Addition–Elimination Reaction in the Trifluoroacetylation of **Electron-Rich Olefins**

Takeshi Moriguchi and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226, Japan

Toshikazu Takata

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Gakuen-cho, Sakai, Osaka 593, Japan

Received December 29, 1994[®]

Reactions of electron-rich olefins such as vinyl ether 1 and vinyl sulfide 2 with trifluoroacetic anhydride in carbon tetrachloride at room temperature proceeded by the formation of addition products 7 and 8, respectively, which were identified as stable intermediates by ^{1}H NMR and IR spectra, eventually giving the corresponding trifluoroacetylated olefins 5 and 6 as substitution products. These reactions were also observed in chloroform and dichloromethane in the absence of base, such as pyridine. These results supported the addition-elimination mechanism. The processes of the addition and elimination were confirmed by the ¹H NMR spectrum and kinetic study which led to the following results: The addition products 7 and 8 were formed through a stepwise *trans* addition, and the trifluoroacetylated olefins 5 and 6 were self-catalytically formed from the addition products 7 and 8 through Ei, E2, or E1, depending on the stability of the cationic intermediates 3 and 4.

Introduction

It has been reported that the reaction of nonfunctionalized olefins with acid chloride¹ or acid anhydride² gives the corresponding acylated olefins. The acylation of olefins proceeds essentially in an addition-elimination mechanism because it is confirmed that the corresponding adducts are always formed as stable intermediates and subsequently transformed to acylated olefins through acid-catalyzed¹ or spontaneous² elimination. On the other hand, the reactions of electron-rich olefins such as vinyl ether, vinyl sulfide, and ketene dithioacetal with trifluoro- or trichloroacetic anhydride or mixed acid anhydrides in the presence of pyridine proceeded by a mechanism like the Friedel-Crafts reaction without formation of the corresponding adducts, as reported by Hojo et al.³ Two mechanisms^{4,5} for these reactions have been proposed: One is the stepwise mechanism in which the initial addition of acyl cation to the vinyl group occurs to form a cationic intermediate 3, followed by rapid elimination of a proton from 3 in the case of vinyl ether 1, and the other is the single-step mechanism in which the addition of an acyl group and the elimination of a proton concertedly occurs without the formation of the cationic intermediate 4 in the case of vinyl sulfide 2, as shown in Scheme 1. The addition-elimination mecha-

* Abstract published in Advance ACS Abstracts, May 1, 1995.



nism has been absolutely excluded from the results of their kinetic study in terms of primary isotope effect.^{4,5}

However, we have recently found that the reaction of electron-rich olefins such as vinyl ether 1 and vinyl sulfide 2 with trifluoroacetic anhydride in the absence of amine base results in the initial formation of corresponding adducts 7 and 8, followed by the slow spontaneous elimination of trifluoroacetic acid to give trifluoroacetylated olefins 5 and 6. This paper discloses this trifluoroacetylation of electron-rich olefins with acid anhydride which undergoes an addition-elimination mechanism.

Experimental Section

Materials. Ethyl vinyl ether, isobutyl vinyl ether, isopropyl vinyl ether, tert-butyl vinyl ether, 2,3-dihydrofuran, 3,4dihydropyran, and phenyl vinyl sulfide were refluxed, distilled

^{*} To whom all correspondence should be addressed.

⁽¹⁾ McMahon, E. M.; Popper, J. N., Jr.; Utermohlen. W. P., Jr.; Hasek, R. H.; Harris, R. C.; Brant, J. H. J. Am. Chem. Soc. 1948, 70, 2971

⁽²⁾ Henne, A. L.; Tedder, J. M. J. Chem. Soc. 1953, 3628.

^{(3) (}a) Hojo, M.; Masuda, R.; Kamitori, Y. Tetrahedron Lett. 1976, 1009. (b) Hojo, M.; Masuda, R.; Kokuryo, Y.; Shioda, H. Chem. Lett. 1976, 499. (c) Hojo, M.; Masuda, R.; Okada, E. Synthesis 1986, 1013. (d) Hojo, M.; Masuda, R.; Sakaguchi, S. Synthesis **1986**, 1016. Hojo, M.; Masuda, R.; Okada, E. *Tetrahedron Lett.* **1986**, 27, 353. (e) Kamitori, Y.; Hojo, M.; Masuda, R.; Yashida, T.; Ohara, S.; Yamada, V.; Yashida, T.; Ohara, S.; Yamada, Y.; Yashida, T.; Ohara, S.; Yashida, T.; Ohara, S.; Yamada, Y.; Yashida, Yash (4) Hojo, M. Juli, J. Chem. 1988, 53, 519.
(4) Hojo, M. Yuki Gosei Kagaku Kyokaishi 1978, 36, 473.

⁽⁵⁾ Hojo, M.; Masuda, R.; Kamitori, Y.; Okada, E. J. Org. Chem. 1991, 56, 1976



over metallic sodium, and stored under nitrogen in a refrigerator. Trifluoroacetic anhydride was refluxed and distilled over phosphorus pentoxide. Carbon tetrachloride was distilled over calcium hydride.

Measurements. ¹H NMR spectra were recorded with a JEOL JNM EX-60 and EX-90 spectrometer, using tetramethylsilane (TMS) as an internal standard in CDCl₃ and CCl₄. FT-IR spectra were obtained with a JEOL JIR-5300 instrument. Distillation of the acylated olefins was conducted with a SHIBATA glass tube oven (Kugelrohr) GTO-250.

Molecular Orbital Calculation. All computations were done on the Apple Macintosch IIci equipped with a 21 MIPS coprocessor board with use of the SONY Tektronix CAChe system version 3.0.4. Geometries were first optimized with molecular mechanics using the CAChe MM2 program and then with MOPAC version 6.00 (QCPE No. 455)⁶ revised as version 6.10 for the CAChe system, using PM3 Hamiltonian. The calculations were carried out by the restricted Hartree–Fock (RHF) method. All calculations were done with full optimization of all geometrical variables (bond length, bond angle, and dihedral angle).

Reaction of Vinyl Ether 1 or Vinyl Sulfide 2 with (CF₃-CO)₂O. To a solution of vinyl ether 1 or vinyl sulfide 2 (5.0 mmol) in CCl₄ (10 mL) in an ice bath was added trifluoroacetic anhydride (5.5 mmol). The reaction mixture was kept at room temperature with stirring, and the reaction's progress was monitored by ¹H NMR. After completion of the reaction, the mixture was poured into water and neutralized with sodium bicarbonate. The CCl₄ layer was separated and washed with water three times. The water layer was extracted with *n*-hexane three times. The extracts were combined and evaporated to give a crude product, which was distilled by Kugelrohr distillation to yield a pure trifluoroacetylated olefin **5** or **6**. Poly(1) or -(2) was also obtained as a residue. The spectral data and boiling points of the trifluoroacetylated olefins **5** and **6** are as follows.

trans-4-Ethoxy-1,1,1-trifluoro-3-buten-2-one (5a): ¹H NMR (90 MHz, CDCl₃) δ 1.41 (t, J = 7.0 Hz, 3H), 4.07 (q, J = 7.3 Hz, 2H), 5.85, 7.90 (d, J = 12.4 Hz, 1H); IR (NaCl, cm⁻¹) 2994, 2948 (ν_{CH_3,CH_2}), 1711 (ν_{CF_3CO}), 1611, 1593 (ν_{C-C-O}); bp 65 °C/15 mmHg (Kugelrohr distillation, lit.^{3a} bp 51 °C/12 mmHg). Anal. Calcd for **5a** (C₆H₇O₂F₃): C, 42.87; H, 4.20. Found: C, 43.03; H, 4.17 (lit.^{3a} C, 43.09; H, 4.35).

trans-4-Isobutoxy-1,1,1-trifluoro-3-buten-2-one (5b): ¹H NMR (90 MHz, CDCl₃) δ 0.98 (d, J = 6.8 Hz, 6H), 2.07 (sep, J = 6.8 Hz, 1H), 3.85 (d, J = 6.4 Hz, 2H), 5.90, 7.99 (d, J = 12.3 Hz, 1H); IR (NaCl, cm⁻¹) 2969, 2882 (ν_{CH_3,CH_2}), 1711 (ν_{CF_3CO}), 1613, 1593 ($\nu_{C=C-O}$); bp 70 °C/15 mmHg (Kugelrohr distillation). Anal. Calcd for **5b** (C₈H₁₁O₂F₃): C, 48.98; H, 5.61. Found: C, 48.68; H, 5.52.

trans-4-Isopropoxy-1,1,1-trifluoro-3-buten-2-one (5c): ¹H NMR (90 MHz, CDCl₃) δ 1.35 (d, J = 6.2 Hz, 6H), 4.41 (sep, J = 6.1 Hz, 1H), 5.89, 7.88 (d, J = 12.2 Hz, 1H); IR (NaCl, cm⁻¹) 2988, 2943 (ν_{CH_3,CH_2}), 1711 (ν_{CF_3CO}), 1611, 1593 ($\nu_{C=C-O}$); bp 68 °C/15 mmHg (Kugelrohr distillation). Anal. Calcd for 5c (C₇H₉O₂F₃): C, 46.15; H, 4.95. Found: C, 45.97; H, 4.97.

trans-4-*tert*-Butoxy-1,1,1-trifluoro-3-buten-2-one (5d): ¹H NMR (90 MHz, CDCl₃) δ 1.43 (s, 9H), 5.95, 8.06 (d, J = 11.7 Hz, 1H); IR (NaCl, cm⁻¹) 2986 (ν_{CH_3}), 1707 (ν_{CF_3CO}), 1603 (ν_{C-C-O}); bp 65 °C/8 mmHg (Kugelrohr distillation). Anal. Calcd for 5d (C₈H₁₁O₂F₃): C, 48.98; H, 5.61. Found: C, 49.35; H, 5.54.

4-(Trifluoroacetyl)-2,3-dihydrofuran (5e): ¹H NMR (90 MHz, CDCl₃) δ 2.97 (t, J = 9.5 Hz, 2H), 4.69 (t, J = 9.9 Hz, 2H), 7.63 (m, 1H); IR (NaCl, cm⁻¹) 2986, 2915 (ν_{CH_2}), 1678 (ν_{CF_3CO}), 1655, 1595 (ν_{C-C-O}); bp 70 °C/15 mmHg (Kugelrohr distillation, lit.^{3d} bp 48.5 °C/10 Torr). Anal. Calcd for **5e** (C₆H₅O₂F₃): C, 43.37; H, 3.01. Found: C, 43.75; H, 3.02.

5-(Trifluoroacetyl)-3,4-dihydropyran (5f): ¹H NMR (90 MHz, CDCl₃) δ 1.63 (m, 2H), 2.34 (t, J = 12.1 Hz, 2H), 4.20 (t, J = 10.6 Hz, 2H), 7.82 (s, 1H); IR (NaCl, cm⁻¹) 2957, 2879 (ν_{CH_2}), 1686 (ν_{CF_3CO}), 1606 (ν_{C-C-O}); bp 75 °C/15 mmHg (Kugelrohr distillation, lit.^{3d} bp 64.6 °C/10.5 Torr). Anal. Calcd for **5f** (C₇H₇O₂F₃): C, 46.67; H, 3.89. Found: C, 46.35; H, 4.04.

4-Thiophenoxy-1,1,1-trifluoro-3-buten-2-one (**6a**): ¹H NMR (90 MHz, CDCl₃) δ 6.24, 8.28 (d, J = 15.3 Hz, 1H, *trans*), 6.63, 7.88 (d, J = 9.9 Hz, 1H, *cis*), 7.44 (s, 10H, Ph); Ir (NaCl, cm⁻¹) 3063 (ν_{Ph}), 1707 (ν_{CF_3CO}), 1553, 1541 (ν_{C-C-S}); bp 110 °C/2 mmHg (Kugelrohr distillation, mixture of *cis* and *trans*). Anal. Calcd for **6a** (C₁₀H₇OSF₃): C, 51.72; H, 3.53. Found: C, 51.22; H, 3.53. The product **6a** obtained by the distillation was a mixture of *cis* and *trans* isomers, which could not be separated.

Results and Discussion

Evidence for the Addition and Elimination Mechanism. The adducts 7 and 8 were confirmed as the initial products in the reaction of vinvl ether 1 or vinvl sulfide 2 with trifluoroacetic anhydride at room temperature by monitoring with ¹H NMR and IR. The most convincing evidence for the formation of the adducts can be seen in the reaction of ethyl vinyl ether 1a with trifluoroacetic anhydride, as shown in Figures 1 and 2. The ¹H NMR spectra in Figure 1 show that all signals of **1a** (t = 0 h) completely disappear, but instead, new signals appear after 1 h. The new signals are completely in agreement with those of the addition product 7a (Table 1). Especially, the methylene (H_b) and methyne (H_d) proton signals are characteristic of the proposed structure 7a. After 24 h, the ¹H NMR spectrum shows clean signals corresponding to trifluoroacetylated olefin 5a which involve typical *trans* olefinic signals at 5.6 (H_{σ}) and

^{(6) (}a) Stewart, J. J. P. J. Comput. Chem. **1980**, 10, 221. (b) Stewart, J. J. P. J. Comput. Chem. **1989**, 10, 209.



Figure 1. ¹H NMR spectral change of the reaction of ethyl vinyl ether 1a with trifluoroacetic anhydride in CCl₄ at room temperature.

7.8 (H_h) ppm. In addition, a highly acidic proton signal at 10.8 ppm can be assigned to trifluoroacetic acid which should be an elimination product from **7a**. The IR spectral change (Figure 2) of this reaction was in good accordance with the ¹H NMR spectral change, where carbonyl absorption based on trifluoroacetic anhydride (1878, 1811 cm⁻¹) in the starting mixture was initially changed to 1875 cm⁻¹ (excess of acid anhydride) and 1792 cm⁻¹ (ester and ketone carbonyls) after 1 h and finally to 1784 cm⁻¹ (free acid) and 1716 cm⁻¹ (unsaturated ketone) after 24 h. Thus, these results unambiguously suggest that the addition product **7a** could be formed as a stable primary product in the reaction of **1a** with trifluoroacetic anhydride.

Several vinyl ethers 1 including cyclic vinyl ethers 1e and 1f and phenyl vinyl sulfide 2a similarly underwent



Figure 2. IR spectral change of the reaction of ethyl vinyl ether 1a with trifluoroacetic anhydride in CCl_4 at room temperature.

the reaction with trifluoroacetic anhydride to quantitatively give the corresponding adducts **7** and **8** which were eventually transformed to the acetylated olefins **5** and **6**, respectively (Table 1). Unfortunately, in the case of *tert*-butyl vinyl ether **1d**, formation of the adduct **7d** could not be confirmed. However, the final acetylated olefin **5d** was selectively obtained in 79% isolated yield. Characteristic ¹H NMR chemical shifts of **7** and **8** are listed in Table 1 along with IR carbonyl absorptions ($\nu_{C=0}$) based on the trifluoroacetyl group.

The reaction of electron-rich olefins such as vinyl ether 1 and vinyl sulfide 2 with trifluoroacetic anhydride was found to proceed *via* the intermediate adducts 7 and 8 to eventually afford the trifluoroacetylated olefins 5 and 6 according to the addition-elimination mechanism (Scheme 2), unlike the previously reported mechanism.³

The Mechanism of the Addition Process. In the addition step, the almost quantitative formation of the adducts 7 and 8 was confirmed as described above; however, there remain two problems as follows: One is how poly(1) and -(2) are formed, and the other is whether the addition proceeds in a *trans* (*anti*) or *syn* manner. The key to solving the problems seems to lay both in yields of the obtained polymers and in a conformation of the adducts.

At first, the final products in the reaction of 1 and 2 with trifluoroacetic anhydride are the trifluoroacetylated olefins 5 and 6 and the poly(1) and -(2) ($M_n < 1000$), respectively (Table 1). No other product was observed. The polymers are to be formed by the cationic polymerization of 1 and 2. In the initiation step, the cationic intermediates 3 and 4 are to be formed as initiation species from the olefins 1 and 2 and trifluoroacetic anhydride. The polymers are to be propagated by repeatedly attacking 1 and 2, leading to the following propagation species originated from 3 and 4. These are

Table 1.	Reaction of	Vinyl Ether	and Sulfide	with Trif	luoroacetic	Anhydride
----------	-------------	-------------	-------------	-----------	-------------	-----------

								trifluoroacetylated olefin and polymer		
		addition				yield ^f (%)				
no.	substrate	time (h)	adduct	¹ H NMR ^b	$\frac{\mathrm{IR^{c}}}{(\nu_{\mathrm{C=O}})}$	total time (h)	5 and 6 (form)	poly(1) and -(2)		
1	1a	1	7a	1.23 (t, $J=7.0~{\rm Hz},$ 3H), 3.25 (d, $J=6.2~{\rm Hz},$ 2H), 3.80 (m, 2H), 6.34 (t, $J=6.0~{\rm Hz},$ 1H)	1792	24	58 (trans)	trace		
2	1b	0.8	7b	$0.86~({\rm d},J=8.0~{\rm Hz},6{\rm H}),1.80~({\rm m},1{\rm H}),3.16~({\rm d},J=5.8~{\rm Hz},2{\rm H}),\\3.42~({\rm m},2{\rm H}),6.35~({\rm t},J=5.8~{\rm Hz},1{\rm H})$	1792	20	63 (trans)	trace		
3	1c	0.5	7c	1.23 (dd, $J = 6.4$ Hz, 6H), 3.22 (d, $J = 6.2$ Hz, 2H), 4.00 (sep, $J = 60$ Hz, 1H), 6.40 (t, $J = 5.4$ Hz, 1H)	1788	4	72 (trans)	trace		
4	1d	_	7d	nd^d	\mathbf{nd}^d	2	79 (trans)	trace		
5	1e	1	7e	1.93–3.07 (m, 2H), 3.73–3.93 (m, 1H), 4.09–4.38 (m, 2H), 6.71 (d, $J = 5.2$ Hz, 1H)	1780	24	78 (-)	trace		
6	1f	24^{e}	7f	1.39-2.31 (m, 4H), $3.07-3.37$ (m, 1H), $3.66-3.84$ (m, 2H), 6.43 (d, $J = 2.6$ Hz, 1H)	1765	144	67 (-)	14		
7	2a	50^{e}	8a	3.25 (d, J = 7.0 Hz, 2H), 6.73 (t, J = 6.6 Hz, 1H), 7.39 (m, 5H)	1797	72	$62~(cis+trans)^g$	38		

^{*a*} Reaction conditions: starting material, 5.0 mmol; (CF₃CO)₂O, 5.5 mmol; solvent, CCl₄ (10 mL); room temperature. ^{*b*} In CCl₄, δ /ppm. ^{*c*} In CCl₄, cm⁻¹. ^{*d*} nd: not detected. ni: not identified. ^{*e*} Yields of **7e** and **8a** were not quantitative. ^{*f*} Isolated yield by Kugelrohr distillation. ^{*g*} Cis:trans = 1:1.



consistent with the fact that trifluoroacetic anhydride is a typical cationic initiator. As shown in Table 1, the yields of the polymers were traces in the cases of 1a - e(within 1 h) but increased with an increase in addition time, like in the cases of 1f(24 h) and 2a(50 h). In addition, the rates of formation of adducts 7 and 8 seem to be much faster than that of the polymerization and depend on the π -electron nucleophilicity of olefins rather than on the dissociation of $(CF_3CO)_2O$ to CF_3CO^+ and CF_3COO^- , judging from the cases of 1f (steric) and 2a (lower nucleophilicity) in Table 1. Therefore, these formations of polymers as well as adducts led us to assume that an equilibrium would exist between the adducts (7 and 8) and the cationic intermediate (3 and 4) in this system, as shown in Scheme 2. To elucidate this equilibrium, the reaction of 1a with trifluoracetic anhydride was further conducted in CHCl₃ and CH₂Cl₂ to indicate that the yield of poly(1a) increased with an increase in solvent polarity, such as the dielectric constant (ϵ) of solvents (CH₂Cl₂ > CHCl₃ > CCl₄), as shown in Table 2. The relationship between the equilibrium and the solvent effect in the cationic polymerization of styrene with trifluoroacetic acids has been extensively discussed by Higashimura.⁷ In this paper, it is reported that the equilibrium should exist between the free ions such as

Table 2.Effect of Solvent in Trifluoroacetylation^a of
Ethyl Vinyl Ether with (CF3CO)2O

			total	yield (%) ^b	
no.	solvent	e	time (h)	5a	poly(1a)
8	CCl_4	2.2	24	58	trace
9	CHCl ₃	4.8	7	59	6
10	$\rm CH_2 Cl_2$	8.9	5	33	26

 a The reaction conditions were similar to those of Table 1. b Isolated by Kugelrohr distillation.



carbenium and carboxylate ions and the nonpolymerizable terminal ester moiety (covalent) to affect the rate of polymerization. Thus, the results in Table 2 are possibly reasonable support for the dissociation of the adduct 7 to cationic intermediate 3 being enhanced by the increasing polarity of the reaction system which accelerates the polymerization. Even if the cationic intermediates 3 and 4 are initially formed by the reaction of olefins 1 and 2 with $(CF_3CO)_2O$ or CF_3CO^+ , as shown in Scheme 2, the polymerization should not instantly occur. Alternatively, 3 and 4 should suffer more rapid nucleophilic attack by CF_3COO^- to give the corresponding adducts 7 and 8 because the adduct 7a could also be confirmed, even in CHCl₃ and CH₂Cl₂, by ¹H NMR, similar to the case in CCl_4 . Consequently, the existence of the equilibrium between the adducts (7 and 8) and the cationic intermediates (3 and 4) should be critical for the formation of poly(1) and -(2) as shown in Scheme 2.

Furthermore, to solve the other problem, namely the *trans* or *syn* addition, the coupling constant J_{ab} between the two methyne protons H_a and H_b (Scheme 3) in the adduct **7e** was estimated by ¹H NMR. In common cyclopentane derivatives,⁸ they are considered to have the *trans* form when their coupling constants are 2–8 Hz, while they are considered to have the *syn* form when the

⁽⁷⁾ Sawamoto, M.; Masuda, T.; Higashimura, T.; Kobayashi, S.; Saegusa, T. Makromol. Chem. 1977, 178, 389.

 $^{(\}bar{8})$ Abraham, R. J.; Fisher, J.; Loftus, P. Introduction to NMR Spectroscopy; John Wiley & Sons Inc.: New York, 1988.



coupling constants are 7–11 Hz. The coupling constant J_{ab} was found to be 5.2 Hz which attributes to **7e** the *trans* form as shown in Scheme 3. This result maintains that the addition of trifluoroacetyl anhydride to 1 and 2 would proceed in a *trans* manner.

As a conclusion from these two pieces of evidence, the addition undoubtedly proceeds in a *trans* manner, but the resulting adducts 7 and 8 are in equilibrium with the cationic intermediates 3 and 4 which are capable of initiating the polymerization of 1 and 2, as shown in Scheme 2.

The Mechanism of the Elimination Process. In the next elimination step, the trifluoroacetylated olefins 5 and 6 can be formed through the following two possible routes: One is Ei or E2, in which the adducts 7 and 8 are converted to 5 and 6, and the other is E1, in which the cationic intermediates 3 and 4 are converted to 5 and 6, respectively (Scheme 2). The isomer ratio of the trifluoroacetvlated olefins 5 and 6 suggests a mechanistic aspect (Table 1). In the cases of linear vinyl ethers **1a-d** (no. 1-4), only trans isomers were obtained, while in the case of phenyl vinyl sulfide 2a (no. 7), a mixture of cis and *trans* isomers (1:1) was obtained.^{4,5} There seems to be an apparent different between the elimination mechanism of 7 to 5 and that of 8 to 6. In the traditional elimination mechanism, preferable conformers (eclipsed, gauche-1, and gauche-2) of the adducts in Ei or E2 and two conformers of cationic intermediates in E1 can be illustrated in Scheme 4. If the adduct 7 has the gauche-2 form, it may give *cis* olefin 5. This assumed elimination process is in conflict with the results in Table 1. The adduct 7 should have the eclipsed or gauche-1 form for the elimination through the Ei or E2 mechanism to selectively give trans olefin 5 (Scheme 4). Similarly, the cationic intermediate 4 should have both of the two possible conformers for the elimination through the E1 mechanism to give a 1:1 mixture of cis and trans olefin 6.

The alternative elimination process probably depends on the stability of the cationic intermediates 7 and 8. In the study of the thermodynamic stability of model cationic intermediates such as α -alkoxy and α -thioalkoxy carbocations, Bernardi *et al.*⁹ have reported an MO calculation (*ab initio*) where π -overlap population in ⁺-CH₂SH (0.1734) is larger than that in ⁺CH₂OH (0.1496), indicating a stronger π -bond between C and S than between C and O. Furthermore, Taft *et al.*¹⁰ have



Table 3.Rotation Barriers and Activation Energies of7a and 8b Found by Molecular Orbital Calculation

CF3		-OCOCF3 - CF3CO			
	7g: Z = O 8b: Z = S	3g: Z = O 4b: Z = S			
adduct	rotation barrier (kcal/mol)	activation energy ΔE (kcal/mol)			
7g 8b	14.91 17.14	150.87 138.48			

reported that the ionization potential for ${}^{+}CH_{2}SCH_{3}$ is lower than that for $^+CH_2OCH_3$ by 5 kcal/mol in the gas phase. The two reports support the idea that these carbocations can be stabilized by the connected S atom more than they can be by the O atom. In order to clarify the stability of the present cationic intermediates 3 and 4. we examined an MO calculation for the estimation both of rotation barriers of methyl vinyl ether 7g and methyl vinyl sulfide 8b and of activation energies either from the adduct 7g to the acetylated olefin 3g or from 8b to 4b. The rotation barriers were calculated from the difference between the highest and lowest (optimized) heats of formations for 7g or 8b, which are confirmed by dihedral angles such as ϕ_1 and ϕ_2 , as shown in Scheme 5. The values of ϕ_1 and ϕ_2 were changed from 0 to 360° with 15° portions. The activation energies were also calculated from the difference between the optimized heats of formations for the adduct (7g and 8b) and that of the cationic intermediate (3g and 4b).

The calculation results are summarized in Table 3 in which it is found that the rotation barrier of 7g is lower than that of 8b by 2.23 kcal/mol. The adduct 7g can be rotated more easily than the adduct 8b, presumably because of the difference between the two atomic sizes of O and S (O < S). However, this difference may hardly affect the preferred conformation of the two adducts. On the other hand, the activation energy from 7g to 3g is much larger than that from 8b to 4b by 12.39 kcal/mol. This difference of the activation energy of 12.39 kcal/mol is considered to affect the elimination mechanism sufficiently. Thus, both 7g and 8b probably have the

⁽⁹⁾ Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Wolfe, S. Can. J. Chem. **1975**, 53, 1144.

⁽¹⁰⁾ Taft, R. W., Jr.; Martin, R. H.; Lampe, F. W. J. Am. Chem. Soc. **1965**, 87, 6521.



Figure 3. Time conversion curves in the elimination from the adducts $7\mathbf{a}-\mathbf{c}$ to trifluoroacetylated olefins $5\mathbf{a}-\mathbf{c}: \bigcirc, 7\mathbf{a}; \bigcirc, 7\mathbf{b}; \triangle, 7\mathbf{c}; \Box, 7\mathbf{a} + \text{trifluoroacetic acid } (0.026 \text{ molar equiv}).$

eclipsed or gauche-1 form as the preferred conformer (Scheme 4), while the adduct 8b would be much more easily dissociated to the cationic intermediate 4b than the adduct 7g would be to 3g. Applied to all the adducts and cationic intermediates obtained in Scheme 2, the equilibrium between the adduct 7 and the cationic intermediate 3 largely lies to the right-hand side (the adduct 7), whereas that between 8 and 4 inclines to 4. The elimination course is, therefore, believed to follow Scheme 2.

The Kinetic Study of the Elimination Step. Rates of elimination from the adducts $7\mathbf{a}-\mathbf{c}$ derived from linear vinyl ether $1\mathbf{a}-\mathbf{c}$ seem to depend on the substituents, Et, *i*-Bu, and *i*-Pr, as shown in Table 1. To evaluate the effect of the substituents, the rates k of the elimination from $7\mathbf{a}-\mathbf{c}$ were examined by ¹H NMR. As shown in the time conversion curves (Figure 3), it is confirmed that the conversion of 7 was accelerated with time like that of a self-catalyzed reaction. The elimination was further accelerated by the addition of a small amount of trifluoroacetic acid (0.026 molar equiv) to the reaction system. Therefore, the elimination should be catalyzed by eliminated trifluoroacetic acid.

Equation 1 was employed for the evaluation of the rate k of elimination. $[A]_0$ is the initial concentration of the

$$\frac{1}{[A]_0 + [P]_0} \ln \frac{([P]_0 + x)[A]_0}{[P]_0([A]_0 - x)} = kt$$
(1)

adduct, $[P]_0$ is the initial concentration of the acid (the concentration of added trifluoroacetic anhydride), and x is the concentration of the adduct at a given time. The rate k followed the order of **7c** (14.4 L·mol⁻¹·s⁻¹) > **7b** (11.2 L·mol⁻¹·s⁻¹) > **7a** (5.75 L·mol⁻¹·s⁻¹). From the resulting rate k, the elimination is closely related to the inductive effect¹¹ of the substituent (*i*-Pr > *i*-Bu > Et).

Conclusion

The successful direct observation of the intermediate adducts 7 and 8 in the electrophilic substitution of olefins with trifluoroacetic anhydride was achieved. The rate of addition then observed appears sufficiently faster than that of the elimination under the present conditions. Carbon tetrachloride as the less polar solvent also seems to contribute to this successful observation by stabilizing the neutral adducts 7 and 8 rather than the ionic structures 3 and 4 (Scheme 2). On the other hand, when an appropriate amine such as pyridine is added to the reaction system,³ the second elimination step may be dramatically accelerated because protons positioned \propto to the trifluoroacetyl group in the adduct 7 and 8 become highly acidic. The abstraction of the proton by amine, therefore, seems to be strongly enhanced. This undoubtedly makes it difficult to find evidence for the formation of 7 and 8 even if the reaction proceeds via the addition process. The primary isotope effect studied by Hojo et al.,^{4,5} namely $k_{\rm H}/k_{\rm D} \simeq 1$ in the reaction of vinyl ether and $k_{\rm H}/k_{\rm D} \simeq 2-3$ in the reaction of vinyl sulfide, certainly implies the possibility of the reaction mechanism in Scheme 1. However, judging from our result that the geometry of trifluoroacetylated olefins 5 and 6 is in complete accordance with Hojo's result,³⁻⁵ the formation of the intermediate adducts 7 and 8 and the following elimination by the Ei, E2, or E1 mechanism would be apparently operative regardless of the presence of amine. In the trifluoroacetylation of electron-rich olefins with trifluoroacetic anhydride, the addition-elimination mechanism, which is either the path of 3 to 7 to 5 in Ei or E2 for vinyl ether 1 or the other path of 8 to 4 to 6 in E1 for vinyl sulfide, is fairly reasonable.

JO942183B

⁽¹¹⁾ Taft, R. W., Jr. Steric Effect in Organic Chemistry; Norman, M. S., Ed.; John Wiley & Sons: New York, 1956; Chapter 13.