

REACTIVITY OF ${}^1n, \pi^*$ STATES OF CONJUGATED CYCLOPROPYL KETONES¹

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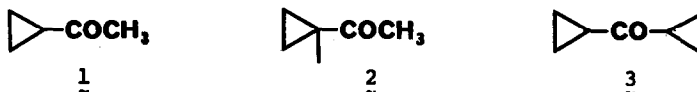
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Although there have been many recent reports of exploratory studies of cyclopropyl ketone photochemistry,² little quantitative information is available about the chemical reactivity of n, π^* excited states of conjugated cyclopropyl ketones. We report here the first measurements of bimolecular rate constants for electrophilic and nucleophilic reactions of cyclopropyl ketone n, π^* excited states. These measurements allow us to directly compare the excited state reactivity of α -cyclopropyl ketones and normal ketones to determine the effect of the introduction of an α -cyclopropyl group. Some effect might be anticipated since significant differences have been reported in the reactivity of alkanones and α -cyclopropylalkanones in bimolecular ground state reactions.^{3,4} For example, cyclopropyl methyl ketone is more basic than the analogous acyclic isopropyl methyl ketone,³ but isopropyl methyl ketone is 16 times more reactive toward NaBH₄ reduction than cyclopropyl methyl ketone.⁴ In addition, the introduction of an α -cyclopropyl group in an alkanone usually lowers λ_{\max} for both the $S_0 \rightarrow {}^1n, \pi^*$ absorption⁵ and the ${}^1n, \pi^* \rightarrow S_0$ fluorescence emission⁶ by 5-10 nm, indicating that α -cyclopropylalkanones have somewhat higher energy ${}^1n, \pi^*$ states than analogous alkanones.

Alkanone n, π^* excited states have two reactive sites: the electrophilic half-vacant oxygen n_o orbital and the nucleophilic half-occupied delocalized π_{CO}^* orbital.⁷ In order to assess the reactivity of each of these sites in ${}^1n, \pi^*$ states of α -cyclopropyl ketones we have studied quenching of the fluorescence of cyclopropyl methyl ketone (1), methyl 1-methylcyclopropyl ketone (2) and dicyclopropyl ketone (3) in benzene by the electron-poor olefin, trans-dicyanoethylene (t-DCE), and two aliphatic amines, diethylamine (DEA) and triethylamine (TEA). t-DCE quenches alkanone ${}^1n, \pi^*$ states by interaction with the

nucleophilic π_{CO}^* orbital,^{7,8} while quenching of ketone n, π^* states by amines results from interaction of the electrophilic oxygen n_o orbital with the nucleophilic amine lone pair electrons.⁹



The fluorescence quenching data were analyzed using the standard Stern-Volmer equation (eqn. 1), where ϕ_f^0/ϕ_f is the ratio of the quantum yield of ke-

$$\frac{\phi_f^0}{\phi_f} = 1 + k_D^S \tau_f [B] \quad (1)$$

tone fluorescence in the absence of bimolecular reactant, B, to the quantum yield in the presence of B, k_D^S is the bimolecular rate constant for quenching of cyclopropyl ketone fluorescence by B, and τ_f is the ketone fluorescence lifetime in the absence of B. The measured fluorescence lifetimes (τ_f) and k_D^S values obtained for 1-3-DCE, DEA and TEA quenching of the fluorescence of 1-3 and a model alkanone, 3-methyl-2-butanone, are given in the Table.

Looking first at the quenching of cyclopropyl ketone fluorescence by 1-3-DCE, we see that k_D^S for quenching the excited singlet states of α -cyclopropyl ketones 1-3 by this electron poor olefin is close to the value of $5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ estimated for diffusion-controlled quenching in benzene.¹⁰ Little variation is observed in the quenching rate constants as a function of cyclopropyl ketone structure. Furthermore, although the k_D^S values for α -cyclopropylalkanones 1-3 are slightly greater than k_D^S for the model alkanone, 3-methyl-2-butanone, it is clear that the reactivity of the nucleophilic π_{CO}^* orbital of alkanone $^1n, \pi^*$ states toward 1-3-DCE is not substantially altered by the introduction of an α -cyclopropyl group.

Similar conclusions can be drawn from the data on DEA and TEA quenching of cyclopropyl ketone fluorescence. Again, (a) the bimolecular quenching rate constants are close to the diffusion-controlled limit in benzene; (b) only minimal changes in k_D^S are observed with variations in α -cyclopropylalkanone structure; and (c) the reactivity of the carbonyl $^1n, \pi^*$ state toward DEA and TEA quenching

is not substantially changed in going from an alkanone to an α -cyclopropylalkanone. Thus the reactivity of the electrophilic half-vacant n_o orbital of the alkanone ${}^1n, \pi^*$ state toward alkyl amines is also relatively insensitive to the introduction of an α -cyclopropyl group.

In conclusion, the differences in the electrophilic and nucleophilic bimolecular reactivity of ${}^1n, \pi^*$ states of conjugated cyclopropyl ketones and alkanones are minimal and are certainly much smaller than the variations observed in ground state reactivity of α -cyclopropylalkanones and alkanones.^{3,4} The insensitivity of the reactivity of alkanone ${}^1n, \pi^*$ states toward t-DCE and alkylamines to the introduction of an α -cyclopropyl group is most likely due to the fact that these bimolecular reactions occur initially at close to the diffusion-controlled rate. Thus the reactions are already sufficiently exothermic that electronic effects and changes in the energy of the alkanone ${}^1n, \pi^*$ state caused by introduction of the cyclopropyl group have little effect on the bimolecular rate constants.

TABLE
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| <u>Ketone</u>       | <u><math>\tau_f</math>, nsec (a)</u> | <u><math>k_b^s, 10^3 M^{-1} sec^{-1} (b)</math></u> |            |            |
|---------------------|--------------------------------------|-----------------------------------------------------|------------|------------|
|                     |                                      | <u>t-DCE</u>                                        | <u>DEA</u> | <u>TEA</u> |
| 3-methyl-2-butanone | 2.3                                  | 3.0                                                 | 1.4        | 1.3        |
| 1                   | 1.5                                  | 3.9                                                 | 2.5        | 2.4        |
| 2                   | 1.9                                  | 3.6                                                 | 1.9        | 1.8        |
| 3                   | 1.1                                  | 3.5                                                 | 2.1        | 1.7        |

(a) Fluorescence lifetimes in benzene, measured using single photon counting technique. Error  $\pm$  15%.

(b) Observed bimolecular rate constants for quenching of alkanone fluorescence in benzene. Calculated using the observed  $\tau_f$  values and the slopes ( $k_b^s \tau_f$ ) of the Stern-Volmer plots for room temperature quenching of maximum fluorescence intensity. Concentration of ketones was adjusted to give optical density equal to 0.8 to 0.9 at  $\lambda_{ex}$  (310 nm). Error  $\pm$  15%.

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