

THERMAL DECOMPOSITIONS OF N-NITROSOHYDROXYLAMINES.  
 VI. SUBSTITUENT EFFECTS ON *t*-BUTYL PERBENZOATE FORMATION

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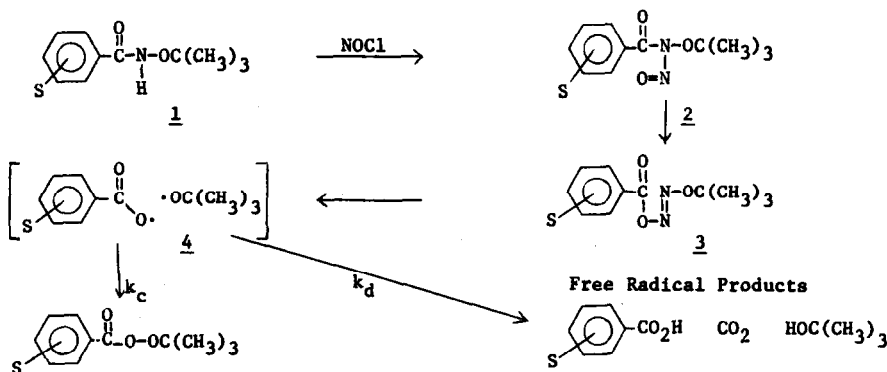
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The observations of Hammet correlations on the thermal decompositions of benzoyl peroxides ( $\rho = -0.4$ )<sup>1</sup> and *t*-butyl perbenzoate ( $\rho = -0.7$ )<sup>2</sup> have been interpreted in terms of differences in starting material stability due to changes in the dipolar repulsion between the oxygen atoms in the O-O bonds. A simple implication of this interpretation is that the reverse reaction should reflect the same perturbation by a reversed sign of the reaction constant ( $\rho$  positive) which should be of reduced magnitude. The reduction in magnitude should be related to the lengthening of the O-O bond in the common transition state for the homolysis-recombination.

We wish to report the results of our experiments which were designed to test this implication. The measured quantities are the isolated yields of *t*-butyl peresters obtained from the overall decomposition of the corresponding N-benzoyl-N-nitroso-O-*t*-butylhydroxylamines (2). These compounds have been shown<sup>3</sup> to undergo rapid rearrangement to the corresponding O-benzoyl-O'-*t*-butyl hyponitrites (3) which subsequently homolyze with the loss of nitrogen, giving the corresponding benzoyloxy-*t*-butoxy radical pair. The radical pair may then combine to form the corresponding perester or diffuse to give the products of the respective free radicals. This overall process is shown as Scheme I.

Scheme I



The t-butyl hydroxamates (1) were prepared by the published procedure.<sup>3</sup> The solvent used for this study was methylene chloride - carbon tetrachloride (1:3) which was chosen primarily because of solubility considerations. An improved procedure for the nitrosation was developed which utilized solid potassium carbonate rather than pyridine to neutralize the hydrochloric acid formed in the reaction. The nitrosations were complete within 20 minutes at -15° and the resulting solutions of the nitrosoamides were simply washed with 5% potassium carbonate at its freezing point, then with water and finally dried over solid potassium carbonate. Aliquots of the resulting solutions were then diluted with the same solvent containing a known amount of dioxane. Integration of the nmr spectra allowed the estimation of the initial nitrosoamide (2)-hyponitrite (3) concentrations. The yields of isolated products were based on these estimates.

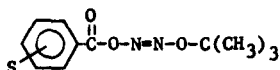
The nmr spectra of the solutions, after complete destruction of hyponitrite, showed the major t-butyl products to be t-butanol and the appropriate t-butyl perester. t-Butyl nitrite, t-butyl ester and acetone were also present. The nitrite and esters are indicative of a small amount of the denitrosation of the nitrosoamide recently reported.<sup>4</sup> The contributions of this reaction to the overall destruction of the nitroso compounds (4) were small enough to be neglected here.

The yields of perester products were determined in two ways. One was by the ratio of the area of the t-butyl perester nmr singlet to the total t-butyl nmr signal. The second was by the area of the t-butyl nmr singlet of the perester remaining in the neutral residue from the product mixtures compared to the area of the methyl signal of added toluene. The agreement between the two methods was satisfactory in all cases. The presence of the peresters was also verified by the infrared spectra of the neutral residues.

The nitrogen yields were determined volumetrically on a calibrated vacuum line. The carbon dioxide yields were determined by weight uptake of ascarite. The carboxylic acid yields were determined by weight of material obtained from base extraction of the product mixtures followed by neutralization. The latter yields refer to the crude material thus obtained. All of these results are summarized in Table I. The fact that significant amounts of carboxylic acids are formed in every case indicates that the decarboxylation of all the substituted benzoyl oxy radicals is too slow to compete with combination. In such cases, the phenomenological scheme for the competition between combination and diffusive separation can be expressed as equation 1.

Table I

Products<sup>a</sup> of O-Benzoyl-O'-t-butyl Hyponitrites  
in CH<sub>2</sub>Cl<sub>2</sub>CCl<sub>4</sub> at 20°C



<u>S</u>	<u>N<sub>2</sub></u>	<u>CO<sub>2</sub></u>	<u>Acid</u>	<u>Perester</u>	<u>CO<sub>2</sub> Balance</u>
p-CH <sub>3</sub> O	1.02	0.29	0.55	0.07 ± .01	0.92
H	1.03	0.76	0.07	0.10	0.93
m-CH <sub>3</sub> O	0.94	0.68	0.11	0.10	0.90
p-Cl	1.00	0.73	0.11	0.12 ± .02	0.96
m-NO <sub>2</sub>	1.00	0.30	0.49	0.18 ± .01	0.97
p-NO <sub>2</sub>	1.02	0.44	0.37	0.20 ± .01	1.01

a) Moles per mole nitrosoamide.

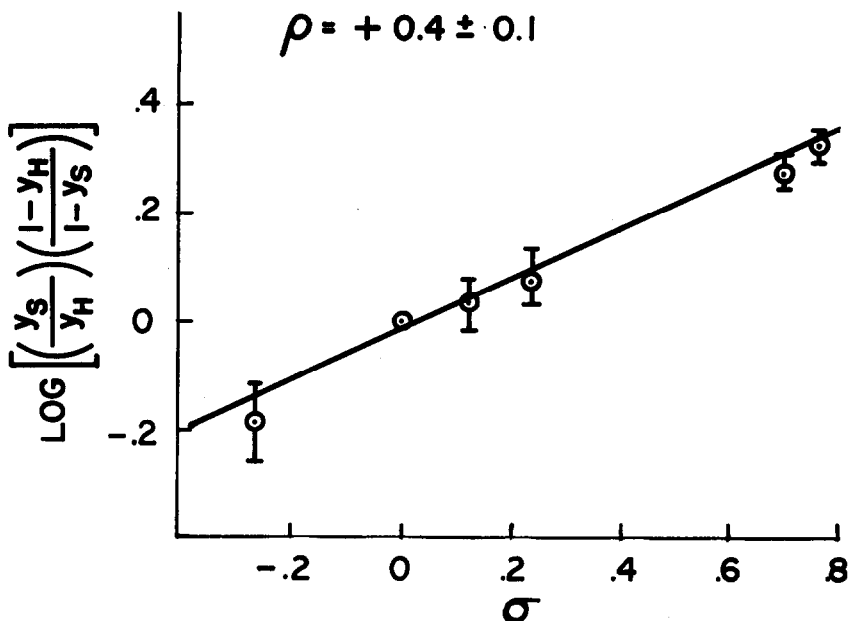
$$\frac{y_{\text{Per}}}{1-y_{\text{Per}}} = \frac{k_c}{k_d} \quad (1)$$

The formal rate constant for diffusion ( $k_d$ ) should be sensitive to the mass and radius of the diffusing particles. However, the calculated variations in these quantities lead to variations in diffusion coefficients which are insignificant throughout the present series. We therefore consider the formal rate constant for the diffusion of all of the substituted benzoyloxy radicals to be the same. This assumption allows the relationship between observed yields of perester and rate constants for combination to be written as equation (2).

$$\log \left[ \frac{(y_s/y_H) \left( \frac{1-y_H}{1-y_s} \right)}{\left( \frac{1-y_H}{1-y_s} \right)} \right] = \frac{k_c^s}{k_c^H} = \sigma\rho \quad (2)$$

The sigma-rho correlation is shown as Figure 1. The points are correlated versus  $\sigma$  values by a  $\rho$  of  $+0.4 \pm .1$ . The large uncertainty is dictated by the large relative errors in the perester yields which are small. In spite of this there seems to be no doubt that a positive  $\rho$  value has been demonstrated. Both the sign and the magnitude of this reaction constant are in line with the simple expectations stated above. More careful consideration of this line of reasoning and the present results leads to the conclusion that an activation energy must be involved for the combination process which can be perturbed by the electronic effects of the remote substituents. The total perturbation difference at 20°C ( $\Delta\Delta G^\ddagger$  from p-nitro to p-methoxy) is ca. 300 cal/mole. What is not clear is the sign of the activation enthalpy.

Figure 1



Either a positive or a negative  $\Delta H^\ddagger$  for combination could give rise to the present results. Our prejudice is towards a negative  $\Delta H^\ddagger$  which is opposed by a negative  $\Delta S^\ddagger$  so that  $\Delta G^\ddagger$  is positive. Regardless of this ambiguity, the present results do suggest variations in rate constants for (re)combination reactions which are outside of strictly statistical (entropy) considerations.

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