

## Fluorescence and Photochemistry of Diacetyl

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Photochemical reactions are chemical reactions which are produced directly, or indirectly, by the absorption of radiation. The most important law in photochemistry is that of Grothus which states that only the radiation which is absorbed is capable of producing chemical reaction. The absorption of the radiation supplies the energy necessary to start the process of chemical reactions. One frequent method for the qualitative study of photochemical reactions has been to radiate with a wavelength which is absorbed and to analyze chemically the end products. However, in order to obtain information concerning the fundamental processes it is necessary to study the material while it is being radiated. This may be done by investigating the fluorescence, when produced, and also by investigating absorption during radiation.

The study of the fluorescence is very useful as it gives a means of investigating various processes which may occur and enter into competition with the fluorescence. Some of the processes are as follows: (1) Dissociation—i.e. the molecule upon becoming excited may dissociate into atoms or radicals. This probability of dissociation depends upon the energy and the lifetime in the excited state. Hence dissociation is a function of the wavelength of the incident radiation and temperature; (2) Collisions of Second Kind—that is, the energy of an excited particle is transferred to another particle by collision. This may mean a loss of electron energy or loss of vibration energy by the excited particle. The number of collisions would be a function of the pressure, i.e., number of particles present; (3) Chemical Reactions—that is, chemical reactions may occur which would not take place between unexcited atoms. Photo-oxidations would be examples of this reaction.

The study of absorption during radiation is very useful as it affords a means of studying the intermediate steps or products of a photochemical reaction. This is important as the intermediate products may exist only a short time. Such would be the case for a photochemical reaction in which free radicals were produced.

Diacetyl vapor absorbs from the blue down to the near ultra violet. Bandedges are found from 4,650 to 4,000  $\text{\AA}$ U. and the continuum goes down to 3,500  $\text{\AA}$ U. Fluorescence of diacetyl may be excited by the 4,358, 4,047, 3,650 lines of the mercury arc. The 4,358 line is most efficient. The apparatus used for the production of diacetyl fluorescence was a tube for the diacetyl vapor placed parallel to a mercury arc. Liquid filters were placed between the arc and fluorescing tube to insure monochromatic radiation and also for focussing purposes. The spectral distribution was obtained by the use of a fast Steinheil spectograph. The fluorescence of diacetyl consists of three broad bands, at 5,120  $\text{\AA}$ °, 5,580  $\text{\AA}$ °, 6,100  $\text{\AA}$ °, on which is superimposed some fine structure. This fluorescence has been studied under various conditions; namely, variation of pressure of diacetyl vapor, variation of intensity, and with admixture of oxygen.

The distribution in the spectrum is independent of the pressure in range of .1 mm. to 50 mm. The intensity of the fluorescence is directly proportional to the pressure over the same range. One can interpret this to mean that there is no self-quenching in this pressure range. That is to say, there is no effect of collisions upon the fluorescence which means that the excited particle must be stable against collisions with the unexcited diacetyl molecules.

The intensity of the diacetyl fluorescence has been found to be directly proportional to the intensity of the incident radiation over a five-fold range. For simple interpretation one would say this seems to indicate a single quantum process.

The intensity of the fluorescence is diminished by small amounts of oxygen. The oxygen is consumed upon continued illumination and the fluorescence increases in brightness. Thus one can follow the photo-oxidation by observing the fluorescence. The data obtained for the quenching of the fluorescence by oxygen show that the quenching does not follow the Stern-Vollmer<sup>1</sup> law.

The absorption of diacetyl vapor in the region of the green fluorescence has been investigated during radiation. No change of absorption is detected during the first illumination. However, if the vapor is radiated for a time then left in the dark for a period and then again radiated, marked changes are produced. In a short time after the second radiation begins the absorption reaches a sharp maximum. The absorption immediately decreases to a minimum which is followed by a broad maximum (in time). This maximum is followed by a plateau which precedes the final decay of absorption. A series of products follow one another, as in a radioactive series, the new substances absorbing light of longer wavelength than does diacetyl. The successive transformations are apparently induced by light and the products are detected by changes in the absorption of the vapor.

The purpose of this investigation is to draw from the above experimental facts and others such conclusions as one can concerning the details of the processes following the absorption of light in this molecule.

<sup>1</sup> Physik Zeit. 20, 183 (1919).