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Acidic Property of Rh and Ru Complexes

Yuan Kou,† Nobuo Yamada, Susumu Akutagawa,* Geng Zhang,†† and Kozo Tanabe*,††
Takasago Research Institute, Inc., 5-38-31, Kamata, Ohta-ku, Tokyo 144
† Lanzoh Institute of Chemical Physics, Lanzoh, China
†† Department of Chemistry, Hokkaido University, Sapporo 060

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The acidic property of [Rh(nbd)(dppb)]ClO_4, [Ru(binap)]$(BF_4)_2$, and [Ru(dmso)$_6$]$(ClO_4)_2$ was measured by using the acetalization of cyclohexanone as a test reaction and the temperature-programmed desorption [TPD] of pyridine. The acid strengths were estimated to be $H_0=-2.1$ for [Ru(dmso)$_6$]$(ClO_4)_2$ and $H_0=-2.2$ for [Ru(binap)]$(BF_4)_2$ and [Rh(nbd)(dppb)]ClO_4 by the test reaction method. The TPD method gave consistent results.

Metal complexes are known to be active and highly selective as catalysts for diversified reactions. For the hydroformylation of camphene, rhodium phosphine complexes, such as $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$, have been reported to be active as catalysts,[1,2] the latter being highly selective in the formation of the aldehyde. We recently found that [1,4-bis(diphenylphosphino)butane](η^4-norbornadiene)rhodium perchlorate[3] (abbreviated to [Rh(nbd)(dppb)]ClO_4), [2,2′-bis[bis(4-methylphenyl)phosphino]-1,1′-binaphthyl]ruthenium bis(tetrafluoroborate)[4] (abbreviated to [Ru(binap)]$(BF_4)_2$), and hexakis(dimethyl sulfoxide)ruthenium diperchlorate[5] (abbreviated to [Ru(dmso)$_6$]$(ClO_4)_2$) showed high catalytic activities for the hydroformylation reaction, the selectivity being different depending on the metal complexes.[6] In order to elucidate the role of the acidic property of the metal complexes regarding catalytic activity and selectivity, the present work was initiated.

Since no study has been made concerning the acidic property of Rh and Ru complexes, a measurement of the acidic property was attempted in the present work. Acidity measurements involving the indicator method, which was applied to uncolored samples;[7] the IR method, which was applied to metal halides by Cook;[8] and the NMR method, which was applied to boron compounds by Pasto and Balasubramaniyan,[9] were found to be unsuccessful in our catalyst system. Therefore, a kinetic method using acetalization of cyclohexanone which is known to be catalyzed by acids and the TPD method were employed in the present research.

Experimental

[Rh(nbd)(dppd)]ClO_4, [Ru(binap)]$(BF_4)_2$, and [Ru(dmso)$_6$]$(ClO_4)_2$ were prepared according to methods described in literature.[3–5] Cyclohexanone and methanol were purified by distillation. Organic acids used as reference catalysts, bases used in the TPD measurement, and indicators used for measuring the acid strength were commercially available and of guaranteed reagent grade. A SiO_2 used as a reference substance in the TPD experiment was Fuji-Davison Type ID.

The acetalization of 37.4 mmol of cyclohexanone in 50 ml of methanol was carried out at 40 °C under a dry nitrogen atmosphere with rapid stirring after 0.01 mmol of the catalyst was added. The products were analyzed by gas chromatography (Shimadzu GC-9A).

The tempeprature-programmed desorption (TPD) experiment was performed as follows. The metal complex catalyst was transferred to an adsorption tube in a dry nitrogen stream and evacuated at room temperature to 1.33×10^{-2} Pa, and then subjected to a TPD run. The TPD background of the sample, itself, was measured at a temperature-increase rate of 5 °C min^{-1}. The relative amounts of desorbed gases were determined as the peak height relative to that of Ar as an internal standard.

The TPD profiles of adsorbed ammonia, pyridine, and triethylamine were obtained by adsorbing ammonia (6.66×10^3 Pa) for 15 min, pyridine (1.33×10^3 Pa) for 10 min, and triethylamine (2.67×10^3 Pa) for 15 min at room temperature on a new sample, respectively, evacuating them at room temperature and desorbing at elevated temperatures at a temperature-increase rate of 5 °C min^{-1}. In the case of an SiO_2 sample evacuated at 600 °C for 2 h, TPD of pyridine was obtained similarly to that mentioned above.

The acid strength of SiO_2 used as a reference substance was estimated by observing the color change of a Hammett indicator adsorbed on the solid sample.[4] The indicators used were *p*-dimethylaminobenzene ($pK_a=+3.3$) and 4-(phenylazo)diphenylamine ($pK_a=+1.5$).

Results and Discussion

Acidic Property by Acetalization. The negative values of the logarithm (p*k*) of the first-order rate constant (*k*) with respect to the concentration of cyclohexanone for acetalization of cyclohexanone with methanol were plotted against the pK_a values[10] of various organic acids used as catalysts. As shown in Fig. 1, an almost straight line was obtained between the p*k* values and the pK_a values. Since the p*k* values obtained in cases of [Ru(dmso)$_6$]$(ClO_4)_2$, [Ru(binap)]$(BF_4)_2$, and [Rh(nbd)(dppb)]ClO_4 are 4.67, 4.70, and 4.70, respepctively, the acid strengths ($H_0\simeq pK_a$) of the metal complexes are estimated to be −2.1, −2.2, and −2.2 from the straight line.

Acidic Property by TPD. Fig. 2 shows some main peaks of the TPD profile of Rh[(nbd)(dppb)]ClO_4, itself, as background. The fact that the desorption

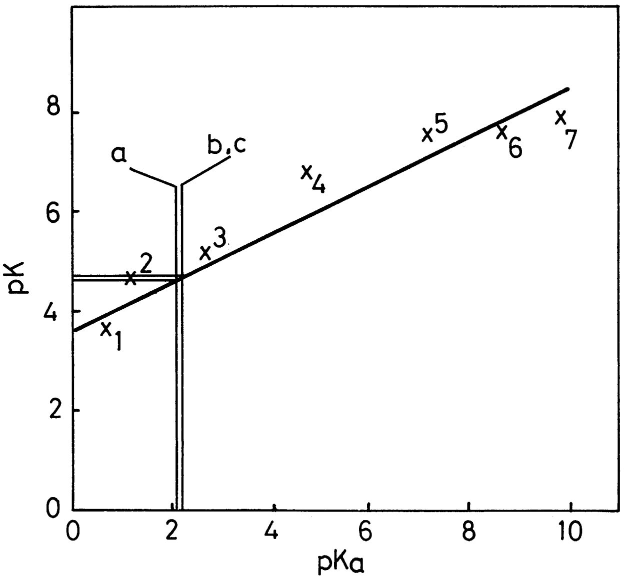

Fig. 1. Relation between the first-order rate constants (p*k*) for acetalization of cyclohexanone in organic acids and their acid strengths (pK_a). (1) trichloroacetic acid; (2) dichloroacetic acid; (3) bromoacetic acid; (4) acetic acid; (5) *o*-nitrophenol; (6) *p*-chlorophenol; (7) phenol; (a) [Ru(dmso)$_6$](ClO$_4$)$_2$; (b) [Rh(nbd)(dppb)]ClO$_4$; (c) [Ru(binap)](BF$_4$)$_2$.

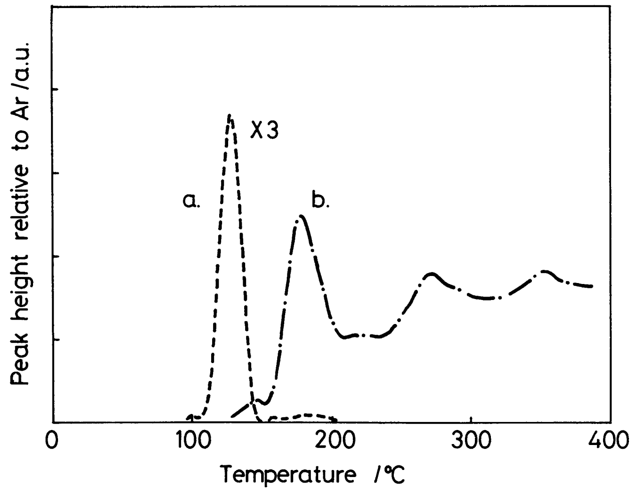

Fig. 2. Temperature programmed decomposition of [Rh(nbd)(dppb)]ClO$_4$. (a) m/z=42; (b) m/z=78.

peak of m/z=42 appeared at 129 °C is considered to be due to a fragment, cyclopropylium ion, formed by the decomposition of dppb, while the peak of m/z=78 appearing at 189 °C seems to be fragments ($C_6H_6^+$) formd by the decomposition of nbd.

The TPD profile of pyridine adsorbed on Rh[(nbd)(dppb)]ClO$_4$ is shown in Fig. 3. A peak of m/z=79 which did not appear in the background profile, attributed to pyridine was observed at 93 °C. When pyridine was adsorbed, the peak at m/z=42 (the fragments of DPPB) shifted to a lower desorption temperature by 20 °C. This indicates that the bond between dppb and Rh is weakened by pyridine adsorption. In the case of ammonia TOD, no desorption peak was observed as long as the Rh complex did not decompose, probably due to the adsorption of small-size ammonia at strong acid sites where pyridine can not approach. Triethylamine whose acid strength is higher than ammonia did not adsorb on the Rh complex, probably because of its larger steric hindrance.

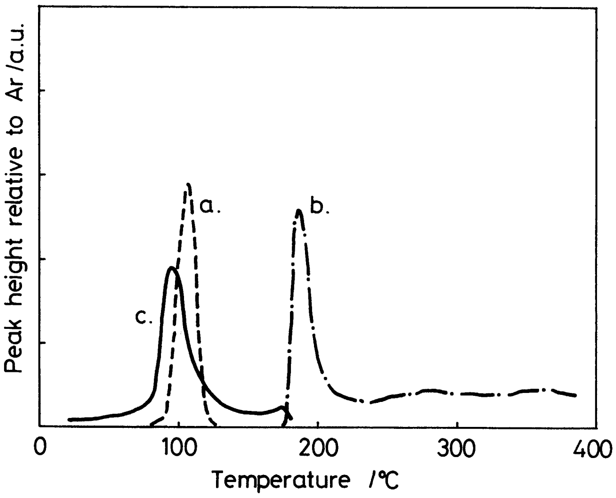

Fig. 3. Temperature programmed desorption of pyridine from [Rh(nbd)(dppb)]ClO$_4$ and temperature programmed decomposition of [Rh(nbd)(dppb)]ClO$_4$ after adsorption of pyridine at room temperature. (a) m/z=42; (b) m/z=78; (c) m/z=79.

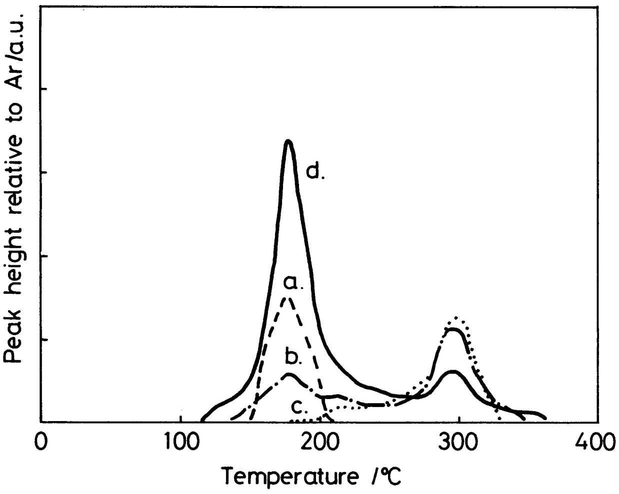

Fig. 4. Temperature programmed decomposition of [Ru(dmso)$_6$](ClO$_4$)$_2$. (a) m/z=63; (b) m/z=35; (c) m/z=52; (d) m/z=79.

The main peaks of the TPD profile of [Ru(dmso)$_6$](ClO$_4$)$_2$, itself a background, are shown by a, b, c, and d in Fig. 4. The peak of m/z=63 at 177 °C is considered due to the fragment (CH_3SO^+) formed by decomposition

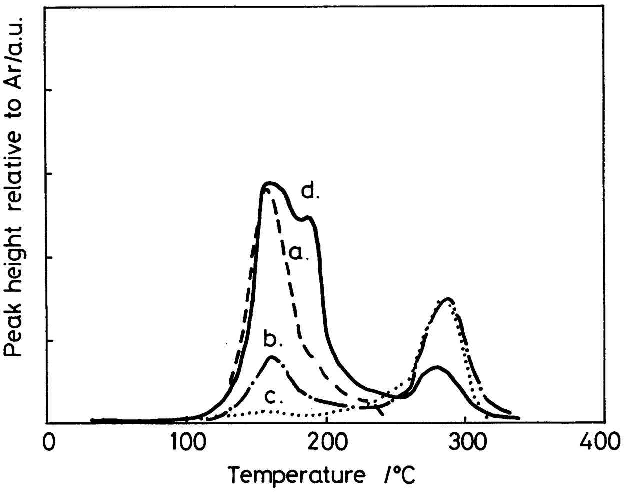

Fig. 5. Temperature programmed desorption of pyridine from $[Ru(dmso)_6](ClO_4)_2$ and temperature programmed decomposition of $[Ru(dmso)_6](ClO_4)_2$ after adsorption of pyridine at room temperature. (a) m/z=63; (b) m/z=35; (c) m/z=52; (d) m/z=79.

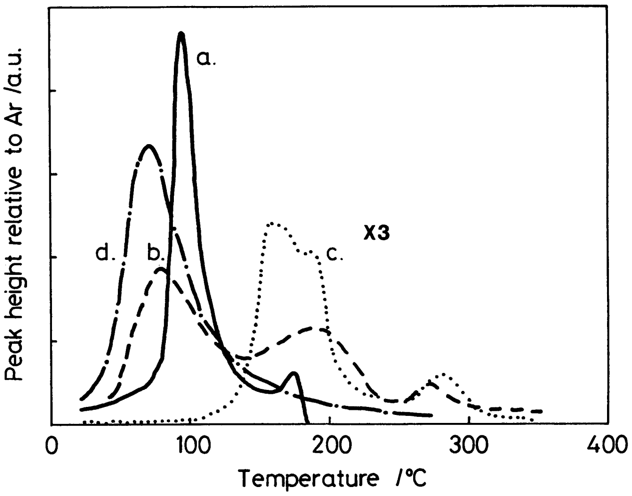

Fig. 6. Temperature programmed desorption of pyridine from (a) $[Rh(nbd)(dppb)]ClO_4$; (b) $[Ru(binap)](BF_4)_2$; (c) $[Ru(dmso)_6](ClO_4)_2$; (d) SiO_2.

of dmso. At 293 °C, the Ru complex is considered to completely decompose, since the peaks of m/z=35 due to the Cl^+ fragment and m/z=52 due to the $HClO^+$ fragment appear. A peak at m/z=79 was also observed in the background. When pyridine was adsorbed on $[Ru(dmso)_6](ClO_4)_2$, a new peak at m/z=79 was observed at 162 °C (Fig. 5); it was assigned to desorbed pyridine by a comparison of Fig. 5 with Fig. 4.

The desorption peak of pyridine (m/z=79) from $[Ru(binap)](BF_4)_2$ appeared at 78, 190, and 268 °C. The decomposition of the complex started at the same temperature, though the TPD profiles are not shown here.

Fig. 6 shows the desorption peaks (a, b, c, and d) of pyridine (m/z=79) adsorbed on $[Rh(nbd)(dppb)]ClO_4$, $[Ru(dmso)_6](ClO_4)_2$, $[Ru(binap)](BF_4)_2$, and SiO_2, respectively. In the temperature range of 70—100 °C, there is no peak of pyridine for $[Ru(dmso)_6](ClO_4)_2$. On the other hand, there is no peak of pyridine for SiO_2 and a relatively small peak was observed for $[Rh(nbd)(dppb)]ClO_4$ in the range of 150—200 °C. In a higher temperature range of 270—300 °C, pyridine desorption peaks were observed only for the Ru complex. Since a material having a higher acid strength shows a higher desorption temperature of pyridine, the order of the acid strength of the metal complexes and SiO_2 is as follows:

$$[Ru(dmso)_6](ClO_4)_2 \simeq [Ru(binap)](BF_4)_2 > [Rh(nbd)(dppb)]ClO_4 \gg SiO_2$$

The highest acid strength of SiO_2 measured by the indicator method was in the range $1.5<H_0<3.3$. Therefore, the fact that the acid strengths of Ru and Rh complexes estimated by TPD method are much stronger than that of SiO_2 is consistent with the result measured by the acetalization method.

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