A Stable, Simple Enol: Ketonization of 2-Methylprop-1-en-1-ol in Nonaqueous Solvents

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Simple aliphatic enols generated by various methods are mostly unstable under the conditions (mostly aqueous solution) under which they are produced,[1,2] while sterically crowded mesityl-substituted enols are so stable that they can be purely isolated.[3] Detailed kinetic studies have been carried out for the ketonization of simple enols in aqueous solution in the presence of acid and base,[1,2a,4,5] while no report has been made on the kinetics in nonaqueous solvents.

In this communication we report the production of a simple aliphatic enol, 2-methylprop-1-en-1-ol, which is quite stable in the absence of solvents as well as in aprotic solvents and kinetic data for the ketonization of the enol in nonaqueous solvents.

Addition of [Rh(CO)(PPh₃)₃]ClO₄ (1) (0.02 mmol) into neat 2-methylprop-2-en-1-ol (2) (12 mmol) under nitrogen at room temperature immediately initiated the exothermic isomerization (eq 1). (Using a greater amount of 1 resulted in boiling the
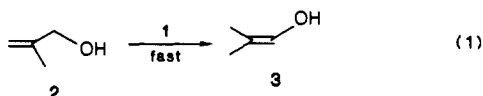
reaction mixture to produce some unknown decomposition products.) The warm-hot reaction mixture was kept at 0 °C for 1 h until all of 2 disappeared in the reaction mixture. Volatile materials, separated from the catalyst (1) by dry ice/acetone trap, contained ca. 95% of 3 and 5% of 2-methylpropanal (4) according to ^{1}H NMR spectra.[6] Almost pure enol ((CH₃)₂C=CHOD, 3D) could be obtained when the deuteriated reactant ((CH₂=C-(CH₃)CH₂OD, 2D) was used (^{1}H NMR spectrum of the fresh product showed no signals of the corresponding aldehyde ((CH₃)₂CDCHO, 4D)). The ^{1}H NMR spectra of 3 in CD₃CO-CD₃ (a sharp doublet at δ ca. 7 (OH) with J (OH–CH) being ca. 5.5 Hz[7] and a multiplet at δ 6.12 (CHOH) with equal inte-

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(7) The sharp doublet (OH) shifts from δ 7.2 to 6.8, and the coupling constant (J_OH–CH) increases from 5.5 to 6.0 Hz with increasing temperature from –50 °C to 0 °C.

Table I. Observed First-Order Rate Constants for the Ketonization of 2-Methylprop-1-en-1-ol (3) in Various Organic Solvents at 27 °C

| solvent	k_{obsd}, s⁻¹
CD₃COCD₃	$(1.5 \pm 0.2) \times 10^{-6}$
C₆D₆	$(2.2 \pm 0.3) \times 10^{-5}$
CH₃OH	$(1.3 \pm 0.2) \times 10^{-4}$
CD₃OD	$(5.3 \pm 0.5) \times 10^{-6}$
H₂O	$(4.6 \pm 0.3) \times 10^{-4}$

grals) indicates that 3 exists mainly in anti conformation.[8]

The enol 3 is quite stable in the absence of a solvent, e.g., only a half of 3 disappears to give 4 and unknown products[9] after 24 h at 25 °C and after more than 10 days at –10 °C, and it shows no sign of reaction for several days at –78 °C where it freezes. Disappearance of 3 in the absence of a solvent was followed by measuring the ^{1}H NMR spectral changes,[6] and the kinetic data could not be fitted into any simple equation of first or second order in 3.

Ketonization of 3 to give 4 was followed by measuring the absorbance at 205 nm in H₂O and 210 nm in CH₃OH and ^{1}H NMR signals of 3[6] in CD₃COCD₃, C₆D₆, and CD₃OD.[10] The rate data conform well to first-order kinetics. The observed first-order rate constants in H₂O is in good agreement with the previously reported value (4.2 × 10⁻⁴ s⁻¹ at 25 °C) by Kresge.[4]

The rate data in Table I may well be understood according to the mechanism involving a fast equilibrium (K_S) between enol and enolate ion followed by protonation of carbon (k_{SH^+}) by protonated solvent (SH⁺) (eq 2), which is identical with the one suggested
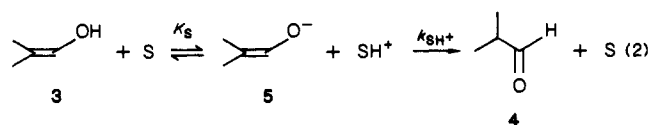
for the water-catalyzed (or uncatalyzed) ketonization of enols in aqueous solution.[4,5] Observed rate constants (k_{obsd} are then products of K_S and k_{SH^+}. The larger k_{obsd} values in protic solvents (H₂O, CH₃OH) than in aprotic solvents (CD₃COCD₃, C₆D₆) may be due to large K_S values for protic solvents (pK_a values for H₃O⁺, CH₃OH₂⁺, and CH₃COHCH₃⁺ are –1.74, –2.0, and –7.0, respectively; no pK_a value has been reported for C₆H₇⁺).[11] Larger k_{obsd} value in C₆D₆ than that in CD₃COCD₃ is somewhat unexpected and may be interpreted by larger k_{SH^+} in C₆D₆ than in CD₃COCD₃. The large value of $k_{obsd(CH_3OH)}/k_{obsd(CD_3OD)}$ = 24.5 is a supporting evidence for the proposed mechanism (eq 2) since it could be considered as the product of the equilibrium isotope effect for the first step (K_S) and the kinetic isotope effect for the second step (k_{SH^+}). A relatively large value of k_{H_2O}/k_{D_2O} = 12 was reported for the ketonization of vinyl alcohol and understood as a product of the equilibrium and kinetic isotope effect.[5] It was found that as the concentration of 4 increases in the reaction mixture, formation of acetal and H₂O from the reaction of 4 with solvent (CH₃OH or CD₃OD) becomes significant, and the rate of the ketonization is accelerated by H₂O. Therefore, k_{obsd} was obtained in CH₃OH and CD₃OD at the early stage of the ketonization.

Finally it might be said that the ketonization catalyzed by the solvent molecule playing the role of acid, whether through the concerted[2a] or stepwise mechanism,[4,5] should be negligible since

(8) Capon, B.; Siddhanta, A. K. Tetrahedron Lett. 1982, 3199–3202 and J. Org. Chem. 1984, 49, 255–257.

(9) It has been found by means of TLC separation and ^{1}H NMR analyses that unknown products contain a significant amount of aldol condensation products from the reaction of 3 and 4.

(10) Ketonization of 3 in CDCl₃ is quite rapid.[6] Careful experiments revealed that CDCl₃ (Fluka 31330; H₂O + D₂O < 0.01%) contains trace amounts of impurities that rapidly catalyze the ketonization. The ketonization rate is considerably slow ($t_{1/2}$ = 3 min) in CDCl₃ treated with molecular sieves (Aldrich 3A) for 24 h. Molecular sieve treatment seems to remove the impurities only in part.

(11) Values of pK_a are approximate and relative to water. See: March, J. Advanced Organic Chemistry; Wiley-Interscience: New York, 1985; pp 220–222.

the pK_a values of solvents (H_2O (15.7), CH_3OH (16), CH_3COCH_3 (20), C_6H_6 (37))[11] are much larger than that of 3 (11.6 in aqueous solution).[4]
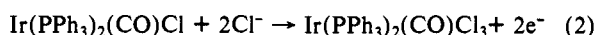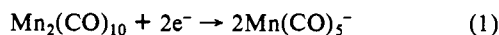
Thermodynamics of Kinetically Irreversible Organometallic Processes. Metal–Metal Bonds

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Organometallic chemistry is rich in descriptive chemistry but often lacking in quantitative insight.[1] For oxidation–reduction reactions such as (1) and (2), kinetic irreversibility precludes the

$$Mn_2(CO)_{10} + 2e^- \rightarrow 2Mn(CO)_5^- \quad (1)$$

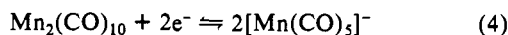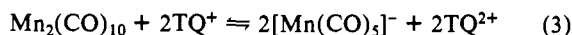$$Ir(PPh_3)_2(CO)Cl + 2Cl^- \rightarrow Ir(PPh_3)_2(CO)Cl_3 + 2e^- \quad (2)$$

direct measurement of free energy changes by standard electrochemical techniques. One approach to the evaluation of thermodynamic parameters is by redox equilibration experiments. This approach has been used previously in other areas of research,[2] and we apply it here to obtain quantitative information for oxidation–reduction reactions involving metal–metal bonds.

In the equilibration experiments we utilized a series of couples based on polypyridyl complexes of Ru and Os, such as [Ru(bpy)$_3$]$^{3+/+}$, [Ru(bpy)$_3$]$^{2+/+}$ (bpy = 2,2'-bipyridine), or bipyridinium ions such as TQ$^{2+/+}$ (TQ^{2+} = 7,8-dihydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepinediium dication).[3] When taken

TQ^{2+}
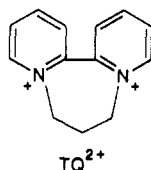
together the couples extend over a range of >3 V in increments of ~50 mV. The IR spectra in the ν_{CO} region in Figure 1 show that the TQ$^{2+/+}$ couple ($E^{\circ\prime}$ = –0.55 V vs SSCE) reaches equilibrium with the Mn$_2$(CO)$_{10}$/2[Mn(CO)$_5$]$^-$ couple in 0.5 M [N(n-Bu)$_4$](PF$_6$)–CH$_3$CN at room temperature. Integration of the ν_{CO} peaks for Mn$_2$(CO)$_{10}$ and [Mn(CO)$_5$]$^-$ compared to predetermined calibration curves give K (22 ± 2 °C) = 1.6(±0.3) × 10^{-5} for reaction 3 and $E^{\circ\prime}$ = –0.69(±0.01) V (vs SSCE) for the couple in reaction 4.

$$Mn_2(CO)_{10} + 2TQ^+ \rightleftharpoons 2[Mn(CO)_5]^- + 2TQ^{2+} \quad (3)$$

$$Mn_2(CO)_{10} + 2e^- \rightleftharpoons 2[Mn(CO)_5]^- \quad (4)$$

Fast scan cyclic voltammetry was performed at 10 μm diameter platinum disk microelectrodes at a scan rate of 5000 V/s with potentials recorded in V vs SSCE. In 0.5 M [N(Bu)$_4$](PF$_6$)–CH$_3$CN the two-electron reduction of Mn$_2$(CO)$_{10}$ to [Mn(CO)$_5$]$^-$
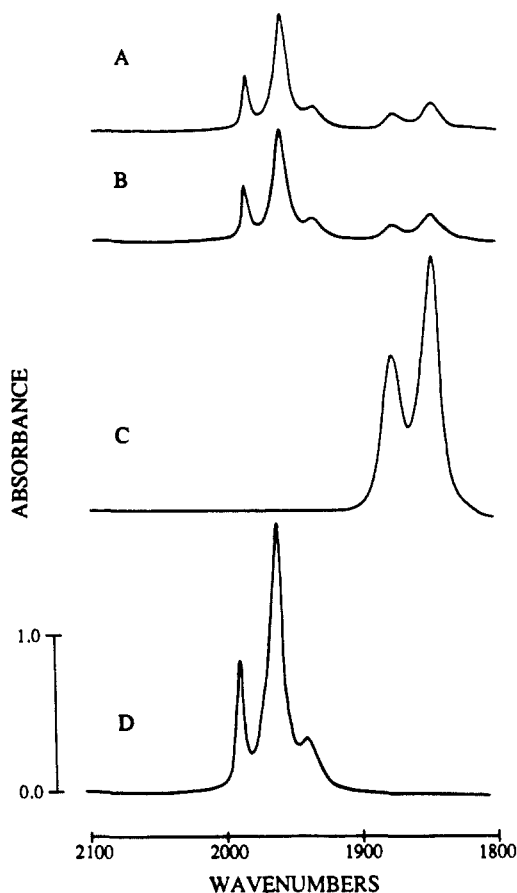
(1) For a review of thermodynamic aspects of organometallic chemistry, see: Connor, J. A. *Topics Curr. Chem.* **1977,** 71, 71.

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(3) (a) Homer, R. F.; Tomlinson, T. E. *J. Chem. Soc.* **1960,** 2498. (b) Salmon, R. T.; Hawkridge, F. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1980,** 112, 253.

Figure 1. FT-IR spectral results of mixing experiments in 0.50 M [N-(n-Bu)$_4$](PF$_6$)–CH$_3$CN solution: A, 1.28 mM Mn$_2$(CO)$_{10}$ + 2.58 mM TQ$^+$; B, 2.56 mM [Mn(CO)$_5$]$^-$ + 2.58 mM TQ^{2+}; C, 5.12 mM [Mn(CO)$_5$]$^-$; D, 2.56 mM Mn$_2$(CO)$_{10}$.
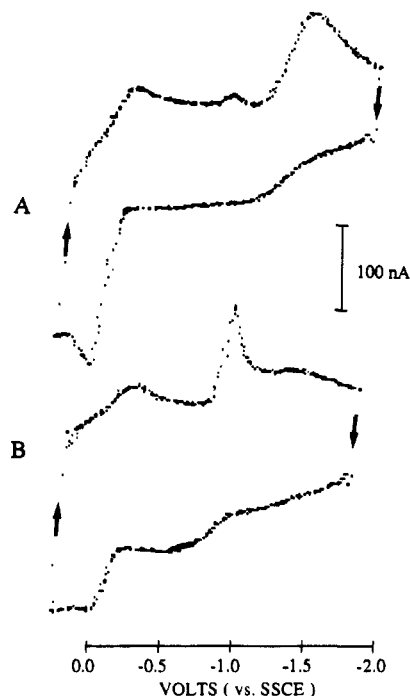

Figure 2. Fast scan cyclic voltammograms in 0.50 M [N(n-Bu)$_4$]-(PF$_6$)–CH$_3$CN solution at a scan rate of 5000 V/s at a 10 μm diameter platinum disk microelectrode: A, 5.0 mM Mn$_2$(CO)$_{10}$; B, 5.0 mM [Mn(CO)$_5$(NCCH$_3$)](PF$_6$).

appears at $E_{p,c}$ = –1.50 V (Figure 2A) and is followed by a reversible wave for the [Mn(CO)$_5$]$^-$/Mn(CO)$_5$ couple at $E^{\circ\prime}$ = –0.15 V. In addition, a wave for the reduction of [Mn(CO)$_5$-(NCCH$_3$)]$^+$ is seen at $E_{p,c}$ = –1.10 V. The cation, [Mn(CO)$_5$-