

Notes

Oxidative Decomposition of *Meso*-Azobis- α -phenylethane by Thianthrene Cation Radical

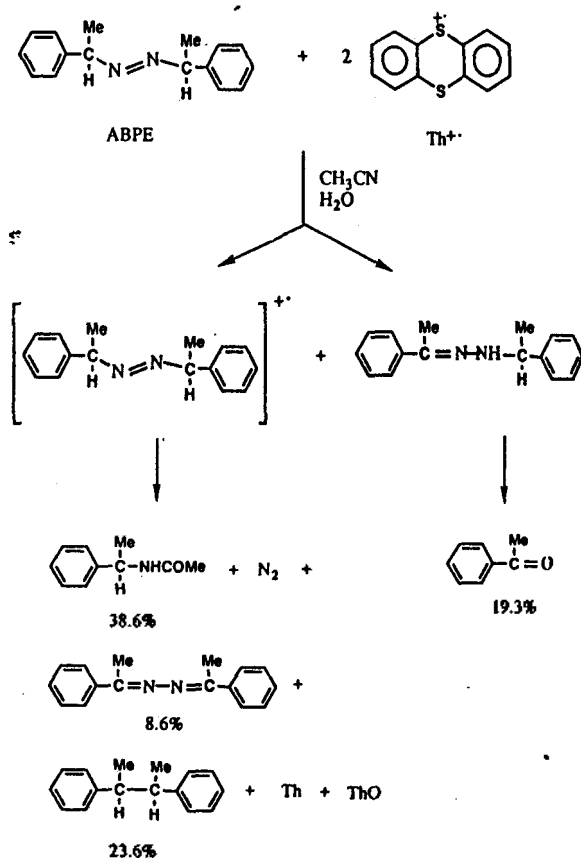
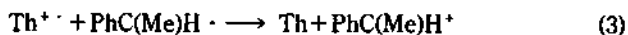
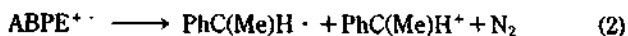
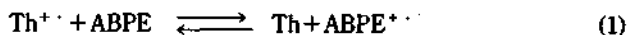
Wang Keun Lee* and Chun Taek Chung

Department of Chemistry Education,
Chonnam National University, Kwang-Ju 500-757

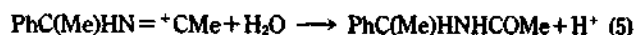
Received April 28, 1992

Cation radical-induced, oxidative chemistry of azoalkane has begun to emerge only in the last few years.¹⁻⁵ For example, azoalkane such as 1,1'-azoadamantane (AA), which has no α hydrogen, is oxidized by thianthrene cation radical perchlorate in acetonitrile solution, affording primarily nitrogen and cation-derived products.¹ However, 1,4-diphenylazomethane (DPAM) possessing two α hydrogens reacts with cation radicals and undergoes facile oxidative cycloaddition with the nitrile solvent to form 1,2,4-triazole.² The results from oxidation of AA and DPAM tell us quite clearly that the type of α -carbon in azoalkanes determines the products of oxidative cleavage. The present investigation arose from questions whether *meso*-azobis- α -phenylethane (ABPE) [1,1'-diphenylazoethane] possessing one α hydrogen is oxidized to its cation radical and decompose to liberate N₂, or tautomerized to its hydrazone and lead to oxidative cycloaddition to the nitrile solvent. The purpose of this study is to know the effects of structure on the oxidation of azoalkane and to validate the reaction mechanism which had been proposed for the oxidation of azoalkane by cation radical.

meso-ABPE undergoes thermolysis into α -phenylethyl radical in solution at reasonable rates at 100-160°C, leading to the 2,3-diphenylbutane (DPB) and rearranges to their hydrazone tautomer more readily than the simple aliphatic azo compounds.⁶ In contrast, this azoalkane reacted with thianthrene cation radical (Th^{•+}) at room temperature rapidly and evolved nitrogen and rearranged to a tautomer of *meso*-ABPE, acetophenone α -phenylethylhydrazone. While Th^{•+} was reduced quantitatively to thianthrene (Th), products from *meso*-ABPE, a traditional source of free radicals,⁷ were *N*- α -phenylethylacetamide (38.6%), 2,3-diphenylbutane (23.6%), acetophenone (19.3%) and acetophenone azine (8.6%). The overall view of the behavior of azoalkane in reaction with Th^{•+} can be explained by Scheme 1. Thus, the major initial trappable products of oxidative decomposition were the α -phenylethyl cations, which reacted with the solvent acetonitrile to give a Ritter-type intermediate PhC(Me)HN=⁺CMe. The Ritter-type intermediate reacted with water during workup to give *N*- α -phenylethylacetamide. One of the possible routes for the formation of the carbocationic product, *N*- α -phenylethylacetamide is shown in Eq. (1)-(5).



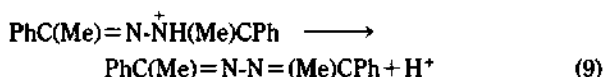
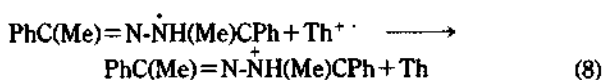
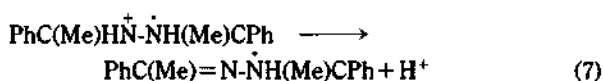
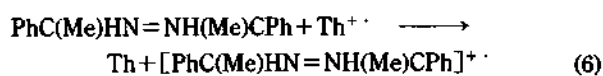
Scheme 1. Mechanism of product formation from *meso*-ABPE and thianthrene cation radical.



All these reactions may involve prior complexation, as was proposed for the cation radical oxidation of anisole.⁸

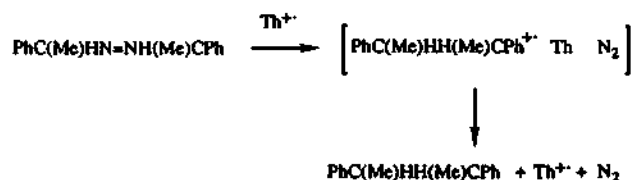
In contrast to the oxidation of AA, and of DPAM with cation radical, acetophenone and small amounts of azine, PhC(Me)=N-N=(Me)CPh were obtained. The formation of acetophenone can be attributed to the hydrolysis of either the corresponding hydrazone or acetophenone azine. However, when an attempt was made to hydrolyze the authentic azine by 70% perchloric acid in acetonitrile solution, the azine was recovered quantitatively. Hence, the formation of acetophenone from the hydrolysis of the azine can be ruled out. Azoalkanes possessing α -protons can tautomerize easily to the more stable isomeric hydrazones.⁹ We are not sure whether the tautomerization occurred in solution prior to the oxidation of *meso*-ABPE or after oxidation, but the cation radical of *meso*-ABPE tautomerized to the cation radical of acetophenone α -phenylethylhydrazone. In this study, 1,2,4-triazole can't be formed from the oxidative cycloaddition of acetophenone α -phenylethylhydrazone cation radical to the solvent MeCN, because ABPE has only one α hydrogen. Acetophenone azine was a product of oxidation of the azo com-

pound. A possible mechanism for the formation of the azine is shown in Eq. (6)-(9).



The formation of the thianthrene 5-oxide (ThO) can be rationalized by hydrolysis of either some of $\text{Th}^{+\cdot}$ by incompletely dried solvent during the course of reaction, or unused $\text{Th}^{+\cdot}$ during workup.¹⁰

No evidence for ethylbenzene was found from the α -phenylethyl radical disproportionation reaction or from hydrogen abstraction from MeCN. When the reaction of $\text{Th}^{+\cdot}$ with *meso*-ABPE was carried out in the presence of BrCCl_3 in MeCN, as we did earlier with AA, the formation of DBP was not stopped. Therefore, we can conclude that DPB is probably not formed in the oxidative reactions by dimerization of α -phenylethyl radical. Generally, radical is destined to abstract hydrogen atom from MeCN rather than to dimerize in the absence of a competing reaction.¹¹ The mechanism for the formation of DPB is rationalized in Scheme 2, which is very similar to that of formation of AdAd by $\text{Th}^{+\cdot}$.¹¹ DPB may have arisen from the DPB cation radical $[\text{PhC(Me)HH}(\text{Me)CPh}]^{+\cdot}$, formed by a cage recombination between α -phenylethyl cation and α -phenylethyl radical, rather than the coupling between two α -phenylethyl radicals. Conversion of DPB cation radical into DPB would have to occur by electron-transfer reaction from $\text{Th}^{+\cdot}$ within solvent cage. In that case, $\text{Th}^{+\cdot}$ would have served as a catalyst for the formation of DPB from *meso*-ABPE. It is interesting to compare the yield of AdAd and DPB from oxidative decomposition of corresponding azoalkane $\text{Th}^{+\cdot}$. Whereas 2.5% of AdAd was obtained from oxidation of AA, 23.6% of DPB was formed in the oxidative of *meso*-ABPE by $\text{Th}^{+\cdot}$. In the oxidation of *meso*-ABPE with $\text{Th}^{+\cdot}$, α -phenylethyl radical would not survive so long enough to be reduced to cation as tertiary adamantyl radical. Therefore, relatively lots of α -phenylethyl radical would recombine with α -phenylethyl cation to form a DPB without further oxidation in the solvent cage. *Meso*-ABPE gave 21.8% of *meso* and 1.8% of non-*meso*-DPB, indicating that some changes in orientations (by out-of-plane rotation) of the cations and radicals are occurring in these original cages prior to combination between α -phenylethylcation and



Scheme 2. Possible reaction pathways for the formation of 2,3-diphenylbutane.

α -phenylethyl radical.

In conclusion, the reaction of $\text{Th}^{+\cdot}$ with *meso*-ABPE, possessing one α hydrogen, in acetonitrile follows not only the carbocationic route but also undergoes tautomerization to its hydrazone, and no oxidative cycloaddition was observed.

Acknowledgement. We thank the Chonnam National University for financial support (1991) and acknowledge Dr. Sung Sik Kim of Conbuk National University for GC-MS.

References

- D. H. Bae, P. S. Engel, A. K. M. M. Hoque, D. E. Keys, W. K. Lee, R. W. Shaw, and H. J. Shine, *J. Am. Chem. Soc.*, **107**, 2561 (1985).
- A. K. M. M. Hoque, A. C. Kovelesky, W. K. Lee, and H. J. Shine, *Tetrahedron Lett.*, 5655 (1985).
- H. J. Shine, D. H. Bae, A. K. M. M. Hoque, A. Kajstura, W. K. Lee, R. W. Shaw, M. Soroka, P. S. Engel, and D. E. Keys, *Phosphorus sulfur*, **23**, 111 (1985).
- J. M. Lee, K. Kim, and J. H. Shin, *Bull. Korean Chem. Soc.*, **6**, 358 (1985).
- P. S. Engel, A. K. M. M. Hoque, J. N. Scholz, H. I. Shine, and K. H. Witmire, *J. Am. Chem. Soc.*, **110**, 7880 (1988).
- S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *J. Am. Chem. Soc.*, **72**, 3947 (1960).
- P. S. Engel, *Chem. Rev.*, **99**, 80 (1980).
- O. Hammerich and V. D. Parker, *Adv. Phys. Org. Chem.*, **20**, 55 (1984).
- P. A. S. Smith, *Derivatives of Hydrazine and other Hydronitrogens having N-N Bonds: Benjamin/Cummings: Reading, Mass.*, pp. 47-70, 176-177, 1983.
- Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969). **Caution:** $\text{Th}^{+\cdot} \text{ClO}_4^-$ is explosive. It should be prepared in small quantities only and used soon after preparation. Sintered glass should not be used for filtration.
- P. S. Engel, W. K. Lee, G. E. Marschke, and H. J. Shine, *J. Org. Chem.*, **52**, 2813 (1987).

The Crystal Structure and Magnetic Properties of Triethylenediaminenickel(II)-Bis(maleonitriledithiolato)nickelate(II); $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_2)_3] \cdot [\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$

Chulmin Keum, Chonhan Kim, Chulsung Kim, Hyontae Kwak, Moonhee Kwon, and Hae Namgung†

Department of Chemical Education, Kookmin University, Seoul 136-702

†Department of Physic Education, Kookmin University, 136-702

Received June 3, 1992

Bidentate dithiolate ligands form very well square planar complexes with Ni-triad ions of different oxidation states,