may be obtained by using the $k_{cat.}$ (40 s^{-1}) for phenyl benzoate under the same conditions. This calculation gives $K_m = 9.8 \times 10^{-5}$ M.

The pH dependence of $k_{cat.}/K_m$ is not pure sigmoidal, but shows clear evidence for the involvement of a group, active in the free base form whose $pK_a' \approx 5.0$.[15]

Thus this work also provides the first example of the catalysis of carbon-carbon bond cleavage by the carboxylesterases.[16]

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(8) Spectral data obtained with $[E]_0 > [I]_0$: ϵ_{252} for ethyl phenylglyoxylate is 6600; in the presence of an excess of enzyme, ϵ_{252}, extrapolated to zero time, is 1560; the absorbance increases in a first-order reaction to a final ϵ_{252} of 13 100, in good agreement with ϵ_{252} for phenylglyoxylate ion (13 200).
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$$k_{obsd} = k_{-OH}[^-OH] + (k_{Tris} + k_b[^-OH])[K_a'/(K_a' + H_3O^+)][Tris]$$

where $k_{-OH} = 707\ M^{-1} s^{-1}$, $k_{Tris} = 0.126_4\ M^{-1} s^{-1}$, $k_b = 1.01 \times 10^4\ M^{-2} s^{-1}$, and the pK_a' of Tris H^+ = 8.55 (kinetically determined).
(14) The maximum solubility of I in this system is ~2.5 × 10^{-6} M in the absence of enzyme.
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Hydrogenation of α-Methylstyrene by Hydridopentacarbonylmanganese(I). Evidence for a Free-Radical Mechanism

Sir:

Recent developments in organo transition metal chemistry have accorded an increasingly important and widespread role to free radical mechanisms.[1] It has been suggested, for example, that the hydrogenation of arenes and alkenes, catalyzed by metal carbonyl hydrides, may proceed through mechanisms in which intermediate free radicals are formed by H-atom transfer from the metal hydride to the substrate.[2] We now wish to present convincing evidence for such a mechanism in the case of at least one reaction, the hydrogenation of α-methylstyrene by hydridopentacarbonylmanganese(I) (eq 1). This evidence encompasses one of the only definitive applications to date of the CIDNP technique to the elucidation of the mechanism of a reaction involving a transition metal complex.

$$C_6H_5C(CH_3){=}CH_2 + 2HMn(CO)_5 \rightarrow C_6H_5CH(CH_3)_2 + Mn_2(CO)_{10} \quad (1)$$

Reaction 1 was found to proceed quantitatively (confirmed by NMR, UV spectroscopy, and GLC) in benzene solution at rates conveniently measurable in the temperature range 40–75 °C. Kinetic measurements, in which the concentrations of $C_6H_5C(CH)_3{=}CH_2$, $C_6H_5CH(CH_3)_2$, and $HMn(CO)_5$ all were monitored by NMR, yielded the second-order rate law, eq 2, with values of (2.65 ± 0.12) × 10^{-5}, (9.0 ± 1.0) × 10^{-5}, and (20.0 ± 1.4) × 10^{-5} $M^{-1} s^{-1}$ for k' at 45.0, 56.2, and 64.5 °C, respectively, corresponding to $\Delta H^{\ddagger} = 21.4 \pm 0.3$ kcal mol^{-1} and $\Delta S^* = -12 \pm 1$ cal $mol^{-1} K^{-1}$.[3] The kinetic results are consistent with the following mechanism (eq 3–5) for which more direct evidence is presented below and according to which $k' = k_3k'_3/(k_{-3} + k'_3)$.[4]

$$-d[C_6H_5C(CH_3){=}CH_2]/dt = k'[C_6H_5C(CH_3){=}CH_2][HMn(CO)_5] \quad (2)$$

$$C_6H_5C(CH_3){=}CH_2 + HMn(CO)_5 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \overline{C_6H_5\dot{C}(CH_3)_2, \dot{M}n(CO)_5} \xrightarrow{k'_3} C_6H_5\dot{C}(CH_3) + \dot{M}n(CO)_5 \quad (3)$$

$$C_6H_5\dot{C}(CH_3)_2 + HMn(CO)_5 \xrightarrow{fast} C_6H_5CH(CH_3)_2 + \dot{M}n(CO)_5 \quad (4)$$

$$2\dot{M}n(CO)_5 \xrightarrow{fast} Mn_2(CO)_{10} \quad (5)$$

Definitive evidence for the proposed free-radical mechanism is provided by the observation of CIDNP effects when the reaction was followed at ~70 °C in the probe of a 60-MHz NMR spectrometer. This is illustrated by the series of stacked spectra in Figure 1, taken at ~75-s intervals over the 90-min duration of a typical reaction. The proton signals of both reactants, i.e., α-methylstyrene and $HMn(CO)_5$, as well as the product 2-phenylpropane, all exhibit polarization. The polarization of the doublet signal at 1.1 ppm due to the methyl protons of $C_6H_5CH(CH_3)_2$, which is observed in emission during the initial stages of reaction, is particularly striking. Analysis of the signal intensities (see below) also reveals polarization of the signals at 5.3, 5.0, and 2.0 ppm due to the two β and the methyl protons of $C_6H_5C(CH_3){=}CH_2$, respectively, as well as the proton signal of $HMn(CO)_5$ (at −7.9 ppm, not shown in Figure 1).

The CIDNP effects can be interpreted in terms of the generally accepted "radical-pair" mechanism[6] involving competition between the back-reaction of the geminate radical pair $\overline{C_6H_5\dot{C}(CH_3)_2, \dot{M}n(CO)_5}$ produced in reaction 3 to re-form the reactants, and the separation (cage escape) of the radicals with ultimate formation of products via reactions 4 and 5. Observations on the corresponding reaction of $C\dot{o}(CN)_5^{3-}$ (which is isoelectronic with $\dot{M}n(CO)_5$) suggest that both reactions (−3 and 4) are very fast as required by the proposed interpretation.[7-9] No species, other than the reactants and products of eq 1 were detected during the course of the reactions. In particular, there was no evidence for the intermediate accumulation of detectable quantities of the cage-combination product, $(C_6H_5)(CH_3)_2CMn(CO)_5$. This compound has not

Table I. CIDNP Data for the Reaction of $HMn(CO)_5$ (1.25 M) with $C_6H_5C(CH_3){=}CH_2$ (0.24 M) at 70 °C

Proton signal (*)	T_1,[a] s	$10^4k'$, $M^{-1}\,s^{-1}$	Arbitrary units α	Arbitrary units β	Enhancement[b]
$C_6H_5CH(CH_3{*})_2$	5.2	3.5	−3920	11.0	$(-3.6 \pm 0.5) \times 10^2$
$C_6H_5C(CH_3{*}){=}CH_2$	6.9	3.8	1360	5.5[c]	$(2.5 \pm 0.4) \times 10^2$
$C_6H_5C(CH_3){=}CH_2{*}$	9.2	3.7	444	1.86[c]	$(2.4 \pm 0.4) \times 10^2$
	8.1	3.7	430	1.86[c]	$(2.3 \times 0.4) \times 10^2$
$*HMn(CO)_5$	3.0	3.8[c]	1200	1.85	$(6.3 \pm 2.5) \times 10^2$

[a] T_1 values were determined by the inversion recovery method under the same conditions as the reaction. [b] Enhancement = $(\alpha - \beta)/\beta$. [c] This parameter was fixed to obtain a reasonable convergence.

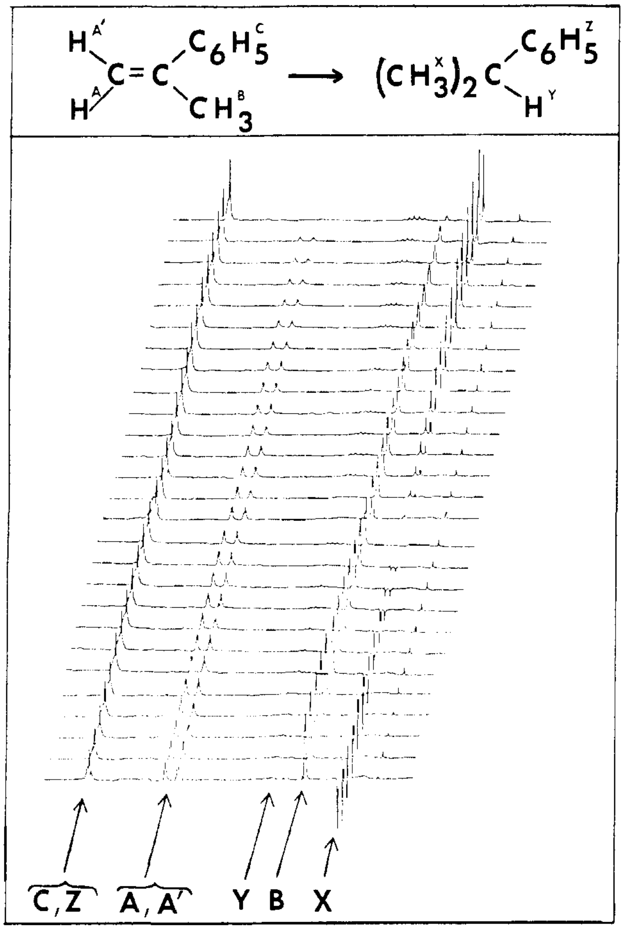

Figure 1. Stacked plot of spectra taken during reaction in the 70 °C probe of a 60-MHz, TT-14 spectrometer (1.31 M $HMn(CO)_5$, 0.17 M α-methylstyrene). The lower left spectrum was taken approximately 50 s after heating of the sample was begun. The first 20 spectra are separated by 75-s intervals. Each spectrum was transformed from four accumulated free induction decays, separated by 4 s (30° tip angle).

been reported in the literature and is expected to be unstable to decomposition via Mn-C bond homolysis under the conditions of our reaction.

The NMR enhancements associated with the CIDNP effect were calculated by fitting the intensity data to equations derived from the Bloch equation modified to account for the initial production of nonequilibrium magnetization by the chemical reaction and for the time dependence (reflecting the concentration dependence) of the equilibrium magnetization, M_0. The form of the Bloch equation for the product, $C_6H_5CH(CH_3)_2$, yielded by this treatment, is given by eq 6 where M_z is the magnetization along the magnetic field axis, α and β are the NMR absorption coefficients of newly formed and equilibrated product, respectively, T_1 is the spin-lattice relaxation time and M_0 is $\beta[C_6H_5CH(CH_3)_2]$.

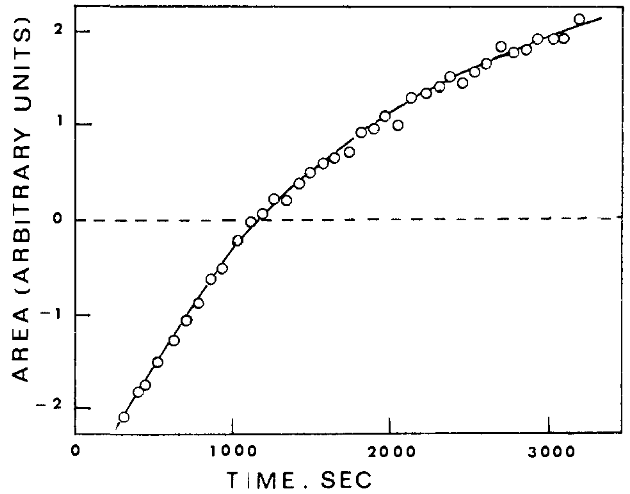

Figure 2. Time dependence of the intensity of the CH_3 doublet (1.1 ppm) of the $C_6H_5CH(CH_3)_2$ product during the reaction of $C_6H_5C(CH_3){=}CH_2$ with $HMn(CO)_5$ (initially 0.22 and 2.28 M, respectively) at 70 °C. The circles represent experimental values while the solid curve is calculated from eq 6 according to the procedure described in the text.

$$dM_z/dt = \alpha k'[C_6H_5C(CH_3){=}CH_2][HMn(CO)_5] - (M_z - M_0)/T_1 \quad (6)$$

Equation 6 was integrated according to a procedure appropriate for accumulated pulsed Fourier transform NMR measurements in a manner related to the treatment of Poranski et al.[12] The resulting calculated time-dependent intensity equation was fitted to the observed data by means of a nonlinear least-squares procedure, using independently determined T_1 values to yield optimum values of the other three parameters, α, β, and k'. Typical results of this treatment are presented in Figure 2 and in Table I which also lists the results of corresponding treatments for several of the reactant proton signals. Very similar results were obtained for another experiment with different initial reactant concentrations (2.28 M $HMn(CO)_5$, 0.22 M α-methylstyrene). Convincing support for the proposed interpretation and treatment is provided by (i) the excellent agreement between the calculated and experimental time-dependent intensities exemplified by Figure 2, (ii) the agreement of the values of k' in Table I, yielded by the above fitting procedure, with the independently determined experimental values (i.e., at 70 °C, $k'_{exp} = 3.8 \times 10^{-4}\ M^{-1}\,s^{-1}$), and (iii) the approximate constancy (within the relatively large uncertainties involved in the determinations) of the enhancements computed for the several reactant and product proton signals. Furthermore, the magnitude of the enhancement, ~300, is sufficiently large to support the view that the proposed free-radical mechanism is indeed a major reaction pathway.

From the polarizations and the assumption of a singlet precursor, it follows that g for $\dot{M}n(CO)_5$ is larger than that for the $C_6H_5\dot{C}(CH_3)_2$ radical. While a reliable g value for $\dot{M}n(CO)_5$ (which has been detected in matrices) has not been reported, g_{iso} for a related isoelectronic Mn(0) complex, bis(1,3-butadiene)carbonylmanganese(0), has been reported to be 2.018.[13] A similar value for $Mn(CO)_5$ would be consistent with the observed CIDNP effects.

Further support for the proposed mechanism is provided by the following observations. (1) When $DMn(CO)_5$ was reacted with $C_6H_5C(CH_3){=}CH_2$, the formation of products was accompanied by isotopic exchange, reflected in the accumulation of $HMn(CO)_5$ and a decrease in the intensity of the CH_3 signal of the unreacted $C_6H_5C(CH_3){=}CH_2$, resulting from deuterium incorporation. This exchange is in accord with the requirement of reversibility of step 3 of the proposed mechanism. The extent of the observed exchange suggests that $k_{-3}/k_3' \gtrsim 1$. (2) The rate constant for the reaction of $DMn(CO)_5$ with $C_6H_5C(CH_3){=}CH_2$ was found to be larger than that for $HMn(CO)_5$ ($k_H'/k_D' \sim 0.4$ at 65 °C). In view of the very low initial frequency of the Mn-H bond ($\sim$1800 cm^{-1}) relative to that of the C-H bond ($\sim$3000 cm^{-1}), such an inverse isotope effect is not unexpected and has indeed been anticipated.[14] Similar inverse isotope effects also have been observed recently in related reactions of $HCo(CO)_4$[15] and $HMn(CO)_5$[16] with arenes.

Qualitatively similar CIDNP effects were observed for the corresponding reaction of $HMn(CO)_5$ with styrene, although the NMR spectra in this case were considerably more complex and have not yet been interpreted in detail. In the case of the reaction of styrene, the NMR spectra did reveal the transient formation in low concentrations of the organometallic coupling product, $C_6H_5CH(CH_3)Mn(CO)_5$. It remains to be established whether this species is associated with the principal reaction pathway or with a minor path.

Finally, we note that although CIDNP effects have been reported for a variety of reactions involving organometallic and coordination compounds, the mechanistic interpretations of these have been incomplete, particularly with respect to the role of the metal species.[17,18] We believe this to be the first definitive demonstration of a CIDNP effect to arise from a reaction in which one of the geminate radical pair is an inorganic metal-centered complex.

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Role of Transition Metal–Dioxygen Complexes in Catalytic Oxidation. Catalysis of the Oxidation of Phosphines by Dioxygen Adducts of Platinum

Sir:

The chemistry of dioxygen adducts of transition metals has been the subject of intensive research in recent years[1] from several standpoints including the *possible* roles of such adducts in catalytic oxidation.[2-6] Several examples have been reported of the catalytic oxidation of organic substrates in the presence of metal–dioxygen adducts or of metal complexes which may form such adducts, but the mechanistic features of these systems have not been elucidated and at least in some cases it appears that free-radical, rather than "molecular", mechanisms are operative.[3,4,7] We report here the detailed elucidation of the mechanism of one class of reactions involving intermediate metal–dioxygen adducts, namely the oxidation of tertiary phosphines catalyzed by platinum(0) phosphine complexes.[8-10]

We have previously demonstrated that the catalysis of the oxidation of PPh_3 to Ph_3PO by $Pt(PPh_3)_3$ proceeds through the following reaction sequence in which the dioxygen adduct $Pt(PPh_3)_2(O_2)$ is an intermediate.[9,10]

$$Pt(PPh_3)_3 + O_2 \rightarrow Pt(PPh_3)_2(O_2) + PPh_3 \qquad (1)$$

$$\underline{Pt(PPh_3)_2(O_2) + 3PPh_3 \rightarrow Pt(PPh_3)_3 + 2Ph_3PO} \qquad (2)$$

$$2PPh_3 + O_2 \xrightarrow{Pt(PPh_3)_3} 2Ph_3PO \qquad (3)$$

The second-order rate law, $k_1[Pt(PPh_3)_3)_3][O_2]$, found for reaction 1[9,10] is consistent with the expected simple bimolecular displacement mechanism. On the other hand, the second-order rate law found for reaction 2, i.e., $k_2[Pt(PPh_3)_2(O_2)][PPh_3]$, clearly demonstrates that this reaction is a multistep process in which only *one* PPh_3 molecule reacts with $Pt(PPh_3)_2(O_2)$ in the initial rate-determining step, i.e.,

$$Pt(PPh_3)_2(O_2) \xrightarrow[k_2]{PPh_3} [\text{intermediate(s)}] \xrightarrow[\text{fast}]{2PPh_3} Pt(PPh_3)_3 + 2Ph_3PO \qquad (4)$$

Various mechanistic schemes for the reaction sequence 4 have been proposed, all involving transfer of *coordinated* oxygen either to coordinated or free phosphines.[9-13] However, these suggestions have not thus far been tested since, unfortunately, the intermediate stages in the reaction sequence 4 could not be detected and characterized, apparently because all subsequent steps are fast relative to the initial one (k_2). As detailed below, we have now successfully accomplished this by invoking the following approaches: (i) using the more reactive phosphines $PMePh_2$ and PMe_2Ph, in place of PPh_3, to increase the rate of the first step (k_2) relative to the subsequent stages and thereby achieving the accumulation of higher steady-state concentrations of the reaction intermediates; (ii) lowering the temperature to increase the lifetime of the reaction intermediates and thus to permit their detection; and (iii)