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Reactivities of Carbonyl Compounds in Acid-Catalyzed Hydride Transfer *vs*. Electron Transfer

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Rate constants for acid-catalyzed hydride-transfer reactions from triethylsilane to a series of carbonyl compounds are compared with those for acid-catalyzed electron transfer from the excited state of $[Ru(bpy)_3]^{2+}$ to the same series of carbonyl compounds in the presence of $HClO_4$ in acetonitrile at 298 K.

Acid catalysis plays an essential role in activating carbonyl compounds for both the one-electron and two-electron reduction, since the protonation of carbonyl compounds enhances the oxidizing ability significantly.1,2) However, it has not been clear whether the reactivity of carbonyl compounds for the two-electron reduction (one-step hydride transfer) is in parallel with that for the one-electron reduction (electron transfer) or not. Moreover, in some cases hydride transfer proceeds *via* electron transfer as the rate-determining step.3) Thus, no comparison of the reactivity of carbonyl compounds in the acid-catalyzed hydride-transfer (one-step) and electron-transfer reactions has so far been made.

In this study we have made for the first time an extensive comparison between rate constants for acid-catalyzed hydride-transfer reactions from triethylsilane to a series of carbonyl compounds and those for acid-catalyzed electron transfer from $[Ru(bpy)_3]^{2+*}$ (bpy = 2,2'-bipyridine and * denotes the excited state) to the same series of carbonyl compounds in the presence of $HClO_4$ in acetonitrile (MeCN).

Alkylsilanes, which are relatively stable to strong acids as compared with other metal hydrides, have been used as effective hydride donors for the acid-catalyzed reduction of carbonyl compounds.1,4) Although triethylsilane shows no reactivity toward carbonyl compounds (ketones or aldehydes) in MeCN at 298 K, the carbonyl compound is readily reduced by Et_3SiH in the presence of $HClO_4$ (70%) to yield the corresponding alcohol (ROH) together with a minor amount of the corresponding ether (ROR).5) In the reduction of aldehydes the yields of the corresponding symmetrical ethers varied slightly with the reaction conditions (10-13%). In the reduction of ketones the corresponding alcohols were obtained exclusively. Triethyl-silanol was the major silane product.[4] When Et_3SiH was replaced by Et_3SiD for the reduction of acetophenone, the deuterium was introduced to the alcohol quantitatively (Eq. 1).[5] Rates of the acid-catalyzed

$$Et_3SiD + PhCOCH_3 + H_2O \xrightarrow{H^+} Et_3SiOH + PhCD(OH)CH_3 \qquad (1)$$

reduction of aromatic aldehydes and ketones were monitored by the decrease of the absorption band due to the carbonyl compounds (λ = 293-335 nm) in MeCN at 298 K. The rates obeyed strictly the second-order kinetics showing the first-order dependence on each reactant concentration. The observed second-order rate constant (k_{obsd}) increased linearly with an increase in $[HClO_4]$ under the conditions that $[HClO_4] > 0.50$ mol dm^{-3}. The k_{obsd} values of aliphatic aldehydes and ketones, which have no appropriate absorption band to monitor the reaction, were determined from the product yields in the competition with the reduction of PhCHO.[6] The k_{obsd} values in the presence of a fixed $HClO_4$ concentration ($[HClO_4]$ = 0.93 mol dm^{-3}) are listed in Table 1. The primary kinetic isotope effects have also been determined from the ratios of the rate constants of Et_3SiH to Et_3SiD, and the k_H/k_D values are also listed in Table 1.

The excited state of $[Ru(bpy)_3]^{2+}$ is a strong one-electron reductant, judging from the largely negative one-electron oxidation potential (E^0_{ox} = -0.81 V vs. SCE).[2] Thus, the luminescence of $[Ru(bpy)_3]^{2+*}$ (λ_{max} = 608 nm) is readily quenched by acid-catalyzed electron transfer from $[Ru(bpy)_3]^{2+*}$ to carbonyl compounds.[2] The rate constants (k_{et}) of the acid-catalyzed electron transfer from $[Ru(bpy)_3]^{2+*}$ to the same series of carbonyl compounds as employed in the reduction by Et_3SiH were determined from the quenching constant and the emission lifetime (s = 850 ns).[2,7] The k_{et} value increased linearly with an increase in $[HClO_4]$. The k_{et} values at $[HClO_4]$ = 2.0 mol dm^{-3} are listed in Table 1. On the other hand, the one-electron oxidation potential of Et_3SiH is at least by 3.1 V more positive than that of $[Ru(bpy)_3]^{2+*}$, since no fluorescence quenching of 10-methylacridinium ion ($AcrH^+$) has been observed by electron transfer from Et_3SiH to $^1AcrH^{+*}$ that is known to be a very strong one-electron oxidant (E^0_{red} = 2.3 V vs. SCE).[8] Thus, there may be no chance for Et_3SiH acting as a one-electron reductant, when the k_{obsd} values can be taken as reliable reference to show the reactivity of carbonyl compounds in the acid-catalyzed one-step hydride-transfer reactions.

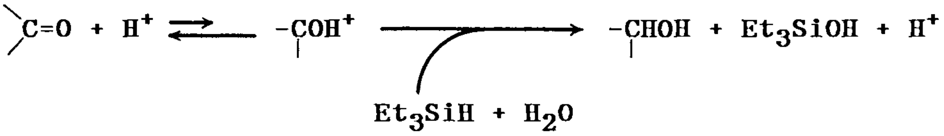
Comparison of the k_{obsd} and k_{et} values in Table 1 reveals no parallel relation in the reactivities of carbonyl compounds for acid-catalyzed

Table 1. Rate Constants (k_{obsd}) for Acid-Catalyzed Reduction of Carbonyl Compounds by Et_3SiH in the Presence of $HClO_4$ (0.93 mol dm^{-3}) in MeCN at 298 K

No.	Carbonyl compound	$\Delta\delta^{a)}$	$k_{obsd}^{b)}$ / dm^3 mol^{-1} s^{-1}	k_{et} / dm^3 mol^{-1} s^{-1}
1	CH_3CHO	2.7	$6.2^{c)}$	1.3×10^6
2	C_2H_5CHO		$6.1^{c)}$	9.8×10^5
3	$(CH_3)_2CHCHO$	2.2	$5.1^{c)}$	6.3×10^5
4	$(CH_3)_3CCHO$	2.0	$3.0^{c)}$	1.8×10^5
5	$(CH_3)_2CO$	8.8	7.4×10^{-1} $(1.3)^{c)}$	1.0×10^5
6	p-MeC_6H_4CHO	2.2	9.1×10^{-1} (1.3)	2.9×10^8
7	C_6H_5CHO	1.5	7.4×10^{-1} (1.4)	9.6×10^7
8	p-ClC_6H_4CHO	1.3	4.0×10^{-1}	1.4×10^8
9	p-CNC_6H_4CHO	0.8	1.8×10^{-1}	1.0×10^8
10	$C_6H_5COC_3H_7$		2.4×10^{-2}	1.2×10^8
11	$C_6H_5COC_2H_5$		2.3×10^{-2}	1.3×10^8
12	p-$MeC_6H_4COCH_3$	5.5	2.1×10^{-2}	3.8×10^8
13	$C_6H_5COCH_3$	4.3	2.0×10^{-2} (1.3)	1.9×10^8
14	p-$ClC_6H_4COCH_3$	3.2	1.2×10^{-2}	1.4×10^8
15	p-$CNC_6H_4COCH_3$		6.3×10^{-3} (1.5)	1.0×10^8

a) Down-field chemical shifts of the carbonyl carbon signals (0.17 mol dm^{-3}) of the ^{13}C NMR spectra in the presence of $HClO_4$ (1.67 mol dm^{-3}) in CD_3CN as compared to those in its absence.[9] b) The values in parentheses are those of the primary kinetic isotope effects (k_H/k_D) determined from the ratios of the rate constants of Et_3SiH to Et_3SiD. c) Determined from the competition with the reduction of PhCHO.[6]

hydride and electron transfer. The aliphatic aldehydes (Nos. 1-4) are more reactive than aromatic aldehydes and ketones in the hydride-transfer reactions. Conversely aromatic aldehydes and ketones (Nos. 6-16) are more reactive than aliphatic aldehydes and ketones in the electron-transfer reactions. The k_{obsd} value (No. 1, 3, 4, 6-9) decreases with a decrease in the down-field chemical shift ($\Delta\delta$) of carbonyl carbon of the ^{13}C NMR spectra of aldehydes in the presence of $HClO_4$ in CD_3CN (Table 1),[9,10] when the degree of protonation decreases. The same trend is observed between the k_{obsd} and $\Delta\delta$ values of ketones (No. 5, 12-14).[11] The small k_H/k_D values in Table 1 indicate that Si-H bond breaking is not extensive in the transition state in the acid-catalyzed hydride-transfer reactions. Thus, the protonation of carbonyl compounds, the equilibrium of which lies far to the left, may be followed by facile hydride transfer from Et_3SiH to the protonated species (Eq. 2), when the reactivity may be determined mainly



(2)

by the protonation ability. In the case of electron transfer, however, the stronger the electron-acceptor ability is, the weaker is the protonation ability, and *vice versa*. Thus, the reactivity of carbonyl compounds in the acid-catalyzed electron transfer may be determined by two reverse effects; the proton- and electron-acceptor abilities.[2)]

References

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5) The product yields were determined by ^1H NMR comparison with authentic materials independently obtained.
6) The ratios of the rate constants (k_A) of aliphatic carbonyl compounds (RCHO) to that of PhCHO ($k_0 = 7.4 \times 10^{-1}$ dm^3 mol^{-1} s^{-1}) were determined from the product yields (Y_A and Y_0 for RCHO and PhCHO, respectively) by using the equation, $k_A/k_0 = \ln(1 - Y_A)/\ln(1 - Y_0)$.
7) In the quenching process, however, no net chemical reaction takes place because of the efficient back electron transfer to the ground state.
8) S. Fukuzumi and T. Tanaka, "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Part C, Chap. 10.
9) The ^{13}C NMR spectra in the absence and presence of $HClO_4$ were measured by using a JEOL JNM-GSX-400 spectrometer (400 MHz).
10) The NMR is generally regarded as a much more adequate technique for the study of protonation of aliphatic ketones than UV; A. Bagno, V. Lucchini, and G. Scorrano, J. Phys. Chem., **95**, 345 (1991).
11) However, no direct comparison between the aldehydes and ketones can be made because of the presence of hydrogen-bonding equilibrium.[10)]

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