A Novel Formyl Complex $[(H_2O)_5CrCHO]^{2+}$. A Pulse Radiolysis Study

Haim Cohen,*[a] Dan Meyerstein,*[b] Alan J. Shusterman,*[c] and Mathania Weiss*[a]

[a] *Nuclear Research Center Negev, Beer-Sheva, Israel*
[b] *Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva, Israel*
[c] *Chemistry Department, Tel-Aviv University, Tel-Aviv, Israel*

The formyl complex $[(H_2O)_5CrCHO]^{2+}$ is formed in aqueous solution *via* the reaction sequence: $Cr^{2+}(aq.) + \cdot CH(OH)_2 \rightarrow [(H_2O)_5CrCH(OH)_2]^{2+} \rightarrow [(H_2O)_5CrCHO^{+2}] + H_2O$, and reduces formaldehyde (k = 1 mol^{-1} dm^3 s^{-1}), yielding CO + CH_3OH; the spectra of $[(H_2O)_5CrCH(OH)_2]^{2+}$ and $[(H_2O)_5CrCHO]^{2+}$ are reported.

Metal-complexed formyl species have been intensively studied as possible intermediates in the metal-catalysed hydrogenation of CO.[1] Most metal formyl complexes have been prepared by hydride reduction of metal carbonyl precursors.[2] Other methods, such as carbonylation of a metal hydride complex,[3a] or formylation of a nucleophilic metal centre,[3b] are also known but appear to lack generality. We report here observations that are consistent with the formation of a Cr^{III} formyl complex, $[(H_2O)_5CrCHO]^{2+}$, (**2**), from the reaction of aqueous Cr^{II} with the dihydroxymethyl radical, $\cdot CH(OH)_2$. The formyl complex reacts with excess of formaldehyde *via* hydride transfer to yield CO and methanol. The results thus describe the first observation of an unstable formyl species in aqueous solutions and the kinetics of hydride transfer from it to an oxidant.

Aqueous Cr^{II} is known to react with a wide range of organic free radicals.[4] These reactions, which are characterized by very large bimolecular rate constants, 10^7—2×10^8 mol^{-1} dm^3 s^{-1} produce Cr^{III} alkyl complexes, $[(H_2O)_5CrR]^{2+}$, wherein chromium is bound to the carbon atom that had previously carried the unpaired electron. The required free radicals are usually generated *via* hydrogen abstraction from the parent hydrocarbon by $\cdot OH$ or $\cdot H$ radicals. In our procedure, aqueous formaldehyde is generated by the acid-catalysed depolymerization of paraformaldehyde (BDH Lab Rg). Aqueous formaldehyde exists almost exclusively in the acetal form,[5] $H_2C(OH)_2$, and previous work has shown that formaldehyde reacts with the $\cdot OH$ radical in water to yield the dihydroxymethyl radical, $\cdot CH(OH)_2$.[6]

Pulse radiolysis of aqueous mixtures of Cr^{II} and formaldehyde between pH 2.8 and 6† generates a transient species, (**1**) whose u.v.–visible spectrum shows maxima at 280 and 380 nm, Figure 1, features which indicate that it contains a Cr^{III}–C bond.[4] The rate of formation of (**1**), which is independent of pH, $[CH_2(OH)_2]$, and monitoring wavelength (λ), agrees with the rate law given by equation (1). These observations suggest that (**1**) is best formulated as the simple adduct: $[(H_2O)_5Cr\text{-}CH(OH)_2]^{2+}$, a hydrated formyl complex.

$$\frac{d[(\mathbf{1})]}{dt} = k[Cr^{II}][\cdot CH(OH)_2] \quad k = (1.3 \pm 0.2) \times 10^8\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1} \tag{1}$$

The hydrated formyl complex (**1**) decomposes rapidly under these reaction conditions and a second chromium complex (**2**) is formed, which then persists for several minutes.The rate of formation of this second transient species, (**2**), obeys the rate law given by equation (2) and is independent of $[Cr^{II}]$, $[H_2C(OH)_2]$, pH, and ionic strength. However, lowering the pH below 2.8 does appear to accelerate the conversion of (**1**) into (**2**). The absorption spectrum of (**2**) shows a maximum at 310 nm and a shoulder at 380 nm, Figure 1, again typical of a complex containing a Cr^{III}–C bond.[4] We propose that (**2**) is the Cr^{III} formyl complex $[(H_2O)_5CrCHO]^{2+}$, formed by the dehydration of (**1**). The kinetics of the decomposition rate, which does depend on $[H_2C(OH)_2]$, conforms to the rate law given in equation (3).

$$\frac{d[(\mathbf{2})]}{dt} = k[(\mathbf{1})] \quad k = (1.0 \pm 0.3) \times 10^2\,\text{s}^{-1} \tag{2}$$

$$-\frac{d[(\mathbf{2})]}{dt} = k[(\mathbf{2})][H_2C(OH)_2] \quad k \sim 1\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1} \tag{3}$$

Further support for the proposed structure of (**2**) and insight into its reactivity is provided by an analysis of the products obtained from the decomposition of (**2**). The same products are obtained regardless of the methods used in generating the required radical precursors to the formyl complex: pulse radiolysis, ^{60}Co-γ radiation, or a Fenton-type reagent (Cr^{II} + H_2O_2). The only observed products from the decomposition of the formyl complex, (**2**), are Cr^{III} and CO.‡ The yield of CO is 95 ± 10% of that of the $\cdot CH(OH)_2$ free radicals.‡ No H_2 or CO_2 was detected in the product mixture.

The stoicheiometry of the decomposition of (**2**) to CO and Cr^{III} necessitates the formation of H^- as well. The absence of H_2 from the decomposition of (**2**) demonstrates that neither H^+ nor the Cr^{III} centre can be acting as hydride acceptors; $[(H_2O)_5CrH]^{2+}$ is known to generate H_2 in aqueous solutions in a rapid reaction.[7] The rate law for the decomposition of formyl complex (**2**) can be rationalized if formaldehyde acts as a hydride acceptor in a reaction that would produce methanol. Unfortunately, we are unable to observe methanol formation since some methanol is invariably present in depolymerized paraformaldehyde.

All of our observations can be rationalized by the reaction scheme given by equations (4)—(6).

$$Cr^{II}\,(aq.) + \cdot CH(OH)_2 \rightarrow \underset{(\mathbf{1})}{[(H_2O)_5Cr^{III}CH(OH)_2]^{2+}} \tag{4}$$

$$(\mathbf{1}) \rightarrow H_2O + \underset{(\mathbf{2})}{[(H_2O)_5Cr^{III}CHO]^{2+}} \tag{5}$$

$$(\mathbf{2}) + H_2C{=}O(aq.) + H_3O^+ \rightarrow CH_3OH + CO + Cr^{III}\,(aq.) \tag{6}$$

---

† Pulse radiolysis experiments were carried out at the LINAC laboratory of the Hebrew University in Jerusalem. The experimental setup and techniques used are reported in detail in ref. 4(b). The ^{60}Co-γ source was a Gammacell Model 3500 produced by Noratom. The g.c. used was a Varian TCD 1420 and the i.r. spectrophotometer used was model MX-S produced by Nicolet.

‡ Cr^{III} was identified by its characteristic u.v.–visible spectrum. Volatile components of the product mixture were analysed using Fourier transform i.r., g.c., and mass spectroscopic techniques.

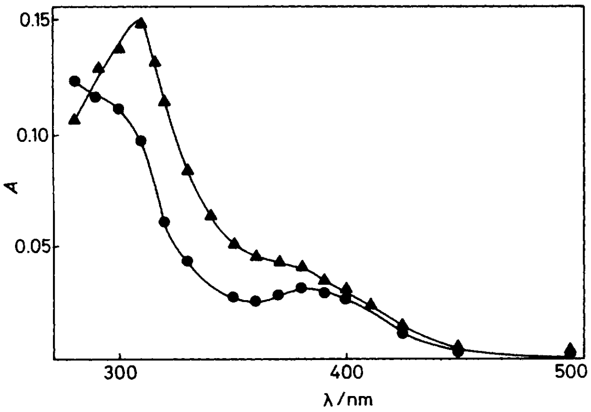

Figure 1. Spectra of $[(H_2O)_5CrCH(OH)_2]^{2+}$: ● measured 200 μs after the pulse and of $[(H_2O)_5CrCHO]^{2+}$: ▲ measured 30 ms after the pulse. Solution composition: 0.3 M $CH_2(OH)_2$, 0.3 M $NaClO_4$, 1 × 10^{-3} M Cr^{2+}(aq.), pH 3.6 and N_2O saturated.

Formyl radicals have been proposed as intermediates in the hydrogenation of CO catalysed by $Co_2(CO)_8$.[8] Presumably, the formyl radical that is formed then couples to the transition metal in a reaction analogous to that proposed for the 'hydrated' formyl radical in equation (4).

We have previously observed that Cr^{III} alkyl complexes containing a β-hydroxy group readily dehydrate yielding Cr^{III}–alkene complexes characterized by a strong alkene donor–Cr^{III} acceptor interaction.[9] Cr^{III}–alkyl complexes containing a single α-hydroxy group are not susceptible to dehydration presumably owing to the inability of the weakly donating Cr^{III} centre to stabilize the positive charge that would develop on the adjacent carbon atom. α-Hydroxyalkyl ligands containing their own donor group [a second hydroxy group in the case of the hydrated formyl complex, (**1**)] should undergo facile dehydration in a manner analogous to equation (5).

The preference of the formyl ligand for the aldehyde form (**2**) over the hydrated form (**1**) stems mainly from the large steric requirements of the $(H_2O)_5Cr$ moiety. A pattern of decreasing hydrate stability with increasing substituent bulk is well known for organic aldehydes and ketones.[5]

Hydride transfer from metal formyl complexes to a variety of hydride acceptors, including formaldehyde, has been reported.[10] Most of these cases involve anionic, or at least, electron-rich metal centres and a stable metal–carbonyl complex is usually obtained as a product.The cationic formyl complex (**2**), contains an electron-poor metal centre but still functions as an efficient hydride donor. No chromium–carbonyl complex, such as $[(H_2O)_5CrCO]^{3+}$, is observed during the decomposition of (**2**), but such a complex would be expected to be short-lived owing to the weak acceptor ability of Cr^{III}.

Preliminary results reveal that between pH 0 and 1 only the transient formyl complex (**2**) is observed, consistent with acid enhancement of the dehydration of complex (**1**), equation (5). Under these conditions (**2**) appears to be somewhat more stable though the same decomposition products that were obtained at higher pH are also observed here.

This study was supported in part by a grant from the Israel-U.S. Binational Science Foundation (B.S.F.), Jerusalem, Israel. One of us, A. J. S., is thankful for the Allon Fellowship. We thank Mr. D. Carmi and D. Shuckron for technical assistance in the experiments.

Received, 19th November 1984; Com. 1636

References

1 For a recent review of metal formyl complexes see: J. A. Gladysz, *Adv. Organomet.Chem.*, 1982, **20**, 1. For recent reviews of CO hydrogenation see: E. L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479; C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61.
2 C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, 1976, **98**, 5395; S. R. Winter, G. W. Cornett, and E. A. Thompson, *J. Organomet. Chem.*, 1977, **133**, 339; J. A. Gladysz and W. Tam, *J. Am. Chem. Soc.*, 1978, **100**, 2545.
3 (a) B. B. Wayland, A. Duttaahmed, and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, 1983, 142; P. J. Fagan, K. G. Moloy, and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6959; (b) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, 1973, **95**, 4089; (c) D. L. Thorn, *J. Am. Chem. Soc.*, 1980, **102**, 7109 and references therein.
4 (a) J. H. Espenson, 'Advances in Inorganic and Bioinorganic Mechanisms,' ed. G. Sykes, Academic Press, London, 1982, vol. 1, p. 1; (b) H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434.
5 T. H. Lowry and K. S. Richardson, 'Mechanism and Theory in Organic Chemistry,' Harper and Row, New York, 1976, p. 403.
6 A. L. Buley and R. O. C. Norman, *Proc. Chem. Soc.*, 1964, 225.
7 H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 1974, 2559.
8 J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.*, 1978, **100**, 3623.
9 H. Cohen, D. Meyerstein, A. J. Shusterman, and M. Weiss, *J. Am. Chem. Soc.*, 1984, **106**, 1876; and unpublished results.
10 C. P. Casey and S. M. Newmann, *J. Am. Chem. Soc.*, 1978, **100**, 2544; C. P. Casey, M. A. Andrews, and D. R. McAlister, *ibid.*, 1979, **101**, 3371.