

Preliminary communication

Bis-arene-vanadium anions as reducing agents towards carbon dioxide and monoxide *

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(Received April 22nd, 1988)

Abstract

A novel way of activating an alkali metal for the reduction of CO₂ and CO involves dissolving potassium in tetrahydrofuran containing [V(C₆H₆)₂], to give a solution of K[V(C₆H₆)₂] as the actual reducing agent. In contact with CO₂ or CO, the formal V^{-I} derivative is immediately re-oxidized to the V⁰ complex and C₁ and C₂ products are formed.

Bis-arene-vanadium anionic derivatives constitute a new class of organo-vanadium complexes and include the first structurally characterized anionic arene sandwich [1]. The known organometallic compounds in which group 5 transition metals formally have a -I oxidation state are all carbonyl derivatives, and behave either as one- or as two-electron reductants, or as nucleophiles [2]. It seemed to us of interest to investigate the reactivity of a carbonyl-free complex.

We chose carbon dioxide and monoxide as test substances, because their conversion is an old and yet important subject owing to their potential in syntheses of C₁ and C₂ chemicals. Reduction of CO₂ and CO by alkali metal requires drastic conditions [3], unless the metal is activated by either dissolution in liquid ammonia [4], amalgam formation [5], or addition of naphthalene [6] or crown ethers [7].

The reactions of carbon dioxide and monoxide with K[V(C₆H₆)₂] (1) are reported here.

Carbon dioxide reacted instantly with a filtered dark blue 0.05 M tetrahydrofuran (THF) solution of 1 [1] at room temperature and atmospheric pressure; the liquid turned red-brown and a very fine solid separated. No CO could be detected chromatographically in the gas phase. After filtration, the precipitate, after being

* Dedicated to the memory of Prof. Camillo Porlezza, who pioneered research on CO₂-reduction by alkali metals.

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Table 1

Yields of the hydrolysis products of **3**

Product	mol per mol of 1
CO_3^{2-} and/or HCO_3^-	0.25
$^- \text{OOC} \text{COO}^-$ and/or $\text{HOOC} \text{COO}^-$	0.41
HCOO^-	0.04 ^a
$\text{HOCH}_2 \text{COO}^-$	0.0012
CO , H_2 , C_2H_2 in the gas phase	absent

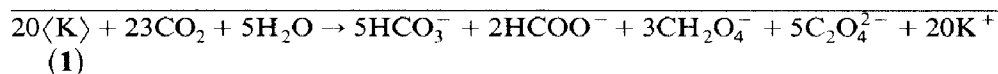
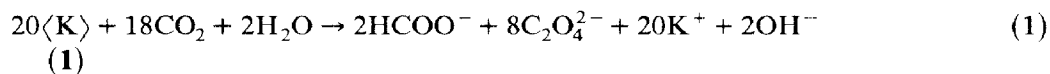
^a This value (GC analysis of the methyl ester formed after azeotropic dehydration of the hydrolysis mixture) is likely to be less than actual [9*].

washed repeatedly with THF and finally dried in vacuo, consisted of a brownish powder, **3**. Vacuum evaporation of the mother liquor, the IR spectrum of which revealed the absence of metal carbonyls, gave $\text{V}(\text{C}_6\text{H}_6)_2$ (**2**) in 95% yield.

When carbon monoxide was brought into contact with a solution of **1**, reaction again took place though somewhat more slowly (about 15 min were required for completion): this can be attributed to the lower solubility of CO than of CO_2 . **2** was produced in 95% yield, and a THF-insoluble, highly pyrophoric brownish powder separated. This reaction is still being studied.

The analysis of **3** was cumbersome and difficult. The results are summarized in Table 1. Hydrolyses were carried out in the absence of oxygen. Carbonate was determined by acidification, with the evolved gas bubbled through a known excess of a standardized barium hydroxide solution and a final titration of the residual hydroxide. Reproducible results for oxalate and glycolate were obtained by the methods used by Büchner [8,9].

The total equivalents of species capable to reduce acidic permanganate in the hydrolysis mixture were numerically equal to the moles of **1** which had reacted with CO_2 . In the light of Table 1, the following overall stoichiometry can therefore be suggested (equations 1,2 and sum thereof):



On the basis of this suggestion the following yields should be expected: HCO_3^- 0.25; HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$ 0.40; HCOO^- 0.10 mole per mole of **1** (cf. Table 1).

When a sealed ampoule containing $\text{KV}(\text{C}_6\text{H}_6)_2 \cdot 1.25 \text{ THF}$ [**1**] was broken in THF saturated with CO_2 , the composition of the insoluble product, **4**, was substantially different (see Table 2).

In the case of the reaction between **1** and CO_2 it therefore seems reasonable to regard **1** as an one-electron reductant, the nature of the CO_2 reduction products being related to the concentrations of the reactants. By taking account of the CO_2^-

* Reference number with asterisk indicates a note in the list of references.

Table 2

Yields of the hydrolysis products of **4**

Product	mol per mol of 1
CO_3^{2-} and/or HCO_3^-	0.29
$^- \text{OOC-COO}^-$ and/or HOOC-COO^-	0.15
$\text{HOCH}_2\text{COO}^-$	0.0020

radical anion postulated as intermediate in the electrochemical formation of $^- \text{OOC-COO}^-$ from CO_2 [10], the higher oxalate yield in the formation of **3** may be attributed to a higher CO_2^{2-} concentration: CO_2 is in fact quickly consumed while diffusing through a solution of **1**, and thus cannot react with the radical anion, that has a relatively high probability of dimerizing.

Acknowledgements. The author thanks Prof. F. Calderazzo and Prof. G. Fachinetti for helpful discussions and Consiglio Nazionale delle Ricerche (C.N.R., Rome), Progetto Finalizzato Energetica II for financial support.

References and notes

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- 9 Conversion of carboxylates to methyl esters, with either diazomethane or BF_3 /methanol, requiring ether extraction of the acids produced by hydrolysis, was hampered by the high solubilities of the latter in water. Better results were obtained on dehydrating an ethereal suspension of the hydrolysis mixture by azeotropic distillation; nevertheless, control experiments carried out on weighed authentic samples of potassium formate and oxalate showed that considerable loss could not be avoided, so that final GC examination gave only qualitative results: in this way, the presence and roughly the order of magnitude of the amounts of formate and oxalate were inferred (see Table 1, analysis of formate).
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