

the molar discrepancy between those isomers that yield *meso*-dideuteriosuccinic acid and those that yield racemic. Since  $\chi_9(0) = 0$ , the observed "high-temperature rate constant" is  $\lambda_7$ . Its components include, but are not limited to,  $k_B$ . Three more critical deductions from Figure 1 and Table I<sup>1</sup> are: (a) the "low-temperature rate constant,"  $\lambda_9 = 4(k_C + k_T)$ , (b) the Doering-Roth experiments<sup>3a</sup> could not distinguish chair from twist mechanisms, and (c) either of these would have sufficed for the *ESRZ/ERSZ* structure proof.<sup>4,13</sup>

A more promising use of Table I is in the design of new experiments to remove such ambiguities. For example, at temperatures where only  $k_C$  and/or  $k_T$  are significant, their relative contributions could be evaluated by measuring either of two rate constants—that for racemizing an optically active mixture containing only *ERSZ* and/or *ESRZ* ( $\chi_4 - \chi_8$ ) or for equilibrating any experimentally convenient members of the *ZRRZ*, *ZSSZ*, *ESSE*, and *ERRE* quartet ( $\chi_4 + \chi_8$ ).<sup>14</sup> In either case, the experimental rate constant ( $4k_C$ ) could then be compared with the known value of  $\lambda_9$ ,  $4(k_C + k_T)$ .<sup>3b</sup>

A comparably complete resolution of  $\lambda_7$  is significantly more difficult and, perhaps, impossible. The relative contribution of [1,3] and [3,3] components is accessible by comparing  $\lambda_7$  with  $8(k_V + k_S + k_H + k_D)$ , the eigenvalue obtained by equilibrating a 1,4-disubstituted 1,5-hexadiene with its 1,6 and 3,4 isomers.<sup>15</sup> Further progress would then either require that  $k_C < \lambda_7$  (which seems unlikely) or  $\lambda_5 > 0$  (in violation of orbital symmetry control).<sup>2f</sup> Otherwise,  $k_C$  would dominate all other possible eigenvalues of both doubly and quadruply labeled 1,5-hexadienes. No further information could then be obtained.

Obviously, the utility of such an analysis in no way disparages the suggestive power of more empirically justified mechanistic criteria.<sup>16</sup> It does, however, emphasize that many, still unrealized, mechanistic distinctions can be made with complete rigor. Others cannot.

**Acknowledgment.** We are grateful for the partial financial assistance provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (GP 15863) and for the careful criticism of R. C. Fay.

(13) M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 5119 (1972).

(14) Gajewski<sup>2i</sup> has independently discovered the equivalent of one such possibility.

(15) Algebraic details of the analysis of doubly and quadruply labeled 1,5-hexadienes have been made available to the Editor and referees of this manuscript and will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-72-7149. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(16) For example,  $\Delta S^\ddagger \approx 4$  is more consistent with a "vault" or "slip" than with a "boat" or "plane" transition state. An extended search for the "twist" has (thus far) yielded no authentic examples,<sup>6b</sup> nor do we know of an authentic symmetry-forbidden thermal reaction of any hydrocarbon.

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 Received June 12, 1972

## Mechanisms of Photochemical Reactions in Solution. LXXII.<sup>1</sup> Electronic Pathways in the Photodissociation of 3-Methyl-1-phenoxybut-2-ene

Sir:

We recently reported evidence that photorearrangement of phenyl acetate to *o*- and *p*-hydroxyacetophenones<sup>2</sup> occurs *via* homolysis of the O-C(acyl) bond followed by radical recombination or hydrogen abstraction,<sup>2</sup> and not by concerted intramolecular pathways as had been previously suggested.<sup>3</sup> The electronic steps which lead to dissociation have not yet been elucidated, although Shizuka, *et al.*,<sup>4,5</sup> have proposed that acetanilide and phenyl acetate dissociate *via* (predissociative) triplet states of the N-C(acyl) or O-C(acyl) bonds. A similar mechanism had earlier been advanced by Porter<sup>6,7</sup> to explain the formation of benzyl radicals in the photolysis of toluene. Even though such a transition is spin forbidden, Porter concluded that the quantum yield was sufficiently low (*ca.*  $10^{-2}$ ) to be in qualitative agreement with known rates of intersystem crossing. In applying this same model to their studies, Shizuka, *et al.*, have concluded that the considerably larger quantum yields for photodissociation of acetanilide and phenyl acetate (0.25 and 0.51, respectively) result from enhanced intersystem crossing due to vibronic coupling of the aromatic  $S_1(\pi, \pi^*)$  and carbonyl  $T_1(n, \pi^*)$  states. In a sense this invokes some of the characteristics which usually lead to efficient crossing of  $S_1(n, \pi^*)$  states of simple carbonyl compounds to triplets.

Analogous photorearrangements of phenyl allyl ethers are of interest since there is no obvious basis for expecting interchromophoric coupling to enhance the rate of an  $S_1(\pi, \pi^*) \rightarrow {}^3\sigma(O-C)$  intersystem crossing (*vide infra*). We therefore chose  $\gamma, \gamma$ -dimethylallyl phenyl ether (3-methyl-1-phenoxybut-2-ene) (1) for photochemical study.<sup>8</sup>

Irradiation of 1 at 254 nm in either isopropyl alcohol or cyclohexane solution at room temperature led to the formation of six products. The quantum yields for the disappearance of 1 and for the appearance of products 2-7 are shown in Table I.<sup>10</sup>

We also irradiated 1 at 254 nm at atmospheric pressure in a gas-phase flow system, which has been previously described.<sup>2</sup> Products 2-7 were observed in relative yields not greatly different from those seen in solution. Addition of 25 Torr partial pressure of nitric oxide quenched the formation of products 3-7; some phenol and several uncharacterized products were detected by glpc.

Product ratios obtained both in solution and in the vapor phase, as well as the total quenching of 3-7

(1) Part LXXI: Y. L. Bahurel, D. J. MacGregor, T. L. Penner, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 637 (1972).

(2) J. W. Meyer and G. S. Hammond, *ibid.*, **92**, 2187 (1970).

(3) D. Bellus, *Advan. Photochem.*, **8**, 109 (1971).

(4) H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Jap.*, **42**, 909 (1969), and references therein.

(5) H. Shizuka, T. Morita, Y. Mori, and I. Tanaka, *ibid.*, **42**, 1831 (1969).

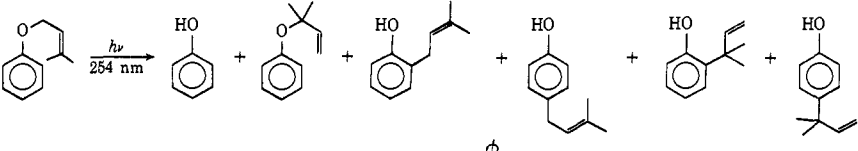
(6) G. Porter, *Chem. Soc., Spec. Publ.*, No. 9, 139 (1957).

(7) G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).

(8) Kelly, Pinhey, and Rigby reported<sup>9</sup> that the compound undergoes photochemical rearrangement, although their study lacked the quantitative character needed for our purposes.

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(10) Details of product isolation and quantum yield determinations will be reported later.

Table I.<sup>a</sup> Quantum Yields for Photoreactions of 3-Methyl-1-phenoxybut-2-ene


Solvent	1, $\phi_{dis}$	2	3	4	5	6	7
Cyclohexane	0.55	0.10	0.05	0.06	0.05	0.02	0.03
2-Propanol	0.75	0.11	0.03	0.18	0.15	0.05	0.07

<sup>a</sup> We suspect that the difference between the quantum yield for the disappearance of 1 and the sum of product appearance quantum yields is largely due to polymerization of 1.

by nitric oxide, suggest strongly that the reaction involves scission to phenoxy and dimethylallyl radicals—*i.e.*, the reaction is analogous to that of phenyl acetate.

The quantum yield for product formation from phenyl acetate in cyclohexane is 0.38,<sup>5</sup> which is not much greater than the quantum yield of product formation from 1 in cyclohexane. Since there is no evidence for the enhancement of intersystem crossing efficiencies by olefins, which themselves undergo intersystem crossing very inefficiently,<sup>11</sup> these results suggest that the photochemical reactivity of 1 is inconsistent with a general model in which enhancement of intersystem crossing is a prerequisite for photochemical dissociation.

The <sup>1</sup>L<sub>b</sub> absorption of 1 is essentially identical with that of anisole in cyclohexane solution. The compounds should, therefore, have the same inherent fluorescent lifetime ( $\tau_s^0$ ),  $3.4 \times 10^{-8}$  sec,<sup>12</sup> and rate constant for fluorescence ( $k_f$ ),  $2.9 \times 10^7$  sec<sup>-1</sup>.<sup>13</sup> For anisole, the observed fluorescence lifetime ( $\tau_s$ ) is  $8.3 \times 10^{-9}$  sec.<sup>9</sup> Therefore,  $1/\tau_s = k_f + k_{isc} + k_d = 1.2 \times 10^8$  sec<sup>-1</sup>.

The fluorescence of 1 also is identical in band shape and position with that of anisole. However, the quantum yield of fluorescence is only 0.011.<sup>14</sup> From the ratio  $\phi_f/k_f$ , we calculate that  $\tau_s$  is about  $3.7 \times 10^{-10}$  sec. We can thus calculate a rate constant for the reaction,  $k_r = \phi_f/\tau_s = 8.6 \times 10^8$  sec<sup>-1</sup>.

The processes of back reaction and radiationless decay must account for the deactivation of the remainder of the S<sub>1</sub> states of 1. Consideration of the data in Table I suggests that in cyclohexane the radicals recombine to give 3 roughly twice as often as to give 6 or 7. If the same ratio holds for the rate of formation of 1 relative to 4 and 5, we might expect the quantum yield for the back reaction in cyclohexane to be *ca.* 0.10. Thus we may estimate the rate constant for enhanced radiationless decay:  $1/\tau_s - (k_{isc} + k_d) - k_r - k_{back} = k_x \cong 1.5 \times 10^9$  sec<sup>-1</sup>. We conclude that nonchemical, nonradiative decay and chemical

reaction are both markedly accelerated in 1, relative to anisole.

Possibly the two accelerated nonradiative processes are closely related. Stretching of the weak C–O bond in the allyl ether should become highly anharmonic in the energy region close to or above the bond dissociation energy. Such anharmonicity may increase the Franck-Condon overlap between high and low vibrational states that is required to make a vibrational mode available as an energy sink in the internal conversion process. If so, the presence of “easily breakable” bonds may lead to acceleration of internal conversion even when the process does not lead ultimately to actual scission, either because the energy deposited initially is less than the dissociation energy or because internal vibrational relaxation removes energy from the dissociative mode before separation occurs.

**Acknowledgment.** This work was supported by the U. S. Army Research Office-Durham. We thank Drs. M. T. McCall and R. G. Weiss for helpful discussions.

(15) National Science Foundation Predoctoral Fellow, 1969–present.

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Received April 24, 1972

### Photochemical Behavior of *trans*-Chloroisothiocyanato-bis(ethylenediamine)chromium(III)

Sir:

From recent investigations on the photochemistry of Cr(III) complexes containing two different types of ligands, the following features have emerged:<sup>1</sup> (i) generally, two distinct photoreactions take place;<sup>2-6</sup> (ii) the relative importance of the two photoreactions depends on the wavelength of irradiation;<sup>3-6</sup> (iii) the

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