

micelles ( $\lambda_{\max}$  255 nm) is red shifted by 5 nm compared with that in acetonitrile solution suggesting that the chromophore resides in a polar site prior to excitation.

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### Geometry of Transition States Involving Allylic Hydrogen Abstraction Elucidated by Isotope Effect Studies

Sir:

The symmetry of the transition state in the abstraction of hydrogen from thiols by a variety of free-radical species has been assessed by Pryor and Kneipp<sup>1</sup> through estimates of the magnitude of the primary kinetic deuterium isotope effect over a range of temperatures. Wiberg and Motell,<sup>2</sup> moreover, have established both the linearity of the hydrogen transfer between carbon and chlorine and the symmetry of the transition state in the conversion of methane to methyl chloride by measurement of  $k_H/k_D$  as a function of temperature, i.e., measurement of  $A_H/A_D$  and  $[\Delta E_a]_D^H$ . We have now obtained, through measurement of the temperature dependence of  $k_H/k_D$ ,<sup>3</sup> evidence supporting the occurrence of nonlinear hydrogen abstraction by radicals, a case in point being the abstraction of allylic hydrogen by alkoxy radicals.

The widely accepted mechanism of allylic acetoxylation of olefins<sup>4</sup> with *tert*-butyl peracetate calls for the rate-determining abstraction of allylic hydrogen by *tert*-butoxy radicals. Consequently, it can be assumed that the kinetic isotope effect for reaction of  $C_6H_5CHDCH=CH_2$  (**1**) would be indicative of the structural features of the prevailing transition state. This isotope effect at a single temperature has been reported by Denny.<sup>5</sup> We have now measured  $k_H/k_D$  for this reaction at a series of temperatures over a range of 90 °C. The results listed in Table I verify the complete temperature independence of  $k_H/k_D$  in this reaction; that is to say,  $[\Delta E_a]_D^H = 0$  and  $A_H/A_D = 2.90$  for allylic hydrogen abstraction by *tert*-butoxy radical from **1**. There seems very little possibility, moreover, that the appearance of temperature independence of  $k_H/k_D$  is a consequence of a fortuitous loss of H and D product radicals via some side reaction occurring at such variable relative rates that at every temperature the product ratio is selectively adjusted to the constant value. The fact that the yields of product, based on the amount of *tert*-butyl peracetate consumed, were in all cases very high ( $\geq 85\%$ ), with no significant amounts of side product evident from the GLC analysis, also militates against this possibility.

It has been previously shown<sup>6</sup> that reaction processes involving nonlinear hydrogen transfer (a bent transition state), characterized by a single rate-determining step,<sup>7</sup> exhibit a temperature-independent isotope effect which is greater than the theoretical maximum,<sup>8</sup>  $A_H/A_D = 1.2$ , for linear transfer. These criteria for a bent transition state,<sup>6</sup> where the angle of H transfer between the reaction centers is considerably less than 180°, are clearly fulfilled in the allylic acetoxylation of **1** and presumably most olefins undergoing this rate-determined

**Table I.** Temperature Dependence of the Primary Deuterium Isotope Effect in the Reaction of **1**<sup>a</sup> with *tert*-Butyl Peracetate<sup>b</sup>

reaction temp, °C	hours at heat	product (H/D) isotope ratio <sup>c</sup>	$k_H/k_D$
25.0	24.0 <sup>d</sup>	0.3410 ± 0.0023	2.93
70.50	35.5	0.3516 ± 0.0036	2.84
79.59	30.25	0.3339 ± 0.0012	2.99
90.48	25.00	0.3530 ± 0.0021	2.83
99.42	12.25	0.3418 ± 0.0014	2.93
114.95	2.00	0.3566 ± 0.0034	2.81
temperature range = 90			av = 2.90 ± 0.06

<sup>a</sup> PhCHDCH=CH<sub>2</sub> (**1**) was prepared by the copper-catalyzed coupling of vinylmagnesium bromide and C<sub>6</sub>H<sub>5</sub>CHDCI. The isotope content at C<sub>3</sub> was determined using chemical ionization mass spectrometric and high resolution NMR methods. This method of synthesis was shown by GLC, NMR, and high resolution chemical ionization mass spectroscopy to yield a product (**1**) which was completely free of any contaminants such as the isomeric 1-phenylpropene and was completely deuterated (>99%) in the  $\alpha$  position. <sup>b</sup> In each run ~100 mg of **1** were charged into a heavy-walled tube along with 1.0 mg of CuBr, 90 mg of 40.8% *tert*-butyl peracetate in benzene, and 0.75 mL of dry acetonitrile. Each tube was degassed in a series of freeze-pump-thaw cycles and sealed at <10<sup>-3</sup>-mm pressure. The sealed tubes were then inserted in a thermostatically controlled bath for a period of hours required to bring about nearly complete decomposition of the perester. The product, worked up in the usual manner, consisted predominantly (~90%) of the cinnamyl isomer and was freed of all residual solvent and starting material by gas chromatography. For purposes of the isotope ratio determinations the (unseparated) isomer composition of the product was introduced directly into the inlet system of the mass spectrometer. <sup>c</sup> Determined by the high precision isotope ratio method described by H. Kwart and J. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976). A minimum of 20 000 mass spectral determinations are averaged in each of the recorded values of the isotope ratio. <sup>d</sup> This result was obtained with photoactivation which has been claimed<sup>4</sup> to produce the identical reaction process.

H-transfer process. A simplistic representation of this conclusion is displayed in Figure 1.

This is intended to illustrate how a *tert*-butoxy radical with one of its p orbitals imbedded in the  $\pi$  orbital of the olefin in the form of a  $\pi$  or charge-transfer complex can effect an angular transfer of the allylic hydrogen by utilizing the orthogonal p orbital to complete a five-membered cyclic transition state. When radical attack occurs at a C-H bond, we can expect that the major interaction is with the HOMO, namely the  $\sigma$  orbital. The SOMO of the oxygen radical is lowered in energy by virtue of the oxygen being complexed with the olefinic orbitals. Its interaction with the HOMO of the adjacent C-H can be expected to be greatly benefited<sup>9-11</sup> thereby in the resulting pericyclic process. In this picture the role of the double bond in facilitating allylic hydrogen abstraction is not merely involved with lowering the energy of the resulting carbon free radical, which is the textbook explanation of the allylic abstraction process; it also provides a kinetic pathway acting to lower the activation energy of the process. Further appreciation of the significance of this factor is to be gained by comparing these results supporting a bent transition state of allylic H abstraction with the results referenced above demonstrating that a temperature-dependent zero-point energy determined  $k_H/k_D$  is observed in the usual case of linear H abstraction from a nonallylic reaction site (for example, in the chlorination of methane<sup>2</sup>).

A similar conclusion has been reached by Walling and Zavitsas,<sup>12</sup> who realized that, while the relative rate constant for H abstraction from *cis*- and *trans*-4-methyl-2-pentane was independent of the source of the *tert*-butoxy radical, the unhindered *trans* olefin underwent this H-transfer reaction with

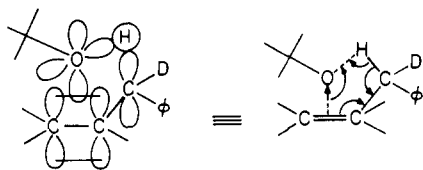


Figure 1.

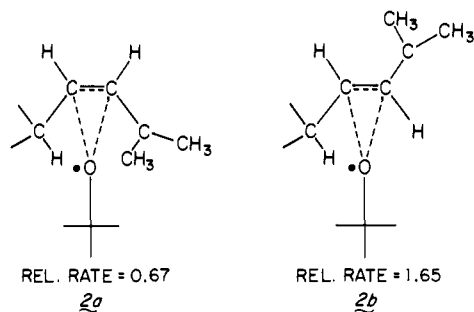


Figure 2.

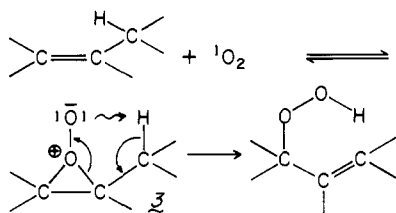


Figure 3.

the bulky *tert*-butoxy radical more than twice as fast as the hindered *cis*. They attributed the rate difference to the relative stabilities of the *cis* (**2a**) and *trans* (**2b**)  $\pi$  complexes shown in Figure 2. (The dotted lines in Figure 2 represent a complexing interaction between the oxygen and the olefinic centers.)

The analogous deduction can be made regarding the geometry of the allylic H-transfer transition state in the electrophilic mechanism of hydroperoxidation of olefins by singlet oxygen.<sup>13</sup> By most criteria which have been previously applied,<sup>14</sup> including the magnitude of  $k_H/k_D$  at a single temperature,<sup>14c</sup> it has not been possible to distinguish unequivocally between a concerted ene-reaction transition state and a chelotropic mechanism involving formation of a transient peroxide intermediate. However, Bartlett and co-workers<sup>15</sup> have provided elegant justification of the peroxide intermediate through a laboriously detailed study of kinetic and product isotope effects in singlet oxygen hydroperoxidation of 4-methyl-2,3-dihydro- $\gamma$ -pyran. This conclusion, implying a bent transition state of H transfer taking place subsequent to the formation of  $\sigma$  peroxide complex **3**, is fully supported by the data assembled in Table II. They confirm a temperature-independent isotope effect greater than the maximum theoretical value of  $A_H/A_D$  in keeping with the mechanistic course illustrated in Figure 3.

Finally, it is of considerable interest to take note of the nature of the kinetic isotope effect in the homolytic abstraction of benzylic hydrogen by *tert*-butoxy radical,<sup>17</sup> where the hydrogen donor substrate, toluene, does not possess the ability to tightly complex the *tert*-butoxy radical acceptor. Larson and Gilliom<sup>18</sup> have studied the case of toluene in reaction with *tert*-butyl hypochlorite under conditions eliminating chlorine atom chains. The steep temperature dependence of  $k_H/k_D$  which they report is taken to be fully consistent with *linear* H transfer involving tunneling, in contrast to the bent transition state (Figure 1) discussed here for allylic olefin centers. The lesser ability of the aromatic nucleus to complex the *tert*-butoxy radical is evident in the fact that the reactant **1**, con-

**Table II.**<sup>a</sup> Temperature Dependence of the Primary Deuterium Isotope Effect in the Hydroperoxidation of  $(\text{CH}_3)_2\text{C}=\text{C}(\text{CD}_3)_2$  by  $^1\text{O}_2$

reaction temp., °C.	$k_H/k_D^b$
14	1.36
0	1.47
-28	1.45
-52	1.36
-70	1.62
$\Delta T = 84$	$k_H/k_D = 1.45 \pm 0.07$

<sup>a</sup> Data of Kopecky and Van de Sande.<sup>16</sup> <sup>b</sup> Each value listed is the average of a number of determinations with a precision of  $\pm 8\%$ .

taining both aromatic and allylic olefin substituents at the site of H abstraction, prefers the bent transition-state pathway conferred by the olefin center.

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- Clearly, the radical with the lower energy SOMO will be more reactive (more negative  $\rho$  value<sup>10</sup>). This is illustrated by the finding<sup>11</sup> that the *t*-BuO• radical, where the  $\alpha$  effect is operating to make an electrophilic radical less reactive, is 10 000 times less reactive in hydrogen abstraction than *t*-BuO•.
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## Transient Proton-Proton Overhauser Effects in Horse Ferrocyclochrome c

Sir:

The nuclear Overhauser effect (NOE) is the fractional change in intensity of one NMR resonance when another resonance is irradiated, and has long been a valuable tool for structural studies of small molecules.<sup>1</sup> More recently theoretical aspects of using NOE's for investigations of biological macromolecules at high frequencies were discussed,<sup>2</sup> and