

Interest in the mechanistic and synthetic aspects of organic photochemistry has been marked during the last few years.<sup>2</sup> However, the nature and behavior of the electronically excited states which are *intermediates* in photochemical reactions probably seem mysterious to many chemists who have not had extensive background in quantum mechanics and molecular spectroscopy. It is the purpose of this paper to clarify some confused and confusing concepts employed by photochemists concerning the reactivity of molecules in related photochemical reactions.

### Photochemical Efficiency, Reactivity and % Yield

Three terms often employed with relation to photochemical reactions are *efficiency*, *reactivity*, and *% yield*. The *efficiency* of a photochemical reaction is an output relative to an input. Generally, the *quantum yield*,  $\Phi$ , is the term used to describe the number of molecules of product formed relative to the number of quanta absorbed by the system which produce the reactive state, i.e., the efficiency of a photochemical reaction (eqn. (1)).

$$\text{Efficiency} = \frac{\text{output}}{\text{input}} \\ = \Phi = \frac{\text{Number of molecules produced}}{\text{Number of quanta absorbed}} \quad (1)$$

For each electronically excited state there exists a number of processes, each of which possesses a characteristic  $\Phi$ . If we ignore chain processes, then the sum of the quantum yields for all processes which occur from an electronically excited state equals unity, i.e., since the excited state is metastable the efficiency of its destruction is unity.

Consider now an electronically excited state  $A^*$  which may undergo two processes: reaction which results in isolatable products (eqn. (2)) or return to the ground state molecule  $A_0$  without any net reaction (eqn. (3)). Equation (3) represents a "waste" mechanism which will cause the efficiency or quantum yield of reaction to be less than unity.



If the steady-state assumption<sup>3</sup> is applied to eqns. (2) and (3), then the quantum yield for product formation may be rephrased in terms of the rates of processes as follows:

$$\Phi_p = \frac{k_1[A^*]}{k_1[A^*] + k_2[A^*]} = \frac{k_1}{k_1 + k_2} \quad (4)$$

In other words, the efficiency of product formation,  $\Phi_p$ , is given by the ratio of the rate of product formation to the sum of the rate of all processes which deactivate  $A^*$ .

It is clear from eqn. (4) that photochemical efficiency as measured by  $\Phi$  and photochemical reactivity as measured by the absolute rate constant for reaction are *not fundamentally related*. For example, if a series of photochemical reactions all have unity quantum yields, there is no guarantee that they have similar rate constants for reaction, only that whatever the rate constant for reaction is, it is much larger than the rate constant for competing reactions. An outstanding example of the possible discrepancies between  $\Phi$  and  $k$  which may arise derives from the work of Wagner and Hammond<sup>4</sup> for the photochemical cleavage of branched ketones into methyl ketones and olefins ("Type II cleavage") as shown in the table.

Quantum Yields and Rate Constants for Type II Cleavage from Triplet Ketones (Based on Unit Efficiency for Triplet Formation)<sup>a</sup>

Compound	$\Phi$	$k(\text{sec.}^{-1})$
$\text{RCOCH}_2\text{CH}_2\text{CH}_2\text{R} \xrightarrow{h\nu} \text{RCOCH}_3 + \text{CH}_2=\text{CHR}$		
$\text{O} \text{COCH}_2\text{CH}_2\text{CH}_3$	0.40	$3 \times 10^6$
$\text{O} \text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.45	$5 \times 10^7$
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	0.36	$2 \times 10^6$
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.38	$1 \times 10^8$

<sup>a</sup> See reference given in footnote

It is striking to note that the measured rate constants vary over nearly three orders of magnitude, yet the quantum yields for reaction are nearly constant. Although this behavior may not be common, it serves to emphasize the hazard and confusion which arise from identifying  $\Phi$  with reactivity.

The % yield of product isolated bears an even more distant relationship to photochemical reactivity. The % yield may be expressed in terms of quantum yields as

$$\% \text{ yield} = \frac{\Phi_p}{\Phi_p + \sum \Phi_i} \quad (5)$$

where  $\Phi_i$  is the quantum yield for all other reactions of

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<sup>2</sup> For recent reviews of photochemistry see: (a) CALVERT, J., AND PITTS, JR., J. N., "Photochemistry," John Wiley and Sons, Inc., New York, 1966. (b) TURRO, N. J., "Molecular Photochemistry," W. A. Benjamin Co., New York, 1965. (c) KAN, R. O., "Organic Photochemistry," McGraw-Hill Book Co., New York, 1966. (d) NECKERS, D. C., "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, 1967.

<sup>3</sup> Reference (b) in footnote 1, p. 145.

<sup>4</sup> WAGNER, P. J., AND HAMMOND, G. S., *J. Am. Chem. Soc.*, **88**, 1245 (1966).

the electronically excited state. Although it is safe to say that quantum yield of product formation close to unity assures a high % yield, the converse statement does not hold. Thus, if

$$\Phi_p = 0.01 \text{ but } \sum_i \Phi_i = 0.0001$$

then the % yield  $\cong 100\%$ . On the other hand, if

$$\Phi_p = 0.50 \text{ but } \sum_i \Phi_i = 0.50$$

then the % yield equals only 50% even though the quantum yield is higher in the latter example.

#### The Rate of a Photochemical Reaction

A final term for consideration here is the *rate* of a photoreaction as given by the number of moles of product produced in a given time. Two questions which occur to the uninitiated are: why does one have to irradiate for hours or days to achieve acceptable yields in some cases, yet the lifetimes of the electronically excited intermediates are of the order of microseconds, and why do two reactions which both have nearly unit quantum efficiency sometimes have grossly different rates?

In order to gain an appreciation of the answer to this question we must recognize that the rate of a photoreaction is dependent on a number of factors as shown in eqn. (6)

$$\text{rate} = I\Phi^*F\Phi_p \quad (6)$$

$I$  is the rate of absorption of light by the system,  $\Phi^*$  is the fraction of absorbed light which produces the reactive state,  $F$  is the fraction of the total incident light which is absorbed, and  $\Phi_p$  is the quantum yield of prod-

uct formed. Thus, the *quantum yield for product formation* does not appear in the rate equation as a dominant term. Other important considerations are the intensity of light utilizable by the system,  $I$ , the fraction of this light absorbed,  $F$ , and the fraction of the absorbed light that leads to the reactive state,  $\Phi^*$ .

Consider the following example of a reaction for which  $\Phi^* = \Phi_p = I = \text{unity}$ , i.e., the best attainable conditions in the absence of a chain reaction. A reasonable intensity of polychromatic light would be  $10^{19}$  quanta/sec which is equal to  $1.7 \times 10^{-5}$  moles of quanta/sec (a mole of quanta is called an Einstein). The rate would then be  $1.7 \times 10^{-5}$  moles of product/sec. It would take  $6 \times 10^4$  sec (about 17 hr) to produce one mole of product.

#### Conclusion

The synthetic organic chemist is accustomed to equating % yield with reactivity for reactions involving related structures. His essential assumption is that the rate constants for various processes possible for a molecule under given conditions behave in a predictable and uniform manner, as the structure of the substrate is varied. The % yield of a photochemical reaction, however, is somewhat distantly related to the inherent reactivity of an electronically excited state. Therefore, attempts to rationalize the reactivity of electronically excited states on the basis of % yields encounter severe pitfalls. Correlation of quantum yields with reactivity must be attempted with caution. The rate constant for reaction of an electronically excited state is the safe and true measure of reactivity in photochemical reactions.