DISCUSSION SECRETARY’S REPORT

B. Stevens
University of Sheffield, U.K.

The discussion was opened by Hochstrasser who re-stated that the aims of his work were concerned with environmental effects on the radiationless transition from the lowest triplet to the ground state of an organic molecule; undoubtedly, the transition probability is considerably enhanced in the crystalline state of aromatic hydrocarbons. The question arises as to whether this enhancement occurs at a singly excited site or whether the extensive transfer of triplet excitation energy (possibly leading to triplet–triplet annihilation) is a necessary precursor. An analysis of the experimental data excludes mutual annihilation as the principal mode of triplet state relaxation and indicates that the crystal triplet state lifetimes of ca. \(10^{-3}\) sec reflect the rate of transition from an excited triplet region into lattice states of the pure crystal. With reference to the rapporteur’s suggestion that the absence of phosphorescence may be due to the presence of impurities, Hochstrasser pointed out that in this case an organic impurity phosphorescence might be expected, yet this was not observed in the spectral region from 300–1000 nm at 4.2°K; moreover, the spectra are sensitive to the presence of aromatic traps at concentrations of ca. \(10^{-4}\) M, whilst extensive repurification and degassing of materials always provides non-phosphorescent crystals.

Holmstrom emphasized that, in the absence of oxygen, the transient produced by the flash excitation of riboflavin in aqueous solution appears to be a semiquinone which decays by a bimolecular disproportionation process. In the presence of oxygen the riboflavin is regenerated from its leuco form whereas the absence of any overall reaction in the presence of ascorbic acid is attributed to oxidation of the semiquinone (which is observed) by dehydroascorbic acid. The overall process appears to involve two one-electron steps. Preliminary investigations indicate that tryptophan reduces riboflavin following flash exposure, the nature of the oxidation product being uncertain;
a second intermediate observed in this system is probably a complex between tryptophan and an excited riboflavin molecule.

In a discussion of the paper on flavin photosensitized decomposition of DNA nucleotides, Knowles pointed out that he was unable to account for the much faster destruction of guanylic acid unless this was due to more efficient energy transfer from flavin. An unpublished contribution to the flash photochemistry of flavins by his associates was described by Terenin; in the presence of diphenylamine as electron donor, electron transfer to lumiflavin was observed in pyridine, dimethylformamide and in glycerol at room temperature, but when the lumiflavin is replaced by lumichrome the transient spectrum of the diphenylamino radical was observed, indicating that hydrogen atom transfer took place in this system.

The dependence of the indole fluorescence spectrum on solvent polarity described by Lumry, Janari and Bovey led Birks to suggest that the red-shifted fluorescence spectrum observed in polar solvents might be an excimer band. Lumry confirmed, however, that this possibility had been considered but that studies of the concentration dependence of the emission spectrum in several solvents revealed no excimer effects; moreover, the indole concentrations were always less than $10^{-4} \text{M}$ and if any indole-indole interaction occurred it was in the dry hydrocarbon solvents and not in the polar solvents where the red-shift can be quantitatively related to the bond moments of the solvent molecule.

Pitts dealt with two contrasting situations in which different modes of photodecomposition of substituted ketones are or are not accompanied by changes in the absorption spectrum of the parent molecule. In the first case a series of ketones containing the cyclopropane group differed considerably in their mode and efficiency of decomposition in the gas phase at 120°C when excited by light of wavelength 313 nm, although their absorption spectra are almost unchanged, as shown in Table 1. The decomposition ranges from an almost complete dissociation into CO and free radicals to a virtually exclusive intramolecular rearrangement involving no free radical or CO formation. In the second case both the quantum yield of ethylene formation in a Norrish type II split and the absorption spectrum of butyrophenone change considerably when substituents are introduced to the benzene ring; these results are summarized in Table 2. The negligible quantum yield of ethylene formation and the marked red shift in the absorption spectrum of the para-NH$_2$ and para-OH derivatives are attributed to
**Table 1.** Quantum yields $\Phi$ of CO in the photolysis of 'model' ketones with cyclopropyl rings (313 nm and at 120° C)

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Structural formula</th>
<th>$\Phi_0$</th>
<th>$\lambda_{max}$ nm</th>
<th>$\epsilon, \lambda_{max}$ (l-mole$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>O</td>
<td>0.04</td>
<td>278</td>
<td>0.27</td>
</tr>
<tr>
<td>II</td>
<td>O</td>
<td>0.88</td>
<td>284</td>
<td>0.34</td>
</tr>
<tr>
<td>III</td>
<td>O</td>
<td>0.65</td>
<td>281</td>
<td>0.28</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>0.009</td>
<td>288</td>
<td>0.34</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>0.76</td>
<td>300</td>
<td>0.27</td>
</tr>
</tbody>
</table>

**Table 2.** Effect of substituents on the reaction:

<table>
<thead>
<tr>
<th>Substituent</th>
<th>none</th>
<th>$p$-CH$_3$</th>
<th>$p$-F</th>
<th>$p$-OCH$_3$</th>
<th>$p$-OH</th>
<th>$p$-NH$_2$</th>
<th>o-OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantum yield of ethylene</td>
<td>0.24</td>
<td>0.20</td>
<td>0.15</td>
<td>0.06</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
a change in the character of the lowest excited state from $^3(n,\pi^*)$ in butyrophenone and the para-CH$_3$ derivative to a triplet state of pronounced charge transfer character in the unreactive compounds in which electron transfer from the para-substituent to the oxygen atom of the carbonyl group inhibits the intramolecular hydrogen atom abstraction process via a six-membered ring intermediate.

Smith asked if the lack of photochemical reactivity of the ortho-hydroxy butyrophenone could be due to a competitive hydrogen bonding process: Pitts agreed that hydrogen transfer from the phenolic group must effectively compete with transfer of the $\gamma$ hydrogen atom in the side chain in the excited molecule, thereby inhibiting eventual photochemical change. In answer to Kleczkowski, who asked why the difference in photochemical activity of the two isomeric bicyclic ketones should be drastically different in view of their spectral similarity, Pitts pointed out that one of these could undergo rearrangement to a conjugated cyclohexenone thus:

\[
\begin{array}{c}
\text{O} \\
\text{CH}_3 \text{C} \quad \text{hv} \quad \text{O} \\
\end{array}
\]

which is similar to the behaviour of méthylecyclo-propenyl ketone:

\[
\begin{array}{c}
\text{O} \\
\text{CH}_3 \text{C} \quad \text{hv} \quad \text{O} \\
\end{array}
\]

whereas such a bond rearrangement is not possible in the other isomer which dissociates into CO and a variety of unsaturated hydrocarbons.

In his discussion of energy transfer between molecules of chlorophyll-$a$ and Cu-pheophytin in monolayers Tweet concluded that the exciton treatment is the correct approach although agreement between theory and experiment is not as good as expected. He pointed out that it is not necessary to postulate triplet-triplet energy transfer to account for the observed results and that the variation in quantum yield of chlorophyll-$a$ fluorescence with packing indicates that the molecules must be rigidly oriented in the chloroplast to account for its relatively
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high fluorescence yield. In reply to Thomas, who asked if the fluorescence yield of chlorophyll in the monolayers is as high as it is in organic solutions, Tweet stated that the maximum yield had not been measured but, on the assumption that its value is 0.3 as in dilute solution, the mean energy transfer distances calculated on the basis of Förster’s theory are in excellent agreement with those measured.

In explanation of his statement that a triplet state will abstract a hydrogen atom rather than a hydride ion, due to rules of spin conservation, Radda replied that the product of hydride ion transfer will be the ionized form of reduced riboflavin which may be expected to have a higher triplet state than that of oxidized FMN; this path would therefore be unfavourable as a result of both energy and spin considerations. He also pointed out that his experiments were performed in the absence of oxygen, and that his results concerning the formation of a complex between the quenching agent in photoreduction and the excited flavin (in the triplet state) might explain Holmstrom’s observation of a new absorption band in the presence of tryptophan.

With reference to his paper on the photodynamic inactivation of trypsin by dyes, Spikes stressed that very little is known about the mechanism of dye-sensitized photo-oxidation of enzymes, and that, indeed, this may be different for different dye molecules. Vladimirov also emphasized that many reactions can occur simultaneously in biological systems and suggested that the main reaction leading to protein inactivation involved an intermediate of the sensitizer which is stable at liquid nitrogen temperatures but which reverts to the ground state when heated. He also suggested that since the production of this intermediate is a two-quantum process at low temperatures, whereas photoinactivation requires one quantum only at room temperature, the effect of the second quantum is to provide the necessary thermal energy at low temperatures.

Commenting on Terenin’s introductory lecture, and in particular on biphotonic processes, Bellin asked if any photochemical reaction had been studied both in the vacuum u.v. region and as a biphotonic process at longer wavelengths, and if it was possible in this way satisfactorily to account for the observed energy requirement of the reaction mechanism. Porter also questioned the possibility of a two-quantum process involving absorption by the triplet state of benzene and toluene when, in fact, triplet–triplet absorption by these compounds has never been observed by flash photolysis. In reply, Terenin stated that the biphotonic reactions described have been
studied only in the near u.v. region of the spectrum since, at shorter wavelengths, absorption by the solvent would be considerable. He also agreed that the failure to observe triplet–triplet absorption in benzene and toluene appears to have been overlooked by Voevodsky and co-workers whose work he had reported, and that, in view of this, the interpretation given should probably be revised.