a contrast to the work of Streitwieser,[16] and implies that in this system reversible polymeric association of base is relatively unimportant.

Finally, we would like to point out the significance of the satellite fine structure. A similar long-range coupling has been observed in acetone, $J = 0.54$ cps, and attributed to interactions with the π electrons of the carbonyl group.[17] The occurrence of this effect in DMSO may provide further indication of whether the electronic structure of the sulfoxide grouping should be best considered as an S–O double bond.[18]

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Nondissociative First-Order Reactions of Some Metal Carbonyls

Sir:

This communication describes some preliminary results which are being reported at the present time because of possible widespread mechanistic significance in the interpretation of the substitution reactions of metal carbonyls.

Nickel tetracarbonyl was previously found to undergo radioactive carbon monoxide exchange in a reaction independent of ^{14}CO concentration.[1] Naturally, the $Ni(CO)_4$ was assumed to be reacting by a dissociative mechanism. This interpretation was apparently verified when the rate of reaction of $Ni(CO)_4$ with triphenylphosphine at 0° in toluene, also independent of phosphine concentration, was found to be about the same as the rate of ^{14}CO exchange.[2]

In a reinvestigation of these reactions, we have found that these two substitutions are separate processes. However, in agreement with earlier work,[1,2] both ^{14}CO exchange and reaction with triphenylphosphine or trimethyl phosphite were found to be first order in $Ni(CO)_4$ and zero order in the entering reagent. The values of ΔH^* and ΔS^*, listed in Table I for three solvents, are quite different for the two reactions, and the agreement in rates at 0° in toluene is entirely fortuitous.

As expected from the lower ΔH^* for ^{14}CO exchange, the ratio of the rate for ^{14}CO exchange to that for reaction with L decreases with temperature, and the ratio is less than 1 at 25° in toluene and heptane.

Similar observations have been made for exchange and substitution reactions of other metal carbonyls. For example, the rate of exchange of ^{14}CO with $Hg[Co(CO)_4]_2$ is first order in the concentration of metal carbonyl but zero order in carbon monoxide. The activation parameters for exchange are $\Delta H^* = 13 \pm 1$ kcal/mole and $\Delta S^* = -24 \pm 2$ eu. Quantitative kinetic data could not be obtained on the reactions of $Hg[Co(CO)_4]_2$ with different phosphines and phosphites to form $Hg[CoL(CO)_3]_2$, but qualitative observations show that these reactions differ in mechanism from the CO-exchange process.

Table I. Activation Parameters for the Reaction of $Ni(CO)_4$ with ^{14}CO and L[a]

Solvent	^{14}Co exchange ΔH^*, kcal	ΔS^*, eu	Reaction with L[b] ΔH^*, kcal	ΔS^*, eu
Acetonitrile	10 ± 1	-36 ± 2	21 ± 1	2 ± 2
Toluene	12 ± 1	-26 ± 2	21 ± 1	2 ± 2
Heptane	10 ± 1	-36 ± 2	21 ± 1	1 ± 2

[a] L = triphenylphosphine or trimethyl phosphite; rate independent of L. [b] Similar results were obtained independently by R. J. Angelici and B. E. Leach (private communication) for L = $P(C_6H_5)_3$ in various solvents.

Also some of the results on the kinetics of exchange and substitution reactions of $CoNO(CO)_3$ (isoelectronic and isostructural with $Ni(CO)_4$) suggest an analogous type of behavior. Substitution reactions of $CoNO(CO)_3$ to form $CoLNO(CO)_2$ are second order,[2] and the reagent reactivity increases with increasing polarizability of the entering ligand atom; *e.g.*, $P(n\text{-}C_4H_9)_3$ is a much better nucleophile toward this substrate than is pyridine. For L = $As(C_6H_5)_3$, a poor reagent, a plot of rate constants *vs.* concentration of L is linear but has a nonzero intercept. The value of this rate constant at zero concentration of L at 25° is about tenfold smaller than that for ^{14}CO exchange with $CoNO(CO)_3$ under the same conditions. The rate of exchange is first order, being zero order in CO. Thus, the substitution path that is zero order in L and the exchange process differ in a manner that appears to be similar to that found for the $Ni(CO)_4$ system.

Thus, many reactions of metal carbonyls, previously presumed to be dissociative reactions, should be reinvestigated in light of these results. To elucidate further the mechanism of reaction of $Ni(CO)_4$, its reaction with other reagents such as ethyl isocyanide is being studied.

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