Maltol.—To 189 mg. of the above hydrochloride in 10 ml. of water was added 1 ml. of N sodium hydroxide and 50 mg. of palladium-on-charcoal catalyst. It was shaken twenty hours at 25° under 20 mm. more than atmospheric pressure of hydrogen. The absorption was 1.05 molar equivalents. The solution was acidified with hydrochloric acid and extracted several times with chloroform. Evaporation of the chloroform left a gummy brown solid from which maltol was isolated by sublimation at 130° followed by crystallization from benzene. The yield was 7 mg., m. p. and mixed m. p. 160–162°.[8]

Anal. Calcd. for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 57.48; H, 4.76.

Many hydrogenations were conducted, and the above is typical. The highest yield of maltol (17%) was obtained when the Mannich base hydrochloride was hydrogenated in absolute alcohol over palladium-on-charcoal at 100° and 100 atmospheres pressure. Adams platinum oxide catalyst and Raney nickel led to no maltol whatever. Chemical reduction with sodium methoxide[9] also failed.

The benzoate of synthetic maltol was prepared with benzoyl chloride in pyridine. It melted at 112–113° and the mixed m. p. was 113–114°.

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[8] We are indebted to The Cliffs Dow Chemical Corporation of Marquette, Michigan, for a sample of pure maltol from wood distillates.

[9] Cornforth, Cornforth and Robinson, *J. Chem. Soc.*, 682 (1942); Woodward and Doering, THIS JOURNAL, **67**, 863 (1945).

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On the Correlation of the Spectroscopic and Thermal Energy Differences between the Fluorescence and Phosphorescence Levels of Dye Molecules

BY M. KASHA AND R. E. POWELL

A general interpretation of the fluorescence and phosphorescence properties of polyatomic molecules on the basis of potential curve crossing suggests a limitation in the validity of the mechanism of luminescence of dyes proposed by Jablonski.[1] Whereas the scheme proposed by Jablonski uses a line energy level diagram, the new interpretation involves a radiationless intersystem "crossing" of potential curves for the first two electronic states above the ground state,[2] as shown in the figure. The potential curves as drawn represent time-average cross-sections, of the potential energy hypersurfaces for the electronic states, along the critical coördinate involved in the excitation of the triplet state[3] of the molecule. An analysis of the rates of the various processes occurring in the S′ state led to the conclusion that for a maximum probability of interaction[4] between the S′ and T states, the "crossing" must occur at the lowest point of the upper curve.

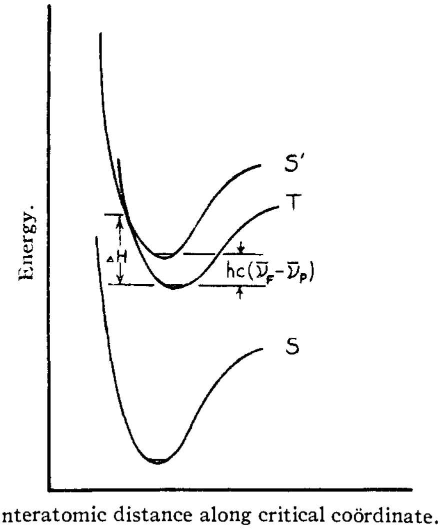

Fig. 1.—Schematic potential energy curves for the three lowest electronic states of a dye molecule.

According to the line energy level scheme of Jablonski, the spectroscopic energy difference between the zero-point energy levels of the fluorescent (unstable) and phosphorescent (metastable) states of a dye should be equal to the heat of activation required for lifting molecules from the phosphorescent to the fluorescent state. This theorem apparently was confirmed by the experiments of Lewis, Lipkin and Magel,[5] in which the fluorescence–phosphorescence energy difference for acid fluorescein dye in boric acid glass was found spectroscopically to be 9 kcal., while the heat of activation as determined by the temperature coefficient of the alpha process[6] of phosphorescence was found to be 8 ± 1 kcal.

However, according to the mechanism of excitation of the phosphorescent state based on potential curve crossing, the two experimental energy quantities may differ considerably in magnitude, if the point of crossing is not at the lowest point of the upper curve. This is shown in the figure, which compares schematically the two energy values for a case of high crossing. According to this picture, the heat of activation should equal or exceed the spectroscopic difference between the zero-point levels of the fluorescent and phosphorescent states.

For the best demonstration of this lack of correlation between the two energy values, (a) the dye should have as small an interval as possible between the zero-point levels of the S′ and T states, and (b) the emission spectra should have

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[1] A. Jablonski, *Z. Physik*, **94**, 38 (1935).

[2] M. Kasha, *Chem. Rev.*, in process of publication.

[3] The triplet state theory of phosphorescence as developed by Lewis and Kasha (THIS JOURNAL, **66**, 2100 (1944); **67**, 994 (1945)) is assumed in this treatment, although metastability of an electronic level may be due to various causes. However, the spectroscopic and magnetic studies of the phosphorescent state conducted in this laboratory have given strong evidence that the relatively long-lived, temperature-independent luminescence (β-phosphorescence) occurring 2000 to 12,000 cm.$^{-1}$ lower than the normal absorption band is, in general, due to a triplet-singlet transition.

[4] In the absence of heavy or paramagnetic atoms, and strong fields.

[5] Lewis, Lipkin and Magel, THIS JOURNAL, **63**, 3005 (1941).

[6] α-Phosphorescence involves a T-S′ thermal activation, followed by S′-S emission. Thus, although relatively long-lived, its spectrum is identical with the normal fluorescence spectrum. β-Phosphorescence corresponds to spontaneous T-S emission.

sharply defined structure, to permit an accurate determination of the interval between the zero-point levels[7] of the electronic states. Furthermore, a low relative quantum yield of phosphorescence (α plus β), compared with fluorescence, indicating a high point of crossing, should correspond to a large discrepancy of the two energy values as shown in the figure. The luminescence properties of such molecules as porphyrin, phthalocyanine and chlorophyll makes them especially suited for use in experiments to test these ideas.

In the case of acid fluorescein dye, aside from uncertainties in determining the spectroscopic energy value due to diffuseness of the emission bands, the high relative quantum yield of phosphorescence probably favored the correlation between the spectroscopic and thermal values.

A recent paper on the luminescence of inorganic crystalline impurity "phosphors" by Williams and Eyring[8] proposes an energy-coördinate diagram somewhat similar to the one discussed here. However, it will be noted that the physical systems and some aspects of the phenomena differ considerably in the two cases. Thus, in the present case the system consists of dilute solutions of the complex molecule in a homogeneous rigid *glassy* medium. Furthermore, the process of luminescence consists of transition between electronic levels of the complex molecule itself, with no electron transfer to the medium. In the phenomena treated by Williams and Eyring, energy levels of the crystal lattice are involved, with electron transfer from the absorbing center.

Although Williams and Eyring studied thermal properties of the inorganic phosphors, no spectroscopic data such as required for the correlation described above were included, although it is possible that an analogous relationship of spectroscopic and thermal energies may exist for inorganic luminescent materials.

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[7] The frequency of maximum intensity of a diffuse emission band (such as is obtained for an ionic dye) does not, of course, give the fundamental energy of the excited state, but merely the frequency of most probable emission, according to the Franck–Condon principle.

[8] F. E. Williams and H. Eyring, *J. Chem. Phys.*, **15**, 289 (1947).

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One-Step Synthesis of 1,2,3,4-Tetrahydrocarbazole and 1,2-Benzo-3,4-dihydrocarbazole

BY CROSBY U. ROGERS AND B. B. CORSON

1,2,3,4-Tetrahydrocarbazole has previously been synthesized in two steps—isolation of cyclohexanone phenylhydrazone followed by ring closure.[1] We have found that certain hydrocarbazoles, such as 1,2,3,4-tetrahydrocarbazole and 1,2-benzo-3,4-dihydrocarbazole, can be prepared by a one-step process which by-passes the isolation of the intermediate phenylhydrazones. There is considerable merit in this abbreviation of the synthesis because these phenylhydrazones are not stable. For example, cyclohexanone phenylhydrazone, although a clean, crystalline compound when first prepared, decomposes in a few days to a sticky, brown mass. An organic acid such as formic, acetic, or propionic can be used as combination solvent and catalyst, or the reaction medium can be water or aqueous alcohol with hydrochloric, phosphoric or sulfuric acid as catalyst.

Experimental

Organic Acid Method.—Phenylhydrazine (108 g., 1 mole) was added during one hour to a stirred, refluxing solution of 98 g. (1 mole) of cyclohexanone in 360 g. of glacial acetic acid. After refluxing and stirring an additional hour, the mixture was cooled to 5° and filtered. The crude solid was washed with water, 75% methyl alcohol, and air dried (yield, 150 g., 88%). Crystallization from methyl alcohol gave a first crop of 120 g. and a second crop of 24 g. The reaction goes equally well if acetic acid is replaced by formic or propionic acid. The solubilities of 1,2,3,4-tetrahydrocarbazole in 10 cc. of various solvents are: methyl alcohol, 0.5, 1.2, 1.8 g. at 10, 35, 55°, respectively; acetic acid, 0.5, 1.1, 2.0, 3.0 g. at 20, 39, 58, 68°, respectively; cyclohexane, 0.1, 0.5, 0.9, 1.5 g. at 1, 54, 69, 77°, respectively.

Aqueous Mineral Acid Method.—To a stirred, refluxing mixture of 500 cc. of water and 172 cc. (2 moles) of concentrated hydrochloric acid (d. 1.18) was added 108 g. of phenylhydrazine during five minutes. α-Tetralone[2] (145 g., 1 mole) was added during one hour, and the mixture was stirred and refluxed for an additional four hours. Worked up as above, the first crop was 123 g. and the second crop was 74 g.; 90% total yield. The solubility of 1,2-benzo-3,4-dihydrocarbazole in 10 cc. of methyl alcohol is 0.2, 0.5 and 0.8 g. at 0, 30 and 50°, respectively.

Aqueous Alcohol–Mineral Acid Method.—A mixture of 108 g. of phenylhydrazine, 920 cc. of 75% ethyl alcohol and 1.5 moles of hydrochloric acid was stirred and refluxed while 98 g. of cyclohexanone was added during one hour. The yield of air-dried 1,2,3,4-tetrahydrocarbazole was about 95%.

Where phosphoric acid was substituted for hydrochloric acid, the usual yield of tetrahydrocarbazole was obtained, but the product was contaminated by ammonium phosphate, although it was readily purified by crystallization from methyl alcohol. Where formic acid was employed in the aqueous alcohol–mineral acid method, the product was β-formylphenylhydrazine.[3] The latter was converted to tetrahydrocarbazole by boiling with an acetic acid or formic acid solution of cyclohexanone. β-Acetylphenylhydrazine remained unchanged upon similar treatment.

Inapplicability of Acetic Acid and Mineral Acid Methods for Synthesis of 6-Nitro-1,2,3,4-Tetrahydrocarbazole.—Refluxing a glacial acetic acid solution containing equivalent amounts of *p*-nitrophenylhydrazine and cyclohexanone produced an 80% yield of β-acetyl-*p*-nitrophenylhydrazine melting at 211–212°. The previously reported melting point of this compound was 205–206°.[4]

Anal. Calcd. for $C_8H_9N_3O_3$: C, 49.2; H, 4.7; N, 21.5. Found: C, 48.9; H, 4.8; N, 21.5.

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[1] Drechsel, *J. prakt. Chem.*, **38**, 69 (1888); Baeyer and Tutein, *Ber.*, **22**, 2178 (1889); Baeyer, *Ann.*, **278**, 88 (1893); Borsche, *ibid.*, **359**, 49 (1908); Perkins and Plant, *J. Chem. Soc.*, **119**, 1825 (1921); Ghigi, *Gazz. chim. ital.*, **60**, 194 (1930).

[2] Where the α-tetralone was not pure, owing to contamination with 5–10% of α-tetralol, the appropriate excess was added to compensate for the lack of purity. The ketone–alcohol mixture was analyzed according to Bryant and Smith, THIS JOURNAL, **57**, 57 (1935).

[3] Hirst and Cohen, *J. Chem. Soc.*, **67**, 829 (1895).

[4] Freund and Haase, *Ber.*, **26**, 1316 (1893); Hyde, *ibid.*, **32**, 1811 (1899).