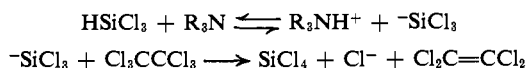


ingly, a simple interpretation of the reduction of hexachloroethane can be written. The other reactions re-



ported can be envisaged as occurring in similar ways.

The concept of a related chemistry between  $\text{R}_3\text{P}$  (and possibly  $(\text{RO})_3\text{P}$ ) and silyl anions generated by base attack on the hydrogen of a silane ( $-\text{SiH}$ ) has far reaching synthetic consequences for both the carbon and silicon chemist. Numerous experiments to extend the scope of these reactions and to establish their mechanisms are presently in progress in our laboratory.

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### Acid Catalysis in Hydrofluoric Acid Buffers<sup>1</sup>

Sir:

Aqueous solutions of hydrogen fluoride and its alkali metal salts possess a number of qualities desired of a good buffer system. The acid is moderately weak ( $\text{p}K_a = 3.17$ ), its anion has low nucleophilic power, both acid and anion are stable toward oxidizing and reducing agents, and their solutions are transparent to visible and ultraviolet light, thus facilitating spectrophotometric measurement of reaction rates and equilibria. Hydrogen fluoride does attack glass vessels, but the present widespread availability of plastic laboratory ware has effectively removed this as a disadvantage. A more serious shortcoming stems from the fact that hydrofluoric acid buffers contain appreciable quantities of the species  $\text{HF}_2^-$  for which an acid catalytic power comparable to that of HF is claimed;<sup>2</sup> this would complicate kinetic analysis of reactions subject to general acid catalysis. We have recently discovered, however, that this complication is absent from a particularly simple example of this kind of reaction.

The hydrolysis of ethyl vinyl ether is known to occur through rate-determining proton transfer from a catalyzing acid to the substrate.<sup>3</sup> This is also the first step of this reaction, and the process is not catalyzed by bases; rates of this hydrolysis, therefore, reflect the catalytic power of general acids in a particularly straightforward way. In order to assess the catalytic strengths of HF and  $\text{HF}_2^-$  in this system, we have carried out kinetic experiments under two sets of conditions: (1) in solutions prepared from hydrogen fluoride alone where the concentration of  $\text{HF}_2^-$  is negligibly low and the only effective catalysts are  $\text{H}_3\text{O}^+$  and HF, and (2) in solutions containing added fluoride ion where the concentration of  $\text{HF}_2^-$  may be made

(1) This research was supported by a grant (GP 6580) from the National Science Foundation.

(2) R. P. Bell and J. C. McCoubrey, *Proc. Roy. Soc. (London)*, **A234**, 192 (1956).

(3) (a) P. Salomaa, A. Kankaapera, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966); (b) A. J. Kresge and Y. Chiang, *J. Chem. Soc., B*, **53**, 58 (1967); (c) M. M. Kreevoy and R. Eliason, *J. Phys. Chem.*, **72**, 1313 (1968).

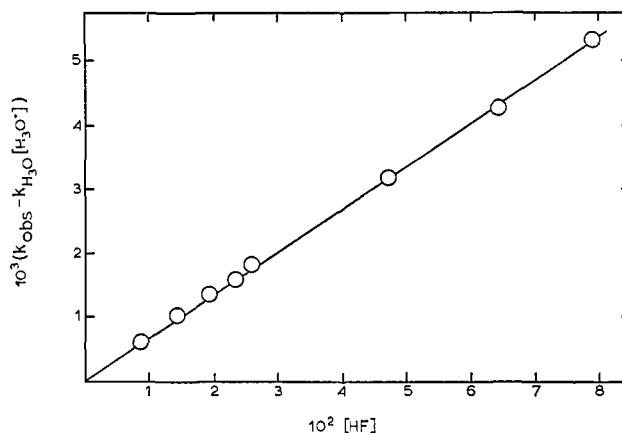


Figure 1. Dependence of  $k_{\text{obs}} - k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+]$  on  $[\text{HF}]$  for ethyl vinyl ether hydrolysis in HF solutions containing NaF; the line is drawn with slope =  $6.71 \times 10^{-2} M^{-1} \text{sec}^{-1} (k_{\text{HF}})$  and designates expected behavior for catalysis by HF (and  $\text{H}_3\text{O}^+$ ) alone.  $\text{HF}_2^-$  concentrations for the experimental points reading from left to right are (in units of  $10^2 M$ ) 0.11, 0.54, 1.05, 1.66, 0.48, 1.55, 3.00, and 4.71.

comparable to that of HF. Using a value of  $k_{\text{H}_3\text{O}^+}$  measured in dilute  $\text{HClO}_4$  solutions ( $1.75 \pm 0.02 M^{-1} \text{sec}^{-1}$  at  $24.9^\circ$ ),<sup>4</sup> we determined  $k_{\text{HF}}$  to be  $(6.71 \pm 0.05) \times 10^{-2} M^{-1} \text{sec}^{-1}$  from the first set of experiments.<sup>5</sup> However, when the latter was used to analyze data from the second series of measurements, in which  $\text{HF}_2^-$  concentrations ranged as high as 70% of HF concentrations, no excess rate assignable to catalysis by  $\text{HF}_2^-$  could be detected. This is demonstrated by Figure 1 where observed rate constants for this series, with contributions to reaction through  $\text{H}_3\text{O}^+$  subtracted out ( $k_{\text{obs}} - k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+]$ ), may be seen to agree remarkably well with rate constants calculated on the basis of the remaining reaction occurring through HF alone. (The latter is represented by the line in this figure.) Since  $k_{\text{obs}} - k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+]$  in these experiments ranged from 60 to 90% of  $k_{\text{obs}}$ , and since rate constants could be measured with an accuracy of  $\pm 1\%$ , we estimate that reaction through  $\text{HF}_2^-$ , if not wholly absent, cannot amount to more than 2-3% of the reaction through HF.

This result prompted us to analyze the published data<sup>2</sup> for the only other reactions examined in this respect, the iodination of acetone and of acetylacetone. Our scrutiny revealed that the claim of equal catalytic powers for HF and  $\text{HF}_2^-$  rests on an error made in calculating the concentrations of the acidic species in these reaction mixtures.<sup>8</sup> When appropriate corrections are made, catalysis by  $\text{HF}_2^-$  vanishes in the reaction of acetylacetone and is reduced to

(4) The value measured here is in good agreement with  $k_{\text{H}_3\text{O}^+} = 1.77 M^{-1} \text{sec}^{-1}$  calculated from the known<sup>8b</sup> temperature dependence of this reaction. Error limits used throughout this paper are standard deviations of mean values.

(5) Solution compositions were calculated throughout this work using  $[\text{H}^+][\text{F}^-]/[\text{HF}] = 6.71 \times 10^{-4}/f_{\pm}$ ,<sup>6</sup>  $[\text{HF}_2^-]/[\text{HF}][\text{F}^-] = 3.86$ ,<sup>6</sup> and  $\log f_{\pm} = -0.50\mu^{1/2}/(1 + \mu^{1/2}) + 0.20\mu$  (this corresponds to the treatment used in ref 2), and were verified by indicator measurements of  $[\text{H}^+]$  employing 2,4-dichloroaniline.

(6) H. H. Broene and T. DeVries, *J. Am. Chem. Soc.*, **69**, 1644 (1947); A. J. Ellis, *J. Chem. Soc.*, 4300 (1963).

(7) C. W. Davis, *ibid.*, 2093 (1938).

(8) Equation 5 of ref 2 is wrong: the coefficient of the second term on its right-hand side should be  $1/2$  rather than  $1/4$ . This mistake produced significant errors in the analysis of rate data collected in the more acidic solutions of that work, but it did not materially affect the conclusions drawn concerning basic catalysis.

half its former magnitude in the case of acetone; it is not certain whether or not the latter is outside the limits of experimental error.

This suggests that  $\text{HF}_2^-$  may in general have an acid catalytic power considerably inferior to that of HF. This would be consistent with the expected greater difficulty of removing a proton from between two electronegative fluorine atoms in  $\text{HF}_2^-$  than from just one such atom in HF. It also agrees with the fact that, although basic catalysis by  $\text{F}^-$  is common,<sup>2,9</sup> no base-catalyzed term in  $[\text{F}^-]^2$  has ever been detected;<sup>2,9</sup> the latter would correspond to basic catalysis by the conjugate base of  $\text{HF}_2^-$ , and, if general acid catalysis by  $\text{HF}_2^-$  were to operate in A2 reactions such as the iodination of acetone and acetylacetone, then the conjugate base of this acid would have to serve as the general base in the second steps of these processes.

(9) R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc. (London)*, **A235**, 453 (1956); J. R. Hulett, *ibid.*, **A251**, 274 (1959); *J. Chem. Soc.*, 468 (1960).

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### An Estimate of the Relative Rates of Conrotatory vs. Disrotatory Electrocyclic Ring Opening

Sir:

A quantitative estimate for the difference in energy between the symmetry-allowed and -forbidden pathways for a thermal electrocyclic cyclobutene reaction has recently been reported by Braumann and Golden.<sup>1</sup> Their value of  $\sim 15$  kcal, in favor of the Woodward-Hoffmann-predicted<sup>2</sup> conrotatory mode, was based on an estimate of ground- and transition-state strain energies, and they correctly pointed out that, for compounds with no added strain for either pathway, only the allowed product can be detected by conventional techniques. In principle, however, it should be possible to obtain a quantitative evaluation for unstrained (or equally strained) compounds by product determination in a cyclobutene-butadiene isomerization in which reversibility has been established at some temperature at which the rate constants are known. We now report the results of such an experiment.

*cis*-3,4-Dimethyltetraphenylcyclobutene (*cis*-I, nmr: 20 phenyl protons at  $\delta$  6.7–7.7, 6 methyl protons at  $\delta$  1.91) was obtained in 82% yield from the reaction of 3,4-dibromotetraphenylcyclobutene<sup>3</sup> with excess  $\text{CH}_3\text{-MgBr}$  in ether. The three geometrical isomers of 1,4-dimethyl-1,2,3,4-tetraphenylbutadiene were prepared by methylation of the appropriate anion generated by the action of BuLi on *cis,cis*-1,4-dibromo-1,2,3,4-tetraphenylbutadiene<sup>4</sup> under varying conditions.<sup>5</sup> Their properties are summarized in Table I.

(1) J. I. Braumann and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).

(2) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(3) H. H. Freedman and G. A. Doorakian, *Tetrahedron*, **20**, 2181 (1964).

(4) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).

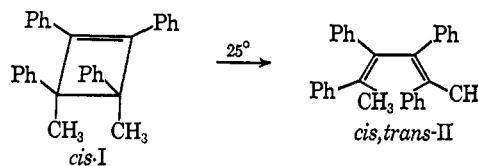
(5) Details of these and similar reactions will be given in a paper describing the preparation and rearrangements of the 1,2,3,4-tetraphenylbutadienyl mono- and dianions.

**Table I.** Properties of the 1,4-Dimethyl-1,2,3,4-tetraphenylbutadienes (II)<sup>a</sup>

Isomer	Mp, °C	Nmr, $\delta_{\text{CH}_3}$ <sup>b</sup>	% at equilibrium <sup>c</sup>
<i>cis,cis</i>	207–208.5	2.40 <sup>d</sup>	61.0 $\pm$ 1
<i>cis,trans</i>	156–157	1.98, <sup>e</sup> 2.18 <sup>e</sup>	36.8 $\pm$ 1
<i>trans,trans</i>	168–170	1.89 <sup>d</sup>	2.2 $\pm$ 1

<sup>a</sup> All new compounds gave satisfactory analyses. <sup>b</sup> In  $\text{CDCl}_3$ ; measured in parts per million. <sup>c</sup> Accomplished by reversible protonation of the anions generated from either *cis,trans*- or *cis,cis*-II by potassium *t*-butoxide in DMSO-THF at 25°. <sup>d</sup> Six-proton singlet. <sup>e</sup> Three-proton singlet.

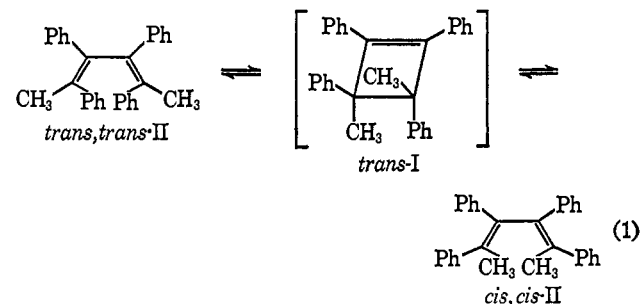
In solution, at room temperature, *cis*-I undergoes the expected, solvent-independent, conrotatory ring opening with complete conversion to *cis,trans*-II, the absence



of disrotatory isomers, *cis,cis*- and *trans,trans*-II, being evident from the nmr spectrum. The first-order rate constants and activation parameters for *cis*-I  $\rightarrow$  *cis,trans*-II were determined in  $\text{CCl}_4$ -pyridine solution. Over the temperature range 26–55° the rate constants varied from  $(1.89 \pm 0.1) \times 10^{-5}$  to  $(7.43 \pm 0.1) \times 10^{-4}$   $\text{sec}^{-1}$ , yielding  $\Delta H^\ddagger = 24.1 \pm 0.5$  kcal/mol,  $\Delta S^\ddagger = 0.5 \pm 1.5$  eu, and  $\Delta G^\ddagger = 24.0 \pm 0.5$  kcal/mol.

Reversibility in a cyclobutene-butadiene electrocyclic reaction can be demonstrated by obtaining the same equilibrium distribution of diene and cyclobutene starting with either component.<sup>6</sup> Alternatively, in the typical case where the equilibrium concentration of cyclobutene is unobservable, reversibility can be inferred if thermal geometrical isomerization of the dienes occurs only between conrotatory isomers to give an equilibrium distribution which is demonstrably different from the normal thermodynamic distribution of isomeric dienes. Though this latter approach may have an element of ambiguity, it is a reasonable postulate, amply supported by the following data.

In pyridine solution at temperatures greater than 100°, both *trans,trans*- and *cis,cis*-II are equilibrated reversibly to the complete exclusion of other products. This is in decided contrast to the thermodynamic distribution of the diene isomers (Table I) and indicates (eq 1) that this thermal equilibration is occurring by both



(6) Cf. G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 3582 (1968).