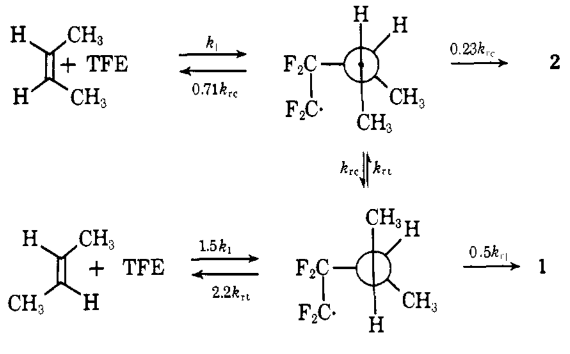
which was held at 150° for 8.5 hr. After the reaction was over, glpc analysis of the cycloadducts showed that the ratio $k_{\text{ethylene}}/k_{\text{butene}}$ was $10.2 \pm 0.3$.

The cycloaddition of 2-butene and tetrafluoroethylene shows two features characteristic of stepwise reactions with biradical intermediates: partial loss of configuration in the products,[2a] and geometrical isomerization of a reactant during, and only during, cycloaddition.[3,4] The formulation of this cycloaddition involves eight rate constants (Scheme I). The information reported here allows us to express these in terms of the three constants $k_1$, $k_{\text{rc}}$, and $k_{\text{rt}}$. By methods previously described,[2ab] the retention ratios $p = 41.8/58.2 = 0.72$, $q = 72/28 = 2.57$, and $pq = 1.85$ lead to $0.23k_{\text{rc}}$ as the rate constant for ring closure to **2** and $0.5k_{\text{rt}}$ the rate constant for ring closure to **1**. In view of the low conversion to product and small fraction of isomerization we neglect the "recycle" effect of product formation from preisomerized olefin, and note that *cis*-2-butene gave 0.129 mol of trans olefin and 0.0298 mol of **1**, indicating that the rate constant for cleavage that competes with closure to **1** is equal to $(0.129/0.0298)0.5k_{\text{rt}} = 2.2k_{\text{rt}}$. Since *trans*-2-butene gave 0.0667 mol of *cis*-2-butene and 0.0125 mol of **2**, the cleavage that competes with closure to **2** has a rate constant of $(0.0667/0.0215)\cdot 0.23k_{\text{rc}} = 0.71k_{\text{rc}}$, as shown in Scheme I.

**Scheme I**



The competition between ethylene and 2-butene is analogous to that between butadiene and 2,4-hexadiene, previously investigated[5] at 80°. The relative rates of addition of 1,1-dichloro-2,2-difluoroethylene ("1122") to one double bond of butadiene, *trans*-piperylene, and *trans,trans*-2,4-hexadiene are 1.0, 1.65, and 0.046. The enhancement due to the methyl group on the allylic system in the biradical is much less than the hindrance imposed by the methyl group at the site of the first bond formation. The overall factor of 10 between ethylene and 2-butene at 175° seems quite in accord with the factor of 22 at 80° between butadiene and 2,4-hexadiene. By contrast, in the concerted Diels–Alder reaction, methyl substitution at the ends of the conjugated system brings about an *increase* in reaction rate (12-fold toward maleic anhydride at 175°[6]).

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*Received January 8, 1972*

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[2] (a) L. K. Montgomery, K. E. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964); (b) but in eq 2, for $(x/y)_{\text{trans}}$ read $(y/x)_{\text{trans}}$.

[3] P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbillich, *ibid.*, **91**, 405 (1969).

[4] P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969).

[5] P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

[6] P. D. Bartlett and K. E. Schueller, *ibid.*, **90**, 6071 (1968).

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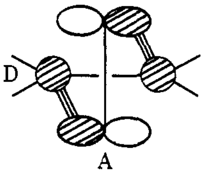
## Nonstereospecific Cycloaddition of Tetrafluoroethylene to Ethylene-*1,2*-$d_2$

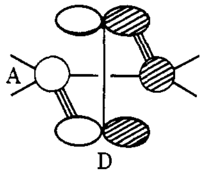
*Sir:*

Concerted (2 + 2) cycloaddition of alkenes from the ground state is required by the orbital symmetry rules to be suprafacial, retaining configuration, in one component and antarafacial, inverting configuration, in the other ($2_s + 2_a$).[1] Although molecular rearrangements have been observed with inversion of the migrating group,[2] the only examples of the ($2_s + 2_a$) cycloaddition mechanism observed to date have involved antarafacial components of special character, *i.e.*, ketenes or allenes, linear systems in which one carbon atom has no protruding substituents to hinder close approach to its reaction partner. The evidence for the mechanism[3] is so convincing as to pose the intriguing question whether any alkene pair exists with low enough barriers to approach and twisting to yield a concerted cycloaddition with inversion at one member of the pair. The most unhindered alkene would appear to be ethylene itself, and the question of what happens to the configuration of *cis*- or *trans*-1,2-dideuterioethylene (**2**) during cycloaddition deserves examination.

Theory affords an imperfect guide to the choice of a reaction partner most likely to make ethylene add antarafacially. In terms of the usual correlation diagrams, two interactions are equally important: **1a**, in which the $\pi$ orbital of the suprafacial component and $\pi^*$ of the antarafacial component interact to yield the new orbital combination $\sigma_1 + \sigma_2$, and **1b**, in which $\pi^*$ of the suprafacial component and $\pi$ of the antarafacial component interact to yield the combination $\sigma_1 - \sigma_2$. However, the most rapid cycloadditions are not those between identical reactants where the donor tendencies are exactly balanced, allowing **1a** and **1b** to contribute equally to the transition state; it is well known that concerted reactions proceed favorably through unsymmetrical transition states in which one bond for-



**1a**



**1b**

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[1] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

[2] (a) J. A. Berson and J. W. Patton, *J. Amer. Chem. Soc.*, **84**, 3406 (1962); (b) J. A. Berson and R. S. Wood, *ibid.*, **89**, 1043 (1967); (c) J. A. Berson and G. L. Nelson, *ibid.*, **89**, 5503 (1967); (d) J. A. Berson and G. L. Nelson, *ibid.*, **92**, 1096 (1970); (e) J. A. Berson, *Accounts Chem. Res.*, **1**, 159 (1969).

[3] P. D. Bartlett, *XXIIIrd Int. Congr. Pure Appl. Chem.*, **4**, 281 (1971), and ref 13–23 cited therein.

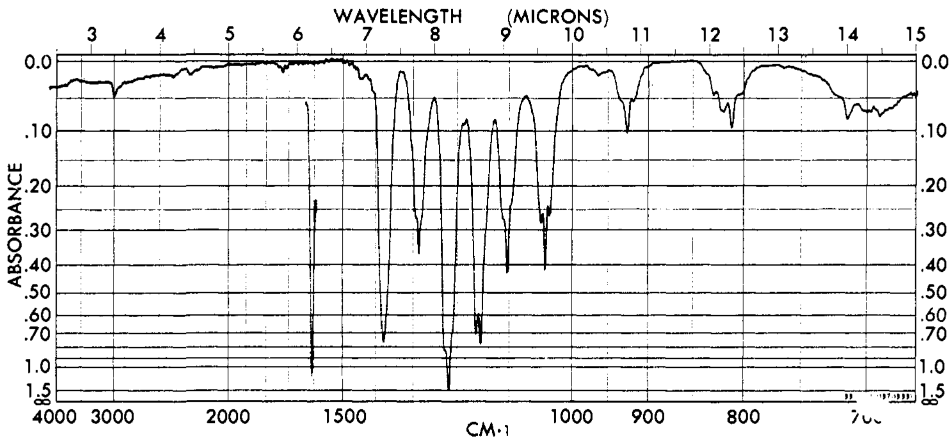

Figure 1. Infrared spectrum of synthetic *cis*-**3**, prepared by catalytic hydrogenation of **7**. The calibration line is at 1601 $cm^{-1}$ in each of the spectra.

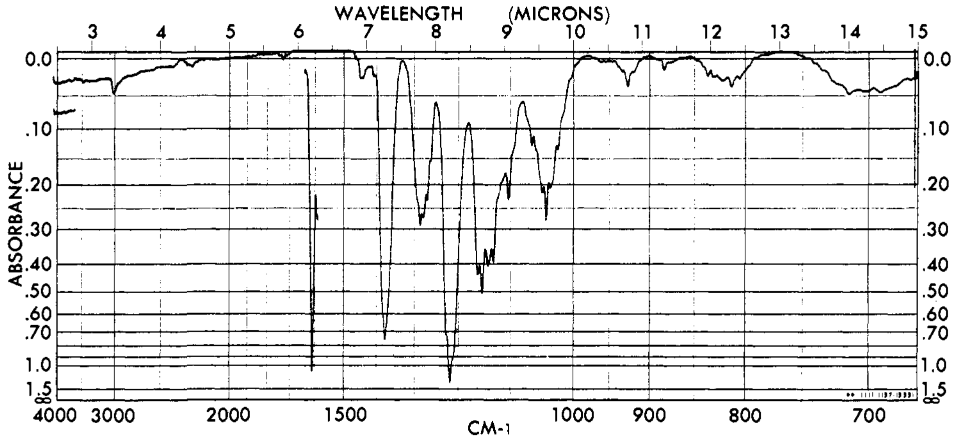

Figure 2. Infrared spectrum of the cycloadduct of *cis*-dideuterioethylene to tetrafluoroethylene.

mation leads over another, guided by well-developed donor–acceptor tendencies. But it does not follow that the donor molecule is any more likely to react suprafacially (**1a**) than the acceptor (as in **1b**). Both transition-state geometries are equally compatible with the requirements of orbital symmetry. The case of ketenes suggests that only the most unhindered reactant has any chance of reacting antarafacially. This report concerns the reaction of *cis*- and *trans*-dideuterioethylene with tetrafluoroethylene, a reagent which adds nonstereospecifically in the (2 + 2) manner to many olefins and dienes.[4-6]

Dideuterioacetylene was prepared from calcium carbide and $D_2O$ (99.88 mol %). *cis*-Dideuterioethylene (*cis*-**2**) was prepared by reduction of $C_2D_2$ with copper-activated zinc and hydrochloric acid.[7] Its ir spectrum[8] showed intense absorption at 842 $cm^{-1}$ and only minute absorption at 725 and 987 $cm^{-1}$. *trans*-Dideuterioethylene (*trans*-**2**) was prepared by reducing $C_2D_2$ with chromous chloride.[7] Its ir spectrum was dominated by strong absorption at 725 and 987 $cm^{-1}$, with no absorption at 842.

Monodeuterioethylene was prepared by the deuterolysis of vinylmagnesium bromide, prepared in THF.[9] It showed characteristic strong peaks at 809, 943, and 1000 $cm^{-1}$ in the infrared.[10] For reference, the cycloadducts of ethylene and monodeuterioethylene with tetrafluoroethylene (**5** and **6**) were prepared in the same way as the dideuterioethylene adducts described below. Authentic *cis*-3,4-dideuterio-1,1,2,2-tetrafluorocyclobutane (*cis*-**3**) was prepared by catalytic hydrogenation (with 0.5% palladium on alumina)[11] of the cycloadduct **7** which was itself prepared by heating dideuterioacetylene, tetrafluoroethylene, and a little hydroquinone for 14 hr at 220° in a bomb packed with stainless steel tubes to increase the surface area. The hydrogenation was conducted at atmospheric pressure without solvent, monitored by glpc, and terminated when 21% complete to minimize H–D exchange. The mass spectrum showed a parent peak at *m/e* 130, and large peaks at 100 and 65; for ir spectrum, see Figure 1.

Tetrafluoroethylene (10.0 g), 6.67 g of *cis*-$C_2H_2D_2$, and a little hydroquinone were loaded into a stainless steel bomb whose capacity had been reduced from 540 to 215 ml by packing with stainless steel rods, the bomb being cooled in liquid nitrogen. After heating for 19 hr at 150°, the product was vented into a trap cooled in

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(4) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962).

(5) P. D. Bartlett, *Science*, **159**, 833 (1968).

(6) W. H. Sharkey, *Fluorine Chem. Rev.*, **2**, 1 (1968).

(7) P. P. Nicholas and R. T. Carroll, *J. Org. Chem.*, **33**, 2345 (1968).

(8) R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.*, **18**, 118 (1950).

(9) D. Seyferth, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 258.

(10) B. L. Crawford, Jr., J. E. Lancaster, and R. O. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953).

(11) I. L. Knunyants, M. P. Krasuskaya, and E. I. Mysov, *Izv. Akad. Nauk SSSR, Otd. Khim.*, 1412 (1960); *cf.* I. L. Knunyants, M. P. Krasuskaya, E. I. Mysov, and I. A. Mukhtarov, *ibid.*, 2141 (1962).

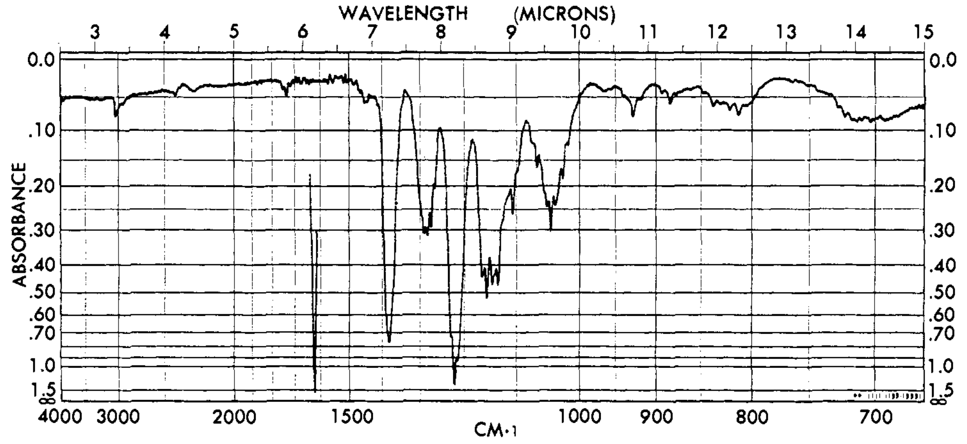


Figure 3. Infrared spectrum of cycloadduct of *trans*-dideuterioethylene to tetrafluoroethylene.

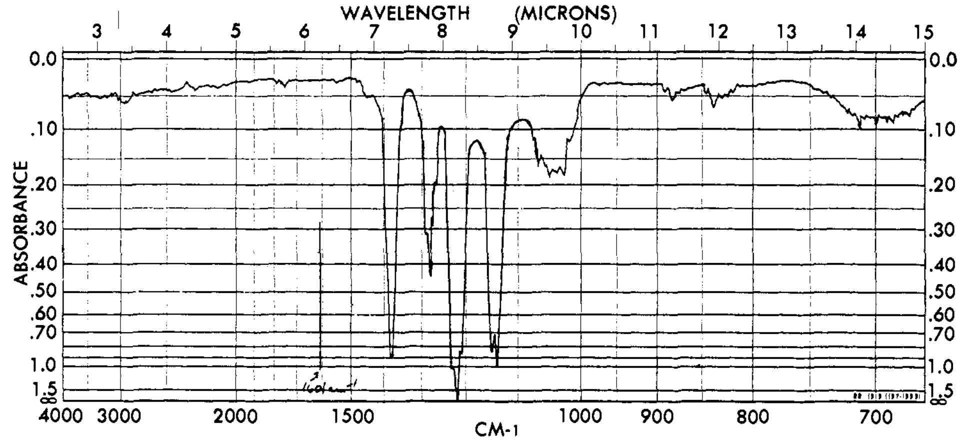
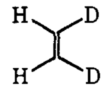
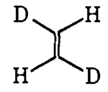


Figure 4. Hypothetical infrared spectrum of *trans*-**3**, calculated by subtracting half of the intensities of Figure 1 from those of Figure 2 or Figure 3.

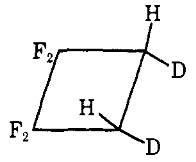
liquid nitrogen, from which the condensate was slowly distilled through a Dry Ice trap into a liquid nitrogen cooled receiver. The Dry Ice trap removed a small amount of octafluorocyclobutane (**4**). The residue, 1.34 g (9.7%), bp 51.5°, was found to be pure by vapor chromatography on Carbowax 20M at 50°. The ir spectrum of a sample purified by preparative glpc is shown in Figure 2.



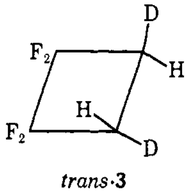
*cis*-**2**



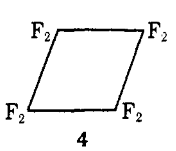
*trans*-**2**



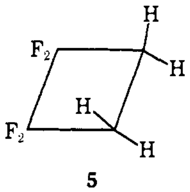
*cis*-**3**



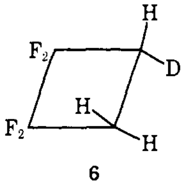
*trans*-**3**



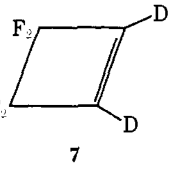
**4**



**5**



**6**



**7**

Repetition of this preparation in a 113-ml stainless steel bomb (150°, 20 hr) gave an identical product. In the same manner a cycloadduct prepared at 200° was isolated in 39% yield from TFE and *trans*-dideuterioethylene; for the ir spectrum of the purified sample, see Figure 3.

Comparison of Figures 1, 2, and 3 indicates that the ir spectra of the cycloadducts from *cis*- and *trans*-dideuterioethylene are indistinguishable from each other, but appreciably different from the spectrum of synthetic *cis*-**3**. The absorption of the latter at 1100 $cm^{-1}$ drops to half-intensity in the spectra of the cycloadducts, while a sharp triplet of *cis*-**3** centered at 1044 $cm^{-1}$ becomes almost lost in a broader absorption of the cycloadducts from 1016 to 1076 $cm^{-1}$; the doublet of *cis*-**3** centered at 1166 $cm^{-1}$ in Figure 1 drops in intensity in the cycloadduct spectra of Figures 2 and 3, and a new, similar doublet appears beside it at 1133 $cm^{-1}$. If we assume that the cycloadducts are both 1:1 mixtures of *cis*-**3** and *trans*-**3**, a comparison of the spectrum of either one with Figure 1 leads to the difference spectrum shown in Figure 4 as probably representing the ir absorption due to *trans*-**3**. Of course, small departures from the 1:1 proportions of stereoisomers in the cycloadducts[12] would not be detectable

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(12) The substantial differences in ir absorption between *cis*- and

by this method. The results, however, are inconsistent with a stereospecific mechanism and are those to be expected from stepwise cycloaddition, with amounts of configuration loss comparable to those observed in known cases of the biradical mechanism.[5]

In the first experiments on this reaction[13] samples of *cis*-**2** and *trans*-**2** yielded cycloadduct samples which differed in infrared absorption, the former showing a peak at 1430 cm$^{-1}$ absent in the latter, which in turn showed absorption at 1370 cm$^{-1}$ which was absent in the former, or at least overlaid by a stronger absorption at slightly lower frequency. Since the 1430 absorption, rather than being a major feature, is barely perceptible in both of our present cycloadducts and the 1370 absorption is strong and identical in both and in synthetic *cis*-**3**, it is clear that neither absorption is in fact diagnostic of configuration in these compounds and we must allow for substantial impurities in the earlier samples. The monodeuterio cycloadduct **6** has a prominent peak at 1430 cm$^{-1}$, and is a likely candidate for the source of this peak in the earlier samples. In addition, the spectra of these samples were more complex than the ones now described in a way that we can account for by the presence of different amounts of TFE and its dimer **4** in the samples which otherwise consisted of *cis*-**3** and *trans*-**3** in similar proportions.

We conclude that even an olefin as unhindered as ethylene reacts with tetrafluoroethylene with a large loss of configuration rather than entering into a concerted reaction antarafacially.

**Acknowledgment.** This work was supported by grants from the National Science Foundation and from the National Institutes of Health.

*trans*-dideuterioethylene enabled J. E. Baldwin and P. W. Ford [*J. Amer. Chem. Soc.*, **91**, 7192 (1969)] to detect net inversions in the *pyrolysis* of 7,8-*cis*,- *exo*-dideuteriobicyclo[4.2.0]octane to ethylene-$d_2$ that was up to 60% trans.

(13) Communicated by C. M. S. to P. D. B., who cited them by permission in a lecture at the 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., July 30, 1971; photooffset publication, ref. 3.

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## Origin of Continuous Infrared Absorption

*Sir:*

A wide variety of hydrogen bonded complexes are now known in which the OH absorption seems to consist of a continuum running from ~2500 to ~800 cm$^{-1}$. The substances which generate such spectra include the hydrated aqueous proton,[1] strong acid solutions in sulfoxides, selenoxides, phosphine oxides,[2-5] and methanol, hydrated polystyrenesulfonic acid,[4] and a variety of carboxylic acids dissolved in amine solvents.[6] However, previous work has mostly involved either pure, isolated complexes or else solutions in which the solvent was a member of the acid–base pair. Attempts to dilute such complexes with an inert solvent have led to the reappearance of a conventional band spectrum. This, plus theoretical calculations on a model in which the proton is a particle in a one-dimensional potential function, has led Zündel and coworkers to conclude that such spectra are inherently cooperative phenomena;[3,7] that is, in dilute solution in non-hydrogen-bonding solvents, only a conventional band spectrum should be observable. We have now examined the complexes of trifluoroacetic acid with dimethyl sulfoxide (DMSO) and with tributylphosphine oxide (TBPO) in dilute solution in sulfolane and found them to exhibit the same sort of continuous OH absorption that is observed in neat mixtures. We have also shown, by means of cryoscopic measurements, that the complexes are monomolecular (not aggregated) in such solutions.

Cryoscopic measurements were made on five systems: trifluoroacetic acid, DMSO, and TBPO in sulfolane, and DMSO and TBPO in a sulfolane solution containing a fixed concentration of trifluoroacetic acid. Plots of $\Delta T_f$, the freezing point depression, against concentration, were linear for trifluoroacetic acid, TBPO, and DMSO, yielding apparent freezing point depression constants of 53.2, 59.3, and 47.3°K kg mol$^{-1}$, respectively. These are different from each other and from the conventional freezing point depression constant for this solvent (64.1°K mol$^{-1}$) because of the known propensity of small molecules to dissolve in *solid* sulfolane.[8] The linearity of the plots, over several orders of magnitude of concentration, and the fact that the apparent freezing point depression constants are not simple fractions of 64.1 give strong evidence that the substances are not aggregated in sulfolane. In the mixed systems, as shown in Figure 1, $\Delta T_f$ is a strongly nonlinear function of the base concentration. This function can be reproduced by assuming complexing constants of 400 $M^{-1}$ for DMSO and infinity for TBPO, with a "normal" freezing point depression constant, 64.1°K kg mol$^{-1}$ for the DMSO complex and 59.3°K kg mol$^{-1}$ for that with TBPO. The concentration of free $CF_3COOD$, as judged by the intensity of the normal OD band, in solutions containing equal quantities of DMSO is consistent with the complexing constant given. If an equal concentration of TBPO or a substantial excess of DMSO is present, the normal OD band disappears, as shown in Figure 2. No simple postulate other than 1:1 complexes seems likely to explain these results.

Trifluoroacetic acid in sulfolane has a conventional OH stretching band in the region 3300–2600 cm$^{-1}$ (2600–2100 cm$^{-1}$ for the deuterated acid). The acid is a strong hydrogen bond donor and sulfolane is evidently a weak acceptor. A strong, sharp absorption at 1787 cm$^{-1}$ is also given by the carbonyl group of the acid.[9] As DMSO or TBPO is added to $CF_3COOH$ solutions in sulfolane, the OH absorption is progressively converted to the continuum described above. The molar extinction coefficients for the continuum, measured in

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