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Autor(en): **Noyes, Albert**

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Some Aspects of Energy Degradation of Excited Molecules

W. ALBERT NOYES, Jr., University of Texas, Austin, Texas

IIInd WERNER KUHN Memorial Lecture, Basle 1966

IUPAP – 12th General Assembly

It is a very great honor for me to be asked to give the Professor WERNER KUHN Memorial Lecture. Especially is it appropriate for this lecture to be given at the University of Basel where Professor KUHN spent a large fraction of the most productive years of his life.

Professor KUHN's great influence on international scientific relations is well known to me and about this I wish first to speak.

When the Section (now called Division) of Physical Chemistry of the International Union of Pure and Applied Chemistry was established in 1951, Professor KUHN became a member of the divisional committee. He successively became Vice-President and then President of that section. In the latter capacity he was also a Vice-President and a member of the Bureau of the International Union itself, a position he relinquished in 1961.

The years during which Professor KUHN presided over the Section of Physical Chemistry of IUPAC were important and turbulent. Far reaching agreements were made about the symbols of free energy and a report was published on definitions and nomenclature. The entire basis for atomic weights was changed by agreement between the International Union of Pure and Applied Chemistry and the International Union of Pure and Applied Physics.

Throughout all of these difficult and sometimes stormy negotiations Professor KUHN showed a soundness of judgement, an equanimity and a common sense which excited our most sincere admiration. The science of chemistry owes him much.

Between 1923 and 1933 Professor KUHN published seven papers in the field of photochemistry. These dealt with such widely diversified parts of the subject as the relationship of the photochemical decomposition of ammonia to the law of photochemical equivalence, the photochemical preparation of optically active substances, and the photochemical separation of isotopes. Professor KUHN showed in photochemistry, as he did in other fields to which he devoted attention later, an extraordinary ability to choose significant problems and to show great originality and insight in their solution.

But there are also other reasons why a talk on photochemistry and particularly at a joint meeting with physicists is appropriate.

Photochemistry prior to World War I had centered mainly around the use of light to obtain atoms and free radicals in controlled amounts. The

beautiful work of BODENSTEIN and his collaborators in Berlin had given the first unequivocal proof of chain reactions, and Professor NERNST, who at one time was a professor in Zurich, contributed greatly to the theoretical understanding of chain reactions. Nevertheless in all of these studies photochemistry was merely a tool and the subject had not emerged from infancy.

It has always seemed to me that the modern era of photochemistry dawned in the years 1924 and 1925. In 1924 VICTOR HENRI, who was then a professor at the University of Zurich and with whom Professor KUHN prepared his doctoral dissertation, published with one of his students, H. TEVES, a paper on predissociation. In studying the absorption spectrum of the sulfur molecule, S_2 , they noted certain diffuse bands. To them this diffuseness implied a dissociation of the S_2 molecule into atoms, an interpretation amply justified by later events. During my student days in Paris, VICTOR HENRI was working in the laboratory of physiology at the Sorbonne.

The Faraday Society held at Oxford on October 1 and 2, 1925, a meeting devoted to photochemistry at which Professor JAMES FRANCK, then a physicist at Göttingen, gave a broad and very fundamental interpretation of the relationship of spectrum type to photochemical behavior of diatomic molecules. The last years of Professor FRANCK's active life were spent at the University of Chicago. Professor ROBERT MULLIKEN, whose most active years were also spent at the University of Chicago, systematized the symbols, the facts, and the interpretation of the spectra of di- and polyatomic molecules.

VICTOR HENRI was a chemist, JAMES FRANCK was a physicist. ROBERT MULLIKEN was trained as a chemist, but he has passed to higher things and has been since 1930 a professor of physics at the University of Chicago. Photochemistry more than almost any other field owes its origins and its progress both to physicists and to chemists.

Photochemists for many years studied atom and free radical reactions. This work is of interest more in the interpretation of thermal reactions than it is from a purely photochemical standpoint. In this lecture I propose to devote attention to the histories, one might almost say the personal histories, of molecules which absorb radiation.

A simple statement of the first law of thermodynamics as applied to photochemistry would be as follows:

Each molecule which absorbs a quantum will either dissociate or be raised to a higher energy level. The active molecules will either radiate, dissociate, or react chemically. All of the absorbed energy must be accounted for either as radiation, as chemical energy or as heat.

The first sentence will be recognized as a statement of the Einstein Law of Photochemical Equivalence. If secondary reactions are initiated so that the products differ from the initially formed dissociation products, the heat of reaction, whether positive or negative, must be added or subtracted as the case may be from the energy of the radiation absorbed in reaching a balance.

These statements are very elementary and very naive. Not to believe in them would be equivalent to saying that science itself has no fundamental basis.

The data accumulated until the 1930's seemed to indicate that photochemical reactions were only initiated either if the absorbing molecule dissociated into active fragments or if the energy could be transferred to another molecule which would then dissociate. The classical researches of CARIO and FRANCK on the mercury sensitized dissociation of hydrogen gave a brilliant example of the energy transfer concept.

We now know how wrong this original attitude toward photochemistry really was. Perhaps two events should be cited which changed the thinking of photochemists. The first was the work of NORRISH and APPLEYARD in 1933 and later of BAMFORD and NORRISH in 1938 in which these investigators showed that certain molecules, mainly aliphatic ketones, could dissociate to give complete molecules without at any time having passed through the stages of free radicals and atoms. This original discovery, for which a later interpretation due to others is now accepted, gave the name Norrish Type II reaction to a phenomenon of extraordinary interest widely studied in many different laboratories.

The second event occurred about 1939 just as the war was starting in Europe. G.N. LEWIS pointed out that many of the phenomena of fluorescence and of phosphorescence could be best interpreted by the use of more than one excited electronic energy level and that one must be considered to be a triplet. The necessity of the use of two or more electronically excited energy levels had already been pointed out by JABLONSKI, and LEWIS's contribution consisted in introducing the triplet state to photochemistry.

It is perhaps difficult for us today to realize how novel and indeed shocking the postulation of a triplet state was less than thirty years ago. Today the forbiddenness of a transition is a relative term. Forbidden transitions are known to be important and given the right circumstances they may overshadow allowed transitions.

Thus I will unhesitatingly assume that photochemical reactions may occur without passing through free atoms or free radicals and furthermore I will assume that several different excited energy levels, including triplet levels, may be involved before absorbed energy has either been transformed to chemical energy or dissipated to the surroundings as heat and radiation.

Let us first consider a very simple hypothetical energy level diagram in which there is a ground singlet state with its own vibrational levels and two excited electronic levels, one singlet and one triplet, each with its own vibrational levels.

One or two generalizations must be kept in mind. For the same set of principal and other quantum numbers the energy of the triplet state always lies below that of the singlet state. As so often happens when a new concept has been introduced into science scientists heed the clarion call and follow along like the rats after the Pied Piper of Hamelin. Thus

it became stylish to interpret photochemical phenomena by use of the triplet state. Now, perhaps, there has been a reversal and some authors even claim that there is no difference between singlet and triplet states and that they may be used interchangeably.

Neither of these extreme positions is correct and before proceeding further we may list important differences in behavior between singlet and triplet states. We must, of course, remember that the multiplicity of a state will not be the only factor which will determine its behavior.

Table I
Some Properties of Singlet and Triplet States

	Singlet	Triplet
Radiative mean life	Short	Much longer
Formation from ground state by absorption of radiation	Yes	Rarely ¹
Reactivity toward diamagnetic gases	Small	No rule
Abstraction of H atoms	Zero (?)	Yes
Reactivity toward paramagnetic gases	Small	May be large
Dissociation	May be rapid	Often requires activation energy
Absorption spectrum	Difficult	Easy often to observe

¹ Easier when heavy atoms are present in a molecule.

In looking at the facts very roughly assembled in Table I three characteristics of triplet states must be kept firmly in mind: (a) their relatively long mean lives which may give them time to perform reactions denied to singlet states; (b) their relatively low energies which may make them require added activation energy for some reactions; (c) their paramagnetic character which will cause them in some instances to react preferentially with other paramagnetic molecules. A paramagnetic molecule has some of the properties of a free radical.

One other characteristic of triplet states will be that double bonds may acquire certain properties, such as free rotation, normally associated with single bonds. For example an unsaturated hydrocarbon such as cis-butene-2 which normally can not have the two ends twisted in opposite directions about the central carbon-carbon bond may in the triplet state have two unpaired electrons and the central carbon-carbon bond may act temporarily as a single bond when it is in the triplet state. Cis to trans isomerization and vice versa may occur through the pathway of triplet states.

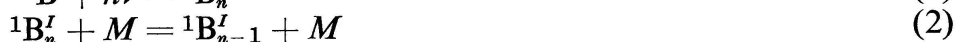
This hasty discussion of the distinction between singlet and triplet states has been given to emphasize that one should whenever possible relate a given type of reaction to a given type of excited state. We will see as we go along how difficult this often proves to be.

The next problem we must consider is that of triplet state formation. First we will present the facts about three different molecules, present our interpretations of these facts and then indicate the kind of information still needed to make the interpretations definite.

The first molecule we mention is biacetyl. Emission from the triplet state of biacetyl lies in the green part of the spectrum. At 25° it has been shown by OKABE to be about sixty times as intense as emission from the singlet state which lies in the blue part of the spectrum.

This ratio is independent of the exciting wave length from 4358 to 3660 Å. From this fact it is possible to conclude that all biacetyl molecules in the first excited singlet state lose vibrational energy before crossing to the triplet state. If crossovers occur at all points on the ladder of vibrational energy levels, the ratio of triplet to singlet state concentrations will be higher the higher the absorbed energy. This is so because the mean radiative lifetime will not vary greatly with vibrational quantum numbers and the higher the initially formed level the longer the time from absorption to emission, on the average.

Perhaps we can make the situation somewhat clearer by stating the mechanism more explicitly. If B represents a biacetyl molecule, $^1B_n^I$, $^1B_{n-1}^I$, ..., etc. biacetyl molecules in the first excited singlet state in the n -th, $(n-1)$ -th, etc. vibration levels, $^1B_0^I$ a biacetyl molecule in the first excited singlet state with vibrational energy equilibrated with the surroundings, 3B a triplet state biacetyl molecule then



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The fluorescent efficiency will be I_f/I_a where I_f is the number of fluorescent photons emitted per unit volume per second and I_a is the number of quanta absorbed per unit volume per second. Then

$$1/Q_f = I_a/I_f = \text{Ratio of } (n)\text{-th degree polynomials in } (M) \quad (12)$$

If all of the steps in this mechanism are important so that none can be neglected a plot of $1/Q_f$ vs. (M) should show an S shaped curve. As the concentration of the colliding molecules M approaches zero $1/Q_f$ vs. (M) will

have a slope k_2/k_3 and an intercept $\frac{(k_3 + k_4)}{k_3}$. In other words the behavior at low pressures will depend on the rate constants of the initially formed excited state. At high pressures steps (2), (5) . . . become rapid and the behavior will depend on the rate constants for the state $^1B_0^f$. The entire plot will approach a horizontal line asymptotically at high pressures with the value

$$\frac{1}{Q_f} = \frac{k_e + \sum k_c}{k_e} \quad (12)$$

where k_e is the rate constant for emission (i.e. $1/k_e$ is the radiative mean life) of the state $^1B_0^f$ and the summation must be carried out for the rate constants of all competing processes. It should be remarked that we have considered the competing processes to be first order because for biacetyl the data indicate this to be the case. It has not been possible to perform experiments at pressures sufficiently low to show any of the processes which compete with fluorescent emission to be second order. Since the value of k_e must be at least to some extent dependent on vibrational quantum numbers, the mean radiative lifetime must be long compared to the time between collisions at the lowest pressure studied. This lowest pressure was about 1 mm and the time between collisions at that pressure is about 10^{-7} sec. The mean lifetime of the excited singlet state of biacetyl as estimated from absorption coefficients is about 5×10^{-6} sec.

The fluorescent emission efficiency of biacetyl is very low, about 0.0025, so that the vast majority of the absorbing molecules undergo some competing first order process. If step (9) (i.e. the crossover $^1B_0^f = ^3B$) is the only first order process which competes with emission from the singlet state then the fraction of the absorbing molecules which pass over to the triplet state is very high, 0.9975. GERALD PORTER and BÄCKSTRÖM and SANDROS have indeed shown that all or nearly all absorbing molecules which do not fluoresce actually become triplet state molecules.

The rate of formation of the triplet state of biacetyl is first order over the pressure range which has been studied. By the same token the rate of disappearance of triplet state molecules is also first order when the colliding molecules are biacetyl, hydrocarbons (including isobutylene), nitrogen and carbon dioxide. And yet the classical work of ALMY and GILLETTE has shown that the fraction of the molecules which emit from the triplet state is only about 0.15 and independent of pressure if the exciting wave lengths are 4358 and 4047 Å. Triplet state biacetyl molecules react rapidly with oxygen molecules which are themselves normally in a triplet state.

At 3660 Å the phosphorescent emission from the triplet state and the fluorescent emission from the singlet state are both pressure dependent. The emission efficiencies increase with increase in pressure. These observations made by HENRIQUES and confirmed by ALMY and his co-workers mean that the vibrational level initially formed at 3660 is sufficiently high to permit dissociation. If vibrational energy is rapidly lost by collision

the molecules may then emit radiation. Since a pressure of 10 to 20 mm will restore emission to the same value as it has at 4047 and 4358 Å, one can estimate the reaction rate constant for dissociation to be of the order of magnitude of 10^7 sec^{-1} . Quite possibly crossover to the triplet state precedes dissociation.

We are confronted, therefore, with a high probability of triplet state formation following absorption by biacetyl. At least 85 percent of the activated molecules either degrade to the ground state or form unrecognized products. It should be noted that the singlet energy level lies about 2.8 eV above the ground state and the triplet state about 2.4 eV above the ground state. The conversion of these amounts of electronic energy either directly into kinetic energy or into vibrational energy is a matter of some concern to theoreticians.

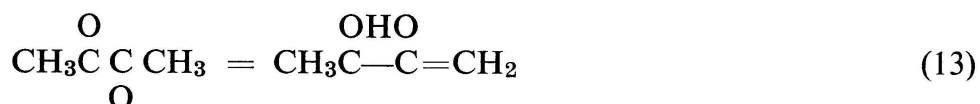
It has often been suggested that polyatomic molecules may be likened to diatomic molecules and within certain limits this must be true. On the other hand diatomic molecules may not undergo unimolecular dissociation for the simple reason that if they possess the requisite amount of vibrational energy it is of necessity in the right mode of vibration to cause dissociation. Possibly one could imagine electronic excitation by thermal collision to a level only very slightly perturbed by a repulsive level so that activation and deactivation by collision could occur. The actual rate would then appear to be first order. Nevertheless for polyatomic molecules with many degrees of vibrational freedom the crossover either to a dissociating state or to another state may have an appreciable time lag. As VICTOR HENRI pointed out in 1924, when one electronic energy level perturbs another the resulting state can not be described in the terms used for either one. The wave function must have contributions from many states but particularly from the two strongly interacting states.

Returning now to biacetyl. The ratio of fluorescence to phosphorescence may be constant because the rate of dissociation of the triplet state is very rapid when it possesses even a little vibration energy. If it dissociates rapidly when formed at 3660 Å and does not dissociate at room temperature when formed at 4047 Å the amount of vibrational energy would be in one case about 0.9 eV and in the other about 0.6 eV. The energy which must be lost for stability is small. The interval over which a stable triplet state molecule may be formed from the singlet state at low pressures is small, only about 0.3 eV. Triplet state molecules radiate so slowly, the mean life is about 10^{-3} sec as observed both by ALMY and GILLETTE and by DUNCAN and KASKAN, that loss of vibrational energy by collision may always occur.

In biacetyl we are faced with two crossovers: first the crossover from the excited singlet to the triplet state. This seems to occur with almost perfect efficiency and with a rate constant of about 10^5 to 10^6 sec^{-1} , nearly independent of temperature since the fluorescence efficiency is essentially independent of temperature. Second, crossover from the triplet to the ground state. At room temperature only 15 percent of the molecules emit and this percentage decreases rapidly with increase in temperature. One

of the processes which destroys the triplet state must have an activation energy of about 15 kcal, 0.6 to 0.7 eV. Logically one of these competing processes must be a dissociation into radicals since decomposition increases rapidly with increase in temperature. Since at 4358 Å dissociation is negligible at room temperature there must be other competing processes. A possibility is a crossover from the triplet state to a high vibration level of the ground state. We know too little about the configuration of the triplet state to predict what modes of vibration would be preferentially excited in the ground state by the operation of the Franck-Condon principle. However, in the triplet state the double bond character of the central carbon-carbon bond is certainly less than in the ground state and one would expect, therefore, more cis form to be present than in the ground state. As suggested by Dr. LEMAIRE a cis form might be stabilized by enolization since a hydrogen bond could be formed between the two oxygen atoms. Evidence for this has been found. The enol form for some cyclic diketones is known to be quite stable.

At present it is impossible to give a precise estimate of the energy required for the reaction



but it must be endothermic. To the extent that (13) is endothermic the amount of electronic energy which must be dissipated immediately as kinetic and vibrational energy can be reduced. The enol form could rearrange to normal biacetyl at its leisure on the walls.

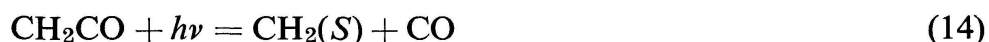
The fact that only 15 percent of the triplet state molecules radiate and the others do not, provides food for thought. Perhaps enough will be known in the future to permit a calculation from quantum mechanics of transition probabilities from geometrical factors. Certainly not enough is known today to give a complete wave function for the biacetyl molecule in the triplet state.

The second molecule we will mention is ketene. This molecule has served for many years as a source of methylene radicals. The behavior of these radicals has been the subject of investigations by KISTIAKOWSKY, by RABINOVITCH, by FREY and others and their absorption spectra have been identified and analyzed by the beautiful work of Dr. HERZBERG.

The methylene radical is isoelectronic with the NH radical and with oxygen atoms and it should exist in both singlet and triplet states. The state of lowest energy would be expected to be the triplet state. The lowest singlet state would lie a few tenths of an electron volt above the ground state. While experimental conditions can be found which produce almost exclusively singlet methylenes, no author, as far as we are aware, has found triplet methylenes to be completely absent. Singlet methylenes must be converted to triplet methylenes by collisions and not much is known about this step at present. We will return to this point later.

Triplet methylenes can be formed exclusively as shown by CVETANOVIC, by HAMMOND, by BELL, by FREY and others. Thus the reactions of singlet as distinguished from triplet methylenes are reasonably well identified although recently RABINOVITCH has given indications that no single reaction is found exclusively for either form. B. S. RABINOVITCH was the first to show clearly that both singlet and triplet methylenes are present during photolysis of ketene.

The primary dissociation of ketene has been known for many years to be



Since the yield of carbon monoxide is about two in pure ketene at 2500–2900 Å the methylene radicals must react with ketene



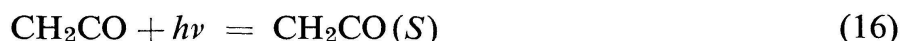
The ratio of carbon monoxide to ethylene is 2.2:1 rather than 2:1, so steps (14) and (15) do not give the complete picture.

STRACHAN showed some years ago that the kinetics of ketene decomposition are quite different at about 2700 Å from what they are at 3660 Å. At the former wave length the yield of two molecules of carbon monoxide per quantum absorbed is essentially independent of pressure and up to about 100° also of temperature.

At long wave lengths the carbon monoxide yield is very dependent both on temperature and on pressure. At constant temperature a plot of the reciprocal of the carbon monoxide yield against the pressure gives a straight line but both the slope and the intercept vary with the temperature.

Neither fluorescence nor phosphorescence of ketene has been reported at any incident wave length. The independence of yield of pressure at 2700 Å strongly suggests either predissociation or an immediately dissociating upper state. If this is true the application of the Wigner Spin Conservation Rule would indicate that the methylenes formed by (14) should be singlet.

To a kineticist the behavior at 3660 Å strongly suggests a series of steps which must include deactivation of an excited molecule by collision



The symbol (S) denotes a singlet state. From this mechanism one finds

$$1/\Phi_{\text{co}} = (k_{18} + k_{20})/2k_{18} + k_{17}(M)/2k_{18} \quad (21)$$

Reaction (20) must be included because without it the intercept would be $\frac{1}{2}$ at zero pressure. This is not true at any temperature although the intercept decreases markedly with increase in temperature. Equation (21)

formally fits the facts but in kinetics agreement between data and a derived equation is never conclusive proof that the mechanism upon which the derivation is based is correct.

Since we are interested in singlet and triplet states of methylene let us now add three more steps to the mechanism. First



where the symbol (*T*) designates a triplet state.

Reactions of methylenes with olefins have been used to determine whether or not the methylenes are in singlet or in triplet states. We do not wish here to examine this question in detail but accept the original proposal of SKELL embodied in the following equations for trans-2-butene



By the introduction of trans-2-butene we now have at least two molecules, viz. ketene and the butene, which may play the roles of *M* in the various steps in the mechanism. Specific effects dependent on the nature of the colliding partner are known to exist for many reactions including loss of vibrational energy and energy transfer in general. When (23) and (24) occur the methylenes are removed from the system and the ethylene yield should decrease. This does in fact occur. Information about the reaction



is meager and not very reliable.

Let us assume first that (23) is very rapid and the mole fraction of the butene is high. Then (22) would be suppressed, as would (19) and the products would be stereospecific. If (18) is the sole reaction which introduces methylene radicals into the system no triplet state radicals would be detected by (24). Such data as exist in the literature are in reasonably good agreement that at wave lengths around 2700 Å the fraction of radicals in the singlet state is high, perhaps 90 percent, although evidence for triplet methylenes is always found. We are forced to conclude that trans-2-butene promotes (22) and reacts by (23). Since the pressure of the butene affects very little the apparent fraction of triplet state one may conclude that the ratio k_{23}/k_{22} is about 9:1. The alternative explanation that there is some stereospecificity to (24) may not be ignored.

The fraction of apparent triplet methylenes is wave length dependent and at 3650 Å 60 to 80 percent seem to be triplet. We ignore the reverse of (22). It must have an activation energy but its value is not at present known.

Carbonyl compounds may exist either in singlet or in triplet excited states and as indicated for biacetyl the triplet state yield may be very high. Let us amplify the ketene mechanism in this respect



The part played by collisions for these three reactions will be discussed briefly in a later paragraph. For many molecules (17) is not important and we will ignore it.

The rate expressions which result from this relatively complex mechanism are difficult to test. We will make only a few statements about the situation. If (26) and (18) are both first order and k_{27}/k_{28} is independent of pressure the dependence of carbon monoxide yield on pressure would be due solely to the effect on (22), i.e. on the rate of transfer of $\text{CH}_2(S)$ to $\text{CH}_2(T)$. This would be most improbable and indeed could hardly agree with the observed change with pressure. Reaction (28) is almost certainly pressure dependent. If $\text{CH}_2\text{CO}(T)$ is formed with considerable vibrational energy, the loss of such energy by collision will in fact favor (28).

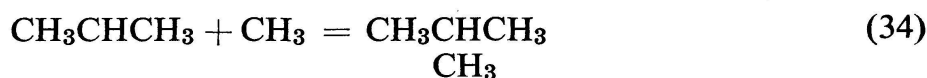
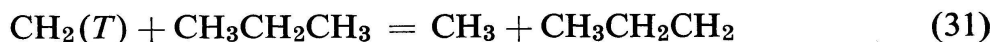
The ratio of triplet to singlet generally increases with pressure. Thus the activated singlet molecules, $\text{CH}_2\text{CO}(S)$, must have long enough mean lifetimes to be capable of loss of vibrational energy before they dissociate provided they are formed at 3650 Å and probably also at 3130 Å.

Mr. Ho has recently made an extensive study of the ketene-propane system. The reactions of singlet methylene with propane should be



If each carbon-hydrogen bond were equally effective in being penetrated by a singlet methylene radical the ratio of (29) to (30) would be 3:1. Actually there are probably steric reasons why all bonds would not be equally effective and the highest ratio obtained was less than 3:1.

Triplet methylenes, on the other hand, will be expected to abstract hydrogen atoms from propane and the butanes will be formed by radical-radical reactions



The activation energy to remove the hydrogens from the central carbon is much lower than for the other 6 so that the rate of (32) is always greater than the rate of (31). The ratio of *n*-butane to isobutane will be expected,

therefore, to be less than unity, just the reverse from the situation for singlet methylene insertion. Table II shows a brief summary of some of Mr. Ho's results.

Table II
Effect of Wave Length on *n*-Butane to Isobutane Ratio in the Ketene-Propane System

Wave Length	Pressure (mm)	Temperature	Ketene/Propane	<i>n</i> -C ₄ H ₁₀ /iso-C ₄ H ₁₀
2400-2850	72	27°	0.200	1.89
	196			1.83
	104		0.100	1.93 ¹
	200			1.98
	200			1.89 ¹
	6	51°	0.200	2.66
	5.5	94°		2.74
	262 ²	27°	0.200	1.68
	590 ²			1.46
3460-3900	59	27°	0.100	0.38
	86		0.091	0.39
	204		0.100	0.38

¹ Light intensity 0.20 and 0.17 respectively of that in other runs.

² 233 mm and 540 mm respectively of CF₄ added.

In addition to the very striking difference in the normal to isobutane ratio at the two wave lengths it should be noted that the addition of large amounts of the neutral gas tetrafluoromethane also cause a marked decrease in the ratio. This certainly means that collisions promote (22), the crossover of singlet to triplet methylenes. Finally it should also be noted that triplet methylenes do abstract hydrogens from propane and that this step has an activation energy since it is more important at high temperatures than at low. Abstraction of hydrogen by molecules in triplet states seems to be a universal phenomenon (see table I).

The case of ketene has been discussed because it is a good example both of the difficulty of disentangling a complicated situation and because in all probability the following conclusions are justified:

(a) At short wave lengths of about 2600 ± 200 Å ketene absorbs and dissociates rapidly to give entirely singlet methylene radicals.

(b) Singlet methylene radicals do cross over to become triplet methylene radicals and the methods of detection of these two forms are not reliable in the sense that they promote the conversion of 10 to 15 percent of singlet methylenes to the triplet state.

(c) At wave lengths around 3650 Å CH₂CO(*S*) will dissociate to give singlet methylenes unless it loses vibrational energy after which it crosses over to form triplet ketene molecules.

(d) The predominance of triplet methylenes at 3650 Å is due to dissociation of triplet ketene molecules.

A completely unique mechanism can not be written and proven at the present time but we feel that good evidence exists for all four of these conclusions.

The third molecule we wish to discuss before we pass on to further generalizations is the benzene molecule. We must state in advance that the data for this molecule are far from complete, partly because they are difficult to obtain.

The benzene molecule absorbs at wave lengths below about 2650 Å and the transition is forbidden for symmetry reasons. Thus the initially formed excited singlet molecule must have an odd number of quanta of an unsymmetrical mode of vibration.

Fluorescence from benzene vapor has long been known. At low pressures resonance fluorescence is observed, that is emission occurs from the initially formed vibration level of the upper singlet state. When pressures of 10 to 20 mm are reached, emission always occurs from low vibrational levels in which the vibrational energy is equilibrated with the surroundings. Since the 0,0 band is forbidden for symmetry reasons absorption and emission do not overlap at pressures over 20 mm.

At very low temperatures, 4 °K and 77 °K, there is not only fluorescence from the singlet state but phosphorescence from the triplet state, and Professor GEORGE PORTER has recently succeeded in photographing the absorption spectrum of triplet benzene at these low temperatures. Moreover LEACH and his co-workers at Orsay have shown that at these very low temperatures in a glassy matrix the benzene molecule opens up and reacts with added molecules such as methanol. Thus the hexatriene adds CH₃ at one end and OH at the other.

There is a slight reaction photochemically between benzene and oxygen in the gas phase to give a peroxide and STEIN and his co-workers in Israel have shown that in liquid benzene there is a reaction both photochemically and with gamma rays with oxygen to give a dialdehyde by addition of the two oxygen atoms from one molecule of O₂ to ortho positions and opening the ring.

Thus there has existed for some time evidence for a triplet state of benzene, particularly at very low temperatures, but until recently no conclusive evidence had been put forward for a triplet state in the gas phase. At very low temperatures the mean life of triplet benzene is very long, about 30 sec, and a triplet state with such a life would be easy to detect in the gas phase if it is formed with an appreciable quantum yield.

The photochemistry of benzene has often been investigated, sometimes with conflicting results. In the Schumann region below about 1700 Å a solid of the appearance of cuprene is formed. Since it deposits on the window precise photochemical work on its formation is meager. Very small amounts of hydrogen are formed concurrently.

Fulvene has been reported as a photochemical product under some experimental conditions. However, the most beautiful work has been done

by WILZBACH, KAPLAN and YANG. The work has been done mainly with benzene derivatives such as 1,3,5,triisobutylbenzene, but the reactions have been shown to occur also with pure benzene. There is isomerization, for example, to the 1,2,4,triisobutylbenzene and to 1,2,3,triisobutylbenzene but the striking fact is also noted that the carbon atoms in the ring to which the isobutyl groups are attached also change position. The reaction is not a free radical reaction and must occur, as these authors indicate, by the formation of isomers which revert to benzene derivatives usually photochemically. These isomers have sometimes been proposed in the last century before KEKULÉ as possible structures of benzene. The Dewar form, prismane, and benzvalene have all been identified. It is true that most of the work has been done in the liquid phase, either in pure benzene or in hydrocarbon solution, but Drs. WILZBACH and KAPLAN have found that similar processes take place in the gas phase.

Thus benzene confronts us with a complex situation and much of what has been said about the behavior of excited states needs to be regarded with skepticism. We will give a brief summary of some of our recent results and indicate the conclusions which have been drawn. We do ask that you receive them in the spirit in which they are offered. We hope that they will stimulate thought on these to us interesting problems.

The identification of the triplet state of benzene in the gas phase has been accomplished by two methods. CUNDALL has sensitized at 2537 Å the isomerization of cis-2-butene by means of benzene. This work at 2537 Å indicated that approximately 0.63 of the absorbing molecules have crossed to the triplet state. ISHIKAWA has shown that benzene preferentially excites biacetyl to a triplet emission. The fluorescence yield in the gas phase has been determined by ISHIKAWA, by POOLE and by others. It may be stated as about 0.18 ± 0.04 at ordinary pressures of a few centimeters and probably is independent of pressure. Thus the fluorescent yield and the triplet state yields add to 0.83 but the uncertainty is such that this may well be unity. There is a marked decrease in the fluorescent and triplet state yields below about 2530 Å and both seem to have become zero by 2417 Å. Perdeuterobenzene shows a higher fluorescent yield than does light benzene.

PARMENTER and KISTIAKOWSKY studied the fluorescent yield to quite low pressures. As the pressure was lowered emission yield increased and then became constant. They accepted ISHIKAWA's yields and found that at the lowest pressure they studied (about 0.03 mm) the fluorescent yield did not exceed about 0.35. On the basis of the conclusion that fluorescent and triplet state yields add to unity PARMENTER and KISTIAKOWSKY concluded that crossover to the triplet state has a rate not dependent on collisions. In this respect their data disagree with work by SIGAL which indicates that the triplet state yield for C_6D_6 , as determined by a modified Cundall technique, is still pressure dependent at the lowest pressure he studied. Their observed variation of fluorescent yield with pressure is hard to understand, although possibly the yield of resonance fluorescence is higher from high than from low vibrational levels. If that conclusion is

accepted it is difficult to understand the chemical observations and the fact that C_6D_6 emits with a higher efficiency than C_6H_6 .

We have accordingly observed the fluorescent yield and also the triplet state yields by the Cundall technique at several wave lengths from 2400 Å to 2660 Å. A grating monochromator was used and for the fluorescence the range of incident wave lengths covered for each measurement was 5 to 10 Å. The sensitivity of the Cundall method is such that the range had to be 30 to 50 Å.

The results are in general agreement with CUNDALL's but do show some trend toward higher triplet state yields with increase in wave length. The fluorescence decreases rapidly below about 2530 Å but at longer wave lengths there are peculiar fluctuations which may not be real but possibly indicate a yield markedly dependent on the initially formed vibrational level.

For benzene, therefore, the data are incomplete and the situation is far from satisfactory. Let us summarize a few of the facts, indicating uncertainties to the best of our ability, and then indicate what we believe to be some of the information needed to permit an improvement.

(a) The fluorescent efficiency in the vapor phase is about 0.18 ± 0.04 and independent of pressure within experimental error from about 20 to 90 mm. The efficiency decreases below 2530 Å.

(b) Triplet state yields by two different methods agree within a large limit of error. Perhaps the best one can say for wave lengths 2530 to 2668 Å is that the triplet state yield is 0.70 ± 0.15 with a trend toward lower values at shorter wave lengths.

(c) Both triplet state yields and fluorescent yields are essentially zero at 2417 Å.

(d) Perdeuterobenzene has a higher emission efficiency than benzene.

(e) Since triplet state yields have not been measured at low pressures except for SIGAL's work on C_6D_6 by the modified Cundall technique it is best to reserve judgement about facts at low pressures.

(f) Some process or processes other than emission and triplet state formation compete successfully with relaxation of vibrational energy at pressures up to 100 mm at 2417 Å and possibly at longer wave lengths.

The important lessons to be learned from this state of confusion seem to be the following:

(1) Photochemists should use monochromatic light, preferably sufficiently monochromatic to excite initially only a single vibrational level of the upper state. Color filters will almost never be adequate for this purpose. The isomerization of benzene might, for example, have a wave length dependence even in the liquid phase. If this is true isomerization is a very rapid process and must take place after a very few vibrations. Otherwise loss of vibrational energy due to collision would remove any effect of wave length.

(2) Absolute fluorescent efficiencies have rarely been determined and agreement between various authors is seldom good. It is very important that attention be given to this matter so that absolute values good to

within 1 or 2 percent can be obtained. Relative values are easier to obtain than absolute ones. A few reliable standards would be of great value.

(3) Improved methods of quantitatively determining triplet states would be very important. The best method is that of flash photolysis as employed by Professor GEORGE PORTER and his co-workers but sometimes it is not applicable, due either to the short mean life of the triplet state or because absorption lies in an inaccessible region of the spectrum. Failure to find a triplet state by this method is insufficient guarantee of its absence. Chemical methods such as isomerization of *cis*-2-butene must always be regarded with some suspicion because of the possibilities of compound formation. WILZBACH, KAPLAN, and YANG have shown, for example, that benzene in one of its photochemically formed isomers does add to the 2-butenes. We have evidence of a small amount of this reaction even in the gas phase. In principle triplet states could be determined by electron spin resonance but rarely are concentrations sufficient for this purpose. When one is fortunate enough, as with biacetyl, to have a readily observable emission from the triplet state the problem is greatly simplified. To say the least much additional work on the quantitative determination of triplet state yields is needed.

We thus leave the discussion of these three molecules: biacetyl, ketene, benzene. These are chemically very different types of molecules. They are all molecules upon which we have worked at one time or another and on two of them work is still in progress. Often our results and our ideas are in disagreement with the results and ideas of others. This always makes work interesting even though sleepless nights and feelings of frustration seem to be the chief rewards.

Photochemistry has changed a great deal in the past twenty years. Rearrangements, cyclizations, additions as well as atom and radical reactions often can be induced by light. Many of these reactions do not take place by the use of the more traditional methods of organic and inorganic chemistry. The organic chemist in particular is now able to use photochemistry as a synthetic method.

However, photochemistry is like other branches of chemistry. The mere accumulation of facts is interesting but soon the facts become so numerous that their storage and retrieval become the bottleneck for their use by the profession. A basic understanding which leads to principles and which therefore permits a rational correlation of the factual material is necessary for progress. Much of photochemistry is in a state of confusion but improvements are just beginning to be visible over the horizon. The basic principles will, we hope, be clarified in the years to come.

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Finally I have decided not to provide a detailed bibliography. The excellent new book on Photochemistry by Professor J. CALVERT and Professor J. N. PITTS has brought references to the literature up to 1965. I have endeavored to mention names in the text when appropriate. If there is a feeling that there are serious omissions and that some photochemists feel slighted I can only express my regret. Some of our own work has not been published but will appear in detail in the near future.