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The Photoisomerization of the o-Nitrobenzaldehydes

I. Photochemical Results

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Numerous disparate explanations have been advanced for the observed quantum yield in the photoisomerization of o-nitrobenzaldehyde. The authors decided to gather further data on this reaction, varying such factors as the weight of the molecule and the physical state of the material. The results indicate that the reaction occurs intramolecularly, but that for o-nitrobenzaldehyde itself the quantum efficiency is nearly one-half in all cases. A detailed consideration of the mechanism is deferred to the second portion of this paper.

INTRODUCTION

THE reaction of o-nitrobenzaldehyde to give o-nitrobenzoic acid upon illumination has been found to proceed entirely by an intramolecular rearrangement¹ with no side or reverse reaction, and the same may be said of the analogous reactions of 2,4-dinitrobenzaldehyde and 2,4,6-trinitrobenzaldehyde.²

The apparent simplicity of the reaction is belied by the quantum efficiency, which for the mono-nitro compound is almost exactly onehalf.³ This surprisingly low quantum efficiency, together with its nearness to a simple fraction, have been the subject of a considerable body of experimental work and theoretical discussion.^{3, 4, 5, 6} Conflicting explanations have been advanced, all but two of which have been either abandoned by their authors or disposed by the work of Zimmer.⁵ The remaining ones are his and that of Wegscheider,⁶ who postulates simply that of the absorbed quanta, half are lost by deactivation and the remainder cause reaction.

Zimmer's hypothesis is that every absorbed quantum splits off an oxygen atom; whereupon half of such atoms return to the nitroso group and the other half react with the neighboring aldehyde. Some objections to this view may be given. First, one might expect some evolution of hyde, at least from nitrobenzene. Second, m- and p-nitrobenzaldehyde should also show photoisomerization, which they do not. Third, the dissociation of a nitro bond by light of wavelength longer than 1900A is energetically improbable, but the reaction occurs at least to 4360A. Fourth, Zimmer's work was with a mixture of the aldehyde and pyrogallol, in which an entirely different reaction might occur.

oxygen molecules, if not from o-nitrobenzalde-

A quantum yield of one-half in the reaction of benzoquinone with ethyl alcohol⁷ was shown to be varied widely upon replacing the hydrogens of the benzene ring with other substituents or upon changing the nature of the solvent,⁸ from which the conclusions were drawn that the low quantum yield was due to a collisional deactivation of part of the quinone molecules which had absorbed light, and that the value of one-half for benzoquinone in pure alcohol was fortuitous.

The possibility of a similar set of circumstances in the nitrobenzaldehyde reaction led the authors to re-investigate the latter, under conditions which might be expected to produce a change in quantum yield. Thus, the number of nitro groups in the molecule was changed, and the reaction in acetone solution was compared with that in a nonpolar solvent and in the solid phase.

Apparatus, Materials and Methods

The arc, prism monochromator, and thermopile used have been described.⁷ As in the investigation of Weigert and Brodmann,³ the conduc-

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¹ Ciamician and Silber, Ber. 34, 2040 (1901).

² Fiedländer and Cohn, Ber. **35**, 1267 (1902); Sachs and Kempf, Ber. **35**, 2707 (1902). ³ Weigert and Kummerer, Ber. **46**, 1207 (1913); Weigert

^a Weigert and Kummerer, Ber. **40**, 1207 (1913); Weigert and Brodmann, Zeits. f. physik. Chemie **120**, 24 (1926); Weigert and Prückner, Zeits. f. physik. Chemie, Bodenstein Festband, 775 (1931).

⁴ Bowen, Hartley, Scott and Watts, J. Chem. Soc. 125, 1218 (1924).

⁵ Zimmer, Zeits. f. physik. Chemie **B23**, 239 (1933). ⁶ Wegscheider, Monats. f. Chemie **62**, 101 (1933).

⁷ Leighton and Forbes, J. A. C. S. **51**, 3549 (1929). ⁸ Leighton and Dresia, J. A. C. S. **52**, 3556 (1930).

tivity of the acid formed in the reaction was used for analysis of the product. The bridge and thermostat possessed no novel features. A dipping electrode in a Pyrex test-tube made the cell.

The manipulations of the solutions were orthodox: solutions were exposed in a fused silica cell behind the exit slit of the monochromator. Those in acetone were then diluted with three volumes of conductivity water for analysis. Solutions in ligroin were evaporated and then extracted with a known volume of acetone after exposure, and the solution diluted with conductivity water as before. The conductivity of a blank or unexposed solution was always subtracted, as in the calibration.

Solids were prepared for exposure by fusing a known quantity to a quartz plate and illuminating through the latter, thus reducing scattering; because the crystal interfaces were then perpendicular or parallel to the beam. Enough sample was used to absorb the beam completely. The plate bearing the exposed sample was placed in a beaker, and the aldehyde dissolved with six cc of acetone. Eighteen cc of conductivity water were added and the whole mixed together. Enough of the mixture to cover the glass shell of the dipping electrode was then poured into the conductivity cell. This was always allowed to stand fifteen minutes in the thermostat at 25°C before the conductivity was read. The room temperature was kept between 22°C and 24°C for all but a few measurements.

Acid formed during the reaction did not precipitate from an acetone solution, but did from one in ligroin. In consequence, the liquid became turbid. Reactions in ligroin were accordingly carried out in a broad flat cell which was slid along behind the monochromator slit every few minutes, so that no acid would cling to the front window. In addition, the solution was stirred. After exposure, the ligroin was evaporated and the solid taken up in the usual mixture of acetone and water.

The transmission before and after exposure was measured for those acetone solutions which were sufficiently dilute to transmit appreciably, but the turbidity of the ligroin solutions prevented accurate observations after exposure. For example, a straightforward calculation for 0.04 precent o-nitrobenzaldehyde in ligroin at 3660A gave $\Phi = 0.57$. If, instead, one calculates what the transmission should have been had there been no scattering and uses this value to compute Φ , the result is 0.52.

The measurements and calculations of quantum efficiencies for the reactions in solution were carried out in the manner reported for the quinone-alcohol reaction,⁷ with such differences as were made necessary by the difference in materials. The calculation of quantum yields in solids presents two difficulties not usually encountered in solutions. The reaction product piles up at or near the surface exposed to light, making a non-uniform filter, and the reflection from the crystal surfaces is difficult to calculate.

Both effects can be circumvented experimentally. The light scattered from crystal interfaces may be collected in large fractions by a lens of wide aperture and short focus and measured with a thermopile, while to avoid absorption by the reaction product one may extrapolate to the start of the reaction.

It remains to discover the proper method of extrapolation. Consider a crystal divided into infinitesimal layers parallel to its front surface. In the first instant of illumination, a certain fraction of the material in the first layer will be changed, and in the next instant, the same fraction of the remainder, and so on. This process leads to a logarithmic decrement of the reaction rate. In the second layer, the same thing happens, but there is the additional complication that the extinction coefficient of the product differs from that of the original material, and accordingly, the intensity, constant on the first layer, will be exponentially changing on the second. The product of these two exponential factors is itself exponential, so that the reaction rate undergoes a logarithmic decrement in the second layer as well. The argument for the third layer is the same. Indeed, we may expect a similar conclusion for the whole crystal.

Now if the logarithm of the instantaneous value of the quantum efficiency, Φ_i , is plotted against the number of quanta absorbed, N_q , the result should be a straight line. The apparent quantum efficiency, Φ_a , calculated on the basis of the total number of quanta absorbed, is what is measured. A plot of this should also give a straight line, with half the slope of the preceding

one. For, using the slope-intercept formula for the equation of the graph of Φ_i against N_q ,

$$\log \Phi_i = m N_q + \log \Phi,$$

where Φ is the true value, obtaining at the start of the reaction, and *m* is the slope. From the relation for the apparent value,

$$\log \Phi_a = (\log \Phi_i + \log \Phi)/2,$$

we have $\log \Phi_a = mN_q/2 + \log \Phi$. One must, then, plot a number of observed values of $\log \Phi_a$ against N_q and fit a straight line to the points.

In this derivation it has been assumed that the extinction coefficients of reactant and product remain constant. As a matter of fact, particularly in ionic crystals, they will change as the reaction progresses, because of the distortion of the crystal lattice. Some such effect is noticeable in the researches of the Göttingen investigators⁹ on the photoreduction of alkali ions in alkali halide crystals. When their results are plotted according to the system here outlined, they yield initial quantum efficiencies close to unity for this process, but the points corresponding to long exposures fall off the line. The high opacity of the alkali halides in the Schumann region may be partly responsible, for the thickness in which most of the reaction occurs is small, and only a short exposure is required to produce almost complete change of the first layers.

The o-nitrobenzaldehyde used was a Kahlbaum product, and was further purified by taking up in benzene to reject the acid which it contained. The solvent was then evaporated and the aldehyde recrystallized four times from dilute alcohol and from hot water. Some of the material was vacuum sublimed, all operations being performed in the dark. The highest melting point reached was 43.5°C. Other reported melting points range from 39.4°C to 46°C.

The 2,4-dinitrobenzaldehyde was synthesized after the method devised by Sachs and Kempf, with the improvements suggested by Lowy and Wescott.¹⁰ After recrystallization from ligroin and from hot dilute alcohol, it melted at 71°C.

The 2,4,6-trinitrobenzaldehyde was obtained from the Eastman Kodak Co. and recrystallized as above. It melted at 119°C. The various nitrosobenzoic acids for calibration of the conductivity-concentration curves were prepared by making successive dilutions of the corresponding aldehydes in acetone and insolating till the conductivity of the most concentrated solution showed no further change. These solutions were then each diluted with three volumes of conductivity water and their conductivities read. From each result there was subtracted the conductivity of a corresponding unexposed solution, and the results were plotted.

EXPERIMENTAL RESULTS

The results for a number of determinations in solution are given in Table I, which includes also some molecular extinction coefficients (α). The Roman numerals refer to the three aldehydes.

TABLE I.

Material	λ	Concentration	1 Solvent	Φ	α
	4040	0.03%	acetone	0.46	35.6
I	3660	0.5	"	0.51	184
	3660	0.04	ligroin	0.52	181
II	3660	0.5	acetone	0.49	
	44	0.5	44	0.49	
	" "	0.1	"	0.48	
	**	0.01	44	0.48	188
III	3660	0.5	acetone	0.65	
	64	0.5	"	0.65	
	44	0.5	**	0.68	
	"	01	44	0.69	192
	**	01	"	0.63	272
	11	01	" "	0.66	
	**	0.04	ligroin	0.17	1030

Most of the solutions were stirred mechanically during the exposure. For two, nitrogen was used as an atmosphere. The observation of Weigert that oxygen, stirring, and concentration differences do not affect Φ for o-nitrobenzaldehyde was found to hold for the other two compounds also. The change of α and Φ with change of solvent in the last measurement is a field for further investigation.

The results for the reaction in the solids are graphed in Figs. 1 to 3. The points in the first diagram of Fig. 1 were taken before the procedure was well standardized, and the line was fitted to them by minimizing the sum of the squares of the normal deviations. The points for

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⁹ E.g., Smakula, Zeits. f. Physik **63**, 762 (1930). ¹⁰ Lowy and Wescott, J. A. C. S. **42**, 852 (1920).

Lony and Wescoll, J. M. C. S. 42, 052 (1920).



FIG. 1. Apparent and actual quantum efficiencies for the photoisomerization of solid o-nitrobenzaldehyde.



FIG. 2. Apparent and actual quantum efficiencies for the photoisomerization of solid 2,4-dinitrobenzaldehyde.



FIG. 3. Apparent and actual quantum efficiencies for the photoisomerization of 2,4,6-trinitrobenzaldehyde.

the mono-substituted compound at 2654A scatter rather badly, but a quantum yield of somewhat less than 0.5 is indicated. The other lines were fitted by inspection; the points are so nearly collinear that analytical devices were unnecessary.

DISCUSSION

Insofar as this work repeats that of Weigert on o-nitrobenzaldehyde in acetone solutions, the two are in agreement. It is true that he found that Φ increased with dilution at 4040A, but he considered this a spurious effect caused by his assumption that α , measured for a concentration of 1 percent, remains constant. Measurement shows that α actually does increase with dilution by the right amount to reduce Weigert's measured Φ 's to about 0.5. Bowen, Hartley, Scott and Watts,⁴ without the refinements in technique used here, obtained an unweighted average of $\Phi = 0.46$ for solid o-nitrobenzaldehyde, in agreement with the value of 0.5 reported in the present paper. The quantum efficiency for this compound is thus seen to be nearly one-half, in acetone and ligroin solutions, and in the solid state, and over a wave-length range from 4360A to 3130A at least.

It is evident that a simple collisional deactivation hypothesis, such as was applied to the quinone-alcohol reaction, will not suffice to explain these results. The yield determining process must be intramolecular, in accord with the apparent intramolecular nature of the reaction.

The same quantum yield is found for the di-substituted compound, both in solid and solution, at 3660A, where the ortho nitro group does the absorbing, and the same conclusions hold. The case of the tri-substituted compound differs because of the effects of a nitro group on both sides of the aldehyde. Discussion of its behavior must await a quantitative discussion of the intramolecular interactions (part II).

The lower quantum efficiencies found at shorter wave-lengths in the solid state may in every case be plausibly assigned to an inner light filter effect of other portions of the molecule, although this is not the only possibility (part II).