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AN ALKOXY RADICAL AS A MODEL FOR THE n,π^* EXCITED STATE

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It is well recognized that the weak absorption band of ketones and aldehydes occurring in the 280-360 millimicron region arises from excitation of a nonbonding 2p electron to the antibonding π orbital. This has been designated as the n-π^* state by Kasha (1). After electron promotion the excited n-π^* state has two electrons in the bonding π orbital, one in the antibonding π^* orbital and the remaining 2p electron still localized on oxygen. Since it is the two bonding electrons which make the molecule planar, the n-π^* excited state still retains planarity and has the remaining 2p electron located in an orbital orthogonal to the plane of the carbonyl double bond. The analogy of this state (which has an unpaired electron localized on the oxygen atom) with an alkoxy radical seems reasonable. Thus the photoreduction (2) and oxetane formation (3) processes of the n-π^* state are analogous to reactions of alkoxy radicals which are known both to abstract hydrogen from hydrocarbons and to add to olefins (4). In order to further demonstrate the validity of this comparison, we have examined the relative reactivities of a number of hydrocarbons with carbonyl compounds that are known to have the n-π^* triplet as their lowest excited state.

Competitive experiments were carried out photochemically on mixtures of hydrocarbons and ketone in sealed degassed tubes. The tubes were placed around a 450 watt Hanovia lamp, irradiated for 82 hours and analyzed by gas chromatography. The ratio of the rate constants for the reaction of each hydrocarbon with the ketone was then calculated using the expression.

$$\frac{k_{R_aH}}{k_{R_bH}} = \frac{\log \dfrac{[R_aH]_i}{[R_aH]_f}}{\log \dfrac{[R_bH]_i}{[R_bH]_f}}$$

where $[R_aH]_i$ and $[R_bH]_i$ are the peak areas of the two hydrocarbons relative to an internal standard prior to reaction, and $[R_aH]_f$ and $[R_bH]_f$ the same quantities after reaction.

The results of competitive measurements are summarized in Table I. It is evident from the data listed that n,π^* triplets show considerable selectivity in their attack on C-H bonds. In each series, the results approximate the order of decreasing C-H bond strengths, except when comparison is made between ethylbenzene and cumene. In view of the different molecules involved and the discrepancies between the other set of measurements, the agreement of the entire series appears satisfactory and supports the hypothesis that the alkoxy radical can serve as a model for the n,π^* triplet state. It should also be noted that the results of relative reactivity determinations for a number of ketones are within experimental error, demonstrating that the unpaired electron localized on the oxygen atom is independent of the alkyl

TABLE I

Relative Reactivities of Hydrocarbons Toward n-π^* Triplets

		------------- Relative Reactivity Per Molecule* --------------				
Compound	Sensitizer:	$PhCOCH_3$	$PhCOC_3H_7$	PhCOPh	4-Me-PhCOPh	t-BuOCl**, 4
Mesitylene		5.51	5.01	5.34	5.27	4.01
Cyclohexane		4.33	4.12	4.08	3.97	6.00
Ethylbenzene		3.06	2.88	3.05	2.96	2.30
Cumene		2.66	2.77	2.88	2.84	2.80
Toluene		1.00	1.00	1.00	1.00	1.00
2,3-Dimethylbutane		0.88	0.82	0.84	0.96	3.15
t-Butylbenzene		0.30	0.30	0.26	0.24	0.32

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* Experimental error is estimated as approximately 5% (spread of duplicate experiments).

** Relative Reactivities of hydrocarbons toward t-butyl hypochlorite at 40°.

substituent on carbon.

The major discrepancy between the relative rate constants for the $n\text{-}\pi^*$ triplet and those for the t-butoxy radical occurs with the two saturated systems. This difference, however, is certainly complicated in both cases by the radical complexing properties of the alkoxy radical and the $n\text{-}\pi^*$ triplet. By analogy with the known solvent participation in the alkoxy radical system (5, 6), one might anticipate a related complexed $n\text{-}\pi^*$ triplet with one or more solvent molecules. It is entirely possible that the rate determining step for both the $n\text{-}\pi^*$ triplet and the alkoxy radical is the formation of a highly solvated "complex". The ease of formation of the "complex" in both the radical and triplet system may be the same with aromatics but differ with aliphatics (7). Thus, the $n\text{-}\pi^*$ triplet and the alkoxy radical may react similarly towards aromatics but differently toward aliphatic hydrocarbons. The observed discrepancy could then be attributed to a difference in the rates of solvation in both systems. Experiments designed to investigate this point are in progress.

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7. Or, alternatively, as has been suggested by a referee, perhaps the complexes form rapidly, and their equilibrium constants with aromatics are the same for alkoxy radicals and triplets, but differ with aliphatics.