Radical-Anion Chemistry of Carbon Monoxide

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The ability of CO to form a radical-anion, $CO^{\bullet -}$, which can react further with CO or $CO^{\bullet -}$ with formation of C–C bonds has been suggested by literature data on (i) the reaction of CO with alkali metals, (ii) the electrochemical reduction of CO to squarate dianion, and (iii) adsorption of CO on metal oxides; we show that solutions containing Na and K anions are also effective reductants.

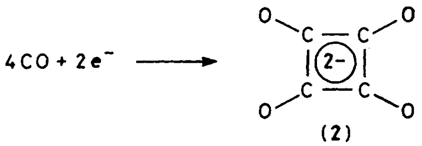
We draw attention to the ability of the CO molecule to acquire an electron, giving the radical-anion $CO^{\bullet -}$, which can react further with $CO^{\bullet -}$ or CO forming carbon–carbon bonds. This feature of CO chemistry, which has been suggested by miscellaneous literature data, does not appear to have been generally recognized. It is, however, of particular interest in view of current efforts devoted to the selective conversion of CO into small organic oxygenates.

The formation and reactivity of the CO radical-anion is illustrated by results from three different areas. (i) An extensive investigation[1] of the reaction of CO with alkali metals in liquid ammonia showed that the product carbonyls, 'MCO', were ethynediolate salts (**1**) for M = Na, K, Rb, and Cs; it was suggested[2] that these compounds were almost certainly formed *via* reactions (1)—(3).

$$M \xrightarrow{NH_3} M^+ + e^- \qquad (1)$$

$$CO + e^- \longrightarrow CO^{\bullet -} \qquad (2)$$

$$2CO^{\bullet -} \longrightarrow \underset{(\mathbf{1})}{{}^-O{-}C{\equiv}C{-}O^-} \qquad (3)$$



(**2**)

(4)

(ii) Dianion (**1**) can be regarded as the first member of the oxocarbon anions,[3] $C_nO_n^{2-}$, which have cyclic structures for $n = 3$—6. The squarate dianion, $n = 4$, (**2**), has been electrochemically synthesized[4] directly from CO, reaction (4). The mechanism of this reaction is unknown, but it seems more probable that $CO^{\cdot -}$ is involved than a concerted reaction or a doubly charged CO^{2-} species. One possibility might be a reaction of $CO^{\cdot -}$ with CO to give $[OCCO]^{\cdot -}$, which then dimerizes.

(iii) The interaction of gaseous CO with oxide surfaces leads to adsorbed species variously described as $(CO)_2{}^{2-}$ and $(CO)_n{}^{x-}$ ($n > 2$) for CO on MgO, CaO, SrO, and BaO,[5] $(CO)_2^{\cdot -}$ for CO on MgO,[6] and $C_2O_2{}^-$ together with $CO_2{}^{\cdot -}$ and a C_4 radical for CO on MgO or CoO–MgO.[7] These formulations bear a strong resemblance to the compounds described under (i) and (ii). It should be noted that Co^{2+} has also been invoked as a one-electron reductant of CO.[7] The ability of MgO to act as a base in these reactions has been stressed.[8]

The observations summarized in (i)—(iii) appear to have in common the formation of a CO radical-anion, with subsequent reactions leading to carbon–carbon bond formation. This chemistry parallels the one-electron reduction of CO_2, which can lead to oxalate formation, possibly *via* a dimerization of $CO_2{}^{\cdot -}$.[9]

In the context of finding methods for reducing CO which are experimentally more convenient than those described in (i)—(iii), we have demonstrated that solutions containing Na and K anions are also effective reductants. These novel species[10] are readily generated[11] from Na–K alloy in tetrahydrofuran (THF) in the presence of a small amount of crown ether. Na–K alloy (12.5 mol. equiv.)[11] and 18-crown-6 (1.25 mmol) were maintained at 0 °C in dry THF (50 ml) and the solution was allowed to absorb ^{13}CO (*ca.* 300 ml at 1 bar,† 12.5 mmol, from a gas burette). The dark blue colour of the solution lightened considerably as the last 5 ml of CO were absorbed. After hydrolysis the water-soluble fraction (1.72 g) was analysed by ^{13}C n.m.r. spectroscopy.‡ Integration of the carbon signals present with respect to the crown ether signal confirmed the stoicheiometry indicated by the volume of gas absorbed of one CO molecule converted per alkali metal atom. Selectivity, defined as carbon efficiency (percentage of converted carbon monoxide present in a given molecule) to the three major products was: glycolate, $HOCH_2CO_2{}^-$ 77%, oxalate, $C_2O_4{}^{2-}$, 6%, and deltate, $C_3O_3{}^{2-}$, 5%. This last assignment is based on the shift of 140.0 p.p.m. [140.0 p.p.m. for $(Li^+)_2$-$C_3O_3{}^{2-}$ in D_2O][12] and the fact that the peak remains a singlet in the ^1H-coupled spectrum. The deltate anion, the cyclic three-membered analogue of (**1**) and (**2**), has not previously been synthesized directly from CO.

The formation with high selectivity of glycolate from CO at 1 bar, at close to ambient temperature and with water as a source of hydrogen, contrasts favourably with the formation of the related ethylene glycol molecule using CO + H_2 at pressures in the range 400—2000 bar, homogeneous Rh catalysts, and temperatures between 190 and 240 °C.[13]

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† 1 bar = 10^5 N m^{-2}.

‡ ^{13}C N.m.r. analysis of water-soluble reaction products (recorded in D_2O) has also confirmed Büchner's finding (ref. 2) that glycolate is the major product in the hydrolysis of (**1**); M = Na formed from Na in liquid NH_3 and CO.