Stopped-Flow/Rapid-Quenching Study of the Reaction of 1,1-Diphenylethylene and CF₃SO₃H*

Kunihide TAKARABE and Toyoki KUNITAKE**

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan.

(Received September 29, 1979)

ABSTRACT: The reaction of 1,1-diphenylethylene (DPE) and CF_3SO_3H was studied in dichloroethane at 30°C by stopped-flow/rapid-scan spectroscopy. The formation of the monomer cation was a fairly clean second-order process with the rate constant of 3400 $M^{-1} s^{-1}$. The absence of the dimer cation in the early stage of the reaction was confirmed by rapid quenching (CH₃ONa in CH₃OH) of the reaction mixture. The monomer cation was slowly converted into a cyclic dimer product (indanic dimer) in a few hours. Linear dimers could not be detected even after prolonged reaction. These results are in sharp contrast with those of Evans and coworkers who observed the exclusive formation of the linear dimer (in benzene with a variety of acidic catalysts). The "autosolvated" dimer cation proposed by Sigwalt and coworkers could not be observed in our experiments.

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

The acid-catalyzed dimerization of 1,1-diphenylethylene has been studied as a model reaction for the cationic polymerization of vinyl monomers. Almost 30 years ago, Evans,¹ and Gold and Tye² observed a new absorption peak in the visible spectrum when diphenylethylene was dissolved in concentrated sulfuric acid, and they ascribed this peak to the diphenylethyl cation. Subsequently, Evans and his coworkers carried out extensive investigation on the dimerization process of diphenylethylene using a variety of cationic initiators.³⁻⁸

More recently, Szwarc and coworkers studied the reaction of diphenylethylene with strong electron acceptors such as $SbCl_5^9$ and tetranitromethane.¹⁰ Sigwalt and coworkers¹¹⁻¹³ examined the reaction of diphenylethylene with metal halides (TiCl₄ and AlCl₃) and CF₃SO₃H at low temperatures and discussed the initiation mechanism in detail. A similar study with BF₃ was reported by Bywater and Worsfold.¹⁴

The stopped-flow/rapid-scan spectrophotometry coupled with the rapid-quenching technique has distinct advantages over previous techniques for following the fast reaction of short-lived intermediates. We have already applied this technique to the cationic polymerization of styrene and its derivatives with the CF_3SO_3H initiator and determined the rate constants of the elementary steps.^{15–18} Similar studies were published on substituted styrenes by Sawamoto and Higashimura.^{19,20}

In this paper, we report on the dimerization process of 1,1-diphenylethylene by CF_3SO_3H as studied by the stopped-flow/rapid-quenching technique.

EXPERIMENTAL

Materials

Commercial 1,1-diphenylethylene (Tokyo Kasei Kogyo Co., purity >99%) was fractionally distilled, bp 107—108°C (3 mmHg) [lit.²¹ bp 119.6°C (5 mmHg)] and the purity was confirmed by gas chromatography and UV spectroscopy. Dichloroethane was washed with dilute aqueous

^{*} Contribution No. 550 from Department of Organic Synthesis.

^{**} Correspondence should be addressed to this author.

sodium hydroxide and water, dried over $CaCl_2$, distilled from P_2O_5 , and stored over Molecular Sieve 4Å. Trifluoromethanesulfonic acid (Wako Pure Chemical Co., special grade) was used without further purification. Quenching solutions were prepared by dissolving calculated amounts of sodium metal in methanol.

Procedures

The reaction was followed by a stoppedflow/rapid-scan spectrophotometer (Union Giken Co., Model RA 1300), in the same procedure as described before.¹⁶ The quenching procedure has been also explained.¹⁶

RESULTS AND DISCUSSION

Reaction of 1,1-Diphenylethylene with Excess CF_3SO_3H

The spectral change in the reaction of diphenylethylene (DPE) and CF₃SO₃H was first studied in the presence of excess CF₃SO₃H. An absorption peak appeared at 435 nm immediately on mixing the two reagents. Olah *et al.*²² reported that the methyldiphenylcarbonium ion I possessed the absorption maximum at 422 nm in FSO₃H–SbF₅ at -60° C. Fleischfresser *et al.*⁹ produced the same cation ($\lambda_{max} = 435$ nm) from 1,1-diphenylethanol and SbCl₅ (CH₂Cl₂, -80° C). The 435-nm species may thus be assigned as I, which is produced by the simple protonation of diphenylethylene. The absorbance becomes maximal in 100–150 ms and then decreases gradually within a period of 2–3 seconds. Another absorption peak appeared at ca. 600 nm only 1—2 seconds after the mixing, and the peak height leveled off in 10 s. The reaction appears to be quite clean during the initial one second. Figure 1 shows the time course of these spectral changes.



This spectral result is in contrast with those observed by Sauvet *et al.*¹¹ These authors noted the formation of (at least) three cationic species in the UV spectra, although NMR spectra indicated that monomeric cation I was the major species. According to them, a main peak at 435 nm is attributable to both the monomeric (I) and dimeric (II) cations, whereas a 520 nm absorption can be assigned to the monomer-solvated form of I and II. Their third absorption at 456 nm was considered to be due to a dimeric cation stabilized through the β -phenyl ring interaction.

The UV spectral observation is made simple in the present study probably because the reaction time is very short and the monomer concentration is low. However, we cannot decide from the spectral data alone whether the species absorbing at 435 nm is monomeric (I) or dimeric (II) cation, or both. This question can be resolved by the rapid-quenching experiment.

Equal amounts (20 ml each) of the dichloroethane solutions of monomer $(1.73 \times 10^{-3} \text{ M})$ and



Figure 1. Time course of the absorbance change: temp, 30° C; solvent, dichloroethane; DPE, 0.45 mM; CF₃SO₃H, 19 mM.

Polymer J., Vol. 12, No. 4, 1980

 $CF_3SO_3H (3.48 \times 10^{-2} \text{ M})$ were mixed at 30°C in the rapid-quenching apparatus and 20 ml of a quenching solution $(8.70 \times 10^{-2} \text{ M CH}_3\text{ONa in CH}_3\text{OH})$ was introduced 100 ms later. This procedure was repeated 15 times and the combined reaction mixtures were washed with water, dried over CaCl₂ and the solvent removed. The oily residue was subjected to high-pressure liquid chromatography: column, Hitachi gel 3019, $8\phi \times 500$; solvent, methanoldichloroethane (4:1); flow rate, 3 ml min^{-1} . Among the three major peaks observed, the first, broad peak at 6-10 min, was attributed to the unidentified reaction product of CF₃SO₃H and dichloroethane (and the quenching solution), since the same peak was found in the absence of monomer. The third peak at 15 min was identified to be the unreacted monomer. The fractions corresponding to the second peak (12.5 min) was collected to give colorless needles, mp 32-33°C, after solvent removal. This compound was shown to be 1-methoxy-1,1diphenylethane III by NMR spectroscopy; NMR $(CDCl_3) \delta 1.75 (s, 3, CH_3), 3.05 (s, 3, CH_3O) and 7.2$ ppm (m, 10, aromatic).



These results clearly show that simple protonation is the only detectable reaction occurring at the early stage (<1 s) in the presence of excess CF₃SO₃H.

$$CF_{3}SO_{3}H + CH_{2}= C \xrightarrow{k} CH_{3}C^{+} CF_{3}SO_{3}^{-} (1)$$

The relative amounts of monomer and the quenched product III in the quenched mixture were readily determined by NMR or UV spectroscopy. In the NMR spectrum, the relative peak area of the singlet methylene proton of DPE and the methoxy proton of III was used. Table I gives some examples of this reaction. Undoubtedly, the reaction is very fast, and appears to have reached equilibria of the monomer and monomer cation in 100 ms, as the monomer consumption is always *ca.* 80%. The extent of the reaction was compared with the absorbance at 435 nm of the molar extinction coefficient of the

cation was estimated to be $31,000 \pm 2,000 \text{ M}^{-1}$ cm⁻¹. This value is close to that given by Fleischfresser *et al.* (33,000 M⁻¹ cm⁻¹),⁹ but is smaller than the one reported by Bertoli and Plesch (39,000 M⁻¹ cm⁻¹),²³ by Sauvet *et al.* (36,000 M⁻¹ cm⁻¹).²²

Subsequently the kinetics of protonation were studied by stopped-flow spectroscopy. The initial rate of the carbocation formation was first-order with respect to monomer and CF_3SO_3H as shown in Figures 2 and 3, respectively.

$$v_{i} = \left(\frac{d[P^{+}]}{dt}\right)_{t=0} = k[DPE][CF_{3}SO_{3}H]$$
(2)

A second-order rate constant of $3,400 \pm 400 \text{ M}^{-1}$ s⁻¹ was obtained. The apparent rate constants were insensitive to the water concentration when it was kept below *ca.* 3 mM.

The lifetime of the monomeric cation is 1-2 min under the conditions of this study. Concurrent with the decrease in the 435-nm absorption, a new absorption appeared at 600 nm as shown in Figure 1. The intensity of this peak becomes maximal in 10 s, and remains constant. This reaction mixture contains a third component as shown by a liquid chromatogram: retention time, ca. 17 min under standard conditions. This component was shown to be an indanic dimer IV as is discussed below. Table II shows the variation in the product distribution of the quenched reaction mixture. In the early stage of the reaction, only the monomeric cation I is formed, since III is the only product of quenching. However, the content of III is decreased very much and a considerable amount of IV is formed instead, when the reaction mixture is allowed to stand for 23 h. This suggests that the indanic dimer is slowly formed from the monomeric cation I. The absorption peak at 600 nm seems to be related to the dimer formation.

Reaction of CF₃SO₃H with Excess Diphenylethylene

In the presence of excess DPE (*ca.* 1 M), the reaction could not be followed by UV spectroscopy due to the large absorbance of the monomeric cation. Therefore, the product characterization was performed by liquid chromatography.

A 10 ml solution of diphenylethylene in dry dichloroethane (0.54 M) and 10 ml of 0.014 M CF_3SO_3H in the same solvent were rapidly mixed at room temperature (16°C). The reaction mixture turned from orange to green and then to dark green. It was

K. TAKARABE and T. KUNITAKE

DPE	CF ₃ SO ₃ H	Methoxylated product, III ^b	Monomer consumption ^b	ε_{max} of cation at 435 nm	
mM	mM	mM	%		
0.072	23	0.056	78	30,000	
0.091	19	0.072	79	33,000	
0.214	23	0.176	82	29,000	

Table I. Protonation reaction of diphenylethylene^a

^a Condition: reaction temp, 30°C, solvent, dichloroethane; reaction time, 100 ms.

^b Determined from liquid chromatograms of the quenched product.



Figure 2. Dependence of the initial rate of protonation on the DPE concentration: temp, 30° C; solvent, dichloroethane; CF₃SO₃H, 23 mM.



Figure 3. Dependence of the initial rate of protonation on the CF_3SO_3H concentration: temp, 30°C; dichloroethane; DPE, 0.143 mM.

quenched with CH₃ONa in CH₃OH 24h later and the mixture was washed and dried over CaCl₂. Three components were detected in a liquid chromatogram of the product. The first and second components were identified to be **III** and DPE by comparison with standard samples. The third component was separated by liquid chromatography and recrystallized from dichloroethane, mp 145—147°C (lit.²³ 143°C). NMR, IR spectra, and elemental analysis results were consistent with the so-called indanic dimer **IV**.²⁴



The product distribution was subsequently determined under several conditions by liquid chromatography, and the results are summarized in Table III. It is seen that the indanic dimer becomes the predominant product after sufficient reaction time. Other products such as linear dimers were not formed.

The Course of Reaction of Diphenylethylene with CF₃SO₃H

The predominant course of reaction of diphenylethylene with CF_3SO_3H can be summarized as in Scheme I on the basis of the present study.

The initial protonation process is very fast and the second-order rate constant determined from the initial rate is 3400 M^{-1} s⁻¹ at 30°C in dichloroethane. However, this reaction is not completed even if an excess of CF₃SO₃H is present. As shown in Table II, 80% of diphenylethylene was protonated in one second, but 10% of the diphenylethylene remained after 23 h under almost the same conditions.

Reaction of Diphenylethylene and CF₃SO₃H

DPE	CF ₃ SO ₃ H	Reaction temp	Prostion time	Product		
mM	mM	°C	Reaction time			
0.45 0.45	19 25	30 26	1 s 23 h	20% DPE, 80% III 10% DPE, 42% III, 48% IV		

Table II. Product distribution^a

^a Reaction conditions: temp, 30°C, solvent, dichloroethane, [DPE] \leq [CF₃SO₃H].

DEP	CF ₃ SO ₃ H	Reaction temp	- Reaction time -	Product distribution ^b /%			Color of the
mM	mM	°C		DPE	III	IV	reaction mixture
169	25	30	50 ms	95	1—2	2—3	Yellow
34	25	30	50 ms	93	7	0	Yellow
320	22	Room temp (16)	1.5 h	13	12	75	Yellow→Wine-red
270	7.0	Room temp (16)	24 h	8	12	80	Yellow→Wine-red
28	26	Room temp (16)	24 h	15	11	74	Yellow→Green

Table III. Product distribution^a

^a Reaction conditions: solvent, dichloroethane; [DPE] > [CF₃SO₃H].

^b Determined by liquid chromatography.



Apparently, the monomer and the monomeric cation become equilibrated in 0.1—1 s (see Figure 1). Thus, the apparent rate constant of protonation k_{app} is actually given by

$$k_{app} = k_1 [CF_3 SO_3 H] [DPE] - k_{-1} [I]$$
 (3)

and the above-mentioned second-order rate constant of protonation is the lower limit of the rate constant of the forward reaction in the protonation process. The k_2 process can be neglected during the early stage of the reaction. The monomer cation may exist in the form of a free ion or an ion pair. However, these species, if present, cannot be differentiated spectroscopically, since it has been shown that the

Polymer J., Vol. 12, No. 4, 1980

polystyryl cation gives a single λ_{max} value (340 nm) without regard to whether or not it is a free-ion or a paired ion.^{17,18}

We could not detect the methoxy-terminated product of the linear dimer cation **II** in the quenching experiment. The indanic dimer must be formed by the intramolecular electrophilic attack of dimer cation **II**. It seems that the equilibrium between the monomer cation and the dimer cation is overwhelmingly in favor of the former, and the dimer cation formed should rapidly revert to the monomer cation or cyclize to the indanic dimer.

The slowly-appearing absorption at 600 nm cannot be attributed to the dimer cation or to an intermediate leading to the indanic dimer.

Sauvet *et al.* reported the observation of a supplementary absorption at 456 nm in the presence of excess diphenylethylene relative to CF₃SO₃H, and assigned it to the "autosolvated" dimeric cation V.



However, this is not likely since the quenching product of linear dimers could not be found in our experiment. Bywater and Worsfold¹⁴ reported the formation of the triphenylmethyl cation from the indanic dimer in the system of DPE–BF₃·H₂O–CH₂Cl₂. We suspect that the 600-nm-absorbing species is a highly delocalized carbocation structurally related to the indanic dimer. The methoxide quenching may convert this species to the indanic dimer.

In earlier days, Evans and his coworkers made extensive kinetic investigations on the linear dimerization of diphenylethylene.

$$CH_2 = C \longrightarrow CH_3 C CH = C \qquad (4)$$

The catalysts used by these authors include trichloroacetic acid,³ iodine,⁴ SnCl₄-H₂O,⁵ SnCl₄-HCl,⁷ TiCl₄-HCl,⁸ and Sb₂Cl₆-HCl²⁵ and the solvent in most cases was benzene. The reaction slowly proceeded to completion, for 10-100 h at 30-40°C. The linear dimer was very slowly (in 100-1000 h) converted to the indanic dimer by SnCl₄²⁶ or by Sb₂Cl₆-HCl.²⁵ These results are quite different from our data and those of the Sigwalt group, in that the indanic (cyclized) dimer is the only dimeric product. In fact, the equilibrium between the monomeric and dimeric cation was shown to shift far to the monomeric side in both this study and that by Sauvet et al.¹¹ Evans and his coworkers followed the very slow reaction of diphenylethylene by dilatometry in the presence of rather large amounts of catalyst. Therefore, they must have been pursuing the secondary reaction characterized by volume decrease. These slow processes cannot be directly related to our spectroscopic/quenching data.

Recently, Higashimura and Nishi reported the simultaneous formation of the linear and cyclic dimers in the acid-catalyzed dimerization of α -methylstyrene.²⁷ The formation of the cyclic dimer increased with increasing polarity of the solvent. These results suggest that the discrepancy between our results and those of Evans also come from the difference in solvent: dichloroethane *vs.* benzene.

The influence of the solvent and initiator on the dimerization process of diphenylethylene will be treated in a future publication.

REFERENCES

- 1. A. G. Evans, J. Appl. Chem., 1, 240 (1951).
- 2. V. Gold and F. L. Tye, J. Chem. Soc., 2172 (1952).
- A. G. Evans, N. Jones and J. H. Thomas, J. Chem. Soc., 1824 (1955).
- A. G. Evans, P. M. S. Jones and J. H. Thomas, J. Chem. Soc., 2095 (1957).
- 5. A. G. Evans and J. Lewis, J. Chem. Soc., 2975 (1957).
- A. G. Evans, P. M. S. Jones and J. H. Thomas, J. Chem. Soc., 4563 (1958).
- 7. A. G. Evans and J. Lewis, J. Chem. Soc., 1946 (1959).
- A. G. Evans and E. D. Owen, J. Chem. Soc., 4123 (1959).
- B. E. Fleischfresser, W. J. Cheng, J. M. Pearson and M. Szwarc, J. Am. Chem. Soc., 90, 2172 (1968).
- S. Penczek, J. Jagur-Grodzinski, and M. Szwarc, J. Am. Chem. Soc., 90, 2174 (1968).
- G. Sauvet, J. P. Vairon, and P. Sigwalt, J. Polym. Sci., Polym. Symp., No. 52, 173 (1975).
- G. Sauvet, J. P. Varion, and P. Sigwalt, J. Polym. Sci., Polym. Chem. Ed., 16, 3047 (1978).
- M. Masure, G. Sauvet, and P. Sigwalt, J. Polym. Sci., Polym. Chem. Ed., 16, 3065 (1978).
- S. Bywater and D. J. Worsfold, *Can. J. Chem.*, 55, 85 (1977).
- T. Kunitake and K. Takarabe, J. Polym. Sci., Polym. Symp., No. 56, 33 (1976).
- T. Kunitake and K. Takarabe, *Polym. J.*, 10, 105 (1978).
- 17. K. Takarabe and T. Kunitake, *Macromolecules*, **12**, 1061 (1979).
- K. Takarabe and T. Kunitake, *Macromolecules*, **12**, 1067 (1979).
- M. Sawamoto and T. Higashimura, *Macromolecules*, 11, 328 (1978).
- M. Sawamoto and T. Higashimura, *Macromolecules*, 11, 501 (1978).
- 21. C. F. H. Allen, S. Converse, Org. Synth., I, 226 (1941).
- G. A. Olah, C. U. Pittman, R. Waack, and M. Doran, J. Am. Chem. Soc., 88, 1488 (1966).
- V. Bertoli and P. H. Plesch, Spectrochim. Acta, 25-A, 447 (1969).
- C. S. Schoepple and J. D. Ryan, J. Am. Chem. Soc., 52, 4021 (1930).
- 25. A. G. Evans and D. Price, J. Chem. Soc., 2982 (1959).
- A. G. Evans, E. A. James and E. D. Owen, J. Chem. Soc., 3532 (1961).
- 27. T. Higashimura and H. Nishi, J. Polym. Sci., Polym. Chem. Ed., 15, 9 (1977).