THE PRIMARY PHOTOCHEMICAL PROCESS IN SIMPLE KETONES[1]

W. ALBERT NOYES, JR., GERALD B. PORTER,[2] AND J. ERIC JOLLEY[3]

Department of Chemistry, University of Rochester, Rochester, New York

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I. Introduction

The primary photochemical process comprises the series of events beginning with the absorption of a photon by a molecule and ending either with the disappearance of that molecule or with its conversion to a state such that its reactivity is statistically no greater than that of similar molecules in thermal equilibrium with their surroundings. There may exist several different paths for loss of the absorbed energy and not all of these may result either in dissociation or in conversion of the absorbing molecule to a new molecular species. The complete elucidation of a primary photochemical process must include an understanding of all that transpires, whether or not a chemical reaction occurs.

The primary photochemical quantum yield is the number of absorbing molecules which either dissociate or react per photon absorbed. If the absorbing species is re-formed in any way by subsequent reactions, the primary quantum yield is not thereby reduced. The primary quantum yield may not exceed unity and it may be zero if, for example, all absorbing molecules fluoresce without reacting.

The energy of the photons absorbed during a photochemical reaction must appear in one or more of the following forms: (1) fluorescence and phosphorescence; (2) thermal energy, which results either in a temperature rise of the absorbing system or in heat loss to the surroundings; (3) chemical energy, i.e., certain molecular species will disappear and new ones will be formed. In the general case one must assume that the absorbed energy will not appear uniquely in any one of these ways.

In principle one may measure the energy absorbed during a photochemical reaction. This may not be easy to accomplish with high accuracy, particularly if the radiation is not monochromatic. The precise measurement of the energy emitted as fluorescence and phosphorescence is far more difficult, since it is almost always diffuse (i.e., emitted in all directions) and since it is not usually monochromatic unless one is dealing with a monatomic gas. Nevertheless the measurement of absorbed and emitted radiation may be accomplished if enough care is exercised.

The measurement or estimation of the final two quantities necessary to achieve an energy balance is far more difficult, particularly if attention is directed solely to the primary process. The absorbing molecules may be re-formed by reactions such as radical combinations, which may follow the primary process. Thus it is often very difficult to determine precisely the number of molecules which dissociate during the primary process. Any temperature rise or loss of heat to the surroundings may be due in part to secondary reactions which follow the primary process. If all reaction products have been determined quantitatively and the heats of formation of the reactants and of the products are known, one may calculate the heat evolved or absorbed due to chemical reaction. This will permit a calculation of energy lost to the surroundings if absorption and emission of radiation are known, but it does not permit a calculation to be made of the number of molecules which dissociate or react during the primary process.

The main difficulties in treating the photochemical primary process quanti-

tatively lie in the determination of the nature of the process and of its magnitude. The photochemistry, the fluorescence, and the absorption spectra of certain simple ketones, notably acetone, biacetyl, and diethyl ketone, have been extensively studied. These molecules present an interesting possibility for discussion of the primary photochemical process, although it will be shown that there are certain gaps in our knowledge, some of which can and should be filled.

II. GENERAL ASPECTS OF PHOTOCHEMICAL PRIMARY PROCESSES

The photochemist should as a minimum determine two things about the primary process: (1) the nature of the chemically active species produced by the absorption of radiation, i.e., whether they are free atoms or free radicals or activated molecules which react without dissociation (usually, but not always, photochemical reactions are started by the formation of free atoms or free radicals); (2) the magnitude of the primary process. More precisely one needs to know the number of free atoms, free radicals, or chemically activated molecules introduced into the system per photon absorbed.

The first of these problems may be approached in a variety of ways and the following types of information will be useful:

(1) The nature of the reaction products. Frequently these can only be formed if the initial dissociation follows a certain pattern.

(2) The strength of the various bonds in the absorbing molecules. It may happen that the absorbed energy will be insufficient to cause certain modes of dissociation and the possibilities may be strictly limited.

(3) The products formed when foreign molecules are present to act as scavengers. Common scavengers are iodine, nitric oxide, unsaturated hydrocarbons, and oxygen. Care must be exercised that the added molecules do not affect the primary process, either by deactivating excited molecules or by reacting with active molecules which might otherwise suffer a different fate.

The second problem, that of determining the magnitude of the primary process, is a very serious one and herein lies the main difficulty in dealing with the primary process. If a chain reaction is initiated by the primary process, there is no way of calculating the magnitude of the primary process unless the chain happens to be terminated uniquely by formation of a molecule formed in no other way. It is obvious that there must be removed from the system by some chain-terminating step two atoms or radicals if two are formed for each molecule which disappears in the primary process. A measurement of the rate of this radical–radical reaction will, therefore, give a measurement of the rate of the primary process unless there are chain-branching steps. This method cannot often be used, because almost invariably either the parent molecule is re-formed or some molecule is formed which is also formed by other reactions.

Nevertheless there are cases for which the magnitude of the primary yield per photon can be determined. These cases may be classified in two ways which are not mutually exclusive: (1) The absorption spectrum is truly continuous so that dissociation must result from the absorption of every photon. This method is

least ambiguous for simple molecules, particularly diatomic molecules, for which the distinction between discrete and continuous absorption can be definitely established. (2) The complete reaction mechanism has been firmly established and particularly the rate constants for all individual steps are known. This ideal situation is not often encountered but in a few instances it is approximated so that one may, from the yields of reaction products, make a good estimate of the primary quantum yield.

We may now turn to a discussion of the methods available for studying the primary process.

A. THE INTERPRETATION OF ABSORPTION SPECTRA

It would not be appropriate at this time to give an extensive review of spectroscopy. The discussion will be limited to points germane to the present subject.

Absorption spectra of gases may vary between two extremes. At one extreme absorption is truly continuous, the absorption coefficients change gradually with wavelength, and there is usually only one maximum whose wavelength may be dependent on temperature. At the other extreme absorption is truly discrete and bands often with well-defined heads can be observed. With sufficient resolution definite structure within each band can be seen.

For diatomic molecules and with equipment presently available the distinction between these extreme cases can easily be demonstrated in the laboratory. Examples of the first case are found in hydrogen iodide (13, 57), hydrogen bromide (112, 117), and the three halogens chlorine, bromine, and iodine below their convergence limits (about 5000 Å.) (86). Examples of the second case are found in the atmospheric absorption bands of oxygen (34, 86), several band systems of nitric oxide (34, 86), and in the halogens at wavelengths longer than their convergence limits (86).

The interpretation of these extreme cases from the standpoint of the photochemical primary process was first given by Franck (30). A continuous absorption implies direct dissociation before the molecule in the upper electronic state has time to rotate or vibrate. Thus the quantum yield of the photochemical primary process is unity. For a diatomic molecule dissociation into two atoms occurs, although these atoms may not be produced in the same electronic state and they will have kinetic energies dependent on wavelength (45).

A truly discrete absorption implies that the molecule in the upper state lasts long enough after it acquires energy from the radiation to execute rotations and vibrations. It may ultimately dissociate or react with some other molecule, but there must be a sufficient time interval after absorption to permit unperturbed rotations and vibrations. If photochemical action occurs after this kind of absorption, it is impossible to state from the character of the absorption spectrum just what the primary photochemical quantum yield really is. Usually the primary yield is very low or even zero for a truly discrete absorption and one expects to find accompanying fluorescent emission.

Between these extremes one finds all gradations from true "discreteness" to true continua, and the appearance of the spectrum of a given molecule may vary

considerably with pressure and with temperature. In a general way fuzziness in the spectrum indicates either dissociation or a perturbation such that the upper state formed by absorption may not be described in simple terms (42). Several things may happen to such molecules after absorption, and precise prediction of the primary photochemical yield is not possible. Indeed, photochemistry may aid the spectroscopist at this point in the interpretation of the data.

The difficulties in the interpretation of absorption spectra of polyatomic molecules are very great. Even for a molecule as simple as that of formaldehyde large dispersion, high resolution, and great care are necessary to obtain discrete lines in the absorption spectrum (20, 24). For highly symmetrical molecules such as benzene (24, 101, 103) and pyridine (102, 104) the interpretation of the spectrum is quite definite, although resolution of the lines within each band has not been achieved. The molecules under consideration in the present review do not have high symmetry and, although quite discrete bands may be observed below 2000 Å. (16, 22, 23, 82, 94, 95), their interpretation in terms of a photochemical primary process is not possible.

Even for a relatively simple molecule such as that of acetone one can show that rotation lines within a given band will not be separated by more than 0.02 or 0.03 Å. Natural half-widths and Doppler broadening make resolution of lines with this separation impossible. Since the simple ketones have many low vibration frequencies, one will expect to find complex absorption spectra which can be interpreted only with considerable difficulty. Crone and Norrish (16) were the first to find some evidence for discrete structure in the near ultraviolet spectrum of acetone and this has been confirmed (14, 79, 82). There is also some observable structure in the fluorescence of pure acetone vapor (61). Nevertheless a detailed interpretation of these spectra has not been possible. Similar difficulties arise with biacetyl (2,3-butanedione), although in this instance considerable progress has been made in understanding the spectrum (99, 100). Structure has not been reported in the near ultraviolet spectra of either ethyl methyl ketone (2-butanone) or diethyl ketone (3-pentanone). Fluorescence studies do indicate that unresolved structure must be present in these absorption spectra (69).

One will expect to find maxima and minima in the absorption coefficients as a function of wavelength, but for the molecules under consideration the degree of fuzziness may not be estimated from the appearance of the spectrum. In general, the spectrum will give no real clue as to the magnitude of the photochemical primary process. Statements in the literature to the effect that certain spectra indicate dissociation to begin at definite wavelengths must, for these molecules, be regarded as unfounded.

### B. THE RELATIONSHIP OF ABSORPTION TO FLUORESCENCE

The existence of fluorescence definitely ascribable to the absorbing molecules and not to some dissociation product or impurity is *prima facie* evidence that the primary photochemical yield is not unity. One may not assume, however, that absorbing molecules only fluoresce and dissociate, since there are other processes which may dissipate energy.

For the reasons given in the preceding section one must assume that absorption of radiation even from a so-called monochromatic source by many polyatomic molecules will lead to formation of molecules in more than one rotation-vibration level of one or more upper electronic states. Thus "resonance" emission (i.e., solely from the states formed by absorption) may appear to be complex. This statement is particularly true if light sources such as high-pressure mercury arcs with broad emission lines are used. These sources are common, since low-pressure arcs with sharp emission lines often give intensities too low for photochemical use.

Let us assume that the molecules prior to absorption are distributed among a series of levels X_0, X_1, X_2 . . ., where X_0 is the lowest level. The distribution at thermal equilibrium will follow the Boltzmann distribution law, so that if the levels are close together, many will be populated. Let the levels of the upper electronic state or states be represented by Y_0, Y_1, Y_2 . . ., where again Y_0 is the lowest level. Selection rules may operate to prevent optical transitions between certain pairs of levels, but let us neglect this point for the present discussion.

If the molecules are exposed to a source of continuous radiation, the absorption spectrum will show transitions as follows:

$$X_0 \rightarrow Y_0, Y_1, Y_2 \ldots; \quad X_1 \rightarrow Y_0, Y_1, Y_2 \ldots; \quad X_2 \rightarrow Y_0, Y_1, Y_2 \ldots \text{ etc.}$$
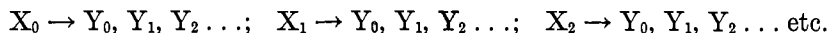
where the magnitude of the absorption will depend on several factors such as the populations of the levels X_0, X_1, X_2 . . . and a transition probability for each pair of levels. The observable long wave limit of absorption will usually be vague. The practical long wave limit will be found for some transition $X_n \rightarrow Y_0$ such that the population of the level X_n multiplied by the proper transition probability will make absorption barely observable. By interposing more molecules in the light beam, either by increasing the pressure or by increasing the path length, it should be possible to extend this limit to longer wavelengths.

At ordinary temperatures the populations of the levels decrease quite rapidly as the energy increases. For example, a level which lies only 2.7 kcal. per mole above the lowest level will be populated by only about 1 per cent of the molecules at room temperature. Thus the main transitions in absorption will occur from the lower X levels.

Absorption of monochromatic radiation may favor transitions from only certain ground-state levels, although for practical purposes absorption will be so weak from high levels that photochemical effects would be small. By absorption of approximately monochromatic radiation, molecules will be produced in a series of upper levels which we will assume to be centered around the Y_n'th level. The shorter the wavelength of the absorbed radiation, the higher the average energy level in the upper state will be.

If the pressure is very low, these upper-state molecules may do one of three things: (1) fluoresce, (2) dissociate, or (3) undergo "internal conversion" (31, 32). The meaning of the latter process is not entirely clear. Presumably the energy may be redistributed within the molecule in such a way that neither dissociation nor fluorescence is rapid. Such a redistribution must be reversible and sooner or

later the energy will be lost by collision, by fluorescence, or by dissociation. If the reverse process is sufficiently slow, internal conversion may effectively lead to degradation of the absorbed energy to thermal energy.

At these low pressures we may write the steady-state condition

$$I_a(n) = (k_2 + k_3 + k_4)(Y_n) \qquad (1)$$

where $I_a(n)$ is the number of photons absorbed per milliliter per second which produce molecules around the Y_n'th level, (Y_n) is the concentration of molecules around the n'th level, k_2 is the first-order rate constant for the process

$$Y_n = X_m + h\nu \qquad (2)$$

k_3 is the rate constant for the process

$$Y_n = D \qquad (3)$$

where D represents dissociation products, and k_4 is the rate constant for internal conversion.

$$Y_n = X_m \qquad (4)$$

X_m represents a molecule (in the normal or at least a lower electronic state) which is incapable of either fluorescence or dissociation. It may or may not be necessary to introduce the colliding molecule M into the rate expression, depending on the detailed nature of the process. Thus the mean life of molecules in the Y_n'th state will be $1/(k_2 + k_3 + k_4)$ and the fluorescence efficiency will be $k_2/(k_2 + k_3 + k_4)$. It should be noted that the sum of the fluorescence efficiency and of the efficiency of the photochemical primary process will not be unity if there is such a process as internal conversion.

The fluorescence observed under these conditions will be resonance fluorescence, that is, the optical transitions giving rise to fluorescence will start from the levels formed by the absorption of radiation. Available data show that resonance fluorescence is not often observed and then only if the pressure is quite low, i.e., less than a few millimeters.

Collisions must under most experimental conditions prevent molecules from staying in the Y_n'th state long enough to fluoresce.

C. POSSIBLE STEPS IN THE PRIMARY PHOTOCHEMICAL PROCESS

A detailed statistical treatment of all of the various collision processes would be difficult; in very few cases are enough data available to make such a treatment useful. One fact, however, is important: the wavelength distribution of fluorescent radiation is nearly always independent of the wavelength of the exciting radiation. This must mean that collisions effectively reduce the energies of the Y molecules to some distribution dependent only on the temperature, i.e., they are reduced to levels not much removed from Y_0 unless a new electronic state is produced which is neither X nor Y.

A detailed analysis of the situation will not be attempted, however. The pos-

sible effects of collisions will be listed and an approximate treatment of the problem will be given.

(1) Loss of vibration energy:

$$M + Y_n = Y_0 + M; \quad -d(Y_n)/dt = k_5(Y_n)(M) \tag{5}$$

(2) Dissociation:

$$M + Y_n = D + M; \quad -d(Y_n)/dt = k_6(Y_n)(M) \tag{6}$$
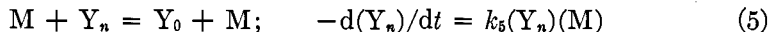
This type of dissociation induced by collisions is known to occur in the case of iodine (113).

(3) Deactivation:

$$M + Y_n = M + X; \quad -d(Y_n)/dt = k_7(Y_n)(M) \tag{7}$$

(4) Transfer to another electronic state:

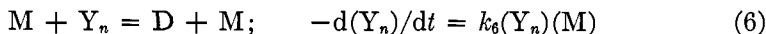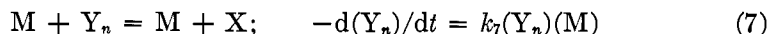$$M + Y_n = M + Z_m; \quad -d(Y_n)/dt = k_8(Y_n)(M) \tag{8}$$

If the energy difference between the Y states and the Z states is not large, this process may be reversible.

Processes 5 and 8 need further examination. Loss of vibrational energy must occur in a stepwise fashion, thus giving rise to a series of states each one of which will have its own rate constants for dissociation, for fluorescence, for internal conversion, for energy loss on collision, and for transfer to other electronic states. Thus for each of the intermediate states there may be several first-order and several second-order steps which compete with one another. If there are n different states (which may or may not be part of the same electronic state), the expression for the quantum yield of the primary process involves a term in $(X)^n$ divided by an $(n - 1)$'th degree polynomial in (X), where (X) is the concentration of ground-state molecules and it is assumed that no foreign gases are present (46). Several cases may now be visualized:

(1) The first state formed dissociates or disappears otherwise so rapidly that this is the only one which needs to be considered. Under these conditions the primary quantum yield will be given approximately by

$$1/\phi = a + b(X) \tag{9}$$

where ϕ is the primary quantum yield for dissociation, $1/a$ is the fraction of the first-order processes which lead to dissociation, and $1/b$ is the ratio of the first-order constant for dissociation to the second-order constant for reactions leading to the disappearance of Y_n.

This case may be expected either when Y_n is not far removed from Y_0 (i.e., there is little vibration energy in the upper state) or when the sum of the primary quantum yield and the fluorescence quantum yield is close to unity. A rapid rate of internal conversion might give rise to this case if the molecules formed are essentially stable.

Generally speaking, this case will show very weak fluorescence unless Y_n is

very close to Y_0 and particularly unless pressures are such that loss of vibrational energy would be rapid. Ketene may possibly provide an example of this case (111).
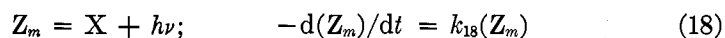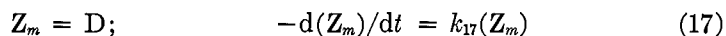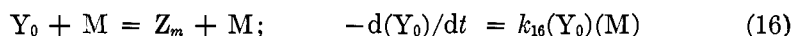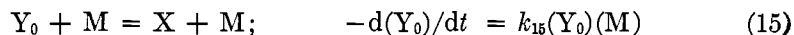
(2) All of the initially excited molecules fail either to dissociate or to fluoresce until they have reached levels near Y_0. This is the case at the other extreme from case 1. Fluorescence data indicate that at pressures over a few millimeters the fluorescence always occurs from the lower levels of the upper electronic state. Under these conditions equations of the same form as 9 will be obeyed, but $1/a$ and $1/b$ are both proportional to the fraction of the absorbing molecules which eventually reach states near Y_0.

Cases 1 and 2 may not be distinguished from each other experimentally unless the spectrum has been analyzed in such a way as to tell whether or not fluorescence comes from the lower levels of the upper electronic state and then only if Y_n is quite different from Y_0.

(3) The intermediate case is the one for which the dissociation of many or all states must be considered. Generally speaking, a plot of $1/\phi$ vs. (X) should have a slope at very low pressures which depends on the rate constants for Y_n and at high pressures on the rate constants for the states near Y_0. It is suspected on the basis of experimental evidence that the ratio of the rate constant for fluorescence to that for dissociation is strongly dependent on the amount of vibrational energy for many gases. Other electronic states than that initially formed must be considered frequently. This would mean that molecules would be in two sets of low levels of two upper electronic states Y_0 and Z_0. The fluorescent lifetimes in these two states are usually quite different.

The third case is really the general one. It is difficult to treat this case rigorously because of lack of information about the behaviors of all intermediate energy levels, but it is necessary to give at least an approximate treatment of it.

Reference to equations 2 to 8 inclusive will show that the states X_m (from equation 4), Y_0 (from equation 5), and Z_m (from equation 8) must still be accounted for. The following reactions seem to be the main ones which need to be considered:
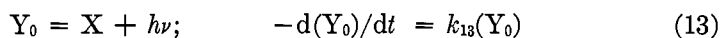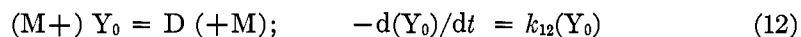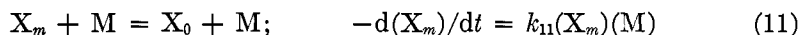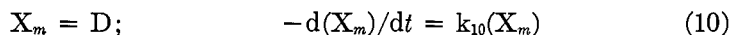
$$X_m = D; \qquad -d(X_m)/dt = k_{10}(X_m) \qquad (10)$$

$$X_m + M = X_0 + M; \qquad -d(X_m)/dt = k_{11}(X_m)(M) \qquad (11)$$

$$(M+)\ Y_0 = D\ (+M); \qquad -d(Y_0)/dt = k_{12}(Y_0) \qquad (12)$$

$$Y_0 = X + h\nu; \qquad -d(Y_0)/dt = k_{13}(Y_0) \qquad (13)$$

$$(M+)\ Y_0 = X_m\ (+M); \qquad -d(Y_0)/dt = k_{14}(Y_0) \qquad (14)$$

$$Y_0 + M = X + M; \qquad -d(Y_0)/dt = k_{15}(Y_0)(M) \qquad (15)$$

$$Y_0 + M = Z_m + M; \qquad -d(Y_0)/dt = k_{16}(Y_0)(M) \qquad (16)$$

$$Z_m = D; \qquad -d(Z_m)/dt = k_{17}(Z_m) \qquad (17)$$

$$Z_m = X + h\nu; \qquad -d(Z_m)/dt = k_{18}(Z_m) \qquad (18)$$
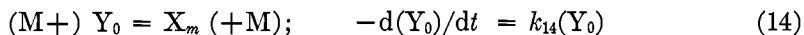
$$Z_m + M = Y_0 + M; \qquad -d(Z_m)/dt = k_{19}(Z_m)(M) \qquad (19)$$

$$Z_m + M = D + M; \qquad -d(Z_m)/dt = k_{20}(Z_m)(M) \qquad (20)$$

$$Z_m + M = X + M; \qquad -d(Z_m)/dt = k_{21}(Z_m)(M) \qquad (21)$$

With the above array of possible reactions and transformations the resulting equations for fluorescence yield and for primary quantum yield contain so many terms that rigorous evaluation of all of the rate constants becomes impossible. One may, however, for certain cases show that some steps are unimportant. From independent data on lifetimes and on fluorescence quenching one may estimate certain constants.

It is necessary now to examine equations 2 to 21 and determine which are unimportant. Reference will be made particularly to the simple ketones under discussion. It would, at the present stage of our information, be unsafe to generalize and to assume that the same reactions would be unimportant in all other cases.

The following facts must be kept in mind:

(1) Except under experimental conditions (high temperatures and short wavelengths) such that the primary quantum yield is high, the primary yield seems to decrease with increase in pressure. In some instances data about primary quantum yields are insufficient to permit conclusions to be drawn.

(2) Plots of the inverse of the fluorescence efficiency against the pressure are linear for both the short-lived and the long-lived states of two of the molecules (acetone and biacetyl), except at 3650 Å. for biacetyl. However, the data have not been extended to very low pressures because of the difficulty of making measurements. It is possible that linearity would not be found at low pressures and that biacetyl at 3650 Å. is not really a special case. Because of the long mean life of one of the upper states of biacetyl this molecule does show certain peculiarities not common to the others.

With these facts in mind, the following statements may be made about the various steps:

Reaction 2: No evidence at all exists for resonance fluorescence under the experimental conditions so far studied. For practical purposes at least, this step may be omitted.

Reaction 3: For all or nearly all of these molecules, there is strong indication that the magnitude of the primary quantum yield depends on wavelength at low temperatures. This is also true at higher temperatures in the presence of scavengers such as iodine. One must assume, therefore, that the energy content of the molecule Y_n affects markedly its rate of dissociation. This step must be included.

Reaction 4: It is relatively unimportant whether one writes reaction 4 followed by $X_m = D$ or whether one retains only reaction 3. Internal conversion followed by energy degradation must be used in some instances. For the moment, we prefer to retain reaction 3 and not to use reaction 4.

Reaction 5: The fluorescence data require this step, since the emitted wavelength is independent of the absorbed wavelength (84).

Reaction 6: No conclusive evidence exists either for or against this step. This is due mainly to the difficulty of measuring the true primary quantum yield. In biacetyl at 3650 Å. the primary yield decreases with increase in pressure. This step will be omitted.

Reaction 7: There is no evidence either for or against this step. It is probable that complete loss of electronic and vibrational energy in a single step does not occur. This step will be omitted.

Reaction 8[4]: Fluorescence occurs from two upper electronic states (43), at least one of which almost certainly differs from the initially formed state. Inclusion of reaction 8 seems to be necessary.

Reaction 10: As already pointed out, reaction 4 followed by reaction 10 is essentially equivalent to reaction 3. Since we have preferred to omit reaction 4, reaction 10 may be omitted.

Reaction 11: This reaction is also not needed if reaction 4 is omitted and especially if reaction 15 is retained.

Reaction 12: If any appreciable fraction of the molecules reach Y_0, a dissociation step for this state is essential. An activation energy seems to be associated with the dissociation and presumably, therefore, collisions are necessary for reaction 12. This step will be retained and the matter of collisions will be considered later.

Reaction 13: The fluorescence data demand this step.

Reaction 14: This is another internal conversion step for which the collision frequency might under some conditions determine the rate. There is no evidence either for or against it. Y_0 must dissociate and it is somewhat immaterial whether one writes reaction 14 followed by dissociation or uses merely reaction 12. Reaction 14 will be omitted.

Reaction 15: The fluorescence data indicate some quenching by collision. This could be due either to dissociation or to energy loss on collision and may be due to both. It seems best to include reaction 15.

Reaction 16: There is no conclusive evidence either for or against this step.

[4] Reaction 8 may be considered as a series of reactions, such as

$$Y_n + M = Z_p + M \tag{8a}$$
$$Z_p + M = Y_n + M \tag{8b}$$
$$Z_p + M = Z_m + M \tag{8c}$$
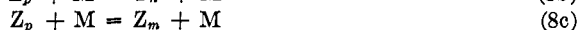
where Z_p is a vibrationally excited state corresponding to Z_m. In order to fit the fluorescence data, the state Y_0 must not be permitted to make the transition to the state Z_m, i.e., there must be a potential barrier between these two states.

An alternative explanation is represented by the reactions:

$$Y_0 = Z_p \tag{8d}$$
$$Z_p = Y_0 \tag{8e}$$
$$Z_p + M = Z_m + M \tag{8f}$$

With this mechanism, it is necessary that the reactions involving loss of vibrational energy of the states Y_n and Z_p, reactions 5 and 8f, respectively, be very much faster than reactions 8d and 8e at all pressures that have been studied experimentally.

These mechanisms predict different fluorescence behaviors at very low pressures, but these experiments are virtually inaccessible.

The ratio of intensity of one type of fluorescence to that of the other varies little with pressure. Y_0 and Z_m should tend to be present to extents dependent on the Boltzmann factor if they can be converted into each other reversibly. Reaction 16 appears to be slow if it occurs at all and it will be omitted.

Reaction 17: If Z_m is formed in appreciable quantity, as it seems to be in some instances, a dissociation step is necessary to explain the photochemical data. The choice between reaction 17 and reaction 20 must be based on whether or not collisions appear to be necessary. Reaction 17 will be tentatively retained.

Reaction 18: The fluorescence data demand a long-lived emitting state and reaction 18 must be included.

Reaction 19: This is the reverse of reaction 16 and both steps must either be included or omitted. For want of more evidence, reaction 19 will be omitted. If Z_m lies at a lower energy than Y_0, conversion into Y_0 will be slow in any case.

Reaction 20: Either reaction 17 or reaction 20 must be included, and the decision between them will depend on trends in the data. Decision will be deferred for the moment.

Reaction 21: Some fluorescence quenching by collision occurs, but it is hard to tell whether this results from reaction 21 or from a dissociation process such as reaction 20. Reaction 21 will be included because it appears to be necessary.

To summarize, the following reactions have been retained: 3, 5, 8, 12, 13, 15, 17, 18, 20, 21. By assumption of the steady state, equations for primary quantity yield and for fluorescence efficiency may now be derived.

The equation for the primary quantum yield is as follows:

$$\phi = \frac{1}{k_3 + (k_5 + k_8)(M)} \left[k_3 + \frac{k_5 k_{12}(M)^2}{k_{13} + (k_{12} + k_{15})(M)} + \frac{(k_{17} + k_{20}(M))k_8(M)}{k_{17} + k_{18} + (k_{20} + k_{21})(M)} \right] \quad \text{(I)}$$

The equations for the quenching of the fluorescences of the two states Y_0 and Z_m are, respectively, as follows:

$$\frac{1}{Q^*} = \frac{k_{13} + (k_{12} + k_{15})(M)}{k_{13}} \cdot \frac{k_3 + (k_5 + k_8)(M)}{k_5(M)} \quad \text{(II)}$$

$$\frac{1}{Q^{**}} = \frac{k_{17} + k_{18} + (k_{20} + k_{21})(M)}{k_{18}} \cdot \frac{k_3 + (k_5 + k_8)(M)}{k_8(M)} \quad \text{(III)}$$

Equations I, II, and III appear to be complex, but it is possible to simplify them under some experimental conditions by comparison with the experimental facts. Certain examples may be cited by way of illustration.

1. The primary quantum yield is very close to unity

This case is found for acetone at 3130 Å. at temperatures over 100°C. in the absence of a scavenger and probably at 2537 Å. at all temperatures (81). It seems to be found in biacetyl at sufficiently short wavelengths (8). If this is to be true, the following conditions must be satisfied: $k_{12}(M) \gg (k_{13} + k_{15}(M))$;

$(k_{17} + k_{20}(M)) \gg (k_{18} + k_{21}(M))$. Thus fluorescence as well as deactivation by collision of Y_0 must be negligible compared to dissociation and the same must be said for Z_m. These statements could have been made, of course, without mathematical proof.

2. Each of the fluorescence quenchings of the two states follows a linear relationship in (M)

This seems to be true for the two states of acetone at 3130 Å. (39) and for the two states of biacetyl at 4358 Å. (15, 38) (but not at 3650 Å.). Experimental evidence for the case of biacetyl is not entirely satisfactory.

Equations II and III may be approximately linear in (M) if the following conditions are satisfied:

Equation II: Either $k_{13} \ll (k_{12} + k_{15})(M)$ or $k_3 \ll (k_5 + k_8)(M)$

Equation III: Either $k_{17} + k_{18} \ll (k_{20} + k_{21})(M)$ or $k_3 \ll (k_5 + k_8)(M)$

There is good reason to believe that the first condition is the correct one in both cases. Since the primary yield depends markedly on wavelength, much of the dissociation must occur by reaction 3, so that k_3 probably cannot be neglected. Possibly a more convincing reason, at least for acetone, lies in the fact that the ratio of slope to intercept for plots of $1/Q$ vs. (M) is the same for both states. Unfortunately, fluorescence data have not been obtained at very low pressures owing to experimental difficulties; hence it is impossible to say whether equations II and III would reproduce the data under such conditions. Equations II and III simplify respectively to the following equations under conditions where data have been obtained:

$$\frac{1}{Q^*} = \frac{k_{12} + k_{15}}{k_5 k_{13}} \cdot (k_3 + (k_5 + k_8)(M)) \qquad \text{(IV)}$$

$$\frac{1}{Q^{**}} = \frac{k_{20} + k_{21}}{k_8 k_{18}} \cdot (k_3 + (k_5 + k_8)(M)) \qquad \text{(V)}$$

and slope/intercept is in each case $(k_5 + k_8)/k_3$.

3. The fluorescence is enhanced by increase in pressure (viz., biacetyl at 3650 Å.)

When this condition is met, equations IV and V are not of the correct form and the following statements must be true:

Equation II: Either $k_{13} \gg (k_{12} + k_{15})(M)$ or $k_3 \gg (k_5 + k_8)(M)$

Equation III: Either $k_{17} + k_{18} \gg (k_{20} + k_{21})(M)$ or $k_3 \gg (k_5 + k_8)(M)$

Probably insufficient information is available to enable one to decide between the various alternatives but because there is a wavelength effect, it seems best to assume that k_3 is wavelength-dependent, that under some conditions it may be neglected, and that under others it may not be neglected. Finally, as pointed out later, it is almost certain that reaction 17 may be neglected.

In the presence of scavengers such as iodine or oxygen one must introduce reactions of Y_n, Y_0, and Z_m with the scavenger. The resulting equations will be similar to the ones already given, and discussion of this matter will be deferred until actual data are considered.

It seems probable, therefore, that a mechanism may be postulated which will account for both the fluorescence and the photochemical data for certain simple ketones. It is recognized that the picture is highly simplified, since there must be involved many rotation-vibration-electronic states each with its own rate constants. Nevertheless if it is possible to reduce the number of steps to manageable proportions and still fit the data, it is believed that progress has been made.

Mention may be made again of the so-called process of "internal conversion" (31, 32). A molecule after absorption which possesses enough energy to dissociate may do so only if sufficient energy is localized in the proper degree of freedom to cause dissociation. If the electronic energy is converted internally into vibrational energy, the probability of proper localization of the vibrational energy may be treated by the ideas of the Rice–Ramsperger–Kassel theory (50). By the principle of microscopic reversibility such an internal conversion of electronic to vibrational energy must be reversible. If, however, vibrational energy is dissipated through collisions, the reverse process may be partially or wholly prevented.

If one considers dissociation to proceed via internal conversion, reaction 3 (Y_n = D) would be replaced by reaction 4 plus the following three steps:

$$X_m = Y_n \tag{22}$$

$$X_m + M = X + M \tag{23}$$

$$X_m = D \tag{24}$$
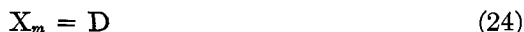
Reactions 5 and 8 would also have to be included. The primary quantum yield for the portion of the reaction which occurs by way of X_m will be given by

$$\phi_{X_m} = \frac{k_4 k_{24}}{k_4[k_{24} + k_{23}(M)] + [k_{22} + k_{24} + k_{23}(M)](k_5 + k_8)(M)} \tag{VI}$$

This may be contrasted with the expression for the primary yield by reaction 3 if X_m is not used.

$$\phi_{Y_n} = \frac{k_3}{k_3 + (k_5 + k_8)(M)} \tag{VII}$$

It is obvious that the condition necessary to give equations VI and VII the same form will be $k_{29} \gg (k_{27} + k_{28}(M))$, in which case VI reduces to

$$\phi_{X_m} = \frac{k_4}{k_4 + (k_5 + k_8)(M)}$$

Hence the rate constant for internal conversion essentially replaces the rate constant for dissociation if dissociation of the state formed by internal conversion is rapid. It should be noted that in view of the fact that fluorescence occurs, one

may not make the rate constant for reaction 4 of a different magnitude from $(k_5 + k_8)(M)$.

Thus one may introduce the concept of internal conversion without changing the forms of the equations used to interpret the data provided the various rate constants have the proper relative values.

A more lengthy discussion of the primary process and its relationship to fluorescence does not seem to be warranted. It is possible to derive certain equations which may be applied to the data. These equations are based on a general mechanism which is recognized to be highly simplified, but they contain enough parameters to be applicable and they should permit certain conclusions to be drawn about the nature of the primary process.

III. THE ABSORPTION SPECTRA OF KETONES

A. THE REGIONS OF ABSORPTION

The simple ketones which contain only one carbonyl group all show absorption in the gas phase which is recognizable in the neighborhood of 3300 to 3400 Å. and extends to shorter wavelengths (87). Maximum absorption coefficients are found around 2700 to 2800 Å. At still shorter wavelengths such ketones become more and more transparent so that absorption is negligible at about 2200 to 2300 Å. As one proceeds to still shorter wavelengths, a brief region of almost complete transparency is followed by strong absorption which usually begins around 2000 Å.

For practical reasons nearly all photochemical studies have been made in the near ultraviolet region of absorption, i.e., from about 2300 to about 3400 Å., and the vast majority of studies have been made with the 2537 and 3130 Å. lines of the mercury arc. Hence only brief mention will be made of the absorption below 2000 Å.

When two chromophoric groups are present in the same molecule, absorption for each of the groups is shifted toward longer wavelengths than for the groups when present alone (41). Thus the absorption spectra for diketones should occur at longer wavelengths than for the monoketones, and this shift should be particularly important for diketones for which the carbonyl groups are adjacent to each other, as in biacetyl.

Gas-phase absorption by biacetyl extends to a long wave limit of approximately 4670 Å. and the maximum occurs near 4000 Å. (2). There is some absorption over the entire region from 4670 Å. down to about 2000 Å. (99, 100). The spectrum at shorter wavelengths does not seem to have been studied.

The ketones which have been investigated with some care (mainly acetone and biacetyl) show at least two types of fluorescence (2, 3, 4, 33, 47, 48, 92). One of these has a short life, i.e., less than 10^{-6} sec., and the other is of much longer life (2×10^{-4} sec. in the case of acetone; 2×10^{-3} sec. in the case of biacetyl). Lifetimes estimated from absorption coefficients are always short and probably correspond more nearly to the short-lived fluorescence than to the long. This indicates that probably the electronic state responsible for the short-lived fluorescence is the one formed by absorption of radiation. The other state

has been described as a triplet state (58, 59). Since singlet–triplet transitions should be extremely weak, one would not expect appreciable absorption from the ground to the long-lived state and there is no evidence for gas-phase absorption of this type even at very long path lengths.

With the above background the various facts about the spectra of the simple ketones discussed in this article may be given.

1. The spectrum of acetone

The long wave limit is about 3350 Å. in a 31-foot tube at a pressure of a few centimeters (82). Since absorption approaches zero slowly, the true long wave limit is probably at greater wavelengths. Absorption through 2 meters of liquid acetone has been reported to about 3450 Å. (48). Thus the true long wave limit cannot be given precisely but may tentatively be placed at 3500 ± 100 Å.

Short wave limit of fluorescence: Fluorescence has not been observed at wavelengths below 3850 Å., but again this is not a precise limit, since the intensity approaches zero asymptotically (61).

The zero-zero band for near ultraviolet absorption: The zero-zero band and bands from neighboring transitions should be observed both in absorption and in fluorescence unless there is some theoretical reason (for example, decidedly different bond lengths and bond angles in the upper and lower states) which makes such transitions extremely weak. Since there is a gap between fluorescence and absorption, one must expect that the Franck–Condon principle (or possibly some selection rule) prevents the zero-zero band from being observed. It is impossible, therefore, to give its wavelength with any precision and it may be placed only tentatively at 3600 ± 200 Å.

Absorption coefficients in the near ultraviolet: Absorption coefficients have been measured in acetone from 3295 to 2235 Å. (91). Additional absorption coefficients have been reported from time to time for specific lines of the mercury arc but since in general high-pressure arcs have been used, these values are not for monochromatic light and they may only be used to calculate the light absorbed in specific experimental situations (39, 44, 47).

In spite of the fact that the reported absorption coefficients show only a gradual increase to a maximum between 2720 and 2820 Å., there is visual evidence for more than one maximum and there is definite evidence of structure in the absorption from about 2950 Å. to the long wave limit of 3350 Å. The reported absorption coefficients must apply, therefore, to acetone at high pressures such that structure is obscured.

Evidence for diffuseness in absorption: Structure has been reported at the long wave end of the near ultraviolet absorption region (14, 16, 82). Thus there is evidence for some stability of the upper electronic state formed by absorption. It is impossible from the appearance of the structure to indicate at what point diffuseness begins. Photochemical decomposition does occur throughout the entire region of absorption, and fluorescence is excited at 3130 and probably at shorter wavelengths, although it is probably not excited at 2537 Å. (29, 68). The appearance of the spectrum is not a safe guide as to the nature of the absorption and of the stability of the upper state or states formed by absorption.

Absorption at short wavelengths: Beginning at about 2000 Å. acetone vapor shows strong absorption with many bands with apparently quite sharp long wave edges (82). Some of these bands can be fitted into Rydberg series (22) which extrapolate to an ionization potential in reasonably good agreement with experiment (47). In this instance a fairly satisfactory interpretation of the spectrum can be given. Very little photochemical work on acetone has been done below 2000 Å. (65). The products are, in general, the same as at longer wavelengths, the chief difference being that some hydrogen is formed. Thus one apparently is dealing with several primary dissociations, at least one of which gives hydrogen atoms and acetonyl radicals.

Bond strengths and absorption spectrum: The energy required to dissociate the molecule of acetone vapor into a methyl and an acetyl radical is not known precisely. It may be as low as 68 kcal. per mole and may be as high as 80 kcal. per mole. Absorption by acetone vapor provides enough energy to cause dissociation, provided both radicals are formed in normal states. No information is available about the electronic states of these radicals.

The situation may be different for molecules which have lost vibration energy. If the zero-zero band has been properly placed at 3600 ± 200 Å., molecules in the lowest vibration level of the upper electronic state may or may not have enough energy to dissociate depending upon the correct value of the dissociation energy. In any case the dissociation of such molecules will not produce radicals of either high kinetic or high vibrational energy and "hot radical" effects from acetone will be small unless wavelengths considerably shorter than 3000 Å. are used.

2. The spectrum of biacetyl

Long wave limit: The long wave limit is about 4670 Å. (3, 60) and is much more definite than it is in the case of acetone.

Short wave limit of fluorescence: The short wave limit of fluorescence is between 4400 and 4500 Å.

The zero-zero band: Since fluorescence and absorption overlap, the zero-zero band almost certainly lies in the region of overlap for transitions to one of the upper electronic states. This band may be placed tentatively at 4500 ± 100 Å. This would be the zero-zero band for the transition in absorption and presumably for the transition in fluorescence with a short life. Much less can be said about the zero-zero band for the long-lived fluorescence. This may lie at an appreciably longer wavelength, about 5000 Å.

Absorption coefficients: These do not seem to have been carefully determined except for specific experimental conditions. There is ample evidence of structure from 4670 Å. to wavelengths below 4000 Å., thus making it difficult to measure absorption coefficients which would have much meaning.

Evidence for diffuseness of absorption: Fluorescence, photochemical behavior, and appearance of the absorption spectrum all undergo changes between 4000 and 3650 Å. and between 3650 and 3000 Å. These changes indicate the possibility of predissociation (43, 60). On the other hand, it is not possible to assign a definite wavelength at which the changes occur.

Nature of upper states: A careful study of the states of biacetyl has just been made (99, 100). Of these there seem to be several, only one of which (in the near ultraviolet) is formed directly by absorption from the ground state. The others are metastable and at least one has been characterized as a triplet state. There is some evidence (88) that the long-lived state of acetone may excite the long-lived state of biacetyl by collisions of the second kind. On the other hand, the long-lived state of acetone seems to excite little or not at all the short-lived state of biacetyl. Thus probably the two long-lived states have the same multiplicity.

3. The spectrum of methyl ethyl ketone

The spectrum of methyl ethyl ketone (2-butanone) lies in the same region as that of diethyl ketone (23), i.e., in the vapor phase in a 10-meter tube it extends from about 2400 Å. to about 3200 Å. As in acetone there are regions of strong absorption beginning at about 2000 Å. and going into the far ultraviolet absorption region. A green fluorescence, due undoubtedly to biacetyl, is excited at 3130 Å. (69).

4. The spectrum of diethyl ketone

The spectrum of diethyl ketone has been studied much less carefully than those of acetone and of biacetyl. There is a very weak fluorescence (69), but it has not been studied with care because of experimental difficulties. Similarly, there is no definite indication of structure in the spectrum but the general region of absorption coincides quite closely with that for acetone.

5. The spectrum of ketene

The absorption spectrum of ketene has been photographed by Norrish, Crone, and Saltmarsh (76) with a grating which gave a dispersion of 5.3 Å. per millimeter. They report completely diffuse bands from about 3700 to about 2600 Å. and continuous absorption below about 2200 Å. The "diffuseness" of the bands may or may not indicate rapid predissociation. Actually, the photochemical data to be reviewed indicate that at 3650 Å. excited molecules of reasonably long life must be produced. At shorter wavelengths the interpretation is less definite, although around 2700 Å. every or nearly every molecule which absorbs must dissociate. Thus the photochemical data aid in the interpretation of the spectrum, and the latter should probably be reëxamined at higher dispersion.

IV. ACETONE

A. THE CALCULATION OF THE PRIMARY QUANTUM YIELD

The photochemistry of acetone has been the subject of a large number of publications, partly because of its convenience as a source of methyl radicals. The field has been ably reviewed recently by E. W. R. Steacie (105).

The products of the vapor-phase reaction are principally carbon monoxide, ethane, and methane. Under some conditions biacetyl (7), methyl ethyl ketone (1, 64), biacetonyl (70), ketene (27), and acetaldehyde (5) are formed. Since the bulk of the work has been without quantitative measurements of these

minor products, the interpretation of mechanism is subject to some ambiguity. It has been conclusively demonstrated that the reaction proceeds by a completely free-radical mechanism (9, 90, 105). A list of the reactions postulated for the system is as follows:

$$CH_3COCH_3 + h\nu = CH_3CO + CH_3 \tag{25}$$

$$CH_3CO = CH_3 + CO \tag{26}$$

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \tag{27}$$

$$CH_2COCH_3 = CH_2CO + CH_3 \tag{28}$$

$$2CH_3 = C_2H_6 \tag{29}$$

$$2CH_3CO = (CH_3CO)_2 \tag{30}$$

$$2CH_3CO = CH_2CO + CH_3CHO \tag{31}$$

$$CH_3 + CH_3CO = CH_3COCH_3 \tag{32}$$

$$CH_3 + CH_3CO = CH_4 + CH_2CO \tag{33}$$

$$CH_3 + CH_2COCH_3 = C_2H_5COCH_3 \tag{34}$$

$$2CH_2COCH_3 = (CH_2COCH_3)_2 \tag{35}$$
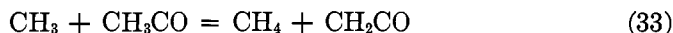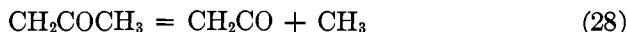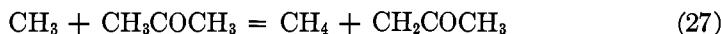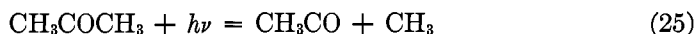
The variables in the system that have been studied are: (a) the wavelength absorbed; (b) the temperature; (c) the intensity absorbed; (d) the pressure of acetone.

Since there have been extensive reviews of the photochemistry of acetone (18, 80, 81, 105), only the salient features will be discussed here. At temperatures above 100°C. the quantum yield of carbon monoxide is within experimental error of 1 at 3130 and 2537 Å. There is no evidence for a chain reaction which forms carbon monoxide, and, therefore, the primary quantum yield must be 1 under these conditions. Acetyl radicals decompose rapidly to methyl radicals and carbon monoxide and undergo no other reactions above 100°C. Methane and ethane are formed by reactions 27 and 29, respectively, although reaction 33 contributes to the methane yield near room temperature. The quantum yields of ethane and methane depend on temperature, intensity, and acetone pressure in a manner that follows directly from the mechanism. The sum of the quantum yields of ketene and methyl ethyl ketone cannot exceed the quantum yield of methane, but there is no quantitative information available.

At temperatures below 100°C. the system is complex. Not only is there the problem of reactions of acetyl radicals which lead to formation of biacetyl and to formation of acetone, but at low acetone pressures the effect of diffusion of radicals to the walls may be important (73). If the pressure of acetone is above about 100 mm., some definite conclusions may be reached.
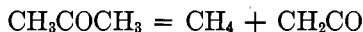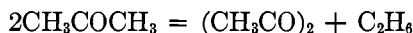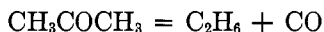
The primary quantum yield is equal to the sum of the quantum yields of products formed by all radical–radical reactions. Under the conditions of low temperature, high acetone pressure, and high intensity, the only radicals present

in the system will be methyl and acetyl. These will react according to equations 29, 30, 31, 32, and 33. The difficulty of the treatment is obvious since, of the products of these reactions, only ethane is known quantitatively.

The primary quantum yield will be given by:

$$\phi = \Phi_{C_2H_6} + \Phi_B + \Phi_{CH_3CHO} + \Phi_{CH_4(33)} + \Phi_{A(32)} \qquad (VIII)$$

where $\Phi_{C_2H_6}$, Φ_B, and Φ_{CH_3CHO} are the quantum yields of ethane, biacetyl, and acetaldehyde, respectively. $\Phi_{CH_4(33)}$ is the quantum yield of methane formed in reaction 33, and $\Phi_{A(32)}$ is the quantum yield for re-formation of acetone by reaction 32. If essentially no methane is formed by reaction 27, the following stoichiometric equations may be used to solve for the quantum yields of bi-acetyl and of acetaldehyde:

$$CH_3COCH_3 = C_2H_6 + CO$$

$$2CH_3COCH_3 = (CH_3CO)_2 + C_2H_6$$

$$2CH_3COCH_3 = CH_3CO + CH_3CHO + C_2H_6$$

$$CH_3COCH_3 = CH_4 + CH_2CO$$

These account for the products formed at low temperature, high acetone pressure, and high intensity. Then it follows that:

$$\Phi_B + \Phi_{CH_3CHO} = \Phi_{C_2H_6} - \Phi_{CO}$$

and

$$\phi = 2\Phi_{C_2H_6} - \Phi_{CO} + \Phi_{CH_4(33)} + \Phi_{A(32)} \qquad (IX)$$

If reactions 31 and 33 are neglected, essentially the same result is found, i.e., equation IX without $\Phi_{CH_4(33)}$, which must be small in this treatment.

The remaining quantum yield to be found is that of the re-formation of acetone. It is here that the inherent difficulty arises and this quantum yield can only be estimated. The ratio $\Phi_{A(32)}^2 / \Phi_B \Phi_{C_2H_6}$ should be constant and independent of all variables in the system, since it is simply equal to a ratio of rate constants $k_{32}^2 / k_{29} k_{30}$, each of which probably has small or zero activation energy. Thus the quantum yield of acetone would be accessible if the value of this ratio were known.

If it is assumed that ϕ_{2537} is one at all temperatures, then ϕ_{3130} is 0.78 and 0.71 at 110 and 180 mm. pressure of acetone, respectively, at 25°C. To the limited extent that this treatment is valid, the data show a slight dependence of the primary quantum yield on pressure at 3130 Å.

These considerations show that the recombination of acetyl and methyl radicals to form acetone must occur to an appreciable extent. The ratio of the rate constants $k_{32}^2 / k_{29} k_{30}$ is about 11 if the treatment given is valid (81, 97). On the basis of the collision theory, if the collision diameter for methyl and acetyl is the mean of the collision diameters for methyl–methyl and acetyl–acetyl, this ratio will be just the ratio of steric factors for the reactions. Plausible values

for the steric factors that fit with a ratio of 11 are 0.5 (35, 53) 2×10^{-2}, and 10^{-4} for reactions 29, 30, and 32.

Additional evidence on the rapidity of these radical–radical combination reactions has recently been obtained (72). Biacetyl with C^{14} in the methyl positions was photolyzed with ordinary acetone. All fractions of the products which contained methyl groups were radioactive and, in particular, the acetone was found to have become radioactive to a considerable extent.

It seems reasonable to assume a quantum yield of 1 for acetone at 2537 Å., independent of temperature in the range studied. This assumption is supported in part by the fact that no fluorescence is observed on absorption of radiation at this wavelength. At 3130 Å. the quantum yield is somewhat less than unity at room temperature, where there is probably a slight dependence on pressure. The steps leading to dissociation must involve activation energies, since the primary quantum yield rapidly increases to 1 at 100°C.

B. PHOTOLYSIS IN THE PRESENCE OF IODINE

Iodine added to a system which contains free radicals will act as a highly efficient trap, so that the rates of radical–radical reactions will be substantially reduced (105). In the photolysis of acetone an iodine pressure of a few millimeters is sufficient to reduce the quantum yields of ethane, methane, and carbon monoxide by more than a factor of 100. The products of the reaction of the methyl and acetyl radicals with iodine are methyl iodide and probably acetyl iodide (10, 36, 37, 66, 90). Unfortunately, most investigators have found that acetyl iodide is particularly difficult to determine. It may undergo further reaction, but it evidently does not decompose to give carbon monoxide in appreciable quantities. In experiments done with radioactive iodine during which separation was made by carrier gas, the acetyl iodide varied from 3 to 120 per cent of the methyl iodide under otherwise identical conditions (66).

The mechanism for the secondary reactions in the presence of iodide is

$$CH_3 + I_2 = CH_3I + I \tag{36}$$

$$CH_3CO + I_2 = CH_3COI + I \tag{37}$$

$$CH_3CO = CH_3 + CO \tag{38}$$

$$2I = I_2 \tag{39}$$

The quantum yield of acetone disappearance is given by the expression:

$$\phi = \Phi_{CH_3I} - \Phi_{CO}$$

This will not be the same numerically as the primary quantum yield in pure acetone. Since the quantum yields of methyl iodide are considerably less than 1 even at 177°C., there must be some deactivation of excited acetone molecules by iodine.

C. THE FLUORESCENCE OF ACETONE

Acetone exhibits a weak blue fluorescence between 3800 and 4700 Å., with a maximum intensity near 4500 Å. at room temperature when excited by 3130 Å.

radiation (17, 39, 47, 48, 49, 61, 62). The fluorescence efficiency (ratio of total fluorescence intensity to absorbed intensity) at 50°C. is about 2×10^{-3} (62).

The shortest wavelength observed in fluorescence does not overlap the longest wavelength in absorption; resonance fluorescence has never been observed. Thus part of the absorbed energy is lost in some way before the emission of fluoresence. Emission must occur from one or more of the lower vibrational levels of the upper electronic state.

Studies of the decay of fluorescence show that it consists of at least two parts, one with a life of about 2×10^{-4} sec. and the other with a much shorter life, less than 8×10^{-6} sec. (39). The long-lived state contributes 90 per cent of the fluorescent intensity at room temperature but is quenched strongly by oxygen and diminishes considerably as the temperature increases. The short-lived fluorescence can therefore be studied alone, whereas the behavior of the long-lived state must be estimated by determining the difference between total fluorescence intensity and that of the short-lived state. The intensity of the short-lived state is found to be independent of the extent to which the long-lived state is removed. This indicates that the long-lived state is not formed reversibly from the short-lived state and is almost certainly a different electronic state.

The mean lifetime of the electronic state reached by acetone in absorption calculated from the integrated absorption coefficient is 3×10^{-6} sec. (48). This estimate neglects the effects of quenching collisions or other forms of degradation and is thus an upper limit to the lifetime. The consistency of this value with the maximum determined experimentally is an indication that the short-lived fluorescence occurs from the same electronic state as is reached by absorption.

Both fluorescences are quenched by acetone. A Stern–Volmer (109) mechanism is obeyed by both species, although there is considerable scatter of the data in the case of the short-lived fluorescence. In addition, the long-lived state follows a similar mechanism for quenching by oxygen. The slope of the Stern–Volmer plot for oxygen is independent of temperature.

D. THE MECHANISM RELATING FLUORESCENCE AND PHOTOCHEMICAL BEHAVIOR

In Section II,C a general mechanism is given to explain the fluorescence and photochemical behavior of these ketones which have been studied extensively. The following experimental facts fix the form of the explicit equations for the primary quantum yield and for the fluorescence efficiencies in the case of acetone.

1. The primary quantum yield is close to unity at 2537 Å. at all temperatures and pressures studied.
2. The primary quantum yield is close to unity at 3130 Å. at temperatures in excess of 100°C. At lower temperatures, the yield is less than 1 and shows a slight pressure dependence.
3. Both the short-lived and the long-lived fluorescences are quenched by acetone according to a Stern–Volmer mechanism.
4. The long-lived fluorescence decreases in magnitude relative to the short-lived fluorescence as the temperature is raised.

5. The ratio of slope to intercept in the Stern–Volmer plots of fluorescence efficiency is the same for both the short-lived and the long-lived fluorescence.

The general expressions for the primary quantum yield and fluorescence efficiencies have been derived in Section II,C. The rates of the fluorescence reactions must be very much smaller than the sum of the rates of the competing reactions which lead to dissociation and degradation. Thus for the short-lived and for the long-lived fluorescence, the conditions imposed by the data at 3130 Å. are: $k_{13} \ll (k_{12} + k_{15})(M)$ and $k_{17} + k_{18} \ll (k_{20} + k_{21})(M)$, respectively. The equations obtained with this degree of approximation are equations IV and V of Section II,C. The ratio of slope to intercept in a plot of $1/Q$ *versus* (M) is $(k_5 + k_8)/k_3$. This has the value 1.5×10^2 mole^{-1} liter for the two fluorescing states Y_0 and Z_m at 50°C. (39). The restriction imposed on the relative rate constants for fluorescence and for dissociation or deactivation would not be expected to hold at very low pressure. However, over the range of pressure studied, equations IV and V are obeyed very well.

As the temperature is raised, both fluorescence efficiencies decrease, an effect that can be attributed to an appreciable activation energy for reaction 3. Since the fluorescence efficiency of the long-lived state decreases more rapidly than that of the short-lived state with increasing temperature, an activation energy must be associated with $k_{20} + k_{21}$ which is greater than that of $k_{12} + k_{15}$.

The primary quantum yield is given by equation I. At 2537 Å., if the primary quantum yield is 1 at all temperatures, $k_3 \gg (k_5 + k_8)(M)$. The fact that no fluorescence is observed at 2537 Å. supports this conclusion. At 3130 Å. at temperatures above 100°C. the primary quantum yield is very close to unity. This is probably due in part to the increase of k_3 with increasing temperature. Since the primary yield is close to unity, reaction 21 cannot be of importance compared with reaction 20 above 100°C., and therefore reaction 20 must have an appreciable activation energy.

The quenching of the long-lived fluorescence by oxygen requires that reaction 40 be included in the mechanism:

$$Z_m + O_2 = X + O_2 \qquad (40)$$

The lifetime of this state in the presence of oxygen is:

$$1/\tau_{(Z_m)} = k_{17} + k_{18} + (k_{20} + k_{21})(M) + k_{40}(O_2)$$

The rate constant k_{40} has the value 8.2×10^9 mole^{-1} liter second^{-1}, independent of temperature from 32° to 75°C. (39). Since only an upper limit to the lifetime of the short-lived state can be measured, the constants in the equation:

$$1/\tau_{(Y_0)} = k_{13} + (k_{12} + k_{15})(M)$$

cannot be evaluated. The data indicate that the short-lived fluorescence is relatively insensitive to changes in temperature.

In the presence of iodine, the following additional reactions are required:

$$Y_n + I_2 = X + 2I \tag{41}$$

$$Y_0 + I_2 = X + 2I \tag{42}$$

$$Z_m + I_2 = X + 2I \tag{43}$$
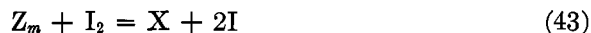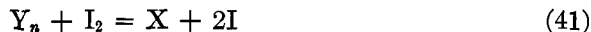
These steps plus the required steps from the general mechanism lead to the following expression for the primary quantum yield in the presence of iodine:

$$\phi = \frac{1}{k_3 + (k_5 + k_8)(M) + k_{41}(I_2)}$$
$$\left[k_3 + \frac{k_5 k_{12}(M)^2}{k_{13} + (k_{12} + k_{15})(M) + k_{42}(I_2)} + \frac{[k_{17} + k_{20}(M)]k_8(M)}{k_{17} + k_{18} + (k_{20} + k_{21})(M) + k_{43}(I_2)} \right]$$

The three terms in the brackets refer to the contributions of Y_n, Y_0, and Z_m, respectively, to the quantum yield of acetone disappearance. The nature of this expression prevents any direct test of its validity. As a first approximation, the contributions of Y_0 and Z_m may be neglected; this reduces the above equation to the form:

$$\phi = k_3/[k_3 + (k_5 + k_8)(M) + k_{41}(I_2)] \tag{X}$$

Equation X may be tested by plotting $[(1/\phi) - 1]/(M)$ against $(I_2)/(M)$. The data obtained at 100°C. and 3130 Å. (66) are presented in this form in figure 1. The intercept of this plot, i.e., at zero iodine pressure, is $(k_5 + k_8)/k_3$ and has the value 10×10^2 mole $^{-1}$ liter. For comparison, the value obtained from the
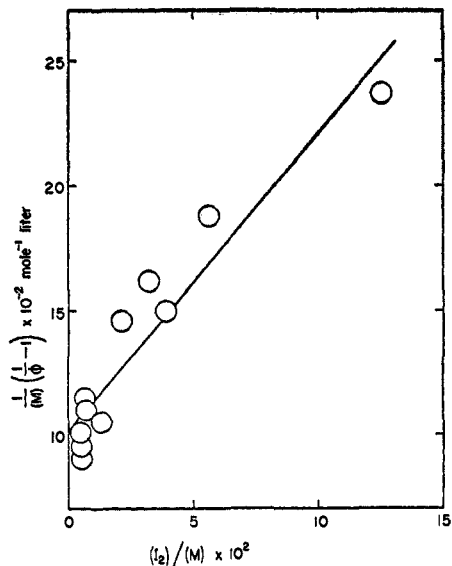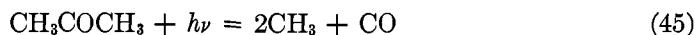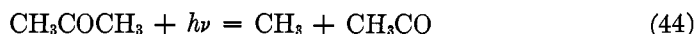

FIG. 1. Test of equation X for the photolysis of acetone in the presence of iodine at 3130 Å. and 100°C.

fluorescence studies at 50°C. is 1.5×10^2 mole^{-1} liter. Considering the approximation made in neglecting the dissociation of Y_0 and Z_m, the agreement is good. The slope of the line in figure 1 gives $k_{41}/k_3 = 1.2 \times 10^4$ mole^{-1} liter. The maximum for k_{41} is about 10^{11} mole^{-1} liter sec.$^{-1}$ Therefore k_3 is less than about 10^7 sec.$^{-1}$ and, similarly, $(k_5 + k_8)$ is less than 10^{10} mole^{-1} liter sec.$^{-1}$

Other data on this system (90) show that Φ_{CH_3I} increases with increasing temperatures, but this is probably due mostly to an activation energy for reaction 3. The fact that Φ_{CH_3I} increases at the shorter wavelengths can with certainty be associated with reaction 3.

E. THE NATURE OF THE PRIMARY PROCESS

Several reactions have been proposed for the primary dissociation step in the photolysis of acetone that have not been definitely excluded:

$$CH_3COCH_3 + h\nu = CH_3 + CH_3CO \qquad (44)$$

$$CH_3COCH_3 + h\nu = 2CH_3 + CO \qquad (45)$$

$$CH_3COCH_3 + h\nu = H + CH_2COCH_3 \qquad (46)$$

The nature of the products is very strong evidence for reaction 44 as the primary step. At higher temperatures, reaction 45 satisfies the data, but, since the quantum yield of carbon monoxide is small in the presence of iodine even at 177°C., it cannot make more than a small contribution to the primary process. Intramolecular rearrangements may be neglected as unimportant, principally on the basis of the work on iodine (66, 90) and on studies with deuterated acetone (9), and are not considered here. Hydrogen is found as a product only when radiation of shorter wavelength is used than is of concern here; therefore reaction 46 will not be considered.

The most important mode of dissociation is certainly represented by reaction 44. It is possible to include the necessary contribution of reaction 45 in another manner; a fraction α of the acetyl radicals produced in reaction 44 retain sufficient energy to undergo a rapid decomposition into methyl radicals and carbon monoxide (44). Thus the reactions:

$$CH_3COCH_3 + h\nu = CH_3 + \alpha CH_3CO^* + (1 - \alpha)CH_3CO \qquad (47)$$

and

$$CH_3CO^* = CH_3 + CO \qquad (48)$$

take the place of a combination of reactions 44 and 45. The rate constant for reaction 48 must be much higher than the rate constant for the corresponding thermal reaction, and α must depend on the wavelength of absorption. For the photolysis of pure acetone, the fraction α has been calculated from the mechanism as 0.07 and 0.22 at 3130 and 2537 Å., respectively. In the presence of iodine, the yields of carbon monoxide are small and probably subject to considerable experimental error. Quantum yields of carbon monoxide in the presence of iodine increase (*a*) with increasing temperature, (*b*) as the wavelength

absorbed is decreased, and (c) as the iodine pressure is decreased. There is too much scatter for any trend with acetone pressure to be apparent. These data may be explained qualitatively by reactions 47 and 48, followed by:

$$CH_3CO = CH_3 + CO \tag{49}$$

$$CH_3CO + I_2 = CH_3COI + I \tag{50}$$

$$CH_3 + I_2 = CH_3I = I \tag{51}$$

These reactions lead to the expression:

$$\frac{\Phi_{CO}}{\Phi_{CH_3I} - \Phi_{CO}} = \frac{k_{49} + \alpha k_{50}(I_2)}{k_{49} + k_{50}(I_2)}$$

Reaction 50 must be fast. Reaction 49 will cause the yield of carbon monoxide to increase as the temperature is raised, since it has an activation energy of 13–18 kcal. per mole (10, 116). The fraction α, which probably does not have the same value in the presence as in the absence of iodine, must increase as the wavelength absorbed decreases. These data cannot be treated quantitatively, owing to insufficient information. Acetyl radicals are generally conceded to undergo reaction 49 essentially to completion above about 100°C., but at 4 mm. iodine pressure even at 177°C. the rate of reaction 49 is small compared to that of reaction 50. Thus the reaction of iodine with acetyl radicals must be efficient and the reaction

$$CH_3CO^* + I_2 = CH_3COI + I \tag{52}$$
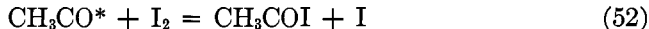
probably cannot be neglected.

V. METHYL ETHYL KETONE

The secondary reactions in the photolysis of methyl ethyl ketone (2-butanone) are similar to, but more complex than, those in acetone (6, 107). Thus, propane, butane, and ethylene are formed as hydrocarbon products as well as methane and ethane (71, 75). The many products render any interpretation of the data very difficult.

Owing to this complexity there is no gain in citing all the possible secondary reactions. In addition to the hydrocarbons mentioned, there may be biacetyl (2,3-butanedione), acetone, diethyl ketone, and bipropionyl (3,4-hexanedione) in the products at low temperature. The re-formation of methyl ethyl ketone by a radical–radical reaction is also expected.

Experimentally, at 3130 Å. and at 25°C., the quantum yield of carbon monoxide is low and of about the same magnitude as in the photolysis of acetone (25). As will be discussed in Section VI, the quantum yield of carbon monoxide in the photolysis of diethyl ketone is approximately 1 under these conditions. Therefore, it is assumed that of the two most probable primary reactions:

$$CH_3COC_2H_5 + h\nu = CH_3CO + C_2H_5 \tag{53}$$

$$CH_3COC_2H_5 + h\nu = CH_3 + C_2H_5CO \tag{54}$$
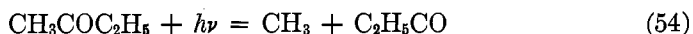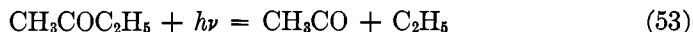
reaction 53 predominates at 3130 Å.

Confirmation of the nature of the primary process comes from the iodine-inhibited photolysis of methyl ethyl ketone (36, 37, 67, 89). At 3130 Å. and 100°C. the relative contributions of reactions 53 and 54, measured essentially by the yields of ethyl and methyl iodide, are in the ratio of about 20 or 30 to 1. The ratio drops to about 5 at 2654 Å. and to about 2 at 2537 Å. The quantum yields of carbon monoxide in the presence of iodine are somewhat higher for methyl ethyl ketone than for acetone. This is to be expected, as propionyl radicals probably dissociate more rapidly than acetyl radicals.

Fluorescence has been observed but is attributed to the photochemical formation of biacetyl (69). No fluorescence of methyl ethyl ketone has been reported.

This is about as far as the analysis can be carried. It is difficult to estimate the primary quantum yields for acetone and even more difficult for methyl ethyl ketone.
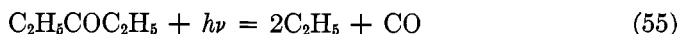
VI. DIETHYL KETONE

In common with the other ketones discussed in this review, diethyl ketone (3-pentanone) decomposes photochemically by a free-radical mechanism (21, 26, 56, 108). The products are more numerous than in the case of acetone, since ethyl radicals may disproportionate as well as combine and since the pentanonyl radicals ($C_2H_4COC_2H_5$) may decompose to give either ethylene and propionyl radicals (C_2H_5CO) or methylketene (40) and ethyl radicals. Chains are induced at lower temperatures than in acetone (110).

Fluorescence has been observed on excitation with 3130 Å. radiation (69). The spectrum of this fluorescence is identical with that observed on irradiation of propionaldehyde. Thus, the green fluorescence almost certainly originates from bipropionyl formed photochemically by the combination of two propionyl radicals. No fluorescence has been found that can be attributed to excited states of diethyl ketone.

At relatively low intensities, the quantum yield of carbon monoxide is 1 within experimental error at all temperatures up to about 150°C. (21). Above this temperature a chain reaction occurs and the yield of carbon monoxide increases to about 3 at 300°C. At high intensities, the quantum yield of carbon monoxide may drop to 0.6 at 25°C. (56). High intensities favor radical–radical reactions. Thus there would be some re-formation of diethyl ketone under these conditions, and further, pentanonyl radicals may be removed from the system by radical-radical reaction which will decrease the importance of the chain reaction. It is almost certain that the primary quantum yield is very close to unity at 2537 Å. and at 3130 Å. at all temperatures investigated.

The primary process

$$C_2H_5COC_2H_5 + h\nu = 2C_2H_5 + CO \qquad (55)$$

has been suggested for diethyl ketone (19, 26). However, from the fact that at high intensity and at 25°C. the quantum yield of carbon monoxide decreases from the value of 1 found at low intensity, it can be concluded that the primary process:

$$C_2H_5COC_2H_5 + h\nu = C_2H_5CO + C_2H_5 \qquad (56)$$

followed by dissociation of the propionyl radical:

$$C_2H_5CO = C_2H_5 + CO \qquad (57)$$

more nearly represents the situation. Additional verification of this mode of dissociation may be drawn from the photoöxidation of diethyl ketone (83, 85). Oxygen suppresses the formation of carbon monoxide. This fact can be accounted for by reaction 56, followed by a competition between reactions 57 and 58:

$$C_2H_5CO + O_2 = ? \text{ (no CO)} \qquad (58)$$
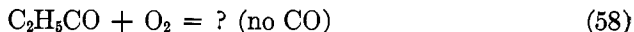
The rate of reaction 58 must be very rapid, since 0.2 mm. of oxygen is sufficient to reduce the quantum yield of carbon monoxide to 0.1. These studies suggest that, as in the case of acetyl radicals formed in acetone, a fraction of the propionyl radicals formed by reaction 56 retain enough energy to dissociate spontaneously. As the pressure of oxygen is increased, the quantum yield of carbon monoxide decreases rapidly at low pressures of oxygen but then decreases slowly up to very high pressures of oxygen. Nitric oxide substituted for oxygen, to facilitate the analysis for carbon monoxide, suppresses the quantum yield of carbon monoxide to a limit of about 0.07 at 35°C. (measured with 35 mm. of nitric oxide) (85).

There is an indication from the photoöxidation work that the fraction of propionyl radicals which undergo a spontaneous reaction increases with increasing temperature, but the interpretation of the data is not certain.

VII. BIACETYL

A. FLUORESCENCE

Fluorescence is excited in biacetyl (2,3-butanedione) by absorption of radiation at 3650, 4047, and 4358 Å. (2, 3, 4, 15, 33, 38, 43, 49, 59, 61, 68, 92, 106). The spectrum overlaps the absorption region, extending from about 4500 to at least 6500 Å. As in the case of acetone, the fluorescence must be ascribed to at least two different states of different lifetimes. One of these states, with a lifetime less than 8×10^{-6} sec. (38), fluoresces weakly from 4500 to about 5000 A. Since the lifetime of this short-lived state agrees with the lifetime calculated from the integrated absorption coefficient, this is probably the same electronic state as is reached by absorption.

The other fluorescence consists of an emission starting at about 5000 Å. with broad maxima at 5100, 5600, and 6100 Å. (33). The state responsible for this green fluorescence has a relatively long lifetime, about 2×10^{-3} sec. (2, 49, 92). For this reason, it has been referred to as a triplet state. This assignment has recently been confirmed (99, 100).

1. Effects of pressure and wavelength

The fluorescence spectrum is independent of pressure and of exciting wavelength. This is evidence that the fluorescence originates from the lowest vibrational levels of the excited electronic states involved, or, at least, from low vibrational levels in thermal "equilibrium" with the surroundings.

The quantum yield, or fluorescence efficiency, is affected by wavelength. At 4047 and 4358 Å. the fluorescence efficiency is almost independent of the

pressure of biacetyl and has a relatively large value, 0.145 at 27°C. (4). There-fore, the rate of degradation of this state by collision is very slow compared with the rate of fluorescence, although there may be other first-order degrada-tions such as internal conversion. Interactions between these metastable mole-cules and normal molecules may be essentially neglected.

Excitation by 3650 Å. radiation leads to abnormal fluorescence behavior in that the efficiency increases with increasing pressure of biacetyl (4, 43). An interpretation of these facts consistent with the photochemical data is as follows: a molecule excited at 3650 A. will be in a high vibration level and will have sufficient energy to dissociate. Unless some of this energy is lost by collision, dissociation will occur. A molecule degraded by collision is essentially the same as one formed at the longer wavelengths and may fluoresce.

There is a slight effect of intensity on the lifetime and on the fluorescence efficiency of the slow fluorescence (49). The effect may be explained by inter-action between metastable molecules, thus removing them from the system either by dissociation or by degradation.

2. Effects of temperature

The long-lived state decreases in importance more rapidly with increase in temperature than does the short-lived state, thus facilitating study of the weak blue fluorescence independent of the green (38). Because of the overlap of fluorescence and absorption, most of these studies have been carried out with 3650 Å. radiation.

The behavior of the green fluorescence as a function of temperature is con-sistent with a reaction which competes with the formation of the long-lived state and which has an activation energy of about 9 kcal. per mole (15). At 200°C. the green fluorescence is completely absent, leaving only the blue. The lifetime of the long-lived state also decreases as the temperature is raised, but the effect is relatively small (49).

There is a decrease of the fluorescence efficiency of the short-lived state with increasing temperature. Here, an activation energy of about 16 kcal. per mole can be associated with the reaction removing the short-lived state from the system by dissociation and by degradation to the long-lived state.

3. Quenching by added gases

The long-lived state is destroyed by oxygen; the short-lived state is not (38, 49). The quenching obeys a Stern–Volmer relationship up to a pressure of oxygen of 350 microns but above about 3 mm. the fluorescence efficiency is constant. The residue is the fast fluorescence unaffected by oxygen.

The slope of the Stern–Volmer plot is independent of temperature, but the intercept increases as the temperature is raised. There must be a reaction re-moving the long-lived state which has a relatively high activation energy.

To investigate the possibility that radicals formed photochemically may react with excited molecules, the fluorescence efficiency was measured in the presence of a fifteen-fold excess of isobutylene (15). There was no effect, a result which indicates that this type of interaction can be neglected.
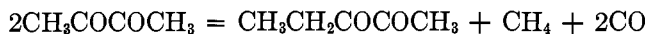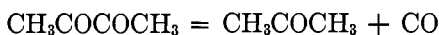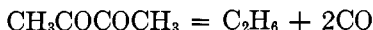
B. THE CALCULATION OF THE PRIMARY QUANTUM YIELD

As in the case of the other ketones, the primary quantum yield is not directly accessible from experimental data unless it is unity. In order to determine this quantity, it is necessary to have a complete understanding of the reaction mechanism. For biacetyl, even this knowledge is insufficient at low temperature. Information must be used about the rate of the reaction which re-forms biacetyl by the recombination of acetyl radicals.

1. From the products based on a mechanism

It is apparent from the experimental data that the same set of secondary reactions occurs regardless of the exciting wavelength. The mechanism is based on the data obtained at wavelengths less than 3200 Å. (8, 11). This same mechanism is used to interpret the photolysis in the longer wavelength region (97, 98).

The products of the reaction are carbon monoxide, ethane, methane, and acetone, all of which have been determined quantitatively at wavelengths less than 3200 Å. (8). Ketene and 2,3-pentanedione are known to be present in the reaction products, particularly at higher temperatures. If these are the only products, the amounts of ketene and of 2,3-pentanedione can be determined from the other products and the stoichiometry. The following overall reactions occur:

$$CH_3COCOCH_3 = C_2H_6 + 2CO$$

$$CH_3COCOCH_3 = CH_3COCH_3 + CO$$

$$CH_3COCOCH_3 = CH_2CO + CH_4 + CO$$

$$2CH_3COCOCH_3 = CH_3CH_2COCOCH_3 + CH_4 + 2CO$$

From these, the quantum yields of ketene and of 2,3-pentanedione are:

$$\Phi_{CH_2CO} = 2\Phi_{CH_4} + 2\Phi_{C_2H_6} + \Phi_A - \Phi_{CO}$$

$$\Phi_{CH_3CH_2COCOCH_3} = \Phi_{CO} - \Phi_{CH_4} - \Phi_A - 2\Phi_{C_2H_6}$$

where Φ_A is the quantum yield for the formation of acetone.

There is some doubt as to the actual nature of the primary process, as will be discussed subsequently. For the present, it suffices to choose:

$$CH_3COCOCH_3 + h\nu = 2CH_3CO \tag{59}$$

The secondary reactions are (8):

$$CH_3CO = CH_3 + CO \tag{26}$$

$$2CH_3 = C_2H_6 \tag{29}$$

$$2CH_3CO = CH_3COCOCH_3 \tag{30}$$

$$CH_3 + CH_3CO = CH_3COCH_3 \tag{32}$$

$$CH_3 + CH_3COCOCH_3 = CH_4 + CH_2COCOCH_3 \tag{60}$$

$$CH_3 + CH_3COCOCH_3 = CH_3COCH_3 + CH_3CO \tag{61}$$

$$CH_2COCOCH_3 = CH_2CO + CH_3CO \tag{62}$$

$$CH_3 + CH_2COCOCH_3 = CH_3CH_2COCOCH_3 \tag{63}$$
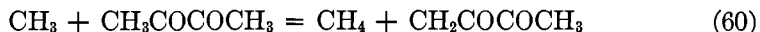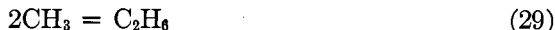
For completeness, the following disproportionation reactions are included (5), but in the treatment to follow, these will be neglected:

$$2CH_3CO = CH_3CHO + CH_2CO \qquad (31)$$

$$CH_3CO + CH_3 = CH_4 + CH_2CO \qquad (33)$$
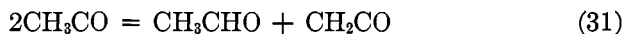
The rate of the primary reaction 59 is equal to the sum of the rates of the radical–radical termination reactions. If the mechanism is complete, reactions 29, 30, 32, and 63 must be included. Additional radical–radical reactions might yield as yet undetermined products which would further increase ϕ. Since acetone is produced by reaction 61 as well as by 32, the source of the acetone must be specified in the expression for the primary quantum yield:

$$\phi = \Phi_{A(32)} + \Phi_{B(30)} + \Phi_{C_2H_6} + \Phi_{CH_3CH_2COCOCH_3}$$

The Φ's are quantum yields: $\Phi_{A(32)}$ is the quantum yield of acetone formed by reaction 32 and $\Phi_{B(30)}$ is the quantum yield for re-formation of biacetyl by reaction 30.

This expression is considerably simplified if only the data at 100°C. and higher temperatures are considered. Under these conditions, acetyl radicals will be unstable with respect to decomposition into methyl radicals and carbon monoxide. The mechanism will then consist of reactions 26, 29, 59, 60, 61, 62, and 63. The primary yield is:

$$\phi = \Phi_{C_2H_6} + \Phi_{CH_3CH_2COCOCH_3}$$

and, with the stoichiometric equation for the quantum yield of 2,3-pentanedione, this becomes:

$$\phi = \Phi_{CO} - \Phi_{C_2H_6} - \Phi_{CH_4} - \Phi_A \qquad (XI)$$

In table 1 are listed the quantum yields for the formation of 2,3-pentanedione and the primary quantum yields at 150°C. at the various wavelengths studied. For purposes of comparison $\Phi_{C_2H_6}$ is included in this tabulation, since it has been suggested that this quantum yield represents the primary quantum yield for $t > 100$°C. (8). The primary quantum yields given in table 1 will be minimum values if there are appreciable quantities of products formed by other radical–radical reactions. If reaction 63 does occur as is predicted by the ma-

TABLE 1

Quantum yields in the photolysis of biacetyl

$t = 150$°C.; (B) $= 1.5 \times 10^{-3}$ moles/liter

Wavelength	$\Phi_{CH_3CH_2COCOCH_3}$	$\Phi_{C_2H_6}$	ϕ
2380	0.28	0.25	0.53
2537	0.30	0.33	0.63
2654	0.23	0.39	0.62
2804	0.13	0.27	0.40
3130	0.15	0.06	0.22

TABLE 2

Ratio of ketene to methane in the photolysis of biacetyl

t, °C	200	150	100
CH_2CO/CH_4	0.8	0.3	0.1

terial balance, there should be contributions from a reaction such as:

$$2CH_2COCOCH_2 = (CH_2COCOCH_3)_2 \tag{64}$$

That 2,3-pentanedione or similar products involving the radical $CH_2COCOCH_3$ are formed is also indicated by the ratio of ketene to methane yields, as shown in table 2 (12).

The primary quantum yield calculated in this manner should be accepted only with reservation, as it involves an algebraic sum of four experimentally determined quantum yields. Thus, the decrease at the shortest wavelengths may not be real and is especially suspect in view of the iodine-inhibited experiments to be discussed in Section VII,B,2. The decrease at the longer wavelengths probably represents the facts more closely, at least in relative values, if not in magnitude.

To calculate the primary quantum yield below 100°C. reactions 30 and 32 must be included. The quantum yield of reaction 32 is the total acetone quantum yield less the quantum yield of reaction 61. From the data at temperatures over 100°C., where reaction 32 can be neglected, the ratio of the rate constants of reactions 61 and 60 can be measured and extrapolated to the lower temperatures. The quantum yield of reaction 32 will be:

$$\Phi_{A(32)} = \Phi_A - (k_{61}/k_{60})\Phi_{CH_4}$$

where Φ_A is the measured quantum yield of acetone formation.

The evaluation of $\Phi_{B(30)}$ requires a ratio of rate constants estimated from the data on acetone (81); $k_{32}^2/k_{29}k_{30}$. The value of this ratio is given only for room temperature, but it should be roughly independent of temperature (see Section IV,A). With this information, the complete expression for the primary quantum yield is:

$$\phi = \Phi_{CO} - \Phi_{C_2H_6} - (1 + k_{61}/k_{60})\Phi_{CH_4}$$
$$+ [k_{29}k_{30}/k_{32}^2][\Phi_A - (k_{61}/k_{60})\Phi_{CH_4}]^2/\Phi_{C_2H_6} \tag{XII}$$

In table 3 are the primary quantum yields as a function of temperature as calculated by equation XII below 100°C. and by equation XI at 100°C. and above. Except for the apparent discontinuity in the primary quantum yield at 2654 Å., a regular increase is observed with increasing temperature.

The primary quantum yield at the longer wavelengths is of special interest, since a correlation may be made with the fluorescence. The available photochemical data at 3650 and at 4358 Å. do not include the quantum yields of acetone and they must be obtained indirectly (97). However, the quantum yield of acetone will be indeterminate to the extent of an unknown constant, since there is insufficient information to find both acetone and 2,3-pentanedione.

TABLE 3

Primary quantum yields as a function of temperature in the photolysis of biacetyl

(M) $\approx 1.8 \times 10^{-3}$ moles/liter; $I_a \approx 6 \times 10^{14}$ quanta/second

t	2654 Å.	3130 Å.	t	2654 Å.	3130 Å.
°C.			°C.		
28, 30	0.39	0.08	125	0.50	—
50	0.41	—	150	0.62	0.22
65	—	0.15	175	0.66	—
75	0.57	—	200	0.71	0.34
100	0.42	0.21			

From the stoichiometric equations, the quantum yield of acetone formed is:

$$\Phi_A = \Phi_{CO} - \Phi_{CH_4} - 2\Phi_{C_2H_6} - \Phi_{C_2H_5COCOCH_3}$$

The expression for the primary quantum yield is:

$$\phi = \Phi_{CO} - \Phi_{C_2H_6} - (1 + k_{61}/k_{60})\Phi_{CH_4}$$
$$+ [k_{29}k_{30}/k_{32}^2][\Phi_{CO} - 2\Phi_{C_2H_6} - (1 + \beta + k_{61}/k_{60})\Phi_{CH_4}]^2/\Phi_{C_2H_6} \quad \text{(XIII)}$$

where the quantity β is a number less than unity representing the fraction of the radicals $CH_2COCOCH_3$ that undergo reaction 63.

When the data at 4358 Å. are analyzed by expression XIII, the primary quantum yields are found to be strongly dependent on temperature, on intensity, and to a lesser extent on the pressure of biacetyl (97, 98). The quantum yields are small, less than 0.03 at room temperature. The primary quantum yield is proportional to the number of quanta absorbed per unit volume per second at 30°C. As the temperature is increased, the primary yield decreases and, at about 70°C., goes through a minimum at high intensity. At low intensity the minimum will not appear. Above this temperature the intensity effect gradually disappears, and at 100°C. the primary yield is experimentally independent of intensity.

The data at room temperature can best be interpreted by the assumption that collisions between excited metastable molecules cause dissociation. The lifetime of the long-lived state is probably determined approximately by the rate of fluorescence at room temperature and is about 10^{-3} sec. Collision cross-sections have been calculated for this reaction based on the lifetime of the long-lived state, the observed primary quantum yields, and the fluorescence efficiency at 4358 Å. and 25°C. Reasonable values were obtained (97). At this wavelength the energy per quantum is small (about 65 kcal./mole) and is probably not sufficient to cause direct dissociation, at least at room temperature. As the temperature is raised, the additional thermal energy permits the long-lived state to dissociate. Thus the primary process changes between 30° and 100°C. At an intermediate temperature, the behavior is complicated by the contribution of both primary processes.

A second explanation of the behavior of the primary quantum yield at 4358 Å. and at room temperature is that the metastable molecule Z_m must absorb another quantum of radiation before it can dissociate (96). However, the molar

extinction coefficient of this state would have to be at least 5×10^6 mole^{-1} liter cm.$^{-1}$, an extremely high value. The molar extinction coefficient of biacetyl in the ground state at 4358 Å. is about 6 mole^{-1} liter cm.$^{-1}$ On this basis, the interpretation that collision of metastable molecules leads to dissociation is preferred.

At 3650 Å. the primary quantum yield is strongly dependent on the pressure of biacetyl (97). Again, the quantum yields are small. A plot of $1/\phi$ against pressure is linear with a finite intercept, as shown in figure 2. As the temperature increases, both the slope and intercept decrease. These data are in excellent agreement with the fluorescence data, in which there is an increase in fluorescence efficiency with increasing pressure and a decrease with increasing temperature.
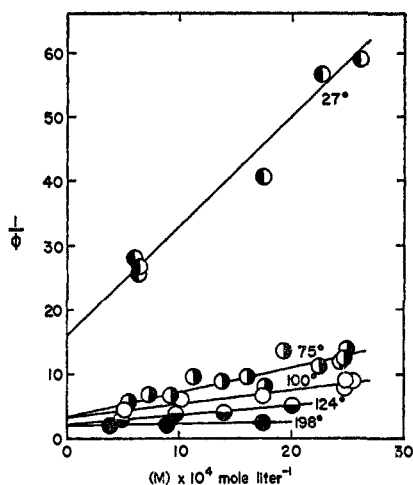
Fig. 2. Primary quantum yield (ϕ) in the photolysis of biacetyl at 3650 Å. as a function of the concentration of biacetyl (M) and of the temperature.

The interpretation is that the initially formed state at 3650 Å. has sufficient energy to dissociate and will do so unless it loses energy by collision. Once an excited molecule has lost energy it becomes essentially the same as the excited molecule formed at 4358 Å.

2. From the iodine-inhibited photolysis

Iodine added to a photochemically decomposing system involving free radicals will remove the radicals as they are formed (106). In the presence of iodine, the mechanism for the biacetyl reaction will consist of the following steps subsequent to the primary dissociation (8):

$$CH_3 + I_2 = CH_3I + I \tag{36}$$

$$CH_3CO + I_2 = CH_3COI + I \tag{37}$$

$$CH_3CO = CH_3 + CO \tag{38}$$

$$I + I = I_2 \tag{39}$$

TABLE 4

Quantum yields in the iodine-inhibited photolysis of biacetyl at 150°C.

Wavelength	Iodine	Biacetyl	Φ_{CO}	Φ_{CH_3I}
Å.	mmoles/liter	mmoles/liter		
2380	0.193	2.23	1.00	0.98
2537	0.178	1.50	0.87	0.81
2654	0.127	1.49	0.72	0.78
2804	0.157	1.65	0.44	0.41
3130	0.146	1.36	0.20	0.19

The iodine-inhibited photolysis of acetone, in which the quantum yield of carbon monoxide is low, shows that reaction 38, the dissociation of acetyl radicals, is negligible in the presence of iodine (90, 105). There is no reason to assume otherwise in the case of biacetyl.

The major products are methyl iodide and carbon monoxide in equal quantities (8). Ethane, methane, and acetone are formed to only a minor extent. No analysis was made for acetyl iodide and, judging from the erratic results obtained in the work with acetone, would not be reliable in any case. The experimental quantum yields as a function of wavelength are given in table 4.

The primary quantum yields from these data are subject to some interpretation. It is evident that the carbon monoxide must be formed in the primary dissociation step, or, at least, from the dissociation of some radical other than acetyl, since the quantum yield for carbon monoxide is very low for acetone-iodine mixtures (see Section IV,B). Therefore the quantum yields of carbon monoxide represent maximum values for the primary quantum yields and will be high to the extent that more than one carbon monoxide molecule is formed by secondary reactions per molecule dissociated in the primary step. The further discussion of this point will be reserved for Section VII,C, in which material relevant to the nature of the primary process will be presented.

The dependence of the primary quantum yield on wavelength from 2380 to 3130 Å., coupled with the low values at the longer wavelengths in this region, means that the initially formed excited molecule is not in a repulsive state. Thus there must be a time lag between absorption and dissociation. It is possible, therefore, that some deactivation by iodine takes place in this system, and the primary quantum yield determined from the experiments with iodine may be even more uncertain than indicated above. There must be deactivation by iodine in the case of acetone and by inference in biacetyl. The values of the primary quantum yields in the presence and absence of iodine are probably not the same.

C. THE NATURE OF THE PRIMARY PROCESS
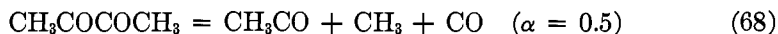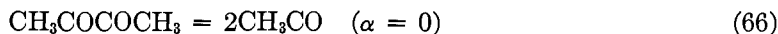
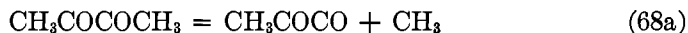The rupture of a biacetyl molecule may be represented by equation 65,

$$CH_3COCOCH_3 = 2(1 - \alpha)CH_3CO + 2\alpha CH_3 + 2\alpha CO \qquad (65)$$

where the fraction α lies between 0 and 1 (97). Three special cases of the primary

process may be cited in which α has the values 0, 1, and 0.5:

$$CH_3COCOCH_3 = 2CH_3CO \quad (\alpha = 0) \tag{66}$$

$$CH_3COCOCH_3 = 2CH_3 + 2CO \quad (\alpha = 1) \tag{67}$$

$$CH_3COCOCH_3 = CH_3CO + CH_3 + CO \quad (\alpha = 0.5) \tag{68}$$

Reaction 68 may be interpreted as:

$$CH_3COCOCH_3 = CH_3COCO + CH_3 \tag{68a}$$

followed by:

$$CH_3COCO = CH_3CO + CO \tag{68b}$$

Intramolecular rearrangements are not included here, as the experimental evidence points to a complete free-radical mechanism.

The fraction α may be calculated from the experimental data and the ratio of rate constants k_{30}/k_{26}^2, estimated from the photolysis of acetone (81). The quantum yield for re-formation of biacetyl is given by the last term in equation XII and also by the expression:

$$\Phi_B = (\Phi_{CO} - 2\alpha\phi)^2 I_a k_{30}/(k_{26})^2 \tag{33}$$

This expression can be evaluated only at room temperature, where $k_{30}/(k_{26})^2$ is known. Such a calculation for α is expected to exhibit considerable scatter. At 2700 Å. α is 0.5 within experimental error (97). The values calculated from data at 3130 and 2654 Å. are 0.35 and 0.61, respectively. If these latter values are correct, it can be assumed that there are two primary processes (reactions 66 and 67), and that the relative contributions are wavelength-dependent. On the other hand, the data at 2700 Å. would indicate that the primary process is best represented by reaction 68. There is reason to believe that this is so.

The photolysis of biacetyl has been investigated by flash techniques (51). For an unfiltered flash, the data may be interpreted to mean that reactions 67 and 66 occur in the ratio 2.8 to 1. When the radiation is restricted to the region around 4200 Å., this ratio is 1.6 to 1. These results may be somewhat high, but are in reasonably good agreement with the low-intensity photolysis.

In the presence of iodine, carbon monoxide is formed at 150°C. to the extents shown in table 4. Under similar conditions the iodine-inhibited photolysis of acetone gives almost no carbon monoxide. The amount so obtained is considerably less than would be calculated from α of the photolysis. The large yields of carbon monoxide for biacetyl–iodine mixtures are conclusive evidence that the carbon monoxide is formed directly in the primary process. It cannot be determined from the data whether the primary process is 66 and 67, or 68. If the primary process is a combination of 66 and 67, and α is wavelength-dependent, then the primary quantum yield is:

$$\phi = \Phi_{CO}/2\alpha$$

In this case, the iodine-inhibited experiments cannot give information about the primary quantum yield in the presence of iodine, since α is not known.

The central carbon–carbon bond in biacetyl has some double-bond character, both in the ground state and in the excited state (63, 99). Thus it is reasonable to assume that the dissociation will occur according to reaction 68a and that the resulting radical will lose carbon monoxide even in the presence of iodine. Then the primary quantum yield in the presence of iodine would be:

$$\phi = \Phi_{CO}$$

The agreement between the quantum yield obtained in this manner and the quantum yield calculated from the photolysis data by equation XI is good at the longer wavelengths studied. The quantum yield of carbon monoxide in the iodine experiments increases regularly with decreasing wavelength to a value of unity at 2380 Å., while the calculated primary quantum yield from the photolysis is almost constant at about 0.6 below 2700 Å. These low results may well be a result of the involved calculation of the primary quantum yield.

At the intermediate wavelength, 3650 Å., α varies with both intensity and pressure (97). At low pressures of biacetyl, α is about 0.2 and increases to almost 0.5 as the pressure is raised. The reason for this effect is not clear.

The primary process seems to be the same at 4358 as at 2700 Å., as α is 0.5 in both cases. This is understandable, since the dissociation at 4358 Å. involves the interaction of two excited molecules and the energies available at these two wavelengths are roughly comparable.

D. THE MECHANISM OF FLUORESCENCE AND OF DISSOCIATION

The experimental facts to be explained by a mechanism are summarized briefly as follows:

At 2380 to 3130 Å.:

(a) The primary quantum yield is less than unity under all conditions except possibly at the shortest wavelength.
(b) The primary quantum yield increases as the wavelength of absorption is decreased.
(c) The primary quantum yield decreases with increasing pressure of biacetyl.
(d) The primary quantum yield increases with increasing temperature.
(e) No fluorescence is observed.

At 3650 Å.:

(a) At all temperatures up to 200°C. the fluorescence efficiency increases and the primary quantum yield decreases as the pressure is increased.
(b) The sum of the two yields is always less than unity.
(c) The character of the fluorescence spectrum is the same whether excited at 3650 or at 4358 Å.
(d) The long-lived fluorescence decreases in importance more rapidly than the short-lived fluorescence as the temperature is raised.

At 4358 Å.:

(a) The primary quantum yield is low at room temperature, varies directly with the intensity, and extrapolates to zero at zero intensity.
(b) The mode of dissociation changes between 30° and 100°C. and the intensity effect disappears.
(c) Above 100°C. the primary quantum yield increases regularly with increasing temperature.
(d) The photochemical and fluorescence quantum yields are essentially independent of the pressure of biacetyl.
(e) There is a slight intensity dependence for the lifetime and for the fluorescence efficiency of the long-lived fluorescence.
(f) The sum of the fluorescence efficiency and of the primary quantum yield is less than unity under all conditions studied.

The mechanism in the short wavelength region from 2380 to 3130 Å. must be considered separately, as a different electronic transition must be involved at these wavelengths than at 3650 and 4358 Å. (99). Since no fluorescence is observed in the short wavelength region, the data require only reactions 3, 5, and 15 of the general mechanism. The primary yield is given by the expression:

$$\frac{1}{\phi} = 1 + \frac{k_5(M)}{k_3}$$

The variation of ϕ with wavelength and with temperature is in accord with the character of reaction 3, in which higher vibration levels are excited as the wavelength is decreased and as the temperature is increased. Data are available to test the pressure dependence of ϕ at 2700 Å. (96), and agreement with the preceding equation is good. The intercepts are subject to some uncertainty, particularly at the higher temperatures, but still lie close to unity. Thus, there can be very little loss of excited molecules through internal conversion at this wavelength.

The data at 3650 and 4358 Å. are consistent with the general mechanism advanced in Section II,C with the addition of another dissociation step:

$$2Z_m = D + X \qquad (69)$$

and with the inclusion of reactions 4 and 14, internal conversion of the states Y_n and Y_0, respectively.

For biacetyl at 3650 and 4358 Å. it is necessary to make the following assumptions: $k_{13} + k_{14} \gg (k_{12} + k_{15})(M)$ and $k_{17} + k_{18} \gg (k_{20} + k_{21})(M)$. In addition, the data at 4358 Å. require that $k_3 + k_4 \ll (k_5 + k_8)(M)$.

With these approximations, equations II and III reduce to:

$$\frac{1}{Q^*} = \frac{k_{13} + k_{14}}{k_{13}} \left[\frac{k_5 + k_8}{k_5} + \frac{k_3 + k_4}{k_5(M)} \right] \qquad \text{(XIV)}$$

and

$$\frac{1}{Q^{**}} = \frac{k_{17} + k_{18}}{k_{18}} \left[\frac{k_5 + k_8}{k_8} + \frac{k_3 + k_4}{k_5(M)} \right] \qquad \text{(XV)}$$

at 3650 Å. and at room temperature. The approximations necessary to arrive at these equations are probably not valid at high pressures, where reactions 12, 15, 20, and 21 must become important. However, over the range studied (up to about 50 mm. pressure of biacetyl) equation XV is obeyed fairly well by the green fluorescence, as shown in figure 3. The ratio of slope to intercept should be the same when the data for the blue and green fluorescences are plotted in the form of equations XIV and XV, but the behavior of the blue fluorescence has not been studied as a function of the pressure of biacetyl at room temperature. The value of $(k_3 + k_4)/(k_5 + k_8)$ obtained from figure 3 is 4.9×10^{-4} mole liter^{-1}.
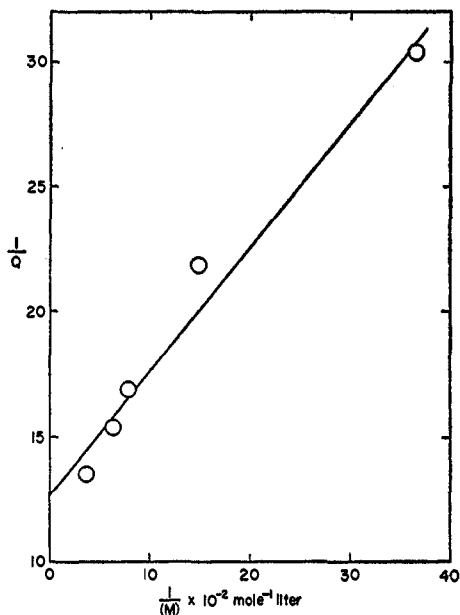

FIG. 3. Test of equation XV for fluorescence efficiency (Q) of biacetyl as a function of the concentration of biacetyl (M) at 3650 Å. and 50°C.

Since the primary quantum yield at 4358 Å. is essentially zero at low intensities and at room temperature, there can be little contribution to dissociation from reactions 12, 17, and 20. Thus, the primary quantum yield at 3650 Å. will be

$$\phi = \frac{k_3}{k_3 + k_4 + (k_5 + k_8)(M)} \tag{XVI}$$

The data fit this equation very well (96, 97). A value of 9.3×10^{-4} mole liter^{-1} for $(k_3 + k_4)/(k_5 + k_8)$ may be obtained from a plot of $1/\phi$ versus (M), in fair agreement with the value from the fluorescence data.

As the temperature is increased, k_3 must increase. Reaction 3 for biacetyl has an activation energy estimated at about 6 kcal./mole higher than the activation

energy for $k_5 + k_8$. Reaction 17 must have an appreciable activation energy to account for the decrease in the green fluorescence efficiency as the temperature is raised. This may correspond to the 16 kcal./mole found from a treatment of the photochemical and fluorescence data (98), but it is not possible with the mechanism used here to put these activation energy differences into an explicit expression.

At 200°C., where only the blue fluorescence occurs, the fluorescence efficiency, although very small, still increases with increasing pressure. The slope of a plot of the photochemical data in the form of equation XVI is zero within experimental error. This latter fact may be due to a contribution to dissociation by the state Z_m (the long-lived state) by reaction 17. The primary yield under these conditions would be:

$$\phi = \frac{k_3 + \left[\dfrac{k_{17}}{k_{17} + k_{18}}\right] k_8(M)}{k_3 + k_4 + (k_5 + k_8)(M)} \tag{XVII}$$

and the pressure effect would be considerably decreased as k_{17} becomes larger than k_{18}.

At 4358 Å. k_3 and k_4 must be small enough to be neglected. The fluorescence efficiencies are:

$$\frac{1}{Q^*} = \frac{(k_{13} + k_{14})(k_5 + k_8)}{k_{13} k_5} \tag{XVIII}$$

and

$$\frac{1}{Q^{**}} = \frac{(k_{17} + k_{18})(k_5 + k_8)}{k_{18} k_8} \tag{XIX}$$

The primary dissociation at 4358 Å. and 25°C. results from the interaction of two long-lived excited molecules, and the expression for the primary quantum yield must involve the intensity to the first power. By including reaction 69 in the mechanism, the steady-state concentration of the long-lived state, Z_m, is

$$Z_m = \frac{k_{18}}{2k_{19}} \left[\left(1 + \frac{4k_8 k_{69} I_a}{(k_5 + k_8)(k_{18})^2}\right)^{1/2} - 1 \right]$$

in which k_{17} is not included, since $k_{17} \ll k_{18}$ at room temperature. In order that this equation reduce to the proper form, the term $4k_8 k_{69} I_a/(k_5 + k_8)(k_{18})^2$ must be small compared to unity. On this basis, the root may be expanded [Note: $(1 - 2a)^{1/2} \approx (1 - a)$ for $a \ll 1$], and the steady-state concentration of Z_m is

$$Z_m = \frac{k_8 I_a}{(k_5 + k_8)k_{18}}$$

The primary yield is given by the expression

$$\phi = \frac{k_{69} k_8^2 I_a}{(k_5 + k_8)^2 k_{18}^2}$$

at 25°C. The slight effect of intensity on the fluorescence is probably due to a contribution of reaction 69, which decreases the concentration and lifetime of the state Z_m.

At higher temperatures reaction 17 is important; above 100°C. the primary quantum yield is represented by the expression

$$\phi = \frac{k_8}{k_5 + k_8} \frac{k_{17}}{k_{17} + k_{18}}$$

and will approach
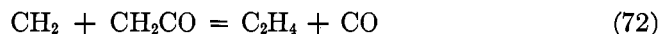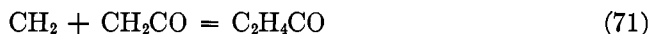
$$\phi = \frac{k_8}{k_5 + k_8}$$

as k_{17} becomes much larger than k_{18}.

VIII. KETENE

A. THE CALCULATION OF THE PRIMARY QUANTUM YIELD

The photolysis of ketene has received considerable attention as a source of methylene radicals (52, 54, 76, 77, 93, 111, 114, 115). In its photochemical behavior ketene resembles biacetyl at 3650 Å. and shorter wavelengths. Fluorescence has not been observed, although there has been no systematic search for it, particularly in the ultraviolet region.

The reaction consists essentially of the following steps:

$$CH_2CO = CH_2 + CO \tag{70}$$

$$CH_2 + CH_2CO = C_2H_4CO \tag{71}$$

$$CH_2 + CH_2CO = C_2H_4 + CO \tag{72}$$

$$C_2H_4CO + xCH_2CO = CO + polymer \tag{73}$$

Reaction 73 must be included as written to explain carbon monoxide quantum yields of 2 at the shorter wavelengths. The ratio of carbon monoxide yield to ethylene yield is 2.2 under all conditions, and polymer has been observed in the cell walls subsequent to photolysis. The reaction of two methylenes

$$2CH_2 = C_2H_4 \tag{74}$$

has been excluded except possibly for conditions of high intensity such as flash photolysis (55).

For the mechanism as written in equations 70 through 73, the primary quantum yield is:

$$\phi = \tfrac{1}{2}\Phi_{CO}$$

B. EFFECTS OF WAVELENGTH AND PRESSURE

The nature of the primary process changes between 2700 and 3650 Å. At the shorter wavelength the primary quantum yield is unity within experimental

error, i.e., the quantum yield of carbon monoxide is 2 (111). It is independent of pressure, of intensity, and of temperature.

At the longer wavelength, 3650 Å., the mode of dissociation is almost identical with that of biacetyl at the same wavelength except that no fluorescence has been found. Thus the mechanism will include reactions 3, 4, 5, and 15. The primary quantum yield is given by the following expression:

$$\frac{1}{\phi} = 1 + \frac{k_4}{k_3} + \frac{k_5(\mathrm{M})}{k_3}$$

The experimental data fit this relation well at all temperatures investigated. Both the slope and the intercept decrease as the temperature is raised, so that an activation energy of about 4.5 kcal./mole must be assigned to reaction 3.

The photolysis has not been studied extensively at 3130 Å. but the available data indicate that the primary quantum yield is about 0.5, intermediate to the results at 2700 and at 3650 Å.

IX. CONCLUSION

A general mechanism consistent with the primary photochemical behavior of several simple ketones has been advanced. This mechanism satisfactorily correlates existing data for acetone, methyl ethyl ketone, diethyl ketone, biacetyl, and ketene, although, as would be expected, the relative importance of some steps varies from compound to compound. Fluorescence data as well as primary photochemical quantum yields may be shown to be consistent with the mechanism.

It must be emphasized first that the mechanism itself is of necessity a simplified version of the true state of affairs, since a detailed statistical treatment based on all possible participating electron-rotation-vibration energy levels would lead to quantum efficiency equations too complex to apply to the data. Certainly not enough is known about the details of the energy-level diagrams to give meaning to such a detailed treatment. Secondly, there are serious gaps in some of the data. These arise partly because much of the work was done before presently available techniques could be used and partly because a reasonably complete picture of the mechanism has been slow in taking shape so that workers in the field did not seek for what is now known to be desirable information. Were one to start over with present knowledge the program could certainly be pursued more efficiently and more elegantly. Hindsight is always easier than foresight.

There are, nevertheless, certain facts which would be difficult to obtain either with presently available techniques or with techniques which one can easily predict to be just over the horizon. These facts are mainly ones which permit the calculation of primary photochemical quantum yields with very high accuracy. Fluorescence efficiencies may not be easy to measure with high accuracy, but on the whole the data are less susceptible of erroneous interpretation than are the photochemical data.

In principle one may calculate a primary quantum yield only under the following idealized conditions: (1) all products are known; (2) secondary reactions do not regenerate molecules of the absorbing substance; (3) secondary reactions do not produce the same radical or radicals as are produced in the primary process. If any one of these conditions is not met uncertainties will always exist in the determination of the primary quantum yield unless there are sound spectroscopic reasons for believing that it is unity.

Even if all three conditions are met, the experimental difficulties are great. Probably no photochemist has ever measured the number of quanta absorbed during a given experiment with an accuracy better than a few per cent. Since the number of quanta absorbed per unit volume per second will vary not only with the position of the volume element in the reaction vessel but with time, the rates of all radical–radical reactions will vary from point to point within the vessel. Thus not only gross quantum yields but especially primary yields which usually must be calculated from sums and differences of gross yields will be subject to great uncertainties except for simple cases where the radical mechanism is well understood. This is not to deny, of course, that there has been much inexcusably poor photochemical work and that both gross and primary yields are subject to errors which careful attention to detail would have avoided.

Thus, one can see two great needs: (a) highly monochromatic light of adequate intensity; (b) better quantitative determinations of all of the reaction products. Great progress in this field will depend on quantum yields of high accuracy obtained under well-controlled experimental conditions. It is much easier to wish for such data than to obtain them. New analytical techniques now available should help, although all too often they are used uncritically by technicians who do not understand the main problem.

Some specific needs for data to complete the picture presented in this review may be cited:

(1) Accurate quantum yields of biacetyl formation from acetone at several wavelengths, pressures, and temperatures. The indirect method of calculation of this quantity from other quantum yields is subject to many uncertainties.

(2) At least reasonably good quantum yields of the minor products from acetone: ketene, ethyl methyl ketone, biacetonyl, and acetaldehyde.

(3) Systematic data on the yields of products in the acetone–iodine system. The primary yield is certainly affected by the presence of iodine, but the experiments suggested should give much information about the behavior of excited molecules.

(4) Systematic determination of yields of ketene and 2,3-pentanedione from biacetyl. Possibly one should look more carefully for dimer or higher polymer.

(5) The absorption spectrum of ketene and a search for possible fluorescence.

(6) The nature of the ketene polymer and of its mode of formation.

Much other pertinent information is needed to complete the picture of the primary photochemical process for even these simple molecules. It is not at first blush rewarding merely to improve techniques to get more accurate measurements in a field in which the cream has already been removed. The authors

feel, however, that much, if not all, of the cream may still be there and that careful experimentation in this field of photochemistry would be rewarding.

X. References

(1) ALLEN, O.: J. Am. Chem. Soc. **63**, 708 (1941).
(2) ALMY, G. M., AND ANDERSON, S.: J. Chem. Phys. **8**, 805 (1940).
(3) ALMY, G. M., FULLER, H. Q., AND KINZER, G. D.: J. Chem. Phys. **8**, 37 (1940).
(4) ALMY, G. M., AND GILLETTE, P. R.: J. Chem. Phys. **11**, 188 (1943).
(5) AUSLOOS, P., AND STEACIE, E. W. R.: Can. J. Chem. **33**, 39 (1955).
(6) AUSLOOS, P., AND STEACIE, E. W. R.: Can. J. Chem. **33**, 1062 (1955).
(7) BARAK, M., AND STYLE, D. W. G.: Nature **135**, 307 (1935).
(8) BELL, W. E., AND BLACET, F. E.: J. Am. Chem. Soc. **76**, 5332 (1954).
(9) BENSON, S. W., AND FALTERMAN, C. W.: J. Chem. Phys. **20**, 201 (1952).
(10) BENSON, S. W., AND FORBES, G. S.: J. Am. Chem. Soc. **65**, 1399 (1943).
(11) BLACET, F. E., AND BELL, W. E.: Discussions Faraday Soc. **14**, 70 (1953).
(12) BLACET, F. E., AND BELL, W. E.: Discussions Faraday Soc. **14**, 131 (1953).
(13) BODENSTEIN, M., AND LIENEWEG, F.: Z. physik. Chem. **119**, 123 (1926).
(14) BOWEN, E. J., AND THOMPSON, H. W.: Nature **133**, 571 (1934).
(15) COWARD, N. A., AND NOYES, W. A., JR.: J. Chem. Phys. **22**, 1207 (1954).
(16) CRONE, H. G., AND NORRISH, R. G. W.: Nature **132**, 241 (1933).
(17) DAMON, G. H., AND DANIELS, F.: J. Am. Chem. Soc. **56**, 2370 (1933).
(18) DAVIS, W., JR.: Chem. Revs. **40**, 201 (1947).
(19) DAVIS, W., JR.: J. Am. Chem. Soc. **70**, 1868 (1948).
(20) DIEKE, G. H., AND KISTIAKOWSKY, G. B.: Phys. Rev. **45**, 4 (1934).
(21) DORFMAN, L. M., AND SHELDON, Z. D.: J. Chem. Phys. **17**, 511 (1949).
(22) DUNCAN, A. B. F.: J. Chem. Phys. **8**, 444 (1940).
(23) DUNCAN, A. B. F., ELLS, V. R., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **58**, 1454 (1936).
(24) DUNCAN, A. B. F., AND HARRISON, G. R.: Phys. Rev. **49**, 211 (1936).
(25) ELLS, V. R., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **60**, 2031 (1938).
(26) ELLS, V. R., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **61**, 2492 (1939).
(27) FERRIS, R. C., AND HAYNES, W. S.: J. Am. Chem. Soc. **72**, 893 (1950).
(28) FINKELSTEIN, A., AND NOYES, W. A., JR.: Discussions Faraday Soc. **14**, 76 (1953).
(29) FISK, C. F., AND NOYES, W. A., JR.: J. Chem. Phys. **2**, 654 (1934).
(30) FRANCK, J.: Trans. Faraday Soc. **21**, 536 (1926).
(31) FRANCK, J., AND HERZFELD, K. F.: J. Phys. Chem. **41**, 97 (1937).
(32) FRANCK, J., AND LIVINGSTON, R.: J. Chem. Phys. **9**, 184 (1941).
(33) FULLER, H. Q., PHILLIPS, L. W., AND ALMY, G. M.: J. Chem. Phys. **7**, 973 (1939).
(34) GAYDON, A. G.: *Dissociation Energies*, Dover Publications, Inc., New York (1950). This book summarizes much of the data on diatomic molecules which are of interest to photochemists.
(35) GOMER, R., AND KISTIAKOWSKY, G. B.: J. Chem. Phys. **19**, 85 (1951).
(36) GORIN, E.: Acta Physicochim. U.R.S.S. **8**, 513 (1938); Chem. Abstracts **33**, 4524 (1939).
(37) GORIN, E.: J. Chem. Phys. **7**, 256 (1939).
(38) GROH, H. J., JR.: J. Chem. Phys. **21**, 674 (1953).
(39) GROH, H. J., JR., LUCKEY, G. W., AND NOYES, W. A., JR.: J. Chem. Phys. **21**, 115 (1953).
(40) HAYNES, W. S., AND GARDNER, P. D.: J. Am. Chem. Soc. **73**, 3065 (1951).
(41) HENRI, V.: *Études de photochimie.* Gauthier-Villars et Cie., Paris (1925).
(42) HENRI, V., AND TEVES, M. C.: Nature **114**, 894 (1924); Compt. rend. **179**, 1156 (1924). No attempt will be made to cite the numerous recent references in this field.
(43) HENRIQUES, F. C., JR., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **62**, 1038 (1940).

(44) HERR, D. S., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **62**, 2052 (1940).
(45) HOGNESS, T. R., AND FRANCK, J.: Z. Physik **44**, 26 (1927).
(46) HOWE, J. P., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **57**, 1262 (1935).
(47) HUNT, R. E., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **70**, 467 (1948).
(48) KASKAN, W. E., AND DUNCAN, A. B. F.: J. Chem. Phys. **16**, 223 (1948).
(49) KASKAN, W. E., AND DUNCAN, A. B. F.: J. Chem. Phys. **18**, 427 (1950).
(50) KASSEL, L. S.: *The Kinetics of Homogeneous Gas Reactions*. The Chemical Catalog Company, New York (1932).
(51) KHAN, M. A., NORRISH, R. G. W., AND PORTER, G.: Proc. Roy. Soc. (London) **219A**, 312 (1953).
(52) KISTIAKOWSKY, G. B., AND MARSHALL, W. L.: J. Am. Chem. Soc. **74**, 88 (1952).
(53) KISTIAKOWSKY, G. B., AND ROBERTS, E. K.: J. Chem. Phys. **21**, 1637 (1953).
(54) KISTIAKOWSKY, G. B., AND ROSENBERG, N. W.: J. Am. Chem. Soc. **72**, 321 (1950).
(55) KNOX, K., NORRISH, R. G. W., AND PORTER, G.: J. Chem. Soc. **1952**, 1477.
(56) KUTSCHKE, K. O., WIJNEN, M. H. J., AND STEACIE, E. W. R.: J. Am. Chem. Soc. **74**, 714 (1952).
(57) LEWIS, B.: Proc. Natl. Acad. Sci. **13**, 720 (1927).
(58) LEWIS, G. N., AND KASHA, M.: J. Am. Chem. Soc. **66**, 2100 (1944).
(59) LEWIS, G. N., AND KASHA, M.: J. Am. Chem. Soc. **67**, 994 (1945).
(60) LIGHT, L.: Z. physik. Chem. **122**, 447 (1926).
(61) LUCKEY, G. W., DUNCAN, A. B. F., AND NOYES, W. A., JR.: J. Chem. Phys. **16**, 407 (1948).
(62) LUCKEY, G. W., AND NOYES, W. A., JR.: J. Chem. Phys. **19**, 227 (1951).
(63) LUVALLE, J. E., AND SCHOMAKER, V.: J. Am. Chem. Soc. **61**, 3520 (1939).
(64) MANDELCORN, L., AND STEACIE, E. W. R.: Can. J. Chem. **32**, 79 (1954).
(65) MANNING, W. M.: J. Am. Chem. Soc. **56**, 2589 (1934).
(66) MARTIN, G. R., AND SUTTON, H. C.: Trans. Faraday Soc. **48**, 812 (1952).
(67) MARTIN, G. R., AND SUTTON, H. C.: Trans. Faraday Soc. **48**, 823 (1952).
(68) MATHESON, M. S., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **60**, 1857 (1938).
(69) MATHESON, M. S., AND ZABOR, J. W.: J. Chem. Phys. **7**, 536 (1938).
(70) McNESBY, J. R., DAVIS, T. W., AND GORDON, A. S.: J. Am. Chem. Soc. **76**, 823 (1954).
(71) MOORE, W. J., JR., AND TAYLOR, H. S.: J. Chem. Phys. **8**, 446 (1940).
(72) NALDRETT, S. N.: Can. J. Chem. **33**, 750 (1955).
(73) NICHOLSON, A. J.: J. Am. Chem. Soc. **73**, 3981 (1951).
(74) NORDHEIM, G., SPONER, H., AND TELLER, E.: J. Chem. Phys. **8**, 455 (1940).
(75) NORRISH, R. G. W., AND APPLEYARD, M. E. S.: J. Chem. Soc. **1934**, 874.
(76) NORRISH, R. G. W., CRONE, H. G., AND SALTMARSH, O. D.: J. Chem. Soc. **1933**, 1533.
(77) NORRISH, R. G. W., CRONE, H. G., AND SALTMARSH, O. D.: J. Am. Chem. Soc. **56**, 1634 (1934).
(78) NOYES, W. A., JR.: J. Chem. Phys. **3**, 430 (1935).
(79) NOYES, W. A., JR.: Trans. Faraday Soc. **33**, 1495 (1937).
(80) NOYES, W. A., JR.: J. Phys. & Colloid Chem. **52**, 546 (1948).
(81) NOYES, W. A., JR., AND DORFMAN, L. M.: J. Chem. Phys. **16**, 788 (1948).
(82) NOYES, W. A., JR., DUNCAN, A. B. F., AND MANNING, W. M.: J. Chem. Phys. **2**, 717 (1934).
(83) NOYES, W. A., JR., AND FINKELSTEIN, A.: Discussions Faraday Soc. **10**, 308 (1951).
(84) NOYES, W. A., JR., AND HENRIQUES, F. C., JR.: J. Chem. Phys. **7**, 767 (1939). The authors discuss this point and give earlier references.
(85) NOYES, W. A., JR., AND JOLLEY, J. E.: In press.
(86) NOYES, W. A., JR., AND LEIGHTON, P. A.: *The Photochemistry of Gases*, pp. 132 et seq. Reinhold Publishing Corporation, New York (1941).
(87) See p. 336 of reference 86, for a summary of spectroscopic data on ketones.
(88) OKABE, H.: Unpublished work done at the University of Rochester.
(89) PITTS, J. N., AND BLACET, F. E.: J. Am. Chem. Soc. **72**, 2810 (1950).

(90) PITTS, J. N., AND BLACET, F. E.: J. Am. Chem. Soc. **74**, 455 (1952).

(91) PORTER, C. W., AND IDDINGS, C.: J. Am. Chem. Soc. **48**, 40 (1926).

(92) RAWCLIFFE, R. D.: Rev. Sci. Instruments **13**, 413 (1942).

(93) ROSS, W. F., AND KISTIAKOWSKY, G. B.: J. Am. Chem. Soc. **56**, 1112 (1934).

(94) SCHEIBE, G., AND LINSTRÖM, C. F.: Z. physik. Chem. **12B**, 387 (1931).

(95) SCHEIBE, G., POVENZ, F., AND LINSTRÖM, C. F.: Z. physik. Chem. **20B**, 292 (1933).

(96) SHEATS, G. F.: Dissertation, University of Rochester (1955).

(97) SHEATS, G. F., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **77**, 1421 (1955).

(98) SHEATS, G. F., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **77**, 4532 (1955).

(99) SIDMAN, J. W., AND MCCLURE, D. S.: J. Am. Chem. Soc. **77**, 6461 (1955).

(100) SIDMAN, J. W., AND MCCLURE, D. S.: J. Am. Chem. Soc. **77**, 6471 (1955).

(101) SPONER, H.: J. Chem. Phys. **8**, 705 (1940).

(102) SPONER, H.: Rev. Modern Phys. **16**, 224 (1944).

(103) SPONER, H., NORDHEIM, G., SKLAR, A. L., AND TELLER, E.: J. Chem. Phys. **7**, 207 (1939).

(104) SPONER, H., AND STÜCKLEN, H.: J. Chem. Phys. **14**, 101 (1946).

(105) STEACIE, E. W. R.: *Atomic and Free Radical Reactions*, 2nd edition, Vol. I, Chap. V, pp. 318–54. Reinhold Publishing Corporation, New York (1954).

(106) See reference 105, pp. 354–8.

(107) See reference 105, pp. 358–62.

(108) See reference 105, pp. 362–8.

(109) STERN, O., AND VOLMER, M.: Physik. Z. **80**, 183 (1919).

(110) STRACHAN, A. N.: Dissertation, University of Rochester (1954).

(111) STRACHAN, A. N., AND NOYES, W. A., JR.: J. Am. Chem. Soc. **76**, 3258 (1954).

(112) TINGEY, H. C., AND GERKE, R. H.: J. Am. Chem. Soc. **48**, 1838 (1926).

(113) TURNER, L. A.: Phys. Rev. **41**, 627 (1932).

(114) VANPEE, M., AND GRARD, F.: Ann. mines Belg. **49**, 37 (1950).

(115) VANPEE, M., AND GRARD, F.: Bull. soc. chim. Belges **60**, 208 (1951).

(116) VOLMAN, D. H., AND GRAVEN, W. M.: J. Am. Chem. Soc. **75**, 3111 (1953).

(117) WARBURG, E.: Sitzber. kgl. preuss. Akad. Wiss. **1916**, 314; Chem. Abstracts **10**, 1299 (1916).