

The structure of metal/bromide catalysts in acetic acid/water mixtures and its significance in autoxidation

W. Partenheimer*

Central Research and Development, E.I. DuPont de Nemours & Co., Inc., Experimental Station, Wilmington, DE 19880-0328, USA

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1. Introduction

Soluble metal/bromide homogeneous liquid-phase catalysts have been used for the industrial and synthetic preparation of hundreds of different alcohols, ketones, aldehydes, carboxylic acids for the last 50 years [1] and continue to be of active interest [2–4]. The most common chemical description of the cobalt/bromide catalyst is ‘cobalt acetate bromide’, often written $\text{Co}(\text{OAc})(\text{Br})$, originally suggested by Hay and Blanchard [5] and subsequently repeated by many others. This description, given for a $\text{Co}(\text{II})$ acetate/HBr mixture in anhydrous acetic acid, is misleading since all reactions necessarily are performed in acetic acid/water mixtures, often 5–15 wt.%, since water is one of the products. As will be shown, once some water is present, little of the bromide is bonded to the metal and a variety of different coordination compounds exist. Structures of the catalyst have been suggested *largely based on solids* isolated from acetic acid/water mixtures. Acetic acid is the second most studied non-aqueous solvent [6] and subsequently there are many pertinent physical-chemical studies from which one can propose reasonable structures. What follows is a description based *on solution studies* of the coordination chemistry of $\text{Co}/\text{Mn}/\text{Br}$ in

acetic acid/water mixtures. Then, using this information, certain conclusions regarding the mechanisms of this catalyst in autoxidation are given.

Only the most common catalyst [1] — a 0.01–0.05 M mixture of $\text{Co}(\text{II})$, $\text{Mn}(\text{II})$ acetate tetrahydrates and hydrobromic acid will be considered. In acetic acid one must distinguish between ionization and dissociation of metal salts:



where the brackets $\{ \}$ denote an ion-pair. The concentration of dissociated species in acetic acid is very small [6,11,12], the overall dissociation constants have pK values >5 , hence dissociated species will be subsequently ignored.

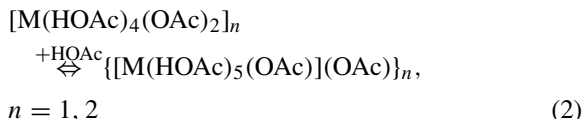
1.1. Metals in anhydrous acetic acid

The solid state crystal structures of $[\text{M}(\text{II})(\text{OAc})_2(\text{H}_2\text{O})_4]$ are octahedral and mononuclear for Co , Ni [7] and polynuclear for $\text{Mn}(\text{II})$ [8]. Compounds with acetic acid ligands, bonded through the carbonyl oxygen atom, of the type $[\text{M}(\text{II})(\text{HOAc})_6]\text{X}_2$ ($\text{X} = \text{BF}_4^-$, ClO_4^- , NO_3^- , $\text{M} = \text{Mn}$, Co , Ni , Cu , Zn) have been characterized [9]. Dissolution of these metals in acetic acid/water mixtures results in significant changes in their coordination chemistry. The dissolution of anhydrous $\text{Co}(\text{II})$ acetate in acetic acid results in $>95\%$ of non-charged species [10] as indicated by

* Fax: +1-302-695-8347.

E-mail address: walter.partenheimer@usa.dupont.com (W. Partenheimer).

ion-migration experiments which is consistent with very small dissociation constants of the acetates from M(II) ($M = \text{Co}, \text{Mn}, \text{Ni}, \text{Cu}$) [6]. Solution physical measurements (osmometry, cryoscopy, etc.) give conflicting information. Some report that M(II) ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$) are mononuclear and Cu(II) is dimeric [10,13] while others indicate partial or complete dimerization for Co and Ni [14–16]. Changes in solubility were noted as a function of time for Co and Ni which may be responsible for the differences [14,16]. Kinetic studies of two-electron oxidants (Pb(IV) and peracids) are second order with respect to the metal for Co(II) [17–19] as is the kinetic dependence of cobalt during of the oxidation of hydrocarbons [20]. This is consistent with the presence of di-nuclear cobalt species. UV–VIS spectra for Co(II) are consistent with an octahedral configuration of the ligands around the metal [10]. One can therefore, conclude that the predominant species present in anhydrous acetic acid are



where the brackets [] denote the ligands in the inner coordination sphere and $n = 1$ and $n = 2$ denote monomer and dimer. The equilibrium lies to the left. Some suggested structures for those on the left side of reaction (2) are given in Fig. 3a and b where $n = 1$ and $n = 2$. One can propose four major species in acetic acid.

1.2. Addition of water to acetic acid

Results in the acetic acid ligands being replaced by aqua ligands. Using the reported values for the stepwise formation constants for Co and Mn [21] and estimating the others [22], one can calculate the distribution of $[\text{M}(\text{HOAc})_m(\text{H}_2\text{O})_{m-4}(\text{OAc})_2]_n$ species, see Figs. 1 and 2. It is assumed that the mono- and di-nuclear species have the same distribution of aqua and acetic acid ligands. One now has

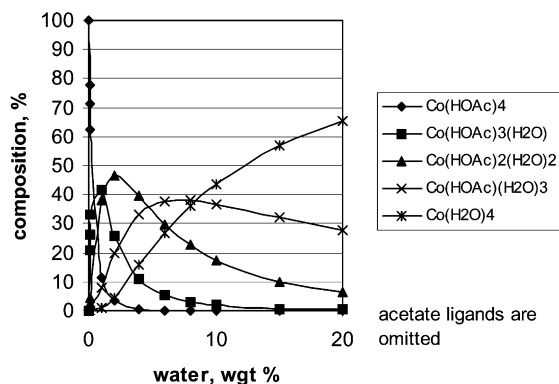
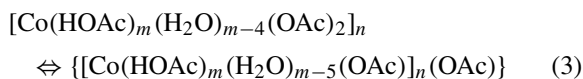


Fig. 1. Distribution of ligands around cobalt(II) in an acetic acid/water mixture, in mol%, calculated from stepwise stability constants.

with m decreasing as the concentration of water increases. There are 10 species on the left and 12 on the right-hand side of Eq. (3). One possible structure for Co(II) for the predominant species in 10% water (one acetic and four aqua ligands) is given in Fig. 3c.

Reports on ion migration experiments on Co(II) acetate as a function of water are in conflict — one stating there is an increase in positively charged species [17] and the other stating there is no change [10]. Since the dielectric constant increases with water concentration, see Table 1, one can assume that the equilibrium in Eq. (3) shifts to the right with increasing water concentration. There is no information on the value of n as a function of water, although kinetic studies [18,19] suggest dimers exist at 5–10 wt.% water concentra-

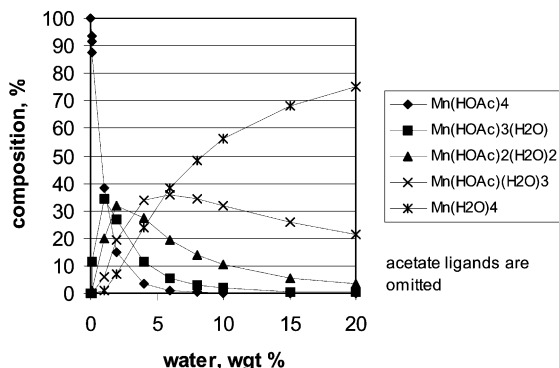


Fig. 2. Distribution of ligands around manganese(II) in an acetic acid/water mixture, in mol%, calculated from stepwise stability constants.

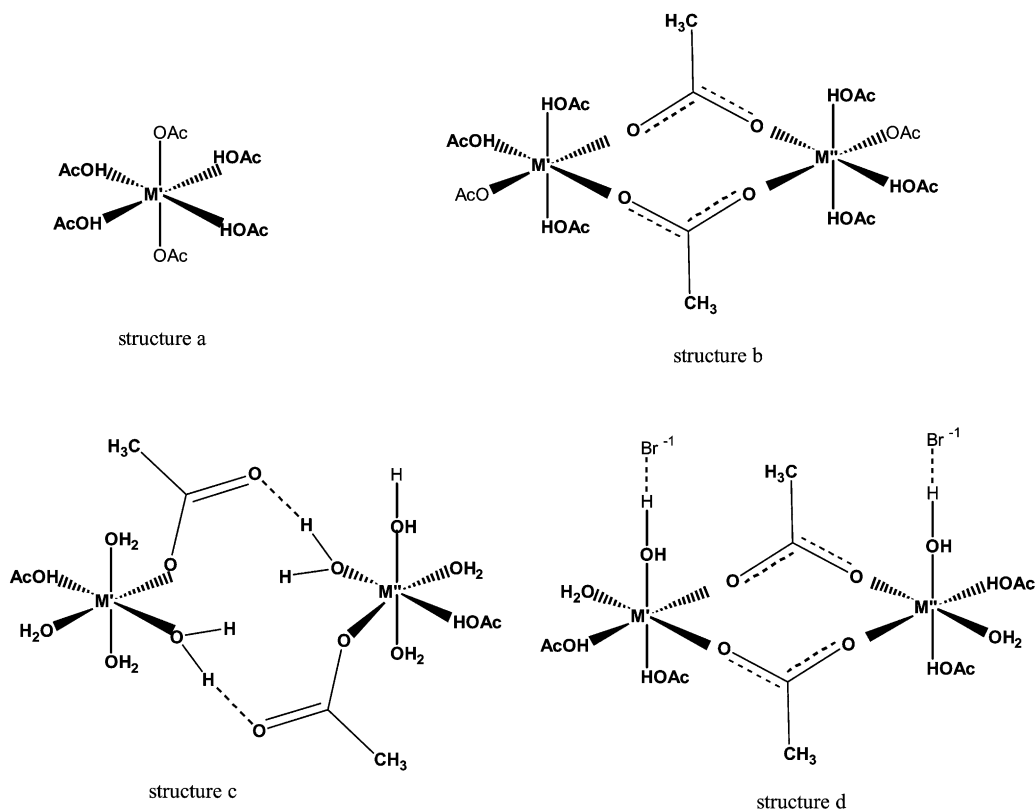


Fig. 3. Some suggested structures for Co/Mn/Br mixtures in acetic acid/water mixtures. M = Co(II, III), Mn(II, III).

tions and esr and UV–VIS studies suggest polymeric species [3].

1.3. Addition of hydrobromic acid

Measurements using the bromide selective electrode indicate that most of the bromide is coordinated

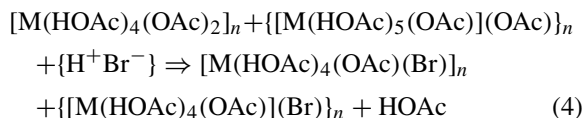
Table 1
Bromide bonded to metal (%)^a

Water (%)	Co	Mn	Co/Mn
0	65.77 ^b	61.78 ^b	66.81 ^b
5	12.5	6	14
10	7.1 ^b	14.4 ^b	3.0 ^b
20	5	–	–
100	1	1	–

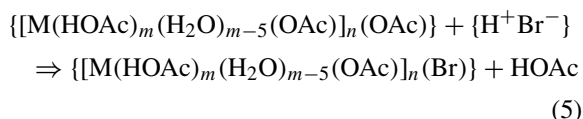
^a As measured by the bromide selective electrode. Experimental error about 8%. Metal concentration or sum of metal concentration is 0.04 M. Br/Metal = 1.0 mol mol⁻¹. Measured using NaBr.

^b Measured with HBr.

in anhydrous acetic acid but rapidly decreases as the water concentration is increased [19], see Table 1. The values obtained in anhydrous acetic acid for the perchlorate metal salts are in agreement with previously reported equilibrium constants [23]. If bromide is added as HBr (M/Br = 1), an acid–base neutralization reaction will occur between the acid HBr and strongest base in acetic acid/water, the acetate anion [6]. In anhydrous acetic acid one has



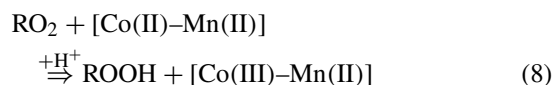
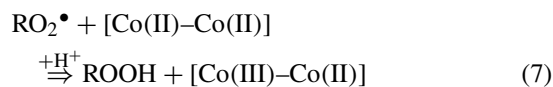
with the neutral metal-bromide species being predominant. If HBr is added with >5% water present, very little of the bromide is coordinated. Therefore, the predominant species is the ion-paired bromide salt:



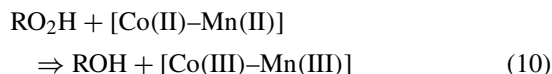
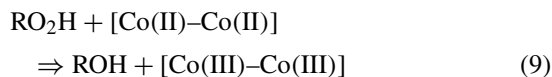
Addition of NaBr will be similar except that $\{\text{Na}^+\text{OAc}^-\}$ will be the product of reaction.

The structural description above leads to the following implications in autoxidation mechanisms:

1. Heteronuclear metal dimers can occur with Co(II) and Mn(II). NMR studies indicate that the acetic acid–metal bond is weak ($5.9 \text{ kcal mol}^{-1}$) ($M(\text{II}) = \text{Co}, \text{Mn}, \text{Ni}$) and exchanges its acetic acid ligands instantaneously at room temperature as the entire molecule, with an dissociative interchange mechanism [24,25]. The labile coordination spheres can lead to compounds of the type $\{[M'(\text{II})M''(\text{II})(\text{HOAc})_m(\text{H}_2\text{O})_{m-5}(\text{OAc})_2(\text{Br})]\}$ where $M = \text{Co}, \text{Mn}$. Indeed recent ESR and UV–VIS studies suggest their existence [3] and heteronuclear species have been isolated from acetic acid ($M = \text{Fe}, \text{Zn}$) [26]. An example of such a structure for a Co,Mn mixtures is given in Fig. 3d, where $m = 1$. We suggest that the bromide is hydrogen bonded to one of the coordinated water molecules, see Fig. 3d.
2. The homogeneous Co/Mn/Br catalyst is not just a single catalyst, but is composed of a large number of different active catalyst species, i.e. different coordination compounds. The ‘active’ catalyst is made when oxidation of the metals via one-electron oxidants such as peroxy radicals and by two-electron oxidants such as peracids occurs. In the Co/M/Br catalysts ($M = \text{Mn}, \text{Co}$) the cobalt becomes initially oxidized. In such a Co/M mixture, the peroxy radicals can react with either the monomer or dimer leading to three different species (ligands are omitted for simplicity):



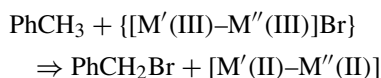
Peracids are known to preferentially react with the metal dimers [16] hence in this case one has



Thus, at least five different metal oxidants, each with varying amounts of aqua ligands, can form.

3. It is known that metal/bromide catalysts require carboxylic acid solvents, particularly acetic acid [1]. One of the functions of the solvent is that the weak, labile acetic acid ligand [23–25], which exists even at high water concentrations, see Figs. 1 and 2, can be displaced by equally weak ligands, such as peroxy radicals, peroxides, and peracids, and hence become incorporated in the metal coordination sphere.
4. The suggested structures (Fig. 3) for the M(II, III) compounds do not contain hydroxo or oxo ligands. Hydroxo and oxo species in acetic acid/water mixtures, which are often suggested [2,3], are essentially non-existent because these species will instantaneously react with the solvent and become ‘leveled’ to the strongest base that can exist in this solvent — the acetate anion [1,6]. Hydroxo and oxo ligands can form when M(III) compounds are precipitated from acetic acid/water solutions but this is an artifact of the water molecule subsequently rearranging during the precipitation and isolation process.
5. We suggest that the Co(III)_a and Co(III)_s forms, discovered by Jones [18], which form instantly (half-lives are in tenths of a second at 60 C), are similar to Fig. 3c and d, respectively. The more ‘open’, hydrogen bonded acetic acid in Fig. 3c is the reason for its known higher reactivity and why it readily closes to Fig. 3d.
6. Even through the bromide is not directly bonded to the metal, it does remain in the second coordination sphere through ion-pairing. Therefore, its reduction by Mn(III) will be more rapid when compared to a bromide completely dissociated in solution, for example, as it would be in water.
7. Benzylic bromide formation reduces the rate in metal/bromide catalyzed autoxidations [1]. There

is evidence they form predominately from within the coordination sphere [27]. The metal species $[M'(III)-M''(III)]$ shown in reactions (9) and (10) are two electron oxidants and hence the formation of benzylic bromides can occur in a *single concerted step*:



rather than in two steps as previously proposed [27].

8. Any structural model must also consider that recent studies indicate that acetic acid/water mixtures contain microphases, one of which is essentially pure acetic acid [28,29]. The complexes described here would be in the water/acetic acid phase.

References

- [1] W. Partenheimer, Catal. Today 23 (1995) 69.
 [2] X.-D. Jiao, J.H. Espenson, Inorg. Chem. 39 (2000) 1549.
 [3] S.A. Chavan, S.B. Halligudi, D. Srinivas, P. Ratnasamy, J. Mol. Catal. A 161 (2000) 49 and references quoted therein.
 [4] W. Partenheimer, V. Grushin, Adv. Synth. Catal. 343 (2001) 343.
 [5] A.S. Hay, H.S. Blanchard, Can. J. Chem. 43 (1965) 1306.
 [6] A.I. Popov, in: J.J. Lagowski (Ed.), The Chemistry of Nonaqueous Solvents III, Academic Press, New York, 1970, p. 214.
 [7] J.N. Van Niekerk, F.R.L. Schoening, Acta Crystallogr. 6 (1953) 609.
 [8] E.F. Bertaut, T.Q. Duc, P. Burlet, P. Burlet, M. Thomas, J.M. Moreau, Acta Crystallogr. B30 (1974) 2234.
 [9] P.W.N.M. Van Leeuwen, W.L. Groeneveld, Recueil 86 (1968) 87.
 [10] C.F. Hendriks, H.C.A. von Beek, P.M. Heertjes, Ind. Eng. Chem. Prod. Res. Dev. 18 (1979) 43.
 [11] O.W. Kolling, J.I. Lambert, Inorg. Chem. 3 (1964) 202.
 [12] P.J. Proll, C.H. Sutcliffe, Trans. Faraday, Soc. 57 (1961) 1078 (there are different interpretations of the data but both indicate large pK values; see comments in [6]).
 [13] K. Sawada, M. Tanaka, J. Inorg. Nucl. Chem. 35 (1973) 2455.
 [14] W.P. Tappmeyer, A.W. Davidson, Inorg. Chem. 2 (4) (1963) 823.
 [15] P.J. Proll, L.H. Sutcliffe, J. Walkley, J. Phys. Chem. 65 (1961) 455.
 [16] A.W. Davidson, W. Chappell, J. Chem. Soc. 3531 (1933).
 [17] D. Benson, P.J. Proll, L.H. Sutcliffe, J. Walkley, J. Chem. Soc. (1960) 60.
 [18] G.H.J. Jones, J. Chem. Soc., Chem. Commun. (1979) 536.
 [19] W. Partenheimer, in: S.T. Oyama, J.W. Hightower (Eds.), Catalytic Selective Oxidation, ACS, 1993 (Chapter 7).
 [20] E.J.Y. Scott, A.W. Chester, J. Phys. Chem. 76 (1972) 1520.
 [21] K. Sawada, K. Agata, M. Tanaka, Inorg. Chim. Acta 30 (1978) 127.
 [22] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 4th Edition, Vol. 70, Wiley/Interscience, New York (values of K_1 , K_2 , K_3 , K_4 used are 1.6, 1.1, 0.56, 0.32 for Mn(II) and 6.7, 1.6, 0.37, 0.21 for Co(II), respectively).
 [23] K. Sawada, M. Tanaka, J. Inorg. Nucl. Chem. 39 (1977) 339.
 [24] A. Hioki, S. Funahashi, M. Ishii, M. Tanaka, Inorg. Chem. 25 (1986) 1360, 2904.
 [25] A. Hioki, S. Funahashi, M. Ishii, M. Tanaka, Inorg. Chem. 22 (1983) 749.
 [26] B. Singh, J.R. Long, F.F. de Biani, D. Gatteschi, P. Stravopoulos, J. Am. Chem. Soc. 119 (1997) 7030.
 [27] T.V. Bukharkina, N.D. Gavrilenko, N.G. Digurov, N.A. Knyazeva, Kinet. Kataliz. 19 (1978) 506.
 [28] N. Nishi, T. Nakabayashi, K. Kosugi, J. Phy. Chem. A103 (1999) 10851.
 [29] U. Kaatze, K. Menzel, R. Pottel J. Phy. Chem. 96 (1991) 462.