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CARBOXYLATE EXCHANGE AMONG DIMOLYBDENUM TETRACARBOXYLATES: THE TRIFLUOROACETATE/FORMATE SYSTEM

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Abstract—^{1}H NMR spectroscopy has been used to study the kinetics and equilibrium properties of solutions, in acetone, made of $(CF_3CO_2)_4Mo_2$ and $(HCO_2)_4Mo_2$. At equilibrium all of the mixed ligand species, $(CF_3CO_2)_3(HCO_2)MO_2$, *cis*- and *trans*-$(CF_3CO_2)_2(HCO_2)_2Mo_2$, and $(CF_3CO_2)(HCO_2)_3Mo_2$, are formed, as well as the end members. The distribution shows almost no significant deviations from that expected statistically, the main one being in a *cis*/*trans* ratio in the 2:2 species that is about 2.5 instead of 2.0. At 21°C, equilibrium was attained too rapidly (<1 h) to permit a detailed rate study but at 10°C and 0°C the growth and decay of the various species was easily followed over 3-5 h periods. The rate behaviour is qualitatively reasonable, but a quantitative kinetic analysis was not undertaken.

In spite of the enormous number of $(RCO_2)_4M_2$ compounds that have now been reported, including some with mixed ligand sets and a few with mixed (MM′) dimetal units,[1] we know of no report[2] on the solution behaviour of a mixed ligand system, i.e. one consisting of two types of carboxyl groups, RCO_2^- and $R'CO_2^-$. This report presents the results of a pilot study in which $M = Mo$, $R = H$ and $R' = CF_3$. This particular choice was dictated by the desire to have two carboxylates that were moderately different in character, while also fulfilling practical requirements pertaining to solubility and having observable NMR signals in a clear region of the spectrum. The chemical shift of the unique proton of the formate ion, which is in a region well removed from most solvent resonances, enabled us to satisfy the last requirement.

The two principal goals of the study were (a) to see if the actual behaviour of the system would deviate significantly from that predicted for a purely statistical situation, and (b) to acquire at least a qualitative idea of the rate and manner by which the system attains equilibrium.

EXPERIMENTAL

The compounds $(CF_3CO_2)_4Mo_2$ and $(HCO_2)_4Mo_2$ were prepared by literature methods.[3,4] Acetone solvent was of spectroscopic grade, predried over molecular sieves and freshly distilled from potassium carbonate.

The NMR measurements were made with a Varian XL-200E spectrometer at 200.1 MHz. Conventional operating conditions were employed. The solutions were prepared and maintained in an inert atmosphere.

RESULTS AND DISCUSSION

Assignments

We begin with the equilibrium mixture obtained by dissolving equimolar quantities of $(CF_3CO_2)_4Mo_2$ and $(HCO_2)_4Mo_2$. The experimental spectrum is shown in Fig. 1. The first task is to assign the six observed signals. This can be done unambiguously. Figure 2 shows the six molecules that must be present and identifies the six types of hydrogen atoms that should each display a different chemical shift. To make the assignments

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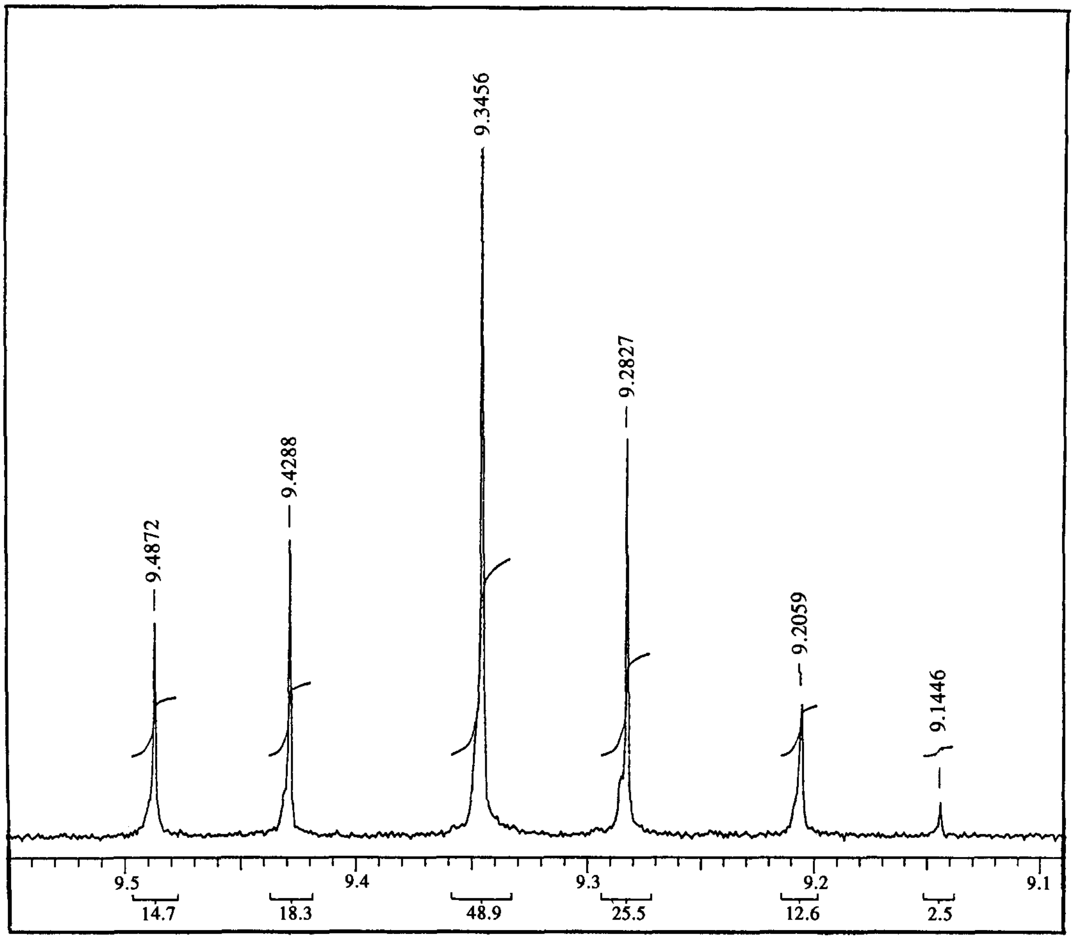
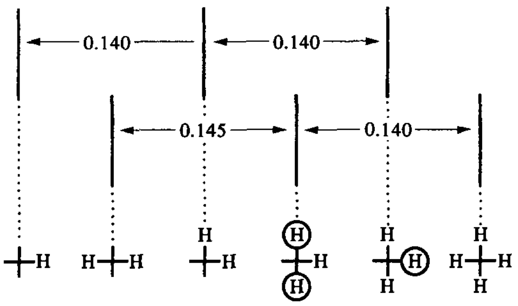


Fig. 1. The observed ^1H NMR spectrum for the 1 : 1 $(CF_3CO_2)_4Mo_2/(HCO_2)_4Mo_2$ solution in acetone at 21 ± 1°C.

we begin by recognizing that the signals should move downfield (i.e. towards less shielding) as the number of CF_3CO_2 ligands increases. In addition, there should be a greater downfield shift in those hydrogen atoms *trans* to CF_3 groups, compared to those that are *cis*. With these criteria alone, we can make the assignment shown in Scheme 1. It can be seen that this embodies a remarkable, but not unexpected, regularity in the intervals between the various chemical shifts.



Scheme 1.

While the above arguments are not by themselves absolutely conclusive, the assignment they lead to is then buttressed by several other criteria to the extent that they can be considered certain. These other arguments are:

(1) The relative intensities are in semiquantitative accord with those expected by a statistical calculation of the equilibrium distribution, particularly its asymmetry towards the low-field side.

(2) Other spectra (see later) obtained for mixtures containing different ratios of CF_3CO_2 to HCO_2 ligands differ from that in Fig. 1 in the ways qualitatively required.

(3) The ratio of signals for H(3*c*) and H(3*t*) must always be 2 : 1 and it always is, not only in Fig. 1, but in all other spectra. This is the only pair

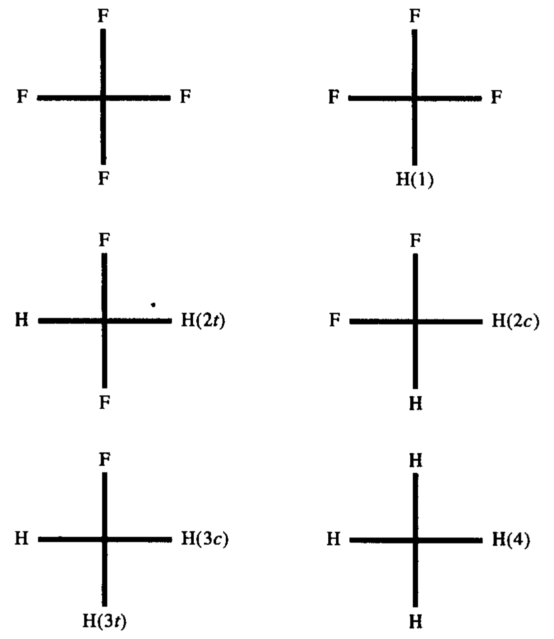


Fig. 2. Schematic representations of the $(CF_3CO_2)_{4-n}(HCO_2)_nMo_2$ molecules (n = 0–4). –F represents an O_2CCF_3 moiety and –H an O_2CH moiety. The molecules are drawn as if seen end-on.

of signals for which the intensity ratio must be invariant.

(4) The ratio of signals for H(2*c*) and H(2*t*) should be 2 : 1 on a purely statistical basis. It could differ from this, but it should be the same in all spectra. It is, indeed, constant within experimental error, namely 2.5 ± 0.2.

(5) The way signals grow [and the H(4) signal declines] as a function of time when a mixture of $(CF_3CO_2)_4Mo_2$ and $(HCO_2)_4Mo_2$ approaches equilibrium is clearly indicative that the H(1), H(3*c*), H(3*t*) and H(4) signals have been correctly assigned.

Equilibrium distribution

We have measured the equilibrium spectra for these mixtures. For a 1 : 1 mixture of $(CF_3CO_2)_4Mo_2$ the results are shown in Fig. 1. In addition, equilibrium spectra (not shown) were recorded for 2 : 1 and 1 : 2 mixtures.

In order to compare the experimental results in these three cases with what would be expected for a purely statistical distribution, these statistical distributions are shown side-by-side with the experimental ones in Fig. 3. It may be noted that we are not aware of any general formula for calculating such statistical results and those shown were worked out on a case-by-case basis.

It is clear that there is very little difference between the experimental and the statistical results. It was established by duplicate runs that the measured percentage for each signal intensity is subject to an error of about ±2%. With that error level

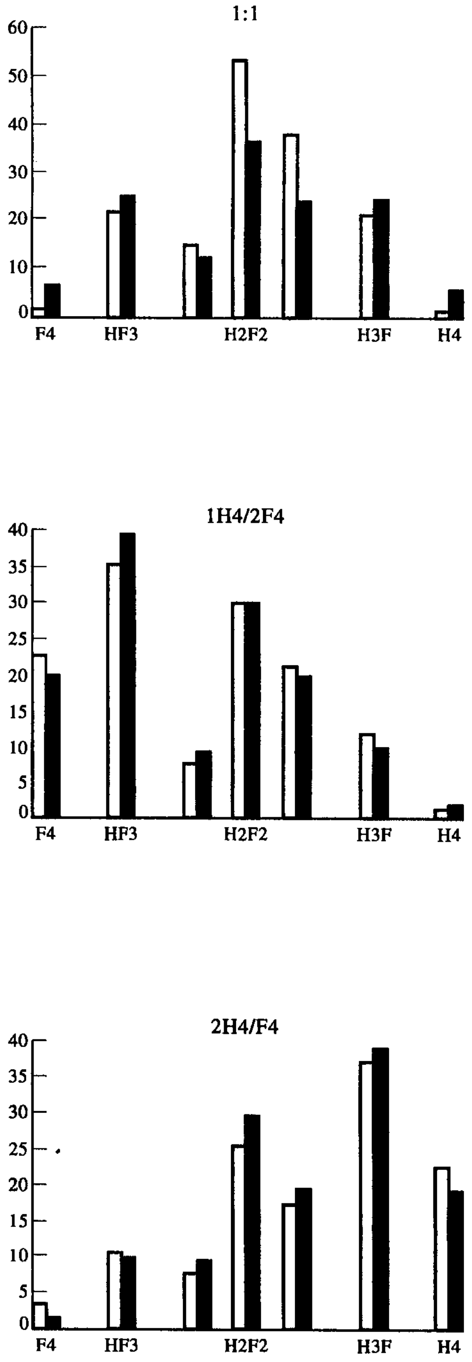


Fig. 3. The observed (open bars) and statistical (filled bars) percentages of the five kinds of $(CF_3CO_2)_n(HCO_2)_{4-n}$ molecules in 1 : 1, 2 : 1 and 1 : 2 mixed solutions. The "observed" values for $n = 4$ (F4) are not literally observed but calculated from the other observed values. In each case the bars for the total H_2F_2 are accompanied by those for the *cis* and *trans* isomers.

in mind, it is clear that the only possible real differences between the observed and the statistical results are the following:

(1) In the 1:1 mixture (only) the F_2H_2 mixed species are more abundant and the H_4 species less abundant than statistically expected. However, the differences are very small and would correspond to only a few tenths of a kilocalorie in free energy.

(2) The *cis*/*trans* ratio is consistently a little higher, 2.5±0.5 vs 2.0, than the statistical one for the F_2H_2 species. This could be due to the effect of a somewhat polar solvent (acetone) favouring the polar *cis* isomers slightly.

On the whole, the conclusion to be drawn is that when $(RCO_2)_4Mo_2$ and $(R'CO_2)_4Mo_2$ species are mixed in solution, the various mixed species as well as the end members are present in very nearly, if not exactly, statistical ratios when equilibrium is attained.

Rate behaviour

It was found that equilibrium is attained within about 30 min at the normal probe temperature of 21±1°C. Therefore, the rate behaviour was studied at 10°C and 0°C. The results at these two temperatures are shown in Figs 4 and 5, respectively. Clearly, 10°C was the ideal temperature for such a study, since numerous intermediate spectra could be recorded and yet the final equilibrium (which is not significantly different from that at 21°C) could be reached in a practical period of time. The results at 0°C are nevertheless useful because they provide data for the earlier stages of the process.

The results are qualitatively entirely reasonable. The H_4 species decline exponentially and the H_1 and H_3 species begin to appear immediately and at essentially the same rate, and with a negative second derivative. Only after the H_1 and H_3 species have begun to accumulate do the isomeric H_2 species grow in, with growth curves having positive second derivatives. Clearly, these observations are consistent with the reasonable expectation that ligand exchanges occur one ligand at a time.

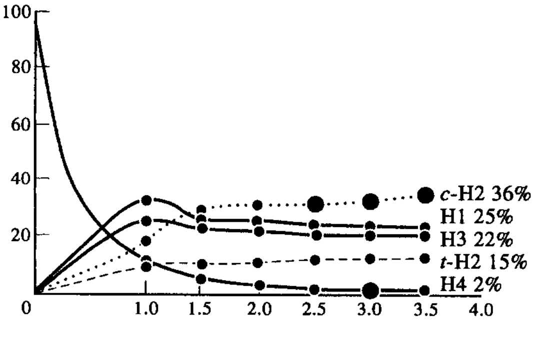


Fig. 4. Time dependence of signals for a 1:1 mixture at 10°C for the five hydrogen-containing species. The percentages plotted are percentages of total ^1H resonance intensity (not, as in Fig. 3, percentage of molecules).

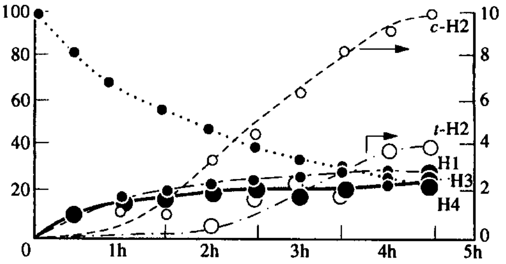


Fig. 5. As in Fig. 4 but at 0°C. Note that the scale for the H_2 species is at the right, while that for the other three is at the left.

It is interesting that at 10°C the production of the H_1 and H_3 species is fast enough to overshoot the final equilibrium values after about 45 min, and then they fall back as the formation of H_2 species catches up. At 0°C the relative rates are such that this overshoot does not occur.

A detailed kinetic analysis of the processes leading to equilibrium would probably be feasible if more data and some straightforward but tedious computer simulation were to be employed. We have not elected to do this, but the specific system we have examined seems to have much to recommend it if such a study is to be attempted.

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