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CIDNP EVIDENCE FOR RADICAL INTERMEDIATES IN THE HYDROFORMYLATION AND REDUCTION OF STYRENE BY $HCo(CO)_4/CO$ *

T. MICHAEL BOCKMAN, JOHN F. GARST *, R. BRUCE KING,
Department of Chemistry, The University of Georgia, Athens, Georgia 30602 (U.S.A.)

LÁSZLÓ MARKÓ and FERENC UNGVÁRY *
Institute of Organic Chemistry, University of Chemical Engineering, H-8200 Veszprém (Hungary)

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Summary

Reactions of styrene with $HCo(CO)_4$ in CH_2Cl_2, CD_2Cl_2 and C_6D_6 give ethylbenzene, 2-phenylpropanal, and probably 2-phenylpropanoylcobalt tetracarbonyl with nuclear spin polarizations consistent with formation through initially singlet radical pairs $[Ph\dot{C}HCH_3\ {}^{\bullet}Co(CO)_4]$. This is the first report of CIDNP in a hydroformylation product.

Reactions of styrene with $HCo(CO)_4$ give ethylbenzene (I) and 2-phenylpropanal (IV) with nuclear spin polarization (Fig. 1a,b). Other polarized product signals are assigned tentatively to 2-phenylpropanoylcobalt tetracarbonyl (III) (Fig. 1a). The observed polarizations are consistent with origins in initially singlet radical pairs $[Ph\dot{C}HCH_3\ {}^{\bullet}Co(CO)_4]$ and the mechanism of Scheme 1.

This is the first report of CIDNP in a hydroformylation product of any reaction. The only previously reported $HCo(CO)_4$-alkene reaction giving CIDNP is that of 1,1-diphenylethylene, which gives a reduction product only [1,2]. Related reactions for which CIDNP has been reported include those of $HMn(CO)_5$ with α-methylstyrene (reduction only) and styrene (products not reported) [3], of $HMn(CO)_5$ with 3,3-dimethyl-1,2-diphenylcyclopropene (CIDNP in reduction product and one assigned tentatively as an alkylmanganese pentacarbonyl) [4], and of several trinuclear alkylidyne cobalt complexes $Co_3(CO)_9CCH_2R$ with H_2 [5].

For the $HCo(CO)_4$-styrene reaction, Scheme 1 has been supported previously only by analogies [1–4,6,7] and kinetics [8,9], which are not discriminatory tests for

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* This paper is dedicated to Professor Jack Halpern on the occasion of his 60th birthday.

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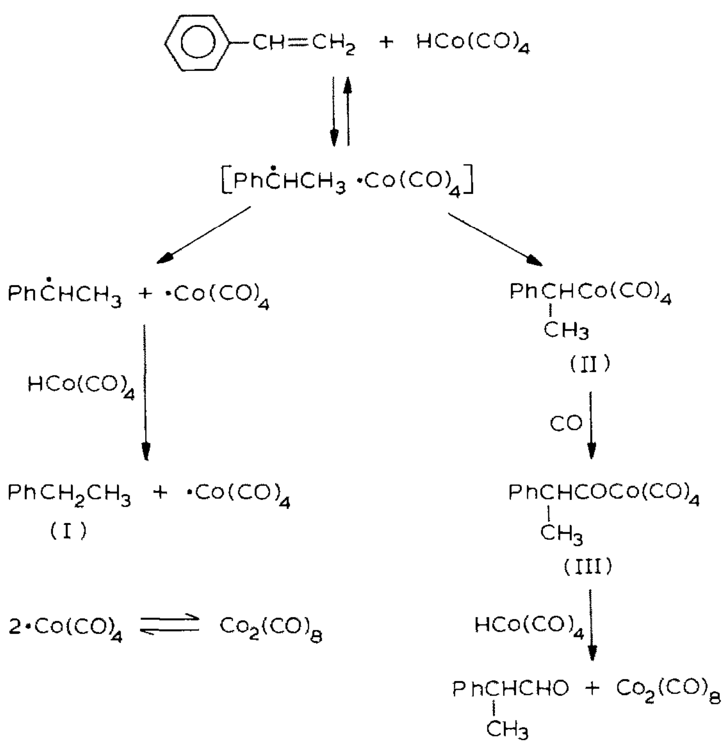

SCHEME 1

radical intermediates. CIDNP implies radical-pair precursors for those products in which it is observed. It is compelling evidence in the sense that no alternative explanation for CIDNP is considered to be viable [10]. The combination of CIDNP and the viscosity effect on the product distribution [11], both predicted by Scheme 1 and fundamental principles, make it clear that hydroformylations (as well as reductions) of arylalkenes by $HCo(CO)_4$ can occur through radical-pair processes. The viscosity effect suggests that there are intermediate molecular pairs that can suffer mutual reaction or diffusive escape; CIDNP identifies these as radical pairs.

NMR tubes containing about 0.5–0.8 ml of 0.2–0.8 *M* $HCo(CO)_4$ in CO-saturated CH_2Cl_2, CD_2Cl_2, or C_6D_6, prepared as described previously [12], were kept in a dry ice/acetone bath. For each experiment, a tube was withdrawn and styrene (10–100 μl, saturated with CO) was injected by syringe. The tube was shaken vigorously and inserted into the probe (ca. 35 °C) of a Varian EM-390 NMR spectrometer (90 MHz; 21 100 gauss). The region of interest was scanned repeatedly at the fastest rate consistent with acceptable resolution (Fig. 1). When C_6D_6 was the solvent, the $HCo(CO)_4$ solution was allowed to melt (near room temperature) before injecting the styrene. The addition of a large amount of $Co_2(CO)_8$ to the reaction mixture had no discernible effect on the CIDNP in ethylbenzene.

$HCo(CO)_4$-styrene reactions are very fast at room temperature and above, being essentially complete in two minutes or less. Consistent with the report of Ungváry and Markó [8], the proton NMR spectra revealed only the branched aldehyde, 2-phenylpropanal; no straight-chain aldehyde, 3-phenylpropanal, was detected at short reaction times (2 min). As determined from the NMR spectra, the ratio of yields of ethylbenzene and carbonylation products (2-phenylpropanal and 2-phenylpropanoylcobalt tetracarbonyl) is about 0.7, similar to those found by Ungváry and Markó [8].

Emissive signals were found for the methyl protons in ethylbenzene (t; δ 1.16 ppm in CH_2Cl_2, 1.04 ppm in C_6D_6), the methine proton in 2-phenylpropanal (q; δ 3.57 ppm in CD_2Cl_2, 3.02 ppm in C_6D_6), and a multiplet at δ 4.2 ppm in C_6D_6. A quartet at δ 4.2 ppm is present in product solutions from reactions of 2-phenylpropanoyl chloride with $NaCo(CO)_4$ in C_6D_6. Therefore it and the emission at δ 4.2 ppm are assigned tentatively to the methine proton of 2-phenylpropanoylcobalt tetracarbonyl.

Because the observed polarizations are very weak, and the normal signals of products being formed are absorptions, it is difficult to detect enhanced absorption with certainty. However, the signal (q; δ 2.55 ppm in CH_2Cl_2, 2.40 ppm in C_6D_6) of the methylene protons of ethylbenzene was found to grow to a maximum, then decrease, in several runs. Since ethylbenzene is believed to be inert under the reaction conditions, we assign this effect to enhanced absorption and its decay by relaxation.

The polarizations appear as pure net effects. Their phases are those predicted by the radical-pair theory of CIDNP [10,13] and Scheme 1. A multiplet effect would be expected if Δg were not large, but Δg for $[Ph\dot{C}HCH_3\ {}^{\cdot}Co(CO)_4]$ is very large, 0.0860 (for ${}^{\cdot}Co(CO)_4$ $g = 2.0886$ [14]; for hydrocarbon π radicals such as $Ph\dot{C}HCH_3$, $g = 2.0026$), so the multiplet effect is "swamped" by the net effect. Similar net polarizations in ethylbenzene are found when the reagent is $DCo(CO)_4$, the methyl group appearing as a doublet and the methylene as a triplet, both poorly resolved. Deuterium NMR spectra reveal that the β protons of excess styrene are deuterated.

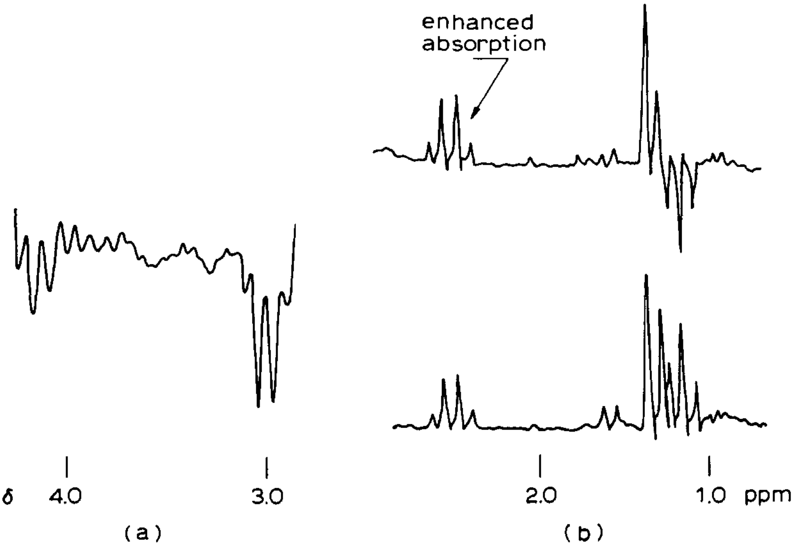

Fig. 1. NMR spectra of reaction mixtures, $HCo(CO)_4$/styrene. (a) Solvent C_6D_6, 25 s following reactant mixing. $[HCo(CO)_4]_0$ 0.81 *M*. [styrene]$_0$ 0.79 *M*. (b) Solvent CH_2Cl_2, 85 (top) and 222 (bottom) s following reactant mixing. $[HCo(CO)_4]_0$ 0.33 *M*. [styrene]$_0$ 0.79 *M*.

The β proton exchange suggests that radical pair formation is rapidly reversible. Similar exchange was reported for related reactions [2,5].

While a qualitative CIDNP observation, such as ours, demands a radical pathway as a component of the reaction mechanism, that component could be a minor reaction pathway. Therefore our results must be combined with other evidence to build a strong case for the mechanism of Scheme 1 as the major reaction path.

The weakness of the observed CIDNP is not itself evidence that it arises through a minor pathway. Weak CIDNP is expected from generating radical pairs with very large values of Δg. The intensity of CIDNP diminishes as $\beta H \Delta g$ becomes much larger than the electron-nuclear coupling of the nucleus under observation. CIDNP depends on nuclear-spin-dependent electronic singlet-triplet transitions of the radical pairs ("intersystem crossings", ISC). The Δg mechanism for ISC is a nuclear-spin-independent pathway that dilutes CIDNP when its contribution is very large. In addition, after more than one minute, some runs in C_6D_6 show the kind of line-broadened deterioration of the NMR spectra that would be expected if paramagnetic species were present. Paramagnetic species greatly enhance proton spin-lattice relaxation times, causing polarization to disappear rapidly. In view of these factors, it might be considered remarkable that any CIDNP can be detected from $HCo(CO)_4$-styrene reactions.

According to the interpretation above, CIDNP in acylcobalt tetracarbonyl III and aldehyde IV is carried over from alkylcobalt tetracarbonyl II through two subsequent reaction steps. This requires that these steps be very fast. It is conceivable that one or both of these steps could occur through intermediate radical pairs. The observed CIDNP is accounted by Scheme I, without considering radical intermediates not shown therein.

CIDNP was observed also from reactions of $HCo(CO)_4$ with 3- and 4-methyl- and 3- and 4-chlorostyrenes, suggesting that there is no change in mechanism with these substituent changes. Thus, the kinetic influences of these substituents should be interpreted in terms of a radical mechanism.

Preliminary experiments show CIDNP from reactions of $HCo(CO)_4$ with methyl methacrylate and from the reaction of $HFe(CO)_3B_3H_8$ [15] with styrene. The latter is the first example of a reaction of an iron hydride giving CIDNP [16].

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