solution. Assuming the density of the micelle to be 0.9, an approximate value of the rate constant in terms of moles reactants per liter of micelle can be calculated. Making this calculation it is found that the rate constants lie between 0.068 and 0.033 liter micelle mole^{-1} min.$^{1-}$. These values are approximately one-fourth to one-tenth the value of 0.29 liter mole^{-1} min.$^{-1}$ to be expected on the basis of the work of Crowell and Hammett.[6]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Effect of Inert Gases on the Quenching of Fluorescence in the Gaseous State[1a,b]

BY H. G. CURME[2] AND G. K. ROLLEFSON

The quenching of the fluorescence of β-naphthylamine by carbon tetrachloride in the gas phase has been studied with respect to its dependence on the wave length of the exciting light and on the concentration of gases which are not in themselves quenchers. It has been found that the quenching constant is about one-fourth as large when λ = 2537–2650 Å. is used for excitation than when λ = 3130 is used. This fact is in accord with Neporent's observations on the lifetimes with these modes of excitation. The addition of ethane or cyclohexane causes the apparent quenching constant to increase and it appears to approach a limiting value. This limit is independent of the nature of the added gas and of the light used for excitation. Such behavior is explained by assuming that the effect of the added gas is to deactivate the photoexcited molecule to the lowest vibrational state of the first excited level. These facts are represented by a set of processes for which rate constants are deduced. The dependence of the apparent quenching constant on the concentration of the added inert gas has been expressed in terms of these constants and it is shown that the theoretical curve is in good agreement with the experimental observations.

Introduction

It is a well known fact that the fluorescence of a substance dissolved in a non-polar solvent is usually independent of the frequency of the exciting light. This observation is explained by saying that the vibrational energy of the photoexcited molecule is removed by contact with the solvent molecules so rapidly that all transitions which lead to the emission of light occur from the lowest vibrational level of the excited state. On the other hand the fluorescence of substances in the gaseous state often shows a marked dependence on the frequency of the exciting radiation. This dependence may take the form of a variation in the quantum yield of fluorescence, a variation of the quenching constant or changes in the energy distribution in the fluorescence spectrum. If the explanation for the lack of such effects in the liquid state is correct it should be possible to eliminate them in the gaseous state by adding inert gases which will not quench the fluorescence but will remove vibrational energy from the excited state. In this paper we wish to present the results of some studies of the fluorescence of β-naphthylamine in which this goal has been achieved.

Experimental

A conventional d.c. resistance bridge circuit was used to measure fluorescent intensities relative to the intensity of a monitoring beam received by a 935 phototube; this arrangement eliminated errors which might be introduced by fluctuations of the light source. Light from the source was collimated by a lens and the beam split by a quartz plate. A portion of the beam passed through the filters, F_2, to the 935 phototube. The remainder passed through the filters F_1, described below, to the fluorescence cell and fluorescent light passed through the filters F_3, also described below, to a 931A photocell.

A 45-volt B.battery was used to power the 935 phototube while the 600–1000 volt stabilizing power supply described by Zimm[3] was used as a power source for the 931A tube. 50,000 ohm resistors were used between the dynodes of the 931A. The resistance legs of the bridge were set at 10,000 ohms and the bridge was balanced with a Rubicon portable galvanometer with a resistance of 1500 ohms and a sensitivity of 6 × 10^{-10} amp./mm. A bucking electromotive force across the resistance arm of the bridge in series with the 931A tube was adjusted until the galvanometer showed no deflection while the entire apparatus was dark. When both photocells were illuminated the balance reading of the bridge was then proportional to the photocurrent from the tube 931A. Tests with screens and filters showed that the response of both tubes and of the bridge was quite linear. In typical operating conditions the current through the 935 tube was about one microampere and that through the 931A tube ranged from one tenth to one microampere. The bridge could easily be balanced to half a per cent. of its total reading. Some variations in sensitivity of the tube with time were noted but these introduced no errors since unquenched and quenched readings were made within minutes of one another. Both phototubes were cooled with jets of compressed air.

The fluorescence cell was immersed in a heating-bath of Dow-Corning silicone oil "DC 200," 100 centistokes viscosity grade. This bath was found to transmit ultraviolet as far as the 2537 A. mercury line at elevated temperatures over a long period of time. The oil was contained by a rectangular 2.5-liter copper vessel with Corning 7910 windows. Temperature was controlled to within about one degree by varying the input to a 250-watt cartridge type heater immersed in the rapidly stirred bath. Temperatures were read on a 100–150 degree thermometer immersed in the oil. The oil bath was surrounded by two inches of glass wool insulation except at the windows where a dead space of two inches was maintained.

β-Naphthylamine.—Eastman Kodak Co. β-naphthylamine (m.p. 109.9°) was purified by sublimation at 180° in a stream of nitrogen. The purified material melted at 110.3°.

Carbon tetrachloride was purified three times by the method of Fieser.[4] The purified material distilled at a constant temperature of 76.6°.

Isoöctane was graciously provided by the Shell Development Co. After one pass through a silica gel column and distillation the liquid was found to be transparent at wave lengths longer than 2250 Å.

Commercial cyclohexane was passed through a silica gel

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(1) (a) From the Ph.D. thesis of H. G. Curme. (b) For material supplementary to this article order Document 3337 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) Eastman Kodak Co. Fellow 1949–1950. Present address: Research Laboratory, Eastman Kodak Co., Rochester, N. Y.

(3) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

(4) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 365.

column until no trace of the benzene absorption was observable on a Beckman quartz spectrophotometer and until the optical density at 2400 Å. through a 1-cm. cell was no higher than 0.02. The product was then distilled.

Ethane was taken from a cylinder of the gas supplied by Ohio Chemical Co.

Light Sources.—Appropriate filters were used in conjunction with a Hanovia low pressure quartz mercury arc type 16200. The set of filters F_2 consisted of a one centimeter solution of 0.2 g./l. potassium chromate and a two centimeter solution of 75 g./l. chrome alum plus 500 g./l. nickel sulfate hexahydrate. For work with the 3130 Å. group of lines the filters F_1 consisted of the above solutions plus three Corning 9863 filters. This exciting light was blocked from the photocell recording fluorescence by means of (F_3) a Corning 5940 filter and a one centimeter solution of the "cn" dye described by Kasha.[5] For work with 2650 and 2537Å. the filters F_1 were three Corning 9863 filters, a two-centimeter solution of 500 g./l. nickel sulfate hexahydrate and a one-centimeter solution of the "cn" dye. This exciting light was blocked from the photocell by using the Corning 5840 filter and the "cn" dye as before.

Absorption Spectra.—Figure 1 shows the absorption spectrum of the β-naphthylamine in isoöctane. This spectrum was obtained with a Cary recording quartz spectrophotometer and is in good agreement with that given in the "International Critical Tables." The addition of carbon tetrachloride in amounts large enough to reduce the fluorescence intensity to one-sixth of its original value produced no change in the absorption spectrum of the amine in the range 2500–3600 Å. The strong absorption of carbon tetrachloride prevents investigation at shorter wave lengths. Neporent[6] reports that gaseous β-naphthylamine at 150° has the following molar extinction coefficients at 3341 Å.: 1300 liters/mole cm. with no added gas; 1400 in the presence of 400 mm. of gaseous pentane; 1200 in the presence of 30 mm. of oxygen. Neporent's data at the other wave lengths show no more variation than this and it is therefore unlikely that isoöctane, cyclohexane or carbon tetrachloride vapors greatly affect the absorption spectrum of the gaseous amine.

Fluorescence Spectra.—Figure 1 also shows the density of plate blackening produced on an Eastman Kodak Co. 103-O spectroscopic plate by the fluorescence of the gaseous amine alone at 120°. The spectra of the amine both in the presence of 100 mm. of gaseous cyclohexane and mixed with 40 mm. of carbon tetrachloride were also photographed, all with a medium Hilger quartz prism spectrograph and all with the amine under 3130 Å. excitation. The lack of structure and the fact that the intensity of fluorescence in the presence of carbon tetrachloride decreased during exposure due to a photochemical reaction (discussed below) make precise comparison of the spectra difficult, but the position of the maximum is the same in all cases within 25–50 Å. and the added gases do not change the shape of the curve.

Quenching Measurements.—Reactors used in the quenching studies consisted of quartz or Pyrex bulbs of 300-cc. capacity connected with auxiliary Pyrex tubing having a volume of about 10 cc.; the large bulb was illuminated while the auxiliary tubing was kept dark. Solid fluorescer and an ampule containing the quencher were introduced into the tubing. Since the vapor pressures of β-naphthylamine are known[7] an amount of the fluorescer was weighed out such that it would vaporize completely to give a pressure about half the saturation value. The amount of quencher used was determined by running carbon tetrachloride into a weighed ampule, freezing it with solid carbon dioxide, evacuating, sealing off and finally reweighing. The sealed ampule was introduced into the apparatus so that a glass enclosed iron weight rested on its capillary tip. The bulb was evacuated, filled with the desired pressure of inert gas, and sealed off. Readings of "I_0," the initial light intensity, were taken after the fluorescer had vaporized; at the same time the quencher had been converted into vapor in the ampule. Then the weight was lifted by means of a solenoid and allowed to fall breaking the tip of the ampule and causing the quencher vapor to mix with the gases in the bulb.

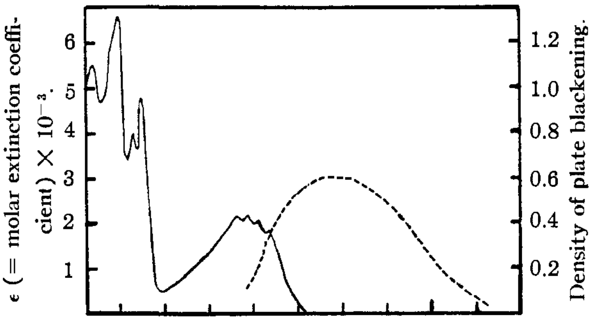

Fig. 1.—Absorption spectrum of β-$C_{10}H_9N$ in isoöctane at 25°, —; plate blackening produced by fluorescence of β-$C_{10}H_9N$ in gas phase at 120°, - - - - -.

Discussion

Immediately after the ampule containing the quencher was broken the fluoresence intensity dropped sharply and then steadied to a constant rate of decrease. This is believed to be due to the nature of the quenching process. It is probable that as a result of the quenching reaction the carbon tetrachloride is broken into a chlorine atom and a CCl_3 radical. West and Miller[8] have shown that ethyl iodide quenches the fluoresence of naphthalene in this manner and Bowen and Norton[9] have observed that carbon tetrachloride chlorinates anthracene in sunlight. The chlorine atoms produced in our system would react with the fluorescer and thus bring about a gradual reduction in the intensity of fluorescence. The rate of these processes was such that a final steady decrease in fluorescence intensity in the presence of quencher amounting to about 5–10% in 30 minutes was observed when the system was continuously illuminated. The intensity measurement made one minute after breaking the ampule was on the average 2% above the value obtained by extrapolating the final steady down drift back to the moment of quenching when only fluorescer and quencher were in the bulb. In the presence of the largest concentrations of cyclohexane and isoöctane used this intensity averaged 4% higher than the extrapolated value. It has been assumed that the back extrapolation gave the correct value of I, the intensity of quenched radiation corresponding to complete mixing of the reactants. All intensity readings have been corrected for a small amount of reflected exciting light which was not absorbed by the filter system. The magnitude of the correction was determined by noting the readings produced by empty bulbs at the temperature of the run to be made. The average correction was about 10% of the measured intensity.

Figure 2 shows a plot of I_0/I against (Q), the quencher concentration, at 120° for the two exciting lights used; the curves in this figure and in Figs. 3 and 4 are drawn in accordance with equations which are to be derived later. Figures 3 and 4 show plots of $(I_0/I - 1)/(Q)$, which is the apparent quenching constant according to the Stern–Volmer[10] equation, against concentration of added gas. It was possible to calculate the quenched intensities by making

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[5] M. Kasha, *J. Optical Soc.*, **38**, 929 (1948).

[6] B. Neporent, *J. Phys. Chem.* (*U. S. S. R.*), **21**, 1111 (1947).

[7] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

[8] W. West and W. E. Miller, *J. Chem. Phys.*, **8**, 849 (1940).

[9] E. J. Bowen and A. Norton, *Trans. Faraday Soc.*, **35**, 44 (1939).

[10] O. Stern and M. Volmer, *Physik. Z.*, **20**, 183 (1919).

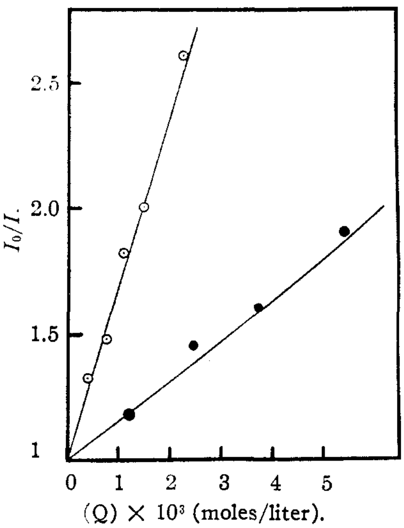

Fig. 2.—β-$C_{10}H_9N$ quenched by CCl_4: 3130 Å. excitation, ⊙; 2537-2650 Å. excitation, ● · t, 120°.

other assumptions: (1) mixing of the gases was complete by the first intensity reading and the remaining down drift was caused by a photochemical reaction, or (2) the back-extrapolated value of intensity was correct but the gas in the side tubing was almost pure quencher, mixing having occurred only in the large bulb. The extremes in calculated quenching constant obtained in these ways are indicated by the lines through the experimental points of Figs. 3 and 4.

It is apparent from an inspection of the figures that the value of the quenching constant depends on the wave length of the exciting light and increases when inert gas is added. The quenching constant appears to approach a limiting value which is independent of the wave length, of the nature of the added gas and of the temperature.

In order to account for the dependence of the quenching constant on the variables involved it is necessary to consider the various events which could happen to a photoexcited molecule. Such a molecule may fluoresce, undergo a monomolecular dark deactivation process, be quenched, or may proceed to another excited state by losing energy to another molecule. A first approximation to the kinetics of such a system may be made by assuming that there are only two excited states. Let F^* represent the fluorescer molecule in the lowest vibrational level of the first excited singlet state and F^{**} represent the molecule in the highly excited state produced by the higher frequency exciting light. F^{**} may be an entirely new excited singlet state or it may be a molecule in the first excited singlet level which has great vibrational energy. Let Q represent the quencher molecules and X molecules which can transform F^{**} into F^* but are otherwise inert

$$F + h\nu \longrightarrow F^{**} \quad (1)$$
$$F^{**} \longrightarrow F + h\nu \quad (2)$$
$$F^{**} \longrightarrow \text{dark products (not } F^*) \quad (3)$$
$$F^{**} + Q \longrightarrow \text{dark products (not } F^*) \quad (4)$$
$$F^{**} + Q \longrightarrow F^* + Q' \quad (5)$$
$$F^{**} + F \longrightarrow F^* + \text{dark products} \quad (6)$$
$$F^{**} \longrightarrow F^* \quad (7)$$
$$F^{**} + X \longrightarrow F^* + X' \quad (8)$$
$$F^* \longrightarrow F + h\nu \quad (9)$$
$$F^* + Q \longrightarrow \text{dark products} \quad (10)$$

(Self quenching has not been considered because it leads to deviations from the Stern–Volmer law in the limiting case of very large concentrations of X and such deviations were not observed experimentally.) Under steady state conditions it follows from the above list of processes that

$$\frac{I_0}{I} = \left[1 + \frac{k_{10}}{k_9}(\mathrm{Q})\right]\left[\frac{k_2 + k_6(\mathrm{F}) + k_7 + k_8(\mathrm{X})}{k_2 + k_3 + k_6(\mathrm{F}) + k_7 + k_8(\mathrm{X})}\right] \times$$
$$\left[\frac{k_2 + k_3 + (k_4 + k_5)(\mathrm{Q}) + k_6(\mathrm{F}) + k_7 + k_8(\mathrm{X})}{k_2\left[1 + \frac{k_{10}}{k_9}(\mathrm{Q})\right] + k_5(\mathrm{Q}) + k_6(\mathrm{F}) + k_7 + k_8(\mathrm{X})}\right] \quad (11)$$

This assumes that the addition of other gases does not change the absorption spectrum of F appreciably; the data of Neporent cited above indicate that this is at least approximately true.

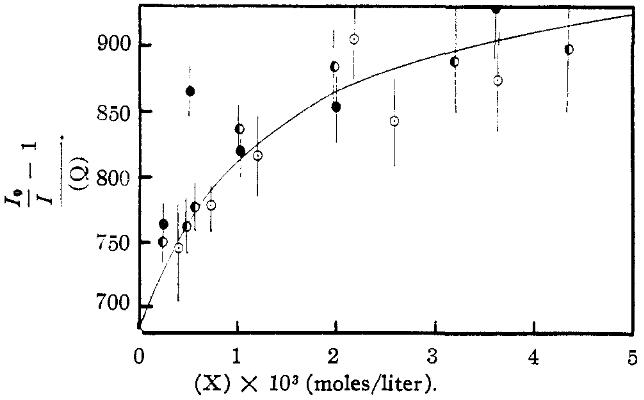

Fig. 3.—β-$C_{10}H_9N$ quenched by CCl_4: ethane added, 120°, ⊙; cyclohexane added, 120°, ●; cyclohexane added, 150°, ◐; λ = 3130 Å. Lines indicate probable error.

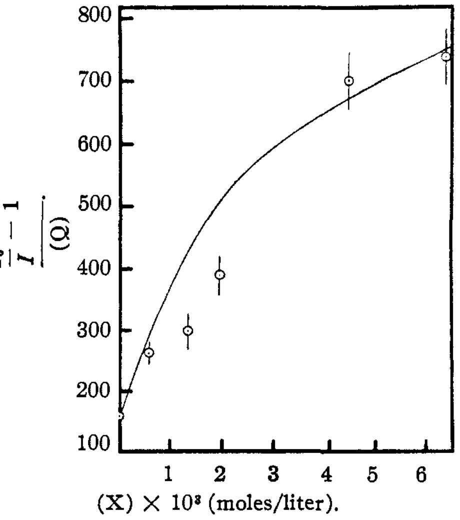

Fig. 4.—β-$C_{10}H_9N$ quenched by CCl_4 at 120°. Ethane added = (X) · λ = 2537-2650 Å. Lines indicate probable error.

The first factor in equation 11 represents Stern–Volmer behavior. All of the reactions involving

F** are presumably dependent on the wave length of the exciting light but those involving F* are not. Since X appears in the same manner in the numerators and denominators of the fractions it follows that at very large values of (X) these fractions will reduce to unity and the system will follow Stern-Volmer behavior with quenching constants which will be independent of the exciting light. Our results show that this condition is approached at moderate concentrations of such a gas as ethane.

It is possible to simplify equation 11 by some consideration of the relative probabilities of the processes (2) to (10). Neporent found that the fluorescent spectrum of β-naphthylamine is practically independent of the exciting light and we have found that carbon tetrachloride made no appreciable change in the fluorescent spectrum. It is rather unlikely that this state of affairs would prevail if both (2) and (9) contributed to the fluorescence, hence we shall assume that k_2 is zero. Process (7) must be considered to have a low probability and we shall assume that k_7 may be considered zero. The ratio $k_6(\mathrm{F})/(k_3 + k_6(\mathrm{F}))$ is the quantum yield of fluorescence of the pure amine relative to the highest yield noted in the gas phase and is a function of the wave length of exciting light. According to Neporent this ratio is roughly 0.75 at 3130 Å. and 0.17 at 2650 Å. In our experiments the 2537 and 2650 lines were not separated. However, when it is considered that in an arc of the type we used the 2537 line is strongly reversed and furthermore is less effective in producing fluorescence than the 2650 line it seems reasonable to conclude that our observations were concerned primarily with fluorescence excited with the 2650 line.

The limiting value of $K_\mathrm{Q} = (k_{10}/k_9)$ has been estimated to be 950 from the data plotted in Figs. 3 and 4. In order to give numerical values to the other constants let us assume that reaction (6) occurs at every collision of F with F**. The construction of a Hirschfelder model for the naphthylamine shows that 3.9 Å. is a reasonable radius to assume for that molecule. Such a value leads a value of 1.5×10^{11} for k_6 at 120°. The fluorescer concentrations were always close to 4×10^{-5} moles/liter therefore $k_6(\mathrm{F}) = 6 \times 10^6$. Then using Neporent's value for the quantum yield we get 2×10^6 for k_3 at 3130 Å. These figures with k_4 assumed negligible and a value of 6×10^9 for k_5 in equation (11) give the curve drawn through the experimental points of Fig. 2. The initial slope of this curve is 700, which is to be compared to the observed 683. Any appreciable value assigned to k_4 would increase the difference so we believe that the assumption that process (4) can be neglected is justified.

A similar set of calculations can be made for excitation by the shorter wave lengths. Since there is more energy to be removed when F** is produced by 2650 Å. radiation than when the 3130 line was used we could expect that k_5 and k_6 would be smaller than the values used for the longer wave length excitation probably by a factor of something less than one half. Taking $k_5 = 2.25 \times 10^9$, $k_6(\mathrm{F}) = 2.25 \times 10^6$ and Neporent's value of 0.17 for the quantum yield we find $k_3 = 11 \times 10^6$ and by using equation (11) the curve drawn in Fig. 2 is obtained.

The experimental results obtained with 3130 Å. excitation which are plotted in Fig. 3 were obtained with an average value of $(\mathrm{F}) = 4 \times 10^{-5}$ mole/liter and $(\mathrm{Q}) = 1.44 \times 10^{-3}$ mole/liter. The curve shown in the figure was calculated by means of equation (11) using these values, $k_3 = 3.75 \times 10^9$, and the values for the other constants given previously. In a similar manner the curve in Fig. 4 for the 2537–2650 Å. excitation was calculated using $(\mathrm{Q}) = 1.78 \times 10^{-3}$, $(\mathrm{F}) = 4 \times 10^{-5}$, $k_3 = 1.5 \times 10^9$, and the values for the other constants already given. In both cases K_Q was taken as 950.

It is apparent that the proposed scheme of reactions accounts for the experimental observations well within experimental errors and fits Neporent's observations on the quantum yield. That the scheme predicts a dependence of the quantum yield and quenching constant on fluorescer concentration slightly greater than Neporent observed is undoubtedly due to the oversimplifications involved. Of course it would be possible to fit the data with somewhat different values of the constants or by assuming more excited states but the constants which we have given form a self consistent set which can be given reasonable physical interpretation. Thus we find that the rate of deactivation of F** to F* is less the more energy that has to be removed regardless of what molecule is removing the energy. The constants we have given correspond to the following average amounts of energy removed from F** per kinetic theory collision with a molecule of the indicated type: β-naphthylamine 4000 cm.$^{-1}$; carbon tetrachloride and cyclohexane 250 cm.$^{-1}$; ethane 100 cm.$^{-1}$.

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