

## Short Communication

---

### The triplet energies of butenedioic acid derivatives

MANFRED J. MIRBACH, MARLIS F. MIRBACH and ALFONS SAUS

Universität Duisburg, Fachbereich 6, Angewandte Chemie, Lotharstrasse 63, D-4100  
Duisburg (F.R.G.)

(Received January 4, 1982)

The oxygen perturbation spectra of butenedioic acid derivatives were measured and the vertical triplet energies were determined to be  $62 \text{ kcal mol}^{-1}$  for fumaronitrile, about  $66 \text{ kcal mol}^{-1}$  for dimethyl fumarate,  $71 \text{ kcal mol}^{-1}$  or more for dimethyl maleate and  $72 \text{ kcal mol}^{-1}$  for maleic anhydride.

Butenedioic acid derivatives such as maleic anhydride (2,5-furandione), maleic acid esters (*e.g.* *cis*-butenedioic acid methyl ester), methyl fumarate (*trans*-butenedioic acid methyl ester) and fumaronitrile (*trans*-butene dinitrile) are frequently used as quenchers or reaction components in photochemical reactions. Despite their importance in photochemistry, the exact values of the triplet energies of these compounds are still uncertain for two reasons: (i) they do not phosphoresce (see below) and (ii) they are powerful electron acceptors, a property which leads to strong charge transfer interactions [1] that obscure triplet energy determinations by the classical Saltiel method [2, 3]. We therefore investigated direct  $S_0 \rightarrow T_1$  absorption in these compounds by the oxygen perturbation method. In this method the enhancement of the strongly forbidden  $S_0 \rightarrow T_1$  absorption by high oxygen pressures is utilized to allow a direct measurement of the "vertical"  $T_1$  energy to be made [4, 5]. In our experiments we measured the absorption spectra of highly concentrated solutions of the compounds in both the presence and the absence of oxygen at a pressure of 150 bar and determined the difference between the two spectra. The oxygen effect was reversible in all cases. The triplet energies measured and those reported in the literature are collected in Table 1.

The oxygen perturbation spectrum of fumaronitrile commences at about 465 nm ( $61.5 \text{ kcal mol}^{-1}$ ) on the long wavelength side and the first maximum appears at 458 nm ( $62.5 \text{ kcal mol}^{-1}$ ). Wong [3] has measured the triplet energy by the Herkstroeter-Hammond method and has found a value of  $59 \pm 2 \text{ kcal mol}^{-1}$ . Thus the vertical triplet energy measured by  $S_0 \rightarrow T_1$  absorption is only slightly higher than the energy of the more relaxed triplet state determined by the Herkstroeter-Hammond method. Furthermore

TABLE 1

Estimated triplet energies of butenedioic acid derivatives

Compound	$E_T$ (kJ mol <sup>-1</sup> (kcal mol <sup>-1</sup> ))	Method <sup>a</sup>	Reference
Fumaronitrile	260 (62)	1	This work
( <i>trans</i> -butene dinitrile)	247 (59)	2	[3]
	≈ 210 (≈ 50)	3	[2]
Dimethyl fumarate	277 (66)	1	This work
(butenedioic acid	≈ 250 (≈ 60)	4	[12]
dimethyl ester)	255 - 280 (61 - 67)	3	[13]
<i>cis</i> -Dicyanoethene	247 (59)	2	[3]
( <i>cis</i> -butene dinitrile)			
Dimethyl maleate	> 297 (> 71)	1	This work
( <i>trans</i> -butenedioic	≈ 293 (≈ 70)	4	[12]
acid methyl ester)	302 - 323 (72 - 77)	3	[13]
Maleic anhydride	302 (72)	1	This work
(2,5-furandione)	302 (72)	4	[8]

<sup>a</sup>1, Oxygen perturbation spectrum; 2, flash photolysis; 3, quenching experiments; 4, perturbation by an external heavy atom.

these results confirm that the value of 50 kcal mol<sup>-1</sup> obtained by the Saltiel method [2] does not reflect the true triplet energy of fumaronitrile; it is too low owing to electron transfer quenching of the donors by fumaronitrile [3].

The  $S_0 \rightarrow T_1$  absorption spectrum of dimethyl fumarate starts at 433 nm (66 kcal mol<sup>-1</sup>) with the first shoulder at 428 nm (66.8 kcal mol<sup>-1</sup>). This suggests that the vertical triplet energy is about 66 kcal mol<sup>-1</sup>, which falls within the limits of 61 - 67 kcal mol<sup>-1</sup> given by Hammond *et al.* [6] but is higher than the value obtained by Cox *et al.* [7].

The oxygen perturbation spectrum of dimethyl maleate commences at about 405 nm (71 kcal mol<sup>-1</sup>) on the long wavelength side and is featureless. Because of the absence of a distinct maximum or shoulder that can be assigned to an  $S_0 \rightarrow T_1$  absorption, we can only put a lower limit (71 kcal mol<sup>-1</sup>) on the triplet energy  $E_T$ . Featureless oxygen perturbation spectra are commonly obtained for carbonyl compounds possessing a lowest  $n\pi^*$  triplet state [8].

As for dimethyl maleate the oxygen-perturbed absorption of maleic anhydride starts at about 405 nm (71 kcal mol<sup>-1</sup>), but it shows a weak shoulder at 397 nm (72 kcal mol). The wavelength of this shoulder coincides very closely with the first maximum of a phosphorescence spectrum reported by Hardham and Hammond [9], but neither we nor other workers [10, 11] have been able to reproduce this emission spectrum. However, the oxygen perturbation spectrum confirms that the vertical triplet energy of maleic anhydride is of the order of 72 kcal mol<sup>-1</sup>.

The oxygen perturbation method gives only indirect evidence of the nature of the triplet states [8], but our results are in agreement with the assignment of a  $\pi\pi^*$  character for fumaronitrile and dimethyl fumarate, an  $n\pi^*$  character for dimethyl maleate and a mixed  $n\pi^*-\pi\pi^*$  character for maleic anhydride [11, 12]. The relatively high energies of the  $\pi\pi^*$  triplet states of the *cis* isomers suggest a non-planar geometry for these compounds. A similar argument has been used to explain the differences between the  $S_0 \rightarrow S_1$  absorption spectra of maleates and fumarates [13].

- 1 R. O. Loutfy, R. W. Yip and S. K. Dogra, *Tetrahedron Lett.*, (1977) 2843.
- 2 P. C. Wong, *Can. J. Chem.*, 57 (1979) 1037.
- 3 P. C. Wong, *Can. J. Chem.*, in the press.
- 4 D. Evans, *J. Chem. Soc.*, (1957) 1351.
- 5 M. F. Mirbach, M. J. Mirbach and A. Saus, *Chem. Rev.*, in the press.
- 6 G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Consell, V. Vogt and C. Dalton, *J. Am. Chem. Soc.*, 86 (1964) 3194.
- 7 A. Cox, P. de Mayo and R. W. Yip, *J. Am. Chem. Soc.*, 88 (1966) 1043.
- 8 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA, 1978, p. 124.
- 9 W. M. Hardham and G. S. Hammond, *J. Am. Chem. Soc.*, 89 (1967) 3200.
- 10 C. J. Seliskar and S. P. McGlynn, *J. Chem. Phys.*, 56 (1972) 275.
- 11 H. D. Scharf and H. Leismann, *Z. Naturforsch.*, 28b (1973) 662.
- 12 R. A. Back and J. M. Parsons, *Can. J. Chem.*, 59 (1981) 1342.
- 13 W. D. Closson, S. F. Brady, E. M. Kosower and P. K. C. Huang, *J. Org. Chem.*, 28 (1963) 1161.