

Figure 1. Silver $3d_{3/2}$ and $3d_{5/2}$ spectra of (a) silver foil evaporated onto a gold foil at 10^{-8} Torr, (b) $\text{Ag}^{\text{II}}\text{OEP}$, and (c) $\text{Ag}^{\text{III}}\text{OEP}(\text{ClO}_4)$ mixed with a small amount of b.

spectrum also shows a single peak presumably composed of both the porphyrin ring carbons and the substituent group carbons. The absence of any additional peaks due to charge differences in the porphyrin ring carbons is in general agreement with Gouterman's calculations⁴ indicating these differences to be less than 0.05 charge unit.

Complexing a metal ion with OEP causes noticeable chemical shifts in the binding energy of the metal, carbon, and nitrogen peaks. For $\text{Ag}^{\text{I}}\text{OEP}$ (Figure 1), the silver peaks are shifted a small amount (0.4 eV) to higher values indicating a slight increase in positive charge relative to silver metal. The spectrum for the (TPP) analog is similar in shape although the effect of the phenyl substituents is to shift the peaks to lower binding energy. This result is in general agreement with previous studies where only slight differences are noted between a variety of $\text{Ag}(0)$, $\text{Ag}(I)$, and $\text{Ag}(II)$ complexes.^{4b,6} The nitrogen 1s spectrum collapses to a single peak with a binding energy value directly in between the OEP doublet. For this molecule, the C 1s peak shows virtually no change indicating the nitrogen σ orbitals are, as predicted,⁷ weakly coupled to the porphyrin ring π system and the positive charge is primarily localized on the silver nitrogen.

The silver spectra of $\text{Ag}^{\text{III}}\text{OEP}(\text{ClO}_4)$ containing some $\text{Ag}^{\text{I}}\text{OEP}$ are shown in Figure 1 and the binding energies are given in Table I. The substantial chemical shift (2.7 eV vs. the $\text{Ag}(II)$ analog and 3.1 eV vs. $\text{Ag}(0)$) clearly confirms the previously assigned oxidized form⁸ to be $\text{Ag}(III)$ formed by removing an electron from the $\text{Ag}(II)$ rather than from the porphyrin ring to form a π cation radical as is believed to be the case for zinc, magnesium, and a number of other metalloporphyrins.¹⁻³ This shift is also in reasonable agreement with a similar shift recently reported for a $\text{Ag}(III)$ biguanide complex (4.2 eV vs. $\text{Ag}(0)$).⁹ The slightly smaller value observed for the porphyrin system may be attributable

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(7) M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959).

(8) K. Kadish, D. G. Davis, and J. H. Fuhrhop, *Angew. Chem., Int. Ed. Engl.*, **11**, 1014 (1972).

(9) D. A. Zatko and J. W. Pather, II, *J. Electron Spectrosc. Relat. Phenomena*, **2**, 190 (1973).

to the strongly coordinated perchlorate³ which would tend to reduce the net positive charge about the $\text{Ag}(III)$.

It is also of interest that the nitrogens are shifted noticeably (~ 1.0 eV) to higher energies thus obtaining a partial positive charge. This observation is consistent with the fact that the greater electronegativity of the $\text{Ag}(III)$ species promotes greater electron withdrawal from the nitrogen through the σ bond which is not replaced by the π system due to poor coupling. The small, reproducible shift to lower binding energy of the porphyrin carbon 1s electrons is somewhat surprising since this result indicates that in removing an electron from $\text{Ag}(II)$ by oxidation the π system slightly increases its electron density. This trend has been predicted^{4a} for an $\text{Fe}(II)/\text{Fe}(III)$ porphyrin system using an extended Hückel molecular orbital treatment.

On the basis of these results, we believe we have obtained conclusive evidence for the presence of a stable $\text{Ag}(III)$ species by preparing a series of complexes with similar structure and by monitoring the chemical shifts of the metal, nitrogens, and carbons. It is apparent that a similar approach on other metalloporphyrin or like compounds can be a valuable aid to estimating molecular charge densities for comparison to available theoretically calculated data.

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The Decomposition of *tert*-Butylperoxy Isobutyrate and Isotopic Derivatives

Sir:

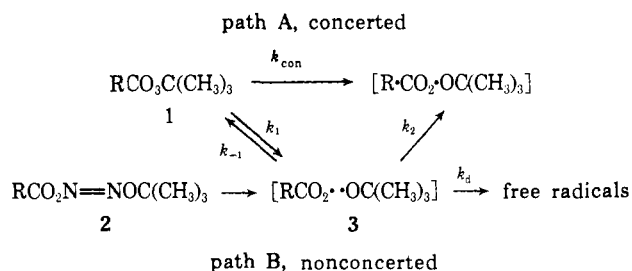
We have developed methods for measuring deuterium secondary kinetic isotope effects in perester¹ and peroxide decompositions² with the twofold purpose of gaining a better understanding of the origin of these effects³ and of extending their use as mechanistic probes. Previous results indicated essentially no isotope effect on the overall rate of decomposition of *tert*-butyl peracetate.^{1a} In contrast, appreciable isotope effects were found for phenylacetates^{1b} ($k_{\text{H}}/k_{\text{D}} > 1.03$ per α deuterium) and *tert*-butyl perpivalate ($k_{\text{H}}/k_{\text{D}} = 1.02$ per β -deuterium). The latter results are consistent with expectations of the transition state for concerted decomposition of the perester in which the starting material and the alkyl-*tert*-butoxy radical pair are separated by a single free energy maximum (Scheme I

(1) (a) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **89**, 2948 (1967); **91**, 2574 (1969); (b) T. Koenig, J. G. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

(2) T. Koenig and R. Cruthoff, *J. Amer. Chem. Soc.*, **91**, 2562 (1969).

(3) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2569 (1969).

Scheme I



path A). The peracetate results^{1b} were interpreted in terms of a nonconcerted reaction involving the intermediacy of the acetoxy-*tert*-butoxy pair (Scheme I path B).

Experiments in which carbonyl labeled *tert*-butyl peracetate was partially decomposed showed that the recovered perester contained oxygen-18 in the peroxy position.^{1b} This is consistent with the nonconcerted reaction if the acetoxy-*tert*-butoxy pair is reversibly formed. The reversibility is given further plausibility through the isolation of the perester as a product of the low temperature decomposition of the corresponding hyponitrite⁴ (2, R = CH₃).

Goldstein and Judson⁵ have raised questions concerning the interpretation of the oxygen-18 randomization process. They found evidence for the existence of this randomization reaction for *tert*-butyl perpivalate (1, R = *t*-Bu), a compound which reacts by the concerted mechanism using the isotope effect criterion. This as well as other data led to the suggestion of a 1,3-sigmatropic shift as the mechanism of the oxygen randomization process.

Another implication of the reversibility of formation of acyloxy-*tert*-butoxy pairs (3) is rate reduction with increased solvent viscosity. During the course of this work, Pryor and coworkers⁶ reported evidence for a slight rate reduction for *tert*-butylperoxy isobutyrate (1, R = *i*-Pr) which would suggest a nonconcerted mode of reaction. However, carbon dioxide yields were not reduced in olefinic solvents so that the isobutyroxy radicals are not scavenged by olefins which do react with the acetoxy species. These workers pointed out the need for study of the isobutyrate using the isotope effect and oxygen-18 criteria. The present report provides the results of such experiments.

The perester and its isotopic derivatives were prepared by the method of Bartlett and Rùchardt⁷ and purified by distillation and recrystallization at low temperature. The rates of decomposition of these compounds were measured by disappearance of the infrared carbonyl band at 1780 cm⁻¹. Added styrene was necessary to obtain reproducible rates.⁸ The rate constants and kinetic isotope effects, obtained in this way, are summarized in Table I. The isotope effects were also measured using the internal isotopic dilution technique^{1,2} in which the oxygen-18 contents of the

Table I. Observed Rate Constants for Decomposition of *tert*-Butylperoxy Isobutyrate at 103.4°

Solvent ^a	$k_{\text{H}} \times 10^4$, sec ⁻¹	$k_{\alpha-d_1} \times 10^4$, sec ⁻¹	$k_{\beta-d_6} \times 10^4$, sec ⁻¹	$k_{\text{H}}/k_{\alpha-d}$	$k_{\text{H}}/k_{\beta-d_6}$
Isooctane	2.10	2.11	1.84	1.00	1.14
Isooctane	2.21	2.07	1.86	1.07	1.19
				Av 1.03	1.16
Nujol	2.21				
Nujol	2.25				

^a Containing 0.2-0.4 M styrene.

carbon dioxide, produced from a mixture of the deuterio and oxygen-18 enriched protio compounds at short and long reaction times, were compared with those obtained from the two components of the mixture reacting separately (Table II). Both the direct and in-

Table II. Internal Isotopic Dilution Isotope Effects^a in Isooctane at 103°

	R_0^*	R_0^d	R_0^m	R_{∞}^*	R_{∞}^d	R_{∞}^m	$k_{\text{H}}/k_{\text{D}}^b$
$\alpha-d_1$	5.580	0.514	3.450	5.648	0.519	3.415	1.06
$\beta-d_6$	5.625	0.711	3.236	5.687	0.739	3.060	1.19

^a R_0^* and R_{∞}^* denote the 46/44 mass spectral ratio for the CO₂ from the protio (oxygen-18 enriched) perester after 7.5 and 300 min, respectively. The R_0^d and R_{∞}^d are the corresponding ratios for the deuterated derivatives. The deuterium oxide used in the synthesis of these compounds was also slightly enriched in oxygen-18. The R_0^m and R_{∞}^m are the ratios for mixtures of the protio and deuterio compounds. ^b $k_{\text{H}}/k_{\text{D}} = ((R_0^m - R_0^d)/(R_0^* - R_0^m))/((R_{\infty}^m - R_{\infty}^d)/(R_{\infty}^* - R_{\infty}^d))$. Instrument and carbon-13 corrections were negligible.

ternal isotopic dilution methods indicate appreciable α - and β -deuterium kinetic isotope effects suggesting the concerted mode (A). The directly observed rate constant in Nujol is the same as that for isooctane which also suggests the concerted mode.

Table III summarizes the results of tests for oxygen-18

Table III. Oxygen-18 Randomization of *tert*-Butylperoxy Isobutyrate Carbonyl ¹⁸O at 103°

Solvent ^a	t_{Δ} , min	$R_{p-\text{NO}_2}^b$	$k_s \times 10^6$, sec ⁻¹	f_{Δ}^c	f_{rec}^d
(Control) ^e	0	0.432 ± 0.015 ^e			
Nujol	100	0.469 ± 0.012 ^d	1 ± 0.4	0.6	0.004
Isooctane	100	0.451	0.6	0.6	0.003
Isooctane ^e	2.2 × 10 ⁴	0.439	<0.001	0.3	0.005

^a 0.15 M perester, 0.35 M styrene. ^b 46/44 mass spectral ratio for the carbon dioxide from the *p*-nitrobenzoate derivative of the *tert*-butyl hydroperoxide from cleavage of the appropriate isobutyrate. ^c Control, average of four determinations of the entire analytical sequence in which the original carbonyl labeled material was cleaved with methoxide, the *p*-nitroperbenzoate isolated and purified by tlc, and decomposed to give CO₂. ^d Average of three identical experiments of the entire sequence. ^e At 50.6°. ^f Fraction original perester decomposed. ^g Fraction recombination, ca. k_2/k_0 .

randomization. To be sure of our results, 10% enriched starting material was used. The analysis was accomplished by the published procedure^{1,4} in which the perester was cleaved with methoxide and the *tert*-butyl hydroperoxide isolated and purified as its *p*-nitrobenzoate derivative. The degree of randomiza-

(4) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **90**, 7014 (1968).

(5) M. Goldstein and H. Judson, *J. Amer. Chem. Soc.*, **92**, 4220 (1970).

(6) W. A. Pryor, E. Morkved, and H. Bickley, *J. Org. Chem.*, **37**, 1999 (1972).

(7) P. D. Bartlett and C. Rùchardt, *J. Amer. Chem. Soc.*, **82**, 1757 (1960).

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tion is reflected by the excess oxygen-18 content of the carbon dioxide from this derivative. The results definitely show that scrambling does compete with the overall destruction of the starting material. Qualitatively the situation is the same as for the pivalate in that the reaction appears to be concerted by the isotope effect criterion yet oxygen-18 randomization is observed. The 1,3-sigmatropic shift could be the explanation. However, a second possibility is that the scrambling reflects the fraction of the overall reaction which proceeds by the nonconcerted path as a competition. The suggestion of an increased k_s ($1 \times 10^{-6} \text{ sec}^{-1}$) in Nujol compared to isooctane ($0.6 \times 10^{-6} \text{ sec}^{-1}$) is consistent with this possibility. Equation 1

$$\frac{k_0}{k_s} = \frac{k_{\text{con}}}{k_1} + \left[\frac{k_{\text{con}}}{k_1} + 1 \right] \left[\frac{k_2}{k_{-1}} + \frac{k_d}{k_{-1}} \right] \quad (1)$$

allows the quantitative treatment of such a competition.

The value of k_1 at 103° is estimated at $2 \times 10^{-6} \text{ sec}^{-1}$ using the reported⁹ activation parameters for *tert*-butyl peracetate. The value of k_{con} can be taken as the observed rate constant for the reaction of the isobutyrate ($2 \times 10^{-4} \text{ sec}^{-1}$). The value of $((k_2 + k_d)/k_{-1})$ is of the order of one for the peracetate at 130° . If the isobutyroxy-*tert*-butoxy pair behave similarly, the k_0/k_s ratio should be *ca.* 2×10^2 which is just what is observed. Thus, in this case, the quantitative analysis of the degree of scrambling is entirely consistent with the radical pair hypothesis.

The rate of scrambling for the isobutyrate at 50.6° is estimated at less than $1 \times 10^{-9} \text{ sec}^{-1}$ or 2 orders of magnitude smaller than that for the pivalate.⁵ The 1,3-sigmatropic shift could explain this discrepancy if it is accelerated by a factor of more than 100 by substitution of a remote methyl group. Such a substituent effect suggests that the 1,3 shift would be too slow for the peracetate or perpropionate to have any bearing on the observed randomization.

The present results are totally consistent with the radical pair hypothesis for scrambling of oxygen-18 in peresters and attest to the sensitivity of this method at detecting the small amount of nonconcerted reaction which competes with the major concerted pathway. The activation parameters,⁹ isotope effects (Table I), insensitivity of rate to fluidity (Table I), quantitative yields of carbon dioxide in the presence of olefins,⁶ negligible amount of oxygen-18 randomization (Table II), and absence of perester formation from the corresponding hyponitrite¹⁰ all lead to the conclusion of concerted conversion of the isobutyrate to the isopropyl-*tert*-butoxy radical pair through a reaction coordinate involving a single transition state which accounts for 99% of the overall reaction.

Acknowledgment. We are grateful to the National Science Foundation and the E. I. du Pont Co. for financial support of this work.

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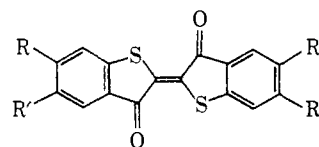
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Photochemical Reactions in Organized Monolayer Assemblies. I. Cis-Trans Isomerization of Thioindigo Dyes

Sir:

Although olefin photoisomerization has been extensively studied in solution,¹ relatively little is known regarding the factors controlling the reaction in other environments.²⁻⁵ Of particular interest is the influence of environment on the cis-trans isomerizations and related reactions which occur in membranes or other semisolid environments in photobiological processes such as vision. In the present communication we report an investigation of olefin photoisomerization in organized monolayer assemblies. Results of this study demonstrate that the membrane-like monolayer environment can exert such a striking influence on reactivity that factors which are relatively unimportant in solution can dominate reactivity in the monolayer.

The olefins employed in this study are the alkyl-substituted thioindigo dyes **1-3**. These olefins undergo



trans-1, R = *n*-C₆H₁₃O; R' = H

trans-2, R = H; R' = *n*-C₄H₉

trans-3, R = H; R' = *tert*-amyl

direct and sensitized cis-trans photoisomerization processes more-or-less analogous to those observed with the stilbenes and other acyclic olefins.⁵⁻⁸ The isomerizations in solution are readily followed by the pronounced changes in spectra accompanying cis-trans isomerization; the rather large differences in spectra between isomers permit the isolation of isomerically enriched isomers by irradiation with selected monochromatic light. It was anticipated that in compounds **1-3** the combination of a polar chromophore with hydrophobic alkyl side chains would result in a surfactant capable of forming spread monomolecular films and monolayer assemblies.⁹ Mixtures of olefin dyes **1-3** and tripalmitine (TP) were found to form monomolecular films that were stable over a pressure range 5-30 dyn/cm; these monolayers were readily transferred to glass supports, and it was found possible to deposit several layers containing the olefins in the usual manner.¹⁰ In addition, **1** forms stable films from the pure

(1) For a comprehensive review see J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafriou, *Org. Photochem.*, **3**, 7 (1973).

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