opposite result is observed experimentally.[20,23] Thirdly, since recent studies indicate that the reaction between alkenes and permanganate is initiated by electrophilic attack,[7-9] as in eq 4, the corresponding reaction with alkynes could proceed via a nucleophilic attack only if permanganate is ambiphilic. It, therefore, seems more likely that the reaction is actually initiated, as it is with alkenes (eq 4), by formation of an organometallic complex. This is consistent with the fact that alkynes are known to be susceptible to electrophilic attack[24] and to readily form π-complexes with various transition metals.[25]



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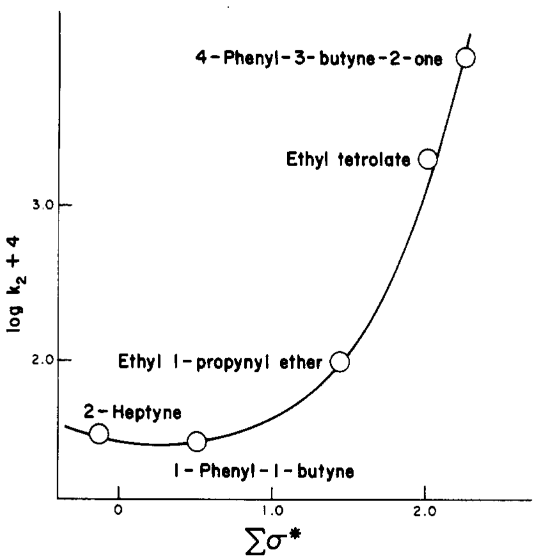
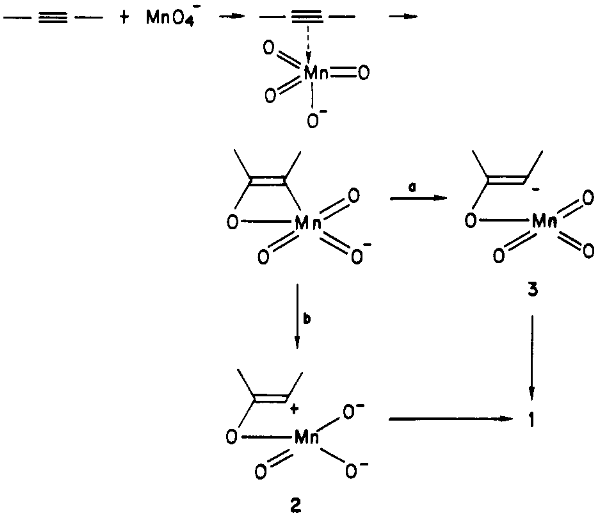


Figure 3. Taft plot for the oxidation of alkynes by tetrabutylammonium permanganate in methylene chloride solutions at 22.0 °C.

When the effect of substitutents on the rates of oxidation of alkenes by permanganate is studied, curved Hammett plots are obtained under certain conditions.[9,26,27] Such curvature is indicative of a change in mechanism caused by the different abilities of the substituents to stabilize positive or negative charges. Since a similarly curved plot is obtained when the rate data from Table II is plotted against the cumulated substituent effects[28] (Figure 3), it appears that the mechanism for the oxidation of alkynes may be similar. Such a mechanism, which includes a choice between an electron-rich carbon and an electron-poor carbon transition state, has been indicated in eq 5. The electron-rich pathway (a) would be followed when electron-withdrawing substituents, such as the acetyl group, are present, whereas the electron-deficient pathway (b) would be followed when substituents capable of sta-



(5)

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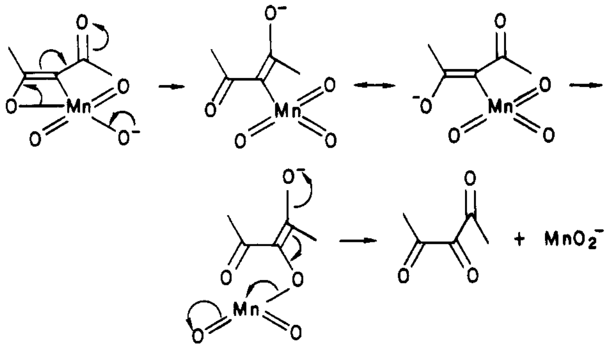
bilizing a cationic center are present. As a consequence, a nonlinear free energy relationship of the type depicted in Figure 3 is obtained. Similarly curved plots, obtained for other dual mechanism reactions, have been documented in the literature.[29,30]

The intermediate, **2**, is actually a substituted vinyl cation, the formation of which has analogies in several other reactions.[31] Anionic intermediates, such as **3**, which are known to occur in a number of alkyne nucleophilic substitution reactions,[21] would be most stable when an α-oxo group is present. In the latter case the charge would be extensively delocalized onto the oxygen to give an enol intermediate similar to the one which has been identified in 1,4-nucleophilic additions to ketoalkynes.[21,32]

The unusually large accelerative effect of an α-oxo group suggests a third possible pathway for the decomposition of the metallocyclooxatene **4**. When an α-oxo group is present, decomposition by opening of an Mn–O rather than Mn–C bond would give an intermediate that could be stabilized by extensive delocalization of the negative change as indicated in eq 6. Migration of carbon from metal to oxygen (a well-known process[7]) then gives a manganate(V) ester which could decompose to the known products of the reaction.



(6)

An examination of the data in Table III indicates that steric factors do not seem to be as important as electronic effects on the rates of reaction. When the logarithms of the rate constants are plotted against ν, the steric parameter defined by Charton,[33] a scattered plot with a statistical slope close to zero (−0.005) is obtained. The low slope suggests that steric factors are not of great importance in this reaction. The scatter found in the plot may be caused by the differing abilities of the various alkyl groups to interact with a charged transition state via hyperconjugation. Superimposition of steric and hyperconjugative effects could lead to scatter. Unfortunately, attempts to fit the data to a Taft dual parameter equation[28] failed, thus leaving undefined the magnitude and significance (if any) of steric effects on this reaction.

The reaction mechanism, summarized in eq 5 and 6, is consistent with the concave Taft plot (Figure 3), with the relatively slow rate of reaction observed for unsubstituted alkynes and with the large increase in rate caused by the presence of α-oxo groups. It also leads to the known products of the reaction and is in agreement with the observed kinetic rate law.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada and the Carus Chemical Company is gratefully acknowledged, as is the assistance of N. A. Noureldin for mass spectrometric analysis.

Registry No. $CH_3(CH_2)_3C{\equiv}C(CH_2)_3CH_3$, 1942-46-7; $(CH_3)_2CHCH_2C{\equiv}CCH_2CH(CH_3)_2$, 56956-29-7; $(CH_3)_3CC{\equiv}CCH_3$, 999-78-0; $(CH_3)_2CHCH_2C{\equiv}CCH_3$, 53566-37-3; ethyl 2-butynate, 4341-76-8; 4-phenyl-3-butyn-2-one, 1817-57-8; ethyl 1-propynyl ether, 14273-06-4; 1-phenyl-1-butyne, 622-76-4; 2-heptyne, 1119-65-9; tetrabutylammonium permanganate, 35638-41-6.

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Steady-State and Laser Flash Photolysis Studies of 1-Aziridinyl-1,2-dibenzoylalkenes[1]

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Received February 25, 1985

Results of a photochemical study based on product analysis and 337.1-nm laser flash photolysis are reported for several *cis*- and *trans*-1,2-dibenzoylethylenes bearing aziridinyl groups at the 1-position. Products isolated from steady-state photolysis suggest facile ring expansion yielding pyrrolines as well as extrusion of alkenes from the aziridine moieties forming nitrene fragments, which subsequently undergo ring closure to give isoxazoles. Laser flash photolysis studies show transient absorption changes, explainable in terms of cis–trans photoisomerization and formation of azomethine ylides. The latter are also observed upon steady-state irradiation of these aziridinyl-1,2-dibenzoylethylenes in an EPA glass at 77 K.

Past investigations have shown that dibenzoylethylenes undergo interesting photorearrangements to give ketene-derived products and lactones, in addition to cis–trans isomerization.[3-8] As part of our continuing interest in the photorearrangements of 1,2-dibenzoylalkenes, we have

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[1] Document No. NDRL-2651 from the Notre Dame Radiation Laboratory.

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