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Fluorescence of Diacetyl: Quantum Yield and Quenching by Iodine

A considerable amount of work has been done on the fluorescence of diacetyl,[1,2] but no measurements of quantum efficiency have been reported. Preliminary measurements of this quantity have just been completed. In the experiments the diacetyl was irradiated with filtered light from a small high pressure mercury arc at $\lambda\lambda$4358, 4047 and 3650. The energy of the fluorescence was measured with a photo-cell and electrometer tube and the incident energy with a photronic cell. Both detectors were calibrated at appropriate wave-lengths against a thermopile whose sensitivity had been determined with the use of a standard lamp.

Absorption coefficients for the diacetyl and tube windows were determined at the appropriate wave-lengths and the energy absorbed in the region seen by the photo-cell calculated. The absorption coefficients per cm path per cm pressure, and the quantum yields, in quanta of fluorescence per quantum absorbed, are listed below. The probable error in quantum yield is about 10 percent at λ4358 and is somewhat higher for the shorter wave-lengths. Between 2 and 5 cm the yield is independent of pressure.

Exciting Wave-length	Abs. Coeff. Diacetyl	Quantum Yield
4358	0.0158	0.033
4047	0.0103	0.0058
3650	0.0042	0.029

The absorption spectrum of diacetyl exhibits discrete structure between 4600A and about 4100A; below 4100A it becomes continuous. Since this change of structure may be due to the onset of predissociation it is not surprising that the fluorescence yield at 4047A should be sharply less than at 4358A. It is surprising that the yield rises again at 3650A.

Iodine has been found to be very effective in the quenching of irradiated diacetyl. With the addition of only 0.007 mm pressure of iodine to 49 mm of diacetyl the intensity of the fluorescence excited by λ4358 was reduced to less than 3 percent of the fluorescence without iodine. From this and other similar observations it appears that the effective cross section for quenching by iodine is at least 50 to 100 times greater than for quenching by oxygen which also strongly quenches the fluorescence.[2]

With continued radiation the fluorescence showed a recovery. Upon irradiating the described mixture of diacetyl and iodine for 3 hours the fluorescence recovered to about 15 percent of the intensity without iodine. In another experiment with a low undetermined pressure of iodine (order of magnitude, 0.001 mm) complete recovery was obtained in 30 minutes.

Diacetyl at a pressure of 49 mm absorbs energy from the source used at the rate of about 2×10^{13} quanta per sec. per cc. Assuming that in 3 hours practically all of 0.007 mm of iodine is used, one can calculate that the total number of excited molecules quenched is 20 to 30 times the number of iodine molecules originally present. One interpretation of this result is that the iodine molecule can quench many excited molecules before it loses its identity. Iodine, which shows discrete absorption at wave-lengths greater than 5000A, may very well be excited by collision with a molecule which fluoresces in the same region. Close resonance may be responsible for the large effective cross section for quenching the diacetyl fluorescence. In further experiments we shall look for sensitized fluorescence of iodine.

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[1] Matheson and Noyes, J. Am. Chem. Soc. **60**, 1857 (1938).
[2] Almy, Fuller and Kinzer, Phys. Rev. **55**, 238 (1939); more complete report of these experiments now in process of publication.