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The Effect of Sulfur Dioxide in the Radical Reactions of Anthracene

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The reaction of anthracene with benzoyl peroxide (BPO) in benzene solution gives 9-benzoyloxyanthracene (I), without forming any 9, 10-dibenzoyloxyanthracene (II). However, in the presence of sulfur dioxide (SO_2), the above mentioned reaction produces II, 9, 9′-dianthrone (III), and anthraquinone (IV), without any I. These reaction mechanisms could be interpreted as follows: It is considered that, in the addition reaction of anthracene with a benzoyloxy radical (PhCOO·), the 9, 10-dihydro-9-benzoyloxyanthryl radical (V) is formed. In the absence of SO_2, an intra-molecular aromatization of V occurs by a hydrogen abstraction and a delocalization of the radical. On the contrary, in the presence of SO_2, the localization of the V radical is enhanced by the interaction with SO_2, thus promoting the reactivity toward the benzoyloxy radical. Moreover, in the experiments using α, α'-azobis-isobutyronitrile (AIBN) in place of BPO, the addition products of 2-cyano-2-propyl radicals with anthracene were isolated. This phenomenon could be explained by the fact that the hydrogen abstractions of the addition products do not occur.

In a previous paper,(1) the reaction of anthracene with SO_2 in the presence of BPO, using as the solvent *n*-heptane, which does not interact with SO_2, was shown to yield anthronyl phenyl sulfone, oligomers (anthracene polysulfones), diphenyl disulfone, and benzenesulfonic acid. However, in the experiment using as the solvent benzene, which interacts with SO_2, the formation of sulfones mentioned above could not be observed; it was replaced by the formation of 9, 10-dibenzoyloxyanthracene (II), 9, 9′-dianthrone (III), and anthraquinone (IV).

Moreover, the *n*-heptane-solvent reaction without SO_2 yielded 9-benzoyloxyanthracene (I) and no II.

The present investigation was undertaken to see if the formation of no sulfone group containing

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1) H. Takeuchi, T. Nagai and N. Tokura, *Tetrahedron,* **23**(4), 1783 (1967).

such compounds as I, II, III and IV might change in the presence or absence of SO_2. Also, the present paper will deal with reactions using AIBN in place of BPO, in which sulfones do not form, perhaps because the hydrogen abstraction does not occur.

Experimental

Material. AIBN was obtained commercially, while the other materials were obtained by the methods reported in the previous paper.[1]

Procedure. As is shown in Exps. 1—9 below, anthracene and BPO (or AIBN) were dissolved in a definite amount of a solvent and the solution was treated under a definite condition. After the solvent had evaporated, the reaction mixtures were chromatographed over silica gel, using chloroform as the solvent. The reaction products that are not described especially were identified by a comparison of their IR spectra and mixed-melting points with those of authentic samples.

Experiment 1. Anthracene (0.045 mol) and BPO (0.100 mol) were dissolved in 400 m*l* of benzene, and the solution was heated at 80°C for 14 hr. The following compounds were isolated and identified: 9-benzoyloxyanthracene (43.0%),[2] biphenyl (8.05%), benzoic acid (43.0%), and unchanged anthracene (20.9%).

Experiment 2. A 120 g portion of SO_2 was passed through the system of Exp. 1. 9, 10-Dibenzoyloxyanthracene (11.3%), 9, 9′-dianthrone (32.6%), anthraquinone (12.1%), benzoic acid (46.0%), biphenyl (trace), and benzenesulfonic acid (trace) were thus obtained.

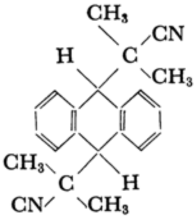
Experiment 3. 9-Benzoyloxyanthracene (5.1mmol) and BPO (7.65 mmol) were dissolved in 45 m*l* of benzene, and the solution was heated at 80°C for 7 hr, while 68 g of SO_2 gas were being passed through. The following compounds were isolated and identified: 9, 9′-dianthrone (31.4%), anthraquinone (13.5%), and benzoic acid (122.5%, based on BPO).

Experiment 4. In this experiment, BPO was eliminated from the system of Exp. 3. The 9-benzoyloxyanthracene was obtained unchanged.

Experiment 5. BPO was dissolved in 400 m*l* of benzene, and the solution was heated at 80°C for 14 hr, while 150 g of SO_2 gas were being passed through. Some of the solvent was evaporated, and the residue after extraction with hot water yielded benzene sulfonic acid (26.2%) and benzoic acid (28.6%). The residue obtained after the evaporation of benzene was chromatographed in the manner described in the Procedure Section, and diphenyl disulfone (7.1%), biphenyl (4.25 %), and unchanged BPO (10.8%) were confirmed to be present.

Experiment 6. Anthracene (0.04 mol) and AIBN (0.089 mol) were dissolved in 355 m*l* of *n*-heptane, and the solution was heated at 90°C for 7 hr, while 105 g of SO_2 gas were being passed through. The following materials were isolated and identified:

***trans*-9, 10-Bis(2′-cyano-2′-propyl)-9, 10-dihydroanthracene (XI).**[3,4]

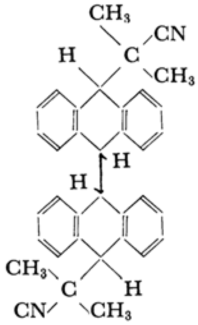


(XI)

Mp 188°C (recrystallized from 95% EtOH), 28.0%. ν_{max}^{KBr} 1370, 1470 and 3000 cm^{-1} (ν_{CH_3}), 2270 cm^{-1} ($\nu_{C\equiv N}$). λ_{max}^{EtOH} 265 mμ (log ε 2.63). NMR: τ; 8.55 (methyl, singlet, 6H), 5.80 (methine, singlet, 1H), 2.5—3.0 (aromatic, multiplet, 4H).

Found: C, 84.25; H, 6.97; N, 8.85%; mol wt, 310. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91%; mol wt, 314.4.

9, 9′-Bis(2′-cyano-2′-propyl) - 9, 9′, 10, 10′-tetrahydrodianthryl-10, 10′ (XII).[3]



(XII)

Mp 196.5°C (recrystallized from acetone), 6.25%. ν_{max}^{KBr} 1490 and 3000 cm^{-1} (ν_{CH_3}), 2260 cm^{-1} ($\nu_{C\equiv N}$). $\lambda_{max}^{dioxane}$ 265 (log ε 3.13), 271.5 mμ (3.05). NMR: τ; 8.55 (methyl, doublet, 6H), 5.98 (9, 9′-methine, singlet, 1H), 4.20 (10, 10′-methine, multiplet, 1H), 2.5—4.0 (aromatic, multiplet, 8H).

Found: C, 87.05; H, 6.75; N, 5.63%; mol wt, 477. Calcd for $C_{36}H_{32}N_2$: C, 87.76; H, 6.55; N, 5.69%; mol wt, 492.6.

Tetramethylsuccinodinitrile (XIII). Mp 165—168°C[5] 52.0%.

Anthraquinone. Mp 280—281°C. It showed no depression of the mixed melting point and had an IR spectrum identical with that of an authenic sample.

Unchanged Anthracene. 20.75%.

Experiments 7—9. *Exp. 7*: SO_2 was eliminated from the system of Exp. 6.

Exp. 8: Benzene was used as the solvent in place of *n*-heptane.

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[2] The yields presented in this paper are based on the anthracene used for the products with an anthracene skeleton, while they are based on the benzoyl peroxide used for the products with no anthracene skeleton.

[3] In the reaction of anthracene with AIBN in a toluene solution, the *cis*-isomer (mp 163—164°C) and the *trans*-isomer (mp 189.0—189.5°C) of XI were isolated by A. F. Bickel and E. C. Kooyman (*Rec. trav. Chim.*, **71**, 1137 (1952)), but in our experiments the *cis*-isomer could not be isolated even though the reaction mixtures were chromatographed over silica gel or active Al_2O_3.

[4] C. la Lau, *Rec. trav. Chim.*, **73**, 931 (1954).

[5] G. S. Hammond, Chin-Hua. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *J. Am. Chem. Soc.*, **82**, 5394 (1960).

Exp. 9: Irradiated by a high-pressure mercury lamp (300 W) in the system of Exp. 6.

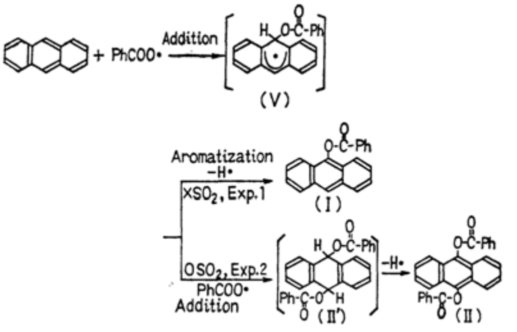
In these experiments, the products were isolated and identified as in Table 1.

TABLE 1

Experiment	Product				
	XI	XII	XIII	Anthraquinone	Unchanged anthracene
Exp. 6	28.0	6.25	52.0	trace	20.75
Exp. 7	29.0	12.1	70.3	trace	28.4
Exp. 8	33.8	12.6	54.7	—	8.1
Exp. 9	25.5	12.4	61.8	—	28.5

Results and Discussions

(1) The Formation Mechanism of 9-Benzoyloxyanthracene (I) and 9, 10-Dibenzoyloxyanthracene (II). In Exp. 1 I was formed, but no II. However, in Exp. 2 II was formed, but no I.



Scheme 1

In the absence of SO_2, the intra-molecular aromatization of the V radical6) occurs by means of the hydrogen abstraction and delocalization of V. Therefore, I forms without the further attack of the benzoyloxy radical.

On the other hand, in the presence of SO_2, it may be considered that the localization of the V radical is enhanced by the interaction7) with SO_2, which promotes the reactivity toward the benzoyloxy radical, and that II forms through the hydrogen abstraction of II′. This mechanism supports the idea that SO_2 does not react with V, but interacts with it, for no anthracene sulfonyl compound can be obtained in Exp. 2. This case shows that the attack of the benzoyloxy radical on V occurs even if V interacts with SO_2,7) because the benzoyloxy radical cannot react with SO_2, as has been established in a previous paper.1)

The energy diagram for these reactions is shown as Fig. 1.

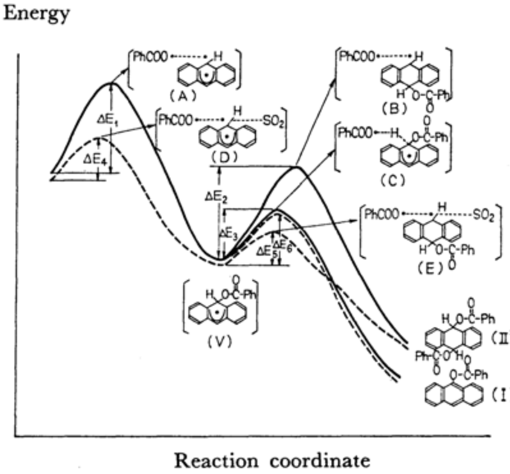


Fig. 1

——; × SO_2 ……; ○ SO_2

ΔE_1, ΔE_2, ΔE_4, and ΔE_5; $\Delta E \propto (L_R+\Delta)$

In the absence of SO_2, it can be expected that PhCOO· and anthracene approach each other to give the V radical through a transition state such as A; in this case the activation energy, ΔE_1, is proportional to $(L_R+\Delta_1)$.8) (L_R: localization energy of anthracene, 33 kcal/mol. Δ_1: energy difference by both hybridization and solvation, based on the difference between the localization and delocalization structures of anthracene.)

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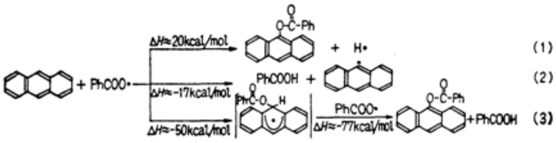
6) Three reactions between PhCOO· and anthracene can be envisioned:



Calculations based on bond energies show that Reaction (1) is endothermic, whereas the sum of (3) is exothermic. Therefore, it may be assumed that a two-step mechanism such as (3) is preferable to a one-step mechanism such as (1). Also, it may be expected that Reaction (2) is a side reaction. A similar discussion of the reaction of Ph· with Ph·H has been reported by D. H. Hey, M. J. Perkins and G. H. Williams (*J Chem. Soc.*, **1964**, 3412). Other similar discussions: M. Levy, M. Steinbery and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 3439 (1954), and Ref. 3.

7) Even if the interaction of SO_2 and anthracene or V shown by D or E prevents the reactivity toward PhCOO·, this prevention seems to be an entropy effect. Therefore, in low-activation-energy reactions, it may be expected that the reactivity is more strongly related to the activation energy than to the entropy effect. Also, in spite of this interaction, it may be assumed that incipient 9-position radicals, such as D or E, can react with PhCOO· by back-side attack, because incipient 9-position radicals presumably have much π-character plus little a σ-character in terms of Hammond's postulate (*J. Am. Chem. Soc.*, **77**, 334 (1955)).

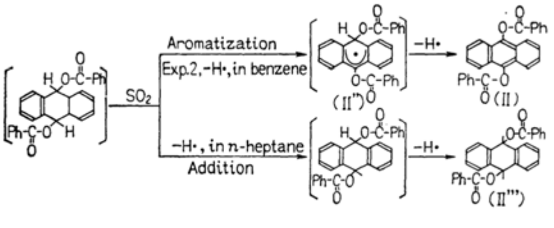
8) a) M. Szwarc, *J. Phys. Chem.*, **61**, 40 (1957). b) M. Levy and M. Szwarc *J. Chem. Phys.*, **22**, 1621 (1954); *J. Am. Chem. Soc.*, **77**, 1949 (1955).

The further attack of PhCOO· on V[9] may be expected. For this the activation energy, $\Delta E_2 \propto (L'_R+\Delta_2)$, is necessary (it may be assumed that L'_R is nearly 27 kcal/mol, because paralocalization energy of anthracene is about 60 kcal/mol[10]). In this case, because the activation energy of hydrogen abstraction from V[9], ΔE_3, is lower than ΔE_2, it may be interpreted that I is given predominantly.

However, in the presence of SO_2, the activation energy forming V, ΔE_4, may be expected to be lower than ΔE_1 because of the electron-withdrawing effect of SO_2 (or complex formation[11] from the localizing electron of anthracene and SO_2 during the reaction process).

Similarly, the activation energy of the formation of II′[12], ΔE_5, may be expected to be lower than ΔE_2, but the activation energy of hydrogen abstraction reaction, ΔE_6, hardly differs from ΔE_3, because no localization occurs in the transition state. Therefore, it may be interpreted that II is formed through II′,[12] while no I is formed.[11]

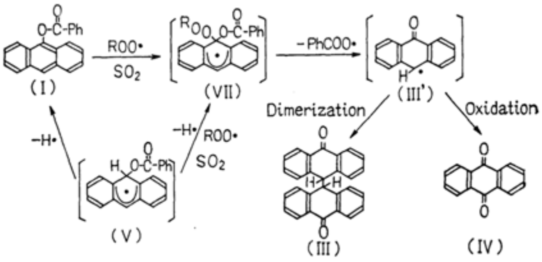
Similarly, in this view, though II is obtained in Exp. 2, oligomers having II‴ units are obtained in the experiment[1] using *n*-heptane in place of benzene as the solvent in Exp. 2. It can be shown by Scheme 2 that a radical such as II″ in the experiment using *n*-heptane localizes more strongly on the 10-position than in the experiment using benzene as the solvent, because the interaction of II″ with SO_2 becomes weak due to the interaction of benzene with SO_2.



Scheme 2

(2) The Formation Mechanism of 9, 9′-Dianthrone (III) and Anthraquinone (IV). The reaction of the anthracene-BPO-*n*-heptane (or benzene) system, when SO_2 exists in the system, yielded products such as 9, 9′-dianthrone, anthraquinone, and anthronyl phenyl sulfone which are derived from an anthronyl radical.

Therefore, in order to investigate the formation mechanism of the anthronyl radical, we carried out Exp. 3, thus forming III and IV from I. In Exp. 4 (without the BPO of Exp. 3), I was unchanged. These results suggest that, in the formation of the anthronyl radical,[13] the existence of BPO and SO_2 is effective.



Scheme 3

Therefore, it can be assumed that, by the interaction with SO_2, the localization of the electron of I is promoted, and it may be predicted that I will react with the peroxide radical (ROO·) presumably formed by BPO and atmospheric oxygen. In this case, the elimination of the PhCOO· radical from VII is obvious from the fact that the yield of benzoic acid is 122.5% (based on BPO).

(3) The Reaction of Anthracene with AIBN. The effects of SO_2 in the reactions using BPO abstracting hydrogen have often been discussed. Next, a reaction using AIBN in place of BPO was carried out in order to investigate whether some

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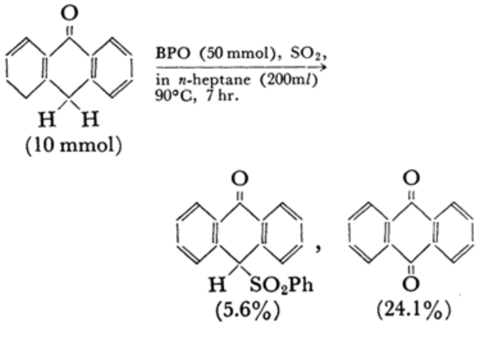
[9] In the case of the attack of PhCOO· on V or the hydrogen abstraction of V, the V radical is also assumed to act as the species responsible for the induced decomposition of BPO. a) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946); **69**, 2299 (1947). b) C. G. Swain, W. H. Stockmeyer and J. T. Clarke, *ibid.*, **72**, 5426 (1950). c) W. Cooper, *J. Chem. Soc.*, **1952**, 2408. d) W. R. Foster and G. H. Williams, *ibid.*, **1962**, 2862. However, judging from the result that about 20% of the anthracene used did not react in Exp. 1, this induced decomposition seems to be unattractive.

[10] R. D. Brown, *J. Chem. Soc.*, **1950**, 691.

[11] As these activation energies are low, it may be predicted that the reaction course is selective, even if some activation energy changes. There is abundant evidence for significant energy effects of complexes or interactions between radical and solvent. a) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957); **80**, 4987, 5002 (1958); G. A. Russel, A. Ito and G. Hendry, *ibid.*, **85**, 2976 (1963). b) C. Walling and A. Padwa, *ibid.*, **84**, 2845 (1962); **85**, 1593 (1963). c) J. C. Martin, J. W. Taylar and E. H. Drew, *ibid.*, **89**, 129 (1967).

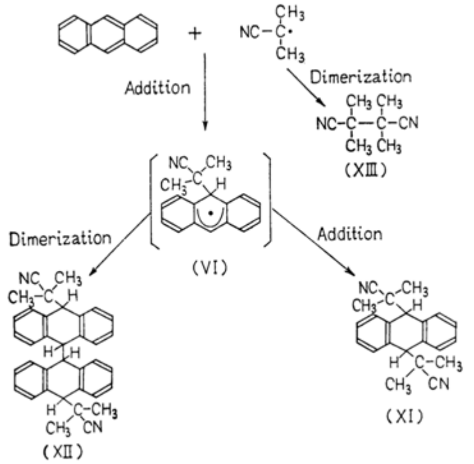
[12] If the formation of II′ occurs through a molecule-induced reaction between anthracene and BPO, the formation of II is prevented by anthracene-SO_2 interaction.

[13] This explanation of anthronyl radical formation may be supported by the following experiment:



sulfone might form in a solvent such as *n*-heptane not interacting at all with SO_2. Also, in these reactions it was investigated whether or not the reaction process changed in the presence or in the absence of SO_2.

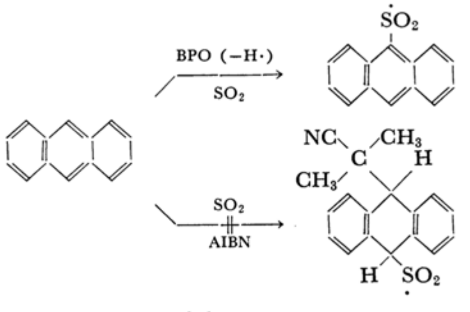
In Exp. 6—9, XI, XII and XIII were the main products,



Scheme 4

The formation of addition products, such as XI and XII, indicates that the VI radical is formed.[3] This fact supports the idea that the addition reactions shown by Schemes 1—3 are more likely.

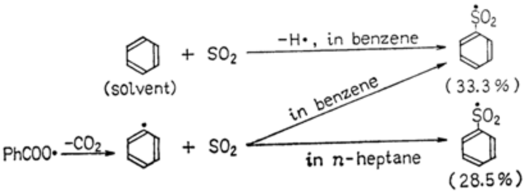
Also, in these reactions, the fact that no sulfone is formed suggests that π-character radicals (such as V, II'', III' and VI) cannot react with SO_2, but that σ-character radicals (such as the phenyl and anthryl radicals) react with SO_2 to form sulfonyl radicals.



Scheme 5

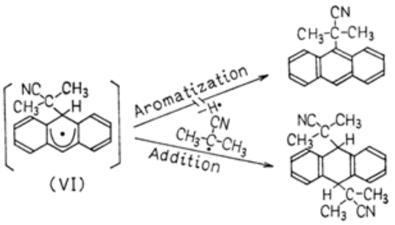
Moreover, the facts that the hydrogen abstraction of such addition product as XI or XII did not occur and no sulfone was formed in the case of AIBN[14] suggest that the anthryl sulfonyl radical occurs, as is shown by Scheme 5, presumably by means of the hydrogen abstraction from anthracene as reported in a previous paper.[1]

This hydrogen abstraction from an aromatic molecule is supported by the facts that, in Exp. 5, benzoic acid (28.6%) is obtained, and that the products (33.3%) derived from $PhSO_2$. are formed in larger amounts than in the experiment[1] using *n*-heptane instead of benzene (Exp. 5), in spite of the benzene-SO_2 interaction, shown by Scheme 6.



Scheme 6

Apparently, the deficiency[14] in the hydrogen abstraction in Exps. 6—9 indicates that the reaction products do not change greatly according as SO_2 is present or absent.



Scheme 7

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[14] In this experiment (XI (5.1 mmol) - BPO(7.65 mmol) - SO_2 - benzene (50 m*l*) system at 80°C for 7 hr), XI was unchanged. Further, in Exp. 9, the methine hydrogens of the addition products could not be eliminated by irradiation. These results suggest that methine-hydrogen abstraction from VI, XI and XII is markedly strained because of steric interference between the bulky substituent group and the hydrogen atoms at the 1- and 8- positions; (Ref. 3).