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Efficient Reduction of Triphenylmethanol to Triphenylmethane by 9,10-Dihydro-10-methylacridine in the Presence of Perchloric Acid

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Synopsis. Reduction of triphenylmethanol (Ph_3COH) to triphenylmethane by an NADH model compound, 9,10-dihydro-10-methylacridine ($AcrH_2$), proceeds very efficiently in the presence of perchloric acid ($HClO_4$) in acetonitrile at 298 K via hydride transfer from $AcrH_2$ to triphenylmethyl cation (Ph_3C^+) which is formed by the dehydration of Ph_3COH with $HClO_4$. Mechanisms of hydride transfer reactions from NADH model compounds to Ph_3C^+ are also discussed.

Acid-stable analogues of dihydronicotinamide adenine dinucleotide (NADH) have been employed as effective reductants in reductions of various carbonyl compounds[1–3] and imines[4] in the presence of acid. It has recently been reported that aryl alcohols can also be reduced by acid-stable NADH model compounds in the presence of acid.[5] However, concentrated acid or high temperature (e.g., refluxing acetonitrile) has so far been required for the reactions to undergo smoothly.[5]

This study reports that very facile reduction of triphenylmethanol occurs by using an acid-stable NADH analogue, 9,10-dihydro-10-methylacridine in the presence of slightly excess concentration of perchloric acid ($HClO_4$) to $AcrH_2$ in acetonitrile at 298 K to yield triphenylmethane. The kinetic investigations have been performed using a stopped-flow technique in order to discuss mechanisms of the facile reduction of triphenylmethanol by $AcrH_2$ as well as those of the hydride transfer reactions from NADH model compounds to triphenylmethyl cation which is prepared independently by the dehydration of triphenylmethanol with $HClO_4$.

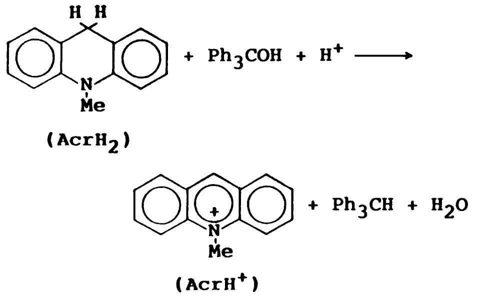
Experimental

Preparation of 9,10-dihydro-10-methylacridine ($AcrH_2$) and 1-benzyl-1,4-dihydronicotinamide (BNAH) was described elsewhere.[6] Triphenylmethyl perchlorate ($Ph_3C^+ClO_4^-$) was prepared by the literature method.[7] Triphenylmethanol (Ph_3COH) and $HClO_4$ (70%) were obtained commercially. Acetonitrile (MeCN) used as a solvent was purified and dried by the standard procedure.[8]

The reactions in the absence and presence of oxygen in CD_3CN were monitored using a Japan Electron Optics JNM-PS-100 ^1H NMR spectrometer. Kinetic measurements were performed using a Union RA-103 stopped flow spectrophotometer. Rates of the reduction of Ph_3COH by $AcrH_2$ in deaerated MeCN at 298 K were followed by the increase in absorbance due to 10-methylacridinium ion ($AcrH^+$) in the visible region ($\lambda_{max}=358$ nm, $\varepsilon=1.80\times10^4$ dm^3 mol^{-1} cm^{-1}). Rates of the dehydration of Ph_3COH with $HClO_4$ in deaerated MeCN at 298 K were determined by the increase in absorbance at $\lambda_{max}=405$, 433 nm due to Ph_3C^+. Rates of the hydride transfer from $AcrH_2$ and BNAH to Ph_3C^+ were also followed by the increase and decrease in absorbance at $\lambda_{max}=358$ and 350 nm due to $AcrH^+$ and BNAH under 4 atm of oxygen (or nitrogen), respectively. All the kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of substrates were maintained at more than 10-fold excess of $AcrH_2$ or BNAH. Pseudo-first-order rate constants were determined by the least-square curve fit using a Union System 77 microcomputer. Second-order rate constants were calculated from the slope of the pseudo-first-order rate constants vs. the concentrations of substrates by the least-squares analysis.

Results and Discussion

Reduction of Ph_3COH by $AcrH_2$ in the Presence of $HClO_4$. Upon mixing $AcrH_2$ with Ph_3COH in the presence of $HClO_4$ in MeCN at 298 K, facile reduction of Ph_3COH by $AcrH_2$ occurs to yield $AcrH^+$ and triphenylmethane (Ph_3CH), Eq. 1. The products were identified by the ^1H NMR and the electronic spectra. The rates obey the second-order kinetics, showing the first-order dependence on each reactant concentration. The observed second-order rate constants k_{obs} increase with an increase in the $HClO_4$ concentration to reach a maximum value at [$HClO_4$] ca. 1×10^{-3} mol dm^{-3}, and then decrease in the higher concentration region as shown in Fig. 1. Such a decrease of k_{obs} in the higher concenration region of $HClO_4$ may be ascribed to the protonation of $AcrH_2$ by $HClO_4$ to form $AcrH_3^+$ (Eq. 2), since $AcrH_3^+$ is known to be much weaker reductant than $AcrH_2$.[2,3] Thus, the reduction of Ph_3COH by $AcrH_2$ is not catalyzed by $HClO_4$. In such a case, the reduction may proceed via the rate-determining hydride transfer reaction from $AcrH_2$ to Ph_3C^+ (Eq. 3) which is formed by the dehydration of Ph_3COH with $HClO_4$ (Eq. 4). In order to confirm this point, the kinetics of both reactions (Eqs. 3 and 4) have been examined independently.



(1)

$$AcrH_2 + H^+ \rightleftharpoons AcrH_3^+ \tag{2}$$

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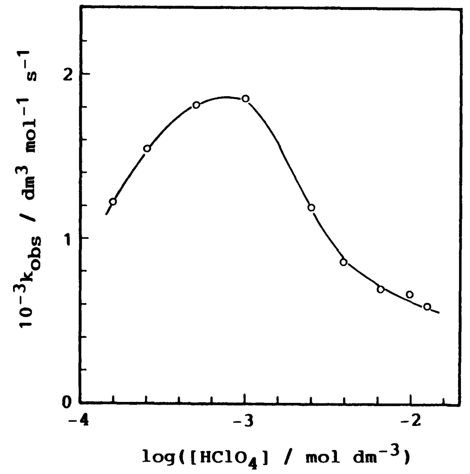


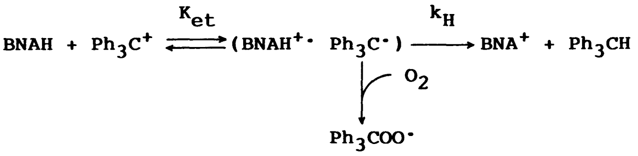
Fig. 1. Dependence of the observed second-order rate constant (k_{obs}) vs. [HClO$_4$] for the reduction of Ph_3COH by $AcrH_2$ in the presence of $HClO_4$ in deaerated MeCN at 298 K.

$$AcrH_2 + Ph_3C^+ \longrightarrow AcrH^+ + Ph_3CH \qquad (3)$$

$$Ph_3COH + H^+ \longrightarrow Ph_3C^+ + H_2O \qquad (4)$$

Rates of both reactions (Eqs. 3 and 4) also obey the second-order kinetics. The observed second-order rate constant of hydride transfer from $AcrH_2$ to Ph_3C^+ (Eq. 4) is determined as 1.7×10^3 dm^3 mol^{-1} s^{-1}. On the other hand, the observed second-order rate constant of the dehydration of Ph_3COH with $HClO_4$ (Eq. 4) is determined as 8.0×10^4 dm^3 mol^{-1} s^{-1} which is much larger than the k_{obs} value of the hydride transfer reaction (Eq. 3). Thus, the dehydration of Ph_3COH with $HClO_4$ to form Ph_3C^+ occurs firstly and then the rate-determining hydride transfer from $AcrH_2$ to Ph_3C^+ takes place to yield $AcrH^+$ and Ph_3CH. In fact, the maximum k_{obs} value (1.8×10^3 dm^3 mol^{-1} s^{-1}) of the reduction of Ph_3COH by $AcrH_2$ at [$HClO_4$]=ca. 10^{-3} mol dm^{-3} (Fig. 1) is nearly equal to the k_{obs} value (1.7×10^3 dm^3 mol^{-1} s^{-1}) of hydride transfer from $AcrH_2$ to Ph_3C^+.

Mechanisms of Hydride Transfer from NADH Model Compounds to Ph_3C^+. With respect to mechanisms of hydride abstraction of Ph_3C^+, it has recently established that hydride transfer from a tungsten-dimethyl complex [$Cp_2W(CH_3)_2$] (Cp=η-C_5H_5) to Ph_3C^+ consists of two-step processes; the exothermic electron transfer from [$Cp_2W(CH_3)_2$] to Ph_3C^+ occurs firstly as indicated by the more negative oxidation potential of [$Cp_2W(CH_3)_2$] (−0.1 V)[9] than the reduction potential of Ph_3C^+ (0.29 V),[10] and the subsequent hydrogen-atom transfer from [$Cp_2W(CH_3)_2$]$^+$ to $Ph_3C\cdot$ occurs to yield Ph_3CH.[11] Evidence for such initial electron transfer has been obtained also for hydride transfer from rhenium–alkyl complexes to Ph_3C^+, although the electron transfer in this case is endothermic.[12] The intermediate radical $Ph_3C\cdot$ formed by the endothermic electron transfer has been successfully trapped by oxygen when the rate of overall hydride transfer is accelerated by the presence of oxygen. Since one-electron oxidation potentials of rhenium-alkyl complexes (e.g., 0.48 V vs. SCE)[12] are rather close to those of NADH model compounds [e.g., 0.57 V vs. SCE for 1-benzyl-1,4-dihydronicotinamide (BNAH)],[6] the hydride transfer from BNAH to Ph_3C^+ may also proceed via initial electron transfer from BNAH to Ph_3C^+, followed by hydrogen transfer from $BNAH^{+\cdot}$ to $Ph_3C\cdot$ to yield BNA^+ and Ph_3CH as shown in Scheme 1.



Scheme 1.

In order to examine the contribution of such an electron-transfer process, the second-order rate constants k_{obs} of hydride transfer from BNAH to $Ph_3C^+ClO_4^-$ in the absence and presence of oxygen were determined under 4 atm of nitrogen and oxygen, respectively. The k_{obs} values are listed in Table 1, together with the reported k_{obs} values of a rhenium–alkyl complex, [CpRe(NO)(PPh_3)(CH_2Ph)].[12] The k_{obs} value of $AcrH_2$ in the presence of oxygen (4 atm) was also determined and the k_{obs} values in the absence and presence of oxygen are also listed in Table 1. In the case of the rhenium–benzyl complex, the k_{obs} value in the presence of air becomes more than 10-fold larger as compared with the value in the absence of oxygen (Table 1). In the case of NADH model compounds (BNAH and $AcrH_2$), however, no acceleration of the rate constant is observed in the presence of oxygen even at 4 atm. It has been confirmed that no oxygen is incorporated into the product, either. Such difference in the effect of oxygen on the reactions of the rhenium–benzyl complex and NADH model compounds may be ascribed to the difference in the reactivities of hydrogen transfer processes of the resulting radical cations formed by the initial electron transfer. According to Scheme 1, the observed overall rate constant consists of the electron transfer equilibrium constant K_{et} of formation of the radical pair and the rate constant of hydrogen transfer k_H as shown in Eq. 5, when the hydrogen transfer is assumed to be the rate-determining step. The K_{et} values can be evaluated from the one-electron oxidation potentials E^0_{ox} of reductants and the one-electron reduction potential E^0_{red} of Ph_3C^+ using Eq. 6. Then, the k_H values can be evaluated from the values of k_{obs}, E^0_{ox}, and E^0_{red} using Eqs. 5 and 6. The k_H values thus determined are also listed in Table 1.

$$k_{obs} = k_H K_{et} \qquad (5)$$

$$\log K_{et} = -F(E^0_{ox} - E^0_{red})/(2.3RT) \qquad (6)$$

The second-order rate constant of the radical trap of $Ph_3C\cdot$ with oxygen is known to be close to the diffusion-limited value, 5×10^8 dm^3 mol^{-1} s^{-1}.[12] In

Table 1. Observed Second-Order Rate Constants k_{obs} of Hydride Transfer Reactions from Reductants (a Rhenium-Alkyl Complex and NADH Model Compounds) to Ph_3C^+ in the Absence and Presence of Oxygen in MeCN at 298 K, the One-Electron Oxidation Potentials E^0_{ox} of Reductants, and the Rate Constants k_H of Hydrogen Transfer from the Radical Cations of Reductants to $Ph_3C\cdot$

Reductant	k_{obs}[a]	E^0_{ox} vs. SCE	k_H
	$dm^3\ mol^{-1}\ s^{-1}$	V	s^{-1}
$PhCH_2$-(Re)[b]	2.3×10[c] (2.4×10^2)[c]	0.48[c]	8.2×10^5
BNAH	8.9×10^4 (8.9×10^4)	0.57[d]	1.3×10^{10}
$AcrH_2$	1.7×10^3 (1.7×10^3)	0.80[d]	7.3×10^{11}

a) The values in parentheses are those determined in the presence of oxygen (4 atm unless otherwise noted). b) $[CpRe(NO)(PPh_3)(CH_2Ph)]$. c) Determined in CH_2Cl_2 at 208 K. The value in parenthesis is determined in aerated MeCN. The data are taken from Ref. 12. d) Taken from Ref. 6.

such a case, 1×10^{-3} mol dm^{-3} oxygen may be sufficient for the oxygen trap to compete with the intramolecular hydrogen transfer process of the rhenium–benzyl complex, resulting in the increase of the overall reaction rate. In contrast, the k_H values of NADH model compounds (Table 1) are too large for the oxygen trap to compete with the hydrogen transfer process, resulting in no effect of oxygen on the observed rate constant k_{obs} of the overall hydride transfer reactions. In the case of BNAH, the rate constant k_{et} of the forward electron transfer from BNAH to Ph_3C^+ is estimated from the E^0_{ox} and E^0_{red} values using Eq. 7. The estimated value 1.9×10^6 dm^3

$$k_{et} = Z\exp[-F(E^0_{ox} - E^0_{red})/(RT)] \qquad (7)$$

$mol^{-1}\ s^{-1}$ is larger than the observed overall rate constant 8.9×10^4 $dm^3\ mol^{-1}\ s^{-1}$. Thus, it is concluded that the hydrogen transfer process (k_H) is the rate determining step following the electron-transfer equilibrium (Scheme 1). In the case of a weaker reductant $AcrH_2$, however, the k_H value becomes close to the frequency factor ($h/kT = 6\times10^{12}\ s^{-1}$) and thus, the electron transfer may occur concertedly with the hydrogen transfer. In such a case, the differentiation between electron-hydrogen transfers and one-step hydride transfer becomes dubious and these two mechanisms should be reconciled into single unified one.

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