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Contribution from the School of Chemical Sciences,
University of Illinois at Urbana-Champaign, 505 S. Mathews Avenue, Urbana, Illinois 61801

Exchange Reactions and Microscopic Reversibility: A Reply[1]

Theodore L. Brown

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Responses are offered to questions raised by W. G. Jackson (*Inorg. Chem.* **1987**, *26*, 3004) regarding the interpretation of experimental work dealing with CO exchange reactions of $M(CO)_5X$ (M = Mn, Re) compounds and application of the principle of microscopic reversibility.

W. G. Jackson has recently published a paper in this journal dealing with the principle of microscopic reversibility as applied to the kinetics and stereochemistry of the CO-exchange reactions of $M(CO)_5X$ (M = Mn, Re) compounds.[2] My purpose in this contribution is to comment on the major issues he raises.

My comments have to do first with Jackson's criticisms of earlier work from our laboratory dealing with application of the principle of microscopic reversibility to interpretation of data for ^{13}CO exchange with $M(CO)_5X$ (M = Mn, Re) compounds. Jackson begins with reference to a 1968 paper[3] in which I invoked the principle of microscopic reversibility in a verbal statement. That statement was later interpreted by Espenson[4] in an equation which Jackson rightly concludes is incorrect. The phrase I employed, "degree of preference", is admittedly imprecise: I meant it to apply to relative rates, not specific rate constants. The discussion in that early paper was focused on the conceptual application of the principle and did not deal with a quantitative interpretation of exchange data. I have no quarrel with Jackson's application of the principle of detailed balancing. Our subsequent work,[5,6] preceding Jackson's paper by more than a decade, is consistent with both microscopic reversibility and detailed balancing.

Jackson goes on to attribute various other views to us. For example, he says "...it was stated that the distribution of labeled CO in the *initially* forming monoisotopically substituted species (the cis- and trans-labeled species) was independent of the question of a fluxional or nonfluxional five-coordinate intermediate. Again, as shown ahead, this is not correct.".[2] But Jackson then goes on to show that for times near zero the ratios of the cis to trans forms are identical for the assumptions of a rigid five-coordinate intermediate on the one hand and a fully fluxional one on the other. An examination of our quantitative analysis of the exchanging system[6] shows that there is no disagreement between our two approaches. Any apparent disagreements have to do with the language employed in describing the exchange phenomena. In this connection, one must distinguish between the *instantaneous* rates at which the five-coordinate species combine with CO to re-form the ground-state six-coordinate molecule and the rates at which the label appears in the axial and radial positions. Of course, the relative quantities of cis and trans monosubstituted forms change as the reaction proceeds, in a manner that depends on the fluxionality or nonfluxionality of the intermediate(s). The quantitative aspects of the changes in concentrations of the variously labeled species are worked out in detail in the Atwood/Brown paper; there is no disagreement between our analysis and Jackson's.

A second kind of issue raised by Jackson has to do with the interpretation of the experimental data relating to exchange of labeled CO with the $M(CO)_5X$ compounds. In the Atwood/Brown paper we reported a detailed study of the exchange of ^{13}CO with $Mn(CO)_5Br$ and $Re(CO)_5Br$, using IR spectra in the carbonyl stretching region to discern the location of labeled CO. This method is both qualitatively and quantitatively reliable and precise. It is possible to determine unambiguously the location of label in the monoisotopically labeled species, and in the more highly labeled species as well. Furthermore, the quantitative extent of incorporation of the label is also obtainable from the intensities of the various IR bands characteristic of the variously labeled species.

The Atwood/Brown work is consistent with other IR studies of CO exchange in showing that label is incorporated into both the axial and radial positions.[7,8] However, quantitative analysis of the results revealed that there is an induction period in the incorporation of label into the axial position. We analyzed the system in terms of a kinetic model that assumes that CO dissociation occurs predominantly from the cis position and that there exists a five-coordinate intermediate or intermediates that are fluxional; that is, they rapidly interconvert during their lifetime. Such a model provides a mechanism for appearance of labeled CO into the axial position. The extent of agreement between the experimental and calculated results for the assumption of a fluxional five-coordinate intermediate is exceptionally good, for both $Mn(CO)_5Br$ and $Re(CO)_5Br$.[6] The model is conceptually and quantitatively correct and is in accord with the principles of microscopic reversibility and detailed balancing. An alternative model, in which nonfluxional five-coordinate intermediates was assumed, was also considered and compared with experiment. Aside from the fact that this model would not be as consistent with the observation that phosphine ligands are preferentially sited in cis positions in substitution processes, the quantitative agreement with the IR results is considerably less satisfactory. There is therefore no reason that I am aware of to doubt the correctness of the general conclusions presented by Atwood and Brown.

Jackson refers to early ^{14}CO radiochemical exchange work on $Mn(CO)_5Br$ which led Wojcicki and Basolo to conclude that only four of the five CO groups in $Mn(CO)_5Br$ undergo exchange.[9] He suggests that this earlier work is more "clear-cut" than the IR work involving use of ^{13}CO or $C^{18}O$. The application of ^{14}CO methods to the study of metal carbonyl reactions represented a pioneering foray into an important and previously unexplored area of organometallic chemistry.[10] However, the accuracy and degree of explicitness with which the incorporation of label can be discerned with use of IR methods that came later are far greater than can be achieved with the radiolabeling methods. The conclusion that only four of the five CO groups of $Mn(CO)_5Br$ exchange with CO is inconsistent with the IR results. As shown in Figure 1 of ref 6, the band growing in at 1958 cm^{-1} is due to incorporation of ^{13}CO in the axial position; the bands growing in to lower wavenumbers of the band at 2135 cm^{-1} are due to incorporation of ^{13}CO in radial positions. It is clear that, although there is an induction period for appearance of the axial label, the labels are appearing in the two locations during the same general period of time. This result is qualitatively the same as that found

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in other IR studies.[7,8] The radiolabeling experiments, if correct, would preclude the appearance of any significant amount of label into the axial position in the time of the IR experiment. It is therefore reasonable to conclude that the earlier radiochemical exchange results are incorrect.

In summary, our applications of the principles of microscopic reversibility and of detailed balancing to the understanding of the exchange reactions of M(CO)$_5$X compounds are in agreement with Jackson's positions. I regard his discussion of the fluxionality of the five-coordinate intermediate, to the extent that it depends on the assumption of the correctness of early radiochemical carbon exchange work, as incorrect. In this connection, Davy and Hall have recently completed extensive calculations of the barriers to CO loss in Mn(CO)$_5$Cl.[11] Their results support the concept of a strong cis-labilizing influence for Cl as heteroligand. Their calculations also predict a high barrier for conversion of the intermediate resulting from radial CO loss to the intermediate resulting from axial CO loss. Thus, the *direct* interconversion between these two intermediates would not, according to these calculations, provide a means for scrambling of the CO groups in the Mn(CO)$_4$X intermediate. However, their calculations show that an indirect process, proposed by Lichtenberger and Brown,[12] permits exchange in the five-coordinate intermediate via a low-energy pathway.

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Contribution from the Department of Chemistry, University of Florence, Florence, Italy,
and Laboratoire de Chimie (UA CNRS 1194), Departement de Recherche Fondamentale, Centre d'Etudes Nucleaires, Grenoble, France

One-Dimensional Magnetism of a Linear Chain Compound Containing Yttrium(III) and a Nitronyl Nitroxide Radical

Cristiano Benelli, Andrea Caneschi, Dante Gatteschi,* Luca Pardi, and Paul Rey

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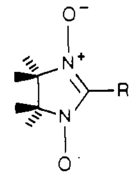
Y(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate; NITEt = 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide) crystallizes in the monoclinic space group $P2_1/n$ with cell parameters $a = 11.245$ (1) Å, $b = 17.257$ (7) Å, $c = 18.357$ (3) Å, $\beta = 98.39$ (1)°, $V = 3524.13$ Å^3, and $Z = 4$. The crystal structure determination converged with $R = 0.132$. The molecular structure consists of linear chains made by Y(hfac)$_3$ moieties bridged by nitronyl nitroxide radicals. Single-crystal EPR spectra and magnetic susceptibility data measured in the 300–4.2 K temperature range are discussed.

Introduction

Nitronyl nitroxides, 4,4,5,5-tetramethyl-2-R-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide, NITR, of the general formula shown below have proved to be versatile ligands towards transition metal and lanthanide ions.[1-3]



They can bind through the oxygen atoms to paramagnetic metal ions, giving rise to exchange interactions that can be either ferromagnetic or antiferromagnetic depending on the overlap between the magnetic orbitals. The nitronyl nitroxides[4,5] and the nitroxides in general[6,7] have also been found to interact with each other, in general in an antiferromagnetic fashion even at relatively long distances. In particular, it has been observed that two NITR radicals bound to one lanthanide ion are antiferromagnetically coupled[8-10] with constants J of ca. 10 cm^{-1}. This result is rather surprising, because the distance between the radicals is too long to justify the observed coupling on the basis of the direct exchange, and the involvement of the metal orbitals in a superexchange pathway has been suggested[10] as a possible origin of the interaction. However, the exact determination of the extent of the coupling between the radicals in these compounds is hampered by the fact that gadolinium(III) is magnetic, and so is europium(III) at high temperature. In order to understand how relevant are the metal orbitals in transmitting the exchange interaction between the nitronyl nitroxides, we synthesized Y(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate), in which the metal ion is nonmagnetic and any deviation from Curie law must be attributed to interactions between the radicals. We wish to report here the magnetic properties and the EPR spectra of Y(hfac)$_3$NITEt, which behaves as a one-dimensional antiferromagnet.

Table I. Crystallographic Data for Y(hfac)$_3$NITEt

formula: YC$_{24}$H$_{20}$F$_{18}$N$_2$O$_8$
formula weight: 895.31
$a = 11.245$ (1) Å
$b = 17.257$ (7) Å
$c = 18.357$ (3) Å
$\beta = 98.39$ (1)°
$V = 3524.13$ Å^3
$Z = 4$
space group: $P2_1/n$ (No. 14)
$T = 18$ °C
$\lambda = 0.71069$ Å (Mo Kα)
$\rho_{\text{calcd}} = 1.69$ g cm^{-3}
$\mu = 17.04$ cm^{-1}
$R(F_o) = 0.132$
$R_w(F_o) = 0.132$

Experimental Section

Synthesis. The NITEt radical was prepared as previously described[11,12] and identified by melting point and EPR spectra. Y(hfac)$_3$·3H$_2$O was prepared according to the literature method[13] and

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*To whom correspondence should be addressed at the University of Florence.

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