

A PHOTOCHEMICAL REACTION INVOLVING UPPER EXCITED STATES

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Among various carbonyl compounds which will undergo photochemical reactions with simple olefins to give oxetanes, 9-anthraldehyde is especially interesting in its behavior. Although it has a low-lying π, π^* triplet state, it reacts with simple olefins to form oxetanes in appreciable quantum yields.¹ It has been suggested that the reactive state in this reaction may be an upper triplet state^{1,2} or a singlet excited state.³ Another interesting aspect of this reaction is that the oxetane formation is dependent on the wavelength of exciting light.¹ Oxetane is the major product if light shorter than 400 m μ is used, while the dimer of anthraldehyde is the major product if light longer than 410 m μ is used. Recent work from our laboratory indicated that the reaction involves two reacting states of anthraldehyde.² Their respective lifetimes may be estimated from the slope of a Stern-Volmer plot to be 3×10^{-10} sec and 1×10^{-9} sec approximately.² The current investigation deals with the identification of these two states.

Hammond and his coworkers demonstrated elegantly that the nature of a reactive state in a photochemical reaction may be determined via photosensitization with sensitizers of various levels of triplet energy.⁴ The method has been applied successfully to many photocycloaddition reactions.⁵ The application of this method is extended to the photochemical reaction between 9-anthraldehyde and 2,3-dimethyl-2-butene. The irradiations were carried out with monochromatic light of 3130 Å in an apparatus previously described.⁶ Benzene solutions containing 0.01 M of 9-anthraldehyde and 1.0 M of 2,3-dimethyl-2-butene and sufficient concentration of a sensitizer which will absorb over 95% of the incident light were prepared and degassed by repeated freezing and thawing before irradiation. The progress

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of irradiation was monitored by examining the absorption of 9-anthraldehyde in 4400-4600 Å region with a Cary-14 Spectrophotometer. The irradiations were carried out in the absence of a sensitizer, and in the presence of xanthone, acetophenone, 3,4-dimethylacetophenone, triphenylene and 2-acetonaphthone. Quantum yields were determined with the aid of a ferrioxalate actinometer as well as by comparison with irradiation in the absence of sensitizer. The data are summarized in the following Table.

| Sensitizer | Conc. | E_T (Kcal/mole) | ϕ |
|-------------------------------|-------|-------------------|--------|
| None | - | -- | 0.015 |
| Xanthone | 0.1 M | 74.2 | 0.070 |
| Acetophenone | 2.0 M | 73.0 | 0.016 |
| 3,4-Dimethyl- acetophenone | 2.0 M | 70.0 | 0.019 |
| Triphenylene | 0.1 M | 66.6 | 0.019 |
| 2-Acetonaphthone | 0.4 M | 59.0 | 0.000 |

The failure of 2-acetonaphthone as a sensitizer for the reaction between 9-anthraldehyde and 2,3-dimethyl-2-butene sets the lower limit for the triplet energy level of either reactive state in this reaction, i. e., both states, if they are triplet, will have an energy level above 58 Kcal. Since the lowest triplet of 9-anthraldehyde is estimated at about 41 Kcal, this experiment excludes the lowest triplet as one of the reactive states in this reaction.

The absorption spectrum of 9-anthraldehyde possesses a group of bands between 350-410 m μ which extends substantially beyond 410 m μ . These bands correspond to the beta-bands (L_a) of anthracene but are more diffuse and red-shifted from the parent compound.⁷ The electronic transition associated with these bands exhibits some charge-transfer character as they are red-shifted in polar solvents. There is also some indication of complexation between anthraldehyde and the olefin as the longest wavelength band is substantially red-shifted in 2,3-dimethyl-2-butene from hexane [from 415-418 m μ to 420-428 m μ]. There may be other less intense transitions masked by these relative intense bands.

Since direct excitation into the last band of anthraldehyde in olefins yields primarily the dimer of anthraldehyde, the lowest singlet excited state cannot be responsible for the formation of oxetane. If an excited singlet state is responsible for the formation of oxetane, it will have to be an upper singlet state.

Recent elegant contributions from various laboratories have shed light into the nature of excited states of aromatic compounds. Kearns demonstrated that n,π^* excited states of

aromatic carbonyl compounds are localized excited states and that n,π^* triplet state of naphthalene carbonyl compounds are not substantially shifted from those of phenyl carbonyl compounds.⁸ Contribution by Liu and Edman indicated that there is a reactive second triplet state of anthracene and its derivatives [T_2] which will sensitize reactions of rigid unconjugated olefins. With exciting light in the 3130-3660 Å region, at least five electronic excited states may be accessible in 9-anthraldehyde. These include two singlet states, the n,π^* and the L_a [π,π^*] state, and three triplet states, the n,π^* triplet, the T_2 state [π,π^*], and the lowest triplet state [π,π^*]. It is highly unlikely that an upper vibrational level of an electronic excited state is involved in this reaction, since the lifetime of the shorter-lived reactive state in 9-anthraldehyde has been estimated which is orders of magnitude longer than the commonly accepted rates of vibrational relaxation in solution.

Our current data indicate that the lowest triplet state and the lowest singlet excited state of 9-anthraldehyde are not the reactive states in its photochemical addition to 2,3-dimethyl-2-butene. The two reactive states are, therefore, very likely the T_2 , the n,π^* triplet or the n,π^* singlet states of 9-anthraldehyde. Since the reactive states may be populated more efficiently by sensitization with xanthone than by direct irradiation (see Table) and the n,π^* triplet state is spin-orbitally coupled with the L_a singlet state,¹⁰ it is very probable that the observed reactive states reported recently² are the T_2 state and the n,π^* triplet state; however, the possibility of the n,π^* singlet state being among them cannot be excluded at this moment.

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