

SCAVENGING OF PHOTOENOLS BY ACIDS AND BASES

J.C.Scaiano^a, Véronique Wintgens^b and J.C. Netto-Ferreira^c

^aDepartment of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

^bLaboratoire de Matériaux Moléculaires, C.N.R.S., Thiais, 94320-France

^cUniversidade Federal Rural do Rio de Janeiro, Departamento de Química, Itaguaí, Rio de Janeiro, Brazil, CEP 23851

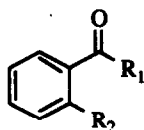
Summary: Photoenols generated by irradiation of *ortho*-methylacetophenone, *ortho*-methylbenzophenone and *ortho*-benzylbenzophenone are readily quenched by acids and bases. The rate constants for these reactions have been determined employing laser flash photolysis techniques.

The mechanism for the photoenolization of *ortho*-alkylphenyl ketones is now well established.¹⁻³ The ketone triplet state, formed via fast intersystem crossing from the singlet state, decays via intramolecular hydrogen abstraction or bond rotation followed by hydrogen transfer to a common rotationally equilibrated biradical. This biradical in turn decays to a short (*Z*) and a long (*E*) lived enol. The former undergoes a rapid 1,5-sigmatropic H-shift to regenerate the starting ketone, while the latter (*E*) lives long enough to be trapped by dienophiles and acids,^{4,5} or to rearrange to a benzocyclobutenol by an intramolecular [2+2] cycloaddition.^{6,7}

It has been generally assumed that the formation of benzocyclobutenols was only efficient from 2,6-dialkylphenyl ketones.⁸⁻¹¹ Recent work by Wilson⁶ and by Wagner,⁷ making extensive use of NMR spectroscopy,¹² demonstrates that irradiation of *ortho*-alkylphenyl ketones leads to the corresponding benzocyclobutenols which are thermally unstable and have as a result been frequently missed in earlier work (where gas chromatography was usually the detection technique). Wagner's detailed mechanistic studies⁷ show that only one isomer of the benzocyclobutenol is formed from the longer-lived, less-congested *E*-enol.⁷ Additional alkyl substitution (i.e. 2,6-) destabilizes the enol, but favors the benzocyclobutenol.

Wagner's work also showed⁷ that acids prevent cyclobutenol formation by acid-catalyzed reversion of the photoenol to the starting ketone. While it is not surprising that acids would have that effect,¹³ we could only find one rate constant in the literature.⁵ We report here that both acids and bases efficiently quench the long-lived *E*-enol formed by laser excitation of *ortho*-alkylphenyl ketones. Presumably, a similar process occurs with the *Z*-enol, although its shorter lifetime would make similar studies more difficult and would require much higher acid or base concentrations.

Ketones 1-3 were selected for this study.

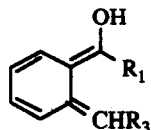


1: R₁ = R₂ = CH₃

2: R₁ = C₆H₅; R₂ = CH₃

3: R₁ = C₆H₅; R₂ = CH₂C₆H₅

The corresponding photoenols were generated by laser excitation of the starting ketone in trifluoroethanol. This solvent was selected because of its ability to dissolve readily the acids used, and because it shortens the lifetime of the *Z*-enol (reflecting that trifluoroethanol is itself a mild acid) to the point where they do not interfere with kinetic studies of the *E*-enols 4-6.



4: $R_1 = \text{CH}_3$; $R_3 = \text{H}$

5: $R_1 = \text{C}_6\text{H}_5$; $R_3 = \text{H}$

6: $R_1 = \text{C}_6\text{H}_5$; $R_3 = \text{C}_6\text{H}_5$

Laser flash photolysis of 1-3[§] leads to *E*-enol absorption spectra with λ_{max} at 390, 400 and 430 nm, respectively. These values are in agreement with literature data where available.¹⁴⁻¹⁶ The lifetimes for the *Z*-enols are relatively short: ca. 250 ns for the *Z*-enols from 1 and 2, and ~100 ns for 3. The *E*-enols derived from ketones 1 and 2 have lifetimes in excess of 200 μs while the *E*-enol from 3 has a lifetime of ~60 μs .

Addition of acids or bases leads to a shortening of the lifetimes for the *E*-enols. The rate constant for the quenching (k_q) by added quenchers (Q; acids or bases) can be obtained from a plot of the pseudo-first order rate constant for enol decay ($k_{\text{obs}} = \tau^{-1}$) against the concentration of Q, equation 1.

$$k_{\text{obs}} = k_0 + k_q[\text{Q}] \quad (1)$$

where k_0 is the reciprocal of the enol lifetime in the absence of added quenchers. Table 1 summarizes our quenching data and representative quenching plots are shown in Figure 1.

Table 1: Quenching rate constants (in units of $\text{M}^{-1}\text{s}^{-1}$) for the quenching of *E*-enols in trifluoroethanol at room temperature.

Reactants $\downarrow \Rightarrow$	4	5	6
NaOH	1.2×10^9	4.0×10^8	4.3×10^8
CH_3ONa	2.6×10^8	2.0×10^8	1.9×10^8
NaN_3	2.3×10^7	1.7×10^7	1.0×10^7
CH_3COONa	5.2×10^6	4.6×10^6	3.1×10^6
Pyridine	7.5×10^5	8.7×10^5	5.9×10^5
HClO_4	1.6×10^7	1.0×10^7	2.7×10^5
CF_3COOH	1.1×10^6	6.8×10^5	$\sim 2 \times 10^4$
CH_3COOH	$\sim 1 \times 10^4$	$\sim 2 \times 10^3$	$< 10^3$

[§] 6 can in fact have *E,E* and *E,Z* configurations; for the purposes of this letter we are only concerned with the *E* configurations at the hydroxylic carbon.

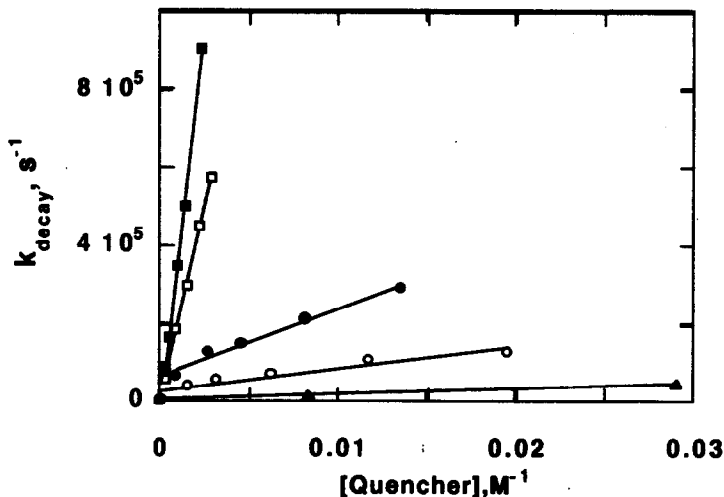
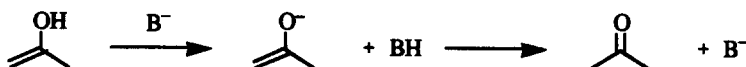
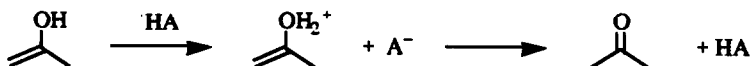


Figure 1: Quenching of the enol **5** produced by excitation of **2** in trifluoroethanol by the following quenchers: ■ : OH⁻; □ : CH₃O⁻; ● : azide; ○ : acetate; and ▲ : pyridine.

Quenching rate constants for organic or inorganic bases are quite high, falling in the 10⁵ to 10⁹ M⁻¹s⁻¹ range. For a given base the reactivities of the three enols examined are very similar. This probably reflects comparable abilities of the three enols to transfer a proton to the base with no dramatic differences in the stability of the enolate, i.e.



Quenching of the enol by acids is generally less efficient than by bases, and occurs with rate constants in the 10³ to 10⁷ M⁻¹s⁻¹ range. Porter and Tchir⁵ report a rate constant of 2 × 10³ M⁻¹s⁻¹ for reactions of acetic acid with the enol from 2,4-dimethylbenzophenone, in agreement with our results. Photoenol **6** is less reactive than **4** and **5** and the rate constants are two orders of magnitude lower. Presumably this reflects increased stability of the enol induced by the additional aromatic ring.



In summary, both acids and bases catalyze the ketonization reaction of the *E*-enol. Given the relative high rate constants for this process, one can assume that the frequent failure to detect benzocyclobutenols may reflect the presence of suitable catalysts in the solvents. This combined with the suggested thermal instability of the

benzocyclobutenol,^{6,7} probably misled researchers in the past. Our data provide for the first time a solid and systematic basis for the understanding of these effects.

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