

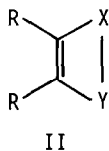
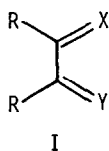
PHOTOSENSITIZED OXIDATION OF ACETYLENES¹

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Abstract: The sensitized (electron transfer) photo-oxidation of acetylenes to yield benzils is described and the mechanism is discussed.

We have recently reported^{2,3} the results of our investigations into the valence tautomerism between α -dithiones, Ia, and 1,2-dithietes, IIa, and between α -ketothiones, Ib, and 1,2-oxathietes IIb, and the existence of these systems led us to consider the possibility of observing the corresponding valence isomers of α -diketones, Ic, i.e. 1,2-dioxetes, IIC.



a, X = Y = S

b, X = O, Y = S

c, X = Y = O

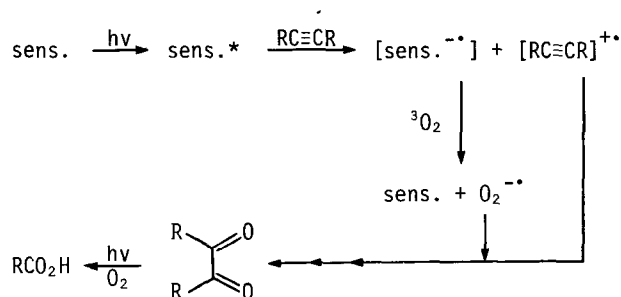
Apart from early reports⁴, not confirmed⁵, no evidence had been presented for the existence of 1,2-dioxetes, IIC, until Turro reported the oxidation of a strained acetylene both with ground state and singlet oxygen, the results of which could be rationalized with the intermediacy of a dioxete⁶. However, oxygen does not normally add to acetylenes, though Foote has demonstrated that singlet oxygen will add to electron rich triple bonds⁷. We have confirmed that simple acetylenes do not react with singlet oxygen generated by methylene blue or rose bengal sensitization in methanol.⁸

Foote has reported⁹ the photosensitized (electron transfer) addition of oxygen to olefins and this suggested to us that acetylenes might also react under these conditions. This was found to be so, and the results are given in the Table.¹⁰ Typical conditions used were as follows: the acetylene and sensitizer, dissolved in air saturated acetonitrile or propionitrile were irradiated with a high or medium pressure mercury arc through a filter (see Table) so that only the sensitizer absorbed light; the reactions were followed to completion by t.l.c. In all cases where any reaction of the acetylene occurred, a major product was the corresponding benzil; in the case of toluene the only other major product was benzoic acid. This was shown to be a secondary photoproduct arising from the photo-oxidation of benzil (direct irradiation of benzil in acetonitrile under identical reaction conditions, except that no sensitizer was present, gave benzoic acid). Other than with toluene, the benzoic acids arising from secondary photo-reactions were not isolated owing to the difficulty of their separation from the sensitizer photo-oxidation products.¹¹ In the case of ortho-methyltoluene, 2-hydroxy-2-phenylindanone¹² was also isolated

and is presumably a secondary photo-product arising from intramolecular hydrogen abstraction by the photo-excited, first-formed ortho-methylbenzil.¹³

By analogy with the mechanism suggested by Foote for the photosensitized (electron transfer) oxidation of olefins⁹, we propose the sequence shown in the Scheme. The excited sensitizer and the acetylene undergo electron transfer to give the sensitizer radical anion and the acetylene radical cation; the former undergoes further electron transfer with oxygen, regenerating sensitizer and superoxide, which recombines with the radical cation of the acetylene to yield, after further reorganization, the benzil product.

Scheme



In agreement with this mechanism, in the absence of sensitizer no reaction occurred and in solvents of low dielectric constant (e.g. benzene or acetone or methylene chloride), where charge separation becomes less favourable, the reaction became slower or more complex. Furthermore, the reactivity of the acetylenes examined is consistent with that predicted by the Weller equation, which relates the free energy of the electron transfer process between an excited acceptor and a donor to the oxidation potential of the donor, the reduction potential of the acceptor and the singlet (or triplet) energy of the excited acceptor.¹⁴ As can be seen from the Table all acetylenes which were reactive are predicted to undergo electron transfer spontaneously, whilst the unreactive acetylenes all possess more positive free energy changes for the process. Also, it would appear that the singlet state of the sensitizer is the acceptor species rather than the triplet excited state, since the free energies of electron transfer to the triplet excited sensitizer are all positive.

The species formed following the recombination of the postulated intermediates, superoxide and the acetylene radical cation, could not be detected. Several intermediates can be written, including a 1,2-dioxete, the latter of which could open to give the observed benzils in an excited state.⁶ Photo-oxidation of toluene using our conditions, but at -30°C or -78°C failed to yield a detectable intermediate and no chemiluminescence (benzil derived emission) was observed when the reaction mixture was warmed to room temperature.

TABLE

	$E_{1/2}^{OX}(V)^a$	sensitizer	Concentration (M) sensitizer	Concentration (M) acetylene	irradiating wavelength (nm)	solvent	ΔG^g (kcal/mol)	ΔG^h (kcal/mol)	Products; (% yield)
diphenyl- acetylene	1.47	DCN ^c	2.2×10^{-2}	6.9×10^{-2}	>300 ^e	MeCN	-15	+16	benzil (34%)
diphenyl- acetylene	1.47	DCA ^d	5.8×10^{-4}	6.3×10^{-3}	>300	MeCN	-5	-	benzil (27%), benzoic acid (54%)
diphenyl- acetylene	1.47	DCA	2×10^{-3}	6.5×10^{-3}	>390 ^f	MeCN	-5	-	benzil (77%), benzoic acid (19%)
phenylacetylene	>2 ^b	DCN	6.7×10^{-3}	5.7×10^{-2}	>300	EtCN	>-3	>+28	no reaction
2-methyl-diphenyl- acetylene	1.39	DCA	1.7×10^{-4}	4.5×10^{-3}	>390	MeCN	-7	-	2-methylbenzil (31%), 2-hydroxy-2- phenylindanone (20%)
1-ethoxy-1- butyne	>2 ^b	DCN	1.6×10^{-2}	1.2×10^{-1}	>300	MeCN	>-3	>+28	no reaction
4-methyl-di- phenylacetylene	1.32	DCA	1.3×10^{-3}	1.9×10^{-2}	>390	MeCN	-8	-	4-methylbenzil (52%)
2-butyne	>2 ^b	DCN	1.4×10^{-3}	1.1×10^{-1}	>300	EtCN	>-3	>+28	no reaction

(a) From cyclic voltammetry; Pt electrode, tetrapropylammonium perchlorate (0.1M) in acetonitrile, vs Ag/AgNO₃ (0.1M): oxidation potentials were irreversible; for a discussion of this problem see ref. 14. (b) Oxidation not observed. (c) DCN = 1,4-dicyanoaphthalene, E_{Red} = 1.67 vs Ag/AgNO₃ (0.1M) from cyclic voltammetry, singlet energy = 86.4 kcal/mol (from ref. 15), triplet energy = 55.5 (from ref. 15). (d) DCA = 9,10-dicyanoanthracene, E_{Red} = 1.23 vs Ag/AgNO₃ (0.1M) from cyclic voltammetry, singlet energy = 66 kcal/mol (from ref. 16). (e) Pyrex filter. (f) Schott GG-400 filter. (g) For singlet excited sensitizer; calculated from the Miller equation, assuming the coulombic term = 1.3 kcal/mol (see Ref. 14). (h) For triplet excited sensitizer. (i) Isolated yield following t.l.c. Experiments typically performed on 30-200 mg of acetylene.

References and Notes:

1. Contribution number 223 from the Photochemistry Unit, University of Western Ontario.
2. W. Kusters and P. de Mayo, J. Amer. Chem. Soc., 96, 3502 (1974); N. Jacobsen, P. de Mayo and A.C. Weedon, Nouveau, J. Chim., 2, 331 (1978).
3. P. de Mayo, A.C. Weedon and G.S.K. Wong, J. Org. Chem., 44, 1977 (1979).
4. R. Willstätter and F. Müller, Chem. Ber., 41, 2580 (1908); A. Schönberg and W. Malchow, Chem. Ber., 55B, 3746 (1922); A. Schönberg and O. Kraemer, ibid., 55B, 1174 (1922).
5. F. Kehrman, Chem. Ber., 44, 2632 (1911); F. Kehrman and M. Cordone, Chem. Ber., 46, 3009 (1913); S. Goldschmidt and F. Graef, Chem. Ber., 61B, 1858 (1928); W.M. Horspool, Quart. Rev., 23, 204 (1969); A. Schönberg and K. Praefcke, Chem. Ber., 99, 205 (1966).
6. N.J. Turro, V. Ramamurthy, K.-C. Liu, A. Krebs and R. Kemper, J. Amer. Chem. Soc., 98, 6758 (1976).
7. C.S. Foote and J.W.-P. Lin, Tetrahedron Letters, 3267 (1968).
8. Acetylenes are, however, oxidized by ozone to give, in the presence of a suitable reducing agent, diketones; see N.C. Yang, and J. Libman, J. Org. Chem., 39, 1782 (1974), and references therein. We thank a referee for drawing our attention to this work.
9. J. Eriksen, C.S. Foote and T.L. Parker, J. Amer. Chem. Soc., 99, 6455 (1977).
10. After the preliminary observations had been made Dr. S. Farid (Eastman Kodak) informed us that he had earlier observed the oxidation of diphenylacetylene, but had not pursued the study.
11. Substantial quantities of sensitizer were destroyed during the reaction to give a complex mixture of polar compounds.
12. A. Padwa and A. Au, J. Amer. Chem. Soc., 98, 5581 (1976).
13. N.K. Hamer, J. Chem. Soc. Perkin I, 1285 (1979); the intramolecular hydrogen abstraction reaction could be partially suppressed in our system by raising the sensitizer concentration. Total suppression of secondary photoreactions giving 2-hydroxy-2-phenylindanone or benzoic acids was not possible because of the low solubility of the sensitizer and the relatively intense absorption by the benzils at long wavelength; at high conversion some light was inevitably absorbed by the products.
14. A.J. Maroulis, Y. Shigemitsu and D.R. Arnold, J. Amer. Chem. Soc., 100, 535 (1978), and references therein.
15. A. Albin and D.R. Arnold, Can. J. Chem., 56, 2985 (1978).
16. R.G. Weiss, J. Amer. Chem. Soc., 97, 4485 (1975).

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