

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.<sup>5</sup>

In the first experiments on this reaction<sup>13</sup> samples of *cis*-2 and *trans*-2 yielded cycloadduct samples which differed in infrared absorption, the former showing a peak at 1430 cm<sup>-1</sup> absent in the latter, which in turn showed absorption at 1370 cm<sup>-1</sup> 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<sup>-1</sup>, 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.

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*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*<sub>2</sub> 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<sup>-1</sup>. The substances which generate such spectra include the hydrated aqueous proton,<sup>1</sup> strong acid solutions in sulfoxides, selenoxides, phosphine oxides,<sup>2-5</sup> and meth-

anol, hydrated polystyrenesulfonic acid,<sup>4</sup> and a variety of carboxylic acids dissolved in amine solvents.<sup>6</sup> 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;<sup>3,7</sup> 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<sup>-1</sup>, respectively. These are different from each other and from the conventional freezing point depression constant for this solvent (64.1°K mol<sup>-1</sup>) because of the known propensity of small molecules to dissolve in *solid* sulfolane.<sup>8</sup> 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 show 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<sup>-1</sup> for DMSO and infinity for TBPO, with a "normal" freezing point depression constant, 64.1°K kg mol<sup>-1</sup> for the DMSO complex and 59.3°K kg mol<sup>-1</sup> for that with TBPO. The concentration of free CF<sub>3</sub>COOH, 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<sup>-1</sup> (2600–2100 cm<sup>-1</sup> 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<sup>-1</sup> is also given by the carbonyl group of the acid.<sup>9</sup> As DMSO or TBPO is added to CF<sub>3</sub>COOH 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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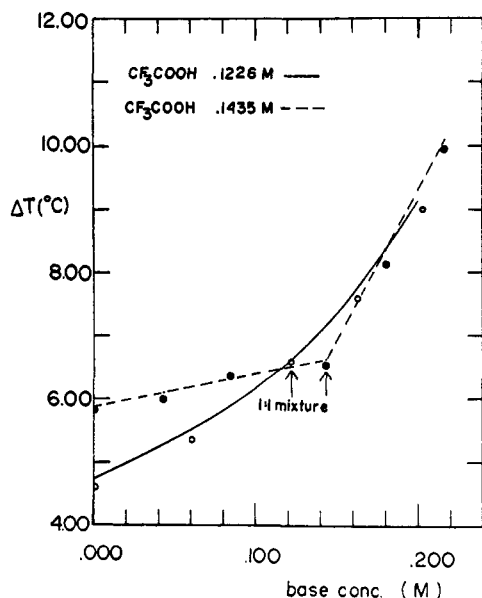
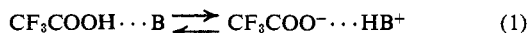


Figure 1. Observed,  $\circ$  or  $\bullet$ , and calculated (lines) freezing point depressions. Open circles correspond to 0.1226 M  $\text{CF}_3\text{COOH}$  and variable concentrations of DMSO. Closed circles correspond to 0.1435 M  $\text{CF}_3\text{COOH}$  and variable concentrations of TBPO. The lines were calculated assuming a complexing constant of  $3^\circ\text{K kg mol}^{-1}$  for DMSO and  $59.3^\circ\text{K kg mol}^{-1}$  for TBPO. The complex with DMSO was assumed to have a "normal" freezing point depression constant,  $64.1^\circ\text{K kg mol}^{-1}$ , and the complex with TBPO was assumed to have a freezing point depression constant of  $59.3^\circ\text{K kg mol}^{-1}$ , the same as that for TBPO itself.

Sulfolane solution at a number of frequencies, are substantially the same as when they are measured on a thin film of an undiluted 1:1 mixture of trifluoroacetic acid and DMSO. Thus the influence of the solvent on the shape and intensity of the continuum is minimal. Simultaneously the carbonyl absorption is broadened and shifted 10–15  $\text{cm}^{-1}$  to lower frequency, although the integrated intensity remains about the same. It is noteworthy that the carbonyl band of the  $\text{CF}_3\text{COOD-TBPO}$  complex occurs at a frequency  $\sim 8 \text{ cm}^{-1}$  lower than that of the  $\text{CF}_3\text{COOH-TBPO}$  complex, although the carbonyl bands of  $\text{CF}_3\text{COOD}$  and  $\text{CF}_3\text{COO}^-(\text{C}_2\text{F}_5)_3\text{ND}^+$  occur at the same frequencies as their hydrogen analogs. Thus the carbonyl bands in the TBPO complexes are, apparently, averages in which the weighting factors change on deuteration. Typical spectra are shown in Figure 2.

To explain these results we postulate a very rapid interconversion of the two possible hydrogen bonded structures, as shown in eq 1. We assume that the



theory relating reaction rate and line shape in nmr spectroscopy<sup>10</sup> is also applicable, at least approximately, to vibrational lines. (This has been shown to be true in the limit of lifetime broadening.<sup>11</sup>) In that case the

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 221–223; spectroscopic frequencies must be expressed in radians reciprocal seconds when they are compared with reaction rates.

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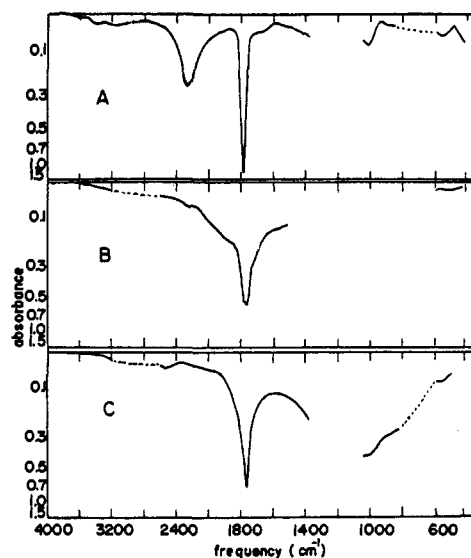


Figure 2. Spectra of solutions in sulfolane. The sulfolane absorption has been removed by subtraction. Regions where the sulfolane absorption was too strong to permit this are left blank. Curve A is for 0.229 M  $\text{CF}_3\text{COOD}$  in sulfolane; curve B is 0.251 M  $\text{CF}_3\text{COOD}$  plus 0.511 M DMSO; and curve C is 0.229 M  $\text{CF}_3\text{COOD}$  plus 0.254 M TBPO, all in sulfolane. Deuterated acid is used to show the hydroxylic spectrum without interference from the sulfolane C–H stretching region. Spectra of TBPO and DMSO in sulfolane show no significant absorption in the regions of interest.

O–H band and the O–H $\cdots$ O (hydrogen bond or breathing) band are seen to be near the coalescence point. Since they were originally separated by something more than 1000  $\text{cm}^{-1}$ ,<sup>12</sup> this implies a lifetime of  $\sim 0.5 \times 10^{-14}$  sec for the individual species shown in eq 1.<sup>10</sup> Such a lifetime also explains the partial re-sharpening of the carbonyl band at a frequency intermediate between those of  $\text{CF}_3\text{COO}^-$  and  $\text{CF}_3\text{COOH}$ ,<sup>10</sup> since those frequencies are separated by only  $\sim 100 \text{ cm}^{-1}$  in the isolated species.<sup>9,13</sup> Previous failure to observe such spectra in dilute solutions was probably due to the low dielectric constants and poor solvating power of the solvents used. This has a tendency to displace eq 1 to the left, increasing the lifetime of the predominant spectroscopic species to the point where the anomaly is no longer observed. Sulfolane has a high dielectric constant (44),<sup>14</sup> and is a fairly good solvent for ions, but is a very weak H-bond acceptor.

It is not likely that a transformation as fast as this can be regarded as a chemical reaction in the conventional sense, and a theory more specifically directed at this problem is clearly needed. A successful theory will probably have to consider the interaction between the O–H mode and the O–H $\cdots$ O mode.

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