The duplication of chromophores, four BChls and two BPheos, combined with the ground-state bleaching and the formation of cation and anion radicals, obviously complicates unambiguous assignments of some of the optical changes that reflect the rapid electron transfer carried out by the RC. However, in further support of the trends predicted by the calculations (Table II), BChl blue shifts are also observed when only the donor is oxidized or the acceptor is reduced under steady-state conditions.[4,10]

**Acknowledgment.** We thank J. Deisenhofer and H. Michel for the coordinates of the *R. viridis* chromophores and C. Kirmaier and D. Holten for valuable discussions. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, under Contract DE-AC02-76CH00016 at BNL and by a University of Florida CRDC Chemical Systems Technology Center award, DAAA15-85-C-0034. M.A.T. is the recipient of an NSF predoctoral fellowship.

## Linear Free Energy Relationship between Keto ⇌ Enol Equilibrium Constants of Stable β,β-Dimesityl and Unstable β,β-Unsubstituted α-Substituted Enols[1]

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*Received March 19, 1987*

There has been a revival in this decade in the study of keto ⇌ enol equilibrium constants ($K_{\mathrm{enol}}$) of simple enols.[2,3] Two types of enols have been studied. Simple unstable aliphatic or α-aryl-substituted enols, such as those of acetaldehyde,[4] acetone,[5] acetophenone,[6] or isobutyraldehyde,[7] were prepared by Capon's,[4a,b] Kresge's,[4c,5,6c,7] and Toullec's[6a,b] groups as short-lived intermediates, and their ketonization rates are recorded. When these are combined with the enolization rates of the ketones, accurate $K_{\mathrm{enol}}$ values in water are obtained. In parallel, $K_{\mathrm{enol}}$ values for sterically crowded polyaryl-substituted enols (Fuson-type enols[8]) that are kinetically and sometimes thermodynamically rather stable, such as β,β-dimesityl α-substituted ethenols[9] or acenaphthenols,[10] were determined accurately by us[9] and by Miller[10] in nonaqueous solvents, starting from both the ketones and the enols.

Are substituent effects correlated in the two types of systems? The question is of interest for three reasons. First, since $K_{\mathrm{enol}}$ values are sometimes determined more easily in one of the systems, coorrelation will permit the estimation of values which are not otherwise available in the other system. Second, $K_{\mathrm{enol}}$ values for the β,β-dimesityl (Mes)-α-alkyl and α-H systems **1** (R = H, Me, Et, *i*-Pr, *t*-Bu) are correlated with Taft's steric parameters,[9b] with the rotational barriers of the correlated two-ring flip in these systems,[11] and with the R—C=C bond angles or the C=C—Mes (cis to R) dihedral angles for **1**.[12] Consequently, a correlation between substituent effects in **1** and in the β,β-unsubstituted α-substituted systems **2** could suggest that a correlation may exist between $K_{\mathrm{enol}}$ values for **2** and steric and structural parameters for this system. Third, the two systems differ in the bulk and the conjugative ability of the β-substituents and probably in the conformation of the OH group.[13] The solvent is also different. Could a correlation be found in spite of these differences?

**Table I.** $\mathrm{p}K_{\mathrm{enol}}$ Values for the Equilibria

$$\mathrm{R_2'CHC({=}O)R} \underset{}{\overset{k_{\mathrm{enol}}}{\rightleftharpoons}} \mathrm{R_2'C{=}C(OH)R}$$

| R | R' = H (H$_2$O, 25 °C) | ref | R' = Mes (hexane, 94.6 °C) | ref |
|---|---|---|---|---|
| Mes | (5.5)[a] | | −1.90[b] | 9b |
| H | 6.23 | 4c | −1.30[b] | 9a |
| *m*-ClC$_6$H$_4$ | 7.57 | 6b | −0.34 | 9c |
| Ph | 7.96 | 6b,6d | −0.01 | 9c |
| Me | 8.22 | 5 | 0.19[b] | 9b |
| *p*-MeOC$_6$H$_4$ | 8.64 | 6b | 0.49 | 9c |
| *t*-Bu | (10.95)[a] | | 2.23[b] | 9b |

[a] Value predicted from the linear regression. [b] At 80.6 °C.

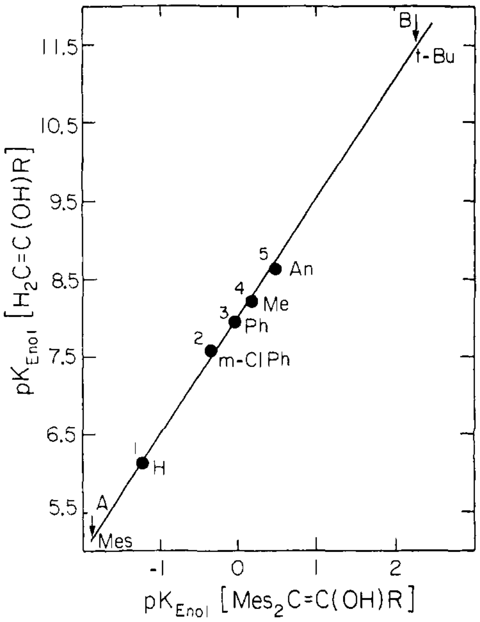

**Figure 1.** Correlation between $\mathrm{p}K_{\mathrm{enol}}$ values for $\mathrm{H_2C{=}C(OH)R}$ in water and $\mathrm{p}K_{\mathrm{enol}}$ values for $\mathrm{Mes_2C{=}C(OH)R}$ in hexane.

$$\underset{\mathbf{1}}{\mathrm{Mes_2C{=}C(OH)R}} \qquad \underset{\mathbf{2}}{\mathrm{H_2C{=}C(OH)R}}$$

Data for correlation of the $K_{\mathrm{enol}}$ values for **1** in hexane and of **2** in water are available for R = H, Me, Ph, *p*-ClC$_6$H$_4$, and *p*-MeOC$_6$H$_4$ (Table I). Data for other substituents in one series have at present no parallel in the other series and are not given, except for the values for R = Mes and *t*-Bu in system **1**. The data are plotted in Figure 1 as a LFER of $\mathrm{p}K_{\mathrm{enol}}(\mathbf{2})$ vs. $\mathrm{p}K_{\mathrm{enol}}(\mathbf{1})$, where $\mathrm{p}K_{\mathrm{enol}} = -\log K_{\mathrm{enol}}$. A linear correlation is obtained with a slope of 1.33 ($r = 0.9991$).

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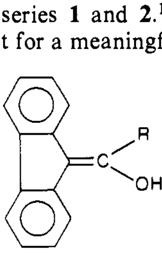
This is a remarkable correlation in view of the differences mentioned above and the fact that the data are from different sources. Also, $K_{enol}$ for the $\alpha$-aryl-substituted **1** are at 94.6 °C whereas the data for the $\alpha$-H and the $\alpha$-Me enols are at 80.6 °C. Nevertheless, we would expect a linear relationship, possibly with a different slope, even if all the data were at the same temperature,[14] but we did not try to correct for this effect since the literature values for system **2** are in the process of minor revision as a result of either better measurements or modification in rate constants used for the calculation.[15]

Although the linearity in Figure 1 may partially result from the fact that the data correlated covers only 2 orders of magnitude in each series,[16] it certainly reflects a proportionality between the substituent effects in both systems. The difference in the solvents used (hexane for compounds **1**, hydrogen-bonding water for compounds **2**) and the partial conjugation of the mesityl groups with the double bond of **1** should increase and decrease, respectively, the sensitivity to a change in the substituent in series **1**. These effects should be reflected in the magnitude of the slope, and we note that for series **3**, where the planarity is presumably higher, the change of R from H to Me reduces $K_{enol}$ more than the parallel change in series **1** and **2**.[17] However, the data available are insufficient for a meaningful analysis of the slope.



**3**

The linearity involving the *meta* and *para* aromatic substituents is not surprising since both Hammett correlations for **1** and **2** (R = *meta*- and *para*-substituted aryl) are linear.[6a,9c] However, the more interesting question as to whether steric effects in series **2** are also playing a dominant role as in series **1**[9a,b] cannot be answered since only R = H and Me appear in Figure 1.

Assuming that Figure 1 applies beyond the limited data, we calculated two $K_{enol}$ values for two extreme cases in series **2**. These are given in Table I. For the $\alpha$-mesityl compound (**2**, R = Mes) the enol is predicted to be relatively stable with a p$K_{enol}$ of 5.4 ± 0.2, whereas the $\alpha$-*tert*-butyl enol (**2**, R = *t*-Bu) is predicted to be the least stable with a p$K_{enol}$ of 11 ± 0.2 (points A and B in the figure). The latter value is of special interest since MO calculations on series **2** (R = H, alkyl) do not show a large difference in p$K_{enol}$ between **2** (R = Me) and **2** (R = *t*-Bu).[18] A direct measurement should resolve this discrepancy.

**Acknowledgment.** We are indebted to Prof. A. J. Kresge and Dr. R. More O'Ferrall for communicating to us unpublished results and to Prof. Y. Apeloig and Dr. M. Karni for calculations. The work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to whom we are grateful.

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(14) This is based on the fact that the main point which determines the slope is that for the H derivative since it is relatively remote from all the other points. Since the enol content in series **1** for R = H at equilibrium is already 95%, even a large change in the equilibrium constants (e.g., to 97% enol) at a different temperature is most likely to be within the experimental error, due to the limitation of NMR integration. Trial shifts of this point indeed still give linear relationships but with different slopes.

(15) For example, a factor of 2 was recently introduced into the calculation of $K_{enol}$ values[6a,b] due to a change in the value of the diffusion-controlled second-order rate constant. The p$K_{enol}$ value for acetophenone has been recently revised from 7.90 to 7.96.[6d] Also, when the previous p$K_{enol}$ value of 6.55 reported by Capon for **2** (R = H)[4b] is used, a linear correlation with a slope of 1.16 still prevails.

(16) The data for each series are more extensive, but the data for common substituents cover only 2 orders of magnitude in $K_{enol}$.

(17) For **3** (R = H), p$K_{enol}$ = −1.23 (Harcourt, M.; More O'Ferrall, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 822. For **3** (R = Me), p$K_{enol}$ = 2.3 (Argile, A.; Carey, A. R. E.; Harcourt, M.; Murphy, M. G.; More O'Ferrall, R. A. *Isr. J. Chem.* **1985**, *26*, 303).

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## Preparation and Structure of $[(Me_3CO)_3W{\equiv}C{-}Ru(CO)_2(Cp)]$, a Heteronuclear, $\mu_2$-Carbide Complex

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Carbon monoxide dissociates to reactive carbide and oxide fragments on many catalytically active metal surfaces. Dissociation is believed to be the first step in the reductive hydrogenation of CO via the Fischer–Tropsch synthesis and related reactions.[1] The remarkable reactivity of these surface carbides is probably due to the fact that they are highly "exposed", with a low coordination number. Most organometallic carbide complexes contain carbon atoms surrounded by at least five metal atoms.[2] However, $[Fe_4C(CO)_{12}]^{2-}$ and related tetranuclear carbide clusters studied by Bradley, Muetterties, and Shriver show high reactivity at the carbide ligand.[3] The chemistry of $[Fe_3(CCO)(CO)_9]^{2-}$ suggests the intermediacy of a very reactive $Fe_3C$ cluster.[4] The sole fully characterized example of a two-coordinate metal carbide complex is $[Fe_2(\mu_2\text{-}C)(5,10,15,20\text{-tetraphenylporphyrinate})_2]$.[5-7] A dinuclear bicarbide complex, $[Ta_2(\mu_2\text{-}C_2)\{OSi(CMe_3)_3\}_6]$, has recently been reported by Wolczanski and co-workers.[8] We report here the first heterodinuclear complex with a two-coordinate carbide ligand.

Schrock, Chisholm, and their co-workers have shown that tungsten–alkylidyne complexes efficiently catalyze alkyne metathesis according to eq 1.[9,10] In general, the largest alkyne

$$[W(\equiv CR)(OCMe_3)_3] + R^1C\equiv CR^2 \rightarrow [W(\equiv CR^1)(OCMe_3)_3] + RC\equiv CR^2 \quad (1)$$

substituent in the system ($R^1$) remains on the alkylidyne, and the

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