

Oxidation of alkynes by cobalt acetate bromide: a new mode of action for an important industrial catalyst

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Abstract

The catalytic oxidation of a variety of alkyne substrates has been studied using the well-known catalyst system, cobalt acetate bromide, under an O₂ atmosphere. Aryl-substituted alkynes generally gave diketones which cleaved to carboxylic acids under prolonged reaction. In some cases the diketone intermediates could be isolated in good yield. For example, reaction of diphenylacetylene with Co(OAc)₂/NaBr and 0.02 eq. Mn(OAc)₂ as a promoter in 95% AcOH/H₂O at 70°C for 7 h gave benzil in 78% selectivity. Whilst [Co(OAc)Br] oxidation catalysis normally involves H-atom abstraction, many of the alkynes used in our study could not proceed by this mechanism. The electron-richness of the alkyne was important in determining reaction rates. Thus, slower reaction was found for PhC≡C–C≡C–Ph than diphenylacetylene itself, and no reaction at all was observed for [PhC≡CC₆H₄–NO₂]. On the other hand, the internal aliphatic acetylene, 4-octyne, did proceed via H-atom abstraction, giving the corresponding acetylenic ketone [CH₃CH₂CH₂C≡CCOCH₂CH₃] in 80% yield. © 1999 Elsevier Science B.V. All rights reserved.

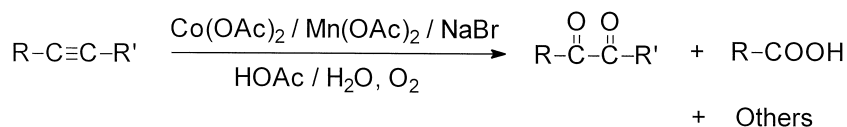
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1. Introduction

The stoichiometric oxidation of alkynes to either 1,2-dicarbonyl compounds or carboxylic acids has been widely investigated with reagents such as permanganate [1–3], ruthenium tetraoxide [4], osmium tetraoxide [5], thallium nitrate [6], peroxyphosphoric acid [7], peroxometalates [8], organic peracids [9–11] and dioxiranes [12–14]. However, studies on the catalytic oxidation of alkynes are fewer in number. For example, Zhu and Espenson [15] reported the

use of hydrogen peroxide with methylrhenium trioxide in the oxidation of alkynes. Internal alkynes yield α-diketones and carboxylic acids while terminal alkynes give carboxylic acids, ester derivatives, as well as α-keto carboxylic acids. Sakaguchi et al. [16] and Ishii and Sakata [17] have shown that diphenylacetylene can be oxidized to benzil in 42% yield with 93% selectivity over 24 h in the presence of cetylpyridinium peroxotungstophosphate (PWCP) under two-phase conditions. Ballistreri et al. [18,19] have reported that diphenylacetylene is cleaved to its acid while terminal alkynes are converted into carboxylic acids or α-keto aldehydes by

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Scheme 1. Oxidation of alkynes by the cobalt acetate bromide.

using hydrogen peroxide in the presence of catalytic amounts of tris(cetylpyridinium) 12-molybdophosphate or 12-tungstophosphate (CMP or CWP) with $\text{Hg}(\text{CF}_3\text{CO}_2)_2$ as a co-catalyst. It has been reported by Rihter et al. [20] that oxo(salen)chromium(V) trifluoromethanesulphonate reacts with diphenylacetylene to give the α -diketone in 86% yield. Furthermore, disubstituted alkynes can be oxidized with iodobenzene in the presence of ruthenium catalysts to afford α -diketones while terminal acetylenes are cleaved to carboxylic acids as reported by Muller and Godoy [21]. As found by Nishinaga et al., cobalt–schiff base complexes can catalyze the oxygenation of alkynes in alcoholic solvents resulting in the incorporation of monooxygen and the alcohol into the triple bond. Thus, phenylacetylene gives acetophenone, mandelic and phenylglyoxylic esters [22]. The above mentioned catalytic systems require either the use of expensive reagents or involve multi-step preparation of catalyst. Thus, there would be interest for investigating readily available and inexpensive transition metal catalysts for the catalytic oxidation of alkynes. These catalysts together with a simple and environmentally favorable oxidant such as oxygen would make a desirable industrial process.

Previously we have investigated the catalytic oxidation of a variety of organic substrates using readily available and cheap first row transition metal catalysts, notably cobalt chloride with molecular oxygen as the oxidant. It is suggested that the oxidation proceeds via a cobalt super-oxo complex which can carry out selective H-atom abstraction [23–26]. Another related catalytic system which has found considerable industrial application is the $\text{Co(OAc)}_2/\text{NaBr}/\text{AcOH}$ system [27]. The Br ions have a pro-

nounced synergistic effect on the cobalt-catalyst by contributing to an enhanced rate of propagation. In most cases the oxidation mechanism is believed to involve H-atom abstraction. In $[\text{Co(OAc)Br}]$, homolysis of a Co–Br bond occurs leading to formation of $\text{Br}\cdot$ radicals which act as the H-atom abstractors [28]. This important catalyst system has already been used in the industrial production of aromatic acids from methylaromatic compounds. For example, terephthalic acid can be prepared in excellent yields from *p*-xylene at atmospheric pressure and at 60°C [29].

In comparison to studies on the oxidation of alkanes and alkenes using cobalt acetate bromide system, oxidation of alkynes using this system has received much less attention. Only Trusov and Madelis [30] reported the kinetics of the oxidation of diphenylacetylene by $[\text{Co(OAc)Br}]$, however, the mode of action of the catalyst was not established.

In this paper, we report the results of the oxidation of a wide range of alkynes using $\text{Co(OAc)}_2/\text{Mn(OAc)}_2/\text{NaBr}/\text{AcOH}$ in the presence of a small amount of water under an oxygen atmosphere (Scheme 1), and discuss the factors affecting both reactivity and selectivity on the oxidation of diphenylacetylene. Finally, a new oxidation mechanism for diphenylacetylene which has not abstractable hydrogen atom is proposed [31].

2. Experimental

Proton and carbon nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 or JEOL EX-400 spectrometer. A Perkin-

Elmer 16RC FT-IR spectrometer was used for recording infrared spectra. Mass spectral determinations were made on a Finnigan TSQ 7000 spectrometer. Gas chromatographic-mass spectrometric determinations were recorded on a Hewlett Packard GC 5890 (Series II Plus), fitted with a HP-5 capillary column in tandem with the Finnigan TSQ 7000 spectrometer. Gas chromatography analyses were carried out on a Hewlett Packard GC 5890 (Series II) equipped with flame ionization detectors.

All alkynes and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were purchased from Aldrich Chemical. *p*-Nitro-tolane and diphenylacetylene were prepared from phenylacetylene following literature procedures [32,33]. Cobalt (II) and manganese (II) acetate tetrahydrate were purchased from Acros Chemicals; and sodium bromide from BDH Chemicals. Oxygen gas was obtained from Hong Kong Oxygen. All chemicals were used as received without further purification.

2.1. General procedure of the oxidation of alkynes

$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (129 mg, 0.5 mmol), NaBr (53 mg, 0.5 mmol) and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.5 mg, 0.01 mmol) were dissolved in a mixture of 19 ml of acetic acid and 1 ml of water and stirred under an oxygen atmosphere at 70°C for 15 min. The alkyne (2.5 mmol) was then added to the solution, and heating was continued for the reaction times as specified in Table 4. The reaction mixture was then cooled to room temperature and poured into 100 ml of distilled H_2O . The solution was extracted with chloroform (3 × 40 ml). The organic layer was washed with 10 M NaOH solution (3 × 10 ml), followed by distilled water (3 × 30 ml), then dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated and products were analyzed by GC and GC-MS. The combined aqueous layers were then treated with 10 M HCl until a pH of 2. The solution was extracted with

chloroform (3 × 40 ml). The organic layer was then washed with distilled water (3 × 30 ml), dried over anhydrous Na_2SO_4 , and filtered. The solvent was evaporated to give the acid product. Pure products were isolated by column chromatography on silica gel using ethyl acetate/hexane mixture as the eluent. Isolated products were determined by $^1\text{H-NMR}$, FT-IR, and mass spectrometry and compared with literature and/or with authentic samples.

2.2. Benzil oxidation

$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (129 mg, 0.5 mmol), NaBr (53 mg, 0.5 mmol) and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (12.5 mg, 0.05 mmol) were dissolved in a mixture of 19 ml of acetic acid and 1 ml of water and stirred under an oxygen atmosphere at 70°C for 15 min. Benzil (210 mg, 1 mmol) was then added to the solution, and heating was continued for 20 h to reach completion. The general work-up procedure was then followed. No product was isolated from the organic layer, while 181 mg, 74% isolated yield of benzoic acid was obtained from the aqueous layer.

2.3. BHT inhibition of diphenylacetylene and benzil oxidations

$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (129 mg, 0.5 mmol), NaBr (53 mg, 0.5 mmol) and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (12.5 mg, 0.05 mmol) were dissolved in a mixture of 19 ml of acetic acid and 1 ml of water and stirred under an oxygen atmosphere at 70°C for 15 min. 2,6-Di-*tert*-butyl-4-methylphenol (BHT, 606 mg, 2.75 mmol) was then added to the solution followed by diphenylacetylene (450 mg, 2.5 mmol) or benzil (525 mg, 2.5 mmol), and heating was continued for 48 h. The colour of the reaction mixture remained purple throughout the course of reaction. The general work-up procedure was then followed. Unreacted starting material or benzil was quantitatively recovered.

3. Results and discussion

At the start of our studies, we were interested in extending the use of CoCl_2 or related compounds as cheap and selective oxidation catalysts to a new class of organic substrates, the acetylenes. Since the mode of action of these cobalt catalysts was predominantly via H-atom abstraction, the successful oxidation of substrates such as diphenylacetylene, which possessed no readily abstractable hydrogens, was not guaranteed. Recently, we had shown that the selective oxidative cleavage of styrenes to acetophenones, by CoCl_2 and O_2 , might involve coordination of the alkene to the metal center [26]. Thus, acetylene binding might provide a possible intra-molecular mechanism for oxidation of such compounds. It was intriguing that although other cobalt salts showed little or no catalytic activity for the oxidation of diphenylacetylene, $[\text{Co}(\text{OAc})\text{Br}]$ system was highly promising in this regard.

The oxidative catalysis of diphenylacetylene (DPA) with $\text{Co}(\text{OAc})_2/\text{NaBr}$ [5:1:1 ratio of substrate: $\text{Co}(\text{OAc})_2$: NaBr] in acetic acid for 48 h at 70°C under oxygen reached 50% conversion and yielded benzil, 1,2-dibromostilbene, and benzoic acid as a mixture of products in 49%, 16%, and 10% isolated yields, respectively, based on the amounts of substrate reacted. The result suggested that the oxidation of diphenylacetylene could be achieved with this simple cobalt catalyst system, giving the α -diketone as well as cleavage products. In order to optimize the conditions for high conversion and selectivity towards the benzil product, we set forth to investigate factors which governed this reaction including the effect of metal catalyst, co-catalyst, catalyst and sodium bromide concentrations, as well as acetic acid concentration.

3.1. Effect of metal catalyst

Various cobalt (II) catalysts were examined for the oxidation of diphenylacetylene in the presence of HOAc, including $\text{Co}(\text{OAc})_2$, CoBr_2 ,

and CoCl_2 . When $\text{Co}(\text{OAc})_2$ or NaBr was used independently, there was no oxidation. There was also no oxidation when CoCl_2 was employed. Oxidation of diphenylacetylene was observed with the use of CoBr_2 in which the conversion rate was comparable to that of the $\text{Co}(\text{OAc})_2/\text{NaBr}$ system, but dibromostilbene yield was doubled. These results suggested the relevance of the bromide ion in conjunction with the cobalt catalyst for this oxidation to occur.

3.2. Effect of co-catalyst

The effect of a co-catalyst for $\text{Co}(\text{OAc})_2/\text{NaBr}$ on the oxidation of diphenylacetylene was explored. When ZrCl_4 was included in the reaction, there was little improvement in both the rate of oxidation and the selectivity as compared with the simple $\text{Co}(\text{OAc})_2/\text{NaBr}$ system. However, when small amounts of $\text{Mn}(\text{OAc})_2$ were added to the reaction, there was a profound effect on both the conversion and selectivity of the oxidation. A detailed study of the effect of varying amounts of $\text{Mn}(\text{OAc})_2$ was performed and is shown in Table 1. Small quantities of $\text{Mn}(\text{OAc})_2$, e.g., up to 0.1 mole ratio, greatly improved the conversion to near completion in only 6 h, while in the absence of the co-catalyst, 12 h was required for the reaction to be completed. However, the rate of oxidation again decreased when too much $\text{Mn}(\text{OAc})_2$ was added, e.g., mole ratios greater than 0.33. In addition, the selectivity towards the benzil product was noticeably decreased while the corresponding acid product increased as more co-catalyst was used. The formation of benzoic acid was likely a result of the over-oxidation of benzil. The yield of the dibromostilbene product remained relatively the same when the mole ratios of $\text{Mn}(\text{OAc})_2$ were varied. A comparison of entries 3, 4, 5 in Table 1 indicated that the use of 5:1:0.02 mole ratio of DPA: $\text{Co}(\text{OAc})_2$: $\text{Mn}(\text{OAc})_2$ gave not only near complete conversion in 6 h, but also resulted in the highest selectivity for the benzil product. This promoting effect

Table 1
The effect of $\text{Mn}(\text{OAc})_2$ on the oxidation of diphenylacetylene (DPA)^a

Entry	Ratio $\text{DPA}:\text{Co}(\text{OAc})_2:\text{Mn}(\text{OAc})_2$	Time (h)	Conversion (%)	Product distribution (%) ^b		
				Benzil	DBS ^c	PhCO_2H
1	5:1:0	12	100	84	6	10
2	5:1:0.01	6	69	80	8	12
3	5:1:0.02	6	96	82	6	12
4	5:1:0.05	6	100	72	5	23
5	5:1:0.1	6	100	67	2	31
6	5:1:0.33	6	90	56	6	37
7	5:1:0.5	6	78	34	9	57

^aReaction conditions: substrate: $\text{Co}(\text{OAc})_2$: NaBr = 5:1:1 under oxygen at 70°C in 95% HOAc.

^bProduct distribution was determined by G.C.

^cDBS = dibromostilbene.

may be due to redox reactions between cobalt and manganese ions which has previously been reported by Partenheimer and Gipe [34]. However, the decrease in conversion that resulted from an excess amount of $\text{Mn}(\text{OAc})_2$ may be a result of $\text{Mn}(\text{OAc})_2$ complexing with bromide ions, therefore, decreasing the amount of bromide ions available for the active catalyst species. Also, the increased amount of $\text{Mn}(\text{OAc})_2$ led to the over-oxidation of benzil to benzoic acid, which is not surprising because $\text{Mn}(\text{OAc})_2$ itself is an effective catalyst to cleave diketones to the corresponding carboxylic acids [35]. The results in Table 1 clearly indicate the importance of the ratio of $\text{Mn}(\text{OAc})_2$ relative to $\text{Co}(\text{OAc})_2$ which is crucial for optimal conversion and selectivity. Our findings are consistent with the study by Partenheimer [36] on the $\text{Co}(\text{OAc})_2$ catalyst in acetic acid which reports that only small amounts of Co^{III} exist in solu-

tion. Therefore, a comparable small amount of $\text{Mn}(\text{OAc})_2$ is needed to react with this species in order to achieve optimal conversion and selectivity. Subsequently, an investigation of the substrate to $\text{Co}(\text{OAc})_2$ ratio was also performed. When this ratio was decreased from 5:1 to 10:1, the conversion was reduced from 96% to 68%. The selectivity towards the benzil product also decreased.

3.3. Effect of sodium bromide

An investigation of how the NaBr concentration effected the conversion and product distribution was performed. Results in Table 2 show that when the $\text{Co}(\text{OAc})_2$ and NaBr ratios were 1:1 (entry 2), the conversion was almost complete and the selectivity for the benzil product was the highest. However, when the $\text{Co}(\text{OAc})_2$ and NaBr ratios were 1:0.5 (entry 1), conversion

Table 2
The effect of NaBr concentration on the oxidation of diphenylacetylene^a

Entry	Ratio $\text{Co}(\text{OAc})_2:\text{Mn}(\text{OAc})_2:\text{NaBr}$	Time (h)	Conversion (%)	Product distribution (%) ^b		
				Benzil	DBS ^c	PhCO_2H
1	1:0.02:0.5	6	50	52	8	40
2	1:0.02:1	6	96	82	6	12
3	1:0.02:2	6	80	69	11	20

^aReaction conditions: $\text{DPA}:\text{Co}(\text{OAc})_2:\text{NaBr}$ = 5:1:1 under oxygen at 70°C in 95% HOAc.

^bProduct distribution was determined by G.C.

^cDBS = dibromostilbene.

was low (50%) and the amount of acid was the highest among the three trials. Since Co(OAc)Br is the active species, its concentration would be limited by the amount of bromide ions present. Thus, less NaBr used results in fewer active species being available for the oxidation of diphenylacetylene to benzil. On the other hand, the oxidation of benzil to benzoic acid can simply be facilitated by Co(OAc)_2 or Mn(OAc)_2 , thus resulting in a higher yield of the acid product. Similarly, the conversion was reduced when a 1:2 ratio of Co(OAc)_2 : NaBr was utilized. Once Co(OAc)Br is formed, excess Br^- may react further to give less-active cobalt bromide species. Furthermore, an increase in the concentration of NaBr resulted in a slight increase of the dibromostilbene product. This increase could be attributed to the bromination of the alkyne by Br_2 which could form upon dimerization of excess Br^\cdot .

3.4. Effect of acetic acid concentration

When small quantities of water together with glacial acetic acid were used as the solvent system, a profound effect on both the rate of oxidation of diphenylacetylene and the selectivity was observed. Table 3 shows the results of varying this $\text{HOAc:H}_2\text{O}$ ratio in both $\text{Co(OAc)}_2/\text{NaBr}$ and $\text{Co(OAc)}_2/\text{Mn(OAc)}_2/\text{NaBr}$ systems. When 95% $\text{HOAc/H}_2\text{O}$ solvent mixture was employed, oxidation of diphenyl-

lacetylene catalyzed by $\text{Co(OAc)}_2/\text{NaBr}$ at 70°C in oxygen, achieved 100% conversion after 12 h, while there was only 50% conversion after 48 h in 100% glacial acetic acid. Increasing the amount of water to more than 10%, however, resulted in a decrease in conversion. Equal amounts of HOAc and H_2O gave no reaction at all. When a 95% $\text{HOAc/H}_2\text{O}$ solvent mixture was used in combination with the $\text{Co(OAc)}_2/\text{Mn(OAc)}_2/\text{NaBr}$ system, optimal conversion and selectivity for the benzil product was accomplished in only 6 h. The improved selectivity resulted in a great decrease in the amount of dibromostilbene produced. The improved rate of oxidation may be attributed by the increase of acetic ion concentration in the presence of a small amount of water. In addition, the possible reaction between water and Br_2 to form HBr can help regenerate the active species $\text{Co}^{\text{II}}(\text{OAc})\text{Br}$. This reaction serves not only to improve the amount of the catalyst species, but also to decrease the amount of the Br_2 addition product, dibromostilbene. However, if too much water is added to the system, hydration of the active cobalt complexes would occur as demonstrated by the considerable decrease in the reaction rate.

3.5. Oxidation of other alkyne substrates

After optimal conditions were discerned for the oxidation of diphenylacetylene, a number of

Table 3
The effect of the $\text{HOAc/H}_2\text{O}$ ratio on the oxidation of diphenylacetylene

Catalytic system	HOAc (%)	H_2O (%)	Time (h)	Conversion (%)	Product distribution (%) ^a		
					Benzil	DBS^b	PhCO_2H
$\text{Co(OAc)}_2/\text{NaBr}^c$	100	0	48	50	60	31	9
$\text{Co(OAc)}_2/\text{NaBr}^c$	95	5	12	100	84	6	10
$\text{Co(OAc)}_2/\text{NaBr}/\text{Mn(OAc)}_2^d$	95	5	6	96	82	6	12
$\text{Co(OAc)}_2/\text{NaBr}^c$	90	10	48	67	82	5	13

^aProduct distribution was determined by G.C.

^b DBS = dibromostilbene.

^c $\text{DPA:Co(OAc)}_2:\text{NaBr} = 5:1:1$ under oxygen at 70°C .

^d $\text{DPA:Co(OAc)}_2:\text{NaBr:Mn(OAc)}_2 = 5:1:1:0.02$ under oxygen at 70°C .

other aryl alkyne substrates were investigated to determine the generality of the catalyst system towards alkyne oxidation. Phenyl-alkyl alkynes, conjugated alkynes, alkynes with an electron withdrawing group and terminal alkynes were examined and the results are tabulated in Table 4.

Most alkynes were found to undergo oxidation similar to the diphenylacetylene case, however reaction rates and product distributions varied greatly. In general, the reactivity of the alkyne substrate was highly correlated with its electron-richness. Thus, substitution of just one strongly electron-withdrawing group into diphenylacetylene, e.g., *p*-nitrodiphenylacetylene, severely reduced the alkyne reactivity. No apparent substrate oxidation was observed even after 48 h. Similarly, diphenyldiacetylene which has a more stable conjugated system than diphenylacetylene itself, also showed diminished reactivity. It was completely oxidized after 24 h to yield benzoic acid. No tetraketone intermediate was detected during the reaction,

indicating that its over-oxidation to benzoic acid and carbon dioxide is relatively facile. The evolution of CO₂ as the other ultimate reaction product was confirmed by formation of a precipitate of Ba(CO₃) after passing the reaction outlet gas through a saturated solution of Ba(OH)₂ · 8H₂O. Ethylphenyl propiolate, which has an electron withdrawing –CO₂Et ester group directly attached to the carbon–carbon triple bond also reacted more slowly than diphenylacetylene, only reaching 100% conversion after 12 h. Again benzoic acid was the predominant product with a smaller amount of brominated side-products. Internal phenyl-alkyl acetylenes PhC≡CR, where R = Me and Bu, were also examined. Complete conversion occurred in less than 12 h. In contrast to diphenylacetylene, these alkynes gave benzoic acid as the predominant product, with only minor amounts of the corresponding diketones being observed. This is presumed to be due to more facile over-oxidation of the less highly conjugated phenyl-alkyl diketones. Interestingly, terminal alkynes were

Table 4
Oxidation of alkynes by the Co(OAc)₂/Mn(OAc)₂/NaBr catalyst system^a

Alkyne	Time (h)	Products (selectivity %) ^b	
Ph–C≡C–Ph	7	PhCO ₂ H (19)	PhC(O)C(O)Ph (78)
Diphenylacetylene			
Ph–C≡C–CH ₃	9	PhCO ₂ H (77)	PhC(O)C(O)CH ₃ (18)
1-Phenyl-1-propyne			
Ph–C≡C–(CH ₂) ₃ CH ₃	12	PhCO ₂ H (91)	PhC(O)C(O)Bu (7)
1-Phenyl-1-hexyne			
Ph–C≡C–C≡C–Ph	24	PhCO ₂ H (99)	Trace
Diphenyldiacetylene			
Ph–C≡C–C(=O)–OEt	12	PhCO ₂ H (94)	
Ethyl phenylpropiolate			
O ₂ NPh–C≡C–Ph	48	No reaction	
<i>p</i> -Nitrodiphenylacetylene			
HO ₂ CPh–C≡C–H	3	HO ₂ CPhCO ₂ H (100)	
<i>p</i> -Carboxyphenylacetylene			
Ph–C≡C–H	2	PhCO ₂ H (100)	
Phenylacetylene			
CH ₃ (CH ₂) ₅ –C≡C–H	5	CH ₃ (CH ₂) ₅ CO ₂ H (100)	
1-octyne			

^aSubstrate:Co(OAc)₂:NaBr:Mn(OAc)₂ = 5:1:1:0.02 under oxygen at 70°C. Reactions were all reached complete conversion at time specified except for the *p*-nitrodiphenylacetylene.

^bProduct selectivity was determined by G.C. after work-up. Others by-products were mainly brominated products and benzaldehyde.

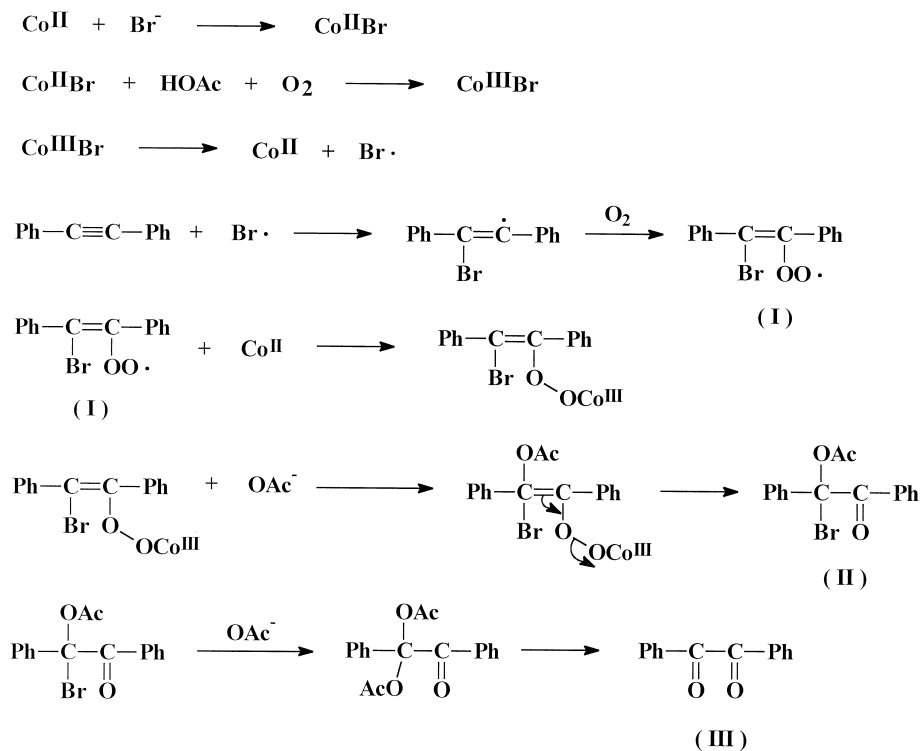
oxidized most rapidly among all substrates tested. Phenylacetylene was almost quantitatively converted to benzoic acid after just 2 h. Even the introduction of a carboxylic acid, an electron-withdrawing group, to the phenyl ring did not hinder the reaction noticeably. An aliphatic terminal alkyne, 1-octyne, was also converted to *n*-heptanoic acid after 5 h reaction. Thus, products with one less carbon atom are formed.

One internal aliphatic acetylene, 4-octyne, was also tested using the catalytic system and conditions described here. Interestingly, this gave the acetylenic ketone [CH₃CH₂CH₂C≡CCOCH₂CH₃] as a major product. Thus, one of the α-methylene groups has been selectively converted to a carbonyl functionality, whilst leaving the alkyne function intact. Since acetylenic ketones are an important class of organic compounds, it is obvious that there is a great potential for this type of functional group

conversion. Details of our studies using a modified catalytic system will be reported elsewhere.

3.6. Proposed mechanisms

An additional experiment was performed in which the Co(OAc)₂/Mn(OAc)₂/NaBr catalyst system was used to oxidize diphenylacetylene in the presence of a radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (BHT). No oxidation was observed, implying that the active species might involve radicals which could be trapped by the BHT. Thus, the cobalt-catalyzed oxidation of alkynes is believed to follow a radical mechanistic pathway as shown in Scheme 2. Co(OAc)₂ is first reacted with NaBr in oxygen to give the Co^{III}Br species. Bromine radical produced from this active catalyst is then reacted with the alkyne in the presence of oxygen to form (bromovinyl) peroxy radical (I). This intermediate has been reported by Yarwood et al. [37] in



Scheme 2. Proposed reaction mechanism for the oxidation of diphenylacetylene.

their FTIR study of the mechanism of Cl and Br atoms initiated oxidation of acetylene. The peroxy radical (I) can react with Co(II) and acetic ions to form a carbonyl compound (II). Further reaction with acetic ion gives the benzil product (III). The electron-richness of the acetylene appears to play a key role in this mechanism. The deactivation of the *p*-nitrodiphenylacetylene to oxidation implies the decrease of electron density of the triple bond, that disfavours attacking by bromine radical, resulting in no oxidation. Finally, the mechanism of oxidative cleavage of diketones to the corresponding acids has been described in the literature [38]. In contrast to the majority of reactions studied here, the formation of the acetylenic ketone from 4-octyne is presumed to occur by the more traditionally accepted role of cobalt acetate bromide, via a hydrogen-atom abstraction mechanism. Thus, in some cases even though α -H atom abstraction appears to be possible, an alternative oxidation mechanism can predominate for the cobalt acetate bromide system. This finding may have practical implications for this industrially important catalyst.

4. Conclusions

The ability of a variety of simple cobalt (II) salts to catalytically oxidize a range of different alkyne substrates using molecular oxygen has been studied. Of these, cobalt acetate bromide shows the most substantial reactivity. Conditions were optimized for the oxidation of diphenylacetylene to the corresponding diketone, using cobalt acetate bromide and employing manganese acetate as a promoter. The optimal conditions obtained were a substrate: Co(OAc)₂:NaBr:Mn(OAc)₂ ratio of 5:1:1:0.02 in 95% HOAc. Further reaction ultimately gave the cleavage product, benzoic acid. A wide range of alkynes were also tested as substrates. Terminal alkynes reacted most rapidly, and electron-deficient alkynes slowly or not at all. In the case of 4-octyne, selective H-atom ab-

straction occurs and the acetylenic ketone is formed. Further studies to elucidate the nature of the proposed new mode of action for cobalt acetate bromide are under investigation.

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