

475 oscilloscope was used (method II). Temperature effects were investigated by placing the sample cuvettes in a metal Dewar with quartz windows, and the temperature was controlled by a constant flow of cold nitrogen gas.

**Acknowledgment.** The cost of the present investigations was

partly defrayed by a Grant-in-Aid from the Ministry of Education of Japan and Mitsubishi Foundation. The authors wish to express their sincere thanks to Dr. Tadashi Okada for his discussion. Thanks are also due to the editor and the reviewers for their comments.

## Photosensitized Dissociation of Di-*tert*-butyl Peroxide. Energy Transfer to a Repulsive Excited State

J. C. Scaiano\*<sup>1a</sup> and Gene G. Wubbels\*<sup>1b</sup>

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and the Department of Chemistry, Grinnell College, Grinnell, Iowa 50112. Received April 28, 1980

**Abstract:** Energy transfer from a variety of aromatic hydrocarbons and ketones to di-*tert*-butyl peroxide has been examined by using nanosecond laser flash photolysis techniques. Triplet energy transfer to the peroxide leads to its efficient cleavage into two *tert*-butoxy radicals. Representative rate constants for triplet quenching in benzene at 25 °C are  $7.9 \times 10^6$ ,  $3.4 \times 10^6$ , and  $7.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for *p*-methoxypropio-phenone, benzophenone, and benz[*a*]anthracene, respectively. The rate of transfer for *p*-methoxypropio-phenone ( $E_T \approx 72.5 \text{ kcal/mol}$ ) is approximately temperature independent; for lower energy sensitizers ca. 0.17 kcal/mol activation energy is required for each kilocalorie per mole decrease in triplet energy. No evidence indicating exciplex intermediacy was found. A model for energy transfer to a repulsive state of the peroxide is proposed in which no activation energy is required if the sensitizer meets the energy requirements at the O-O equilibrium distance. For sensitizers of lower triplet energy, energy transfer to a repulsive state is proposed to occur from a thermally activated ground state having a greater than equilibrium oxygen-oxygen bond length. The same mechanism may apply in other systems where the acceptor lacks low-lying excited states. A few rate constants for the quenching of singlet sensitizers have also been determined by using fluorescence techniques.

### Introduction

Investigations of electronic energy transfer by the electron-exchange mechanism<sup>2-4</sup> have dealt with a variety of effects including those of separation<sup>5</sup> and orientation<sup>6</sup> of donor and acceptor, steric hindrance,<sup>7</sup> the energy change accompanying transfer,<sup>8</sup> and the influence of medium viscosity.<sup>9</sup> In most studies the acceptors have been molecules having energetically accessible, bound excited states. Few quenchers possessing energetically accessible repulsive excited states have been studied. Photosensitized dissociation of a quencher is, of course, not rare, but the process often involves a bound excited state which requires thermal activation for dissociation.<sup>10</sup> Several studies concerned with the photosensitized dissociation of peroxides have been published.<sup>11-17</sup> Among studies

Table I. Kinetics of Triplet Quenching by Di-*tert*-butyl Peroxide

sensitizer	solvent	$k_q^a$	$\tau_{T^1}^b$ (perox) <sup>b</sup>	$\gamma^c$
propio-phenone	benzene	$9.6 \times 10^6$		
<i>p</i> -methoxypropio-phenone	benzene	$7.9 \times 10^6$	23	0.57
benzophenone	benzene	$3.4 \times 10^6$	60	0.72
benzophenone	acetonitrile	$3.7 \times 10^6$		
phenanthrene	benzene	$1.8 \times 10^6$	98	0.85
phenanthrene	acetonitrile	$3.0 \times 10^6$		
naphthalene	benzene	$1.1 \times 10^6$	150	0.62
benzil	benzene	$2.8 \times 10^4$	3000	
fluorenone	benzene	$2.4 \times 10^5$	680	
benz[ <i>a</i> ]anthracene	benzene	$7.0 \times 10^4$	2200	
anthracene	benzene	$9.7 \times 10^4$	1500	

<sup>a</sup> Units of  $\text{M}^{-1} \text{ s}^{-1}$ , at 25 °C. <sup>b</sup> In nanoseconds, in neat peroxide. <sup>c</sup> Efficiency of *tert*-butoxy radical generation (see text below), neglecting any differences in cage recombination between direct and sensitized photodecompositions.

of energy transfer to dissociative states of other molecules,<sup>11,18,19</sup> the kinetic study by Wallace, Van Duyne, and Lewis<sup>18</sup> on singlet and triplet quenching by dialkyl disulfides is the most extensive, but a general model for energy transfer to a dissociative state remains to be described.

In this paper we report a study of the quenching of several sensitizers by di-*tert*-butyl peroxide. We have obtained absolute

(1) (a) University of Notre Dame. Address correspondence to the Division of Chemistry, National Research Council, Ottawa K1A 0R6, Canada. (b) Grinnell College.

(2) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836-850.

(3) Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7-17.

(4) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978-1989.

(5) Ermolaev, U. L. *Sov. Phys.-Dokl. (Engl. Transl.)* **1967**, *6*, 600.

(6) De Schryver, F.; Boens, N. *Adv. Photochem.* **1977**, *10*, 359.

(7) Wamser, C. C.; Medary, R. T.; Kochevar, I. E.; Turro, N. J.; Cheng, P. L. *J. Am. Chem. Soc.*, **1975**, *97*, 4864-4869.

(8) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355-2374.

(9) Birks, J.; Salet, M.; Leite, S. C. P. *J. Phys. B* **1970**, *3*, 417-424.

(10) (a) Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W.-K. *J. Am. Chem. Soc.* **1979**, *101*, 6435-6437. (b) Engel, P. S.; Bishop, D. J.; Page, M. A. *Ibid.* **1978**, *100*, 7009-7017.

(11) Kuz'min, M. G.; Guseva, L. N. *High Energy Chem. (Engl. Transl.)* **1970**, *4*, 19-22.

(12) Ivanov, V. L.; Filimonova, G. V.; Kuz'min, M. G. *High Energy Chem. (Engl. Transl.)* **1972**, *6*, 446-448.

(13) Fahrenholtz, S. R.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1971**, *93*, 251-253.

(14) Ng, N. C.; Guillet, J. E. *Macromolecules* **1978**, *11*, 937-942.

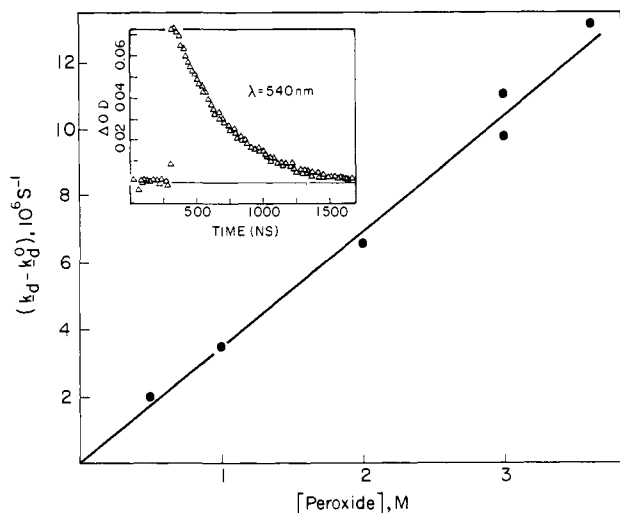
(15) Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 3413-3417.

(16) Levy, M.; Steinberg, M.; Szwarc, M. *J. Am. Chem. Soc.* **1954**, *76*, 5978-5981.

(17) Geuskens, G.; David, C. *Pure Appl. Chem.* **1979**, *51*, 2385-2393.

(18) Wallace, W. L.; Van Duyne, R. P.; Lewis, F. D. *J. Am. Chem. Soc.* **1976**, *98*, 5319-5326.

(19) (a) Pavlik, J. O.; Plooard, P. I.; Somersalt, A. C.; Guillet, J. E. *Can. J. Chem.* **1973**, *51*, 1435-1440. (b) Encina, M. V.; Lissi, E. A. *J. Photochem.* **1974**, *3*, 237-239.



**Figure 1.** Determination of  $k_q$  for benzophenone in benzene, according to eq 1. Insert: trace obtained for  $[t\text{-BuOO-}t\text{-Bu}] = 0.5 \text{ M}$  (average of four laser shots).

quenching rate constants by using laser flash photolysis techniques. Our study centers on the triplet state reaction; whenever possible we have also determined the quantum yields of alkoxy radical generation and, in a few selected cases, the activation energy for the quenching process.

In a few systems, we have also determined rates of singlet quenching in order to differentiate singlet and triplet components in the determination of quantum yields and to compare the singlet reaction characteristics with those of the triplet state process.

## Results

All of our experiments involving triplet quenching have been carried out by using laser flash photolysis techniques. Our instrument uses the pulses from a nitrogen laser (8 ns,  $\sim 3 \text{ mJ}$ , 337.1 nm) for excitation and a detection system with nanosecond response.

Quenching by di-*tert*-butyl peroxide of the triplet states of a series of aromatic hydrocarbons and ketones in benzene and acetonitrile was observed by monitoring directly triplet-triplet absorptions in the presence of various concentrations of peroxide. At sufficiently low excitation doses, all the triplets examined underwent clean first-order decay. The pseudo-first-order rate constants of triplet decay ( $k_d = \tau_T^{-1}$ ) correlate with the rate constants of quenching ( $k_q$ ) and that of decay in the absence of peroxide ( $k_d^0$ ) according to eq 1.

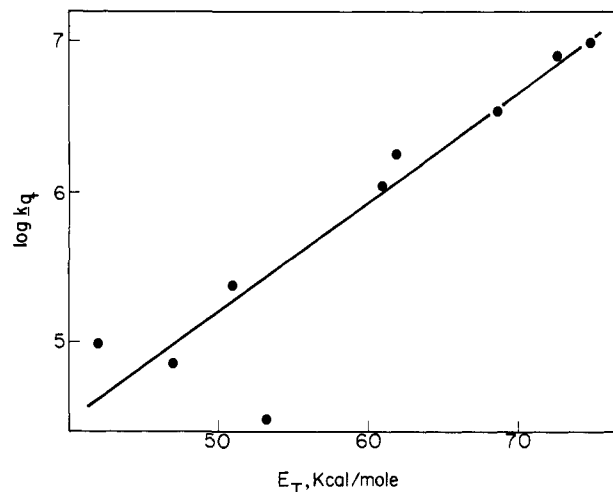
$$k_d = k_d^0 + k_q[t\text{-BuOO-}t\text{-Bu}] \quad (1)$$

The rate constants obtained by using this approach are summarized in Table I. Figure 1 shows a typical plot according to eq 1 and the corresponding triplet decay trace (insert).

Naphthalene does not absorb at 337.1 nm; its triplet state was generated by sensitization by using benzophenone as an absorber. For example, when the concentrations are naphthalene = 0.028 M and peroxide = 3.6 M, at most 6% of the benzophenone triplets could be quenched by peroxide.

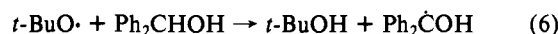
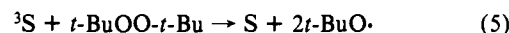
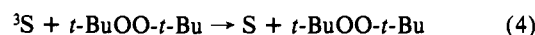
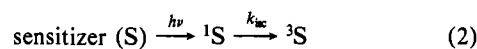
The triplet sensitizers selected span a range of triplet energy from ca. 75 to 42 kcal/mol. When  $\log k_q$  is plotted against  $E_T$  (Figure 2), a reasonably linear correlation is observed.<sup>20</sup> The slope of this plot (0.072 mol/kcal) is considerably less than that observed for normal endothermic energy transfer at 25 °C (0.733 mol/kcal).<sup>8</sup>

The efficiency of sensitized homolysis of the peroxide O-O bond was estimated for four sensitizers (Table I). For most of the other systems (not examined) the errors can in general be expected to



**Figure 2.** Dependence of  $\log k_q$  in benzene on the triplet energy of the sensitizer.

be large, either because of the slow rate of quenching or because of extensive involvement of singlet state processes (vide infra). The reactions involved in these experiments are shown in eq 2-7.



The experimental rate constants for triplet quenching ( $k_q$ ) by peroxide include all quenching events, regardless of whether they lead to alkoxy radical generation, i.e.,  $k_q = k_4 + k_5$ . Reaction 7 includes all pseudo-first-order components, in particular, attack on the peroxide by  $t\text{-BuO}\cdot$  and cleavage of  $t\text{-BuO}\cdot$  to give acetone and methyl radicals. Radical-radical reactions (e.g., recombination) can be ignored by using sufficiently low excitation doses<sup>21</sup> and are not important in the time scales used in this work. Diphenylmethanol was used as a probe<sup>21-23</sup> (see below). For three of the sensitizers, *p*-methoxypropiophenone, benzophenone, and naphthalene (benzophenone sensitized), only triplet quenching needs to be considered, since the excited singlets are too short-lived to participate in energy transfer to the peroxide. For phenanthrene, however, quenching of the singlet is significant (see below), and it was necessary to take it into consideration in determining the efficiency of the triplet reaction. The efficiency of quenching the singlet and triplet manifolds may be estimated by eq 8. For

$$\Phi_q = \tau_s k_q^s [t\text{-BuOO-}t\text{-Bu}] + (k_{isc} \tau_s) \tau_T k_q^T [t\text{-BuOO-}t\text{-Bu}] \quad (8)$$

phenanthrene in 1.12 M peroxide we estimate that 33% of the excited singlets and 70% of the triplets would be quenched. Using the rates of triplet quenching and triplet lifetimes from our experiments, we estimate that for *p*-methoxypropiophenone, benzophenone, and naphthalene, 95, 75, and 62% of the triplets decay via peroxide quenching in 1.12 M peroxide. In addition, in the case of naphthalene, ca. 2% of the benzophenone triplets would be quenched by peroxide.

Alkoxy radicals are not easy to detect by using absorption spectroscopy, particularly when in the presence of strong UV

(21) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520-4527.

(22) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 296-298.

(23) Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49-51.

(20) Benzil is the only sensitizer whose behavior deviates significantly from that observed for all the other sensitizers studied; this result is probably related to the exceptional geometric differences between its ground and excited states: Morantz, D. J.; Wright, A. J. C. *J. Chem. Phys.* **1971**, *54*, 692-697.

Table II. Arrhenius Parameters for Triplet Quenching in Neat Di-*tert*-butyl Peroxide

sensitizer	$E_a^a$ , kcal/mol	$A^b$ , $M^{-1} s^{-1}$
<i>p</i> -methoxypropiophenone	~0	$7.8 \times 10^6$
benzophenone	0.78	$1.4 \times 10^7$
phenanthrene <sup>c</sup>	1.67	$2.6 \times 10^7$
fluorenone	3.94	$1.3 \times 10^8$

<sup>a</sup> Typical errors are ca. 0.3 kcal/mol, except in the case of fluorenone where the error is probably ca. 0.7 kcal/mol. <sup>b</sup> The  $A$  factors have been corrected to bimolecular values dividing the intercept of the  $-\log \tau_T$  vs.  $T^{-1}$  plot by 5.5 M. <sup>c</sup> For example in this case the  $k$  values at  $-50, -30, -28, -5,$  and  $+23$  °C are  $3.62 \times 10^6, 3.78 \times 10^6, 5.17 \times 10^6, 6.83 \times 10^6,$  and  $8.59 \times 10^6 s^{-1}$ , respectively, in neat peroxide.

absorbers, as in the case with most of the sensitizers used. The yield of *t*-BuO• can be determined if these radicals are scavenged by a molecule which generates easily detectable absorptions, as in the case for diphenylmethanol which leads to the diphenylhydroxymethyl radical (reaction 6),<sup>24</sup> which can be easily monitored at 540 nm. We have used the direct photodecomposition of di-*tert*-butyl peroxide as a reference reaction, effectively an actinometer. The yields are then determined from the absorption due to Ph<sub>2</sub>COH correcting for the fraction of excited states quenched and the fraction of the 337-nm pulse absorbed.<sup>25</sup> The efficiencies given in Table I are subject to total cumulative errors of the order of 20%. It should be emphasized that the efficiencies “ $\gamma$ ” given in Table I are not quantum yields but rather,  $\gamma$  represents the fraction of the quenching events which leads to the formation of a pair of *tert*-butoxy radicals.<sup>26</sup> In the case of *p*-methoxypropiophenone, benzophenone, and naphthalene the value of  $\gamma$  refers exclusively to triplet quenching, while for phenanthrene it is a combined singlet-triplet efficiency; that is, it was normalized to the total number of quenching events. The values of  $\gamma$  do not seem to vary systematically with the energy of the sensitizer; the fact that the values are all in the neighborhood of 0.7 indicates that quenching does indeed cause efficient photodissociation. Around 30% of the quenching events do not seem to lead to photodissociation; while the difference between the values of  $\gamma$  and unity is close to the experimental error, it is also systematic enough to suggest that it may be significant.

Quenching rate constants were also determined in acetonitrile for two of the sensitizers, benzophenone and phenanthrene, in order to assess the importance of solvent polarity. The rate constants increased by 9 and 67%, respectively, when compared with the values in benzene, indicating that quenching is relatively unresponsive to large changes in the dielectric character of the solvent.

In order to gain further insight into the quenching mechanism, we determined the triplet lifetimes of all the sensitizers at 25 °C in pure di-*tert*-butyl peroxide; the corresponding values have been included in Table I. The triplet lifetimes under these conditions are determined by peroxide quenching, which, with the exception of the case of anthracene (where it could be around 80%), is responsible for well over 90% of the triplet decay. This conclusion is based on the rates of quenching given in Table I and the experimental triplet lifetimes in benzene.

(24) Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144. Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038.

(25) As long as *tert*-butoxy radicals do not react with the sensitizer, the fraction of radicals trapped by diphenylmethanol will be controlled only by the concentration of the latter. Under these conditions the ratio of transient absorbances due to diphenylhydroxymethyl radicals (monitored at 540 nm) reflects the yields of *tert*-butoxy in the sample and peroxide reference. This ratio has to be corrected by the ratio of absorbed light intensities by sensitizer and reference peroxide sample and by the fraction of triplets actually quenched by peroxide; only experiments where this fraction is relatively high can yield reliable values, since this minimizes the magnitude of the correction.

(26) We have ignored any differences in the extent of cage recombination of *tert*-butoxy radicals between the direct photodecomposition (effectively used as a reference reaction) and the sensitized process. This is not expected to be an important source of error, since reported efficiencies of radical generation are in the 88–95% range: Lissi, E. A. *Can. J. Chem.* **1974**, *52*, 2491–2492; Kiefer, H.; Traylor, T. G. *J. Am. Chem. Soc.* **1967**, *89*, 6667–6671.

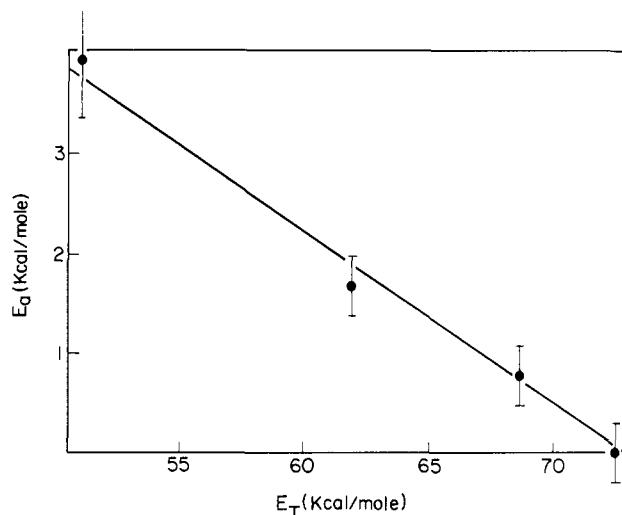
Figure 3. Dependence of the experimental activation energies for energy transfer on the triplet energy of the sensitizer.<sup>27</sup>

Table III. Fluorescence Quenching Data in Benzene at Room Temperature

sensitizer	$k_q \tau_s$ , $M^{-1}$	$k_q$ , $M^{-1} s^{-1}$	$\lambda_{exc}/\lambda_{emi}$
phenanthrene	0.12	$9 \times 10^6$	378/401
fluorenone	0.30	$7.3 \times 10^7$	420/480
benzil	0.03 <sup>a</sup>	$<3 \times 10^7$	400/496
benz[a]anthracene	0.31	$3 \times 10^7$	388/411
anthracene	0.29	$7 \times 10^7$	390/424

<sup>a</sup> Quenching of benzil fluorescence ( $\tau_s < 1$  ns) was not appreciable at 1 M peroxide.

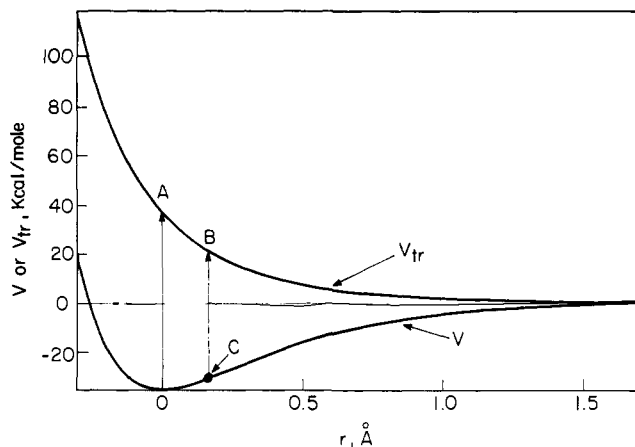
Table IV. Redox and Spectroscopic Properties of the Sensitizers Used<sup>a</sup>

sensitizer	$E_T^b$	$E_s^b$	$\tau_s^c$	$E_{red}^b$	$E_{ox}^b$
propiophenone	74.5			-48.9 <sup>d</sup>	58.9 <sup>d</sup>
<i>p</i> -methoxypropiophenone	72.5				
benzophenone	68.6			-39.7	54.7
phenanthrene	61.9	82.8	13.4	-54.2	38.5
naphthalene	60.9			-56.5	40.8
benzil	53.4	59.0	$\leq 1$	-24.0	
fluorenone	51	63	4.1	-31.1	
benz[a]anthracene	47	74.5	10.4	-46.6	30.0
anthracene	42	76.3	4.2	-45.4	29.7

<sup>a</sup> Sources of information: Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 5656–5659; Kalinowski, M. K. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1970**, *18*, 685–692; Mann, C. K.; Barnes, K. K. "Electrochemical Reaction in Non-Aqueous Systems"; Marcel Dekker: New York, 1970; Loutfy, R. O.; Loutfy, R. O. *J. Phys. Chem.* **1973**, *77*, 336–339; Yoshihara, K.; Kearns, D. R. *J. Chem. Phys.* **1966**, *45*, 1991–1999; Loutfy, R. O.; Loutfy, R. O. *J. Phys. Chem.* **1972**, *76*, 1650–1655; Fang, T.-S.; Brown, R. E.; Kwan, C. L.; Singer, L. A. *Ibid.* **1978**, *82*, 2489–2496. <sup>b</sup> In kcal/mol. <sup>c</sup> In air-saturated benzene (nanoseconds); see text. <sup>d</sup> Values for acetophenone.

The role of the triplet energy in determining the kinetics of peroxide quenching can also be examined from a plot of  $-\log \tau_{(peroxide)}$  vs.  $E_T$ . This plot (not shown) is virtually coextensive with the one shown in Figure 2; the slopes of the plots based on  $k_q$  and  $\tau_T$  are 0.072 and 0.067 mol/kcal, respectively.

For four of the sensitizers (Table II), we also examined the temperature dependence of the triplet lifetimes in neat peroxide in the  $-48$  to  $+25$  °C range. The activation parameters given in Table II were obtained from conventional Arrhenius plots of the triplet decay rates obtained at four to seven different temperatures. Figure 3 shows a plot of  $E_a$  vs.  $E_T$  for the four sensitizers examined; the slope of this approximately linear plot is  $-0.174$ , meaning that activation energy increases 0.174 kcal/mol for each 1 kcal/mol



**Figure 4.** Attractive ( $V$ ) and repulsive ( $V_{tr}$ ) potentials calculated according to eq 9 and 10, respectively. The bond dissociation energy was taken as 36 kcal/mol and the Morse parameter  $\beta$  as  $2.69 \text{ \AA}^{-1}$ .

decrease in triplet energy. The  $A$  factors are rather low and show an increase with decreasing triplet energy.<sup>27</sup>

We have also examined the quenching of the fluorescence of three aromatic hydrocarbons and two aromatic ketones (Table III). In the case of benzil, we could not observe quenching of its fluorescence, even at di-*tert*-butyl peroxide concentrations of 1 M. The rate constants were obtained by combining the Stern-Volmer slopes with literature singlet lifetimes. Table IV gives a summary of singlet lifetimes, as well as other spectroscopic and redox properties of the sensitizers used. The quenching rate constants in Table III are subject to errors on the order of 25% resulting from the use of literature values which we corrected for oxygen quenching (see Experimental Section). The rate constants, which fall in the vicinity of  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ , are well below the diffusion limit for benzene but generally exceed the rates for the corresponding triplet state processes.

Finally, we have also calculated potential energy profiles for the cleavage of the O-O bond in di-*tert*-butyl peroxide. While plots of this type can only be regarded as a very coarse approximation, they do provide a better basis for mechanistic discussion than a purely qualitative plot. For the bonding interaction we have used a simple Morse potential,<sup>28</sup> eq 9, and for the repulsive triplet term we have used a Sato-Morse function,<sup>29,30</sup> eq 10, where

$$V = De[\exp(-2\beta r) - 2 \exp(-\beta r)] \quad (9)$$

$$V_{tr} = (De/j)[\exp(-2\beta r) + 2 \exp(-\beta r)] \quad (10)$$

$V$  and  $V_{tr}$  are the attractive and repulsive energy terms, respectively,  $r$  is the displacement from the equilibrium bond distance,  $De$  is the bond energy, and  $\beta$  is the Morse parameter, which for the peroxide bond we have taken as  $2.69 \text{ \AA}^{-1}$ .<sup>31</sup> The parameter  $j$  was taken as 2 by Sato,<sup>29</sup> although in some cases  $j = 4$  gives a better repulsive curve.<sup>30</sup> We have used  $j = 2.9$ ; our choice was carried out by optimizing for  $E_a \approx 0$  at  $E_T = 72.5 \text{ kcal/mol}$  (see Discussion). That is, the vertical transition ( $r = 0$ ) corresponds to  $(V_{tr} - V) = 72.5 \text{ kcal/mol}$ . Figure 4 shows the plots obtained.

## Discussion

Gas-phase spectroscopic studies suggest that the first excited singlet state of dialkyl peroxides corresponds to a dissociative state.<sup>32,33</sup> There is also no evidence for the involvement of pre-dissociative excited states.<sup>33,34</sup> CNDO calculations for hydrogen

peroxide<sup>35</sup> indicate that three excited singlet states and four triplet states exhibit no minima with changes in the O-O distance and correlate with the ground state of two hydroxyl radicals; further, the author<sup>35</sup> speculated that the results should also apply to di-*tert*-butyl peroxide,<sup>36-39</sup> since the oxygen orbital degeneracies of the scission products are the same as in the case of hydrogen peroxide.

Whereas singlet energy transfer can take place by several mechanisms,<sup>3,40</sup> triplet-triplet energy transfer from the sensitizers to the peroxide can only occur by the electron-exchange mechanism.<sup>3,40-42</sup> A recent study of quenching by dialkyl disulfides<sup>18</sup> concludes that the electron-exchange mechanism also applies to singlet quenching by disulfides on the ground that the overlap of donor fluorescence and acceptor absorbance is too small to permit resonance or emission-absorption transfer. Inasmuch as di-*tert*-butyl peroxide absorbs UV light more weakly than the disulfides,<sup>18,32a,43</sup> we propose that the exchange mechanism must also apply to singlet quenching by di-*tert*-butyl peroxide.

Previous studies of energy transfer to peroxides have proposed a variety of mechanisms; Ng and Guillet<sup>14</sup> suggest that energy transfer from carbonyl triplets in polymers to di-*tert*-butyl peroxide involves the intermediacy of an exciplex in which vibronic coupling permits transfer of the electronic energy to vibrational modes of the peroxide.<sup>44</sup> A similar mechanism has been proposed by Lohdi<sup>45</sup> for quenching of triplet naphthalene by di-*tert*-butyl peroxide. Kuz'min et al.<sup>11,12</sup> propose that excited state quenching by acetyl peroxide involves the formation of a charge-transfer exciplex followed by O-O bond dissociation, a mechanism which they suggest is analogous to predissociation in a nascent complex between donor and acceptor. In each case the authors reject normal electron-exchange energy transfer on energetic grounds. The basis for this conclusion is the assumption that the only accessible excited state of the peroxide is the one that would be reached by Franck-Condon excitation of the ground state at the equilibrium distance. We show below with a general model for energy transfer to a repulsive state that this is too limited an assumption concerning the accessible energies of a peroxide quencher.

The question of exciplex formation was examined in detail by Wallace, Van Duyne, and Lewis<sup>18</sup> for both singlet and triplet transfer to dialkyl disulfides from aromatic hydrocarbons and aromatic ketones. The criteria for the absence of exciplex formation were (i) a change in solvent from benzene to acetonitrile caused only a small increase in the rate constant for quenching and (ii) in both the singlet and triplet manifolds, the rate constants for quenching showed no correlation with the electron-donating or -accepting characteristics of either the sensitizers or quenchers. Application of these criteria to our results yields the same conclusion. Figure 2 clearly shows that the rate of energy transfer is controlled by the triplet energy, regardless of other sensitizer characteristics such as the nature of the excited state (e.g.,  $n, \pi^*$

(34) Similar conclusions have been advanced in the case of hydrogen peroxide: Volman, D. H. *Adv. Photochem.* **1963**, *1*, 43-82.

(35) Evleth, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 1637-1639.

(36) The calculations<sup>35</sup> assumed a trans geometry; the dihedral angle between the *tert*-butyl groups in di-*tert*-butyl peroxide is  $166^\circ$ ,<sup>37</sup> and the barrier to rotation in di-*tert*-butyl peroxide to the  $180^\circ$  geometry should be practically negligible.<sup>38</sup>

(37) Kaess, D.; Oberhammer, H.; Brandes, D.; Blasehette, A. *J. Mol. Struct.* **1977**, *40*, 65-75.

(38) Batich, C.; Adam, W. *Tetrahedron Lett.* **1974**, 1467-1470.

(39) In fact there is little question that the lowest triplet state is repulsive. In the case of the excited singlets, the indications are that in the gas phase those states are also repulsive. In solution there are some indications that the lowest singlet state can be quenched.<sup>21</sup>

(40) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, California, 1978; Chapter 9.

(41) Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1042-1052.

(42) Turro, N. J. *Pure Appl. Chem.* **1977**, *49*, 405-429.

(43) Bell, E. R.; Rust, F. F.; Vaughn, W. E. *J. Am. Chem. Soc.* **1950**, *72*, 337-338.

(44) This mechanism appears to correspond to that proposed for quenching of dimethoxybenzene by  $\sigma$ -bonded quenchers: Carroll, E. A.; McCall, M. T.; Hammond, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 315-318.

(45) Lodhi, S. A. K. *Pak. J. Sci. Ind. Res.* **1971**, *14*, 173-176. Lodhi, S. A. K.; Moghal, G. R. *Ibid.* **1969**, *12*, 27-30.

(27) For reasons elaborated in the Discussion section, we note that the linear fitting shown in Figure 3 has been used simply for convenience.

(28) Morse, P. M. *Phys. Rev.* **1929**, *34*, 57.

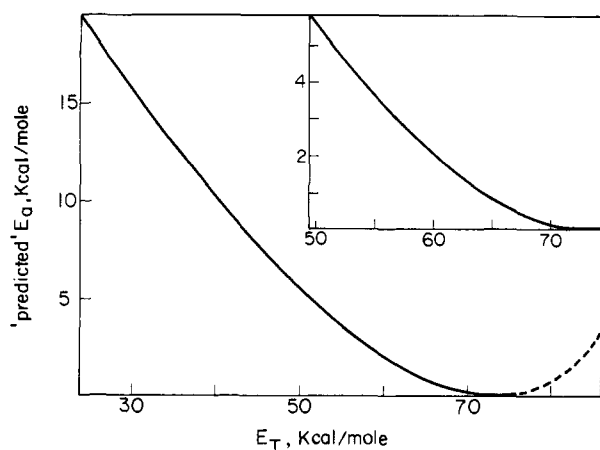
(29) Sato, S. *J. Chem. Phys.* **1955**, *23*, 2465.

(30) Johnston, H. S. "Gas-Phase Reaction Rate Theory"; Ronald Press: New York, 1966; Chapter 4.

(31) Reference 30, p 210.

(32) (a) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; pp 443-449. (b) *Ibid.*, pp 172-174.

(33) Dorer, F. H.; Johnson, S. N. *J. Phys. Chem.* **1971**, *75*, 3651-3655.



**Figure 5.** Predicted activation energies obtained from the difference between the two potentials in Figure 4. The insert shows an expansion of the region of interest (same units as the main figure). The dashed curve corresponds to hypothetical transfers to the left of the equilibrium distance.

or  $\pi, \pi^*$ ), the type of molecule or its dipole moment. This conclusion is also supported by the lack of any correlation of the types used by Weller<sup>46</sup> or Guttenplan and Cohen<sup>47</sup> of the quenching rate constants with the redox parameters of the sensitizers (Table IV). Moreover, the slight increase in rate constants observed when the solvent is changed from benzene to acetonitrile is quite small when compared with changes observed in systems involving considerable charge transfer. For example, a similar solvent change caused a 25-fold increase in the rate of quenching of fluorenone triplets by triethylamine.<sup>47</sup>

The mechanism which we propose involves transfer to a triplet repulsive state. Energy transfer to the peroxide at its equilibrium geometry is represented by the vertical arrow at point A in Figure 4. If the sensitizer is able to supply energy matching the gap at point A, energy transfer would require no activation energy. As pointed out before, the value of "j" in eq 10 was optimized so that this condition would be fulfilled. For a sensitizer possessing less energy than that required at point A, we propose that vertical energy transfer could occur at a point somewhere to the right of point A; this would naturally be an activated process. If, for purposes of illustration, the sensitizer energy corresponded to the gap at point B, the activation requirements would correspond to the difference in energy at point C and that at the equilibrium distance, but the energy required to reach the repulsive state at point B would be greatly reduced because of the sharp downward slope of the excited state energy curve. The actual values of the activation energies are largely determined by the curvature at the bottom of the potential energy well. The expected dependence of  $E_a$  on the triplet energy can be approximated by plotting the difference in potential energies at  $r$  and  $r_0$  vs. the difference between the two curves in Figure 4 (or eq 9 and 10); this plot is shown in Figure 5, the insert showing an expansion of the region of interest. While the plot is far from linear, the region corresponding to triplet energies between 50 and 75 kcal/mol can, given the rough approximations already used, be approached by a linear expression; this leads to a slope of ca.  $-0.24$  which compares reasonably well with the value of  $-0.174$  obtained experimentally (Figure 3). For comparison, for normal endothermic energy transfer between bound states, the slope of the corresponding plot is expected to be  $-1.0$ .<sup>8</sup>

The  $A$  factors observed deserve some comment. The values obtained are quite low and show an increasing trend with decreasing triplet energy. Typical  $A$  factors for endothermic quenching would be expected to be in the neighborhood of  $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>48</sup> It is conceivable that the low  $A$  factors with di-*tert*-butyl

peroxide reflect unusually stringent orientational requirements for successful energy transfer. Examination of space-filling models suggests that the orbitals on oxygen are well shielded by the *tert*-butyl groups. Comparison with models of di-*tert*-butyl disulfide and azo-*tert*-butane indicates that the center orbitals in both, but specially for the disulfide, are substantially more accessible than are those of the peroxide. Benzophenone triplets are quenched by di-*n*-butyl disulfide 3.3 times faster than by di-*tert*-butyl disulfide.<sup>18</sup> Steric effects in the case of azoalkane quenching are larger;<sup>7</sup> azo-*tert*-butane quenches triplet triphenylene about 10 times slower than does azo-*n*-butane, the difference being attributed to a steric effect.<sup>7</sup> Though we have no directly comparable data, steric hindrance of approach to the heteroatom orbitals seems likely to be larger for di-*tert*-butyl peroxide than for the comparable azo or disulfide compounds.

That steric hindrance should depress the rate constant ( $k_{ET}$ ) for energy transfer by the exchange mechanism can be seen by examining eq 11,<sup>2,40</sup> in which  $K$  is related to specific orbital

$$k_{ET} = KJ \exp(-2R_{DA}/L) \quad (11)$$

interactions of the donor and acceptor,  $J$  is a spectral overlap integral, and  $R_{DA}$  is the donor-acceptor separation relative to their van der Waals radii,  $L$ . Since  $J$  is normalized for the extinction of the acceptor,<sup>40</sup>  $k_{ET}$  of energetically permitted transfers is predicted to be independent of the absorption characteristics of the acceptor.<sup>49</sup> Steric hindrance, by forcing a larger value of  $R_{DA}$ , would substantially decrease  $k_{ET}$ .<sup>7</sup> The van der Waals radii, which vary in the order  $S > N > O$ , would also make the orientational requirements of the peroxide more severe than those of the azo or disulfide compounds.

The reasons for the increase of the  $A$  factors with decreasing triplet energy are not entirely clear. It seems possible that those transfers with higher activation energy occur at geometries where a higher density of vibrational states is available. These conditions could lower the entropic requirements for energy transfer and lead to a looser transition state. In other words, if energy requirements are met, the probability of transfer would be higher for those structures which deviate from the equilibrium geometry.

In view of the variation in the  $A$  factor and the expected curvature of the  $E_a$  vs.  $E_T$  plot (see Figure 5) one could argue that the correlation of Figure 2 should not necessarily lead to a straight line; while this is true, the linear representation is an experimental fact and should be regarded as a convenient basis for discussion and is useful simply in this sense.

The limited singlet quenching data (Table III) show no simple correlation with singlet energy nor with any other sensitizer characteristic listed in Table IV. Due to the limited data available and the considerable errors involved in the case of the singlet state, we hesitate to draw any firm conclusions about the singlet quenching mechanism.

## Conclusion

The quenching of triplet states by di-*tert*-butyl peroxide involves exchange transfer to a repulsive state of the peroxide. Energy transfer leads to efficient bond cleavage. It is suggested that transfers from sensitizers which do not meet the energy requirements at the equilibrium O-O bond distance takes place by vertical excitation at nonequilibrium distances. Semiempirical calculations using Morse-Sato potential are consistent with these assumptions.

## Experimental Section

**Materials.** All the sensitizers were of the highest purity commercially available and were recrystallized or distilled prior to use. Di-*tert*-butyl peroxide was an MCB product; it was distilled and treated on an alumina column to eliminate all traces of *tert*-butyl hydroperoxide. Diphenylmethanol (Aldrich) was doubly sublimed. The solvents, benzene and acetonitrile, were Aldrich, Gold Label.

(48) E.g., fluorescence quenching of pyrene by di-*n*-butyl disulfide ( $E_a = 3.65 \text{ kcal/mol}$ );<sup>18</sup> an  $A$  factor of  $6.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  may be calculated.

(49) We were surprised by the conclusion<sup>18</sup> that spectral overlap differences for di-*tert*-butyl vs. di-*n*-butyl disulfide can account for the threefold difference in their quenching rate constants.

(46) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257. Leonhardt, H.; Weller, A. *Ibid.* **1963**, *67*, 671.

(47) Guttenplan, J. B.; Cohen, S. G. *Tetrahedron Lett.* **1972**, 2163-2166.

**Singlet Quenching.** Fluorescence quenching measurements were carried out by using a Spex fluorolog digital spectrofluorimeter. Sensitizers selected for study were those with significant absorption at wavelengths greater than 380 nm, so that competitive absorption by di-*tert*-butyl peroxide ( $\epsilon_{380} = 0.031 \text{ M}^{-1} \text{ cm}^{-1}$ ) was minimized. Quencher concentrations ranged from 0.1 to 1.5 M, and the resulting Stern-Volmer plots were acceptably linear. The solutions (in benzene) were not deaerated. Fluorescence lifetimes for fluorenone<sup>50</sup> and anthracene<sup>51</sup> in air-saturated benzene were available in the literature. The literature values for phenanthrene ( $\tau_F = 57.4 \text{ ns}$ )<sup>18</sup> and benz[*a*]anthracene ( $\tau_F = 26 \text{ ns}$ )<sup>52</sup> were corrected for oxygen quenching by the formula  $\tau_{\text{air}} = 1/(\tau_F^{-1} + k_{\text{O}_2}[\text{O}_2])$ . The values of  $[\text{O}_2]$  and  $k_{\text{O}_2}$  were taken to be  $1.91 \times 10^{-3} \text{ M}$  and  $3.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>53</sup> This procedure and the use of literature lifetimes introduce the possibility of up to 25% error in our quenching rate constants.

**Triplet Quenching.** Our laser flash photolysis facility makes use of a Moletron UV-400 nitrogen laser for excitation. The pulses (8 ns,  $\sim 3$

mJ, 337.1 nm) are concentrated on the sample and are incident at an angle of approximately  $15^\circ$ . The excitation doses were adjusted with suitable neutral density filters in order to avoid triplet-triplet annihilation processes. The system is fully interfaced with a PDP 11/55 computer; further details on the instrument and technique have been given elsewhere.<sup>54,55</sup>

The concentration of sensitizers was chosen so as to obtain an optical density between 0.3 and 1.0 at 337.1 nm in a cell with an optical path of 3 mm.

**Acknowledgment.** The research described herein was supported by the office of Basic Energy Sciences of the U.S. Department of Energy. This is Document No. NDRL-2132 from the Notre Dame Radiation Laboratory. Most of the experiments described in this paper were carried out during visits of G.G.W. to the Notre Dame Radiation Laboratory; the support of the laboratory for those visits is gratefully acknowledged.

(50) Monroe, B. M.; Groff, R. P. *Tetrahedron Lett.* **1973**, 3955-3958.

(51) Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455-458.

(52) Thomas, J. K. *J. Chem. Phys.* **1969**, *51*, 770-778.

(53) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(54) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146-2152.

(55) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1980**, *13*, 815-820.

## Acid-Catalyzed Reactions of *N*-Arylhydroxylamines and Related Compounds with Benzene. Iminium-Benzenium Ions

Koichi Shudo, Toshiharu Ohta, and Toshihiko Okamoto\*

Contribution from the Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan. Received March 24, 1980

**Abstract:** *N*-Arylhydroxylamines react with benzene in the presence of trifluoroacetic acid (TFA) at room temperature to give diphenylamines. When TFA was replaced by a strong acid, trifluoromethanesulfonic acid (TFSA), the major products were aminobiphenyls. The nature of the reaction was explored by reactions of 4-substituted phenylhydroxylamines and dialkylaniline *N*-oxides with benzene. Thus, it was demonstrated that the reactive intermediates are onium-benzenium dications which are trapped by benzene to give aminobiphenyls by a mechanism similar to the Friedel-Crafts alkylation. Further evidence for the proposed reaction mechanism was the observation that nitrosobenzene and azoxybenzene reacted with benzene to give analogous products in the presence of the stronger acid.

### Introduction

Although *N*-arylhydroxylamines have been known since the last century,<sup>1,2</sup> their nature and reactivity are still not sufficiently understood.<sup>3</sup> The chemistry of *N*-arylhydroxylamines is currently important in the study of the metabolism of nitrogen compounds.<sup>4</sup> Particularly, interesting are the metabolically activated forms of many nitro and amino carcinogens, which are often *N*-arylhydroxylamine derivatives.<sup>5,6</sup> Some activated carcinogens have been shown to react with bionucleophiles via attack at the nitrogen atom or the carbon atom of an intermediate *N*-arylhydroxylamine.<sup>6-8</sup>

Acid-catalyzed "rearrangement" of *N*-phenylhydroxylamine to 4-aminophenol in sulfuric acid was reported by Bamberger.<sup>1,9,10</sup>

His excellent work and later studies by others<sup>11-14</sup> have shown that the reaction is intermolecular with water (or sulfate) and other groups such as halogen and alkoxy as the attacking nucleophile. Bamberger also reported that *N*-phenylhydroxylamine reacts with aniline, phenol, and 4-nitrotoluene.<sup>10</sup>

In 1920, Kliegl and Huber reported that aminobiphenyl and diphenylamine are formed in the  $\text{AlCl}_3$ -catalyzed reaction of *N*-(4-methylphenyl)hydroxylamine with benzene.<sup>15</sup> More recently Whiting reported a similar reaction catalyzed by tetrafluoroboric acid in sulfolane.<sup>16</sup>

We have explored further the reactivity of *N*-arylhydroxylamines, attempted to rationalize and generalize their reactions, and to clarify the mechanism involved.<sup>17</sup> In this paper regiose-

(1) Bamberger, E. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 1347; **1895**, *28*, 251.

(2) Wohl, A. *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 2543.

(3) Zeeh, B.; Metzger, H. "Houben-Weyl, Methoden der Organischen Chemie", 4th ed.; Miller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1971; Vol. X/1, pp 1097-1279.

(4) Gorrod, J. W. "Biological Oxidation of Nitrogen"; Elsevier/North-Holland Biomedical Press: Amsterdam, 1978.

(5) Miller, J. A. "Chemical Carcinogenesis"; Ts'O, Paul, O. P., DiPaolo, J. A., Eds.; Marcel Dekker: New York, 1974; Part A, pp 61-85.

(6) Miller, J. A. *Cancer Res.* **1970**, *30*, 559 and references therein.

(7) Kawazoe, Y.; Araki, M.; F-Huang, G.; Okamoto, T.; Tada, M.; Tada, M. *Chem. Pharm. Bull.* **1975**, *23*, 3041.

(8) Hashimoto, Y.; Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1979**, *27*, 1058, 2532.

(9) Bamberger, E. *Justus Liebigs Ann. Chem.* **1921**, *424*, 233, 297; **1925**, *441*, 297.

(10) Bamberger, E. *Justus Liebigs Ann. Chem.* **1912**, *390*, 131.

(11) Heller, H. F.; Hughes, E. D.; Ingold, C. K. *Nature (London)* **1951**, *168*, 909. Hughes, E. D.; Ingold, C. K. *Q. Rev., Chem. Soc.* **1952**, *6*, 34.

(12) Yukawa, Y. *Nippon Kagaku Zasshi* **1950**, *71*, 547, 603.

(13) Dewar, M. J. S. *Nature (London)* **1946**, *156*, 784; *J. Chem. Soc.* **1946**, 406; "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963, Part 1, pp 295-344.

(14) Patrick, J. A.; Schield, J. A.; Kirchner, D. J. *J. Org. Chem.* **1974**, *39*, 1758.

(15) Kliegl, A.; Huber, H. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 1646.

(16) Parish, J. H.; Whiting, M. C. *J. Chem. Soc.* **1964**, 4713.