Tetrahedron Letters,Vol.23,No.29,pp 2943-2946,1982 0040-4039/82/292943-04$03.00/0
Printed in Great Britain

SUBSTITUENT EFFECTS ON THE DECOMPOSITION OF 1,2-DIOXETANES

A HAMMETT CORRELATION FOR SUBSTITUTED 1,6-DIARYL-2,5,7,8-TETRAOXABICYCLO[4.2.0]OCTANES

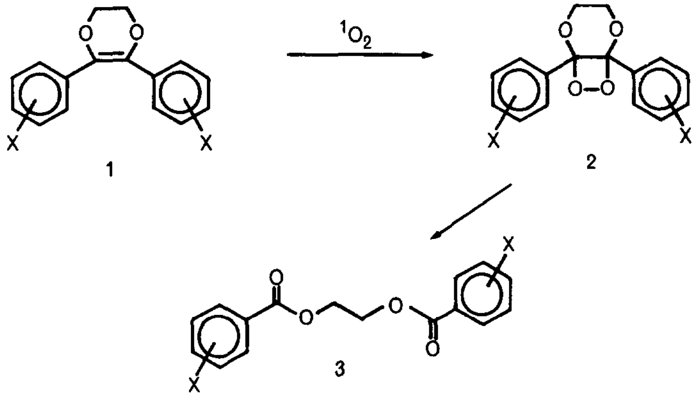
A. Paul Schaap*, Steven D. Gagnon, and K. A. Zaklika

Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Summary. Rates of decomposition for 1,2-dioxetanes obtained from addition of singlet oxygen to substituted 2,3-diaryl-1,4-dioxenes have been found to obey a Hammett relationship with $\rho^+ = -0.24$ ($n = 15$, $r = 0.92$). The results are taken as support for a biradical mechanism.

The chemiluminescent decomposition of 1,2-dioxetanes has generated considerable interest during the last few years.[1] The involvement of these peroxides in some bioluminescent systems has also been established.[2] Although a large number of dioxetanes have now been synthesized, wide variations in structural type have made comparisons difficult and hampered the detection of mechanistic trends. To avoid these problems and to probe the mechanism(s) for dioxetane decomposition, we have investigated a series of dioxetanes derived from 1,4-dioxene, in particular 1,6-diaryl-2,5,7,8-tetraoxabicyclo[4.2.0]octanes <u>2</u>.

Concerted[3] and biradical[4] mechanisms have been proposed for the cleavage of dioxetanes. More recently, it has been suggested that dioxetanes bearing easily oxidized substituents may decompose <u>via</u> intramolecular electron-transfer processes.[5] We now describe the results of a study which indicate that "normal", stable dioxetanes cleave by a stepwise mechanism involving rate-limiting homolysis of the O-O bond.



Dioxetanes <u>2a-p</u> were prepared by photooxygenation of the corresponding olefins <u>1a-p</u> in methylene chloride or acetone at -78°C with polymer-bound Rose Bengal[6] (SENSITOX I) and a 400-W high pressure sodium lamp. The dioxetanes were identified by ^1H and ^{13}C NMR spectroscopy and by their quantitative cleavage to diesters <u>3a-p</u> which have been fully characterized.

Rate constants for the decomposition of dioxetanes 2b-p were obtained at 45-90°C from measurements of the decay of chemiluminescence intensity of $10^{-4} - 10^{-5}$ M solutions in o-xylene. A fluorescer, 9,10-dibromoanthracene (10^{-5} M), was added to the solutions in order to visualize the excited triplet states of 3b-o.[7] The thermolyses were cleanly first order. Rates showed variations of less than 3% and gave excellent Arrhenius plots ($r > 0.999$). Relative rates of decomposition for the dioxetanes calculated at 25°C are listed in the Table. As shown in the Figure, dioxetanes 2b-p were found to obey a Hammett relationship where $\rho^+ = -0.24$ ($n = 15$, $r = 0.92$) for a correlation with σ^+ and $\rho = -0.38$ ($n = 15$, $r = 0.84$) with σ. It should be noted that this correlation includes unsymmetrically substituted dioxetanes 2g and 2h.

Table Activation Parameters and Rates of Decomposition for 1,2-Dioxetanes 2

dioxetane (X)[a]	E_a (kcal/mol)[b]	log A	k_{rel} (25°C)	σ^+ [e]	σ [g]
2a (NMe_2, NMe_2)	19.3[c]	10.99	382	-1.7	-0.83
2b (OiPr, OiPr)	23.6	12.25	5.46	-0.99[f]	-0.45[f]
2c (OMe, OMe)	24.1	12.38	3.51	-0.78	-0.27
2d (OH, OH)	24.2	12.50	3.43	-0.92	-0.37
2e (OPh, OPh)	24.0	12.24	2.93	-0.5	-0.32
2f (NHAc, NHAc)	24.6	12.65	2.48	-0.6	0.00
2g (OH, H)	24.4	12.38	2.10	-0.92, 0	-0.37, 0
2h (OMe, H)	24.5	12.50	2.07	-0.78, 0	-0.27, 0
2i (Me, Me)	25.1	12.54	1.21	-0.31	-0.17
2j (Ph, Ph)	24.7	12.56	1.66	-0.18	-0.01
2k (Cl, Cl)	24.3	12.28	1.17	0.11	0.23
2l (H, H)	24.8	12.39	1[d]	0	0
2m (m-OMe, m-OMe)	24.4	12.22	1.42	0.05	0.12
2n (m-Cl, m-Cl)	25.1	12.51	0.85	0.4	0.37
2o (m-CF_3, m-CF_3)	24.4	12.16	1.04	0.52	0.43
2p (3,4-C_4H_4,3,4-C_4H_4)[h]	24.6	12.49	1.94	-0.14	0.04

[a] Unless otherwise indicated the substituents are located at the para positions of phenyl groups. [b] Precision of E_a values is ±0.2 kcal/mol or less. Temperature control for kinetic experiments was ±0.05°C in o-xylene from approximately 45 to 90°C. [c] In toluene from 5 to 45°C. [d] Corresponding to a rate constant of $1.61 \times 10^{-6} s^{-1}$ in o-xylene at 25°C. [e] H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958). [f] C.G. Swain and E.C. Lupton, Jr., J. Am. Chem. Soc., 90, 4328 (1968). [g] D.H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420 (1958). [h] 2-Naphthyl.

For comparison, the relative rate for the dimethyamino-substituted dioxetane 2a is also shown on the plot. As described previously, the properties of 2a are distinct being relatively unstable and exhibiting a singlet chemiexcitation efficiency of 22%.[8] Further, the stability of 2a is dramatically diminished in polar solvents whereas the unsubstituted dioxetane 2l shows no significant solvent effect on the rate. These observations are consistent with the proposed intramolecular electron-transfer mechanism for the decomposition of 2a.

Dioxetanes 2b-p, on the other hand, are "normal" dioxetanes being relatively stable and yielding predominately triplet excited cleavage products.[8] For example, the half-life of dioxetane 2l at 25°C in o-xylene is 120 h. The modest ρ value for the decomposition of 2b-p provides additional support for a biradical mechanism. A substantically more negative ρ value might be anticipated for a concerted process in which an unsaturated carbonyl carbon bearing a partial positive charge is developed in the transition state. Model reactions for the biradical process which exhibit similarily small negative reaction constants include thermolyses of substituted benzoyl peroxides[9] (ρ = -0 38), substituted 2-thenoyl peroxides[10] (ρ = -0.44), and substituted tert-butyl peroxybenzoates[11] (ρ = -0.29). Richardson[12] has recently found that substituted 3-aryl-3-methyl-1,2-dioxetanes also exhibit a Hammett correlation with ρ = -0.22. Although the present results are inconsistent with a fully concerted mechanism, the lower activation energies for 2b-e suggest that a small degree of C — C bond stretching may occur in the transition state for the cleavage of dioxetanes with electron-releasing substituents.

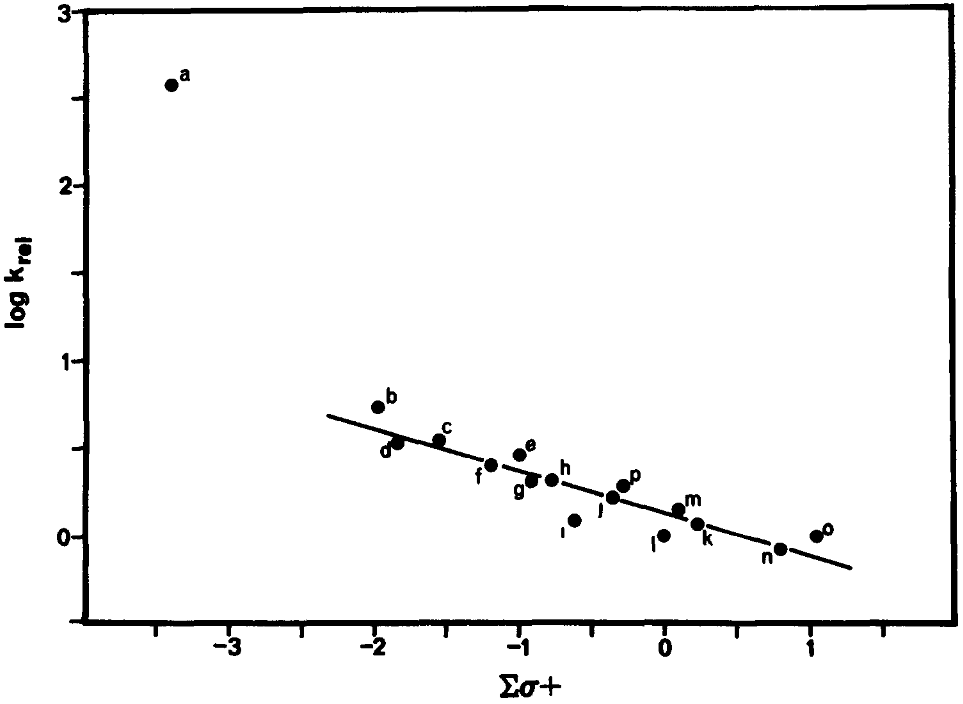


Figure. Hammett plot for the decomposition of dioxetanes 2a-p in o-xylene at 25°C against the sum of the σ^+ substituent constants ρ^+ = -0.24 (n = 15, r = 0.92).

Acknowledgement. Support from the U.S. Army Research Office is gratefully acknowledged

References and Notes

(1) For reviews of the chemiluminescent decomposition of 1,2-dioxetanes, see: (a) T. Wilson, Int. Rev. Sci Phys. Chem Ser. 2, 9, 265 (1976), (b) K A Horn, J -Y Koo, S. P. Schmidt, and G B. Schuster, Mol Photochem., 9, 1 (1978), (c) P D. Bartlett and M. E. Landis, In "Singlet Oxygen", H. H Wasserman and R. W. Murray, Eds., Academic Press, New York, 1979, Chapter 7, (d) N J Turro, P. Lechtken, N. E. Shore, G. B. Schuster, H.-C. Steinmetzer, and A. Yekta, Acc. Chem. Res., 7, 97 (1974).

(2) O. Shimomura and F. Johnson, Photochem. Photobiol., 30,89 (1979) and references therein.

(3) (a) F. McCapra, Chem. Commun., 155 (1968), (b) F. McCapra, Pure Appl Chem., 24, 611 (1970); (c) D. R. Kearns, Chem. Rev., 71, 395 (1971).

(4) (a) W. H. Richardson, J H. Burns, M E. Price, R. Crawford, M. Foster, P. Slusser, and J. H. Anderegg, J. Am. Chem. Soc., 100, 7596 (1978), (b) J.-Y. Koo and J. B Schuster, Ibid, 99, 5403 (1977).

(5) (a) K. A. Zaklika, A. L. Thayer, and A. P. Schaap, J. Am. Chem. Soc., 100, 4916 (1978); (b) F. McCapra, J. Chem. Soc. Chem. Commun , 946 (1977), (c) H. Nakamura and T. Goto, Photochem. Photobiol , 30, 29 (1979); (d) C. Lee and L. A Singer, J. Am. Chem. Soc., 102, 3823 (1980).

(6) (a) A P. Schaap, A. L. Thayer, E. C. Blossey, and D C. Neckers, J. Am Chem. Soc., 97 3741 (1975), (b) A. P. Schaap, A. L Thayer, K. A. Zaklika, and P C. Valenti, Ibid., 101, 4016 (1979). This sensitizer is available under the tradename SENSITOX I from Hydron Laboratories, Inc., Chemical Sales Dept., New Brunswick, NJ 08902.

(7) (a) T. Wilson and A. P. Schaap, J Am. Chem. Soc., 93, 4126 (1971), (b) T Wilson, Photochem. Photobiol., 30, 177 (1979).

(8) K. A. Zaklika, T Kissel, A. L Thayer, P A. Burns, and A. P. Schaap, Photochem. Photobiol , 30, 35 (1979)

(9) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, J Am Chem. Soc , 72, 5426 (1950).

(10) R. D. Schuelz and D. M. Teller, J. Org. Chem., 27, 410 (1962)

(11) W. A. Pryor and W. H. Hendrickson, Jr., J. Am. Chem. Soc., 97, 1580 (1975).

(12) W. H Richardson and D. L. Stiggall-Estberg, J. Am. Chem. Soc., in press. We thank Prof. Richardson for a preprint of his paper.

(Received in USA 16 March 1982)