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Substituent Effects in Dimethylsulfoxide-promoted Carbon Monoxide Insertion into Iron–Alkyl Bonds*

J. D. COTTON**, G. T. CRISP and LATIFAH LATIF

Department of Chemistry, University of Queensland, Brisbane, 4067 Qld., Australia

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The insertion reaction of carbon monoxide, induced by dimethylsulfoxide, into iron–carbon sigma bonds in the complexes, $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$*, has been extended to a wide variety of primary and secondary alkyl substituents. Rate constants for the forward* (k_1) *and reverse* (k_{-1}) *reactions, together with the second order rate constant* (k_2)*, for the further reaction of the solvated acyl complex with triphenylphosphine, have been measured and evaluated. The major substituent effect is seen in* k_1 *and appears largely to reflect steric enhancement of reaction. The relative reactivity of a series (methyl through n-octyl) of straight chain alkyl complexes has been compared with a recent theoretical prediction. Thermodynamic and kinetic parameters for the formation of the solvated acyl have been measured and evaluated.*

Introduction

Previously we reported [1] our study of the electronic effects of *meta-* and *para-* substituents on the triphenylphosphine-induced insertion of carbon monoxide into molybdenum to carbon sigma bonds in a series of benzyl complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4X)]$. In this paper, we describe an extension of this work to the reactivity of a variety of simple primary and secondary alkyl groups (R = Me, Et, ^{i}Pr, CH_2Cy *etc.*) bound to a transition metal, in the readily accessible compounds, $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$.

In polar solvents, such as acetonitrile, the ligand (L)-induced carbonyl insertion reaction to yield acyl-iron complexes, $[(\eta^5\text{-}C_5H_5)(CO)LFe(COR)]$, is known [2] to follow the same reaction pathway as the corresponding molybdenum compounds, with the formation of an acyl intermediate $[(\eta^5\text{-}C_5H_5)(CO)Fe(COR)]$ in the first stage in a solvent-assisted [3] process, followed by the reaction of the intermediate with ligand (*e.g.* triphenylphosphine), to give the final product. In these systems, the rate constant, k_{obs}, for the overall reaction (measured under conditions where the ligand concentration is effectively constant thus making the reaction effectively first order) tends towards a limiting value, k_1, (the forward rate constant associated with the formation of the intermediate), as the concentration of ligand is increased. Much interest has centred particularly on k_1, because of the likely [3] substantial role of metal–carbon bond breaking in this step of the reaction. However, unlike the situation for molybdenum complexes, the k_1 values for the iron compounds can be obtained only with some difficulty and with moderate accuracy because of the fact that the limiting k_{obs} is reached at high, and inaccessible, concentrations of ligand. For this reason we sought an alternative means of evaluating k_1 and have based our work on a unique variation of the carbon monoxide insertion reaction observed by Nicholas, Raghu and Rosenblum [4] for the complex, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2Cy)]$, in dimethylsulfoxide solution.

The variation involves the direct observation of a solvated species, which formally corresponds to the hitherto undetected 'intermediate' in the general reaction scheme, *i.e.*

$$[(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2Cy)] + DMSO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COCH_2Cy)].$$

This solvation stage of the reaction can be carried out separately, yielding an equilibrium constant, and individual values of k_1 and k_{-1}. The subsequent reaction of the solvated species with triphenylphosphine gives the rate constant k_2 for the second order process;

$$[(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COCH_2Cy)] + PPh_3 \xrightarrow{k_2} [(\eta^5\text{-}C_5H_5)(Ph_3P)(CO)Fe(COCH_2Cy)] + + DMSO$$

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*No reprints available.

**Author to whom all correspondence should be addressed.

TABLE I. Rate and Equilibrium Constants for Reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ Complexes at 29 °C.

R	K	$10^6\ k_1$ (s^{-1})	$10^6\ k_{-1}$ (s^{-1})	$10^6\ k_2$ $(l\ mol^{-1}\ s^{-1})$
Me	0.075	1.5	20	–
Et	0.54	21.8	40.3	35
^{n}Pr	0.42	19.4	46.3	–
^{n}Bu	0.40	17.6	43.9	94
^{n}Hexyl	0.41	18.8	45.7	–
^{n}Octyl	0.41	18.8	45.7	–
^{i}Bu	1.00	91	91	136
$CyCH_2$	1.16	75.1	64.7	–
Me_3SiCH_2	0.25	103	414	751
^{i}Pr	2.35	277	118	–
^{s}Bu	3.4	780	220	420
Me_3CCH_2	4.6	910	200	330
$(Me_3Si)_2CH$	1.15	very large	very large	24000

The reactions thus conveniently allow for the separate measurement of k_1, k_{-1} and k_2. These separate rate constants, when substituted in the kinetic expression

$$k_{obs} = \frac{k_1k_2[L]}{(k_{-1} + k_2[L])}$$

established for the overall ligand-induced carbonyl insertions in polar solvents with a steady-state concentration of intermediate, gave a value which agreed closely with that measured for the direct reaction of triphenylphosphine with the cyclohexylmethyl-iron complex in dimethylsulfoxide [4].

In our study, we were interested in exploring the generality of this reaction for a variety of alkyl-iron complexes, and, given this, in assessing substituent effects on the three rate constants involved. It should be noted that, for the molybdenum system, in acetonitrile and other polar solvents, only k_1 and the ratio k_{-1}/k_2 are accessible.

Results and Discussion

The formation of DMSO-solvated iron acyl complexes was found to occur for a wide variety of alkyl substituents (see Table I). In fact the only compounds which failed to give an observable reaction were the benzyl (including activated *p*-methoxybenzyl) systems, which is compatible with the generally noted lower reactivity of benzyl compared with methyl substituents in this reaction [5]. The reactions were essentially clean, except for the formation of small amounts of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$ in the case of the more thermally unstable alkyls, and were unaffected by light and the presence of the free-radical inhibitor, 1,1′-diphenylpicrylhydrazyl.

Kinetic comparisons of reactivity with dimethylsulfoxide were conveniently studied at 29 °C, at which temperature a reasonable compromise between overall reaction rate and the equilibrium constant, (decreasing with increasing temperature), for the first stage of reaction was obtained. The reactions were monitored by a ^{1}H NMR method [4]; the formation of the solvated species, $[(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COR)]$, was followed by the appearance of a singlet cyclopentadienyl resonance (observed as a doublet for ^{s}Bu because of the presence of diastereoisomers) at around 4.7 ppm, relative to the disappearing cyclopentadienyl resonance for the starting material at around 5.0 ppm. The second stage of reaction, corresponding to the replacement of DMSO in the acyl complex by triphenylphosphine, was studied by the addition of an approximately 50% molar amount of the phosphine to the equilibrium mixture and was monitored, again by ^{1}H NMR, by the appearance of a cyclopentadienyl doublet ($J_{^{31}P-^1H} \sim 1$ Hz) at around 4.3 ppm. The kinetic analysis used is summarised in the Experimental section; in the case of the calculation of k_2, a modification of the method described earlier [4] was employed which took account of the changing concentration of the solvated acyl complex throughout the reaction.

The kinetic results at 29 °C are shown in Table I. For R = $(Me_3Si)_2CH$, the k_1 and k_{-1} values could not be obtained as the reaction reached equilibrium within the time of mixing. The effect of the substituent is most clearly seen in the values of k_1, where there is an approximately 200-fold difference between the fastest measurable reaction (Me_3CCH_2) and the slowest (Me), compared with k_{-1} (a 16-fold difference for the same substituents) and k_2. Such observations give strong support to the traditional reaction scheme [3] in which substantial breaking of a metal–carbon bond has occurred in a three-centre transition state leading to the formation of the intermediate, which in this case is the DMSO-solvated acyl complex. The interpretation of the reactivity order in k_1, [$(Me_3Si)_2CH \gg Me_3CCH_2 > {}^sBu > {}^iPr > Me_3SiCH_2 > CyCH_2 > {}^iBu > Et > {}^nPr \sim {}^nBu \sim {}^nHexyl \sim {}^nOctyl > Me$], must involve both steric and electronic factors. With respect to the latter, a naive interpretation of the trends, *e.g.* ${}^sBu > {}^iPr$, $Me_3CCH_2 > Et$, ${}^sBu > {}^iBu$, in keeping with our observation [1] of electronic enhancement of reactivity in substituted molybdenum-benzyl compounds in acetonitrile, might simply occur in terms of increased substitution of weakly electron-donating substituents at either the α- or β-carbon in the substituent. However, there is considerable controversy surrounding the interpretation of such electronic effects, which, in a recent report [6], were claimed to be essentially constant. Our feeling is that the results can more reasonably be evaluated on steric grounds. The reactivity order correlates with intuitive feeling of size of the alkyl groups, and with substituent parameters of such groups which reflect 'front strain' effects [7], *i.e.* the steric repulsion associated with the attacking or leaving group in a reaction. The explanation on steric grounds allows, for example, for the interpretation of the higher reactivity of Me_3CCH_2 over Me_3SiCH_2 in terms of the longer Si–C, compared with the C–C bond, which would result in a relatively reduced steric influence for Me_3SiCH_2. The results suggest that enhancement of reactivity could be substantially associated with the relief of steric strain in the three-centre transition state, as the metal–alkyl bond becomes longer and partially broken.

Although previous studies of alkyl substituent effects have been limited in scope, similar trends have been observed; for example, for [$(\eta^5\text{-}C_5H_5)(CO)_3MoR$] and triphenylphosphine in acetonitrile, a reactivity order, $Et > Me > PhCH_2$, was noted [5], for [$(CO)_5MnR$] with carbon monoxide in 2,2'-diethoxydiethylether, ${}^nPr > Et > Me > PhCH_2$ [8]; and for [$(\eta^5\text{-}C_5H_5)(CO)_2FeR$] and triphenylphosphine in acetonitrile, ${}^iPr > Et > Me$ [2]. The preferential insertion of carbon monoxide into the $ZrCH(SiMe_3)_2$ rather than the Zr–Me bond in the complex, [$(\eta^5\text{-}C_5H_5)_2ZrMe(CH(SiMe_3)_2)$], albeit to give an η^2-acyl product [9], is also compatible with our observations.

The observed alkyl substituent effect series has practical relevance to the hydroformylation reaction in which there is a high preference, particularly for the catalyst, [$(Ph_3P)_3Rh(CO)H$] [10], for the formation of a linear product alcohol. The various factors which affect product distribution have recently been summarised [11]. We believe that our observations, which show that carbonylation of a secondary carbon centre (leading to a branched chain product) is favoured over a primary centre (linear chain), indicate that the reactivity preference in the hydroformylation process is being expressed at an earlier stage of reaction, and perhaps in the steps which involve the coordination of olefin and/or its reaction to produce a metal-alkyl species. In a similar manner, our reactivity series may lend support to the interpretation [12] of steric preference in asymmetric hydroformylation, where the induction was concluded to take place during the formation of the diastereomeric alkyl complexes.

TABLE II. Variation of k_1 with Temperature for [$(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2Cy)$] Reaction with DMSO.

Temp (°C)	$10^6\ k_1\ (s^{-1})$
25	45.9
29	75.1
34	190
35	217
40	332
45	752
46	840
50	903

The equilibrium constants associated with the formation of the DMSO-solvated acyl complex also show a substantial variation with alkyl substituent which is generally in line with the trend in k_1. However, the low value for Me_3SiCH_2 is striking and defies interpretation. To our knowledge, the only other series of equilibrium constants for acyl formation are those of Baird and co-workers [13] for the reaction, in $CDCl_3$ at 25 °C,

$$[RhRCl_2(CO)(PPh_3)_2] \rightleftharpoons [RhCl_2(COR)(PPh_3)_2].$$

For this system, for R = Me, K had a value of 3.5, but for Et, ${}^nPr$ and $PhCH_2$ was greater than 50 (*i.e.* alkyl complex was undetectable).

Our experimental observations are useful for evaluating a recent theoretical study [14] on the relative reactivity of simple primary alkyl ligands towards carbonyl insertion in the [$(CO)_5MnR$] system. The calculated activation energies (Me, 0.85 eV; Et, 0.66 eV; ${}^nPr$, 0.64 eV), together with estimates of entropies of activation, which were assumed to decrease with increasing chain length, were used to derive a plot of the variation of the free energy of activation for the insertion process. The analysis predicted a significant increase in reactivity from

TABLE III. Thermodynamic and Kinetic Parameters for Reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ with DMSO.

R	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
Me	99.6	−26.8	−30.1	−121
Et	107.1	19.3	−39.8	−121
^{n}Pr	115.1	45.6	−32.6	−117
^{n}Bu	110.9	33.9	−39.3	−138
^{i}Pr	94.6	2.5	−36.0	−105
$CyCH_2$	106.3	28.5	−37.2	−121
Me_3CCH_2	95.4	20.1	−31.8	−92

TABLE IV. Solvent Effects on k_1 for Reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2Cy)]$ at 37 °C.

	10^5 k_1 (s^{-1})	Taft π Parameter	Solvent Donicity
DMSO	21.0	1.00	29.8
CH_3CN	13.3	0.86	14.1
THF	6.1	0.58	20.0

methyl to ethyl to n-propyl ~ n-butyl, followed by a steadily decreasing reactivity at longer chain lengths. Our experimental results partly support this conclusion. The k_1 values certainly increase significantly from methyl to ethyl and, although uncertainties in measurement are relatively large, perhaps show a slight decrease thereafter.

We attempted to provide a better evaluation of the theory by obtaining separate values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ by measurements over a range of temperatures (which was severely restricted by the freezing point of DMSO and by the onset of thermal decomposition of the metal alkyls at around 45 °C). Some representative reactivity data (k_1) are shown in Table II. The same general reactivity trend for the several straight chain alkyls was observed at all temperatures. The calculated $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for straight chain, and other, alkyl substituents are given in Table III. Experimental uncertainties, particularly in $\Delta S^\ddagger$, are high, and, not surprisingly, swamped the necessarily (on the basis of relative k_1 values) small differences between the alkyl substituents. The average $\Delta H^\ddagger$ value, for all substituents, is around 104 ± 8 kJ mol^{-1} and $\Delta S^\ddagger$ (calculated at 302 K) around 17 ± 24 J K^{-1} mol^{-1}. These values agree quite well with those observed ($\Delta H^\ddagger$, 109 kJ mol^{-1}; $\Delta S^\ddagger$, −16 J K^{-1} mol^{-1}) by earlier workers [15] for the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2FeMe]$ with $^nBu_3P$ in tetrahydrofuran. However, our results suggest that the large variation of $\Delta H^\ddagger$ with substituent which was claimed [2] for the reaction of several iron alkyls, $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$, with triphenylphosphine in acetonitrile, is unlikely. (Our attempted recalculation of these values, which was hindered by our inability to calculate meaningful k_1 values from the experimental data presented, gave very substantially different results and huge uncertainties. We believe that the $\Delta H^\ddagger$ values, and the large negative $\Delta S^\ddagger$ values, should be treated with caution).

Values of ΔH° and ΔS° for the formation of the solvated acyl complex were also calculated from the temperature variation in K. Again, experimental uncertainties swamp any possible trends, and probably only the average values (ΔH°, −35 ± 4 kJ mol^{-1}, ΔS°, −117 ± 12 J K^{-1} mol^{-1}) are of significance.

The observation of a solvent-stabilised 'intermediate' acyl compound in the reactions of the iron alkyls with triphenylphosphine in dimethylsulfoxide is pertinent to the vexed question as to the degree of involvement of polar solvents in the first stage of the insertion process. For evaluative purposes, we have measured k_1 values (by the extrapolation method) for the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2Cy)]$ with triphenylphosphine in acetonitrile and tetrahydrofuran. These results, together with the k_1 value in dimethylsulfoxide at the same temperature, are shown in Table IV. The values correlate with the Taft π scale of generalised solvent polarities [16], although not with the enthalpy-derived solvent donicity scale [17]. The solvent effects show a similar, if less marked, trend to those for molybdenum complexes in corresponding reactions [1]. Although the theoretical analysis [14] of the insertion reaction suggests that solvent molecules may stabilise the intermediate, but not the transition state, we believe that the experimental results generally are compatible with the concept [3] of a solvent-assisted process.

Experimental

General

All preparative and kinetic work was carried out under nitrogen using Schlenk methods. The following solvents were distilled under nitrogen, immediately prior to use, from the drying agents noted: tetrahydrofuran and hexane (calcium hydride), acetonitrile (Merck "Sicapent"). Dimethylsulfoxide-d_6 was dried over molecular sieve 4A, degassed and stored under nitrogen. Infrared spectra were recorded on a PE457 spectrophotometer. Proton NMR spectra for kinetic runs were run on a Jeol PS100 spectrometer, and routine spectra on a Varian EM360 spectrometer.

Preparation of $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ *Complexes*

The preparation of the iron alkyl complexes was unexceptional and followed the existing procedure [18]. Crude product was purified by column chromatography (alumina, grade II/III, in hexane) followed by crystallisation from cooled hexane (for the solids, R = CH_2Cy and $(Me_3Si)_2CH$) or by short path distillation (~50–60°/10^{-2} mm).

Kinetic Studies

The reactions of iron-alkyl compounds with d_6-DMSO were carried out in evacuated NMR tubes at a substrate concentration of 0.25 *M*. The disappearance of the cyclopentadienyl resonance of the reactant at around 5.0 ppm, and the appearance of the cyclopentadienyl resonance of the product, $[(\eta^5\text{-}C_5H_5)(DMSO)(CO)Fe(COR)]$, at around 4.7 ppm was monitored by the peak height method until the establishment of equilibrium. The first order rate constant for the reaction ($k = k_1 + k_{-1}$) was obtained by the standard method [19], namely a plot of ln $(A_o - A_e/A_t - A_e)$ *versus* time, where A_o, A_e and A_t refer to the concentrations of the iron alkyl complex initially, at equilibrium, and at time, t. Application of $K = k_1/k_{-1}$ gave the individual values of the forward and reverse rate constants. The measurement of k_2 was carried out by the addition of an approximately 50% molar amount of triphenylphosphine to an equilibrated mixture of iron alkyl and dimethylsulfoxide, and was monitored by the appearance of the cyclopentadienyl doublet ($J_{^{31}P-^{1}H} \sim 1$ Hz) at around 4.3 ppm and the disappearance of the cyclopentadienyl resonances of the alkyl and solvated acyl complexes. Experimental observation showed that the rate of the second order substitution of triphenylphosphine was slow compared with the re-establishment of the solvation equilibrium. Accordingly, if the initial concentration of triphenylphosphine is p_o, of the iron alkyl a_o, and the concentration of the phosphine substituted acyl product at time t is x_t, it can be shown that a second order process will give a linear plot of $[1/(a_o - p_o)]\ln[p_o(a_o - x_t)/a_o(p_o - x_t)]$ *versus* time, of gradient $k_2K/(K + 1)$. As the value of K has been obtained previously, the k_2 value could be calculated. Temperature control was achieved in thermostatted water baths (±0.05 °C) for slower reactions, or in the thermostatted NMR probe (±0.5 °C). Apportionment of errors is difficult for the style of analysis carried out and is necessarily variable from experiment to experiment. Generally K values should be regarded as accurate to ±5%, and the linear least squares error in the overall rate constant (*i.e.* $k_1 + k_{-1}$) for the first reaction stage as ±5% and in k_2 ±10%. The significance of the k_1 values are probably best gauged by the reproducibility of measurement which would give errors of around ±5% at 29 °C and ±10% at 40 °C *e.g.* in the straight chain alkyl series. Values of k_1 in acetonitrile and tetrahydrofuran were obtained at 0.02 *M* substrate concentration using the infrared technique [1].

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