Since A_DH is formed by several reactions besides the abstraction reaction, its yield is considerably the larger. Therefore, only the yield of A_HD, which is formed only by the abstraction reaction, can be used as a measure of the formation of AM_0B. Statistical and isotope-effect considerations lead to a total G_{AM_0B} of eight times that for G_{A_HD}. Therefore, the G_{A_HD} of 0.2 in the high dose rate experiment leads to a G_{AM_0B} of 1.6. This is an unrealistically high upper limit because the analytical sensitivity required such a high dose that only 3% of the butene remained unreacted; this means that the rate of the propagation reaction is quite diminished during much of the reaction, so that the yield of AM_0B should be enhanced. The true G_{AM_0B} is probably less than unity.

Mechanisms of Photochemical Reactions in Solution. XXVIII.[1] Values of Triplet Excitation Energies of Selected Sensitizers

BY WILLIAM G. HERKSTROETER,[2] ANGELO A. LAMOLA,[2] AND GEORGE S. HAMMOND

The triplet excitation energies of a number of compounds have been determined by emission spectroscopy. Some of the principles involved in the choice of photosensitizers are discussed.

Introduction

Intermolecular transfer of electronic energy has become a powerful tool for uncovering new photochemical reactions,[3] for directing the course of photochemical reactions,[4] for elucidating the mechanisms of photochemical reactions,[5] and for obtaining information about molecular excited states not possible to obtain by ordinary spectroscopic methods.[6] Transfer of triplet excitation energy,[7] generally more efficient than transfer of singlet excitation in solution, has found extensive application in photochemical reactions. Of special interest are recent studies in this laboratory which have demonstrated a strong dependence of the reaction course upon the triplet excitation energy of the sensitizer (donor).[8,9] For these studies it was necessary to have available a series of sensitizers with triplet excitation energies distributed over a large range.

Only a limited number of triplet state energies have been reported in the literature and, for the most part, the values reported were not satisfactory for our use, either because of discrepancies among these values or because the solvents employed in these determinations differed from those in our experiments. Solvent effects on triplet energy levels depend upon the nature of the transition involved, and significant spectral shifts have been observed. Almost without exception, the literature values were determined with the compounds dissolved in rigid alcohol-containing solvents. The correlation of our results with these reported values was not possible since nonpolar hydrocarbon solvents were employed in our experiments.

We report herein the triplet-state energy values of a large number of compounds, mostly hydrocarbon and carbonyl compounds, as determined from phosphorescence spectra in rigid hydrocarbon solvents at 77°K.

Experimental

The triplet-state energies reported here, unless stated otherwise, were determined from phosphorescence spectra of the compounds dissolved in rigid glasses at 77°K. These spectra were recorded by either of the two methods described below.

Spectrographic Method.—Light from a General Electric AH-4 mercury lamp was filtered through a Corning 7-54 glass color filter and focused on a frozen, degassed solution of the sample contained in a sealed Pyrex tube held in a Pyrex dewar containing liquid nitrogen. The phosphorescence emission, separated from source emission and sample fluorescence by means of a Becquerel phosphoroscope, was focused on the entrance slit of a Bausch and Lomb 0.5-m. quartz prism spectrograph and the spectrum photographed on glass spectroscopic plates. Microdensitometer tracings (Joyce-Loebl recording microdensitometer) were recorded directly from the plates. Mercury lines photographed along with the sample phosphorescence were used to calibrate the spectra.

Spectrophotometric Method.—A photoelectric spectrophosphorimeter consisting of a Jarrell-Ash Ebert scanning monochrometer ($f/9$), an EMI 9558 photomultiplier tube, a "rotating can" phosphoroscope, an electrometer amplifier, and a Bristol 1-sec. strip chart recorder was used to record the spectrum of the phosphorescence emission. The samples were frozen, degassed solutions contained in sealed Pyrex tubes held in a Pyrex dewar containing liquid nitrogen. A G.E. AH-4 source was employed along with interference filters or Corning color glass filters to isolate the groups of mercury lines centered at 3130 and 3660 Å. The spectra were scanned at a rate of 50 Å. per min. A correlation of scanning rate and recorder chart speed allowed wave length determination (± 5 Å.) directly from the recorded spectra. The wave length indicator on the monochrometer was calibrated from time to time using the mercury lines as standards. Spectra recorded in this manner were better resolved than those obtained by the photographic method and more accurate determinations of the wave lengths of band maxima could be made.

Solvents.—A variety of solvents or solvent mixtures will form clear glasses when cooled to liquid nitrogen temperatures.[10] Those used in these determinations were 3-methylpentane (MP); methylcyclohexane–isopentane 5:1 by volume (MCIP); iso-pentane–methylcyclohexane 1:5 (IPMC); ether–isopentane–ethanol 5:5:2 (EPA); and ether–ethanol 1:2 (EA). The hydrocarbon solvents were distilled prior to use. All solvents and solvent mixtures were checked for impurity emission before use.

(1) Part XXVII: R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1892 (1964).

(2) National Science Foundation Predoctoral Fellow, 1961–present.

(3) See G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(4) See G. S. Hammond, C. A. Stout, and A. A. Lamola, *ibid.*, **86**, 3103 (1964).

(5) See F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

(6) See G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

(7) (a) See G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961); (b) A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

(8) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(9) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

(10) (a) W. J. Potts, Jr., *J. Chem. Phys.*, **21**, 191 (1953); (b) K. Rosengren, *Acta Chem. Scand.*, **16**, 1421 (1962).
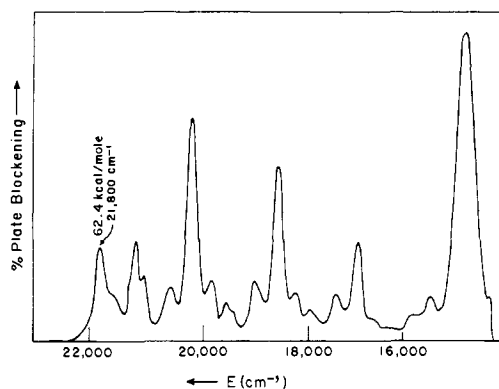
Fig. 1.—Densitometer tracing of the phosphorescence of 9,10-anthraquinone in MCIP at 77°K. measured spectrographically. The intense band near 15,000 cm.$^{-1}$ is due to Pyrex emission observed here because a phosphoroscope was not used.
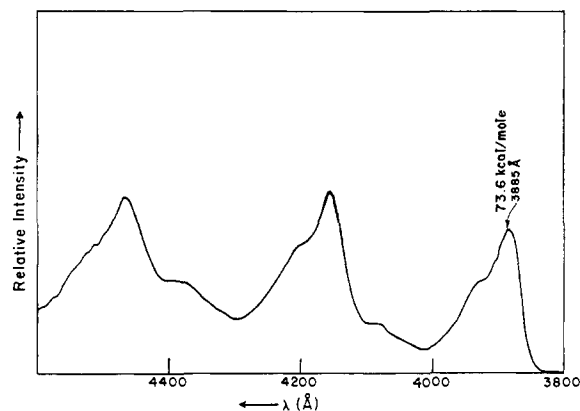

Fig. 2.—Phosphorescence from acetophenone in MCIP at 77°K. measured spectrophotometrically.

Samples.—All samples were purified by alumina chromatography followed by recrystallization, distillation, sublimation, or a combination of these procedures. The solutions were approximately 10^{-3} M in solute and were checked to make sure that they formed clear glasses (not clouded with microcrystals) at 77°K. The sample solutions contained in Pyrex test tubes were degassed (one or two freeze–pump–thaw cycles) and sealed under vacuum.

Results and Discussion

Phosphorescence from organic molecules is attributed to radiative return to the ground singlet state from the lowest triplet state.[11] At low temperatures and in viscous solvents, phosphorescence can compete more favorably with quenching processes which destroy triplets in fluid solutions, and it is under such conditions that phosphorescence is usually studied. The triplet-state energies reported here are based on phosphorescence spectra of the samples dissolved in clear, rigid solvent mixtures at 77°K.' Phosphorescence was separated from short-lived emission (fluorescence) by means of conventional mechanical delay systems (phosphoroscopes).

It has been pointed out[12] that spectral shifts due to solvent effects depend upon the type of transition involved. For example, the phosphorescence from carbonyl compounds where the transition is n ← π* shows a large hypsochromic shift in polar, hydrogen-bonding solvents compared to nonpolar solvents, while phosphorescence due to π ← π* transitions such as those oc-

(11) For a general discussion of luminescence from organic systems, see M. Kasha, *Radiation Res. Suppl.*, **2**, 243 (1960).

(12) For a discussion of solvent effects on electronic transitions of organic molecules, see C. Reid, "Excited States in Chemistry and Biology," Butterworths, London, 1957, p. 61, and references therein.
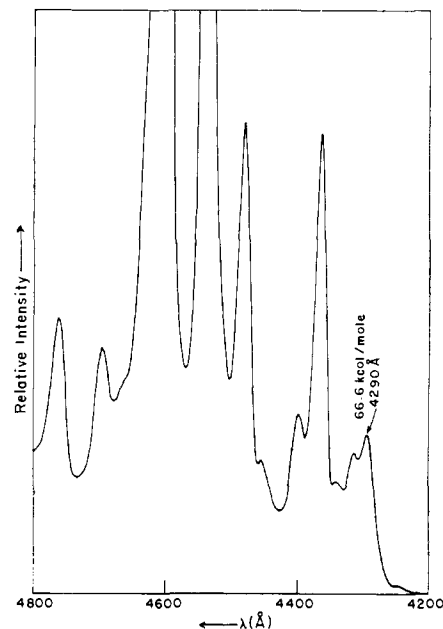

Fig. 3.—Phosphorescence from triphenylene in MCIP at 77°K. measured spectrophotometrically.

curring in aromatic hydrocarbons usually shows a small bathochromic shift in polar solvents compared to nonpolar solvents. The interpretation of experiments based upon energy transfer must take solvent effects into account. The data reported in Table I are based upon the phosphorescence spectra of the samples dissolved in hydrocarbon mixtures. Also included are data based upon phosphorescence spectra of samples in solvents containing ether and ethanol, as well as selected data from the literature.

The triplet-state energies reported in Table I correspond to the highest energy band maxima in the respective phosphorescence spectra. At 77°K. only the lowest vibrational level of the triplet state is significantly populated. The radiative transition of highest energy corresponds to the transition between the 0th vibrational levels of the triplet state and ground state, respectively (the 0'–0 band). In accord with the Franck–Condon principle,[13] if the triplet and ground states have significantly different geometries, the 0'–0 band may not be the band of maximum intensity. For most of the phosphorescence spectra recorded in these experiments, little difficulty was encountered in assigning the 0'–0 band since vibronic structure was usually well developed.

Some examples of the spectra recorded by both methods described are shown in Fig. 1–5. In three, acetophenone, anthraquinone, and triphenylene, an energy assignment is unequivocal. In the other two examples, thioxanthone and benzil,[14] the broadness of the bands makes precise assignments of the position of the 0'–0 bands more difficult.

Knowledge of the electronic energy levels of a compound may permit application of that compound as

(13) For a discussion of the Franck–Condon principle as applied to the spectroscopy of organic molecules, see H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 134.

(14) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960), have reported a similar emission from benzil in benzene solution. The same authors[15] have also tabulated triplet energy levels.

(15) See K. Sandros and H. L. J. Bäckström, *ibid.*, **16**, 958 (1962), for a number of compounds not included in this survey.
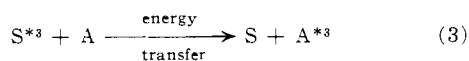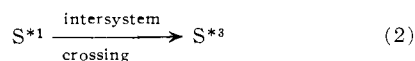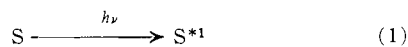
TABLE I

Compound	$E_T{}^a$ (kcal./mole)	
	Hydrocarbon solvent[b]	Polar solvent[c]
Propiophenone	74.6	
Xanthone	74.2[d] in MP	
Acetophenone	73.6	76.3[e]—
1,3,5-Triacetylbenzene	73.3	
Isobutyrophenone	73.1	
1,3-Diphenyl-2-propanone	72.2	
Benzaldehyde	71.9	
Triphenylmethyl phenyl ketone	70.8	
Carbazole	70.1	70[f]
Diphenylene oxide	70.1	
Triphenylamine	70.1	70.1[f]
Dibenzothiophene	69.7	69.3
o-Dibenzoylbenzene	68.7	
Benzophenone	68.5	69.2
4,4'-Dichlorobenzophenone	68.0	
p-Diacetylbenzene	67.7	
Fluorene	67.6	
9-Benzoylfluorene	66.8	
Triphenylene	66.6	67.2[g]
p-Cyanobenzophenone	66.4	
Thioxanthone	65.5	
Phenylglyoxal	62.5	
Anthraquinone	62.4[d]	63.3[e]
Phenanthrene	62.2	61.8[g]
α-Naphthoflavone	62.2	
Flavone	62.0[d] in IPMC	
Ethyl phenylglyoxalate	61.9	63.0[d]
4',4-Bis(dimethylamino)-benzophenone	61.0[d]	62[f]
Naphthalene	60.9	61[f]
β-Naphthyl phenyl ketone	59.6	
β-Naphthaldehyde	59.5[d]	
β-Acetonaphthone	59.3[d]	59.5[d]
α-Naphthyl phenyl ketone	57.5[d]	57.7[d]
α-Acetonaphthone	56.4[d]	58[b]
α-Naphthaldehyde	56.3	56.3
5,12-Naphthacenequinone	55.8	55.8 in EA
Biacetyl	54.9[d]	57.2[d]
Acetylpropionyl	54.7[d]	57.2[d]
Benzil	53.7[d]	57.3[d]
Fluorenone	53.3	
Pyrene	48.7	

[a] These values refer to the maximum of the 0'-0 band of the phosphorescence measured spectrophotometrically at 77°K. [b] In MCIP unless otherwise noted. [c] In EPA unless otherwise noted. [d] Measured spectrographically. [e] C. A. Parker and C. G. Hatchard, *Analyst*, **87**, 664 (1962). [f] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944). [g] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949) (value for 0'-0 band head).

either a sensitizer (donor) or a quencher (acceptor) in photochemical studies. This report concludes with a brief discussion of those factors other than energy content which make a compound a "good" triplet sensitizer.

A good sensitizer (S) is a compound which functions efficiently in the following reaction sequence.

$$S \xrightarrow{h\nu} S^{*1} \qquad (1)$$

$$S^{*1} \xrightarrow[\text{crossing}]{\text{intersystem}} S^{*3} \qquad (2)$$

$$S^{*3} + A \xrightarrow[\text{transfer}]{\text{energy}} S + A^{*3} \qquad (3)$$

In addition to having high efficiency in intersystem crossing and energy transfer, the sensitizer should have other desirable characteristics. Ideally the sensitizer should absorb strongly at longer wave lengths than those
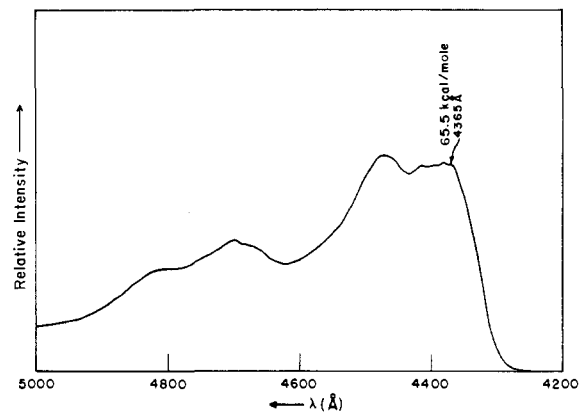

Fig. 4.—Phosphorescence from thioxanthone in MCIP at 77°K. measured spectrophotometrically.
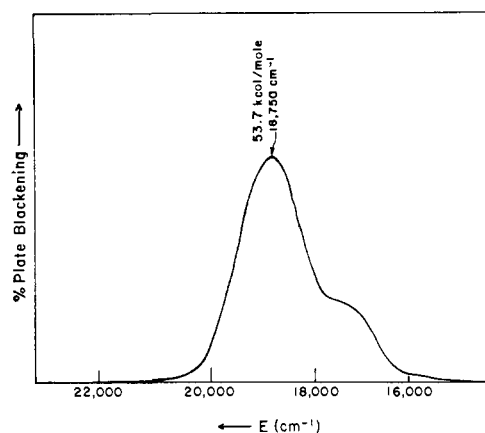

Fig. 5.—Phosphorescence from benzil in MCIP at 77°K. measured spectrographically.

at which the acceptor (A) absorbs. High efficiency in reaction 3 requires that the triplet excitation energy of S be higher than that of A.[16] Combination of these two requirements suggests that good sensitizers are likely to be compounds in which there is a relatively small separation between the excitation energies of the lowest excited singlet and triplet states. This condition, which is also a factor favoring efficient intersystem crossing, is often fulfilled in simple carbonyl compounds in which the lowest excited states both have n → π* configurations. All of the compounds listed in Table I absorb significantly at 3200 Å. and longer wave lengths, many absorb the 3650 Å. mercury line strongly, and some absorb as far into the visible as 4500 Å. The yield of triplets by intersystem crossing varies widely, however. The values[18] range from 33% (carbazole and fluorene) to 100% (benzophenone and acetophenone) for compounds listed in Table I.

The photochemistry of the sensitizers themselves is of considerable importance, since the efficiency will be decreased if the sensitizer is lost through a photoreaction. A more subtle problem may arise if the sensitizer is converted to a new compound having a low-lying triplet state since such by-products may act as quenchers and shut off the reaction entirely. However, it should be

(16) As has been reported,[6,17] excitation of acceptors to nonspectroscopic states sometimes occurs with significant efficiency in cases in which the sensitizer triplet has insufficient excitation energy to excite the acceptor to a spectroscopic state.

(17) G. S. Hammond, N. J. Turro, C. D. DeBoer, and P. Wyatt, *J. Am. Chem. Soc.*, **86**, 2532 (1964).

(18) These are data of G. S. Hammond and A. A. Lamola for solutions in benzene at room temperature. A full report describing these determinations is in preparation.

noted that sensitizers need not always be absolutely photostable since energy transfer to the substrate, reaction 3, will often reduce the photoreactivity of the sensitizer. Many carbonyl compounds undergo photoreduction in solvents that serve as hydrogen donors.[19,20] For this reason we have often chosen to carry out sensi-

(19) A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).

(20) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

tized reactions in benzene, a poor hydrogen donor. *Triphenylene is recommended as an especially good sensitizer for orienting experiments* since it absorbs at relatively long wave lengths (ϵ 100 at 3450 Å.), undergoes intersystem crossing with high efficiency (95%), gives triplets with relatively high excitation energy ($\sim$67 kcal.), and is exceptionally photostable.

Formation of Diamond. III.
Effects of Silicon on the Nucleation and Growth of Diamond. Comparison of Effects with Other Light Atom Impurities

BY P. CANNON AND E. T. CONLIN, II

The effects of silicon on the catalyzed diamond-forming reaction have been studied and are found to depend on the form and purity of the Si compound used to dope the reaction mix. Oxidation yielding SiO_2 or dissolution of Si in the catalyst metal took place at diamond-stable, high-pressure, high-temperature conditions. Diamond is found intergranularly in a coesite matrix, in the first case, if a suitable excess of carbon is present. In the second case, some diamond is found with N-containing SiC in a Ni-Si acid-resistant matrix. Decomposable compounds of silicon, like $CaSi_2$, reduce diamond nucleation, slow growth, and promote the formation of rotation twins of diamond on (111). The crystals have very smooth (111) faces, and appreciable amounts of Ni and CaO may be demonstrated to be present in some of these diamonds. The quantitative effect of Si upon nucleation and growth is not so pronounced as that of either boron or aluminum, and it is thus not possible to say that Si is a cocatalyst for diamond formation when employed in conjunction with, *e.g.*, nickel. Strong qualitative effects of these various impurities upon diamond-crystal color are observed, and these are discussed in the Appendix.

Introduction

It was previously observed[1] that the presence of silicon had an unusual effect on the nucleation of diamond in the Ni–Al–C system. Silicon also appears to be involved in the formation of natural diamond. In crystals from the Congo, silicon is widely supposed to cause the tough opaque character of the outer layer. Custers[2] questioned this supposition; he examined the opalescent skin of such stones and found no evidence of any solid material other than diamond carbon to be present, beyond a few small unknown inclusions. The origin of the supposition may lie in the approximate petrographic similarity between opaque, layered diamond and some forms of silica-like agate, but the matter is not that simple, since we have obtained an analysis of 0.13% Si contained in Congo diamond. It would seem that the best statement is that the opalescent character is not necessarily dependent on Si. That small but measurable amounts of silicon are in fact present in natural diamond has also been demonstrated by spectrographic and neutron activation analysis.[3] The presence of silicon must, of course, reflect the nature of the matrix from which the crystals were formed. Silicon might be expected to influence the solubility of carbon in the matrix, and generally to impede diffusion through the bulk of the medium involved, by occupying, *e.g.*, interstitial sites in a metal, thus altering the pattern of nucleation-growth events, as well as the final

(1) P. Cannon and E. T. Conlin, 5th International Congress on the Reactivity of Solids, Munich, 1964; see also General Electric Research Laboratory Report RL-3461-C.

(2) J. F. H. Custers, *Am. Mineralogist*, **35**, 51 (1950).

(3) (a) F. G. Freedman, *J. Chem. Phys.*, **26**, 347 (1952); (b) F. G. Chesley, *Am. Mineralogi t*, **27**, 23 (1942); (c) F. A. Raal, *Proc. Phys. Soc.*, **71**, 846 (1958).

product. Again, at all temperatures up to $\sim$1850°K., SiO_2 has a higher free energy of formation than does CO, and so Si might serve as a preferred sink for oxygen. If these considerations are significant in the nucleation of diamond, experimental verification should be possible.

It is also important to know, as far as general questions of reaction mechanism are concerned, whether the enhanced diamond nucleation characteristics described earlier[1] are due to a modification of catalyst function or to the action of the impurities as heterogeneous nucleating sites. The problem is complex; prior information shows that many impurities introduced in elemental form do alloy with nickel and that they are actually incorporated into the growing diamond. No clear evidence exists that the inclusions in laboratory-prepared diamond are in general heterogeneous-growth nuclei, and in those cases where noncarbon material has been specifically identified, it seems to be randomly distributed with respect to the cubic axes of diamond. In this connection, carbide needles may be observed in diamond prepared using a Ni–Cr catalyst, but no obvious mutual orientation is apparent. The formation of solid chromium carbide and diamond seems to have taken place simultaneously and very rapidly. Again, the color associated with boron incorporated by growth into diamond is frequently nonuniform. However, in both these latter cases the impurities were alloyed with the nickel in advance of the reaction and thus probably existed as a dilute second phase in the main nickel phase in the solid or solidifying state and as a simple dilute solution in the liquid state. As a consequence it might seem very reasonable that the second component of the catalyst would be bound to appear in the final product,