

A Stopped-Flow/Rapid-Quenching Study of the Reaction of 1,1-Diphenylethylene and Sulfuric Acid*

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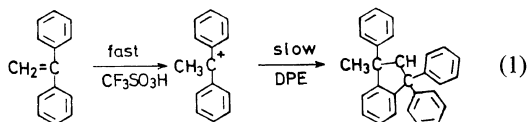
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ABSTRACT: The reaction of 1,1-diphenylethylene with sulfuric acid was studied at 30°C in dichloroethane by stopped-flow/rapid-scan spectroscopy coupled with the rapid-quenching technique. Rapid-scan spectra showed the formation and decay of two species absorbing at 435 and 465 nm during a period of less than one second. These species were detected only when sulfuric acid was 100% or more. The 435-nm species was the monomeric cation formed by protonation, and the 465-nm species was conceivably a charge-transfer complex of diphenylethylene and SO₃. The latter species eventually gave cyclic sulfones.

KEY WORDS Diphenylethylene / Sulfuric Acid / Cationic Polymerization / Stopped-Flow Technique / Rapid-Scan Spectroscopy /

In a previous article, we described the stopped-flow/rapid-quenching study of the reaction of 1,1-diphenylethylene (DPE) and CF₃SO₃H.¹ The reaction was fairly straightforward and the very fast protonation was followed by the slower formation of the cyclic dimer:



In contrast, the reaction of diphenylethylene with other cationic initiators appears much more complex. For example, Masure *et al.*² observed three successive stages of initiation (formation of the carbocation) in the reaction with AlCl₃. Having completed the stopped-flow/rapid-quenching study of the CF₃SO₃H-catalyzed dimerization, we next chose to examine the reaction of diphenylethylene with sulfuric acid. The H₂SO₄-initiation of vinyl monomers has been extensively studied, and the present study is expected to help elucidate the initiation mechanism by sulfuric acid. It also appeared advisable to study this system prior to working on the more complex system initiated by

Friedel-Crafts catalysts.

EXPERIMENTAL

Materials

The purifications of diphenylethylene and dichloroethane are described in the accompanying paper.¹ The "100%" sulfuric acid was prepared by mixing calculated amounts of commercial concentrated sulfuric acid (95%) and 30% fuming sulfuric acid.³ Sulfuric acids other than 100% were prepared similarly. These mixtures were added to dry dichloroethane and allowed to stand at room temperature for 2—3 days or one week and the organic supernatant was used as the initiator solution. The concentration of the H₂SO₄ moiety in dichloroethane was determined by titration with thymol blue as indicator. The original initiator solution was diluted with dry dichloroethane when necessary.

Reaction Procedure

The reaction was followed by a stopped-flow/rapid-scan spectrophotometer (Union Giken Co., Model RA 1300). The experimental procedure was described before.⁴

Diphenylethylene-H₂SO₄ Adduct

Under conditions of vigorous shaking, ten ml of a

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dichloroethane solution of diphenylethylene were injected to 50 ml of a dichloroethane solution of 106% sulfuric acid in 1–2 s under dry nitrogen. The final concentrations were 56 mM for diphenylethylene and 24 mM for sulfuric acid. The reaction was quenched after 20 min by adding 20 ml of 0.5 M CH_3ONa in CH_3OH . The resulting mixture was washed with water, dried over CaCl_2 and the solvent was stripped off. The residue was recrystallized from methanol to give colorless plates; mp 154–155°C, yield 34%.

RESULTS AND DISCUSSION

Rapid-Scan Spectra and Influence of Percentage of Sulfuric Acid on the Reaction

When 8.8×10^{-5} M of diphenylethylene was mixed with excess sulfuric acid (15.6 mM) in dry dichloroethane ($[\text{H}_2\text{O}] = 2.1$ mM), complex rapid-scan spectra shown in Figure 1 could be observed. The spectra were composed of two independent peaks with λ_{max} at 435 and 465 nm. The 465-nm peak appeared at an early stage of the reaction (e.g., 20 ms). Two peaks could be seen within 40–60 ms of the reaction period, but these spectra consisted mainly of the 435-nm peak at 100–300 ms. A new peak at 600 nm appeared at a later stage. The species with $\lambda_{\text{max}} = 465$ nm was more sensitive to the water concentration than the other species, and its formation depended very much on the preparation of the sulfuric acid. Therefore, sulfuric acid of different percentages was intentionally prepared and the effectiveness of the sulfuric acids as initiator was examined.

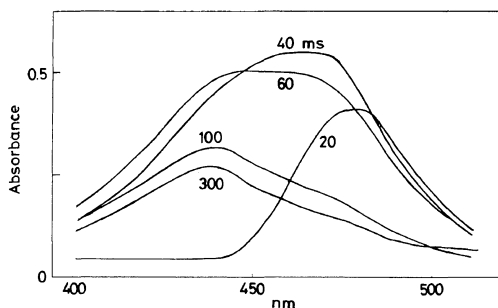
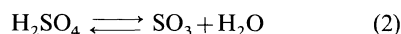


Figure 1. Rapid scan spectra at different reaction times: 30°C; solvent, dichloroethane; DPE, 8.8×10^{-5} M; 106% sulfuric acid, 16 mM; H_2O , 2.1 mM.

95% and 98% Sulfuric Acids as Initiator. The sulfuric acid in these percentages was not sufficiently soluble in dichloroethane (at most 2 mM) and were ineffective as initiator. The peaks at 435 and 465 nm were very small in rapid-scan spectra or did not appear at all. These sulfuric acids are commercial 95% sulfuric acid itself and a mixture of the necessary amounts of 95% sulfuric acid and fuming (30% excess) sulfuric acid. However, the exact percentage of sulfuric acid in dichloroethane is not known since the percentage of H_2SO_4 may change during its dissolution in dry dichloroethane due to the following equilibrium.



Nevertheless, the present observation suggests that extra water readily suppress the fast reaction of sulfuric acid and diphenylethylene.

100% Sulfuric Acid as Initiator. The effectiveness of 100% sulfuric acid as an initiator was found to depend on the period of dissolution of the sulfuric acid in dry dichloroethane. In one series of experiments, 100% sulfuric acid with a dissolution period of 2–3 days was used as the initiator:

$$[\text{H}_2\text{SO}_4] = 5.4 \times 10^{-3} \text{ M}, [\text{DPE}] = 4.4 \times 10^{-4} \text{ M}.$$

Only the 465-nm peak appeared immediately after mixing (20–40 ms), but the 435-nm peak became predominant 150–200 ms later. When 1 mM of H_2O was added to the monomer solution, only the 435-nm peak was seen with less absorbance. On the other hand, when 100% sulfuric acid with a dissolution period of one week was used

$$([\text{H}_2\text{SO}_4] = 1.94 \times 10^{-2} \text{ M}, [\text{DPE}] = 1.21 \times 10^{-4} \text{ M}),$$

only the 435-nm peak appeared and its intensity reached a maximum in 100–150 ms.

106% Sulfuric Acid as Initiator. Similar to the above experiments, the two types of 106% sulfuric acid in dichloroethane were prepared with different dissolution periods. When the dissolution period was 2–3 days, the rapid-scan spectra contained only one peak at 465 nm which reached its maximal values at 50 ms:

$$[\text{H}_2\text{SO}_4] = (7.95\text{--}11.0) \times 10^{-3} \text{ M},$$

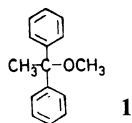
$$[\text{DPE}] = (2.15\text{--}51.8) \times 10^{-5} \text{ M}.$$

When the dissolution period was one week, the 465-nm peak was broader and the 435-nm peak could be seen as the shoulder; see Figure 1. The latter peak became more apparent at a later stage of the reaction.

Determination of Reaction Products

According to the preceding results, the formation of the unstable intermediates depends very much on the preparation of the dichloroethane solution of sulfuric acid. Two peaks were observed at 435 and 465 nm in the rapid-scan spectrum. The 435-nm peak is assigned to the monomer cation as discussed in detail in a preceding paper.¹ On the other hand, the 465-nm peak was observed only when the percentage of sulfuric acid was 100 or more, and this peak was shorter-lived and more sensitive to water than the monomer cation. Thus, we attempted to characterize this species by a rapid-quenching experiment.

The initiator used was 106% sulfuric acid with a dissolution period of 2–3 days, since it produced only a 465-nm peak. After a given reaction period, the reaction mixture was quenched, washed with water, and subjected to liquid chromatography. Three major peaks appeared, depending on the reaction condition. The monomer peak appeared at a retention time of 11 min under standard chromatographic conditions, when the reaction period was short (<1 s). With longer reaction periods, the monomer peak disappeared completely, as seen from the liquid chromatogram of the quenched mixture in Figure 2. The absence of the methoxy-terminated product of the monomer cation **1** was confirmed by NMR spectroscopy.



This is consistent with the fact that the 435-nm peak was not observed in the rapid-scan spectrum under these particular reaction conditions. Broad peaks appearing at 5–7 min in liquid chromatography are attributed to unidentified reaction products formed in the absence of monomer.* The two products eluting at 8 min 30 s and 9 min should thus be associated with the 465-nm peak. It must be noted that these products were obtained

* Fifty ml of a dichloromethane solution of 98% sulfuric acid (80 mM) was thoroughly mixed with 20 ml of 1 M CH₃ONa in methanol, washed with water and dried. The resulting mixture gave rise to several broad peaks at 5–10 min under the standard condition of liquid chromatography. Its NMR spectrum possessed triplets at 3.7 and 4.5 ppm and complex peaks at 0–2 ppm.

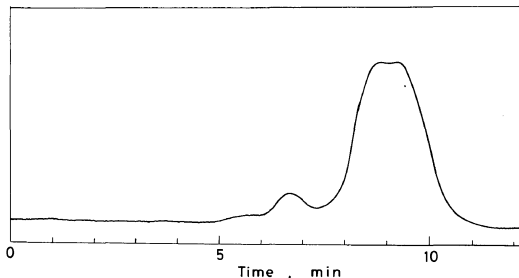
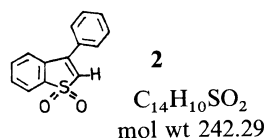


Figure 2. Liquid chromatogram of the quenched mixture. Reaction condition: temp, 30°C; solvent, dichloroethane; DPE, 0.58 mM; 106% sulfuric acid, 27 mM; quenched by 60 mM CH₃ONa in CH₃OH. Chromatographic condition: instrument, Hitachi HLC 635; Hitachi gel 3019; 8φ × 500; methanol/dichloroethane = 4; 4 ml min⁻¹; UV detector (250 nm).

irrespective of whether quenching was conducted during the time scale of rapid-scan spectroscopy (*i.e.*, the reaction period of 50–200 ms) or the quenching time was much longer (10–60 min) than the lifetime of the 465-nm peak. This indicates that the product was not derived directly from the quenching of the unstable intermediate.

When the initial ratio of H₂SO₄ to the monomer was less than 10, the 8.5-min peak was predominant. This fraction was collected after recycling, removal of solvent *in vacuo* and recrystallization of the resulting solid from methanol to give colorless plates, mp 154–155°C. The same compound can be synthesized on a larger scale as described in the EXPERIMENTAL. The analytical data of this compound are as follows: mass spectrum (70 eV) *m/e* 241 (P⁺); IR (KBr) 3060 (ν_{C-H}), 1265, 1145 cm⁻¹ (ν_{SO₂}); molecular weight (vapor pressure osmometry), 234. *Anal.* Calcd for C₁₄H₁₀SO₂: C, 69.40%; H, 4.17%. Found: C, 69.25%; H, 4.12%. An ¹H NMR spectrum of this compound is shown in Figure 3a. There is a multiplet peak at 7.4–7.9 ppm (9H) attributable to the aromatic protons and a singlet at 6.6 ppm (1H). These data are consistent with 3-phenylbenzo[2,3-*b*]thiophene-1,1-dioxide:



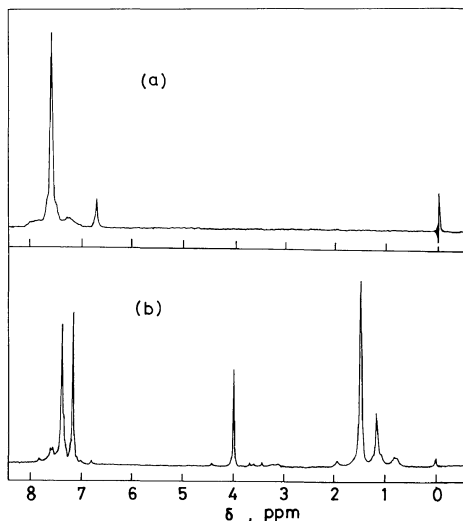
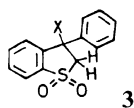


Figure 3. ^1H NMR spectra of the quenched product in CDCl_3 : a, component eluting at 8 min 30 s; b, run 5 in Table I.

When the $[\text{H}_2\text{SO}_4]/[\text{DPE}]$ ratio was larger than 10, the 9-min peak was commonly observed in liquid chromatograms. This fraction was separated and the solvent removed to leave a trace amount of white solid. An NMR spectrum was obtained without further purification. The spectrum is rather complex as shown in Figure 3b, since the sample contains unidentified quenching products formed in the absence of the monomer. The NMR peaks of Figure 3b at 0–2 ppm are very similar to those of the sample obtained in the absence of monomer. The sharp singlet (6.6 ppm) observed in Figure 3a is lacking. Instead, a sharp singlet is found at 4.0 ppm. This is assigned to the methylene proton adjacent to phenyl sulfone.* The relative area of this peak and the phenyl proton peak (7.0–7.5 ppm, the chloroform peak at 7.25 ppm excluded) is approximately 1:4.5. These data strongly suggest that the products have the structure of **3**. In this structure, X is probably the sulfate moiety, though this could not be confirmed.



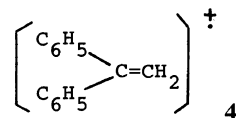
* $\delta = 4.3$ ppm is given for the α -methylene proton of *p*-hexadecylsulfonylaniline⁵

Table I summarizes the relation of the product ratio (**2** vs. **3**) with the reaction condition. Under the condition of $[\text{H}_2\text{SO}_4]/[\text{DPE}] \geq 10$ (entry 1–3), the ratio of **3** increased with the reaction time. The formation of **3** is favored when $[\text{H}_2\text{SO}_4]/[\text{DPE}]$ is large (compare entry 2, 4, and 6). These data suggest that **3** is formed from **2** by the action of sulfuric acid.

Reaction Scheme

The reaction of diphenylethylene with sulfuric acid is intrinsically more complex than that with $\text{CF}_3\text{SO}_3\text{H}$. The rapid-scan spectrum obtained immediately after the mixing of diphenylethylene and sulfuric acid usually gives two absorption maxima. The one at 435 nm may certainly be assigned to the monomer cation derived from simple protonation. This process was studied in detail in the previous publication¹ with $\text{CF}_3\text{SO}_3\text{H}$ as initiator. The assignment of the 465-nm species is less unambiguous. This species is formed when the concentration of sulfuric acid is 100% or more, and is more short-lived. These sulfuric acids should contain the SO_3 species. In fact, the 465-nm peak appeared when gaseous SO_3 was bubbled into a dichloroethane solution of DPE in a separate experiment.⁸ Under the reaction conditions where only the 465-nm peak was observed in the rapid-scan spectrum, the major quenching products were the 1:1 adduct of diphenylethylene and H_2SO_4 or its elimination product (**2** and **3**).

Some years ago, Fleischfresser *et al.* studied the electron transfer from diphenylethylene to SbCl_5 and found the formation of an unstable intermediate absorbing at 465 nm.⁶ They assumed this species to be a charge-transfer complex of diphenylethylene and SbCl_5 . Hayashi and coworkers recently studied primary ionic species of diphenylethylene produced by high-energy radiation and concluded that monomeric radical cation **4** absorb at 395 and 550 nm.⁷ These results suggests that the 465-nm species formed from diphenylethylene and SO_3 is a charge-transfer complex.



The reaction of diphenylethylene and sulfuric acid may now be summarized as in Scheme I.

The course of the formation of the cyclic sulfones

Reaction of Diphenylethylene and Sulfuric Acid

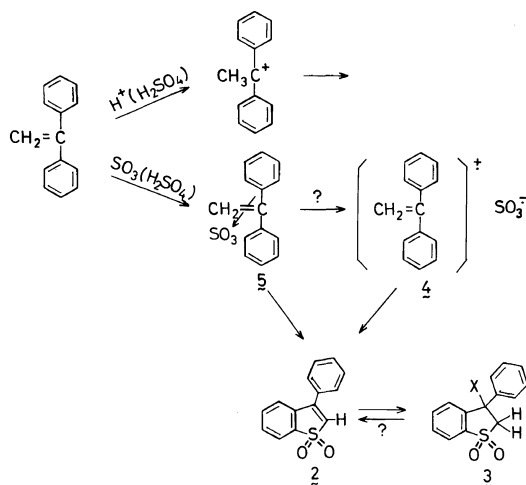
Table I. Quenching experiment

No.	DPE	H ₂ SO ₄ ^a	[H ₂ SO ₄]/[DPE]	Reaction time	Conversion ^b	Approximate product distribution ^c /%	
	mM	mM				%	2
1	0.45	21	47	0.05 s	20—30	100	0
2	0.58	23	40	20 min	100	63	37
3	0.58	27	47	60 min	100	50	50
4	8.7	13	1.5	15 min	80—90	100	0
5	37	56	1.5	90 min	80—90	100	0
6	4.8	27	5.6	16 min	100	92	8

^a 106% Sulfuric acid.

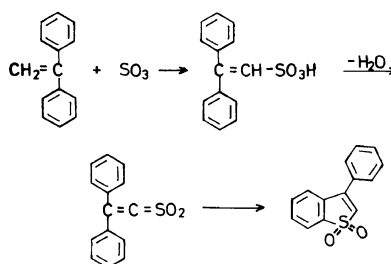
^b Determined from liquid chromatograms of the quenched product.

^c Determined by the relative height of peaks at 8 min 30 s (2) and at 9 min (3) in liquid chromatograms. The extinction coefficient of these compounds at 254 nm was assumed to be close.



Scheme I

cyclization.* The cyclization process may in fact be the same in both schemes. The observation of the charge-transfer band at 465 nm indicates a strong interaction of diphenylethylene and SO₃, even in Scheme II.



Scheme II

from charge-transfer complex 5 is not confirmed. In the reaction of diphenylethylene and SbCl₅,⁶ the initially-formed charge-transfer complex is supposedly transformed into a radical pair of DPE⁺ and SbCl₅⁻ which eventually gives the dimer dication of diphenylethylene. Sulfone 2 may thus be formed directly from 5 or *via* radical pair 4. The latter pathway remains a possibility, though the radical cation was not observed spectrally. Sulfone 3 may be formed by the addition of H₂O or H₂SO₄ to 2.

An alternative mechanism for the sulfone formation involves the insertion of SO₃ onto the methylene C—H bond, followed by dehydration and

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* This mechanism was suggested to us by Prof. A. Senning of University of Aarhus during his visit to Kyushu University.

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