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# Quantitative Assessment of Electron-Donor Properties of Enol Silyl Ethers: Charge-Transfer Complex Formation, Photoelectron Spectra and Transient Electrochemical Oxidation

Rajendra Rathore and Jay K. Kochi

Chemistry Department, University of Houston, Houston, Texas, 77204-5641, U.S.A.

***Abstract:*** Enol silyl ethers are excellent electron donors by virtue of their ionization and oxidation potentials which can be as low as IP = 7.5 eV and $E_p$ = 1.0 V *vs.* SCE, respectively. Such donor properties are shown by the ready formation of 1 :1 electron donor-acceptor complexes with quinones, in which the distinctive colors associated with charge-transfer transitions ($h\nu_{CT}$) correlate linearly with IP in accord with Mulliken's prediction.

Keto-enol tautomerization effectively converts a (relatively electron-poor) carbonyl acceptor into a (correspondingly electron-rich) olefinic donor;[1] and such an umpolung allows the conventional nucleophilic additions at the carbonyl center (*e.g.* Grignard reaction) to be replaced by electrophilic substitutions at the α-carbon (*e.g.* bromination) of ketones, aldehydes, *etc.*[2] For synthetic purposes, the deliberate transformation of enols to the corresponding ethers circumvents the kinetics problem associated with their substitution lability.[3] Among these derivatives, trimethylsilyl (TMS) and related congeners have found broad synthetic applicability.[4] Especially noteworthy are the facile α-substitution of enol silyl ethers with N-bromosuccinimide, nitronium and diazonium salts, chloranil and DDQ, silver oxide, tetranitromethane, ceric ammonium nitrate, *etc.*[5] The wide diversity of such reagents, that include cationic and neutral electrophiles as well as strong and weak 1-electron oxidants, raises the question as to whether a unified mechanistic formulation pertains to enol silyl ethers as electron donors.[6] Since the energetics consideration for any electron-transfer pathway requires a quantitative assessment of the electron-donor properties of enol silyl ethers, we now report three independent measures of electron detachment and how they vary with the structure of the enol silyl ether.

The visual indication that enol silyl ethers are electron donors derive from the vivid charge-transfer colors that are observed when they are exposed to various quinones. For example, an intense purple coloration developed in solution of cyclohexanone enol silyl ether **5** in dichloromethane immediately upon the addition of chloranil. Similarly, the other substituted enol silyl ethers in Table I and chloranil afforded brightly colored solutions of varying shades of red, blue and green. The quantitative effect of the color changes is illustrated in Figure 1A by

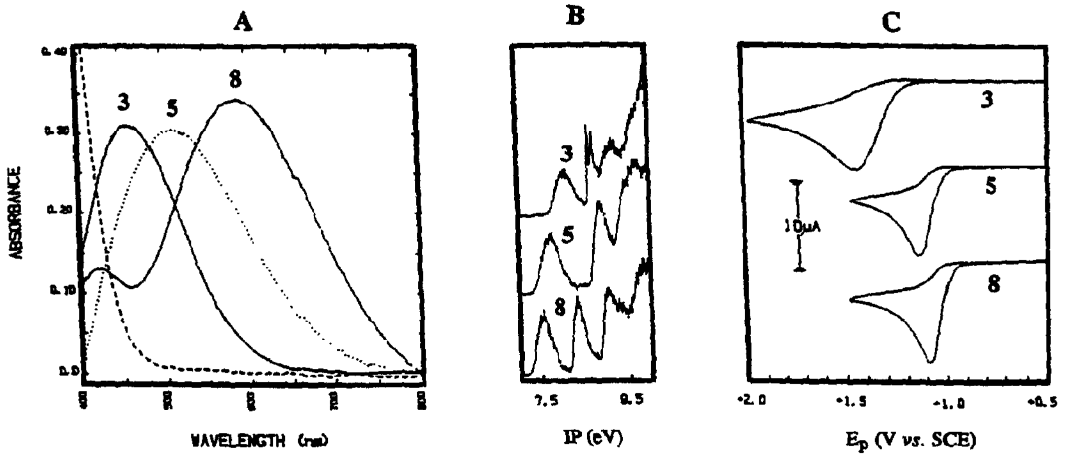
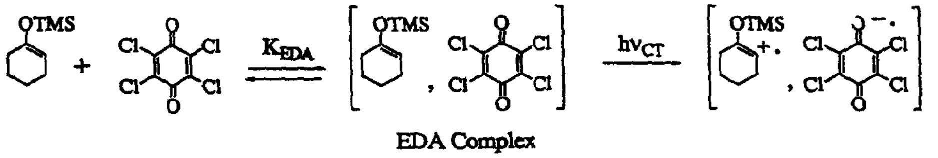


**Figure 1:** (A) Charge-transfer absorption spectra of EDA complexes of the enol silyl ethers **3**, **5** and **8** and chloranil in dichloromethane at 25 °C. (B) Low-energy portion of the photoelectron spectra of enol silyl ethers **3**, **5** and **8**. (C) Cyclic voltammograms of enol silyl ethers **3**, **5** and **8** (0.01M) in dichloromethane containing 0.3 M electrolyte (TBAH) at a scan rate of v = 200 mV $s^{-1}$ at 25 °C.

the systematic spectral shifts of the new electronic absorption bands derived from the cyclohexenyl, methylcyclohexenyl and dihydronaphthalenyl analogues **3**, **5** and **8**, respectively. [Note that neither chloranil nor the enol silyl ethers alone absorbs beyond 400 nm.] These well-resolved, but featureless absorption bands are characteristic of weak intermolecular EDA complexes in which the colors derive from the electronic transition $h\nu_{CT}$ in eq.1.[7]

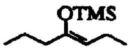
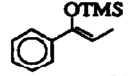
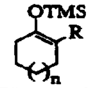
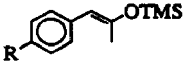
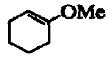
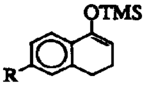
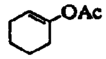
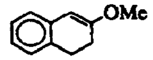
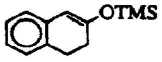
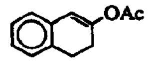


(1)

Furthermore, the charge transfer absorbance ($A_{CT}$) grew monotonically with incremental additions of enol silyl ether (TMSE) to a solution of chloranil (CA) according to the linear (spectrophotometric) relationship of Benesi and Hildebrand: $[\mathrm{TMSE}] / A_{CT} = \varepsilon_{CT}^{-1} + K_{EDA}\, \varepsilon_{CT}\, [\mathrm{CA}]^{-1}$, from which the values of $K_{EDA}$ were readily extracted.[8] The structural variations of the CT transition energy ($h\nu_{CT}$) and the formation constant ($K_{EDA}$) of the 1 : 1 chloranil EDA complexes with different enol silyl ethers are collected in Table I.[9]

The more precise determination of the energetics of electron detachment is available from the gas-phase measurement of the ionization potentials (IP) determined from the helium (I) photoelectron spectra (PES) of the enol silyl ethers. Importantly, Figure 1B presents the progression of well-resolved (HOMO) bands of **3**, **5** and **8** to successively lower energies in the same order as the bathochromic shifts of the charge-transfer absorptions (compare with Figure 1A). Similarily, the correlation of the ionization potentials of enol silyl ethers and the charge-transfer transition energy ($h\nu_{CT}$) in the chloranil EDA complex as illustrated in Figure 2 confirms Mulliken's prediction that

**Table I.** Ionization Potentials (IP) and Anodic Potentials ($E_p$) for Various Enol Derivatives. The EDA Complex Formation With Chloranil in Dichloromethane at 25 °C.

|  | Donor | IP (eV) | $E_p$ (V) | $\lambda_{max}$ (nm) | $K_{EDA}$ |  |  | IP (eV) | $E_p$ (V) | $\lambda_{max}$ (nm) | $K_{EDA}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 |  | 8.3 | 1.50 | 469 | 1.1 | 9 |  | 8.0 | 1.43 | 515 | 1.0 |
|  |  |  |  |  |  |  |  |  |  |  |  |
| 2 | R = H, n = 0 | 8.3[a] | 1.33 | 466 | 2.1 | 10 | R = H | 7.7 | 1.26 | 566 | 0.8 |
| 3 | R = H, n = 1 | 8.4 | 1.41 | 460 | 1.1 | 11 | R = $NO_2$ | 9.7 | b | c | b |
| 4 | R = H, n = 2 | 8.3[a] | 1.50 | 468 | 1.5 |  |  |  |  |  |  |
| 5 | R = Me, n = 1 | 7.9 | 1.14 | 524 | 1.0 | 12 |  | 8.4 | 1.36 | 450 | 1.3 |
|  |  |  |  |  |  | 13 |  | 8.8 | 1.79 | c | b |
| 6 | R = H | 7.8 | 1.30 | 538 | 3.7 | 14 |  | 7.6 | 1.10 | 606 | 0.9 |
| 7 | R = OMe | 7.5[a] | 1.02 | 600 | b |  |  |  |  |  |  |
| 8 |  | 7.5 | 1.10 | 590 | 1.0 | 15 |  | 8.0 | 1.48 | 492 | 2.3 |

a. Estimated from Fig. 2. b. Not measured. c. No new charge-transfer band observed in UV-vis absorption spectrum.

$h\nu_{CT}$ = IP − EA − ω,[10] where the electron affinity (EA) of the chloranil acceptor and the electrostatic interaction (ω) of the CT ion pair in eq. 1 are constant in considering the series of related EDA complexes.[11]

The adiabatic measure of the donor property of enol silyl ethers was obtained by linear sweep voltammetry at a platinum electrode in dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. Thus a well-defined anodic wave was observed in the initial positive-scan cyclic voltammogram of **3** at v = 200 mV $s^{-1}$ (Figure 1C), but no cathodic wave was observed even at enhanced scan rates. However, the irreversible anodic peak potentials ($E_p$) shifted negative in the order: **3**, **5** and **8** in accord with the trend in the

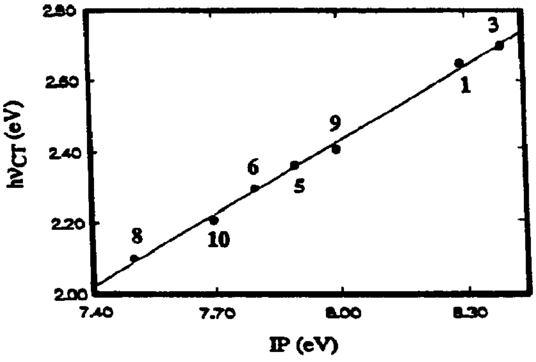


**Figure 2.** Correlation of the ionization potentials (IP) of various enol silyl ethers with the charge-transfer transition energy ($h\nu_{CT}$) of their EDA complexes with chloranil in dichloromethane.

ionization potentials. Such a direct correlation indicates that the kinetic factors affecting $E_p$ are rather constant for the series of related silyl enol ethers.[12] As such, we consider the anodic peak potentials in Table I to be indicative of the donor properties of the enol silyl ethers in solution. [Note that methyl and trimethylsilyl ethers are of comparable donor strengths, whilst corresponding enol acetates are much weaker electron-donors (see Table 1)].

We have thus clearly demonstrated that enol silyl ethers are excellent electron-donors and from an energetics consideration, an electron-transfer mechanism should be feasible when electron-rich enol silyl ethers are treated with various oxidants and electrophiles. Furthermore, the oxidative substitution reactions should be particularily efficient in the light of the facile cleavage of the labile O-Si bond in the cation radical of the enol silyl ether ($TMSE^{+\cdot}$) to allow effective competition with the energy-wasting back electron transfer.[13] The quantitative relationship between the donor strengths of a graded series of enol silyl ethers and their reactivity in electrophilic (oxidative) substitution is being explored.[14]

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