[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Quenching of Iodine Fluorescence by Benzene Vapor

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In connection with studies of the photochemical halogenation of benzene and of some of its derivatives[1] it was thought that it might be of interest to determine the mechanism of the quenching of iodine fluorescence by benzene vapor. The mechanism of this quenching must be more complex than that encountered in monatomic vapors such as mercury because of the large number of energy levels which may be involved.

Many previous studies of iodine fluorescence and of its quenching both by foreign gases and by magnetic fields have been made. Auto quenching has been studied by Stern and Volmer,[2] while the effect of argon has been studied by Turner[3] and by Koehler.[4] Elyashevitch[5] has studied the addition of hydrogen and of nitrogen, while Ramsauer[6] and Loomis and Fuller[7] have investigated the noble and electronegative gases and oxygen, respectively. The effect of a magnetic field in quenching the fluorescence has been investigated theoretically by Van Vleck[8] and studied experimentally by several authors.[9] Other references could be cited but have little bearing upon the work herein reported.

I. Experimental

Figure 1 shows a diagram of the apparatus. The iodine was Mallinckrodt reagent quality further purified by sublimation and drying with anhydrone and stored in the bulb A. The benzene had been purified for freezing point measurements in the laboratory of Professor Kraus.[10] It was fractionally distilled, dried with anhydrone and stored in the bulb B. Magnetic stopcocks were used to obviate the use of stopcock grease. The plungers of these stopcocks were sufficiently well ground in to allow a pressure increase of less than one millimeter per hour with a pressure difference of one atmosphere.

The fluorescence cell J was made of 25 mm. Pyrex tubing with plane Pyrex ends. The end opposite the photoelectric cell K was bent around to prevent back reflection as much as possible. For absorption measurements a quartz cell with plane ends and 20.5 cm. in length was employed.

The pipet for introducing known amounts of benzene is shown between the magnetic stopcocks D and E. The volume of this pipet was obtained by weighing the water it contained. Benzene vapor was admitted to the pipet when the reservoir B was maintained at a constant temperature and after closing D allowed to enter the apparatus by opening E.

Prior to making a run the trap G was immersed in liquid air and all stopcocks left open to remove mercury vapor and other condensable impurities.

A General Electric Sodium Lab Arc (H) was used as a source of exciting radiation. When operated at constant voltage it was found to give an exceptionally constant radiation of which only the sodium D lines would be appreciably absorbed by iodine vapor. The light was focused through the cell by means of a 12.7 cm. planoconvex lens (I). For absorption measurements a beam of parallel radiation was obtained by focusing the light from a 1-cm. aperture by means of the lens.

A photocell (GM visitron 73 A) and amplifying circuit were used to measure intensities. The amplifying circuit was essentially that designed and described by Horton.[11] The only important change consisted in operating the last tube by separate batteries from the amplifying and impedance tubes as this added somewhat to the stability. The entire amplifier and the photocell and leads were carefully shielded as a good deal of difficulty was experienced due to stray fields. A microammeter in the plate circuit was the indicating device. The plate current was first adjusted to zero for zero input. The response was found to be linear to impressed voltage over the range used. Since the photoelectric current is linear with light intensity for low intensities, the micrometer readings were proportional to the light intensity. This statement was further verified by taking readings of intensity from a point source of radiation and assuming the inverse square law of intensities.

For absorption measurements the potential drop of the photoelectric current across a 20-megohm resistor was impressed directly on the grid of the last tube since the beam was of high intensity. Since the point at issue here concerned the effect of benzene on the absorption coefficient, the direct relation of light intensity to plate current was not determined.

To determine the fluorescence the procedure was as follows. Iodine was admitted to the cell at its vapor pressure at 20°[12] and the intensity of the fluorescence determined. The iodine was then condensed with liquid air and a measurement made to make sure that no radiation other than fluorescent reached the photocell. The ben-

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[1] See Hart and Noyes, THIS JOURNAL, **56**, 1305 (1934), and earlier papers.

[2] Stern and Volmer, *Physik. Z.*, **20**, 183 (1919).

[3] Turner, *Phys. Rev.*, **41**, 627 (1932).

[4] Koehler, *ibid.*, **44**, 761 (1933).

[5] Elyashevitch, *Physik. Z. Sowjetunion*, 1, 510 (1932); *Phys. Rev.*, **39**, 532 (1932); *J. Exptl. Theoret. Phys.* (U.S.S.R.), **2**, 59 (1932).

[6] Ramsauer, *Z. Physik*, **40**, 675 (1927).

[7] Loomis and Fuller, *Phys. Rev.*, **39**, 180 (1932).

[8] Van Vleck, *ibid.*, **40**, 544 (1932).

[9] Turner, *Z. Physik*, **65**, 464 (1930); Genard, *Compt. rend.*, **197**, 1104 (1933); *Z. Physik*, **77**, 791 (1932); *Physica*, 1, 849 (1934).

[10] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

[11] Horton, *J. Franklin Inst.*, **216**, 749 (1933).

[12] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907).

zene reservoir had been surrounded by a bath to give the desired vapor pressure[13] and the pipet was now filled to the equilibrium pressure. The benzene was then condensed onto the iodine with liquid air and both were allowed to vaporize. Sufficient time (5 to 10 mins.) was allowed for equilibrium to be attained by diffusion. The intensity of the fluorescence was again measured. The pressure of the benzene was calculated from the ratio of the volumes. The average of a large number of readings was used for each point.

The fluorescent spectrum was photographed with a Hilger E-3 spectrograph using a glass train. Results similar to those already reported were found.[14] Attempts to photograph the fluorescence with benzene present failed, even though the diminution in total intensity amounted to only about 5%. This is probably due to the fact that transfer to so many energy levels occurs that the fluorescence, which is weak at best, is distributed among so many spectral lines as to be unobservable.

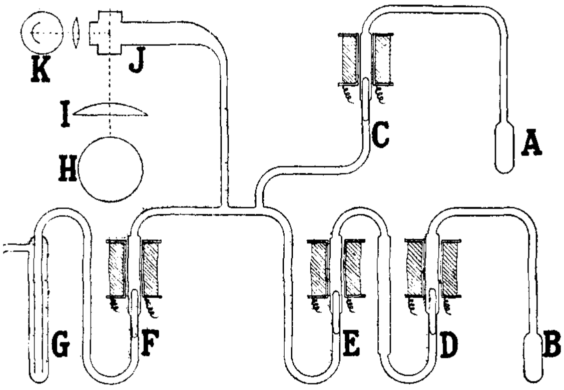

Fig. 1.

II. Results

With iodine at a pressure of 0.124 mm. and a path length of 20.5 cm., the fraction of the radiation absorbed was 0.087. This did not vary by more than 0.005 (about the maximum experimental error) with benzene pressures below 0.756 mm. We are justified, therefore, in assuming constant absorption over the range used.

The data on the fluorescence are summarized in the graph in Fig. 2 in which $1/Q = I_0/I_f$ is plotted against the benzene pressure. I_0 is the fluorescent intensity at zero benzene pressure and I_f is the intensity at a given benzene pressure. The points come from several different runs.

Attempts to iodinate benzene photochemically seem to have resulted always in failure and the present one is no exception. The light from the sodium arc was split into two parallel beams each incident on a photocell. The cell of iodine and benzene was placed in the path of one of the beams and the photocells balanced by resistances using a simple balanced vacuum tube circuit as a null indicator. The gases were illuminated by the entire radiation from a quartz mercury arc for twenty-four hours, the reaction vessel being of Pyrex. No time change in absorption could be found indicating the absence of reaction.

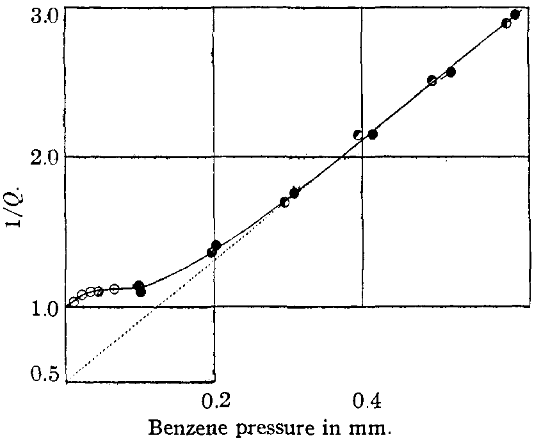

Fig 2.—●, Run 3; ◐, run 4; O, run 5.

III. Discussion of Results

The simplest mechanism for fluorescence and its quenching would be represented by equations (1)–(4).

$$I_2 + h\nu_1 = I^\circ \qquad (1)$$
$$I_2^\circ = I_2 + h\nu_2 \qquad (2)$$
$$I_2^\circ + B = I_2 + B \qquad (3)$$
$$I_2^\circ + I_2 = I_2 + I_2 \qquad (4)$$

This mechanism leads to

$$1/Q = 1 + k_3 P_1/(k_2 + k_4 P_2) \qquad (5)$$

where P_1 is the benzene pressure and P_2 is the pressure of iodine (here kept constant). Equation (5) is inadequate to represent the curve in Fig. 2 since the variation of $1/Q$ with benzene pressure should be linear.

The fluorescence of iodine is polarized to the extent of about 10% and this figure does not vary appreciably with iodine pressure.[15] This indicates that while iodine quenches its own fluorescence it exerts little influence in causing transfer of iodine molecules between various rotation and and vibration levels of the excited state. Foreign gases such as helium do, however, produce such an effect.[16] Such a decrease in polarization in the absence of true quenching would lead to an apparent increase in the intensity of the fluorescent radia-

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[13] "International Critical Tables," McGraw-Hill Book Co., New York, 1928, Vol. III, pp. 208, 221.

[14] Pringsheim, "Fluorescenz und Phosphorenz," Verlag von Julius Springer, Berlin, 1928, p. 56.

[15] *Cf.* Ref. 14, p. 108.

[16] *Cf.* Ref. 14, p. 136.

tion since observation is made at right angles to the incident beam. This effect is in the proper direction but is too small to make the above mechanism fit the facts. An increase in absorption due to the presence of benzene would also provide a change in the right direction, but no such increase was observed.

The inability to photograph the fluorescence in the presence of benzene indicated that this substance exerted a large influence in causing transfer of iodine molecules between various rotation and vibration levels of the excited state. With this in mind the complete mechanism for the fluorescent system would be represented by the following set of equations

$$I_2 + h\nu_1 = I_2^\circ \qquad (6)$$

$$I_2^\circ + B = I_2^j + B\ (j = 1,2,\ldots.n)\ k_2 \qquad (7)$$

$$I_2^j = I_2 + h\nu_j\ (j = 0,1,2,\ldots..n)\ k_3 \qquad (8)$$

$$I_2^j + B = I_2 + B\ (j = 0,1,2,\ldots..n)\ k_4 \qquad (9)$$

$$I_2^j + I_2 = 2I_2\ (j = 0,1,2,\ldots..n)\ k_5 \qquad (10)$$

$$I_2^j + B = I_2^i + B\ (j = 1,2,\ldots.n;\ i = 1,\ldots n)\ i \neq j)\ k_6 \qquad (11)$$

Reformation of the I_2° state is neglected because one of the other states will differ from this state only in being oriented in random fashion. This mechanism leads to equation (12).

$$1/Q = [1 + P_1(k_4^\circ + \Sigma_j k_2^j)/(k_3^\circ + k_5^\circ P_2)]/[1 + k_3^1\alpha_1(P_1)/Fk_3^\circ + k_3^2\alpha_2(P_1)/Fk_3^\circ + \ldots] \qquad (12)$$

$1/F$ is the factor by which the intensity of fluorescence from state I_2° must be multiplied to give the intensity with random orientation. $\alpha_1, \alpha_2, \ldots$ are ratios of the concentrations of the various states to that of the molecules in the state I_2°. The α's are all ratios of nth degree polynomials in the benzene pressure and tend toward constancy at high benzene pressures.

At relatively high benzene pressures the curve in Fig. 2 becomes a straight line. The slope divided by the intercept for this straight line should be $(k_4^\circ + \Sigma_j k_2^j)/(k_3^\circ + k_5^\circ P_2)$. As P_1 approaches zero the slope becomes approximately $k_4^\circ/(k_3^\circ + k_5^\circ P_2)$ since $1/F$ is not far from unity.

It can be shown conclusively that equation (12) based on only one intermediate state ($j = 1$) cannot be made to fit the data. With two intermediate states the fit is well within experimental error, although in the actual system many more states must be involved. The inclusion of more states would unquestionably improve the agreement slightly since more arbitrary constants would at the same time be introduced.

Constants were evaluated for the case with two intermediate states resulting in equation (13)

$$1/Q = (348\ P_1^3 + 42.3\ P_1^2 + 5.50\ P_1 + 1)/(86.2\ P_1^2 + 1.465\ P_1 + 1) \qquad (13)$$

Table I shows the applicability of equation (13) to the three different runs included in Fig. 2.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED QUENCHING OF IODINE

(Pressure of I_2, 0.2 mm.)

Run	Pressure of benzene (P_1), mm.	Average deflection	1/Q (obsd.)	1/Q (calcd.)	Δ(1/Q)
3	0.00	67.6	1	. .	. .
	.101	61.3	1.10	1.16	0.06
	.202	47.7	1.42	1.39	− .03
	.308	34.8	1.76	1.75	− .01
	.414	31.5	2.15	2.15	.00
	.520	25.4	2.56	2.56	.00
	.607	22.9	2.95	2.90	− .05
4	0.00	69.3	1	. .	. .
	.098	61.0	1.14	1.15	0.01
	.196	50.8	1.36	1.37	.01
	.295	41.0	1.69	1.70	.01
	.394	32.3	2.14	2.07	− .07
	.494	27.6	2.51	2.47	− .04
	.595	24.0	2.89	2.86	− .03
5	0.00	76.9	1	. .	. .
	.011	74.8	1.03	1.04	0.01
	.022	71.1	1.08	1.07	.01
	.033	69.9	1.10	1.09	− .01
	.044	70.0	1.10	1.11	.01
	.055	70.0	1.10	1.11	.01
	.066	68.4	1.12	1.12	.00

The initial slope as obtained from equation (13) is 4.03. The ratio $k_5^\circ P_2/k_3^\circ$ may be obtained approximately from the work of Koehler,[4] who used the yellow line of mercury among others in studying the auto quenching of iodine fluorescence. He gives 4.16 for this ratio. If the kinetic theory radius of 2.23 Å. is used for iodine and 2.90 Å. is taken for the radius of the benzene molecule, the mean life of the I_2° molecule is found to be 2.1×10^{-6} sec. This may be compared to 3.8×10^{-6} seconds obtained by making a similar calculation based on the auto quenching experiments of Koehler.[4] Uncertainties in the radii could easily account for the difference. To put the matter in a slightly different way, if 10^{-7} second is taken as the mean life of the I_2° molecule, the sum of its effective radius and that of the benzene molecule is 23.7 Å.

The situation as regards the high pressure part of the curve is somewhat more complex. The straight line representing this part of the curve has a slope divided by intercept of 8.06. It is now seen that

$$k_4^\circ + k_2^1 + k_2^2 = 8.06\, k_3^\circ (1 + k_5^\circ P_2/k_3^\circ) = 41.6\, k_3^\circ \quad (14)$$

Since $k_4^\circ = 20.8k_3^\circ$ from the initial slope it follows that $k_2^1 + k_2^2 = k_4^\circ$ and the amount of quenching of the I_2° molecule is approximately equal to the amount of transfer to other energy levels. While from equation (13) the initial and high pressure slopes are equal, the figure for the initial slope cannot be obtained with high precision.

While it is not possible to draw quantitative conclusions concerning the life times and quenching of the intermediate states there is no reason to assume that they differ radically in these respects from the initially formed state. Probably their quenching would be slightly lower if anything.

The curve may be described in words as follows. At the beginning one excited state predominates and it either fluoresces or is quenched by a Stern–Volmer mechanism (equations (1–5)). During the horizontal portion of the curve the importance of intermediate state formation becomes greater and greater until the relative concentrations of all excited states attain approximately constant values, after which the high pressure straight line portion is reached.

In conclusion the authors wish to express their appreciation to Dr. R. M. Fuoss for evaluating the constants in equation (13).

Summary

1. The quenching of iodine fluorescence by benzene at pressures of the latter below 1 mm. has been studied.
2. The quenching is not of the simple type encountered in some systems and a complete explanation necessarily involves the assumption of several excited states which may be formed from the primarily excited state by collision. The use of two such states leads to a satisfactory equation, but a larger number probably take part in the phenomenon.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Constants of Acetylenic Compounds. VI. Acetylenic Acids

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It has been shown by the authors[1] that the members of the fatty acids are not associated in dioxane and this is undoubtedly true for at least the majority of organic acids. In their work on acetylenic compounds the authors obtained a certain number of propiolic acids as intermediates in their preparations and it was felt that the moments of these compounds might be of some interest. While the carboxyl group is quite complex, it was thought that it might be possible to determine whether or not the triple bond has an effect on that moment. The article also reports data obtained on some substituted benzoic acids, benzoic acid and phenylacetic acid.

Preparation of Compounds

The substituted phenylpropiolic acids were made from the corresponding substituted toluenes. These substituted toluenes were oxidized to aldehydes with chromic acid, converted to the corresponding cinnamic acids by means of the Perkin synthesis and the acids changed to the ethyl esters. The ethyl esters were brominated and the dibromo esters treated with alcoholic potassium hydroxide. The phenylpropiolic acids were precipitated in a rather impure condition by the addition of water and hydrochloric acid. They were purified by dissolving them in a basic solution followed by fractional precipitation from an ice-cold solution by the addition of hydrochloric acid. The acids were further purified by crystallizing them from acetic acid until a constant melting point was obtained.

Propiolic acid was prepared by first brominating fumaric acid in a bomb at a temperature of 130°. The impure α,β-dibromosuccinic acid was purified by crystallization from water. The dried dibromosuccinic acid was treated with alcoholic potassium hydroxide, the solution filtered and the filtrate acidified with sulfuric acid. After refluxing for an hour the acid was extracted with ether, the ether distilled and the acid purified by fractional distillation under reduced pressure. The acid was further purified by crystallization from carbon bisulfide until a constant melting point was obtained.

In the preparation of tetrolic acid, acetoacetic ester was chlorinated to form β,β-dichloroethyl butyrate. The chloro compound was dehydrohalogenated by treating it with an aqueous solution of potassium hydroxide to which a few cc. of ethyl alcohol had been added. The alkaline solution was acidified with dilute hydrochloric acid and the tetrolic acid extracted with ether. The ethereal solution was dried over calcium chloride, the ether distilled and the acid fractionally distilled under reduced pressure. After

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[1] Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).