Tetrahedron Letters, Vol.22, No.44, pp 4363 - 4364, 1981
Printed in Great Britain

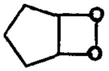
0040-4039/81/444363-02 \$02.00/0

THERMOLYSIS OF 3,4-DIALKYL-1,2-DIOXETANES: EFFECT OF CYCLIC SUBSTITUENTS

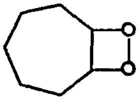
Alfons L. Baumstark* and Catherine E. Wilson, Department of Chemistry
Laboratory for MBS, Georgia State University, Atlanta, Georgia 30303, USA

Summary: In 3,4-dialkyl-1,2-dioxetanes, the effect of ring size of cyclic substituents on E_a was found to be $5 \approx 7 < 8 < 6$ while little or no effect was observed on $\Delta S^{\neq}$.

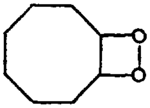
The thermolysis of alkyl-1,2-dioxetanes has been shown[1] to produce two carbonyl fragments, one of which may be produced in an excited state (direct production of high yields of excited triplets). Two mechanistic extremes have been traditionally proposed[1] to describe the thermal decomposition of alkyl substituted dioxetanes: a) diradical and b) concerted. Calculation of some dioxetane activation parameters by a group additivity method[2] was taken as support for the diradical mechanism.[3] The insensitivity[4] of dioxetane activation parameters to many[5] substituent effects and changes; including deuterium substitution[6] and additional ring strain[7] seem to favor the diradical interpretation.[8] Studies of the effects of cyclic substituents on the activation parameters are scarce. We have previously shown[9] that the activation energy for the thermal decomposition of 3,4-tetramethylene-1,2-dioxetane was substantially lower than those of cyclic or acyclic model compounds. We wish to report a study of the thermal decomposition of 3,4-trimethylene-1,2-dioxetane (**1**), 3,4-pentamethylene-1,2-dioxetane (**2**), and 3,4-hexamethylene-1,2-dioxetane (**3**).



1



2

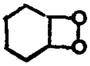


3

1, **2**, and **3** were prepared in low yield by closure of the corresponding bromohydroperoxides[10] with base at low temperature. The products of the thermolysis of **1**-**3** were the expected cleavage products. Without added fluorescers, the thermolyses of **1**-**3** were only weakly chemiluminescent. Thermolysis of **1**-**3** directly produced high yields (~10%) of excited triplet carbonyls as determined from the intensities of chemiluminescence of varying concentrations of dibromoanthracene or diphenylanthracene. The yields of excited singlet products were low in all three cases (<0.1%). The rates of thermal decomposition of **1**-**3** were determined by monitoring the decay of chemiluminescence intensity in aerated xylenes with or without added fluorescers. The rates were cleanly first order, showed no dependence on added fluorescer, and were unaffected by addition of $EDTA^{=}$. The activation parameter data for **1**-**3** are summarized in Table 1.

The effect of cyclic substituents on the activation parameters of 3,4-disubstituted-1,2-

Table 1. Activation Parameters for the Thermal Decomposition of 1-3 in Xylenes.

Dioxetane^{a}	k_{60}sec^{-1}	Ea kcal/mole	log A^{b}	$\Delta S^{\neq b}$ eu
1	3.8×10^{-4}	26.0 ± 0.3	13.6	+1.6
	1.1×10^{-2}	$22.5^{c} \pm 0.3$	12.8^{c}	-2.1
2	4.0×10^{-4}	25.9 ± 0.3	13.6	+1.9
3	4.5×10^{-4}	24.8 ± 0.3	13.0	-1.6

a) Initial Concentration ~10^{-4}M. b) Calculated at 60°. c) See Ref 9.

dioxetanes yielded an interesting result. The order of the effect on the activation energy is 5 ≈ 7 > 8 > 6 while little or no effect is observed in $\Delta S^{\neq}$ term. As for the decomposition of many dioxetanes[1], the values of $\Delta S^{\neq}$ for the present cases are within experimental error of 0 ± 5 eu. Consistent with the present data, Lechtken found[11] that several trisubstituted dioxetanes showed similar effects. A ring-size effect has been reported[12] on the product distribution of the decomposition of postulated dioxetanes in the photooxygenation of sulfur-substituted cycloalkenes.

3 is the first example of a dioxetane containing an eight membered ring. The Ea value for 3 is close to that of an acyclic cis-3,4-dialkyl-1,2-dioxetane.[9] The observed trend in the activation energies for cyclic substituents is not readily explained by the diradical mechanism[4]. Extra ring strain, due to the substituents, has been shown[6] not to effect dioxetane activation parameters. The conformation of a cyclic substituent could affect the activation energy of dioxetane thermolysis if a twisting mode[9] of O-O bond cleavage were involved in dioxetane cleavage. Such a process would require that dioxetanes that have rigid substituents show higher activation energies. The present data seem consistent with the involvement of a twisting mode for dioxetane cleavage. The conformation of the 5- and 7-ring lead to unusually high activation energies for disubstituted dioxetanes suggesting the lack of the specific interactions[9] observed for the 6-ring containing dioxetane.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to the GSU Research Fund.

References and Notes

1. For recent reviews see: a) Wilson, T., MTP Int. Rev. Sci.: Phys. Chem. Ser. Two, 1976, 9, 265; b) Adam, W., Adv. Hetero. Chem., Vol 21, 1977, 437; and c) Horn, K.A., Koo, J., Schmidt, S.P. and Schuster, G.B., Molecular Photochem., 1, 1978-9, 9(1).
2. O'Neal, H.E. and Richardson, W.H., J. Am. Chem. Soc., 1970, 92, 6553 and correction, ibid, 1977, 93, 1828.
3. Doubts have been raised as to the predictive value of the calculations. See: Bechara, E.J.H., and Wilson, T., J. Org. Chem., 1980, 45, 5261.
4. Richardson, W.H., Burns, J.H., Price, M.E. Crawford, R., Foster , M., Slusser, P., Anderegg, J.H., J. Am. Chem. Soc., 1977, 99, 5403 and references therein.
5. For an example of a large substituent effect see: Baumstark, A.L., Wilson, T., Landis, M.E. Bartlett, P.D., Tetrahedron Lett., 1976, 2397.
6. Wilson, T., Golan, E.D., Harris, M.S., Baumstark, A.L., J. Am. Chem. Soc., 1976, 98, 1086.
7. Koo, J. and Schuster, G.B., ibid, 1978, 100, 7596.
8. The unique electron transfer mechanism(s) that occur(s) with certain peroxides does not occur readily with the dioxetanes described here.
9. Baumstark, A.L. and Wilson, C.E., Tetrahedron Lett., 1979, 2569.
10. Prepared by the method of: Kopecky, K.R., Filby, J.E., Mumford, C., Lockwood, P.A., Ding, J.-Y., Can. J. Chem., 1975, 53, 1103.
11. Lechtken, P., Reissenweber, G., Grubmueller, P., Tetrahedron Lett., 1977, 2881.
12. Ando, W., Watanabe, K., and Migita, T., Tetrahedron Lett., 1975, 4127.

(Received in USA 30 June 1981)