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Kinetics of protonation of tungsten hydrides $WH(CO)_2(NO)L_2$ by weak OH-acids

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The kinetics of protonation of tungsten hydrides $WH(CO)_2(NO)L_2$ (**1**, L = PMe_3, PEt_3, $P(OPr^i)_3$, PPh_3) by weak OH-acids (PhOH, $(CF_3)_2CHOH$, $(CF_3)_3COH$) in hexane was studied by IR spectroscopy. The study of the reactions of compounds **1** with OH-acids at 190—270 K revealed that the first step involves the formation of dihydrogen-bonded $W(CO)_2(NO)L_2(H)...HOR$ complexes. When the temperature increases to ambient, the proton transfer and evolution of molecular hydrogen occur, affording the final products: organyloxy derivatives $W(OR)(CO)_2(NO)L_2$. The study of the kinetics at 298 K found that the proton transfer is the rate-determining step. The rate constants k_{app} are $2.2 \cdot 10^{-5}$—$6.3 \cdot 10^{-4}$ s^{-1}, and the free activation energies are $\Delta G^{\neq}_{298K}$ = 22—23 kcal mol^{-1}. The rate constants depend on the proton-accepting properties of the hydride and the acidic properties of the OH-proton donor and increase in the same order as the enthalpy of hydrogen bond formation.

Key words: tungsten hydrides, dihydrogen bonds, proton transfer, kinetics, IR spectroscopy.

Protonation of transition metal hydrides is a well known method for the synthesis of cationic dihydrogen complexes. These continue to attract researcher´s interest due to their fundamental significance for catalysis and biochemistry.[1] Using a series of tungsten hydrides $WH(CO)_2(NO)L_2$, we have found[2] for the first time the existence of complexes with an M—H...HX intermolecular hydrogen bond involving the hydride ligand (so-called dihydrogen bonds). It was shown[3] that these hydrogen-bonded complexes are formed in the first step of proton transfer yielding a dihydrogen complex (Scheme 1). The equilibrium and activation thermodynamic parameters of the reaction for a series of hydrides of Groups VI—VIII metals were obtained.[4]

Scheme 1

$$[MH] + HX \rightleftharpoons MH{-}{-}{-}HX \rightleftharpoons [M(\eta^2\text{-}H_2)]^+[X]^-$$

In some cases, the $(\eta^2\text{-}H_2)$-complexes, stable in the presence of weakly coordinating counterions ($X^- = BF_4^-$, PF_6^-), lose hydrogen in the presence of conjugated anions of weaker acids ($X^- = OCOR^-$, OR^-) to form organyloxy derivatives. An example can be found in the earlier studied complexes $[MeC(CH_2CH_2PPh_2)_3]ReH(CO)_2$,[5] $Re(CO)H_2(NO)(PR_3)_2$,[6] and $CpRuH(CO)[P(cyclo\text{-}C_6H_{11})_3]$.[7] The majority of thus synthesized organyloxy complexes were characterized spectrally *in situ*, except for $ReH(OC_6H_4NO_2)(CO)(NO)(PMe_3)_2$ [6] and $[MeC(CH_2CH_2PPh_2)_3]Re(CO)_2(OCOCH_2Cl)$.[5] However, the kinetics of protonation of transition metal hydrides accompanied by H_2 evolution has not been studied earlier.

In this work, we present the results of IR spectroscopic studies of the kinetics of protonation and formation of the organyloxy derivatives for tungsten hydrides $WH(CO)_2(NO)L_2$ (**1**) (L = PMe_3 (**a**), PEt_3 (**b**), $P(OPr^i)_3$ (**c**), PPh_3 (**d**)) reacting with proton-donors of different strength (phenol, fluorinated alcohols) in nonpolar media (hexane, pentane).

Experimental

Hydrides **1** were synthesized as described previously.[8] Solvents (hexane, pentane) were dehydrated by reflux over metallic sodium and distilled under argon atmosphere prior to use. All procedures were carried out under dry argon using the Schlenk technique. IR spectra were measured on a Specord M-82 spectrophotometer using a cryostat (Carl Zeiss Jena), which made it possible to maintain a necessary temperature. The cell thickness was 0.127—1.2 mm, and the cell volume was 0.1—0.6 mL. The molar absorption coefficients ε of the ν_{CO} bands of hydrogen-bonded complexes **2** were determined at 270 K under the conditions without proton transfer.

The Iogansen "rule of factors" [9] was used for the estimation of the proton-accepting ability of hydrides **1**. According to this

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rule, the proton-donating (P_i) and proton-accepting (E_j) properties of the partners during hydrogen bonding are mutually independent and constant: $\Delta H_{ij} = \Delta H_{11} P_i E_j$, where ΔH_{11} is the enthalpy of hydrogen bond formation for the standard pair PhOH—Et$_2$O ($P_1 = E_1 = 1.00$).

The k_{app} rate constants were determined from the analysis of the linear plots of ln*A* *vs.* time using the MS Excel program, and standard deviations were calculated using the SolverAid macros.[10]

Results and Discussion

The reactions of hydrides WH(CO)$_2$(NO)L$_2$ with fluorinated alcohols ((CF$_3$)$_2$CHOH, (CF$_3$)$_3$COH) and phenol were studied in a wide temperature range (190—300 K) in a medium of low polarity. At temperatures of 190—270 K, no proton transfer is observed, and only the initial hydride and dihydrogen-bonded (DHB) complex are present in the system.[2] The formation of the DHB complex is characterized by the appearance of broad low-frequency bands $\nu_{OH}{}^{bond}$ ($\Delta\nu_{OH} = -(236—448)$ cm^{-1}, $\Delta\nu_{1/2} = 176—390$ cm^{-1}), whose parameters ($\Delta\nu_{OH}$, $\Delta\nu_{1/2}$, and intensity $A_{OH}{}^{bond} = (7.6—12.9) \cdot 10^4$ L mol^{-1} cm^{-2}) increase with the enhancement of the proton-accepting properties of the alcohol and phenol or the proton-accepting properties of hydride hydrogen. In the region of stretching vibrations of the ligands ν_{CO}, ν_{WH}, and ν_{NO}, the formation of H-complexes is indicated by new low-frequency bands ν_{WH} ($\Delta\nu = -(5—15)$ cm^{-1}) of the WH groups bonded by the hydrogen bonds and high-frequency bands ν_{CO} and ν_{NO} ($\Delta\nu = 10—17$ cm^{-1}) of the CO and NO ligands that are not bonded with the proton donors. The proton-accepting ability (E_j) of hydride hydrogen in complexes **1** (Table 1) is independent of the strength of the acid and medium and determined only by the electronic and steric properties of the phosphine ligands, increasing in the order PPh$_3$ < P(OPr^i)$_3$ < PEt$_3$ < PMe$_3$.[2] At ambient temperature spectral changes related to H$_2$ evolution can be observed in time. The evolution of H$_2$ is irreversible and occurs even in the presence of equimolar amounts of proton donors in the case of the strongest donor ligands L = PMe$_3$, PEt$_3$ to which the maximum E_j values of the hydride ligand correspond. In this case, the IR spectra exhibit a gradual decrease in the intensity down to the complete disappearance of the ν_{CO}, ν_{WH}, and ν_{NO} bands of the initial hydride **1** and hydrogen-bonded complex **2** and an increase of new higher-frequency bands ν_{CO} and ν_{NO} of the W(OR)(CO)$_2$(NO)L$_2$ products (**3**). The appearance of the products, as well as DHB complex formation, is easily detected in the region of stretching vibrations of the ligands. For instance, for the reaction of hydride **1a** with (CF$_3$)$_2$CHOH, ν_{CO}(**1**) = 1918 cm^{-1}, ν_{CO}(**2**) = 1930 cm^{-1}, and ν_{CO}(**3**) = 1944 cm^{-1} (Fig. 1). The reaction products with the proton donors studied, *viz*., complexes **3**, turned out to be unstable and, hence, were characterized only spectrally *in situ*. The obtained IR spectral characteristics agree with the available published data for W(OPh)(CO)$_2$(NO)(P(OPr^i)$_3$)$_2$, W(OMe)(CO)$_2$(NO)(P(OPr^i)$_3$)$_2$, and W(OPh)(CO)$_2$(NO)(PMe$_3$)$_2$,[11] that confirms our assignment of the bands in the IR spectra to ν_{CO} and ν_{NO} of complexes **3** (see Table 1).

Table 1. IR spectroscopic data for the protonation products of tungsten hydrides **1** with phenol and fluorinated alcohols W(OR)(CO)$_2$(NO)L$_2$ in hexane

L	E_j [2,9]	OR	ν_{CO}	ν_{NO}
			cm^{-1}	
PMe$_3$	0.91	OPh	1940	1632
		OCH(CF$_3$)$_2$	1944	1633
		OC(CF$_3$)$_3$	1940	1626
PEt$_3$	0.87	OPh	1936	1625
		OCH(CF$_3$)$_2$	1940	1630
		OC(CF$_3$)$_3$	1943	1616
P(OPr^i)$_3$	0.72	OPh	1945	1615
		OCH(CF$_3$)$_2$	1948	1618
		OC(CF$_3$)$_3$	1968	1635

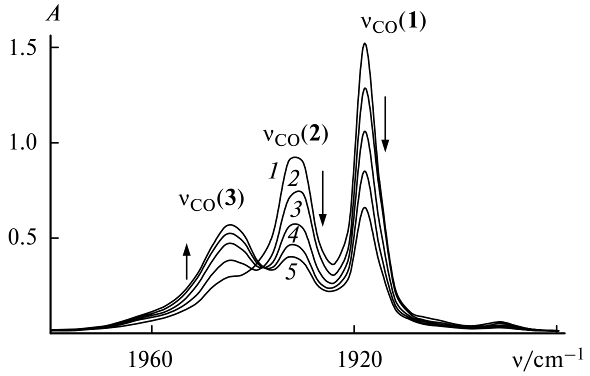
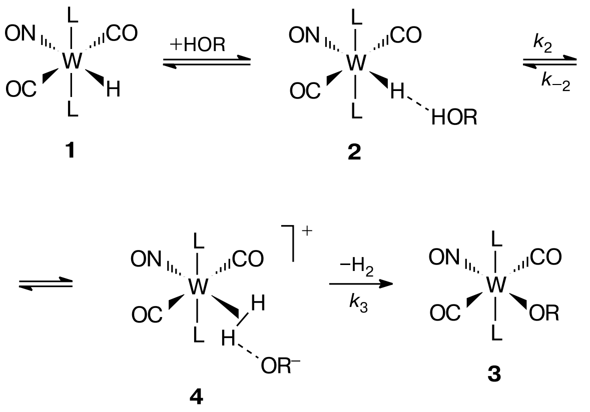


Fig. 1. IR spectra in the ν_{CO} region for the reaction of WH(CO)$_2$(NO)(PMe$_3$)$_2$ (**1a**, $C = 0.005$ mol L^{-1}) with tenfold excess (CF$_3$)$_2$CHOH in hexane 10 (*1*), 24 (*2*), 90 (*3*), 157 (*4*), and 218 min (*5*) after mixing of the reactants; $d = 1.06$ mm.

Based on the results of spectral studies, we can propose the scheme of the reaction (Scheme 2).

The formation of DHB complex **2** precedes the proton transfer and formation of a dihydrogen complex (**4**), which immediately loses H$_2$ and transforms into the corresponding organyloxy derivative **3**. We failed to experimentally detect the dihydrogen complex; however, the corresponding minimum on the potential energy surface of the reaction was determined by the quantum chemical investigation of the reaction of the model hydrides MH(CO)$_2$(NO)(PH$_3$)$_2$ (M = Mo, W) with the proton donors HR of increasing strength (R = OH, F, H$_2$O$^+$).[12] The dihydrogen complex **4** is very unstable for

Scheme 2



obvious reasons and cannot be detected even at low temperatures. Let us compare this (η^2-H_2) complex with the synthesized and isolated[13] non-classical hydride $W(H_2)(CO)_3L_2$ in which the (η^2-H_2) ligand is in the *trans*-position to the carbonyl ligand and rather labile. The substitution of the carbonyl group for the nitrosyl group (with stronger π-acidic properties) decreases the backward donation to the σ^*-orbital of the coordinated H_2 ligand due to which the W—(H_2) bond in the $[W(\eta^2\text{-}H_2)(CO)_2(NO)L_2]^+$ complex becomes very unstable.[14]

Hydrogen bond formation that occurs, as known, with the diffusion-controlled rate is the pre-kinetic step. To determine the reaction order and rate of the next step, we used the data obtained by changing the absorbance of the ν_{CO} bands of hydrogen-bonded complex **2** and product **3** in time. The linear plots of ln*A* *vs.* time for the bands ν_{CO}(**2**) of the H-complex (Fig. 2) and ν_{CO}(**3**) of the organyloxy product indicate the first-order reaction. It follows from this that the proton transfer with the formation of non-classical hydride **4** and the substitution of the (η^2-H_2) ligand for OR⁻ are intracomplex processes. The apparent rate constants $k_{2,\mathrm{app}}$, determined from the decrease in the absorbance of the band of the H-complex ν_{CO}(**2**), coincide with $k_{3,\mathrm{app}}$ obtained from changes in the ν_{CO}(**3**) band.

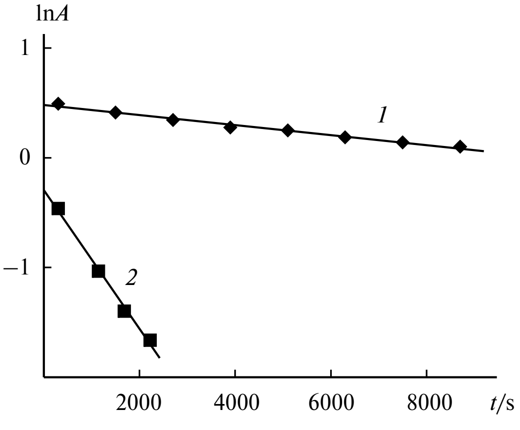


Fig. 2. Time plots of ln*A* of the ν_{CO}(**2**) band of hydride $WH(CO)_2(NO)(PEt_3)_2$ (**1b**, $C = 0.04$ mol L⁻¹) in the presence of $(CF_3)_2CHOH$ (*1*) and $(CF_3)_3COH$ (*2*); $d = 0.127$ mm.

The kinetics of the process can be described by the following equations:

$$d[WH...HOR]/dt = -k_2[WH...HOR] + k_{-2}[W(H_2)], \quad (1)$$

$$d[WOR]/dt = k_3[W(H_2)], \quad (2)$$

$$d[W(H_2)]/dt = k_2[WH...HOR] - k_{-2}[W(H_2)] - k_3[W(H_2)]. \quad (3)$$

Under the condition $d[W(H_2)]/dt = 0$, we obtain from Eq. (3)

$$[W(H_2)] = k_2[WH...HOR]/(k_{-2} + k_3). \quad (4)$$

Then

$$-d[WH...HOR]/dt = [k_2k_3/(k_{-2} + k_3)]/[WH...HOR] \quad (5)$$

and

$$-d[WOR]/dt = [k_2k_3/(k_{-2} + k_3)]/[WH...HOR]. \quad (6)$$

The experimentally observed fast elimination of H_2, which does not allow one to detect the (η^2-H_2) complex, implies that $k_3 \gg k_{-2}$ and, hence, $k_2k_3/(k_{-2} + k_3) \approx k_2$. Thus, proton transfer is the rate-determining step of the reaction.

Let us compare the obtained values of the rate constants (Table 2) with the proton-donating ability of HOR, on which the proton-transfer rate should depend, and nucleophilicity of the conjugated OR⁻ anions, which should determine the formation rate of the W—OR derivatives. The reaction of hydride **1a** with isopropyl alcohol ($P_i = 0.63$) does not start within 6 h even under the conditions of its tenfold excess. The reaction rate increases on going to less nucleophilic but more acidic phenol and then to somewhat stronger proton donor $(CF_3)_2CHOH$. For less basic hydride **1b**, the reaction rate

Table 2. Rate constants and activation free energies $\Delta G^{\neq}_{298K}$ of the protonation of hydrides **1a,b** with phenol and fluorinated alcohols

Hydride	L	HOR	P_i[9]	$k_{app} \cdot 10^5$ /s⁻¹	$\Delta G^{\neq}_{298K}$ /kcal mol⁻¹
1a	PMe_3	HOPr^i	0.63	No reaction	
		HOPh	1.00	3.2±0.3	23.5
		$HOCH(CF_3)_2$	1.05	9.9±0.4	22.9
1b	PEt_3	HOPh	1.00	2.2±0.3	23.6
		$HOCH(CF_3)_2$	1.05	4.6±0.2	23.3
		$HOC(CF_3)_3$	1.33	63.3±0.3	21.9

constants k_{app} with this proton donor are lower than that for **1a** but also increase with an increase in the proton-donating ability of the alcohol. For instance, on going from phenol to hexafluoroisopropyl alcohol, the reaction rate constant increases two times, whereas the rate constant increases by an order of magnitude when going to perfluoro-*tert*-butyl alcohol (see Table 2). When the proton-donating ability of HOR becomes higher (CH_3COOH, CF_3COOH), the hydrogen evolution and appearance of the ν_{CO}(**3**) band of the product occur virtually immediately. We could not determine the reaction rate, although the nucleophilicity of $RCOO^-$ is much lower than that of PhO^-.

The reactivity of the hydrides under study changes in the same series as the above-mentioned proton-accepting ability E_j of the hydride ligand ($PPh_3 < P(OPr^i)_3 < PEt_3 < PMe_3$). For example, the half-life $t_{1/2}$ for the reaction of hydride **1a** (L = PMe_3) with 10 equiv. of $(CF_3)_2CHOH$ is ~2 h, the reaction with hydride **1c** (L = $P(OPr^i)_3$) is slower even when stronger alcohol $(CF_3)_3COH$ was given in tenfold excess, and no reaction for the complex with L = PPh_3 is observed even during 24 h.

Thus, the rate constants of the reactions of hydrides **1** with the proton donors increase with an increase in the proton-accepting ability of the hydride ligand and proton-donating ability of HOR, *i.e.*, the reaction rate increases with an increase in the strength of the DHB complexes. The data obtained confirm the assumption that the rate-determining step is the intracomplex proton transfer **2** ↔ **4** rather than the next step including the evolution of a hydrogen molecule and the interaction of the metal complex with the OR^- anion.

Based on the obtained rate constants k_{app}, one can calculate the activation free energies of proton transfer $\Delta G^{\neq}_{298K}$ (see Table 2), which are close and equal to 22—23 kcal mol^{-1}. These values are substantially higher than those obtained for the earlier studied hydrides. For example, for more basic (in hydrogen bond) molybdenum trihydride $Cp^*MoH_3(Ph_2PCH_2CH_2PPh_2)$ ($E_j = 1.45$),[15] the activation energy of proton transfer from $(CF_3)_2CHOH$ in toluene is $\Delta G^{\neq}_{293K}$ = 15.8 kcal mol^{-1}, whereas for the protonation of closer (in the proton-accepting properties) $CpRuH(CO)[P(cyclo\text{-}C_6H_{11})_3]$ (E_j = 1.04) with perfluoro-*tert*-butyl alcohol in hexane $\Delta G^{\neq}_{298K}$ = 16.7 kcal mol^{-1}.[7b] The results obtained in this work together with published data suggest the scheme of the total energy profile of the reaction (Fig. 3). The first minimum belongs to the DHB complex, and the second minimum is attributed to the dihydrogen complex. The depth of the first minimum ΔG_1, as well as the height of the barrier $\Delta G^{\neq}_1$, is determined by the nature (basicity) of the organometallic complex and proton-donating ability of HOR. The depth of the second minimum depends on the stability of the (η^2-H_2)-complex, which is unstable in the case of $[W(\eta^2\text{-}H_2)(CO)_2(NO)L_2]^+$. The relative values of the barrier of proton transfer ($\Delta G^{\neq}_1$) and the barrier of hydrogen evolution and addition of OR ($\Delta G^{\neq}_2$) differ for different hydride complexes of transition metals. For instance, for the reaction of $Cp^*MoH_3(Ph_2PCH_2CH_2PPh_2)$ with the proton donors, which also affords the organyloxy derivatives,[16] $\Delta G^{\neq}_1 < \Delta G^{\neq}_2$, whereas for hydrides **1** studied in the present work, $\Delta G^{\neq}_1 > \Delta G^{\neq}_2$, because it is this proton transfer which is the rate-determining step.

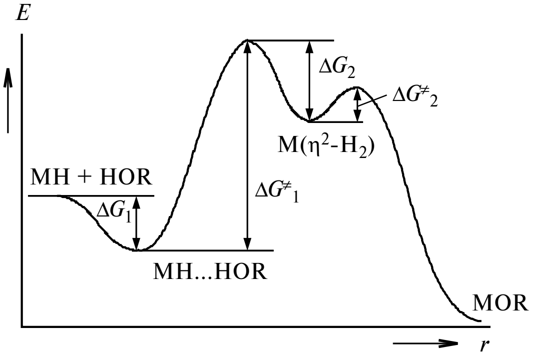


Fig. 3. Scheme of the total energy profile of the reaction; *r* is the reaction coordinate.

Thus, we studied the kinetics of the protonation and formation of the organyloxy derivatives of tungsten hydrides $WH(CO)_2(NO)L_2$ reacting with weak OH-acids in a wide temperature range (from low to ambient temperatures) by IR spectroscopy. The use of low temperatures (190—270 K) makes it possible to distinguish and estimate the first step: formation of the DHB complexes. The temperature increase results in the proton transfer and evolution of molecular hydrogen leading to the formation of the final products, *viz.*, organyloxy derivatives. The study of the reaction kinetics allowed us to distinguish the rate-determining step, namely, proton transfer, and show the dependence of the rate on the factors determining the strength of the DHB complexes: proton-accepting properties of the hydrides and proton-donating properties of the OH-acids rather than on the nucleophilicity of the OR^- groups. The activation energy of proton transfer $\Delta G^{\neq}_{298K}$ for studied hydrides **1** (22—23 kcal mol^{-1}) is much higher than the barriers of proton transfer obtained earlier for the protonation of the hydrides with the higher basicity.

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