The Photochemistry of Some Simple Aromatic Molecules in the Gaseous State[1]

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I. Introduction

Simple aromatic molecules which possess only one aromatic ring all show many regions of absorption, but under experimental conditions customarily employed the one at longest wavelengths begins at 270–290 nm. The long wave limit depends on the molecule and on the experimental conditions. With long path lengths and at moderate temperatures such that it is possible to observe transitions which arise from relatively high vibrational levels of the ground state, the long wave limit may extend to about 300 nm. Since the lowest excited triplet electronic levels all lie at lower energies than those of the corresponding excited singlet levels, special experimental conditions (*e.g.*, addition of paramagnetic molecules to the system or the presence of a magnetic field) are necessary for absorptions of the singlet–triplet type to be observed. Such absorptions always occur at longer wavelengths than the corresponding singlet–singlet absorptions.

Increasing attention is being devoted to photochemical work at short wavelengths where transitions to higher than the first excited singlet state, including Rydberg transitions, are observed. In this article discussion will be confined to incident wavelengths longer than about 230 nm, *i.e.*, to transitions lying below about 5.4 eV. It must be further stated that discussion will be mainly limited to molecules which have been studied in our own research group. We believe it wise from time to time to review our own work. In the course of time, new and often better data have become available and interpretations need modifications which lead to improvements.[1]

It was true at the beginning and it is still true that good methods for some of the essential measurements are not available. Precise determinations of emission (fluorescence and phosphorescence) yields are always difficult. Triplet state yields are also difficult because most methods involve addition of monitoring substances which may alter the system under investigation. These difficulties will not be discussed in detail.

Incident radiation may be considered to be monochromatic only if the absorbing species has a single absorption coefficient. This is never true if the absorbing species possesses an unresolved fine structure, for absorption coefficients vary many times from small (or zero) values to high values and back in the range covered by the incident radiation. Thus, extrapolation from concentrations such that absorption can be easily measured to low concentrations may lead to large errors. In some instances rigorous corrections are impossible.

It must be emphasized that the apparent constancy of the constants in Beer's law ($I_{\text{trans}} = I_{\text{incident}} \exp(\alpha_\nu C l)$) is not a very sensitive test of the monochromaticity of radiation. (I_{trans} is the intensity of radiation transmitted after passage through a distance l of an absorbing substance at concentration C. α_ν is the absorption coefficient at frequency ν; I_{incident} is the intensity of the incident radiation expressed in energy units or photons per square centimeter per second. The beam must be parallel.)

Ishikawa[2] has considered in some detail the problem of calculating fractions of light absorbed when incident radiation is not truly monochromatic. Noyes, Mulac, and Harter[3a] and Phillips[3b] have dealt with the specific case of measurement of emission efficiencies.

"Radiative lifetimes" may be calculated for certain molecules by use of absorption coefficients integrated over a given electronic transition.[4] "Radiative lifetime" is $1/k_{\text{rad}}$, where k_{rad} is the rate constant for emission if there are no competing processes.

If there is unresolved fine structure, the integration may be in error. Integrations performed by different authors often disagree for the same molecule.[4a] If incident radiation has several absorption coefficients, absorptions which approach totality vary little with concentration. At

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low concentrations, high-absorption coefficients are important and low-absorption coefficients become increasingly important as concentrations increase. There may also be sound quantum mechanical reasons why the equations used for calculating radiative lifetimes do not apply to certain molecules.[4b] The cause of difficulty may not always be apparent.

If products are formed unimolecularly from excited species, quantum yields may be determined without reference to the distribution in space of the absorbed photons. Products may be formed by reactions between radicals, by reactions between excited molecules (*i.e.*, triplet-triplet interactions), or possibly by reactions between radicals and excited species. In such cases it is necessary to calculate local concentrations of intermediates and to perform an integration over volume to obtain the total yield. If the intermediates are short lived, this can be done if the distribution of intensity in a cross section of the incident light beam and absorption coefficients are known. If the lifetimes are sufficiently long, concentrations of intermediates throughout the cell may approach uniformity. The situation may be complicated.[5]

II. Outline of the Spectroscopy of Simple Aromatic Molecules

The benzene molecule in its ground electronic state is one of high symmetry. In addition to the identity, the following symmetry operations may be performed: (1) rotation around three twofold axes of symmetry; (2) rotation around one sixfold axis of symmetry; (3) reflection in four planes of symmetry; (4) displacement through a center of symmetry. This high symmetry has made benzene attractive to theoreticians and the number of papers and treatises dealing with energy states and spectroscopy of this molecule is very great. A summary of great clarity appears in a review article by Parmenter.[6]

The electronic transition in the region under question (230–270 nm) is of the $\pi\pi^*$ type; *i.e.*, it involves a transition of one of the π electrons to an upper π state.

For symmetry reasons the electronic transition $^1A_{1g} \rightarrow {}^1B_{2u}$ is forbidden. If the molecule in either the ground or in the excited state possesses an odd number of quanta of an antisymmetric vibration, the forbiddenness is largely eliminated and transitions can occur. Integrated absorption coefficients indicate a relatively long radiative lifetime of about 397 nsec.[7] Deuterated benzene shows a radiative lifetime of 377 nsec.[8]

The lowest antisymmetric vibration in benzene is at 620 cm^{-1}. The fraction of molecules with this amount of vibrational energy at 298°K is about 0.05 and absorption based on that vibrational level in the ground state will be weak. The strongest progression is based on one unit of this mode of vibration which has a frequency of 520 cm^{-1} in the upper state combined with an integral number of quanta of the symmetrical "breathing" vibration which in the upper state has a frequency of 920 cm^{-1}. These bands are located at 259, 253, 248.4, and 242 nm, respectively. With polychromatic incident light, absorption in them overshadows that in other bands. Other bands are so numerous that it is unsafe to assume that a high fraction of the absorption lies in any one of these strong bands.

If there is substitution in the benzene ring, the symmetry is altered unless there are six atoms substituted for the six hydrogens as would be the case in C_6D_6 and in C_6F_6. Two general types of substitution must be considered. (1) Those which involve introduction of groups of saturated entities made of light atoms such as CH_3, C_2H_5, $i\text{-}C_3H_7$, $n\text{-}C_3H_7$, etc. For example, if CH_3 is considered to be concentrated at a point (*e.g.*, toluene), there are only two planes of symmetry instead of four, there is only one axis of symmetry, and there is no center of symmetry. Thus, the electronic transition to the first excited singlet state is no longer as forbidden as it is in the case of benzene, and the radiative lifetime calculated as for benzene becomes 178 nsec[9] instead of 397 nsec.[7] (2) Substitution of other atoms or groups such as F, CF_3, NH_2, etc., on which there are nonbonding electrons. In some cases there ceases to be any plane of symmetry in either the ground state or in the excited state. Generally speaking radiative lifetimes are very much shorter: 31 nsec for aniline, 69 nsec for fluorobenzene (see below).[10] For such molecules care must be exercised not only to avoid high absorptions in calculating radiative lifetimes but also to ensure that the equations are applicable.

It should be noted that in the cases of polyatomic substitution groups the number of modes of vibration increases. Thus, $3n - 6$ for toluene is 39 and the bands are far more crowded together than they are for benzene. Since absorptions are higher than for benzene and overlap is considerable, the chance of being able to excite *single vibrational levels in the upper electronic state* is low. Nevertheless, for all aromatic molecules with one ring made only of carbon atoms, the absorption regions are similar and so are the regions of emission. There is some displacement with unsaturated side chains and for compounds with rings for which some orbitals overlap those of the π electrons of the aromatic ring. These effects are qualitatively understood but quantitative treatments of such spectra lie in the future.

An aromatic molecule with an atom such as nitrogen included in the ring has transitions which resemble closely those of benzene, *i.e.*, they are classified as $\pi\pi^*$, but in addition there are transitions which lie at somewhat longer wavelengths which are classified as $n\pi^*$. These latter arise because the nitrogen atom possesses electrons not associated with the aromatic character of the ring. The general theory of the spectra of such molecules is well understood. If the heterocycles include more than one nitrogen atom in the ring, there may be several $n\pi^*$ transitions. The nonradiative transitions between these various states are numerous since there will be a triplet state of lower energy corresponding to each singlet state. The rules governing such transitions may not be too well understood but they have been made the subject of extensive investigations, particularly in the laboratory of Professor Magat at Orsay.[11]

Pyridine and the picolines do not show light emission, either fluorescence or phosphorescence.[12,13] While photochemical isomerization of benzene and of benzene derivatives is a well-established fact[14,15] and it is probable that these isomerizations occur from the singlet excited state, no evidence for the isomerization of pyridine has been found and isomerization yields for the picolines are extremely low[13] and not fully understood.

Research on the diazines is not very extensive. 1,2-Diazine and 1,3-diazine neither fluoresce nor phosphoresce, but they isomerize with relatively low yields.[11,16] On the other hand 1,4-diazine (pyrazine) in the gaseous phase both fluoresces and phosphoresces.[17] Very few molecules show this characteristic. One of the few is biacetyl.[18] Because of this characteristic, pyrazine may be used to determine triplet state yields. It has one advantage over biacetyl: the ratio of fluorescence to phosphorescence[17] is near unity whereas that of biacetyl is about 1:60.[19] Pyrazine has the serious disadvantage that both fluorescence and phosphorescence have very low yields and are hard to measure accurately. Nevertheless, Nakamura obtained by the use of pyrazine a triplet yield for benzene[17] in good agreement with the value generally accepted.[15,20]

For certain aromatic hydrocarbons, the sum of fluorescent and triplet state yields is near unity if absorption occurs at wavelengths near the 0,0 band. As the wavelength of the incident light decreases, the fraction of incident photons not thus accounted for generally increases. The sum of these two yields for the azines is always far from unity. Errors in determining fluorescent yields may be large, but it is inconceivable that these yields could be large enough to make the sums near unity.

III. Light Emission (Fluorescence and Phosphorescence) from Simple Aromatic Molecules

The 0,0 bands for aromatic molecules which have single aromatic rings generally lie in the region 260–280 nm. At shorter wavelengths other transitions (often members of Rydberg series) are found, but they do not concern us in this review.

Light emission sometimes described as "resonance fluorescence" is found in a few cases at low pressures.[21,22] Resonance fluorescence is defined as light emission from initially formed excited energy levels. Thus, emission must occur before vibrational energy has been lost. For polyatomic molecules the identification of resonance fluorescence is rarely rigorous. Emission at short wavelengths which does not appear if vibrational relaxation is complete is so classified.

Except for resonance fluorescence, emission occurs at wavelengths longer than the 0,0 bands and extends often to wavelengths longer than 350 nm. A combined plot of intensity of fluorescent emission against wavelength and of absorption coefficients against wavelength will show generally two broad maxima, one for each part, and the emission plot will be very roughly the mirror image of the absorption plot. In making these statements we neglect mention of minor peaks and valleys which are related to fine structure based on vibrational levels.

Most fluorescent emissions for polyatomic molecules are studied under conditions such that vibrational energy in the emitting state is equilibrated with the surroundings. The spectrum will thus be complex.

The emission efficiency involves determination of the number of photons emitted per unit time divided by the number of photons absorbed per unit time. The latter is a relatively easy measurement, since the incident light is or should be more or less monochromatic. The determination of the number of photons emitted per unit time involves several integrations: (a) over an entire sphere so that all emitted photons are counted; (b) over all emitted wavelengths. Since sensitivities of most photomultiplier tubes are wavelength dependent and the emitted intensity is also wavelength dependent, these integrations may be difficult.

For aromatic compounds discussed in this article the mean wavelength of the emitted photons from fluorescence does not vary greatly and conclusions would be little affected if it were considered to be the same for all of them. The best results are usually obtained by using an aromatic compound as a standard, but one must always be careful to avoid the "round-the-corner effect."[80,81]

Gas-phase phosphorescence is not often observed. Biacetyl and pyrazine[17,18,23] are exceptions. On the other hand, phosphorescence can often be observed in glassy matrices and it often has a very long life. Benzene in a glassy matrix shows a phosphorescent mean life of several seconds.[24]

TABLE I. Comparison of Calculated and Measured Lifetimes of Excited Singlet States[a]

	Gas		Liquid	
	Q_f(259 nm) × τ_{rad}, nsec	τ_{true}, nsec	Q_f × τ_{rad}, nsec	τ_{true}, nsec
C_6H_6	0.19 × 397 = 75	75	0.07 × 397 = 28	29
$C_6H_5CH_3$	0.29 × 178 = 52	56	0.17 × 178 = 30	34
o-Xylene	0.36 × 155 = 56	56	0.19 × 155 = 30	32
m-Xylene	0.30 × 171 = 51	49	0.17 × 171 = 29	31
p-Xylene	0.50 × 96 = 48	44	0.40 × 96 = 38	30

[a] Radiative lifetimes are from I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York, N. Y., 1971. Decay times are also from Berlman. Fluorescent yields in the gaseous phase are from Noyes, and Harter, ref 15, except for toluene which is from C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, **49,** 1705 (1968). True lifetimes are from Breuer and Lee, ref 52. Values of Q_f are relative to those for benzene as a standard.[27]

It is not immediately obvious why a phosphorescent lifetime in the gaseous phase should be much shorter than in a glassy matrix. Trace impurities may have more effect in a gas because diffusion would be important. Two methods have been used in benzene gas to estimate the mean lifetime of the triplet state, and the results differ.[25,26] The explanation for the difference has not been made although it is suggested that an impurity (possibly oxygen) may be responsible.

In the studies reviewed in this article, mean lifetimes of molecules in excited states have not been measured, but some have been measured in other laboratories. We will have occasion to mention this matter so that the basic equations will be given.

The following simple mechanism can serve as a basis

$$\mathrm{M} + h\nu = {}^a\mathrm{M} \qquad \Phi_T I_a \tag{1}$$

$${}^a\mathrm{M} + \mathrm{X} = \,? \qquad k_2(\mathrm{X}) \tag{2}$$

$${}^a\mathrm{M} = \mathrm{M} + h\nu \qquad k_3 \tag{3}$$

$$= \mathrm{Y} \qquad k_4 \tag{4}$$

where M is the absorbing molecule and a state ^{a}M of multiplicity *a* can undergo reactions of the types of (2), (3), or (4) which are either first or second order. The quantum yield of formation of ^{a}M is Φ_T and I_a is the number of photons absorbed per unit volume per second.

The radiative lifetime which in principle can be calculated from integrated absorption coefficients (see above) is $1/k_3$. The true lifetime is $1/(k_2(X) + k_3 + k_4)$. Hence one may write

$$\tau_{\text{true}}/\tau_{\text{rad}} = \frac{k_3}{k_2(\mathrm{X}) + k_3 + k_4} = \Phi_e \tag{5}$$

where Φ_e is the emission quantum yield. Thus

$$\tau_{\text{true}} = \Phi_e \tau_{\text{rad}} \tag{6}$$

Since τ_{true} is the lifetime of the emission which would be measured in the laboratory, Φ_e is the emission yield which would be measured in the laboratory, and τ_{rad} is the calculated radiative lifetime, the applicability of (6) can be tested from data and calculations available in the literature. Table I shows data for a few molecules covered in this article. The fluorescent yields were determined in the laboratory,[15,27] the true lifetimes were obtained from the data of Lee,[52] and the radiative lifetimes were taken from the work of Berlman.[4] Data are given for both liquid and gaseous phases, although data for the liquid phase were not obtained in this group.

The data in Table I indicate an extraordinarily good agreement between calculated and true lifetimes in the gaseous phase. Even in the liquid phase, where emission yields are much lower, the agreement is better than one would expect. As we shall see, the agreement is much less good for some other aromatic compounds.

IV. Type Reactions of Simple Aromatic Molecules

Excited aromatic molecules may isomerize, may under certain circumstances dissociate, may dimerize or polymerize, and may in the presence of suitable acceptors lose energy of excitation by collision of the second kind. Efforts have been made for several years to associate these various processes with definite electronic levels.

Triplet yield determinations are made by several methods. A physical method for the gas phase based on magnetic susceptibility is presently not available. Indeed, were triplet molecule concentrations sufficiently high to permit use of such methods, triplet–triplet interactions would occur, thus invalidating the results. The method of flash photolysis based on absorption by molecules in triplet states has been developed by Porter.[28] To obtain yields per photon by this method, the absorption coefficients for the triplet state in question must be known. Sometimes reasonably reliable estimates can be made of these important quantities, but they can be measured accurately only if yields are already known.

Since physical methods are rarely if ever applicable, recourse must be had to addition of monitoring substances. There are several, but, in fact, they are all based on equations of the type

$$^3M + A = {}^3A + M \qquad (7)$$

where A is an acceptor molecule whose behavior in the triplet state is accurately known. These methods have been discussed in the literature, and we will not belabor this subject here. We will mention briefly some of the requirements for these methods. (a) The donor molecule ^3M must provide enough energy to raise A to ^3A. (b) The concentration of A must be enough to quench ^3M quantitatively (or at least to quench a definite and determinable fraction of ^3M). (c) The behavior of ^3A must be definite; *i.e.*, its behavior must not depend on the energy provided by ^3M, nor may it depend on steric factors. (d) There must not be troublesome side reactions which prevent eq 7 from being quantitative.

The two most commonly used methods in the gas phase are based on *cis*- and *trans*-2-butene (method of Cundall[29]) or on biacetyl.[2,15,30] For the former, the isomerization yield of cis to trans (or trans to cis) per photon absorbed by the donor is determined. ^3A must be assumed always to revert to the same ratio of cis to trans in the ground state.[31] The slight difference between heats of formation of cis and trans should not be important.[32] For biacetyl, the preferential excitation of triplet biacetyl is assumed, and the phosphorescent yield of the biacetyl is determined.

Each of these methods appears to give useful results for certain donor molecules. For the 2-butenes the energy provided by the donor must be considerably greater than for the biacetyl. This may restrict its usefulness, but simple aromatic molecules provide enough energy almost invariably. Quenching of ^1M by the 2-butenes can be neglected, but it may not be zero.[33] In some instances a chain isomerization of the 2-butenes appears to occur, thus making the method inapplicable.[34,35]

Biacetyl quenches singlet states of many molecules. Excitation to the second excited singlet state causes a problem only in so far as it reduces the triplet yield. A correction for this must be applied. Excitation to the first excited singlet state of biacetyl followed by crossover to the triplet may lead to phosphorescence which is not ascribable to ^3M.[36,37] A correction for this must be applied.[15]

Neither method can be guaranteed to be useful in all cases.[15] The Cundall method is more generally useful than the biacetyl method, and the slight difference in enthalpies of formation of the cis and trans isomers[32] seems to be of little importance. The two methods often agree within experimental error, and occasionally the biacetyl method can be used when the other fails.

As so often happens in kinetics, more than one mechanism may be used to interpret data. If instead of energy transfer by eq 7 an adduct serves as an intermediate, the same form of rate and yield equations may result, but the meanings of the rate constants would be different. Any of these methods will fail if the behavior of ^3A varies from one donor molecule to another.

Pyrazine both fluoresces and phosphoresces[17] and hence may be used to determine triplet state yields under certain circumstances.

Brief mention should be made of energy levels. If triplet state methods depend on simple energy transfer, the energy level of the donor must lie higher than that of the corresponding level of the acceptor. The lowest triplet level of biacetyl lies at about 2.4 eV, well below that of the lowest triplet level of any of the molecules here considered. The lowest singlet level at about 2.6 eV also lies well below the excited singlet states of these molecules, and even the second excited singlet state at about 4 eV lies below those of the aromatic molecules here considered. Corrections for excitation of biacetyl to its lowest excited singlet state have been described.[15]

V. Mechanisms for Photochemical Behavior of Individual Molecules

A. Benzene

Several isomers of benzene are known but only four are of real importance in photochemistry. They are illustrated in Figure 1 and are named as follows: (a) benzvalene; (b) Dewar benzene; (c) prismane; (d) fulvene.

Benzvalene has been used as an intermediate by Wilzbach and Kaplan[38,39] to explain isomerization of substituted benzenes without having recourse to free radicals and atoms. Recently benzvalene has been synthesized by nonphotochemical methods, and several of its properties are known.[40,41] It may revert to benzene photochemically either by direct absorption of radiation or by photosensitization.

Dewar benzene is not planar and seems not to be formed photochemically from pure benzene. It also has been synthesized by nonphotochemical methods.[42] It reverts thermally to benzene with a rate which has a high temperature coefficient.

Thus, the behaviors of benzene isomers and their relationships to the photochemistry of benzene have received much attention in recent years.[38-44]

Prismane has been identified by nuclear magnetic resonance. If, for example, an ortho-substituted benzene isomerizes to give a para-substituted benzene in addition to a meta-substituted benzene, one suspects that a prismane form is an intermediate.[45] Its properties are, however, less well known than those for the other isomers.

Fulvene is a colored gas and is formed photochemically mainly by radiation below 200 nm.[44,46-48] We will have little occasion to refer to fulvene.

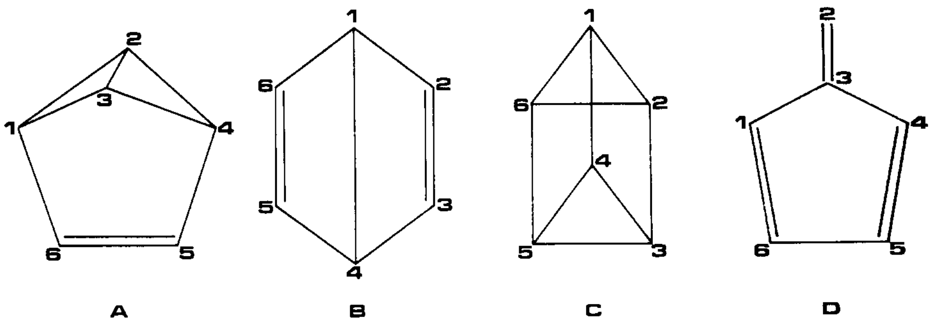


Figure 1. Some isomers of benzene. The six carbons in benzene are numbered consecutively 1 through 6, and the numbers in the isomers correspond to those in the original ring. (A) Benzvalene. It can revert to benzene by breaking two pairs of bonds: 1-3 and 2-4 or 1-2 and 3-4. The former would restore benzene in its original form and the latter would form benzene with carbon atoms in the order 1,3,2,4,5,6, and 1,2 ortho compound would become a meta compound. (B) Dewar benzene. It is not formed photochemically from benzene but is formed from hexafluorobenzene. When it reverts to benzene the original order of the carbon atoms is found. (C) Prismane. It can revert to benzene by breaking three bonds at a time as follows: (a) 1-2, 3-4, and 5-6 to give the order 1,4,5,3,2,6. A 1,2 ortho compound could become meta, a 5,6 ortho compound could become para, a 1,3 meta compound could become para, and a 1,4 para compound could become ortho; (b) 1-6, 5-4, and 2-3 to give the order 1,4,3,5,6,2. Isomerizations of all types are possible if prismane is the intermediate. (D) Fulvene. It is an isomer of benzene long known to be formed. Probably it is formed photochemically from benzvalene and it can revert to benzene photochemically.

To account for all of the photons absorbed to form the initially excited singlet state, it would be necessary to measure the number of molecules per absorbed photon which dissociate or isomerize from that state. If the initially formed reaction products are for any reason, either photochemical or thermal, not stable, the energy balance may be difficult or even impossible to achieve.

The light used in most photochemical work is not truly monochromatic so that with a given monochromator setting several different vibrational levels of the upper electronic state will be produced. Parmenter,[6] Ware,[49] Jortner, Rice, and Hochstrasser,[50] and Spears and Rice[51] have studied these problems in detail. Benzene molecules with about 2500 cm^{-1} of vibrational energy in the excited $^1B_{2u}$ state do not fluoresce, and, while triplet yields for such molecules are not known, they are probably zero. At this point, ability to interpret data quantitatively ceases since the quantitative determination of yields of isomers has not been made. It is impossible from the information at present available that the yields would be as much as unity. Wilzbach and Kaplan estimate that the primary yield of benzvalene might be as much as 0.1[39] at wavelengths less than 250 nm.

It is assumed that a molecule of benzene vapor which absorbs a photon will diffuse a negligible distance before it either emits or crosses over to the triplet state, since its mean life is only about 8×10^{-8} sec.[52,53] It may, however, transfer energy to a biacetyl molecule. The green emission from the biacetyl and the fluorescent emission from the absorbing molecules should be emitted essentially from the same volume elements; *i.e.*, they will show the same round-the-corner effect. Thus, the ratio Q_f/Q_p should be constant as the concentration of the absorbing molecules is increased, provided Q_f/Φ_T is independent of concentration. It should be noted, however, that an impurity which quenches excited singlet molecules would have the same effect provided it has no effect on the emitting biacetyl molecules and provided it bears a constant concentration ratio to the absorbing molecules.

Reference may now be made to the work of Ishikawa.[2] The lines incident were 253.7 and 265.4 nm of mercury, and the apparent molar extinction coefficient decreased, as would be expected, as the pressure of the benzene increased. The higher the pressure, the greater the relative importance of the less absorbed portions of the radiation would be.

Table II gives the values of $Q_f{}^0$ in pure benzene at several benzene pressures and the corresponding values of Q_p, the green emission yield of the biacetyl when added at 0.16 Torr to benzene at the same pressures. These values are uncorrected for round-the-corner effect and for any possible excitation of the biacetyl to the first excited singlet state which could cross over to the emitting triplet state.

TABLE II. Effect of Benzene Pressure on Fluorescent Yield of Benzene (Q_f) and on the Triplet Emission Yield of Biacetyl (Q_p)[a]

Benzene pressure, Torr	Q_p	$Q_f{}^0$	Q_p/Q_f
5.0	0.135	0.247	0.547
10.0	0.130	0.236	0.551
20.0	0.120	0.220	0.545
30.0	0.112	0.204	0.549
32.0	0.110	0.201	0.547
		Av	0.548 ± 0.002

[a] Pressure of biacetyl = 0.16 Torr. Values from the Ph.D. Thesis of H. Ishikawa, University of Rochester, 1962.

Table II shows there is some apparent self-quenching of benzene fluorescence. The apparent cross section for self-quenching is a few hundredths of a square angström unit, much less than is found from the data of Morikawa and Cvetanovic.[33] Some authors find in this pressure range essentially no self-quenching.[54] Since nearly all errors would make for too much quenching, it seems safe to conclude that except in the low-pressure region, where some resonance emission would be expected, self-quenching is essentially zero.

By use of the data from Table II it is possible to calculate the triplet yield of benzene[15] provided certain points are kept in mind: (1) the values of $Q_f{}^0$ in the third column were obtained in pure benzene; (2) since biacetyl quenches the singlet state of benzene and hence also the amount of crossover to the triplet state, the values of Q_p should be multiplied by 1.086.[2,15] The average ratio in the fourth column should be multiplied, therefore, by 1.086, and it becomes 0.595.

The value of $Q_f{}^0$ was found to be 0.18 at 253 nm, but the incident radiation was not strictly monochromatic and may have included a small amount of radiation for which $Q_f{}^0$ would have been lower. The value at 259 nm might be as much as 0.20. For the work of Ishikawa we accept 0.19 ± 0.02. Thus, the apparent triplet yield of benzene is 0.75$_3$, where 0.15 ± 0.01 is the phosphorescent yield of biacetyl.[37] A small correction must be made for excitation of biacetyl to its lowest singlet state. Thus, $\Phi_T = 0.73 \pm 0.02$. This agrees satisfactorily with the value accepted by Birks.[55]

On the basis of the best information presently available, it appears necessary to conclude that $(Q_f^0 + \Phi_T)$ is significantly less than unity at pressures of benzene over about 10 Torr. Better data applicable to single vibrational levels in the $^1B_{2u}$ state would probably help to determine (a) whether the energy balance is or is not good, and (b) if not, what happens to the other excited molecules.

Ermolaev[56] has summarized data on many molecules and indicates that for many, $\Phi_T + Q_f = 1$, mainly in the liquid phase. Both entities in this sum seem to be maxima when absorption is near the 0,0 band.

B. Molecules Composed of Carbon and Hydrogen

1. Methylbenzenes

Toluene and the three xylenes are considered. Integrated absorption coefficients for these four molecules are all higher than for benzene, and they increase in the order toluene, *m*-xylene, *o*-xylene, and *p*-xylene.[4] These other molecules have lower symmetries than does benzene. For this reason the 0,0 bands for them will not be forbidden as it is for benzene, and absorption coefficients will be higher.

As indicated in Table I, the calculated radiative lifetimes vary inversely to the order of integrated absorption coefficients. *p*-Xylene has the highest emission efficiency and the shortest measured true lifetime in the first excited singlet state.

The 0,0 band for benzene is at 38,086 cm^{-1},[57] that for toluene is at 37,477,[58] and those for *o*-, *m*-, and *p*-xylene lie respectively at 36,900, 36,700, and 36,500 cm^{-1}.[15] For toluene, in contrast to benzene, the 0,0 band has the highest absorption peak,[15,59] and this is also true for the three xylenes.[15]

Even though these five molecules all absorb and fluoresce in roughly the same wavelength regions and emission in each case is roughly the mirror image of absorption, there are distinct differences in their spectroscopic and photochemical behaviors. Presumably toluene can isomerize photochemically, but no stable or metastable isomer has been isolated.

The toluene spectrum has been analyzed[58-61] in terms of six excited state frequencies. Some of these differ little from excited state frequencies in benzene.

The fluorescent efficiency of toluene vapor excited at 266.8 nm at 14.5 Torr is about 0.30.[59] Q_f decreases with increase in temperature and decrease in incident wavelength, and emission is strongly quenched by oxygen. At short wavelengths addition of substances which cause vibrational relaxation, including the 2-butenes, enhance fluorescent yields.[59] Xenon causes quenching of the fluorescence with an effective cross section of 0.189 Å^2 [59] For krypton the value is 0.101, and lower molecular weight noble gases and sulfur hexafluoride give effects less than experimental error. High atomic weight gases enhance crossover to the triplet state by their effects on spin-orbit coupling.

No evidence for photochemical isomerization of toluene could be found, and over the wavelength range 250 to 266.8 nm and at temperatures up to 150° no products with quantum yields greater than 10^{-3} volatile at $-165°$ were found. At 266.8 nm and 24°, $Q_f + \Phi_T = 1.02 \pm 0.04$.

Thus, the data for toluene combine to form a satisfactory mechanism for the photochemical behavior of this substance, except that under many experimental conditions the steps by which the excited molecules degrade to the ground state remain unidentified. It is interesting to speculate about possibilities.[62]

One further point may be mentioned, although we will return to it later. Other simple aromatic compounds with single substituents composed of carbon and hydrogen atoms, *e.g.*, phenylcyclobutane and *trans*-phenyl-2-butene,[63-65] have fluorescent yields almost the same as that of toluene unless there is unsaturation adjacent to the ring in the substituents. In that event fluorescent yields are usually higher[66-68] (see Table IV).

Equations 5 and 6 are probably applicable within experimental error even in the liquid phase (see Table I as well as Berlman[8]). Since the spread of measured lifetimes in the liquid phase is less than in the gas phase, agreement between measured and calculated values may be somewhat fortuitous. Emission yields in the liquid phase are more difficult to measure than in the gas phase, partly because impurities can be very important and partly for optical reasons.

The three xylenes all undergo photoisomerization. If dimethylbenzvalenes are the sole intermediates, the following processes can occur (see Figure 1)

o-xylene → *m*-xylene

m-xylene → either *o*-xylene or *p*-xylene

p-xylene → *m*-xylene

If prismane is also an intermediate, any one of the xylenes can isomerize photochemically into any other. The data in the gas phase[15] show virtually no ortho to para isomerization, but in the liquid phase[45] ortho-para is 10 to 11% that of ortho-meta. If the ratio were the same in the gas phase, that of ortho-para would be so low as to make it uncertain. Isomerization yields are pressure dependent in the gas phase as well as wavelength dependent. As the pressure increases, the isomer yields approach those at wavelengths near the 0,0 bands, and these in turn are only slightly higher than in solution in *n*-hexane.

It is concluded that isomerization is most rapid from higher vibrational levels of the excited singlet states and that isomerization is, therefore, at least one of those processes which prevents fluorescence and crossover to the triplet state. It is legitimate to ask why yields of isomers are so low when yields of fluorescence and of crossover have become essentially zero. A complete answer to this question cannot be given.

Let us consider *m*-xylene as an example. There are six pairs of bonds which can be formed to give dimethylbenzvalene. Of these six dimethylbenzvalenes, all can revert to *m*-xylene, two could give *o*-xylene, two could give *p*-xylene, and two can only revert to *m*-xylene. The probabilities of breaking the new bonds *vs.* the probabilities of breaking old ones are not known, but for the sake of argument let us say that the probabilities are equal. Thus, there are twelve possible results eight of which restore *m*-xylene, two give *o*-xylene, and two give *p*-xylene. With this idealized model if the quantum yield of dimethylbenzvalene formation is unity, the quantum yield of *o*-xylene would be 0.16 and that of *p*-xylene would also be 0.16. Actual quantum yields are well below these figures. This implies either that the benzvalenes are not formed with unit yield or that for some reason benzvalenes tend preferentially to revert to the aromatic molecules from which they were formed. In making these simplified calculations, it is assumed the fluorescent yields are negligible at short wavelengths.

If dimethylprismanes are the intermediates, there are six ways of forming them from *m*-xylene. Each prismane can return to *m*-xylene or break new bonds to form different aromatics. Of the 18 ways of breaking bonds, ten will still give meta, four will give ortho, and four will give para. Thus, if all rearrangements are equally probable, the quantum yield of *o*-xylene would be 2/9 = 0.22 and of *p*-xylene would be the same. These are much higher than the observed yields at 248 nm.[15]

This rapid and somewhat naive treatment merely shows that isomerization yields should be low. The fact that they are even lower than these considerations merely shows that the problem is complex. The yields are never high enough to give an energy balance. *p*-Xylene is photochemically very stable and yields of meta and of ortho when starting with para are scarcely greater than zero by more than experimental error.[15,45]

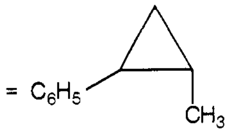
2. *Monosubstituted Benzenes with Alkyl Substituents*

A few alkyl benzenes have been studied other than the methylbenzenes, and these are all of types which could have reactions in the substituent groups.

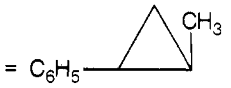
a. Cyclobutylbenzene[63,64]

Two major and two minor products are found upon gas-phase irradiation of cyclobutylbenzene.

$$C_6H_5(c\text{-}C_4H_7) + h\nu = C_2H_4 + C_6H_5CH{=}CH_2 \qquad (8)$$



(9)



(10)

The styrene yields were low due to polymerization. This can be prevented by careful treatment of the vessel walls.[64]

Styrene yields seem to depend markedly on the condition of the walls. Acid-treated walls induce polymerization. At 266 nm and 40°, $\Phi_{\mathrm{styrene}} = 0.49 \pm 0.01$ and $\Phi(C_2H_4)$ is within experimental error of being the same. Φ_{10} averages about 0.069 and Φ_9 about 0.052. Table III shows fluorescence yields at several wavelengths and temperatures.

The material balance is not perfect since 0.49 + 0.28 + 0.069 + 0.052 = 0.89 with an uncertainty of about 0.05. Thus, there is probably some other process with a small yield. Possibly a benzvalene-type isomerization could occur.

Addition of xenon should give an external heavy atom effect by its effect on spin-orbit coupling. Thus, fluorescence yields should decrease, and, if products are formed from triplet states, added xenon should cause the yields of such products to increase. The following trends are observed: (1) the fluorescence is quenched by xenon, (2) the yield of eq 8 is increased by addition of xenon, (3) the yields of eq 9 and 10 both decrease as xenon is added. Triplet sensitizers enhance the yield of eq 8. Sensitizers such as *p*-xylene which have high fluorescence yields and low triplet state yields lower the yield of styrene. The trends are more or less consistent with (8) coming from the triplet state although conceivably it could arise either from the singlet or from the triplet state. Reactions 9 and 10 seem to come from the singlet state at high vibrational levels.

TABLE III. Fluorescent Yields from Cyclobutylbenzene[63]

	Wavelength: 266.0 ± 0.4 nm, *P* = 3.5 Torr (at 40°)						
Q_f	0.28	0.26	0.24	0.19	0.18	0.14	0.12
T	40	60	80	103	123	145	163
	Wavelength: 254.0 ± 0.4 nm						
Q_f	0.093	0.075	0.051				
T	40	62	81				
	Wavelength: 248 ± 0.4 nm						
Q_f	0.024	0.017	0.006				
T	40	62	81				

One may conclude tentatively that (8) arises from the triplet state, and (9) and (10) almost certainly arise from the singlet state. Details of this work will appear shortly.[64]

Effective cross sections (cm^2 × 10^{16}) from fluorescence quenching of phenylcyclobutane at 266 nm are: Xe, 0.18; Kr, 0.065; Ar, 0.022.[63] This trend with decrease in atomic number is similar to that found for toluene.[59]

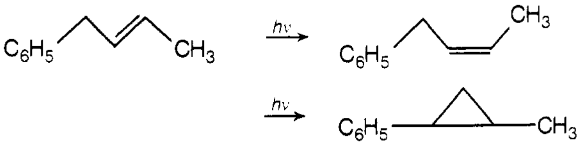
The trends shown in Table III are similar to those shown for benzene, toluene, and the xylenes, *viz.*, Q_f decreases as wavelength decreases and decreases as temperature increases. Unfortunately, for molecules such as this, triplet state methods are not reliable.

It may be possible to perform experiments which will relate the chemical reactions to the multiplicity of the electronic state.

b. *trans*-1-Phenyl-2 butene[65]

trans-1-Phenyl-2-butene was studied on the basis that the phenyl group would be the absorber and that it might "sensitize" reactions in the side chain. This is an oversimplified point of view since it is not possible to treat absorption in one part of a molecule while ignoring the remainder.

Two principal reactions result from the exposure of *trans*-1-phenyl-2-butene: (1) cis-trans isomerization in the side chain; (2) formation of 1-methyl-2-phenylcyclopropane.



(11)

(12)

The fluorescent yields of the phenyl-2-butene vary from about 0.01 at 240 nm to about 0.27 at 268 nm and are thus almost within experimental error of those for toluene.[59] The 0,0 band lies at 266 nm and yields of products are greatest at this wavelength, *i.e.*, $\Phi_{11} = 0.18$ and $\Phi_{12} = 0.14$. Thus the sum of product yields and fluorescent yield at this wavelength is about 0.6.

Cis-trans isomerizations are visualized most easily as arising from triplet states which permit free rotation around the single bond located where the double bond was found in the ground state. On this basis one would expect (11) to arise from a triplet state.

Although data are somewhat fragmentary since triplet state methods almost always cause vibrational relaxation, they tend to indicate that both fluorescence and crossover to the triplet state are optimum in the vibrationless excited singlet state. The yields of both (11) and (12) decrease with decrease in wavelength, but the yields of (11) and (12) both increase at short wavelengths with increase in pressure of an inert gas such as butane. Since the ratio of the two yields is not independent of pressure and even 100 Torr of butane only increases the yield of (11) to about half of its long wave value, Comtet concluded with good reason that (11) and (12) do not arise from the same triplet state. Reaction 11 must occur very rapidly after the triplet state from which it arises is formed. The reasoning is based on an analogy with toluene for which Burton[59] found that at wavelengths around 250 nm the addition of butane increased both the fluorescence and the crossover to the triplet state.

This brings up the interesting question of two triplet states, each responsible for a different reaction. Comtet visualizes one as similar to the $^3B_{1u}$ state of benzene and the lowest triplet of toluene; *i.e.*, it depends on the aromatic character of the absorbing molecule. The other would then be formed, possibly by intramolecular energy transfer, from the electrons in the double bond in the side chain. The formation of the cyclopropane derivatives is an example of photochemical rearrangement of 1-4 nonconjugated dienes and seems to come from a higher triplet state than cis-trans isomerization.

A reasonable and fairly complete picture can therefore be given for the photochemical behavior of *trans*-1-phenyl-2-butene. If one assumes that each reaction arises from an intermediate which can either revert to the parent molecule or give a product, one can account qualitatively for about 90% of the absorbed photons.

3. Other Substituted Benzenes Containing Only Carbon and Hydrogen

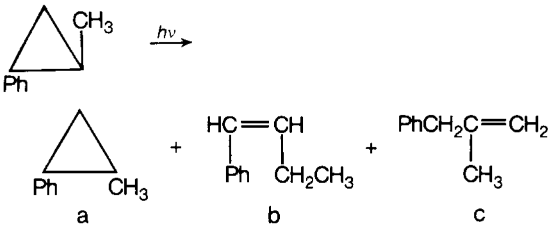
Table IV summarizes data on some substituted benzenes, a few from the literature but mostly based on work from this group. Some data discussed above are included.

The data in Table IV need relatively little discussion except to point out that the values of Q_f for all of these monosubstituted benzenes are within experimental error of that for toluene unless the substituent has a cyclopropyl ring adjacent to the aromatic ring. The overlap between the orbitals of the carbon-hydrogen bonds in the cyclopropyl ring adjacent to the aromatic ring and the π electrons in the aromatic ring would tend to increase the radiative transition probability to the ground state.

Benzylcyclopropane has Q_f about the same as toluene, but phenylcyclopropane is very much higher (about 0.47). Phenylbut-1-ene with the unsaturation well removed from the aromatic ring is slightly below toluene but probably within experimental error.

Salisbury has studied the photochemistry of certain compounds included in Table IV.[66-68]

trans-1-Methyl-2-phenylcyclopropane in the liquid phase gives several different reactions,[69] but in the gas phase three principal products are formed.[68]



(13)

TABLE IV. Alkyl-Substituted Benzenes

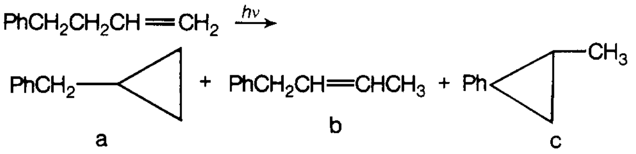
Compd	Q_f	Ref	τ_0(calcd), nsec
$C_6H_5C_2H_5$	0.28	66	
$C_6H_5(n\text{-}C_3H_7)$	0.29	66	145
$C_6H_5(sec\text{-}C_4H_9)$	0.28	66	170
$C_6H_5(c\text{-}C_3H_5)$	0.47	66	130
$C_6H_5CH_2(c\text{-}C_3H_5)$	0.25	66	150
$C_6H_5CH_2CH_2CH{=}CH_2$	0.24	68	
$C_6H_5(c\text{-}C_4H_7)$	0.28	63, 64	
$C_6H_5(c\text{-}C_3H_4CH_3)$	0.47	66	
trans-1-Methyl-2-phenylcyclopropane	0.47	68	140[66]

From 254 to 275 nm Φ_{13a} is almost constant at about 0.12, but at 248 nm it is 0.10 and at 240 nm less than 0.005. The radiation is never truly monochromatic so that a setting at 248 nm almost certainly includes some radiation for which the yield is about 0.12 and some for which it is less, possibly even zero. A sharp cutoff above a certain vibrational level probably will be found to be the rule when better data are available. Over the same wavelength range Φ_{13b} increases from 0.011 to 0.015, and while the trend is not much more than experimental error it is probably definite. Φ_{13c} is small, about 0.007. From Table IV the fluorescent yield is about 0.47 so that the energy balance is not complete and only about 61% of the absorbed photons are accounted for even near the 0,0 band. The radiative lifetime is 140 nsec, and if eq 6 is obeyed the true lifetime would be about 66 nsec. Neither added butane nor added *cis*-2-butene affects the yields of product a, while they both after a slight decrease cause increases in the yields of b. They cause a very marked increase in the yields of product c.

cis-2-Butene is not isomerized if added to the *trans*-1-methyl-2-phenylcyclopropane and irradiated. Either the yield of the triplet is very small or it disappears quite rapidly after it is formed. Benzene sensitization gives product formation but with lowered yields. Salisbury concludes that two explanations are possible. (1) The observed chemistry comes from one or the other of two trimethylene derivatives formed by breaking bonds in the cyclopropane ring when in the excited singlet state. Formation of other intermediates such as benzvalene would account for the energy loss since these might revert to the ground state. This could explain products b and c in eq 13. (2) The chemistry might result from the triplet state in which case the trend in Q_f and in product yields would require an increase in intersystem crossing with decrease in incident wavelength. Salisbury concludes that probably products are formed from both singlet and triplet states.

This molecule is a good example of the difficulty of reaching unambiguous conclusions about mechanism. While some experiments can be imagined which would give support to one mechanism or another, it is doubtful whether an unambiguous answer could be obtained by presently available techniques. It is for this reason, if for no other, that this molecule and phenylcyclobutane studied by Autard are so interesting.

The photochemistry of 4-phenylbut-1-ene has also been studied by Salisbury.[67] Three major products were found.



(14)

From Table IV one notes that the fluorescent yield is about 0.24. All product yields increase with increase in wavelength in the gas phase over the wavelength range 248 to 266 nm: (a) 0.061 to 0.19; (b) 0.011 to 0.024; (c) 0.010 to 0.023. It is evident, therefore, that nearly 70% of the absorbed photons are not accounted for by either fluorescence or product formation. Since the fluorescent yield is almost within experimental error equal to that of toluene, one is again tempted to say that all of the photochemistry occurs from the triplet state. The values of Q_f decrease to about 0.075 at 248 nm, and it is often noted that the triplet yield and the fluorescent yield decrease hand in hand as the wavelength decreases. There is thus circumstantial evidence, but not full proof, that the reactions occur from the triplet state. The ratio of a to b to c in eq 14 is 6:1:1 and independent of wavelength in all quenching experiments and at all wavelengths. The quenching gases used were neopentane, *cis*-2-butene, and *trans*-piperylene. Thus, piperylene is known to quench singlet states of many aromatic molecules,[70] whereas the 2-butenes do little if anything to singlet-state molecules because their singlet energy levels lie too high. They are fairly good quenchers of triplet states with electronic energies above about 3.6 eV.

There are not enough data to prove any mechanism conclusively, but Salisbury suggests that after absorption, following which some excited singlet molecules emit, there is a crossover to the triplet state by the remainder. Then a vibrationally excited intermediate is formed (possibly also a triplet) very rapidly and the products are formed from this. Vibrational quenching of this intermediate causes formation of ground state molecules. Since it is easy to imagine two types of triplet, one essentially benzenoid and the other not, and since at present there is no way of determining which would be formed by the crossover, the postulation of an intermediate seems logically unnecessary although it may exist. Quite possibly there will develop means of elucidating some of these details in the years to come.

In concluding this section devoted to aromatic molecules made solely of atoms of carbon and of hydrogen, one may express certain generalizations and cite some bearing that they may have on the photochemistry of such molecules.

1. Under ordinary experimental conditions as used by most photochemists, absorption and emission of radiation only occur between states of the same multiplicity. If ground states are singlets (as they almost invariably are), absorption of radiation leads initially only to singlet states. This rule may be violated in the presence of reasonably high concentrations of paramagnetic molecules,[71] in the presence of magnetic fields and also, since no transition is totally forbidden, in long path lengths and with very high incident intensities. Since heavy atoms tend to cause a breakdown of spin-orbit coupling, the presence of heavy atoms may cause triplet formation which would not otherwise be expected.[24] These heavy atoms may either be in the molecules being studied or external to them.

2. Processes which are not accompanied by absorption or emission of radiation do not obey a spin conservation rule with the same rigor. Thus, light emission from states initially formed by the absorption of radiation is, except under special conditions, invariably singlet-singlet, but quite often all of those molecules which do not emit fluorescence will cross over to a triplet state. The main things which can prevent this from happening are competing chemical reactions from the singlet state such as dissociation and isomerization. These latter seem usually, but not always, to be more rapid when vibrational energy is present, and hence fluorescence and crossover to a state of different multiplicity almost invariably have highest yields in molecules excited near 0,0 bands and at low temperatures.

These two generalizations help to explain much of the photochemistry of simple aromatic molecules made solely of carbon and hydrogen. However, molecules in excited triplet states are not thermodynamically stable, and they must disappear either by light emission or by energy transfer to the surroundings provided they do not disappear by chemical reactions.

Light emission from a triplet state to a ground singlet state violates the selection rule that in a radiative process spin must not change. Rate constants for such processes are low, much lower than for similar transitions of the singlet-singlet or triplet-triplet type. Few molecules show phosphorescent (triplet state) emission.

In some instances (*e.g.*, sulfur dioxide[72]) singlet-triplet absorption may be strong enough to permit direct excitation to the triplet state by radiation from lasers.

It must also be kept in mind that the importance of the electronic state may sometimes be exaggerated and that the really important matter may be the vibrational level. Since vibrational relaxation is slower in the gaseous phase than in condensed phases, this aspect of the problem is best studied in gases. Nevertheless, even in condensed phases effects of incident wavelength should be explored.

C. Heterocycles with Nitrogen in the Ring

Superficially, conversion of a benzene derivative to a heterocycle containing a single nitrogen atom in the ring involves merely substitution of a nitrogen atom for a CH. There is, however, an important difference between benzene and pyridine. In a qualitative way one can say that in both cases 18 electrons determine the aromatic character of the ring, but in benzene all 18 are responsible for carbon-carbon bonds, while in pyridine 12 are responsible for carbon-carbon bonds and 6 are responsible for carbon-nitrogen bonds. In addition, two electrons on the nitrogen atom may be described as nonbonding. The latter, when radiation is absorbed, provide one antibonding electron in the excited state.[12] One expects, therefore, two types of singlet-singlet absorption: $n-\pi^*$ and $\pi-\pi^*$. The former lies at a somewhat longer wavelength than the latter.[12]

No fluorescent emission for pyridine has been reported, and, although isomer formation has been sought for, no isomers similar to those for benzene have been positively identified.[73] That such isomers may have transient existences is indicated by work on the diazines in the laboratory of Magat.[11,16]

The picolines also do not fluoresce[13] and, although isomerization occurs, yields are extremely low. We will return to this matter.

The situation with the diazines is spectroscopically more complicated because several singlet and several triplet states are possible. The relationships between these states and possible transitions between them have been the subject of several studies.[11,16] Discussion in this article will be confined to 1,4-diazine (pyrazine).

1. Pyridine

Recent work by Heicklen and his coworkers[74] has described in some detail the photochemical behavior of pyridine in the gaseous phase so that only a brief mention will be given of this molecule.

The work of Linnell[75] showed pyridine to decompose little at 253.7 nm, but it did give some gaseous products at shorter wavelengths. Triplet yields were determined by Lemaire[12] by the Cundall method.[29] Yields in both the $n-\pi^*$ and the $\pi-\pi^*$ bands were quite low with the former being the higher of the two. Since all authors seem to agree that product formation at the wavelengths we are considering is negligible, a discussion of mechanism does not seem to be in order. Roquitte[76] by flash photolysis found acetylene and some hydrogen cyanide as products. However, the wavelength was not well defined and the results were not quantitative.

One can conclude that some at present ill-defined pathway must be responsible for return of both excited singlet and excited triplet molecules of pyridine to the ground state. At 213.9 and 228.8 nm acetylene is the main product, but the yield at 228.8 nm is low.[74] A polymer is also formed.

2. *Picolines*

The picolines have been studied by Roebke.[13] If aromatic compounds with nitrogen atoms in the ring are able to isomerize to benzvalene and prismane, the picolines should isomerize as do the xylenes. 3-Picoline and 4-picoline were formed from 2-picoline when irradiated in the π–π^* band at wavelengths 238, 248, and 266 nm at pressures of about 1 Torr. Yields per photon were always low: Φ for 3-picoline respectively was 5.1, 3.4, and 0.9 $\times 10^{-4}$; Φ for 4-picoline was respectively 4, 3, and 0 $\times 10^{-5}$. At the two longest wavelengths, 275 and 280 nm, both in the n–π^* band, no isomerization was observed.

The isomerization yields of the picolines, while very low, follow the same general trends found for other aromatic compounds such as the xylenes; *viz.*, they increase with decrease in incident wavelength and decrease with increase in pressure. There is, however, an intensity effect not noticed with the xylenes. Since yields increase with increase in intensity, some process involving two intermediates seems indicated. Roebke[13] has proposed the following mechanism.

$$\mathrm{M} + h\nu = {}^1\mathrm{M_v} \tag{15}$$

$${}^1\mathrm{M_v} = \mathrm{I} \tag{16}$$

$${}^1\mathrm{M_v} + \mathrm{X} = {}^1\mathrm{M_0} + \mathrm{X} \tag{17}$$

$${}^1\mathrm{M_v} = {}^1\mathrm{M_0} \tag{18}$$

$${}^1\mathrm{M} = {}^3\mathrm{M} \tag{19}$$

$$\mathrm{I} + \mathrm{wall} = \mathrm{M} \tag{20}$$

$$\mathrm{I} + {}^3\mathrm{M} = \mathrm{isomers} \tag{21}$$

$$\mathrm{I} + h\nu = \mathrm{isomers} \tag{22}$$

$${}^3\mathrm{M} + \mathrm{X} = \mathrm{M} + {}^3\mathrm{X} \tag{23}$$

where ${}^1\mathrm{M_v}$ and ${}^1\mathrm{M_0}$ are vibrationally excited and vibrationally equilibrated excited singlet state molecules, respectively. I is an intermediate isomer, possibly of the benzvalene or prismane type. Reaction 21 would be responsible for increased yields at high intensities. Reactions 17 and 18 both seem kinetically to be necessary even though it is recognized that ultimate loss of vibrational energy must occur by collision.

Triplet yields obtained by the biacetyl method vary from 0.031 to 0.210 over the wavelength range covered. Since light emission must be less than 0.01, much of the absorbed energy is not accounted for although one can suggest possibilities such as large scale reversion of I to M.

The radiative lifetime of ^{1}M is calculated to be 19 nsec, and hence if the emission yield is less than 0.01 the true lifetime must be less than 0.19 nsec.

The mechanism proposed by Roebke[13] thus fits the facts at least qualitatively, but some of the rate constants, particularly those related to the triplet state, may not be estimated from the data. The nature of the wall surface seems to affect yields. A detailed discussion of this point is not possible.

TABLE V. Fluorescent and Phosphorescent Yields of Pyrazine[17] at 3 Torr and 25°

	Wavelength, nm				
	326.7	313.0	300.0	290.000	280.0
Q_f	0.00173	0.00174	0.00129	0.00084	0
Q_p	0.00166	0.00170	0.00128	0.00084	0
Q_f/Q_p	1.05	1.03	1.01	1.00	

3. *Diazines*

The diazines have formed the object of an extended series of investigations in the laboratory of Professor Magat at Orsay.[11,16] Pyrazine only will be discussed here.

Since the diazines have two nitrogen atoms in the ring, there will be several n–π^* and π–π^* states, both singlet and triplet. The group at Orsay has elucidated many of the relationships between these states and the character of the triplet states which are formed. It is impossible to use sufficiently monochromatic light to disentangle all of the steps completely.

Pyrazine proved to be of particular interest because it is one of those rare molecules which both fluoresce and phosphoresce in the gas phase. Table V gives values of Q_f and Q_p for pyrazine at several wavelengths (from Nakamura[17]). All of the emission from pyrazine is excited by absorption in the n–π^* band and emission is zero following absorption in the π–π^* band. The trend in Q_f/Q_p is probably real although it is scarcely greater than experimental error.

The benzene-sensitized emission of pyrazine was also studied. The exciting radiation was at 253 nm, which does not excite pyrazine to emission so that the triplet emission of pyrazine must have been excited by energy transfer. No sensitized singlet emission of pyrazine was observed.

It is, therefore, possible to use the sensitized triplet emission of pyrazine to calculate the triplet yield in benzene. Nakamura[17] found this to be 0.69 ± 0.07, well within experimental error of the values obtained by other methods. The pyrazine method for triplet yield determinations has one advantage over the biacetyl method; Q_f and Q_p are nearly equal. The chief disadvantage is in low values of Q_f and of Q_p, which make precise measurements difficult.

Jones and Brewer[77] have determined triplet yields for several molecules, including pyrazine, by both the Cundall and the biacetyl methods. It has already been indicated that there is no basis for calculating triplet yields if the branching ratio (ratio of *cis*-2-butene to *trans*-2-butene formed from the intermediate) is not constant from one donor molecule to another. Jones and Brewer[77] used both the Cundall and the biacetyl methods at three different wavelengths. In both cases reciprocals of yields were plotted against reciprocals of pressures of biacetyl or of olefin, respectively. Extrapolation to the intercept for which the inverse of the pressure has become zero permits calculation of yields at infinite pressure of acceptor molecules.

At 313 nm with pyrazine the two methods for determining triplet yields disagree, and results differ from one laboratory to another.[11,77] Since *trans*-2-butene is thermodynamically more stable than *cis*-2-butene by about 1 kcal,[32] possibly the difficulty resides in the ability of triplet pyrazine to effect transfer of energy. Small differences in wavelength distribution in the light sources and in trace impurities could be crucial. The butene method probably is not giving good results even though the quantity $\Phi_{CB} + \Phi_{TB}$ is not far from unity. The triplet yield by the biacetyl method is about unity as it probably should be since Q_f is only about 0.002. At shorter wavelengths triplet yields by both methods are small and the two methods agree within experimental error.

Isomerization yields for the diazines are very low.[11,16] Near the long wave end of the n–π^* absorption region the triplet yield is about unity. Thus, the photons absorbed are accounted for through the singlet state within experimental error. In the π–π^* region the photon balance as regards the singlet state is incomplete. Fluorescence yields are low and are probably zero, triplet yields are well below unity, and isomerization yields are small. Formations of prismane and of benzvalene type intermediates of the diazines[11,16] have been suggested, but positive proof of their transitory existence is largely lacking. More data of types not now available would be necessary to establish mechanisms beyond reasonable doubts.

D. Simple Aromatic Molecules Containing Fluorine

The carbon–fluorine bond is highly polar, and for this reason substitution of fluorine in aromatic compounds changes the spectral characteristics markedly. Fluorine atoms as in fluorobenzene have a great perturbing effect on the electronic system of the ring, and the band system with which we are mainly concerned becomes almost completely "allowed" instead of "forbidden" as it is in benzene.[78] Absorption is thus far more intense in fluorobenzene than it is in either benzene or substituted benzenes with substituents composed only of carbon and hydrogen.

The decrease in the forbiddenness has several effects on the photochemistry of fluorine-substituted benzenes. In the first place, the very high absorption accentuates the round-the-corner effect, and great care must be exercised in measuring fluorescent efficiencies. It must be remembered that there is no exact way to correct for errors introduced by this effect other than to use concentrations or pressures such that absorption is never more than about 25% in the peaks of the unresolved fine structure.

In the second place, the calculation of the radiative lifetimes from integrated absorption coefficients may be considerably in error, both because the integration cannot be performed with high accuracy if there are high peaks of absorption and because the perturbations caused by the fluorine atoms render the equations used for such calculations nonrigorous. Effects on the infrared spectra have been discussed by Varsanyi.[79]

The atomic number of the fluorine atom is relatively low, and one would not expect serious effects on spin–orbit coupling due to a "heavy atom." Neon does not show appreciable heavy atom effects when added to gases discussed in previous sections.[59]

1. Fluorobenzene

The 0,0 band for fluorobenzene is placed at 264.4 nm[78] and is the most intense band in the absorption spectrum. Several calculations of the radiative lifetime have been made, and the agreement among them is not perfect. The lowest value is 69 nsec[4] and several values from 100 to 120 nsec are reported.[4,21] From eq 6 it is possible to calculate the true lifetime, and this requires knowledge of the fluorescent yield.

TABLE VI. Approximate Effective Cross Sections for Vibrational Quenching of Excited Singlet Fluorobenzene[21]

Foreign gas	Wavelength, nm	Effective cross section
H_2	253	0.438×10^{-16} cm^2
	256	0.418
	258	0.304
CH_4	253	1.24
	256	1.21
	258	0.835
C_2H_6	253	2.03
	256	1.46
	258	0.994
cis-2-Butene	253	5.66
	256	2.94
	258	1.18

Fluorescent yields in fluorobenzene vapor were first determined before the consequences of the round-the-corner effect were fully appreciated.[80,81] The best value seems to be about 0.19.[82] Thus, the true lifetime of fluorobenzene excited at about 260 nm should be in the range 13 to 23 nsec. The best value of the measured true lifetime by Lee and his coworkers[52] is 8.4 nsec.

The agreement between measured and calculated true lifetimes for the excited singlet state of fluorobenzene is poor, certainly not as good as for the compounds shown in Table I. The reason for this cannot be stated with certainty, but it is most probably in the difficulty of obtaining a good calculated lifetime for a molecule which absorbs as strongly as fluorobenzene.

Isomerization and dissociation of fluorobenzene in the spectral region covered by this report have not been reported.

The triplet yield of fluorobenzene has been determined by several authors.[80,81] The biacetyl method is subject to the same round-the-corner effect as the fluorescence provided diffusion does not cause migration of the triplet biacetyl away from the places where the triplet fluorobenzene molecules are formed. Nakamura[83] was the first to recognize that quenching of the fluorescence of a molecule like fluorobenzene by biacetyl leads to excitation of biacetyl to both the first and the second excited singlet states. Since the former crosses over almost quantitatively to the triplet state which emits, a correction for this fact must be applied.[15] At 264.7 nm Nakamura gives a triplet yield of 0.81 (which he believes may be slightly high) and a fluorescent yield of 0.22. The two add to unity within experimental error (however, see ref 82). Thus, the fates of the initially formed singlet molecules in the neighborhood of the 0,0 band are accounted for.

At a pressure of 1 Torr Nakamura[21] recognized some short wave emission lying below the 0,0 band and ascribed it to "resonance" emission. Since the incident radiation excited several vibrational levels of fluorobenzene, a quantitative treatment of the data is not possible. Nevertheless, qualitatively effective cross sections for quenching of vibrational energy in the excited singlet state could be calculated. These data are summarized in Table VI and indicate clearly that the 2-butenes are very effective vibrational relaxants. The data on fluorobenzene furnish valuable information about the behavior of aromatic molecules which contain fluorine atoms.

2. Other Fluorobenzenes

For the difluorobenzenes (see Table VII), the sums of fluorescent and triplet state yields in the neighborhood of the 0,0 bands are probably within experimental error of unity. For these highly absorbing substances the errors

TABLE VII. The Fluorobenzenes ($C_6H_4F_2$)

Compd	Wavelength	Fluorescent decay time[a]	Q_f	Φ_T	Ref
o-$C_6H_4F_2$	266	5.5	0.15	0.71	84
m-$C_6H_4F_2$	274	6.0	0.16	0.81	85
p-$C_6H_4F_2$	278	8.0	0.50	0.20	84

[a] From ref 52 and 53.

TABLE VIII. The Fluorobenzenes

Compd	Wavelength, nm	Fluorescent decay time, nsec	Q_f	Φ_T	Ref
		$C_6H_3F_3$			
1,2,4-$C_6H_3F_3$	278		0.28	0.64	86
1,3,5-$C_6H_3F_3$	264		0.035	0.40	86
		$C_6H_2F_4$			
1,2,3,4-$C_6H_2F_4$	264.5		0.19	0.22	87
1,2,3,5-$C_6H_2F_4$	268		0.03	0.14	87
1,2,4,5-$C_6H_2F_4$	267		0.34	0.52	87
		C_6HF_5 and C_6F_6			
C_6HF	272	1.6[89]	0.04	0.08	88
	265		0.017	0.02	88
C_6F_6	280	3.6[89]	0.02	0.05	53

TABLE IX. Monofluorotoluenes[a]

Compd	Symmetry group	Wavelength, nm	Fluorescent decay time, nsec	Φ_T	Q_f	Ref
o-$FC_6H_4CH_3$	C_s	265	9.8	0.57	0.22	90, 92
m-$FC_6H_4CH_3$	C_s	265	10.7	0.73	0.21	90, 92
p-$FC_6H_4CH_3$	C_{2v}	265	11.2	0.68	0.35	90, 92

[a] $P = 1$ Torr for lifetime measurements.

TABLE X. CF_3- and F-Substituted Benzenes

Compd	Wavelength, nm	Fluorescent decay time, nsec	Q_f	Φ_T	$\Phi \times 10^3$ isom	Ref
$C_6H_5CF_3$	265	19	0.16	0.73		93
1,3-$C_6H_4(CF_3)_2$	265	11.5	0.14	0.83		93
1,4-$C_6H_4(CF_3)_2$	265	6.3	0.16	0.90		93
o-$FC_6H_4(CF_3)$	265	6.0	0.32	0.58	0.1[a]	93, 94
m-$FC_6H_4(CF_3)$	265	4.0	0.35	0.65	0.08[b] 0.10[c]	93, 94
p-$FC_6H_4(CF_3)$	265		0.23	0.75	0.12[d]	93, 94

[a] 0.16 (253.7 nm); 0.29 (248 nm). [b] Ortho yield: 0.07 (253.7 nm); 0.03 (248 nm). [c] Para yield: 0.21; 0.09. [d] 0.35 (253.7 nm); 0.36 (248 nm) (ref 93, 94).

due to the round-the-corner effect may be large and such errors always make fluorescent yields too low.

Data on variations of yields with wavelength are not extensive but they indicate the same trend as for other aromatic molecules; *i.e.*, both fluorescent and triplet state yields decrease as the incident wavelength decreases. Isomerization occurs as it does for the xylenes (see above), and this certainly is one of the ways by which excited molecules disappear.

Insufficient data are available for the trifluorobenzenes to permit rigorous conclusions to be drawn. The sum of fluorescent and triplet state yields for 1,2,4-trifluorobenzene is within experimental error of unity, but this is not true for the 1,3,5-trifluorobenzene although the wavelength is shorter for this molecule. See Table VIII.

Of the tetrafluorobenzenes only the 1,2,4,5 compound has a sum of fluorescent and triplet state yields approaching unity at 267 nm. For the other two the sum is far below unity. Since isomerization yields are not known, conclusions about energy balance are not possible.

Pentafluorobenzene and hexafluorobenzene have very small fluorescent and triplet state yields. However, Phillips[89] concludes that in all probability the methods for triplet yield determinations are not satisfactory for hexafluorobenzene because the lifetime of the triplet state molecules may be very short.

Isomerization of hexafluorobenzene has been observed, and it is interesting to note that the dewar form results in contradistinction to benzene.[91] Further work on the isomerization of the fluorobenzenes is obviously needed.

3. *Fluorotoluenes*

Table IX shows data for the three fluorotoluenes. Probably within experimental error near the 0,0 bands of these three molecules the sums of fluorescent yields and triplet state yields are unity. However, it is unwise to assume that this is a very exact statement.

Isomerization yields of the fluorotoluenes have not been determined. By analogy with other compounds they would be expected to increase as the wavelength of the incident radiation decreases.

4. *Fluoro- and Trimethylfluoro-Substituted Benzenes*

The substitution of CF_3 for CH_3 does not seem to affect fluorescent yields very markedly. Table X shows data for several substituted benzenes with CF_3 and fluorine atoms.

For all of the compounds listed in Table X the sums of fluorescent and of triplet yields add to unity within experimental error. Thus, isomerization yields should be very small or nearly zero as they are. The lifetimes of excited singlet state molecules as shown in this table are all very small, and what evidence there is would indicate that the lifetimes of these molecules in the triplet state are also very short.

It is interesting to note that for the three isomers of $FC_6H_4(CF_3)$ the isomerization yields increase with decrease in wavelength except for the meta compound where they may pass through a maximum. It has been suggested by Al-Ani[94] that possibly this indicates an optimum rate of isomerization as distinct from reversion to the parent molecule in a certain range of vibrational levels of the excited singlet state. Further investigation of this matter might be warranted.

Except for possible unusual trends in quantum yields of photoisomerization, these fluoro compounds show the same trends as do most of the other aromatic molecules herein discussed. It must be emphasized, however, that for all of them absorption coefficients are high and radiative lifetimes and true lifetimes are short, thus indicating that the presence of carbon-fluorine bonds has very substantially changed the character of these molecules from the corresponding molecules made only of carbon and hydrogen.

5. *Mixed Halogeno Benzenes*

Chlorobenzene and other compounds for which a chlorine atom is substituted for hydrogen on the benzene ring

TABLE XI. Mixed Halogen Aromatic Compounds[95]

Compd	Wavelength, nm	Q_f	Radiative lifetime (calcd), nsec
C_6H_5Cl	269.7	0.005	603
o-ClC_6H_4F	269.5	0.015	121
m-ClC_6H_4F	269.9	0.015	154
p-ClC_6H_4F	275.5	0.042	111
o-ClC_6H_4Br	269.0	0	
m-ClC_6H_4Br	270.0	0	
p-ClC_6H_4Br	270.0	0	

all fluoresce very little. Chlorofluorobenzenes are no exception to this rule. In the absence of data on possible photochemical products, there is little one can discuss about mechanism. Table XI summarizes some data on fluorescent yields in the gaseous phase of a few mixed halogen aromatic compounds.

The *p*-chlorofluorobenzene shows the highest fluorescent yield and the shortest calculated radiative lifetime of the three isomers. This trend resembles those found for other substituted benzenes. The dissociation energies of carbon-chlorine bonds are certainly less than for the carbon-fluorine bonds in these compounds so that the possibility of some dissociation photochemically to give chlorine atoms must be kept in mind. This could mean that the methods customarily used to determine triplet state yields would not turn out to be useful.

The biacetyl method was used to determine triplet state yields for a few of the compounds in Table XI.[95] For this method a plot of $1/Q_p$ *vs.* $1/P_{Bia}$ should give a straight line if certain assumptions about relative rate constants are made. For *o*- and *p*-chlorofluorobenzenes reasonably straight lines are obtained with intercepts of 4 and 7.25, respectively. Since according to Calvert and Horowitz[37] the phosphorence yield of biacetyl is 0.15 ± 0.01 and $Q_p/0.15$ should be the maximum possible value for the triplet state yields, the triplet yields appear to be $0.25/0.15 = 1.7$ and $0.138/0.15 = 0.92$, respectively. The first value is impossible and the second is improbable.

One must conclude that the extrapolation is not valid although the mechanism upon which the calculation is based may occasionally go astray.[15] In any case it appears probable that the singlet chlorofluorobenzenes may excite biacetyl to its first excited singlet state from which it can cross over to triplet biacetyl and phosphoresce.

Nakamura[83] actually measured the emission from $^1BiA^I$ and by use of the known ratio of green to blue emission for biacetyl as determined by Okabe[19] he was able to estimate the correction for Q_p. Thus, about 40% of the quenching of fluorobenzene singlet by biacetyl was due to excitation of the biacetyl to its first excited singlet state.

As regards the chlorofluorobenzenes there is the possibility of some dissociation and also the possibility of some isomerization, and the triplet yields thus could not be determined with accuracy. Further work on these molecules would be useful.

VI. General Remarks

There have been presented data on many aromatic molecules of several different types. No pretence is made that the data are all inclusive, nor is it contended that the methods used always give the right answers. For certain important measurements the methods leave much to be desired and sometimes methods which work well for one molecule are open to suspicion when used for others. This is particularly true for methods dependent on energy transfer to monitoring substances. This situation sometimes places the investigator in the unenviable position of having to choose the data he likes best rather than those susceptible of unambiguous proof of validity.

In spite of many difficulties some generalizations seem to be useful and quite possibly they will bear the test of time. Since this is the case the question can legitimately be raised as to whether extensive programs based on present methods would be useful or whether breakthroughs both in experimental methods and in theory may not be essential for real progress. A brief discussion will be given of this matter even though the authors recognize the dangers both of philosophizing and of either predicting or trying to guide the future.

In this article some 29 compounds are listed for which the fluorescent yields (Q_f) and the triplet state yields (Φ_T) have been determined in the neighborhood of the 0,0 bands. If both n-π^* and π-π^* transitions have been observed only the n-π^* transitions are included in these statistics. Of the 29 compounds the sum of ($Q_f + \Phi_T$) is within experimental error of unity for 19 and three undergo dissociation or isomerization so that triplet state yields probably have little meaning as at present determined. Of the remaining seven two with nitrogen in the ring do not fluoresce and for them it is only fair to say that triplet yields also seem to be low. Thus, at least for these three compounds the above sum is far from unity. It may be questioned, however, whether presently available triplet methods give correct answers. One is *m*-xylene which may isomerize appreciably even at the 0,0 band, and methods for determining the primary isomerization yield as distinguished from the net yield after some isomer destruction are not yet available. It is understandably impossible to achieve an energy balance for this molecule.

The remaining four molecules all have fluorine atoms attached to ring carbon atoms. For these latter molecules both more and different kinds of information are needed. Even for the 19 compounds which seem to behave "normally" errors are such that any generalization is subject to uncertainty. Nevertheless, Ermolaev[56] finds that in the liquid phase a very large number of molecules obey this simple rule. Vibrational relaxation should almost always be complete in the liquid phase before light emission occurs.

A second generalization to which few if any exceptions have been noted is to the effect that $(1 - Q_f - \Phi_T)$ increases as the wavelength of the incident radiation decreases and that for all molecules discussed in the present article this difference approaches unity between 240 and 250 nm. However, once again a word of caution is necessary since inert added gases cause vibrational relaxation (see below) and hence tend to increase fluorescent yields at wavelengths below the 0,0 bands. Presumably, the same would be true for triplet state yields. This question is worthy of a more complete investigation. Unfortunately, the 2-butenes are very efficient at causing vibrational relaxation.[21] Also, Morikawa and Cvetanovic[96] have shown that *cis*-2-butene electronically quenches the $^1B_{2u}$ state of benzene to a slight extent. Presumably, this quenching is small enough not to be of great importance in triplet yield determinations.

A third generalization has its origins in some work done many years ago on biacetyl.[97] At 366 nm biacetyl vapor shows an increase in fluorescent efficiency as pressure is increased, thus indicating that some process (presumably first order) destroys excited biacetyl molecules before they emit radiation but that they are "saved" for emission if vibrational energy is removed by collision. Recently Calvert, *et al.*,[37,72] have suggested that wall effects are very important, particularly at low pressures. Similar trends are not observed at 404.7 and at 435.8 nm. It should be mentioned in passing that in using the biacetyl method to determine triplet yields an error may be introduced if the energy received by the biacetyl molecule is too large and the pressure is too low to provide adequate vibrational relaxation.

Since fluorescence and crossover to the triplet state do not account for all of the absorbed photons as the frequency of the incident radiation increases beyond that of the 0,0 band, there must be some process or processes which account for the remainder of the singlet state excited molecules. The main possibilities are dissociation and isomerization. Very tentatively we restrict the dissociation to certain types. This is suggested by the work of Autard[63] and of Ho and Gorse[64] on the dissociation of phenylcyclobutane into its various products, but particularly dissociation into ethylene and styrene has yields which decrease as the frequency of the incident radiation increases, and in addition the yields are lowered by addition of *cis*-2-butene and of 1,3-pentadiene. Both of these molecules quench triplet states although the pentadiene is reasonably effective in quenching singlet excited states of aromatics.[69] The major dissociation of this molecule appears to occur from the triplet state.

It should be noted that the two principal photochemical dissociations of phenylcyclobutane are into complete molecules and not into radicals and atoms.

Thus, with the possible exception of dissociations into complete molecules, we note that isomerizations and dissociations have yields which tend to increase with the amount of vibrational energy in the excited singlet state. In the liquid phase where vibrational relaxation is rapid and at relatively high pressures of inert gases in the gas phase, isomerization yields should be lower than at short wavelengths at low pressures.

This statement is in agreement with the facts, but a study of fluorescent yields permits estimates to be made of the effectiveness of collisions in causing vibrational relaxation. Some such studies have been made for molecules discussed in this article. Brewer[85] concludes that for *m*-difluorobenzene vibrational relaxation, in agreement with Kemper and Stockburger,[98] must take place by two or more processes one of which appears to be first order and the other(s) second order. Obviously energy will not be lost permanently by the first-order process, but it may be intramolecularly redistributed so that fluorescence could only occur with a very low rate. The energy lost per collision appears to be wavelength dependent but is of the order of 50–70 cm^{-1} per collision.

Table VI gives some results obtained by Nakamura[83] on the effective cross sections for quenching of the excited singlet state of fluorobenzene by several gases.

As would be expected, the shorter the wavelength, and hence the more vibrational energy present in the excited molecule, the higher the probability of loss of vibrational energy on collision. Also as one would expect, the more complex the colliding molecule the greater the probability of vibrational energy loss.

VII. Summary

For many of these simple aromatic molecules fluorescence, isomerization, and crossover to the triplet state account for all or nearly all of the initially excited singlet state molecules. The data, particularly for triplet yields, are such as to make this statement only approximate.

When nitrogen atoms form part of the ring, fluorescence is rarely encountered. Pyrazine (1,4-diazine) is an exception. Fluorinated aromatics absorb strongly and errors due to the round-the-corner effect can, therefore, be relatively serious. Fluorescent yields and triplet state yields are now known for many of these molecules, and in a general way they do not form marked exceptions to the generalizations put forward above.

Finally we must refer to the simplest aromatic compound, benzene. For this molecule the 0,0 band is forbidden either in emission or in absorption. This is for symmetry reasons. Data on fluorescent yields and on triplet state yields mainly in the strong bands at 259 and at 253 nm show them to be in the ranges 0.18 to 0.20 and 0.70 to 0.75, respectively. The sums appear to be definitely less than unity even though the accuracies of the results may still leave something to be desired. The work of several authors[6,49-51] on the behaviors of excited $^1B_{2u}$ benzene molecules in single vibrational levels shows that fluorescent efficiencies vary from one level to another and that emission ceases when the excited molecules have more than about 2500 cm^{-1} of energy.[6]

For most of the aromatic molecules discussed herein the 0,0 band is the one for which absorption is the strongest. It is also the one which gives the highest fluorescent efficiency and also probably, although the data are less good, the highest efficiency of crossover to the triplet state.

Thus, benzene may appear to be an exception to the general rule that fluorescent and triplet state yields add to unity because absorption in the 0,0 band is negligible. There are other possible reasons. Birks[54] has studied excimer formation and emission for many aromatic molecules in the liquid phase. Conceivably even though excimer formation seems to be relatively unimportant in the gaseous phase, it might account for some of the failure to have the sum equal to unity.

Finally, only recently has the theory of these processes begun to receive adequate attention.[50,51] The beaten path may not prove to be very fruitful but there are signs of a possible brilliant future.

VIII. References and Notes

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