

Benzyne by Pyrolysis of *o*-Sulphobenzoic Anhydride

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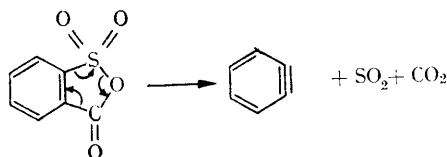
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PHTHALIC ANHYDRIDE at 690° loses carbon dioxide and carbon monoxide to give benzyne, closely

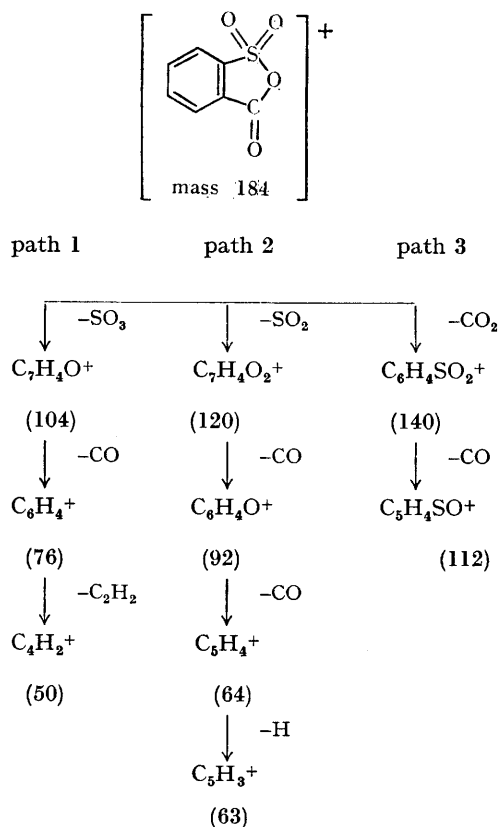
paralleling its behaviour in the mass spectrometer.¹ *o*-Sulphobenzoic anhydride possesses potentially

two good leaving groups, sulphur dioxide and carbon dioxide, and could also yield benzyne upon pyrolysis:



Compounds of somewhat similar structure, 1,2,3-benzothiadiazole 1,1-dioxide² and indanetrione³ decompose in this manner at 0° and 500° respectively.

The mass spectrum of *o*-sulphobenzoyl anhydride furnishes evidence for three competing decomposition paths:

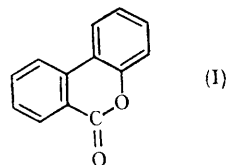


Relative contributions of the three paths can be estimated by summing the intensities of the ions arising by each of them in the 70v spectrum; (I), 68.7%; (II), 30.9%; (III), 0.4%. However, voltage-dependence measurements show that the appearance potential of C₇H₄O₂⁺ is lower than that of C₇H₄O⁺. At 9.5 ionizing volts (uncorrected),

intensity of the C₇H₄O₂⁺ ion is about five times that of C₇H₄O⁺, in sharp contrast to the situation at 70 volts, where intensity of C₇H₄O⁺ is twice that of C₇H₄O₂⁺. Loss of SO₂ is thus preferred at low energies, and might therefore be expected to be the preferred primary process also in pyrolysis.^{4,5}

To test this prediction, a solution of *o*-sulphobenzoyl anhydride (3.68 g.; 0.02 mole) in benzene (35.5 ml.; 0.4 mole) was pyrolyzed in a Vycor tube filled with Vycor beads at 690°, with a contact time of 18 seconds. The pyrolysate, after removal of benzene, weighed 2.2 g. The product mixture was examined by mass spectrometry. The Table shows relative intensities of parent peaks of components in the low-voltage (7.5 volts, uncorrected) spectrum—taken as a first approximation to relative concentrations—together with those from identical pyrolyses of benzene (35.5 ml.) alone (0.3 g. product) and of phthalic anhydride (2.96 g.; 0.02 mole) in benzene (35.5 ml.) (2.6 g. product) for comparison. Relative concentrations (vol. %) of the three components for which we have the requisite calibration data—naphthalene:biphenyl:3,4-benzocoumarin = 71:100:21—differ but little from the relative intensities shown in the Table.

The data strongly suggest the formation of benzyne from *o*-sulphobenzoyl anhydride—from the products of its reaction with benzene by 1,2- and 1,4-addition (naphthalene, phenylnaphthalene) and insertion (biphenyl, about 4 times as much by weight as from benzene alone). The uncondensed gases from the reaction, caught in barium hydroxide, proved to be a 1:1 mixture of sulphur dioxide and carbon dioxide. This, in addition to the other products, indicates that the first step of Path 2, loss of sulphur dioxide, is the dominant primary process. However, the resulting zwitterion, unlike its cationic counterpart in the mass spectrometer, does not go on to lose carbon monoxide; it stabilizes itself more easily by losing carbon dioxide and going to benzyne. Another possible course for the zwitterion is to attack the benzene and give either biphenyl or the lactone of 2-hydroxybiphenyl-2'-carboxylic acid (I):



The pyrolysate contained an appreciable amount of product of mass 196, which could be either xanthone or the lactone (I). Directly coupled gas

chromatography-mass spectrometry⁶ identified it as (I). The retention time and mass spectrum of this product agreed closely with those of an authentic sample of (I),⁷ which was clearly

unidentified peaks of masses higher than 230; these did not appear in the spectrum of the pyrolysate from phthalic anhydride under the same conditions. To elucidate further the products of thermal

TABLE
Mass-spectral intensities of pyrolysis products

Mass	Identity	Benzene	Relative intensities ^a	
			Phthalic anhydride in benzene	<i>o</i> -Sulphobenzoic anhydride in benzene
128	Napthalene	0.2	23.1	67
152	Biphenylene	—	2	—
154	Biphenyl	100	100	100
180	Fluorenone	—	0.9	3
196	3,4-Benzocoumarin ^b	—	—	20
204	Phenyl ⁿ aphthalene	—	9	10
230	Terphenyl	4	2.5	10

(a) Normalized to a value of 100 for biphenyl.

(b) See text.

distinguishable from xanthone on both counts. The formation of (I) parallels that of fluorenone from phthalic anhydride and benzene.¹

The spectrum of the pyrolysate from *o*-sulphobenzoic anhydride in benzene showed many small

decomposition of *o*-sulphobenzoic anhydride, further work on the pyrolysis in various solvents is in progress.

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¹ E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474.

² G. Wittig and R. W. Hoffmann, *Angew. Chem.*, 1961, **73**, 435.

³ R. F. C. Brown and R. K. Solly, *Chem. and Ind.* 1965, 181.

⁴ H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, ed., Academic Press, New York, 1963, p. 453; S. Meyerson and J. D. McCollum, *Adv. Analyt. Chem. Instrumentation*, 1963, **2**, 179.

⁵ Similar considerations seem to be relevant in attempts to extrapolate from unimolecular ionic processes in the mass spectrometer to photolytic and radiolytic reactions on a macro-scale. Cf.: S. Meyerson, *J. Phys. Chem.*, 1964, **68**, 968; N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *J. Amer. Chem. Soc.*, 1965, **87**, 4097.

⁶ R. S. Gohlke, *Analyt. Chem.*, 1954, **3**, 535; L. P. Lindeman and J. L. Annis, *Analyt. Chem.*, 1960, **32**, 1742; J. T. Watson and K. Biemann, *ibid.*, 1964, **36**, 1135.

⁷ The lactone (I) was synthesized by the method of C. Graebe and P. Schestakow, *Annalen*, 1895, **284**, 306.