

REACTIONS OF AROMATIC RADICAL ANIONS. III.  
REACTION WITH SULFUR DIOXIDE (1)

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While sulfur dioxide reacts with typical organometallic reagents to give salts of sulfinic acids (2) and with the tetraphenylethylene dianion to give the corresponding disulfinic acid salt (3), the reaction with aromatic radical anions has not been studied. As part of our continuing interest in reduction and addition reactions of aromatic radical anions, the reaction of sulfur dioxide with select aromatic radical anions was investigated.

At room temperature, sodium naphthalene in tetrahydrofuran reacts exothermically with sulfur dioxide with a color change and the formation of a white solid. Gas chromatographic analysis of the liquid using an internal standard reveals that 38.2% of the naphthalene is recovered. The solid isolated from the reaction was determined to be a mixture of sodium thiosulfate (35%), sodium sulfite (35%) and sodium dithionite (30%). The yield based on sodium was 90%. Accordingly, electron transfer is the sole reaction between sodium naphthalene and sulfur dioxide. Moreover, variations in the reaction conditions give no evidence for an addition reaction. Variation of temperature in the range of -20° to 40°, change of solvent to dimethoxyethane and inverse mode of addition of reactants all resulted in identical products and yield.

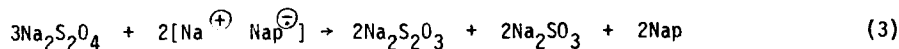
A reasonable mechanism involves first electron transfer to form the sulfur dioxide radical anion which is well known (4).



This is followed by dimerization of the  $\text{SO}_2^{\ominus}$  to give dithionite ion.



Finally secondary reactions of the dithionite, known to be unstable toward disproportionation (5), lead to thiosulfate and sulfite.



The electron transfer reaction (equation 1) depends upon the electron affinity of naphthalene,  $-0.01$  eV (6), and sulfur dioxide,  $1.0$  eV (7). Since variation of the electron affinity of the radical anion by suitable selection of the aromatic could alter the reaction path, the reaction with aromatic radical anions of varying and known electron affinity was investigated. Table 1 records these results.

TABLE 1  
Reaction of Sulfur Dioxide with Aromatic Radical Anions

Aromatic	Red. Pot. <sup>a</sup> , (volts)	Electron Affinity <sup>b</sup> (E.V.)	%Electron <sup>c</sup> Transfer	%Addition
Naphthalene	2.48	-0.01	100	>1%
Phenanthrene	2.44	+0.05	100	<1%
Pyrene	2.11	+0.42	100	<1%
Anthracene	1.96	+0.71	98	<1%
Fluoranthene	1.77	+0.93	99	<1%
Acenaphthylene	1.68	1.1	90	8% <sup>d</sup>
Azulene	1.62 <sup>e</sup>	—	—	—

a. I. Bergman, *Trans. Far. Soc.*, 50, 829 (1954); G. J. Hoijtink, *Rec. Trav. Chim. Pays. Bas.*, 73, 355 (1954), 74, 1525 (1955) and references therein.

b. Reference 6.

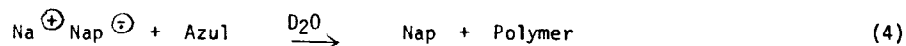
c. As determined by naphthalene recovery and yield of inorganic salts. The mixture of sulfite, dithionite and thiosulfate was comparable in all cases.

d. In addition to naphthalene loss a small amount of an aromatic sulfur-containing product was obtained.

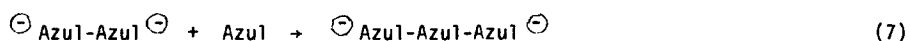
e. Estimated from the reduction potential in glyme, D. F. Shriner, D. E. Smith and P. Smith, *J. Am. Chem. Soc.*, 86, 5153 (1964).

As predicted, aromatics with electron affinities less than sulfur dioxide react only by electron transfer. Moreover, when the aromatic has a comparable electron affinity (acenaphthylene) some of the reaction involves addition. This addition product was characterized as a sulfur-containing aromatic compound. Further characterization was not possible due to the low yields and the instability of sulfinic acids. Finally, attempts to increase the addition reaction by the use of azulene, an aromatic with a greater electron affinity than sulfur dioxide, were thwarted by a polymerization reaction.

Azulene radical ion has been prepared in dilute solutions where it appears to be stable (8). In contrast, attempted preparation of the anion in more concentrated solution (0.5 M) and quenching with  $D_2O$  led only to polymer rather than to any deuterium containing products (equation 4). The polymer was not further characterized.



At higher concentrations the chemistry of the azulene radical anion appears to be similar to that of the styrene radical anion where a polymerization reaction prevents study of the radical anion (9). By analogy the following steps can be postulated for azulene (equations 5, 6, 7, 8).



This rapid polymerization is not surprising since the dimer dianion (and succeeding growing anions) probably incorporates the highly stable cyclopentadiene anion structure.

Surprisingly, the reaction of the anthracene dianion with sulfur dioxide gave only electron transfer. This contrasts with the behavior of the tetraphenylethylene dianion where addition has been observed. Since the reduction potentials are comparable it was thought that differences in the charge densities at the reactive sites and/or localization energies might account for the results. However, from molecular orbital calculations, the charge densities in the 9 and 10 position of the anthracene dianion are  $-.386$  whereas the charge density for the 1 and 2 positions for the tetraphenylethylene dianion are  $-.312$ , and the difference in localization energies is  $0.439$  B less for anthracene, thus favoring addition. The source of this contrasting behavior appears to be some unusual factor.

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