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The Reduction of Molybdenum(II) Trifluoroacetate by Pulse Radiolysis in Methanol[1]

Sir:

Previous studies of the redox reactions of molybdenum(II) carboxylates have included the oxidation of $[Mo_2(O_2CC_3H_7)_4]$ to $[Mo_2(O_2CC_3H_7)_4]^+$ by cyclic voltammetry[2] and the conversion[3] of $[Mo_2(O_2CR)_4]$ species by halogens to such products as $[Mo_2(O_2CR)_4]I_3$. However, no reductions of these compounds appear to have been characterized. Preliminary studies have indicated that $[Mo_2(O_2CCF_3)_4]$ reacts with certain reductants; however, no molybdenum-containing products could be isolated in a pure state from the resultant mixtures. In view of these observations and the difficulties encountered by Cotton et al.[2,4-6] in isolating pure compounds subsequent to redox reactions of compounds containing multiple metal-metal bonds, an alternative approach to the reduction of $[Mo_2(O_2CCF_3)_4]$ was adopted. Pulse radiolysis techniques[7] were used since they allow the production of solvated electrons (e_s^-) in solution and have been shown[8] to be effective in the production of reduced metal ions such as Ni(I) and Zn(I). We have thus established that oxygen-free methanol solutions of $[Mo_2(O_2CCF_3)_4]$ do indeed react with e_s^-, by following the kinetics of the decy of the e_s^- absorption[9] at 550 nm in the presence and the absence of the compound.

$[Mo_2(O_2CCF_3)_4]$[10] was dissolved in freshly distilled, argon purged, methanol ("Analar", B.D.H.) and an atmosphere of argon was maintained above all solutions used, unless stated otherwise. The concentration of these solutions (typically $\geqslant 5 \times 10^{-3}$ mol l.$^{-1}$) was chosen such that, assuming a rate constant for the reaction of $[Mo_2(O_2CCF_3)_4]$ with the electron to be $\sim 10^{10}$ l. mol^{-1} s^{-1}, the electrons (available in solution in a molar ratio $[e_s^-]$: $[Mo_2]$ of typically ca. 1:100) should react with the compound in preference to the solvent. From such measurements, a rate constant for this reaction of $4.0\ (\pm 0.5) \times 10^9$ l. mol^{-1} s^{-1} was obtained.

The value of the rate constant for the reaction of $[Mo_2(O_2CCF_3)_4]$ with e_s^- is in the range expected[11] for a diffusion controlled process, suggesting that the species thus formed is the primary product (A) of this reaction and is presumably therefore $[Mo_2(O_2CCF_3)_4]^-$. (It has been established[12] that e_s^- reacts only very slowly with trifluoroacetate groups.) The absorption spectrum of this product was obtained by measurements of the post-pulse absorption (400-1000 nm) produced in $[Mo_2(O_2CCF_3)_4]$ solutions ($\geqslant 5 \times 10^{-3}$ mol l.$^{-1}$) where more than 90% of the e_s^- reacted with the compound. This spectrum[13] is shown in Figure 1 and its principal feature is an absorption at 780 ($\pm$20) nm (ϵ 2.6 ($\pm$0.3) $\times 10^3$ l. mol^{-1} cm^{-1}).

A is very short lived, the 780-nm absorption decays very rapidly to ca. 20% of its maximum intensity and then more slowly to <1% of this value. Both of these decay processes follow second-order kinetics with respective rate constants[14] of $4.5\ (\pm 1.0) \times 10^9$ and $2.5\ (\pm 1.0) \times 10^8$ l. mol^{-1} s^{-1}. It seems possible that one of these decay processes is the electron exchange,

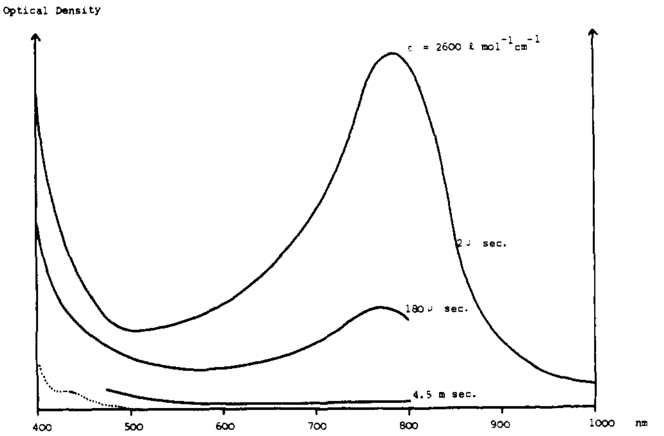

Figure 1. The electronic spectrum of the product of the reaction between $[Mo_2(O_2CCF_3)_4]$ and an electron in MeOH (recorded after the times shown; the spectrum of $[Mo_2(O_2CCF_3)_4]$ in MeOH shown for comparison (···)).

$$2[Mo_2(O_2CCF_3)_4]^- \rightarrow [Mo(O_2CCF_3)_4] + [Mo_2(O_2CCF_3)_4]^{2-}$$

In order to provide some confirmation of the above conclusions the following observations were carried out. (a) In radiolyzed methanol solution $\cdot CH_2OH$ radicals as well as e_s^- are transient products and possible reducing agents. To examine this latter possibility, solutions of $[Mo_2(O_2CCF_3)_4]$ in methanol were saturated with nitrous oxide which is known to react with e_s^- to produce O^-, the latter then forming $\cdot CH_2OH$ by reaction with methanol. The irradiation of such solutions produced a transient absorption at ca. 500 nm but none at ca. 780 nm. (b) To further support the formulation of A as a reduction product, the rate of decay of the 780-nm absorption was monitored in the presence of known amounts[15] of dioxygen. This rate of decay was found to be accelerated by the presence of dioxygen and the second-order rate constant for this process was determined as $5.9\ (\pm 0.3) \times 10^9$ l. mol^{-1} s^{-1}. The product of the reaction obtained under these conditions was not simply $[Mo_2(O_2CCF_3)_4]$ but a species with an absorption which extended through the visible region of the spectrum. (c) Glasses formed by dissolving $[Mo_2(O_2CCF_3)_4]$ (ca. 10^{-2} mol l.$^{-1}$) in methanol-1-propanol (100:3) and rapidly freezing to liquid nitrogen temperature, were subjected to γ-irradiation from a ^{60}Co source at ca. 1 krad min^{-1} over varying time intervals (15 min-2 h). The ESR spectra of these glasses maintained between 77 and 130 K contained, in addition to a strong signal characteristic of $\cdot CH_2OH$ radicals, a reasonably intense and broad (ca. 65 G in width) signal centered at $g = 1.91$, the profile of which suggested that the paramagnetic center involves some anisotropy. These observations strongly suggest that some of the electrons produced on γ-irradiation become trapped on the dimolybdenum center. The electronic structure of this reduced center would be anticipated to be $\ldots(\delta)^2\ (\delta^*)^1$, the magnetic properties of which, in view of the suggested electronic structure[16] for $Mo \equiv Mo$ units, might reasonably be expected to be similar to those of the corresponding oxidized species having the $\ldots.(\delta)^1$ configuration. The observed g value is in fact very similar to those reported[2,6] for $[Mo_2(O_2CC_3H_7)_4]^+$ and $[Mo_2(SO_4)_4]^{3-}$.

We conclude that these experiments have shown that it is possible to add an electron to $[Mo_2(O_2CCF_3)_4]$, the probable product being a molybdenum ($1\frac{1}{2}$) species which is very short-lived. Therefore the possibility of isolating this and related simple reduction products of the molybdenum(II) carboxylates appears to be considerably more remote than for related technetium and rhenium (2½) complexes.[17]

One feature of the above data which merits some comment is the origin of the low energy absorption (λ_{max} 780, ϵ 2600 l. mol^{-1} cm^{-1}) apparently characteristic of the $[Mo_2(O_2CCF_3)_4]^-$ moiety. The absorption contrasts markedly with the lowest known absorption of $[Mo_2(O_2CCF_3)_4]$ (λ_{max} 430 nm, ϵ 130 l. mol^{-1} cm^{-1}) which is assigned[16] to the forbidden $\delta \rightarrow \pi^*$ or $\pi \rightarrow \delta^*$ transition of the metal center. If, as suggested above, the additional electron is accommodated in the δ^* orbital, possible electronic rearrangements which could give rise to the low energy absorption include (i) a $\delta^* \rightarrow \pi^*$ transition on the metal center and (ii) a $\delta^* \rightarrow$ carboxylato-π^* transition. Of these two possibilities the latter is favored since its metal ligand charge-transfer character is more consistent with the rather considerable intensity observed for this low energy absorption and a small $\delta^* \rightarrow \pi^*$ promotion energy is inconsistent with the interpretation that dimeric Mo(1½) and Mo(2½) species have similar *g* values.

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(13) Extinction coefficients were calculated assuming an electron yield G = 1.8 electrons per 100 eV.
(14) The faster of these processes was monitored at both 800 and 425 nm and essentially the same rate constant was obtained. The rate constants for both processes were calculated assuming ϵ_{780nm} 2600 l. mol^{-1} cm^{-1}. However, if the slower process is not the decay of A but that of a secondary product, this assumption does not hold.
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Complexation of Carbonyl Oxide Zwitterions[1]

Sir:

In earlier papers[2-4] π (or charge transfer) complexes of ozone were described for the first time. Among the complexing agents employed were 1-mesityl-1-phenylethylene, toluene, mesitylene, and hexaethylbenzene. It was also shown that the cis-trans ozonide ratios obtained from ozonation of *cis*- and *trans*-1,2-diisopropylethylene with complexed ozone differed from those obtained with "free" ozone.[4]

We wish now to report evidence which indicates that these differences in results obtained with complexed and uncomplexed ozone are due to complexation of Criegee carbonyl oxide zwitterions with the complexing agent rather than to different mechanisms of ozone attack and/or ozonolysis with complexed and "free" ozone. Accordingly, these results further strengthen and support the concept that stereospecificity of ozonide formation results from the preferential manner in which syn or anti zwitterions are produced from cis or trans olefins during ozonolysis.[5,6]

Table I. Cis/Trans Ozonide Ratios from Ozonation of *cis*- and *trans*-1,2-Diisopropylethylenes with Ozone Complexes

Temp, °C	Complex agent	Freon-12 Cis isomer	Freon-12 Trans isomer	Isopentane Cis isomer	Isopentane Trans isomer
−78	None	50:50	49:51	54:46	49:51
−150	None	55:45	51:49	67:33	58:42
−150	Toluene	*a*	*a*	74:26	62:38
−150	*o*-Xylene	61:39	48:52	76:24	65:35
−150	Isodurene	61:39	51:49	75:25	57:43
−150	HEB	*b*	*b*	75:25	65:35
−150	MPE	64:36	50:50	78:22	54:46

[a] Complex is stable in Freon-12 only at lower temperatures. [b] The complexing agent is too insoluble in Freon-12 to use in the usual concentration. [c] HEB = hexaethylbenzene. [d] MPE = 1-mesityl-1-phenylethane.

Table II. Comparison of Normal and Inverse[a] Ozonation with Complexing Agents

DIPE[b] isomer	Solvent	Complex	Cis/trans normal	ozonide ratios inverse
Cis	Freon-12	*o*-Xylene	61:39	60:40
Cis	Freon-12	Isodurene	61:39	58:42
Cis	Freon-12	MPE[c]	64:36	62:38
Cis	Isopentane	*o*-Xylene	76:24	75:25
Cis	Isopentane	Isodurene	75:25	74:26
Cis	Isopentane	MPE[c]	78:22	77:23
Trans	Freon-12	*o*-Xylene	48:52	47:53
Trans	Freon-12	Isodurene	51:49	49:51
Trans	Isopentane	Toluene	62:38	64:36
Trans	Isopentane	*o*-Xylene	65:35	65:35
Trans	Isopentane	Isodurene	57:43	55:45
Trans	Isopentane	HEB[d]	65:35	65:35
Trans	Isopentane	MPE[c]	54:46	53:47

[a] Inverse ozonation refers to ozonation with "free" ozone followed by addition of the complexing agent before warm-up. [b] DIPE = 1,2-diisopropylethylene. [c] MPE = 1-mesityl-1-phenylethane. [d] HEB = hexaethylbenzene.

Table I shows cis-trans ozonide ratios obtained by ozonizing *cis*- and *trans*-1,2-diisopropylethylene with "free" and with complexed ozone, using several different complexing agents and two different solvents.[7] The differences observed between complexed and uncomplexed ozone and between the two solvents are real. Most of the values are averages of several runs which varied by no more than ±1%.

The values do differ in some cases from those reported earlier,[4] but this was due to undeveloped technique in the preliminary work, particularly in regard to the nature of the warm-up. We have found, like Murray and Hagen,[9] that a fast warm-up gives scattered results which differ greatly from those obtained using a slow warm-up, at least with the trans olefin. The results in Tables I and II were from a very slow warm-up, from −150 °C to room temperature in the Dewar flask over a period of 24 or more h.

That the differences in cis-trans ozonide ratios observed between complexed and "free" ozone are not due to different mechanisms of ozone attack was established in three ways. First, the primary ozonide of *trans*-1,2-diisopropylethylene was observed by NMR using either "free" or complexed (*o*-xylene) ozone.[10] The characteristic ring proton doublet was present in equal intensity in both cases (δ