

Preliminary communication

DIRECT EXPERIMENTAL EVIDENCE FOR COMPLEX FORMATION BETWEEN $\text{RhH}(\text{PPh}_3)_4$ AND ALCOHOLS IN BENZENE SOLUTION

D. BEAUPERE, P. BAUER*, L. NADJO and R. UZAN

Laboratoire de Chimie Organique Physique, Université d'Amiens (France)

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Summary

An IR spectroscopic study has shown that a range of alcohols form complexes with $\text{RhH}(\text{PPh}_3)_4$ in benzene and relevant equilibrium constants are given.

Much effort has been devoted during recent years to the study of transfer hydrogenation of an acceptor, e.g. a ketone, by a donor, for example an alcohol, catalyzed by Rh [1], Ru [2] or Ir [3] complexes. Usually, the explanations of the results assume the intermediate formation of complexes between the catalysts and the donors. Some suggestions have been made about the nature of the association [1,2,4], but to the best of our knowledge no direct evidence for such complexes has been presented, despite the importance of the matter for the complete elucidation of the transfer hydrogenation mechanism. We describe below the observation of the complex between a Rh catalyst and alcohol donors, and present equilibrium constants for the association. The catalyst complex we used was $\text{RhH}(\text{PPh}_3)_4$.

1-Phenylethanol (2×10^{-2} M) in benzene has an IR spectrum with a $\nu(\text{OH})$ band at 3588 cm^{-1} (this value is different from that obtained in CCl_4 solution (3619 cm^{-1}) and indicates that there is some association between the alcohol and benzene). Introduction of $\text{RhH}(\text{PPh}_3)_4$ (2×10^{-2} M) leads to a rapid decrease of the intensity of the $\nu(\text{OH})$ band at 3588 cm^{-1} with concomitant appearance of a strong band at 3355 cm^{-1} (Fig. 1). There is also a slow build-up of a small concentration (up to 10%) of acetophenone, as indicated by the appearance of the characteristic CO band at 1688 cm^{-1} .

In Table 1 are shown the results of an IR spectroscopic study of a series of alcohols in benzene. For each alcohol the concentration was varied over the

*ITODYS, Université de Paris VII.

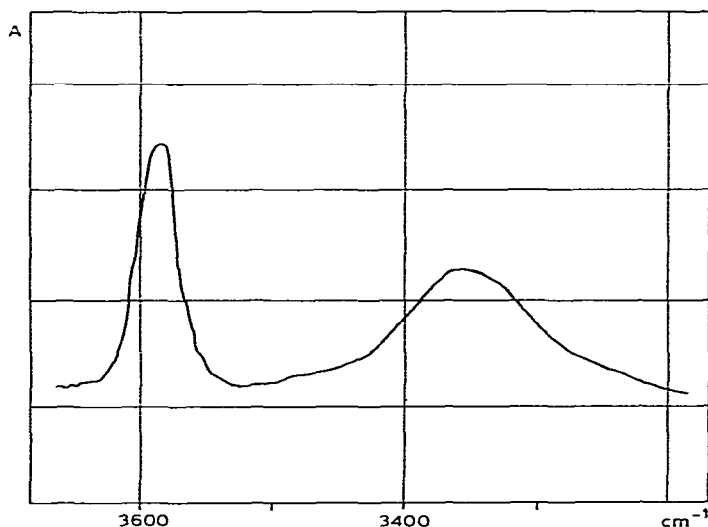


Fig. 1. Infrared spectrum of a benzene solution of $\text{RhH(PPh}_3)_4$ ($2 \times 10^{-2} M$) and PhCHOHCH_3 ($4 \times 10^{-2} M$).

TABLE 1

INFRARED DATA AND K VALUES FOR Alcohol- $\text{RhH(PPh}_3)_4$ COMPLEXES

$[\text{RhH(PPh}_3)_4] 2 \times 10^{-2} M$; $10^{-2} M \leq [\text{alcohol}] \leq 4 \times 10^{-2} M$; $30 \pm 1^\circ \text{C}$ in C_6H_6 under Argon; K values $\pm 15\%$.

Alcohol	$\nu(\text{OH})$ alcohol (cm^{-1})	$\nu(\text{OH})$ complex (cm^{-1})	K ($\text{mole}^{-1} \text{ l}$)	
			a	b
PhCHOHCH_3	3588	3355	13.5	11.1
PhCH_2OH	3592	3362	9	8
$4\text{-OMePhCH}_2\text{OH}$	3590	3364	14.2	12.4
$4\text{-NO}_2\text{PhCH}_2\text{OH}$	3592	3322	62	52
PhCHOH-t-Bu	3590	3350	2.9	2.9
$\text{CH}_3\text{CHOHCH}_3$	3598	3392	5.6	5.1

a Assuming that the ketone is completely complexed with the catalyst. b Assuming that no complex is formed between the ketone and the catalyst.

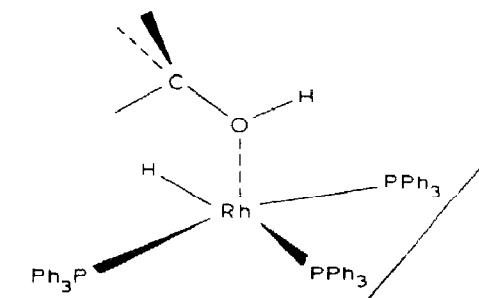
range $10^{-2} M$ to $4 \times 10^{-2} M$, with the catalyst concentration being maintained at $2 \times 10^{-2} M$. Kinetic results described in one of our previous [1c] papers indicated that complexation of the catalyst with the acceptors (namely ketones) is also very likely. Thus determination of the association constant between the alcohols and the catalyst requires use of the previous knowledge of the partial complexation of the catalyst by the ketone formed, for example by acetophenone formed from 1-phenylethanol. Taking this case as an example we observed no change in the CO band intensity of a benzene solution of acetophenone, without or with catalyst. There are several possible explanations of this observation; e.g. the complex between the ketone and the catalyst may have a band falling in the same region as the free CO band, with similar ϵ .

values, or the concentration of the complex may be very low and its ϵ values small, so that any new band has too low an intensity to be detected. Calculations have thus been based on the two extreme hypotheses: (i) that the ketone formed is completely associated with the catalyst, or (ii) that the association with the catalyst can be neglected. In the first case the association constant between the catalyst and the alcohol varies in the range 13.5 to 2.9, depending on the nature of the alcohol. On the second hypothesis, the range is from 11.1 to 2.9, except that 4-NO₂C₆H₄CH₂OH gives an anomalously high value. On either hypothesis the maximum error in the association constant is less than 20%.

The very small association constant obtained for PhCHOH-*t*-Bu reveals the importance of steric effects in the complexation, and in this case no ketone formation is observed on the IR spectrum, probably due to the low value of the association constant. In the case of *p*-nitrobenzyl alcohol, the strong complexation ($52 \leq K \leq 62$) cannot be attributed solely to electronic effects because, comparison of 1-phenylethanol and its *p*-MeO derivative shows that the electronic effect of the methoxy group is weak and causes an increase of only 10% in the K value. Further work on this feature is in progress.

An NMR study of benzene solutions of the catalyst RhH(PPh₃)₄ shows, in the light of results obtained by Dewhurst et al. [5] that the catalyst is present as RhH(PPh₃)₃. Furthermore, introduction of 1-phenylethanol causes no variation in the doublet from the hydrogen initially attached to the catalyst (δ -8.16 ppm, J 12.7 Hz) and the signal for the hydroxylic proton is shifted to lower fields. An NMR study shows the build up of acetophenone.

Scheme 1 shows a possible representation of the complex between alcohol and catalyst.



Spectroscopic results, associated with the fact that phenoxide formation results from the complexation of phenol by RhH(PPh₃)₃ [5,6], indicate that the alcohols are probably associated with the catalyst by interaction of the lone pair of the OH group with the rhodium atom. This hypothesis is consistent with the fact that RhH(PPh₃)₄ has a planar structure [7]. Our NMR study revealed no evidence for the trihydride catalyst postulated by Imai et al. [1a] nor did we find any evidence for insertion of Rh between O and H as described by Sharf et al. [4].

Further studies of the transfer hydrogenation reactions are in progress.

References

- 1 (a) H. Imai, T. Nishiguchi and K. Fukuzumi, *J. Org. Chem.*, **39** (1974) 1622;
(b) B. Heil, S. Törös, J. Bakos and L. Markó, *J. Organometal. Chem.*, **175** (1979) 229;
(c) D. Beaupère, P. Bauer and R. Uzan, *Can. J. Chem.*, **57** (1979) 218;
(d) D. Beaupère, L. Nadjó, R. Uzan and P. Bauer, *J. Mol. Catal.*, **14** (1982) 129.
- 2 (a) Y. Sasson and J. Blum, *J. Org. Chem.*, **40** (1975) 1887;
(b) W. Smadja, G. Ville and C. Georgoulis, *J. Chem. Soc., Chem. Commun.*, (1980) 594.
- 3 (a) G. Mestroni, G. Zassinovich, A. Camus and F. Martinelli, *J. Organometal. Chem.*, **148** (1980) 87;
(b) Y.M.Y. Haddad, H.B. Henbest, J. Husband, T.R.B. Mitchell and J. Trocha-Grimshaw, *J. Chem. Soc. Perkin I*, (1974) 596.
- 4 V.Z. Sharf, L.Kh. Freidlin and V.N. Krutii, *Bull. Acad. Sci. USSR*, **26** (1977) 666.
- 5 K.C. Dewhirst, W. Keim and C.A. Reilly, *J. Org. Chem.*, **7** (1968) 546.
- 6 W. Keim, *J. Organometal. Chem.*, **8** (1967) 25.
- 7 S.H. Strauss, S.E. Diamond, F. Mares and D.F. Shriver, *Inorg. Chem.*, **17** (1978) 306.