STUDIES OF CHEMICAL REACTIONS OF EXCITED SPECIES USING INTENSE LIGHT SOURCES[1]

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ABSTRACT

The use of measurements of the products of flash photolysis as a means for studying the reactions of electronically-excited molecules is discussed. With intense light sources the problem of isolating these reactions from others involving free radicals is simplified. The flash sources also have their limitations, and misleading information which can result from the presence of inert gases is noted. A diagnostic test is proposed for detecting the effects (if any) of a possible adiabatic temperature rise of the flash.

Some recent studies in the author's laboratory are summarized. Evidence is presented that in the flash photolysis of acetone acetyl radicals arise from an excited molecule. Several deactivation processes are described and compared with results from fluorescence studies.

INTRODUCTION

The study of the chemical products of photochemical systems using low light intensities has yielded a considerable body of knowledge about the reactions of free radicals and some information about the behavior of electronically-excited molecules (13, 18). The short-lived species are produced in these systems in a well-defined way at a definite temperature. At the usual wavelengths employed there is no formation of ions which result from many other sources of radiation, nor are there the high temperatures which accompany the use of shock waves for producing these intermediates. Various methods of production and observation of unstable chemical species have been the subject of a recent symposium (19) and survey (10).

A number of detailed investigations have served to point up some of the information which can be derived about the electronically-excited molecules by these low light intensity techniques and at the same time have revealed their limitations. The experimental results show that the problem of distinguishing between the reactions of excited states and reactions involving free radicals is frequently a matter of some difficulty. Several such examples will be discussed.

In the method of flash photolysis, an intense light source is used, such as a flash lamp (11, 12), a spark (7), or an exploding wire (14). In these systems the concentration of the free radicals is so high that radical–radical reactions are usually favored over all others unless the radical is "hot". The reaction products thus become a more direct measure of the primary photochemical steps and of the reactions of the resulting electronically-excited molecules. However, since low intensity light sources have certain compensating features, the two techniques provide complementary rather than alternative approaches for the investigation of the reactions of excited states.

The study of unstable species and their reactions, by spectroscopic observations of the flashed system, has been reviewed recently (12). We shall be principally concerned here, instead, with flash studies based on a determination of reaction products.

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EXAMPLES OF LOW LIGHT INTENSITY STUDIES—THEIR FINDINGS AND LIMITATIONS

In the photolysis of acetone, Noyes and his collaborators have shown that traces of oxygen (*ca.* 0.02 mm.) can quench the fluorescence of a long-lived electronically-excited acetone molecule (3) and can inhibit ethane formation at low light intensities (8, 9). A considerable amount of information was obtained about the latter process, but it is difficult to separate the reactions of oxygen with the excited molecules from those with the methyl radicals. However, from the rate constant estimated in the above study it can be computed that 10 mm. of oxygen will not react with methyl radicals under the usual flash photolysis conditions, thereby permitting the reaction with excited molecules to be studied in the absence of competing free radical processes.

Another important reaction of excited states is unimolecular dissociation. Some evidence described later suggests that acetyl radicals, but not carbon monoxide, may arise from the unimolecular dissociation of an excited acetone molecule which can be quenched by acetone at moderate pressures. This unimolecular reaction undoubtedly has some temperature coefficient, but its amount has not been definitely established. Complicating features occur, such as an increasing dissociation of acetyl radicals themselves with increasing temperature. The study of this system with intense light sources will serve to eliminate the latter reaction and permit an assessment of the temperature dependence of the former. Recently, flash experiments have provided some information on this process (17).

The photolysis of perfluoroacetone has been recently shown to result in the formation of carbon monoxide from an excited perfluoroacetone molecule (2). The unimolecular reaction rate constant was studied as a function of temperature. Since no perfluoroacetyl compound could be detected, it was not certain whether the dissociation first resulted in a short-lived perfluoroacetyl radical or whether there was a direct split into carbon monoxide. Supplementing this study by one employing flash photolysis could serve either to detect the radical or to place a lower limit on the latter's unimolecular rate constant, of the order of 10^6 sec.$^{-1}$ or so (depending on the light intensity).

SOME LIMITATIONS OF FLASH PHOTOLYSIS

While flash photolysis experiments have much to offer, they also have their limitations, whose importance depends upon the purpose for which they are being used. One problem is that of obtaining sufficiently monochromatic light by filters without reducing the intensity unduly and without having to use an inordinate number of flashes. Again, depending upon the flash time, there may be a more or less appreciable departure from steady-state conditions for the transient species. This situation will complicate the mathematical treatment of certain reaction schemes but not that of others. This problem will be analyzed in detail elsewhere.

Computation of variations in the light absorbed accompanying changes in the experimental conditions can be a difficult problem. It was not one in the present study, however, (except at wavelengths below 2000 Å where the absorption of acetone was not proportional to pressure at the pressures employed). The type of light source used in this study serves to alleviate the difficulty. Calculation of absolute quantum yields is a more formidable problem, partly because of the polychromatic nature of the light.

The reaction temperature may be uncertain because of some increase caused by the flash. Its amount can be reduced by increasing the heat capacity of the gaseous system, i.e. by adding large amounts of inert gas. This procedure, we shall see, has resulted in misleading information when excited states are present. An alternative way is simply to investigate the effects of reducing the intensity and, thereby the temperature rise, of the flash. At these high light intensities, the quantum yields of products would probably not vary with light intensity if no temperature change occurs. Thus, when no intensity effect is found, this is evidence that either temperature changes do not occur or that if they do, their effect on the reaction products is negligible.

STUDIES IN THE FLASH PHOTOLYSIS OF ACETONE

The flash apparatus used in the present experiments (14) was of a standard type, but the customary flash lamp was replaced by an exploding wire. It proved to be convenient, cheap, and reproducible within several per cent. It was found that the light intensity could be easily varied in a known way merely by changing the distance from this line source, a long thin wire, to the axis of a parallel, cylindrical quartz reaction vessel (14). On the other hand, in any experimentation where an extremely large number of flashes is required, a flash lamp is preferable since it can be automatically flashed many times. In most of the experiments reported below the number of flashes varied between one and three, and the total per cent decomposition was about 0.1%. The flash period was fairly long, about 300 μsec.

Preliminary Studies with Unfiltered Light

In some preliminary experiments (15) using light containing radiation of wavelengths near 1900 Å, ethane, carbon monoxide, and methane were measured. No hydrogen was formed. The ratio of ethane to carbon monoxide was greater than one, averaging about 1.25 and indicating the presence of biacetyl.

Using 400 mm. carbon dioxide, the ethane to carbon monoxide ratio fell to about 0.95. Traces of biacetyl (0.1 to 0.7 mm.) also reduced the ratio to slightly below unity, even though they were present in too small an amount to absorb the radiation. When the 1900 Å light was removed by interposing a cellophane filter, these amounts of biacetyl had no effect at all on the products, showing that the electronically-excited molecule which it quenched arises from light in the 1900 Å region.

In the experiments in this and in the following sections the ratio of methane to carbon monoxide was about 0.1. There is evidence from these studies that this methane is not formed from a disproportionation between methyl and acetyl radicals. For example, the acetyl radicals could be reduced to zero concentration by addition of carbon dioxide, without appreciably affecting the methane to carbon monoxide ratio. Instead, the methane appears to arise either from a primary photochemical act or from the collision of a hot methyl radical with acetone. If the primary photochemical step is indeed the origin of the methane at high light intensities, the photolysis of mixtures of acetone and acetone-d_6 should result in the formation of methane and methane-d_4, but not any other deuterated methanes. Such experiments are in progress.

A methane to carbon monoxide ratio of 0.1 has also been obtained in experiments made with a fairly intense light source (1). These authors detected ketene.

In an earlier flash photolysis study using unfiltered radiation (5), Khan, Norrish, and Porter photolyzed acetone to high conversions and in the presence of 480 mm. carbon dioxide. This gas was added to reduce the temperature rise. Their ratio of methane to carbon monoxide was the same as ours but their ethane to carbon monoxide ratio was about 0.9. This is quite consistent with our subsequent results on the deactivating effects of carbon dioxide and of traces of biacetyl. It also serves to indicate the limitations of using inert gases to reduce the temperature rise when excited states are present.

Studies with Filtered Light

In these experiments (16), a cylindrical cellophane filter was employed. It surrounded the reaction vessel and was protected from the exploding wire by a concentric close-fitting quartz tube. The quantum yields of carbon monoxide and ethane, or more precisely the ratios of each of these products to the acetone pressure, were independent of light intensity when it was varied by a factor of five. The quantum yield of carbon monoxide was constant over a range of acetone pressures varying from 7 to 160 mm. (though there may be a 15% drop at high pressures, ∽220 mm.). The yield of ethane decreased markedly with increasing acetone pressure, as in Fig. 1. This curve lies approximately between the curve found by Herr and Noyes at 3130 Å and their curve at 2537 Å (4). These authors used low light intensities and worked at constant absorbed intensity to reduce the effects of changing the relative amounts of the secondary free radical reactions as the radical concentration varies. The shape of our curve suggests the presence of two excited acetone states.

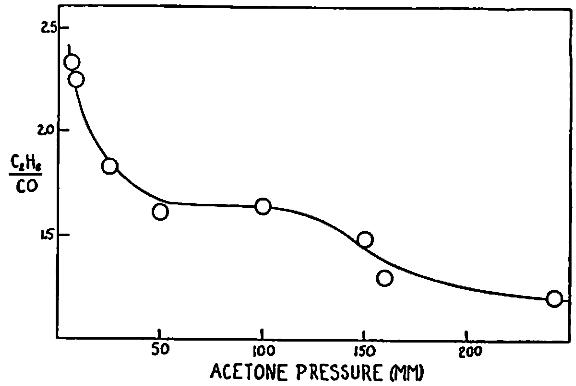

FIG. 1. Plot of ethane to carbon monoxide ratio vs. acetone pressure at room temperature. The point at 100 mm. is the mean of 1.62, 1.65, 1.66.

Since our yields were independent of the light intensity, either the temperature of the system in these experiments is that of the room or temperature effects can be neglected. We can compare these results, then, with some obtained in fluorescence studies made at a definite temperature.

Acetone has been shown to fluoresce from two excited states, both of which can be quenched by acetone molecules (3). No fluorescence enhancement was reported at any pressure. At 50° C. the quenching occurs appreciably at acetone pressures of about 150 mm. for both states. Studies as detailed as this do not appear to have been reported for 25° C., but the behavior of total fluorescence with pressure is about the same at 25° C. and 50° C. (6). Purely for the present purposes of discussion, it will be assumed that this behavior is also the same for each state at the two temperatures.

From the photolysis studies, in conjunction with those of Herr and Noyes and the foregoing results, it is inferred that the excited state which yields acetyl radicals and is deactivated in the low pressure region of Fig. 1 is probably not responsible for the fluorescence, although the one deactivated in the higher pressure range may be. Carbon monoxide also does not appear to be a product of either fluorescing excited state, unless the fluorescence behavior at 25° C. and 50° C. is rather different.

Studies in Progress

Studies in progress in this laboratory include the effects of added hydrocarbons, of oxygen. and of increased temperature on the lifetime of the excited acetone molecules.

CONCLUSIONS

The determination of the chemical reaction products of flash photolysis is particularly suited for studying the reactions of electronically-excited molecules. It is shown that the addition of inert gases, for purposes of reducing the possible temperature rise of the flash, has led to misleading information. These gases can deactivate excited molecules and so change the reaction scheme. A preferable procedure, it is suggested, is to test for the effects of any temperature rise, and a diagnostic test is proposed.

Results obtained on the flash photolysis of acetone in several studies in this laboratory are described.

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