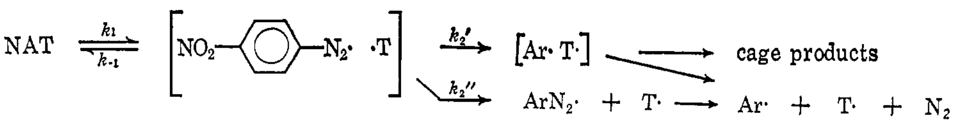
Scheme I



suggest that the amount of internal return from the first formed geminated pair will *always* exceed the amount of cage product from any subsequently formed geminate pair.[4]

Figure 1 also presents data for NAT in hydrocarbon solvents at 60°. *It is clear that NAT and acetyl peroxide show very similar behavior, and that internal return must occur for NAT.*

Notice that k_1 is obtainable from the intercept of Figure 1, and k_{-1}/k_2 can be calculated from k_{obsd}/k_1 using eq 3. The branching ratio k_{-1}/k_2 is perhaps the most interesting description of the amount of internal return for an initiator. This ratio was determined for acetyl peroxide by Taylor and Martin,[6] and it is desirable to compare our data with theirs. Their work was at 80° whereas the viscosity data of Eirich applies at 60°; nevertheless, a rough comparison can be made by the following method. Taylor and Martin found $k_{obsd}/k_1 = 0.62$. Now, we can take as an approximation of the activation energy for step k_1 that observed for the gas phase decomposition, since no internal return would occur in the vapor phase.[8] Szwarc[9a] has found $E_{gas} = 29.5$ kcal/mole; we therefore assume $E_1 = 29.5$. Szwarc[9b] also obtained 32.2 kcal/mole as the activation energy for the over-all decomposition in isooctane, the solvent Taylor and Martin used, and we therefore take $E_{obsd} = 32.2$. Using these two activation energies, we estimate $k_{obsd}/k_1 = 0.49$. From Figure 1, we obtain $k_1 = 1.31 \times 10^{-5}$ sec^{-1} for acetyl peroxide; k_{obsd} at 60° in isooctane is 4.85×10^{-6} from Szwarc's data[9b] and 2.9×10^{-6} sec^{-1} from Eirich's.[4] Therefore, our estimate of k_{obsd}/k_1 at 60° is 0.37 or 0.22.

At this point, the agreement between Taylor and Martin's value of $k_{obsd}/k_1 = 0.49$ (extrapolated to 60°) and our value of 0.22–0.37 must certainly be considered satisfactory. The discrepancy could arise from several factors. (1) The mechanism in eq 1 is an oversimplification (see below). (2) The use of only first terms of expansions leads to eq 4 being only an approximation. (3) Taylor and Martin's and Eirich's data are not comparable for any of several possible reasons; for example, different amounts of induced decomposition might have occurred under the different conditions employed. (4) Our extrapolation of Taylor and Martin's value of k_{obsd}/k_1 to 60° is inaccurate.

It is worth pointing out, however, that our analysis appears to lead to acceptable values of the branching ratio k_{-1}/k_2 much more easily than does ^{18}O labeling. Furthermore, our analysis can be applied to all initiators, whereas only certain chemical types can be studied by the ^{18}O method.

The results provide evidence that NAT decomposes by the scission of one C–N bond at a time. The mechanism of the decomposition of NAT can be represented as shown in Scheme I, where $k_2 = k_2' + k_2''$. If it is assumed that $k_2 = k_2' + A'/\eta$, then the intercept of Figure 1 is $[\log k_1 - 0.868(1 + 2k_2'/k_{-1})]$. For acetyl peroxide, an analogous expression can be written, where k_2' is the constant for the loss of CO_2. In both cases, if $k_2' \gg k_{-1}$, then the intercept of graphs like Figure 1 will give essentially the correct value of k_1. If k_2'/k_{-1} is finite, Figure 1 will lead to erroneously small values of k_1 and large values of k_{obsd}/k_1. This complication could explain part of the discrepancy between the value of k_{obsd}/k_1 obtained from Figure 1 and that from the ^{18}O study on acetyl peroxide.

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Optical Rotatory Dispersion Effects of Transient Species by Flash Excitation

Sir:

In the last decade optical rotatory dispersion (ORD) has become an important tool in organic chemistry for the study of stereochemical and structural problems in optically active compounds.[1] Also during approximately the same period, many spectroscopic studies of transient species having lifetimes as short as 10^{-6} sec have been undertaken by the technique of flash photolysis.[2] We report here a preliminary study demonstrating the feasibility of combining the two techniques in order to determine possible structural changes occurring on electronic excitation as well as absolute configurations of excited states (assuming retention of optical activity in the transient species). Benzoin was chosen as a model system, since it is one of the simpler optically active compounds involving a carbonyl group, the chromophore on which most of the ORD characterization and structural correlation studies have been made.[1] Very little modification of the asymmetric environment would be expected in benzoin on electronic excitation.

A block diagram of the flash spectropolarimeter is shown in Figure 1. The flash lamp consists of two parallel quartz tubes with tungsten electrodes, filled with Xe (80 mm) and O_2 (*ca.* 3 mm). These are connected in series electrically, triggering of the discharge (20 kv, 5000 joules maximum) being effected by a 30-kv pulse. The polarizer, P, and analyzer, A (each a 12-mm aperture Glan-Taylor Type A quartz prism), are mounted within 1 cm of the cell windows, with the polarizer in a fixed position and the analyzer attached to a 360° angle divider. The continuous analyzing light from the stabilized 450-w Xe lamp is rendered

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[8] This is probably a better assumption than to equate k_1 (liquid phase) with k_{obsd} (gas), as do Taylor and Martin. It is safe to assume that k_1 (gas) = k_{obsd} (gas), but k_1 would not necessarily have the same value in the gas and liquid phase (F. R. Mayo, private communications).

[9] (a) A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5975 (1954); (b) M. Levy, M. Steinberg, and M. Szwarc, *ibid.*, **76**, 5978 (1954); (c) see also M. Szwarc, "Peroxide Reaction Mechanisms," Interscience Publishers, Inc., New York, N. Y., 1962, pp 153–174.

(1) (a) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960; (b) P. Crabbe, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965.

(2) G. Porter in "Technique of Organic Chemistry," Vol. VIII, Part II, 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 1055.

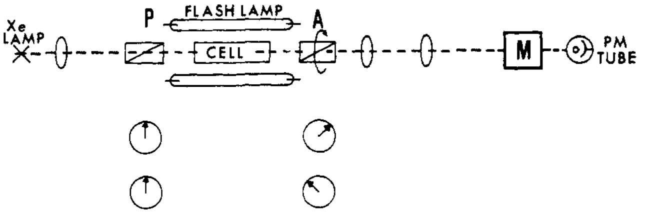

Figure 1. Block diagram of flash spectropolarimeter.

monochromatic by M, a Zeiss MM12 double monochromator. Transient output from the 9558B or Q photomultiplier tube, corresponding to a change in transmitted light, is dc coupled through a cathode follower amplifier to an oscilloscope and photographically recorded. The cylindrical quartz reaction cell (10-cm light path, 2.5 cm i.d.) has evacuated 2-cm cylindrical chambers at each end; surrounding the cell compartment and approximately 75% of each end section is an annular jacket through which is circulated the thermostated saturated aqueous nickel(II) chloride filter solution.

The intensity of light transmitted by the polarizer and analyzer at an angle of rotation θ relative to each other is

$$I = I_0 K \cos^2 (\theta + \alpha) \qquad (1)$$

where I_0 is the incident light, K is a constant for the apparatus and absorption cell which accounts for all light losses by reflection, etc., and α is the rotation of the solution. In practice, the observed change in transmittancy following initiation of the flash results from scattered flash light and absorbance changes as well as from rotational change. Accordingly, transmittancy change measurements as a function of time are made with the analyzer rotated $+\theta'$ and $-\theta'$; the transitory change in rotation at a specific wavelength λ and time t after initiation of the flash, $\alpha_t(\lambda)$, is then given by eq 2 if $\alpha_t(\lambda)$ is small compared to θ'.

$$\alpha_t(\lambda) = -\frac{\Delta I_+ - \Delta I_-}{4I' \tan \theta'} \qquad (2)$$

In this expression $\theta' = \theta + \alpha_0$, where α_0 is the steady (assumed constant) rotation of the solution resulting from ground-state optical activity, ΔI_+ and ΔI_- are the changes in transmittancy at $+\theta'$ and $-\theta'$, respectively, and I' is the steady transmitted intensity at $+\theta'$ or $-\theta'$, measured just prior to flash initiation. The best value for θ' is a compromise between photomultiplier tube shot noise and constant measurement errors; for the conditions of oscilloscope sensitivity, etc., used in this work, the best value for θ' was ±80°. The transitory ORD curve is thus constructed from the above measurements taken as a function of wavelength.

Short- and long-lived transient species, as well as extensive photochemical decomposition, result from the flash excitation of benzoin (benzene solvent). However, transient optical activity was observed in this work only during the lifetime of the short-lived transient (*ca.* 50-μsec half-life and tentatively identified as a benzoin triplet state), and the solutions became completely inactive (from photochemical decomposition processes) after repeated flashings. (For this reason, data were used from oscillograms taken on freshly outgassed solutions flashed less than four times.)

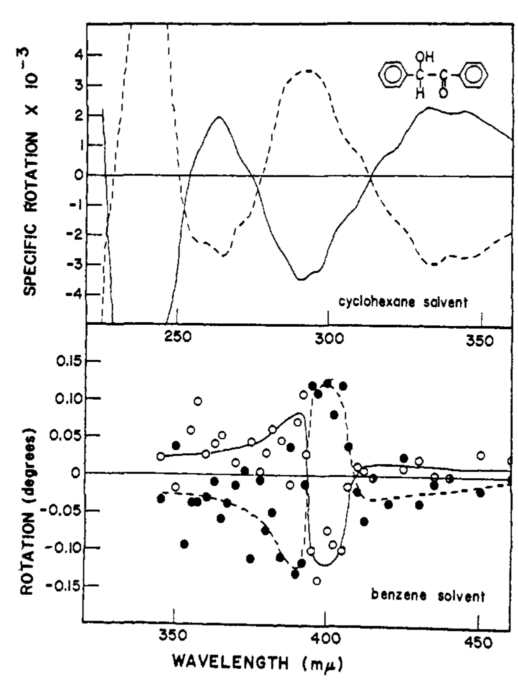

Figure 2. Optical rotatory dispersion curves of the ground and excited states of benzoin: ———, ground-state *d*-benzoin; -----, ground-state *l*-benzoin; —○—, excited state *d*-benzoin; ---●---, excited state *l*-benzoin.

The ORD curves for the excited state, measured at 50 μsec after flash initiation, are given in Figure 2 for both *d*- and *l*-benzoin in the region of triplet–triplet absorption,[3] and are compared with the ground-state ORD curves below 355 mμ obtained on a conventional spectropolarimeter. The experimental accuracy of this technique involving transitory measurements is still relatively low as indicated by the scattering of experimental points. Nevertheless, the excited-state curves are roughly mirror images of each other, and very definite similarities in multiple Cotton effects are shown between the ground and excited states. Electronic excitation not involving bond rupture will not effect the asymmetric environment of the carbonyl chromophore in a molecule such as benzoin; these similarities thus suggest that basic asymmetry and not the specific type of electronic transition may determine the character of the ORD effect.

Work is continuing in this laboratory on related systems.

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(3) G. Porter and M. W. Windsor, *Proc. Roy. Soc.* (London), **A245**, 238 (1958).

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The Oxidation by Iodine of Tryptophan 108 in Lysozyme

Sir:

Canfield[1] and Jolles, *et al.*,[2] have shown that the six tryptophans of lysozyme are located at sequence posi-

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(1) R. E. Canfield, *J. Biol. Chem.*, **238**, 2698 (1963).

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