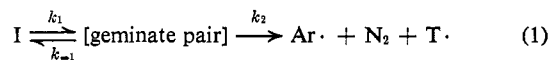


Evidence of the Re-formation of an Initiator from a Geminate Pair (Internal Return from the Cage)¹

Sir:

In this communication we wish to present a general method for determining the fraction of the geminate pairs from an initiator which returns to re-form the initiator. (We shall call this step internal return). We present new experimental data on *p*-nitrophenylazotriphenylmethane (NAT)² and a reexamination of published data on acetyl peroxide.

The simplest mechanism which includes internal return is shown for a PAT-type initiator I

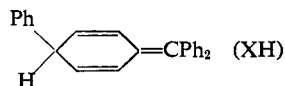


where k_2 is a rate constant for an irreversible step which destroys the cage and $\text{T}\cdot$ is the trityl radical. If internal return did occur, then the first formed geminate pair would be formulated as $\text{ArN}=\text{N}\cdot$ and $\text{T}\cdot$, rather than $\text{Ar}\cdot$, N_2 , and $\text{T}\cdot$, since it is not reasonable to expect the readdition of two radicals to a nitrogen molecule in the cage. This, in turn, would imply that the two C-N bonds in the initiator did *not* undergo simultaneous scission. Current evidence has been interpreted as indicating simultaneous scission of both C-N bonds in most azo compounds.³

Our terminology for describing cage processes must be expanded to include the possibility of several different geminate pairs arising for a particular initiator. For example, for PAT there are two possible geminate pairs, $(\text{ArN}_2\cdot\text{T}\cdot)$ and $(\text{Ar}\cdot\text{T}\cdot)$. For acetyl peroxide, there are three possible pairs: $(\text{AcO}\cdot\text{AcO}\cdot)$, $(\text{AcO}\cdot)$

(1) Reactions of Radicals. XIV.

(2) (a) W. A. Pryor, J. T. Echols, and K. Smith, *J. Am. Chem. Soc.*, **88**, 1189 (1966). (b) W. A. Pryor and H. Guard, *ibid.*, **86**, 1150 (1964). (c) We have found that both phenylazotriphenylmethane (PAT) and NAT give less than 100% yields of scavenged $\text{Ar}\cdot$ radicals under a wide range of conditions using either iodine or CBr_4 as scavenger and either CCl_4 or toluene as solvent. (Unpublished data of K. Smith, J. Echols, W. Bushey, and J. Schreck.) Therefore, some cage products are formed. It had appeared that ArH was a major cage product since its yield remained finite upon extrapolation to infinite dilution. [See ref 2a and also R. G. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).] However, ArH is not produced in the presence of iodine or CS_2 ^{2a} or CBr_4 as scavengers. Furthermore, by using very low initial concentrations of PAT or NAT, we now have found that the yield of ArH drops precipitously toward zero. Thus, ArH is not a cage product. However, CPh_4 and XH



which result from the combination of $\text{Ar}\cdot$ radicals with the ambient trityl radical, are formed from PAT in CCl_4 and are reduced in yield but not eliminated by scavengers. (XH was analyzed as its aromatized derivative $p\text{-PhC}_6\text{H}_4\text{CHPh}_2$.) Therefore, the ArH which is produced from these initiators in pure CCl_4 results from the reaction of $\text{Ar}\cdot$ with XH and other hydrogen donors which are themselves formed, in part, in cage reactions. This explains the abruptness in the dropoff in graphs of per cent ArH vs. the initial concentration of initiator. A detailed discussion of NAT chemistry and many more k_{II}/k_{CI} values will be published later. [For other reactions of trityl acting as an ambident radical, see J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *ibid.*, **88**, 1257 (1966), and J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).]

(3) The article by S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 137 (1966), is the most recent review of this topic. S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965), have concluded from isotope effect studies that α -phenylethylazomethane decomposes one C-N bond at a time. Also see S. Seltzer, *ibid.*, **83**, 2625 (1961). At -196° , there is epr evidence for a nitrogen-containing radical ($\text{RN}_2\cdot$) from AIBN but not from azomethane; see P. B. Ayscough, B. R. Brooks, and H. E. Evans, *J. Phys. Chem.*, **68**, 3889 (1964). S. Kodama, *Bull. Chem. Soc. Japan*, **35**, 652 (1962), has concluded that azomethane undergoes internal return since it has a lower quantum yield at lower temperatures.

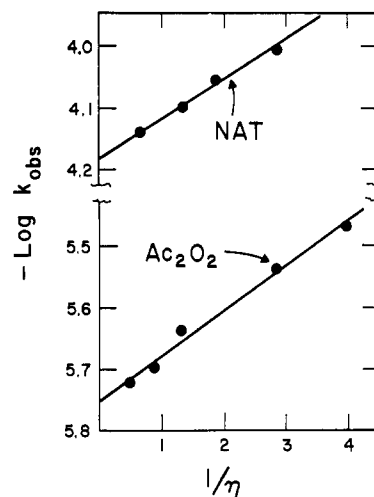


Figure 1. A graph of $\log k_{\text{obsd}}$ vs. the inverse of the viscosity of several hydrocarbon solvents, all data at 60° . The data for acetyl peroxide are those of W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

$\text{Me}\cdot$), and $(\text{Me}\cdot\text{Me}\cdot)$.⁴ Traditionally, the amount of internal return has not been included in the figures for per cent cage reaction, since internal return does not lessen the moles of radicals produced from a mole of initiator (*i.e.*, the efficiency). Note that for acetyl peroxide, internal return, ester formation, and ethane formation all occur from different geminate pairs; presumably, for PAT, internal return and cage products such as $\text{C}(\text{Ph})_4$ are produced from different pairs also.^{2c}

Evidence on internal return can be obtained from a study of the viscosity dependence of the observed rate constant for disappearance of an initiator. In solvents of higher viscosity the geminate pair separates more slowly, and larger amounts of internal return should occur and k_{obsd} should be observed to decrease. The relation of k_{obsd} to the constants given in eq 1 is

$$-dI/dt = k_{\text{obsd}}(I) \quad (2)$$

$$k_{\text{obsd}} = k_1 k_2 / (k_2 + k_{-1}) = k_1 / (1 + k_{-1}/k_2) \quad (3)$$

If k_1 and k_{-1} are assumed to be independent of viscosity, and k_2 is assumed to have the dependence $k_2 = A\eta^{-1}$ where A is a constant, then eq 4 can be obtained.⁵

$$\log k_{\text{obsd}} = (\log k_1 - 0.868) + \frac{1.737}{Ak_{-1}\eta} \quad (4)$$

Eirich⁴ has studied the dependence of k_{obsd} for acetyl peroxide on the viscosity of a series of hydrocarbon solvents. Figure 1 shows these data plotted according to eq 4. A straight line is obtained, and k_{obsd} does decrease with $1/\eta$ as expected. Acetyl peroxide is known to undergo internal return; oxygen-18 labeling experiments show that 38% of the geminate acetate radicals re-form the peroxide in isooctane at 80° .⁶ In fact, this is the most important generalized cage reaction acetyl peroxide undergoes, since the yields of ester and ethane are only about 15 and 5%⁷. We

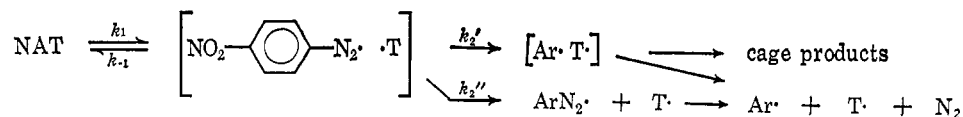
(4) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

(5) Equation 4 is derived by expanding the expression for $\log k_{\text{obsd}}$ and $1/(1+x)$, retaining only the first terms.

(6) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3650 (1966).

(7) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 89. The conclusions concerning internal return given here, based on the older tracer experiments which are now known to be in error, must now be revised.

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 $k_{\text{obsd}}/k_1 = 0.62$. 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 $E_{\text{gas}} = 29.5$ 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 $E_{\text{obsd}} = 32.2$. Using these two activation energies, we estimate $k_{\text{obsd}}/k_1 = 0.49$. 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 $k_{\text{obsd}}/k_1 = 0.49$ (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 ¹⁸O labeling. Furthermore, our analysis can be applied to all initiators, whereas only certain chemical types can be studied by the ¹⁸O method.

The results provide evidence that NAT decomposes by the scission of one C-N bond at a time. The mech-

anism 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 CO₂. 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 ¹⁸O study on acetyl peroxide.

Acknowledgment. This work was supported in part by U. S. Public Health Service Grant GM 11908-02.

William A. Pryor, Kennedy Smith

Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Received December 8, 1966

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 O₂ (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

(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.