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The Transformation of the Triphenylmethyl Radical into the Triphenylmethyl Cation in the Sulfur Dioxide - Oxygen System

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The decomposition of phenylazotriphenylmethane (I) in the presence of SO_2 and O_2 in benzene at 60°C gives *p*-hydroxytetraphenylmethane (II) by the reaction of the trityl cation and the phenol formed in the reaction system. However, in the absence of O_2 or SO_2, the above-mentioned reaction produces trityl phenyl sulfone (III) or bistrityl peroxide (IV), without forming any II. Also, 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (Gomberg's trityl) (V) has been chosen as the trityl radical source, and reacted with phenol in the presence of SO_2 and O_2 to give II as the product. However, in the absence of SO_2, IV and a trace of II are formed. Moreover, in the absence of O_2 in the above system, *p*-benzhydryltetraphenylmethane (VI) and a small amount of II are formed. The benzene solution of VI is stable on exposure to air at 60°C. Further, the UV spectrum of V in the liquid SO_2-O_2 system shows λ_{max} at 405 mμ ($\log \varepsilon$ 4.1) and 434 mμ ($\log \varepsilon$ 4.1) (trityl chloride in 98% H_2SO_4: λ_{max} 430 mμ ($\log \varepsilon$ 4.58)). However, the UV spectrum of VI in the liquid SO_2-O_2 system has no absorption in this range. The NMR spectrum in the liquid SO_2-O_2 system of V exhibits only aromatic protons (2.6—3.1 τ). These facts indicate that the trityl radical generated from V is transformed into the trityl cation in the SO_2-O_2 system at room temperature, whereas VI does not dissociate into the trityl radical even at 60°C in benzene.

We have previously established[1] the reaction of SO_2 with a radical source such as phenylazotriphenylmethane (I) which is able to liberate both the π- and the σ-character radicals[2,3] (the trityl and phenyl radicals). The nearly-quantitative formation of trityl phenyl sulfone (III) in the above reaction could be considered to be the result of the intramolecular radical recombination of the radical pairs (the phenylsulfonyl and trityl radicals) surrounded by SO_2 molecules.

On the other hand, the reaction of I with SO_2 in the presence of O_2 gave *p*-hydroxytetraphenylmethane (II) and benzenesulfonic acid, but neither III nor bistrityl peroxide (IV). Busch and Knoll have reported[4] the formation of II from the ionic reaction of Ph_3CCl with PhOH. Therefore, the formation of II from I in the presence of SO_2 and O_2 was expected to result by means of the trityl cation formed from the trityl radical. The thermal electron-transfer reaction[5] in the presence of SO_2 and O_2 has been recongnized as reasonable in the polymerization of *N*-vinylcarbazole.

The present study was concerned with the ionic behavior of the trityl radical in the SO_2-O_2 system by using I and using 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (V) as the trityl radical source. Phenol was used as a trapping reagent of the trityl cation.

Further, the transformation of the trityl radical into the trityl cation in the liquid SO_2-O_2 system was proved by a study of the UV and NMR spectra. This fact arouses our interest in the field of polymerization.

Results and Discussion

The Effect of Oxygen - Sulfur Dioxide in the Reaction of Phenylazotriphenylmethane (I) with Phenol. In a previous paper,[1] we reported that the reaction of I with SO_2 in benzene or *n*-heptane gave trityl phenyl sulfone (III) in a good yield:

$$\underset{\text{(I)}}{\text{Ph-N=N-CPh}_3} + \text{SO}_2 \xrightarrow[\text{in benzene or } n\text{-heptane}]{-\text{N}_2} \underset{\text{(III)}}{\text{Ph-SO}_2\text{-CPh}_3}$$

In the presence of O_2, the above reaction gave *p*-hydroxytetraphenylmethane (II), benzenesulfonic acid, and a small amount of phenol, but neither III nor bistrityl peroxide (IV) was found, although the reaction of I with only O_2 gave IV, without

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[1] H. Takeuchi, T. Nagai and N. Tokura, *Tetrahedron*, **25**, 2987 (1969).

[2] H. Takeuchi, T. Nagai and N. Tokura, *ibid.*, **23**, 1783 (1967).

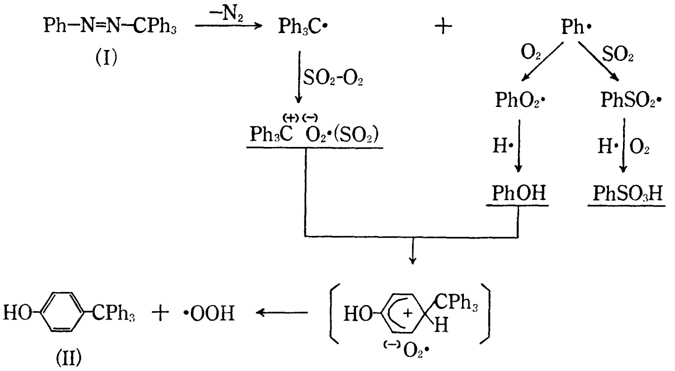
[3] H. Takeuchi, T. Nagai and N. Tokura, This Bulletin, **40**, 2375 (1967).

[4] M. Busch and R. Knoll, *Ber.*, **60**, 2240 (1927).

[5] T. Nagai, T. Miyazaki and N. Tokura, *J. Polym. Sci., Part B*, **6**, 346 (1968).

any II. These facts suggest that the reaction in the presence of SO_2 and O_2 is ionic. Actually, Busch and Knoll[4] reported a 98% yield of II from the reaction of Ph_3CCl with PhOH. Therefore, it was expected that II was formed by the reaction of the trityl cation with phenol.

Then, phenol (five equivalents to I) was added to the system (Exp. 1). In this reaction, the yield (58%) of II increased in comparison with the yield (18—24%) of II in the reaction without phenol. However, in the absence of O_2 in Exp. 1, III was formed without giving II (*cf.* Exp. 2). These facts suggest the formation of II by the reaction of the trityl cation with phenol, as in Scheme 1:

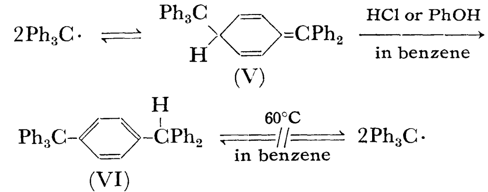


Scheme 1

The Effect of Oxygen - Sulfur Dioxide in the Reaction of 1-Diphenylmethylene-4-trityl-2,5-cyclohexadiene (V) with Phenol. The reaction of V with phenol in the presence of SO_2 and O_2 in benzene at 60°C gave II (52%) (*cf.* Exp. 3). However, in the absence of SO_2, IV (41%) and II (trace) were formed in Exp. 4. Moreover, in the absence of the O_2 of Exp. 3, *p*-benzhydryltetraphenylmethane (VI) (45%) and a small amount of II were formed (*cf.* Exp. 5).

These observations support the idea that the transformation of the trityl radical into the trityl cation in the SO_2-O_2 system occurs as Scheme 1 shows.

The Formation of *p*-Benzhydryltetraphenylmethane (VI). As is indicated in Exp. 6, VI was obtained by the reaction of V with phenol under Ar gas. When HCl was used in place of phenol, VI was also produced (Exp. 7).



Scheme 2

It has been reported by Lankamp, Nauta and MacLean[6] that Gomberg's trityl has a cyclohexadiene structure, as is shown in Scheme 2. Gomberg *et al.*[7,8] have reported that the reaction of V with HCl or CH_3COOH gives hexaphenylethane. However, it was found that the product was not hexaphenylethane, but VI, on the basis of the IR, NMR and mass spectral data (*cf.* Exp. 5). The details of the reaction mechanism of the formation of VI will be reported in the near future.[*1]

The UV spectrum of VI has $\lambda_{\max}^{\text{cyclohexane}}$ at 263 mμ (log ε 3.11). The NMR spectrum of VI shows aromatic protons (2.6—3.1 τ) and a methine proton (4.6 τ) in CCl_4. The mp (225—227°C) of VI is higher than the mp (145—147°C) of V. Further,

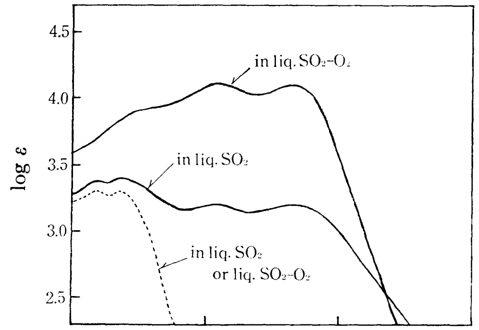


Fig. 1. The electronic spectra of Gomberg's trityl (V).
—— Gomberg's trityl (V)
---- *p*-Benzhydryltetraphenylmethane (VI)

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6) H. Lankamp, W. Th. Nauta and C. MacLean, *Tetrahedron Lett.*, **1968**, 249.

7) M. Gomberg, *Ber.*, **35**, 2877 (1902).

8) F. Ullmann and W. Borsum, *ibid.*, **35**, 3914 (1902).

[*1] In the experiment using I in place of the V of Exp. 3, VI was never found. Similarly, the treatment of 1-(phenyl-*p*-tolylmethylene)-4-(diphenyl-*p*-tolylmethyl)-2,5-cyclohexadiene with HCl in benzene afforded α,α,α'-triphenyl-α,α'-ditolyl-*p*-xylene by the isomerization of the cyclohexadiene structure.

Table 1. The UV spectra of V in liquid SO_2 and liquid SO_2-O_2

Number	log ε in liquid SO_2				log ε in liquid SO_2-O_2		
	360 mμ *max*	368 mμ *max*	405 mμ *max*	434 mμ *max*	374 mμ shoulder	405 mμ *max*	434 mμ *max*
1	3.26	3.25	3.0	3.0	3.91	4.11	4.10
2	3.36	3.37	3.3	3.3	3.94	4.01	4.0
3	3.44	3.44	3.3	3.3	—	—	—
Average	3.4	3.4	3.2	3.2	3.9	4.1	4.1

This transformation is shown as Fig. 1.

the benzene solution of VI is stable on exposure to air, even at 60°C.

The Transformation of the Trityl Radical into the Trityl Cation in the Liquid SO_2-O_2 System. The UV spectra of Compound V were measured in liquid SO_2 and liquid SO_2-O_2 systems at room temperature. The results are summarized in Table 1.

This transformation is shown as Fig. 1.

In the liquid SO_2-O_2 system, no absorption corresponding to the trityl radical[9] appears. The values of log ε at 405 and at 434 mμ in liquid SO_2 were 3.2,*[2] whereas those in the liquid SO_2-O_2 system were 4.1. The UV spectra of the trityl cation have been established to be as follows:

Trityl chloride[10]: $\lambda_{max}^{98\%\ H_2SO_4}$ 430 mμ (log ε 4.58).

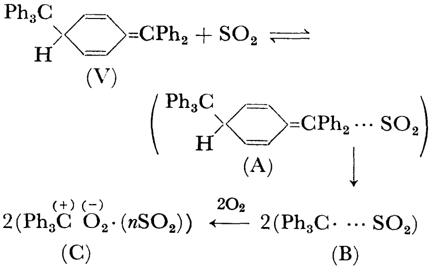
Compound V[11]: $\lambda_{max}^{H_3PO_4}$ 400 mμ and 440 mμ (log ε 4.5).

Compound V[11]: $\lambda_{max}^{POCl_3}$ 420 mμ and 440 mμ (log ε 4.2).

Therefore, the peaks at 405 and 434 mμ in the liquid SO_2-O_2 system may be said to correspond to the absorptions of the trityl cation.

The absorption with $\lambda_{max}^{SO_2}$ at 360 and 368 mμ is observed characteristically in liquid SO_2. Also, the UV spectrum of VI was measured as: $\lambda_{max}^{SO_2 \text{ or } SO_2\text{-}O_2}$ 360 mμ (log ε 3.3) and 368 mμ (log ε 3.3). The UV spectrum of VI does not have the absorption corresponding to the trityl cation in the liquid SO_2-O_2 system, indicating that the dissociation of VI into the trityl radical does not occur as in Scheme 2, since the trityl radical is transformed into the trityl cation in this system. This finding is in fair agreement with the chemical evidence. In a cyclohexane solution, the absorption with λ_{max}= 360 and 368 mμ did not appear in the case of either V or VI.

These observations indicate that the absorption with λ_{max}=360 and 368 mμ is attributable to a C–T complex of SO_2 with V (*cf.* A in Scheme 3).

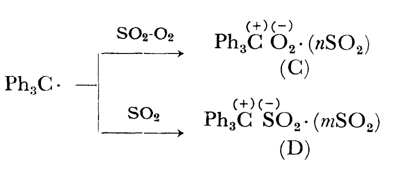


Scheme 3

Therefore, the transformation of V into C may be assumed to proceed *via* an A complex. The oxygen counter anion is stabilized by a solvated SO_2 such as $\overset{(-)}{O_2}\cdot(nSO_2)$.

The NMR spectrum shows that the cation formed from V in this system is not the 1-diphenylmethylene-2,5-cyclohexadienyl cation, but the trityl cation having only aromatic protons (2.6—3.1 τ).

Although the electron affinity of SO_2 (0.2—0.3 eV)[5] is larger than that of O_2 (0.15 eV),[5] the promotion*[3] of the transformation of the trityl radical into the trityl cation in SO_2-O_2 rather than SO_2 may be expected to proceed as follows:



Scheme 4

The interaction energy between an anion and solvated SO_2 molecules with a dipole moment may

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[9] W. Theilacker and M. L. W. Ewald, *Ann.*, **594**, 214 (1955).

*[2] The dissolved oxygen in liquid SO_2 was eliminated by the method described in the Experimental section. However, this absorption may arise from a very small amount of oxygen, or else from the trityl cation already generated in liquid SO_2.

[10] A. G. Evans, J. A. G. Jones and G. O. Osborne, *J. Chem. Soc.*, **1954**, 383.

[11] T. L. Chu and S. I. Weissman, *J. Chem. Phys.*, **22**, 21 (1954).

*[3] Because of the following reasons, it seems feasible that a trityl cation such as D is formed even in the liquid SO_2 system, as is shown in Scheme 4. The UV spectrum of V even in liquid SO_2 shows peaks corresponding to those of the trityl cation, as Fig. 1 shows. Further, the reaction of V with phenol in the presence of SO_2 and Ar gas, as in Exp. 5, gives II (11%) and thus corresponds to the reaction of the trityl cation with phenol.

be represented by the following formula:

$$\overset{(-)}{O_2}\cdot \underset{r_i}{\longleftrightarrow} SO_2 \quad E_1 = \sum_{i=1}^{n}\{N(-e)\mu_{SO_2}\cos\theta_i/r_i^2\}$$

$$\overset{(-)}{SO_2}\cdot \underset{r_j}{\longleftrightarrow} SO_2 \quad E_2 = \sum_{j=1}^{m}\{N(-e)\mu_{SO_2}\cos\theta_j/r_j^2\}$$

$-e$: electric charge.
μ_{SO_2}: dipole moment of SO_2 (1.61 debye).
r: distance between dipole and ionic center.
θ: angle between the direction of r and that of μ_{SO_2}.
N: Avogadro number.

Since $\overset{(-)}{SO_2}\cdot$ is bulkier than $\overset{(-)}{O_2}\cdot$, the value of r_i is smaller than r_j. Therefore, the absolute value of the interaction energy between $\overset{(-)}{O_2}\cdot$ and SO_2, E_1, becomes greater than that between $\overset{(-)}{SO_2}\cdot$ and SO_2, E_2, so that the difference between the above interaction energies appears to compensate sufficiently for the electron affinity difference between SO_2 and O_2. Also, the Coulombic enregy stabilization by $Ph_3\overset{(+)}{C}$ and $\overset{(-)}{O_2}\cdot$ is greater than that by $Ph_3\overset{(+)}{C}$ and $\overset{(-)}{SO_2}\cdot$. These stabilization energies of the trityl-cation formation due to the oxygen counter anion, $\overset{(-)}{O_2}\cdot(nSO_2)$, may act as the driving force to transform the trityl radical into the trityl cation in the SO_2-O_2 system.

Experimental

Apparatus. The IR spectra were run on an EPI-S2-type Hitachi IR spectrometer. The NMR spectra were obtained with a Japan Electron Optics Lab. spectrometer (JNM3H-60). The UV spectra were taken on an EPS-3 Hitachi recording spectrometer.

Materials. The liquid SO_2 was dehydrated with P_2O_5 and distilled. The benzene was purified by an ordinary method. The phenol was obtained commercially. The phenylazotriphenylmethane (I) (mp 111°C dec.) was synthesized by the method of Cohen and Wang.[12] The 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (V) was synthesized by the method of Gomberg and Cone.[13]

Experiment 1. Compound I (4.7 mmol) and phenol (23.5 mmol) were dissolved in 95 m*l* benzene; the solution was then heated at 60°C for 2 hr with stirring while 70 g of gaseous SO_2 and O_2 were being passed through. The benzene was distilled under reduced pressure. The residue was chromatographed over silica gel, using benzene as the eluent; we then isolated and identified the *p*-hydroxytetraphenylmethane compound (58%), showed no depression of mp in a mixed-melting-point determination and which had an IR spectrum identical with that of an authentic sample.[4]

Experiment 2. Compound I (8.6 mmol) and phenol (43 mmol) were dissolved in 60 m*l* benzene; the solution was then heated at 60°C for 2 hr while 30 g of gaseous SO_2 were being passed through. The benzene was distilled under reduced pressure. The residue was crystallized from MeOH - ether, and trityl phenyl sulfone (55%) was isolated and identified. This compound showed no depression of mp in a mixed-melting-point determination with an authentic sample,[1] and the IR spectra were identical.

Experiment 3. Compound V (4.7 mmol) and phenol (47 mmol) were dissolved in 65 m*l* benzene; the solution was then heated at 60°C for 2 hr with stirring while 32 g of gaseous SO_2 and O_2 were being passed through. *p*-Hydroxytetraphenylmethane (52%) was confirmed as has been described above.

Experiment 4. In this experiment, SO_2 was eliminated from the system of Exp. 3. The residue obtained after the evaporation of the benzene was chromatographed over silica gel, using a petroleum ether - benzene mixture as the eluent by changing the polarity of the eluting medium. Bistrityl peroxide (IV) was isolated and identified, along with a small amount (3%) of *p*-hydroxytetraphenylmethane.

Bistrityl Peroxide (IV). Mp 183°C (recrystallized from toluene), 41%. This compound showed no depression of mp in a mixed-melting-point depression with an authentic sample[14] and had an identical IR spectrum.

Experiment 5. This experiment was carried out much as in Exp. 3, but Ar gas was used in place of O_2. The residue after the distillation of the benzene was chromatographed over silica gel, using a petroleum ether - benzene mixture as the eluent by changing the polarity of the eluting medium. The following compounds were isolated and identified (*p*-hydroxytetraphenylmethane (11%) was also confirmed, as has been described above):

***p*-Benzhydryltetraphenylmethane (VI).**[15] Mp 225—227°C (recrystallized from benzene - acetic acid), 45%, IR: 2880 (ν_{C-H}), 840 cm^{-1} (*p*-substituted phenyl). $\lambda_{max}^{cyclohexane}$ 263 mμ (log ε 3.11), shoulder; 255 mμ (log ε 3.15), 269 mμ (log ε 2.99) and 272 mμ (log ε 2.67). NMR (in CCl_4): τ; 2.6—3.1 (aromatic, multiplet, 29H), 4.6 (methine, singlet, 1H). Mass spectrum: *m*/*e*; 486, 409, 243 and 167.

Found: C, 93.71; H, 6.41%. Calcd for $C_{38}H_{30}$: C, 93.79; H, 6.21%.

Triphenylmethane. Mp 92°C (recrystallized from MeOH), 6%. This compound showed no mixed-mp depression.

Experiment 6. In this experiment, Ar gas was used in place of the SO_2 and O_2 of Exp. 3. *p*-Benzhydryltetraphenylmethane (68%), *p*-hydroxytetraphenylmethane (3%), and triphenylmethane (3%) were confirmed as has been described above.

Triphenylcarbinol. Mp 164°C, 5%. The IR spectrum of this compound coincided with that of a specimen synthesized by another method; this compound was confirmed by a mixed-mp determination.

Experiment 7. Compound V (2.9 mmol) was dissolved in 15 m*l* of benzene saturated with HCl; the solution was then allowed to stand at room temperature for half an hour. The benzene was distilled by reduced

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[12] S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **75**, 5504 (1953).

[13] M. Gomberg and L. H. Cone, *Ber.*, **37**, 2034 (1904).

[14] M. Gomberg and L. H. Cone, *ibid.*, **37**, 3538 (1904).

[15] M. Gomberg, *ibid.*, **36**, 376 (1903).

pressure, and 25 m*l* of ether was added to this residue. *p*-Benzhydryltetraphenylmethane (82%) was confirmed as has been described above.

Measurement of the UV and NMR Spectra. The dissolved oxygen in liquid SO_2 was eliminated by the following method. The dehydrated and distilled liquid SO_2 was frozen by liquid N_2 and evacuated at about 10^{-3} mmHg. Subsequently, this solvent was melted at room temperature by introducing Ar gas. This operation was repeated six times. This liquid SO_2 was used in the measurement of the UV and NMR spectra at room temperature.