High-Resolution Rhodium-103 Nuclear Magnetic Resonance Spectra of $Rh[(C_6H_5)_3P]_2COCl$ and $Rh[(C_6H_5)_3P]_3Cl$

Sir:

This note describes the first application of a double-resonance "tickling" experiment[1] to the problem of determining rhodium chemical shifts. Several years ago this technique was shown to be useful in determining ^{129}Xe chemical shifts in the various xenon fluorides,[2] measurements which would be very difficult to obtain by traditional methods. Recent experiments on phosphine-platinum complexes have indicated that transition metal chemical shifts can be very sensitive to the extent of π bonding to the central atom.[3,4] Also, the phosphorus nmr spectra of several phosphine-rhodium complexes have previously been reported;[5] however, in addition to obtaining rhodium chemical shifts, the present experiments allow a determination of the relative signs of the various rhodium-phosphorus and phosphorus-phosphorus coupling constants.

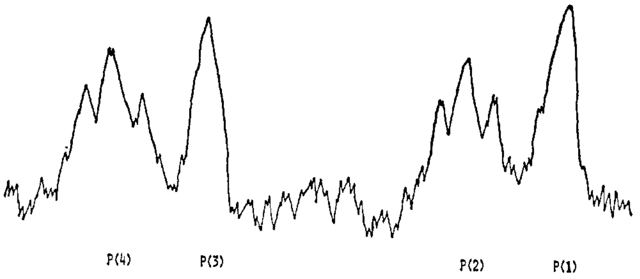

Figure 1. High-field ^{31}P quartet in $Rh[(C_6H_5)_3P]_3Cl$ with simultaneous irradiation of the ^{103}Rh transition at 2.844125 MHz.

The low natural sensitivity of the ^{103}Rh nucleus ($I = {}^1/_2$, abundance = 100%) due to its small magnetic moment, in addition to problems of relaxation times, makes its detection by standard techniques difficult. However, in the double-resonance "tickling" experiment,[1] the lines in the rhodium spectrum are irradiated with a small radiofrequency field while simultaneously observing another nucleus to which it is coupled, in this case phosphorus. The phosphorus spectra were obtained from saturated solutions in 13-mm spinning sample tubes *vs.* an external P_4O_6 reference, with a Bruker 90-MHz frequency-sweep spectrometer. The rhodium frequencies were provided by a phase-locked Schomandl frequency synthesizer. Because of the low solubility of these complexes, an additional radiofrequency field was applied to simultaneously decouple the phenyl protons, to increase the signal-to-noise ratio of the phosphorus lines, and to improve resolution. The phosphorus frequencies are reported for a field strength such that the proton signal from TMS falls exactly at 90 MHz.

After proton decoupling the phosphorus spectrum of the compound $Rh[(C_6H_5)_3P]_3Cl$ in methylene chloride consists of a high-field quartet (labeled P_1) due to the *trans*-phosphorus atoms split first by the rhodium atom and then by the *cis*-phosphorus atom, and a pair of low-field triplets (labeled P_2) due to the *cis*-phosphorus atom. The corresponding rhodium spectrum is predicted to consist of two overlapping triplets separated by $J(Rh-P_2)$. As illustrated in Figure 1 as well as in Table I the highest field line in the rhodium spectrum is connected to lines 2 and 4 in the P_1 spectrum; from the energy-level diagram this establishes that $J(Rh-P_1)$ and $J(Rh-P_2)$ have the same sign. Similarly, the highest field line in the rhodium spectrum is also connected to lines 7 and 10 in the P_2 spectrum, and this establishes the sign relationship between $J(Rh-P_1)$ and $J(P_1-Rh-P_2)$.

Table I. Connected Transitions Observed by Double Resonance in the Nmr Spectrum of $Rh[(C_6H_5)_3P]_3Cl$

^{103}Rh line irradiated[a]	Irradiating[b] frequency, MHz	Connected ^{31}P line	Observing frequency, MHz
Rh(1)	2.844125	P(2)	36,433,777
		P(4)	36,433,919
		P(7)	36,434,375
		P(10)	36,434,564
Rh(6)	2.844598	P(1)	36,433,739
		P(3)	36,433,881
		P(5)	36,434,299
		P(8)	36,434,488

[a] Numbered for each nucleus in the order of decreasing magnetic field strength. [b] Reported for each nucleus at a field strength such that TMS falls exactly at 90 MHz.

Studies of phosphine complexes of platinum(II)[6] have shown that the sign of J(Pt-P) is positive when referred to the presumably known sign of the proton-proton coupling in the ethyl groups directly bonded to the phosphorus atom. For the purposes of assigning appropriate signs to the coupling constants in this work, we assume that the reduced coupling constants[7] K(Pt-P) and K(Rh-P) have the same sign, *i.e.*, are positive. Since the magnetic moment of the rhodium nucleus is negative while those of platinum and phosphorus are positive, we arrive at the signs of the coupling constants given in Table II, *i.e.*, that $J(Rh-P_1)$, $J(Rh-P_2)$, and $J(P_1-Rh-P_2)$ are all negative.

Table II. Coupling Constants and Chemical Shifts for Rhodium-Phosphine Compounds

	$Rh[(C_6H_5)_3P]_3Cl$	$Rh[(C_6H_5)_3P]_2COCl$
$J(Rh-P_1)$, Hz	−142[a]	−124[a]
$J(Rh-P_2)$, Hz	−189	...
$J(P_1-Rh-P_2)$, Hz	−38	...
$\delta(P_1)$, ppm, *vs.* H_3PO_4	−31.5[b]	−29.1
$\delta(P_2)$, ppm, *vs.* H_3PO_4	−48.0	...
δ(Rh), ppm, *vs.* Rh metal	−1499	−1211

[a] For the absolute sign convention, see text. [b] The chemical shifts are calculated according to the equation $\delta(X)$, ppm = $(H_s - H_r)/H_r \times 10^6$ where H_s and H_r are the resonant magnetic fields for the sample and reference, respectively.

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(1) R. Freeman and D. H. Whiffen, *Mol. Phys.*, 4, 321 (1961).

(2) (a) T. H. Brown, E. B. Whipple, and P. H. Verdier, *Science*, 140, 178 (1963); (b) *J. Chem. Phys.*, 38, 3029 (1963); (c) in "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963.

(3) W. McFarlane, *Chem. Commun.*, 7, 393 (1968).

(4) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, *A*, 1970 (1968).

(5) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Letters*, 2, 205 (1966).

(6) W. McFarlance, *J. Chem. Soc.*, *A*, 1922 (1967).

(7) J. A. Pople and D. P. Santry, *Mol. Phys.*, 8, 1 (1964).

The phosphorus spectrum of the compound *trans*-Rh[$(C_6H_5)_3P]_2$COCl in chloroform, after proton decoupling, consists of a doublet split by J(Rh-P). Both lines in the phosphorus spectrum are equally perturbed into triplets by irradiation at rhodium frequencies of 2.843420 and 2.843668 MHz and into doublets at a frequency of 2.843544 MHz. This confirms that the rhodium spectrum consists of the expected 1:2:1 triplet and gives the rhodium chemical shift directly.

The rhodium chemical shifts listed in Table II are arbitrarily reported relative to the resonance frequency of rhodium metal which was reported *vs.* D_2O.[8] This frequency (2.840104 MHz) has been calculated for a field strength such that TMS falls directly at 90 MHz by measuring the chemical shift of D_2O from TMS. A detailed discussion of the rhodium chemical shifts will be presented when additional compounds have been studied.

[8] P. B. Sogo and C. D. Jeffries, *Phys. Rev.*, **98**, 1316 (1955).

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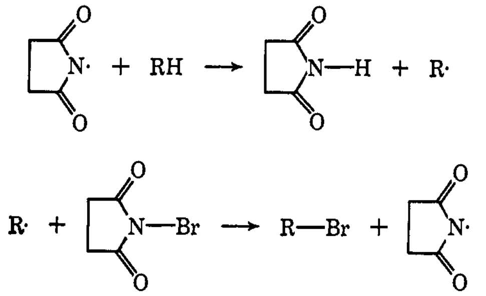
Oxidation of 1-Phenylethanol by the Succinimidyl Radical

Sir:

In 1942 Ziegler[1] first demonstrated the allylic brominating ability of N-bromosuccinimide (NBS). Two years later Bloomfield[2] proposed a radical chain mechanism which involved the succinimidyl radical in a chain-carrying sequence.



Goldfinger[3] in 1953 proposed an alternative mechanism whereby the chain-propagating step involved a bromine atom as the hydrogen-abstracting species rather than the succinimidyl radical. Bromine was formed in the reaction mixture by the reaction of NBS with traces of HBr in the reaction mixture.

$$\text{Br}\cdot + \text{RH} \longrightarrow \text{HBr} + \text{R}\cdot$$

$$\text{R}\cdot + \text{Br}_2 \longrightarrow \text{RBr} + \text{Br}\cdot$$

A series of articles[4] appeared in 1963 giving experimental evidence that supported the proposal of Goldfinger. For example, Russell[4b] studied competitive photobromination of aralkyl hydrocarbons by NBS and molecular bromine, and both reactions appeared to involve the bromine atom as the hydrogen-abstracting species.

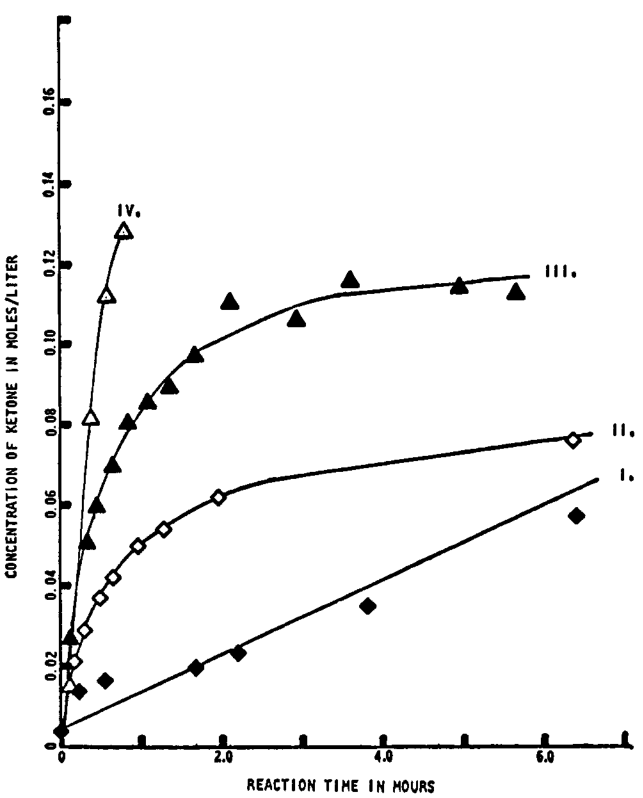


Figure 1. Rates of oxidation of 1-phenylethanol by NIS in benzene at reflux. All rates are with 0.004 mol (0.4 *M*) of alcohol and 0.002 mol of NIS: (I) chloranil inhibited; (II) benzoyl peroxide initiated; (III) benzoyl peroxide initiated, with silver acetate present; (IV) irradiated, with silver acetate present.

To our knowledge evidence for the involvement of the succinimidyl radical in chain-propagating steps as a species capable of abstracting hydrogen atoms has not been demonstrated. In fact, when N-iodosuccinimide (NIS) was heated[5] at reflux with toluene in CCl_4 in the presence of benzoyl peroxide and strong light no radical reactivity was found.

We wish to report a set of experiments to establish the ability of the succinimidyl radical to propagate a radical chain reaction. We have investigated the oxidation of 1-phenylethanol to acetophenone with N-iodosuccinimide (NIS) in dry benzene at reflux. Using 0.002 mol of NIS and 0.004 mol of 1-phenylethanol in all runs but varying reaction conditions we obtained four different ketone formation rates. Reactions III and IV (see Figure 1) were initiated with 1 mol % benzoyl peroxide and tungsten light, respectively, and both reactions showed very fast initial rates as compared with reaction 1 which was inhibited with 5 mol % chloranil. This suggests that the oxidation of the alcohol in runs III and IV was a radical-chain reaction. In runs III and IV silver acetate was used to prevent the hydrogen iodide product from reacting with the NIS to form molecular iodine. No iodine color was observed in these reactions.

In runs I and II no silver acetate was used and an immediate iodine color appeared. This iodine formation consumed NIS and should result in lower yields

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[1] K. Ziegler, A. Spaeta, E. Schaaf, W. Schumann, and E. Winkelman, *Ann.*, **551**, 80 (1942).

[2] C. F. Bloomfield, *J. Chem. Soc.*, 14 (1944).

[3] J. Adams, P. A. Gosselain, and P. Goldfinger, *Nature*, **171**, 704 (1953); *Bull. Soc. Chim. Belges*, **65**, 533 (1956).

[4] (a) C. Walling and A. L. Rieger, *J. Am. Chem. Soc.*, **85**, 3134 (1963); (b) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963); (c) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963).

[5] C. Djerassi and C. T. Lenk, *ibid.*, **75**, 3494 (1953).