Oxidation of Ethane and Propane with Cobalt(II) Catalyst: Unexpected Formation of 1,2-Diol Esters and C–C Bond Cleavage

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Ethane reacts with both cobalt(III) and O_2–cobalt(II) in trifluoroacetic acid solution to form ethyl trifluoroacetate and 1,2-bistrifluoroacetoxyethane in successive reactions, along with the products of C–C bond cleavage; propane undergoes similar oxidative reactions.

The selective functionalization of alkanes is a challenging problem.[1] Recently, methyl trifluoroacetate was obtained in 90% yield by oxidation of methane in CF_3CO_2H (Ac_fOH) solution using $Co(OAc_f)_3$ or O_2–$Co(OAc_f)_2$. Studying the oxidation of methane homologues under the same conditions, we have found that these substrates form the corresponding glycol esters and products containing one carbon atom less than the parent hydrocarbon. This would not be expected on the basis of mechanisms involving H-atom or hydride-ion abstraction from the substrate as the first step of an oxidation reaction.

The reactions were carried out in sealed glass tubes at 130–200 °C with 5–40 atm initial alkane pressure and 0–10 atm of O_2 for 1–4 h using 0.3 mol dm^{-3} solution of the Co^{III} or Co^{II} salt in Ac_fOH. In the absence of O_2 the conversion of Co^{III} to Co^{II} was 80–100%, and that of alkanes was 1–3%. The products were identified by GLC and ^1H NMR spectroscopy.

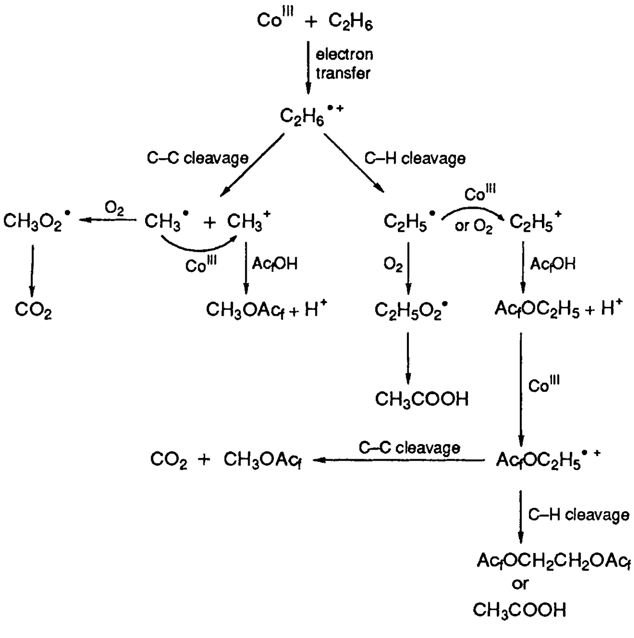
Ethane and propane were found to react with $Co(OAc_f)_3$ in Ac_fOH solution to form the corresponding alkyl trifluoroacetates as the main products, see eqns. (1) and (2).

$$C_2H_6 + 2Co(OAc_f)_3 \rightarrow C_2H_5OAc_f + 2Co(OAc_f)_2 + Ac_fOH \quad (1)$$

$$C_3H_8 + 2Co(OAc_f)_3 \rightarrow iso\text{-}C_3H_7OAc_f + 2Co(OAc_f)_2 + Ac_fOH \quad (2)$$

The reactions were accompanied by decarboxylation of Ac_fOH catalysed by the Co salt to form CO_2 and CHF_3. This side reaction was found to proceed independently of the presence of alkanes.[2]

The isomer composition of the C_3 esters obtained seems to be a result of the acid-catalysed isomerization of the esters rather than the regioselectivity of reaction (2). Thus, added Pr^nOAc_f was isomerized to Pr^iOAc_f much faster than propane was oxidized.



Scheme 1

The oxidation of the C_2 and C_3 alkanes was found to be less selective than that of methane (see Table 1). Thus, acetic acid, methyl trifluoroacetate and 1,2-bistrifluoroacetoxyethane besides $EtOAc_f$ were detected in the products of the reaction of ethane. Propane oxidation yielded small amounts of acetic acid, acetone, $MeOAc_f$, $EtOAc_f$ and traces of 1,2-bistrifluoroacetoxypropane and Pr^iOAc_f.

These minor products are formed by further oxidation of the primary oxidation products, $EtOAc_f$ and Pr^iOAc_f, respectively. We have shown that both these esters are oxidized by Co^{III} and O_2–Co^{II} in Ac_fOH solution. Thus, 18% of initial $EtOAc_f$ was converted to a mixture of $Ac_fOCH_2CH_2OAc_f$, AcOH and $MeOAc_f$ (5:3:2) (see Table 1) in ~85% total yield based on $EtOAc_f$ reacted. Similarly, Pr^iOAc_f was oxidized to a mixture of $MeOAc_f$, $EtOAc_f$, AcOH, acetone and $Ac_fOCHMeCH_2OAc_f$.

Ethylene glycol was obtained recently in substantial yield by oxidation of ethanol with Pt^{IV}–Pt^{II} chloride complexes in aqueous solution.[3] However, in the case of Co^{III}, a typical one-electron oxidant, oxidative attack at the methyl group of alkyl esters is an unexpected direction of reaction. Further, formation of the products of C–C bond cleavage, $MeOAc_f$ (from C_2 substrates) and $MeOAc_f$ + $EtOAc_f$ (from C_3 substrates), in the absence of O_2 (see Table 1) are also unexpected on the basis of the normal mechanism of alkane oxidation by M^{3+} ions.[1,4,5]

Table 1 Products distribution, mol%, for oxidation of C_2 and C_3 alkanes and alkyl trifluoroacetates[a]

Substrate	Products	With Co^{III}	With O_2–Co^{II}[b]
C_2H_6[d]	$C_2H_5OAc_f$	77[e]	67[f]
	$Ac_fOCH_2CH_2OAc_f$	3	3
	CH_3CO_2H	11	19
	CH_3OAc_f	9	11
$C_2H_5OAc_f$[c]	$Ac_fOCH_2CH_2OAc_f$	46	60
	CH_3CO_2H	33	17
	CH_3OAc_f	21	23
C_3H_8[d]	*iso*-$C_3H_7OAc_f$	76	56
	$Ac_fOCH_2CHMeOAc_f$	~0.1	~0.1
	CH_3CO_2H	3	5
	CH_3COCH_3	4	3
	CH_3OAc_f	12	25
	$C_2H_5OAc_f$	5	11
i-$C_3H_7OAc_f$[c]	$Ac_fOCH_2CHMeOAc_f$	10	4
	CH_3CO_2H	22	37
	CH_3COCH_3	38	20
	CH_3OAc_f	18	23
	$C_2H_5OAc_f$	12	16

[a] *General conditions*: 0.3 mol dm^{-3} solution of Co salt in Ac_fOH, 180 °C for 1 h. [b] 20 atm initial O_2 pressure. [c] 0.8 mol dm^{-3} solution in Ac_fOH. [d] 40 atm initial pressure. [e] Initial rate (r_0) = 1.1 mol dm^{-3} h^{-1} (equiv. Co^{III})$^{-1}$. [f] r_0 = 1.6 mol dm^{-3} h^{-1} (equiv. Co^{III})$^{-1}$.

These facts might reasonably be explained by a mechanism including direct electron transfer from an alkane molecule RH to Co^{III} ion to give a radical cation $RH^{\cdot +}$ as the first step, as was proposed earlier for oxidation of alkylarenes and alkenes with Co^{III} and Mn^{III},[6,7] as well as for alkane oxidation with $Co(OAc)_3$.[8]

Radical cations, *e.g.* $C_2H_5^{\cdot +}$ (with weakened C–H and C–C bonds in comparison with those in C_2H_6), could decompose to give CH_3^+ and $CH_3^{\cdot}$(C–C cleavage) as well as $C_2H_5^+ + H^{\cdot}$ or $C_2H_5^{\cdot} + H^+$ (C–H cleavage). Similar transformations of ester radical cations, *e.g.* $Ac_fOC_2H_5^{\cdot +}$, could lead to the glycol ester or acetic acid as shown in Scheme 1. The alkyl radicals can be captured by either Co^{III} or O_2. Under the experimental conditions, reaction with Co^{III} seems to be preferred.

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