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The Photoisomerization of the o-Nitrobenzaldehydes

II. Mathematical Treatment

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The probable course of the reaction, from the absorption of light to the formation of the isomer, is followed in roughly quantitative detail. In this manner, the low quantum yields, surprising at first sight for intramolecular processes, are explained by a consideration of the physical properties of the molecules.

IN the preceding paper it was stated that the process which determines the observed quantum efficiency of one-half in the isomerization of o-nitrobenzaldehyde to o-nitrobenzoic acid must be intramolecular. A consideration of the possible nature of such a process will involve an examination into, first, the bond or group which absorbs the actinic light, second, the relative orientation of the reacting groups, and third, the relative probabilities of energy transfer by resonance between bonds, of deactivation, and of reaction.

A comparison of the absorption spectra of o- and m-nitrobenzaldehyde, nitrobenzene and benzaldehyde[1] shows clearly that for wavelengths longer than about 3100A, the nitro group is the only portion of the molecule which appreciably absorbs. This absorption is presumably effected by the electrons of the two nitrogen-oxygen bonds, the absorption probability in the two being equal.

THE ORIENTATION OF THE NITRO AND ALDEHYDE GROUPS

The relative orientation which may be assumed for the nitro and aldehyde groups involves the question as to whether these groups are freely rotating, or are constrained to a particular position by intramolecular forces. The constraints which need to be treated are those varying with the rotation of the substituents, aldehyde and nitro, which together with the phenylene residue will be chosen as constituents of the molecule. The position-sensitive interactions of these groups, since they bear no free valences, will be made up of second and higher order terms.

It will be recognized that, if one plots the energy of a given configuration as altitude on a contour map, using the rotation of the nitro group as abcissa and that of the aldehyde as ordinate; then the lowest point is the position of stable equilibrium and the height of the lowest pass is the energy required to produce rotation. The first-order interaction between the nitro and aldehyde will be a slight steric hindrance because they are somewhat closer than the sum of their kinetic theory radii. If the groups are supposed to be surrounded by spheres of influence, there will be no change in the magnitude of repulsion on rotation, but this is probably too crude a picture; prolate spheroids doubtless better represent the facts. However, since the shape of these is unknown, the first order repulsion will not be further considered.

The second-order interactions, if calculated according to the theory of London,[2] would also give no constraint to free rotation. However, this theory assumes that the groups possess isotropic polarizabilities, i.e., that an impressed electric field induces the same electric moment for any relative orientation of group and field. This is far from being true in the present case. No measurements of the actual components of the polarizability tensors are possible for the groups under consideration, but such measurements have been made for molecules closely analogous to the groups considered here.[3] Benzene, sulphur dioxide and hydrogen cyanide, that is, are similar to phenylene, nitro and aldehyde. To change the molecular values to fit a corresponding radical, one has to multiply each component for the mole-

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[1] Purvis and McCleland, J. Chem. Soc. **103**, 1088 (1913).

[2] London, Zeits. f. Physik **63**, 245 (1930).

[3] Wolf, Briegleb and Stuart, Zeits. f. physik. Chemie **B6**, 195 (1930).

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cule by the ratio of the mean polarizabilities of radical and molecule. The radical components, which we shall call α_{11}, α_{22} and α_{33} in descending order of magnitude, are obtained for the principal axes of the group. They are transformed to a coordinate system (x, y, z) embedded in the molecule by the customary formula. For example:

$$\alpha_{xz} = \alpha_{11}\cos(1, x)\cos(1, z) + \alpha_{22}\cos(2, x) \times\cos(2, z) + \alpha_{33}\cos(3, x)\cos(3, z). \quad (1)$$

Here α_{xz} is numerically equal to the x-component of the moment induced by a unit field in the z-direction, i.e., the xz-component of the polarizability tensor referred to the (x, y, z) system.

For the calculation of the second-order interaction it is also necessary to know the size of the dipoles associated with the nitro and aldehyde groups. Now the total moment of a dipole molecule is made up of the intrinsic moment belonging to the electrically asymmetric part and the induced moment which this produces in the (polarizable) remainder of the molecule. Calling the intrinsic moment ξ, the induced moment η and the total μ, we have the equation $\xi + \eta = \mu$, and also $\eta = \alpha \cdot \mathbf{F}$, where $\mathbf{F}$ is the field strength caused by ξ and α is the polarizability of the remainder. These equations may be solved simultaneously for ξ, taking the tensorial nature of α into account.

The nitro ξ was resolved along the two N–O bonds. Each ξ was allocated to the centroid of the corresponding group, for this is the centroid of positive charge, and that of negative charge must be close by.

The second-order interaction is conveniently expanded, for computation, in terms of the electric moments connected with transitions between the various energy levels. As London has shown,[2] the simple formulation is not valid for that portion which is expanded in terms of the rotational energies. This portion, however, makes up the dipole interaction and the induction effect of classical theory. The remainder of the second-order interaction energy is called the dispersion effect by London. The first two take the forms:

$$E_{\text{dip}} = -\frac{1}{R^3}[2\xi_x'\xi_x'' - \xi_y'\xi_y'' - \xi_z'\xi_z''] \quad (2)$$

and

$$E_{\text{ind}} = -\frac{1}{2R^6}[4\alpha_{xx}'\xi_x''^2 + \alpha_{yy}'\xi_y''^2 + \alpha_{zz}'\xi_z''^2] - \frac{1}{2R^6}[4\alpha_{xx}''\xi_x'^2 + \alpha_{yy}''\xi_y'^2 + \alpha_{zz}''\xi_z'^2]. \quad (3)$$

These interactions are computed for the three groups taken pair-wise, and the prime and second refer to the members of such a pair. The phenylene residue was considered to be dipole-free. The x-axis, of course, joins the centroids of the pair for which calculation is being made.

The dispersion effect demands a more thorough treatment. We have used Cartesian coordinates throughout, instead of the polars employed by London. His equation for the interaction in terms of the displacement components thus becomes

$$E_{00}^{(2)} = \frac{-e^4}{R^6} \sum_{k'l'} \left\{ \frac{[2(X_1)_{0k'}(X_2)_{0l'} - (Y_1)_{0k'}(Y_2)_{0l'} - (Z_1)_{0k'}(Z_2)_{0l'}]^2}{E_{k'} - E_0 + E_{l'} - E_0} \right\}. \quad (4)$$

Here, for example, the x-component of the displacement associated with the transition $O \rightarrow k'$ in group 1 is represented by $e(X_1)_{0k'}$. $E_{00}^{(2)}$ is the dispersion interaction, i.e., the second-order shift of the ground state expanded in terms of those transitions for which the system is originally in the ground state at room temperatures. R is the intercentroid distance. It will be seen that k' is a variable quantum number for group 1, as is l' for group 2. Each denominator is the sum of the energies of the corresponding transitions.

When the square is expanded, the numerators become

$$(4X_1^2X_2^2 + Y_1^2Y_2^2 + Z_1^2Z_2^2 + 2Y_1Y_2Z_1Z_2 - 4X_1X_2Y_1Y_2 - 4X_1X_2Z_1Z_2). \quad (5)$$

The quantum numbers are understood, having been omitted for compactness. Such electric moments can in principle be evaluated quantum-mechanically, but it is preferable to make use of the relation

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with the polarizability $\mathbf{m}=\alpha\cdot\mathbf{F}$; whereby sums of the unknown displacement components may be replaced by known polarizability components. Consider for example α_{xz}, again the x-component of the displacement induced by a unit field in the z-direction.

The eigenfunction of a group perturbed by a field F_z is[4]

$$\psi=\psi_0-eF_z\sum_i\frac{\psi_i\int\tilde{\psi}_iz\psi_0d\tau}{E_i-E_0}. \tag{6}$$

Multiply both sides by $\tilde{\psi}ex$ and integrate over configuration space:

$$e\int\tilde{\psi}x\psi d\tau=e\int x\left(\tilde{\psi}_0-eF_z\sum_i\frac{\tilde{\psi}_i\int\psi_iz\tilde{\psi}_0d\tau}{E_i-E_0}\right)\left(\psi_0-eF_z\sum_i\frac{\psi_i\int\tilde{\psi}_iz\psi_0d\tau}{E_i-E_0}\right)d\tau. \tag{7}$$

The first parenthesis is $\tilde{\psi}$ written in full. Performing the indicated multiplication:

$$e\int\tilde{\psi}x\psi d\tau=e\left[\int\tilde{\psi}_0x\psi_0d\tau-eF_z\sum_i\frac{\int\tilde{\psi}_0x\psi_id\tau\int\tilde{\psi}_iz\psi_0d\tau}{E_i-E_0}-eF_z\sum_i\frac{\int\tilde{\psi}_ix\psi_0d\tau\int\tilde{\psi}_0z\psi_id\tau}{E_i-E_0}+\cdots\right]. \tag{8}$$

The first term in brackets is the energy of the ground state, and it can be made to vanish by convention. The left side is the x-component of displacement produced by F_z. Accordingly, with the previous notation for matrix components of displacement:

$$\alpha_{xz}=-2e^2\sum_i[X_{0i}Z_{0i}/(E_i-E_0)]. \tag{9}$$

Finally, by selecting an effective average energy V for the denominators of our various expressions one obtains

$$E_{00}{}^{(2)}=-\frac{V}{8R^6}[4\alpha_{xx}{}'\alpha_{xx}{}''+\alpha_{yy}{}'\alpha_{yy}{}''+\alpha_{zz}{}'\alpha_{zz}{}''+2\alpha_{yz}{}'\alpha_{yz}{}''-4\alpha_{xy}{}'\alpha_{xy}{}''-4\alpha_{xz}{}'\alpha_{xz}{}'']. \tag{10}$$

This V was empirically found, in the cases investigated by London,[2] to lie near to the ionization potential of the groups involved. Accordingly, 12 v.e. were used in the present work. A more accurate determination could be made by integrating the measured absorption of the groups, but the necessary data are not at hand. The method of Mayer[5] might be used or the actual spectrum, appropriately plotted, might be planimetered.

The values of R were read from a diagram of the molecule, drawn to scale. Centroids were found by graphic statics. The aromatic C—C distance was assumed to be 1.42A, and the others were made up from Pauling's table.[6] All valence angles were assumed tetrahedral except O—N—O. Following Kohlrausch[7] this is taken to be 103°.

The sum of the dipole, induction, and dispersion effects is then calculated for a number of orientations and plotted in Fig. 1. The equilibrium configuration, represented by the lowest point, is that for which the molecule is coplanar. The lowest pass is seen to be that connecting successive equilibria of the nitro group.

Any attempt to rotate the aldehyde group more than about 90° would produce large repulsions in addition to those shown on the diagram because of steric hindrance between the oxygens of the nitro and aldehyde groups. In any case, it seems probable that in 2,4,6-trinitrobenzaldehyde the aldehyde group stands more or less perpendicular to the plane of the ring as a result of interaction with nitro groups on both sides of it.

The pass for the ortho compound has a height of 1380 cal./mol., i.e., 2.4 RT. In consequence, the rotation will be greatly hindered, but not altogether eliminated. For the tri-substituted

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[4] Sommerfeld, *Wellenmechanischer Ergänzungsband*, p. 173, Vieweg, Braunschweig, 1929.

[5] Mayer, J. Chem. Phys. **1**, 270 (1933).

[6] Pauling, Proc. Nat. Acad. **18**, 293 (1932).

[7] Kohlrausch, *Der Smekal-Raman-Effekt*, p. 194, Berlin, 1930.

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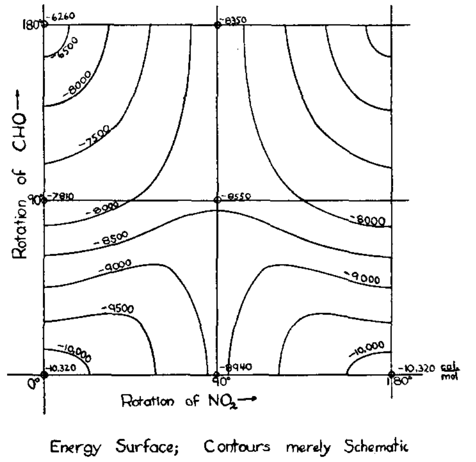

FIG. 1. Altitude, energy of o-nitrobenzaldehyde; abscissa, angular rotation of nitro; ordinate, angular rotation of aldehyde.

compound, rotation of the nitro groups should be fairly easy. If the ortho compound is treated by the method discussed by Pauling,[8] the motion of the nitro group is seen to be that of a quantized torsional oscillator, with the lower levels separated by about one-fifteenth of the height of the potential barrier. Half of the molecules will be found in the lowest four vibrational levels, and about ten percent will be rotating. As the vibrational energy of the nitro group is gradually increased from zero, the periods start with $\pi/(V/I)^{\frac{1}{2}} = 3.27 \times 10^{-13}$ sec. for the lowest level and go to infinity when the energy is just equal to the height of the potential barrier, $2V$. I is the moment of inertia of the nitro group, determined by graphic statics. Beyond this unstable equilibrium, more energy will cause rotation, at first with a very long period, then more rapidly, until the rotation approximates that of an unhindered rotator. The periods for most of the rotating molecules lie between 10^{-12} and 10^{-13} sec.

ENERGY TRANSFER, DEACTIVATION AND REACTION

The third question mentioned in the opening paragraph must unfortunately be treated with still less exactitude. It was stated that the actinic radiation is absorbed in the nitro group, presumably by the electrons of the N—O bonds. With the molecule constrained to a flat configuration, the observed quantum efficiency of one-half could be very simply explained by saying that light absorbed by the bond more distant from the aldehyde is lost; whereas light absorbed by the bond nearer the aldehyde causes reaction. This, however, neglects the possibility of a transfer of activation between the two bonds, as well as the possibility of some deactivation in the proximal bond, and a more detailed consideration is required.

We may assume that energy is absorbed by a virtual oscillator in one or the other of the bonds. Let us call the state of the system in which the distal bond is excited ψ_1, and the state in which the proximal bond is excited ψ_2. The virtual oscillator perturbs the other bond. Then if it were impossible for the group ever to lose its energy, the latter would resonate between the two bonds, and the state of the system at any time would be given by a superposition[9]

$$\psi = c_1\psi_1 + c_2\psi_2.$$

In such a case the c's would be undamped periodic functions of the time, or, according to the quantum-mechanical view, the absolute square of c_i. at a given instant would give the probability of finding the energy in ψ_i.

This transfer process is very like that studied by Kallmann and London.[10] Indeed, an evaluation of the probability by the standard theory of coupled vibrations gives their Eq. (32). We shall write this equation in the form

$$|c_2|^2 = \sin^2(2\pi p^2 t/hR^3), \qquad (11)$$

for the case in which ψ_1 is originally excited at a time t before c_2 is being evaluated. The other symbols have the following definitions: p^2 is the square of the average absolute magnitude of the moment of the virtual oscillator produced by the absorption of radiation, h is Planck's constant, and R is the effective distance between 1 and 2. The latter is taken as 2.1A, the intercentroid distance of the two nitro bonds, and the former is found from the experimentally determined

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[8] Pauling, Phys. Rev. **36**, 440 (1930).

[9] Dirac, *Quantum Mechanics*, pp. 18, 162, Oxford, 1930.

[10] Kallmann and London, Zeits. f. physik. Chemie **B2**, 207 (1929).

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effective cross section for absorption, by using the formula[11]

$$p^2=3cha/8\pi^2\nu. \qquad (12)$$

Here c is the velocity of light, a is the effective cross section per unit time for absorption, and ν is the incident frequency. For 3660A, a is 2.4×10^{-4} cm^2/sec., and is found by easy transformations from the observed molecular extinction coefficient. The meaning of this value is that if a layer of molecules of o-nitrobenzaldehyde is exposed, each to a quantum of 3660A radiation, then on the average 2.4 out of every 10^4 quanta will be absorbed.

The least value of t in Eq. (11) for which the argument of the sin^2 goes to $\pi/2$, and hence for which $|c_2|^2$ goes to unity, is 2.2×10^{-13} sec. This time will be denoted by T_1 and called the time of transfer. Accordingly,

$$T_1=hR^3/p^2=2.2\times10^{-13}\text{ sec.} \qquad (13)$$

Deactivation by the remainder of the molecule and by the surrounding solvent molecules occurs by a similar process, but more rapidly. The effective distance to the surrounding molecules is indeed greater than to the other nitro bond, and, other things being equal, the time varies with the cube of this. Kinetic theory molecular diameters are usually about 3.5A. On the other hand, the unexcited nitro bond obscures a relatively small solid angle, perhaps one-tenth of a sphere surrounding the excited one. Thus the time of deactivation will be approximately

$$T_2=T_1(1/10)(3.5/2.1)^3\backsimeq10^{-13}\text{ sec.} \qquad (14)$$

It is assumed that the quasi-static polarizability, which conditions p, is of the same order for the surroundings as it is for the nitro bond.

No strictly analogous time can be given for the reaction process because of the different mechanism involved. Should the probability of reaction per unit time depend merely on the probability of finding the molecule still in the initial state for $|c_2|^2=1$ at $t=0$, then one might expect the curve of probability/time to behave like $1-e^{-t}$. However, this means that the rate of reaction is greatest at $t=0$. If, on the other hand, the reaction always takes a finite time, then the curve will possess a toe, as does the graph of sin^2 t. Thus for a short interval near $t=0$, the curve will resemble that for transfer, except that the probability will approach unity asymptotically rather tangentially.

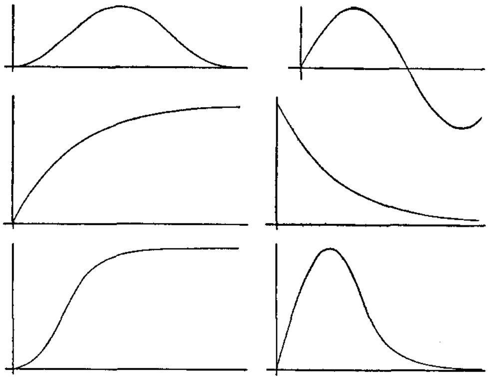

FIG. 2. Type curves. The left column contains $W=\sin^2 t$, $W=1-e^{-t}$, and a composite curve. The scales are arbitrary. The right column contains the time derivatives of these curves in the same order.

A similar conclusion holds for the deactivation process; since activation transferred to an acetone molecule stands little chance of returning to the nitro bond. The derivative curve, expressing the rate of deactivation of reaction, will be the derivative of sin^2 x at the start, i.e., sin $2x$, and e^{-x} at the end. The two may be multiplied or fitted as are the two wave functions in the process of finding a self-consistent field (Fig. 2). Since for all three processes, the curves are similar for a considerable time, we may allot a time T_3 to the reaction process on the same footing as the others. An evaluation of this is pure guesswork, but it is no doubt of the order of a few vibration periods, say 10^{-13} sec. also.

We shall assume that the processes of transfer, deactivation, and reaction are independent, i.e., that only one of them is occurring in any one molecule at any given time. This corresponds to assuming that the absorbed quantum retains its identity as long as it remains an electromagnetic phenomenon. In order for the excitation energy to be degraded and finally lost as heat, it must go over to relative motional energy of different systems. This can occur by a coupling between electronic and nuclear vibrations within one molecule and a dissipation of the resulting vibrational energy by collisions. This degradation is presumably rather slow on the whole, because of the great disparity between the masses of the

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[11] Reference 9, p. 232 inf.

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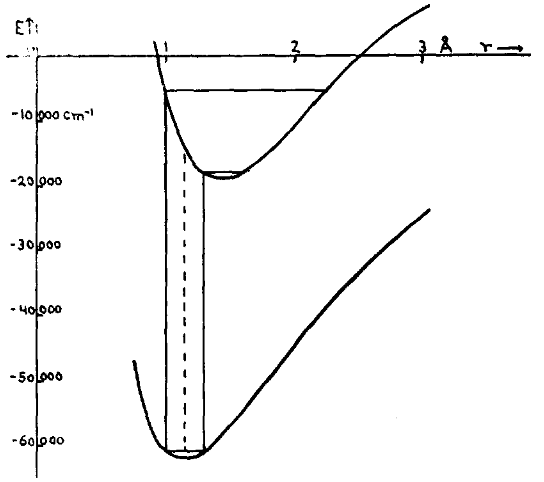

FIG. 3. Morse curves for nitric oxide, showing the bond extension following the absorption of light. A similar effect may occur in the nitro group.

nuclei and the electrons and the resulting large number of vibrations required to transfer the energy. However, one may expect that a certain amount of the excitation goes into vibrational energy at once if the higher state is an upper vibrational level of the electronically excited bond.

The spectrum of o-nitrobenzaldehyde has not been analyzed, but that of NO has. The Morse curves for the ground state and the excited state which gives the β-bands may be plotted from the data so obtained[12] (Fig. 3). They show that light absorption by molecules at room temperature yields molecules having a few Cal. of vibrational energy, with a maximum internuclear distance considerably greater than that of the ground state. That a similar situation exists for the nitro group seems plausible.

The nitro group, of course, has three fundamental vibrations, and the sudden extension of one of its bonds corresponds to the excitation of all three modes, but principally the unsymmetrical valence vibration and the deformation vibration are excited, in the proportion of about two to one, as may be seen from a diagram of the molecule and a consideration of the various restoring forces. There will not be time for appreciable transfer of this vibration from one bond to the other, especially if 2 is the excited one, but in the latter case the vibration may well be important in causing the reaction. If the rest of the molecule remained rigid, the vibrational motion would swing the oxygen nucleus near enough to the aldehyde hydrogen so that an hydroxyl group with normal nuclear separation could form by a mere redistribution of the electron cloud (Villars' allegiance exchange). At the same time a chemically saturated nitroso group could form from the remainder of the nitro group, leaving the hydroxyl to react with the carbonyl.

The actual process probably does not fall into steps, but is a continuous shift of the oxygen from one group to the other, expressible in the Eyring manner. However, it may well be that the molecule must oscillate into a favorable position to cross the energy barrier, so that T_3 is taken as 10^{-13} sec. rather than as some shorter time.

It seems fair to assume that the relative frequency of deactivation and reaction is the ratio of the rates of the two processes considered separately. Since there is one chance in two that the activated system is initially in ψ_1 and the like for ψ_2, the probability of reaction may be expressed as $\frac{1}{2}(P_1+P_2)$, where P_1 is the probability of reaction if the system is originally in the state ψ_1 and P_2 is the probability of reaction if the system is originally in ψ_2. In the second case, the probability is the partition coefficient for the separation of excited molecules into the reacted or deactivated forms. The latter group includes those molecules in which transfer of activation to 1 occurs, for energy, one transferred from 2, has a negligible chance of causing reaction. The rate of reaction from ψ_2 is the ratio of the slopes of the graphs of probability against time. Near $t=0$, for example, it is

$$\frac{2}{T_3}\sin\frac{2t}{T_3}\Big/\left(\frac{2}{T_1}\sin\frac{2t}{T_1}+\frac{2}{T_2}\sin\frac{2t}{T_2}\right). \qquad (15)$$

The average of P_2 during a short interval a is then, by the standard formula,

$$P_2=\frac{\displaystyle\int_0^a\left[\sin\frac{2t}{T_3}\Big/\left(\frac{1}{T_1}\sin\frac{2t}{T_1}+\sin\frac{2t}{T_2}\right)\right]dt}{\displaystyle\int_0^a dt}. \qquad (16)$$

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[12] International Critical Tables, 5, 415, 417 (1929).

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The terms in T_2 and T_3 change to exponentials after about 0.8×10^{-13} sec., as noted above. This expression is most conveniently handled graphically. Analogously,

$$P_1=\frac{\int_0^a\left(\frac{1}{T_1}\sin\frac{2t}{T_1}\Big/\sin\frac{2t}{T_2}\right)dt}{\int_0^a dt}\cdot P_2.$$

That is, there is a partition of the energy into deactivation and transfer, and then, in the transferred portion, a further partition expressed by P_2.

Graphical integration gives $P_2=0.80$, $P_1=0.20$. Since ψ_1 and ψ_2 are equally probably *a priori*, the quantum efficiency is the arithmetical mean of these, namely $\Phi=0.50$, exactly as found experimentally.

This result is rather surprising at first; a further inspection shows it to come from the assumption that $T_2=T_3$, and, from other assumptions made above. It might have been assumed at the start that Φ has the experimental value and that T_2 and T_3 are to be adjusted accordingly. Assuming a different value for T_1 without changing the others will not change Φ, the quantum efficiency, but only the relative values of P_1 and P_2.

Of course, T_2 and T_3 may change in different manners with change in temperature. In particular, rising temperature probably increases T_3 by throwing a considerable fraction of the nitro groups into high states of torsional oscillation and rotation. Such molecules will spend most of their time in orientations unsuitable for reaction, and the temperature coefficient will accordingly be negative. Indeed, a negative temperature coefficient was actually found by Zimmer.[13]

The quantum efficiency $\Phi=0.67$ found in acetone solutions for 2,4,6-trinitrobenzaldehyde may be interpreted simply on the basis of the foregoing computations. As noted above, the contour map (Fig. 1) shows that the three vicinal groups cannot easily be coplanar. The aldehyde group is doubtless forced to within 30° or so of perpendicularity to the plane of the ring. In such a case, the nitro groups are no longer hindered by a very high potential barrier and can rotate somewhat, say with a period of about 10^{-13} sec. at room temperature. This is rapid enough so that all four bonds become more nearly equivalent than in the mono-substituted compound. That is, P_2 is the most important partition coefficient and $P_2>\Phi>0.5$. The lower quantum efficiencies found for this compound in ligroin solution and in the solid state may be due either to a reduction in the amount of rotation or a reduction in P_2. Lower quantum efficiencies at shorter wave-lengths may in every case be plausibly assigned to an inner light filter effect of other portions of the molecule than those which can be active in causing reaction, but may partly be caused by a decrease of T_2 for higher frequencies of exciting light.

CONCLUSION

A calculation of the position-sensitive interactions of the nitro and aldehyde groups in o-nitrobenzaldehyde indicates that at room temperature these groups will be for the most part constrained to a flat configuration, coplanar with the phenylene ring, and that rotation of the nitro group will precede that of the aldehyde group. A consideration of the possible processes following upon the absorption of a quantum of light in one of the $N-O$ bonds leads to the conclusion that the observed quantum efficiency of one-half is due principally to an equality between times of deactivation and reaction. Most of the absorption in the proximal bond produces reaction; while most of the energy absorbed in the distal bond is lost by deactivation, and the yield is independent of energy transfer between the two bonds.

The explanation, although approximate in character, contravenes no accepted ideas on the structural arrangement of the molecule, and contravenes no physical principle. The description is still not complete; in particular it does not cover the Eyring diagram for the motion of the oxygen atom.

The authors wish to express their gratitude to Drs. W. V. Houston and F. Bloch for stimulating conversations on this problem as well as for specific assistance in certain instances.

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[13] Zimmer, Zeits. f. physik. Chemie **B23**, 239 (1933).

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