Table I

Expt	Bromo ketone	Reagent	Solvent[a]	Product	% yield	Atoms of D[b]	Mechanism
1	I(6)	NaOD	EtOD–D_2O	II(6), R = H	95	0.00	Semibenzilic
2	I(6)	KO-*t*-Bu	*t*-BuOD	II(6), R = *t*-Bu	94	0.026	Semibenzilic
3	I(7)	NaOD	EtOD–D_2O	II(7), R = H	80	0.01	Semibenzilic
4	I(7)	NaOMe	MeOD	II(7), R = Me	96	0.00	Semibenzilic
5	I(7)	KO-*t*-Bu	*t*-BuOD	II(7), R = *t*-Bu Recovered I(7)	67	0.83[c] 0.00	Cyclopropanone
6	I(7)	$AgNO_3$	EtOD–D_2O	II(7), R = H	85	0.00	Semibenzilic
7	I(8)	NaOD	EtOD–D_2O	II(8), R = H	88	0.90[c]	Cyclopropanone[d]
8	I(8)	$AgNO_3$	EtOD–D_2O	II(8), R = H	25	0.005	Semibenzilic

[a] Reactions were carried out at the reflux temperature of the solvent except for reactions 6 and 8 which were done at room temperature. [b] Combustion deuterium analyses (per molecule of product) by J. Nemeth, Urbana, Ill. [c] Value expected for rearrangement entirely by a cyclopropanone when allowance is made for OH introduced into the solvent and for $k_H/k_D \sim 4–5$ in the irreversible carbanion protonation (T. Riley and F. A. Long, *J. Am. Chem. Soc.*, **84**, 522 (1962)). [d] An optically active sample of I(8), $[\alpha]^{19}D$ $-10°$ (*c* 3.03, chloroform), was divided into two portions, one of which was rearranged in sodium hydroxide–ethanol–water to give 67% *cis*-II(8) of rotation $[\alpha]^{20}D$ $+1.1°$ (*c* 6.20, chloroform), and the other was rearranged in the silver nitrate–ethanol–water reagent to give 52% *cis*-II(8) of rotation $[\alpha]^{19.6}D$ $+31.3°$ (*c* 4.26, chloroform). The loss in optical activity shown by the product from the sodium hydroxide reaction corresponds to 96% racemization.

corporation alone is sufficient provided that no α'-hydrogen exchange occurs before rearrangement. With these criteria and the fact that the stereochemistry of II from all reactions was exclusively *cis*[10] (required by a semibenzilic path, permitted by cleavage of a cyclopropanone), the results shown in Table I were obtained.

Under typical Favorskii conditions (NaOD–D_2O–EtOD or NaOMe–MeOD) I(6) and I(7) rearrange by the semibenzilic path, but when the ring size reaches that of I(8), the α' hydrogen becomes comparable in acidity to that of α-chlorocyclohexanone, and rearrangement by the symmetrical path taken by the latter ketone[2] becomes faster. However, under other conditions I(8) can rearrange by the semibenzilic path as revealed by its reaction with silver nitrate. While this change of mechanism undergone by I(8) might be considered exceptional since silver nitrate is not a typical Favorskii reagent, the change from a semibenzilic intermediate for rearrangement of I(7) with hydroxide or methoxide as base to a symmetrical intermediate for reaction with *t*-butoxide must be regarded as occurring under normal basic Favorskii conditions. We have considered four possible causes for the change in mechanism: (a) difference in base strength, (b) inability to form dianion IV, conceivably a required intermediate for semibenzilic rearrangement, (c) insufficient concentration of anion III(7) (R = *t*-Bu) for rearrangement *via* III(7) to compete with cyclopropanone formation, and (d) change in solvent polarity. The fact that I(7) will rearrange with methoxide ion by a semibenzilic path excludes IV(7) as a *required* intermediate. Of the remaining three possibilities, at present we favor a since I(6) with *t*-butoxide undergoes rearrangement by the semibenzilic path.

The demonstration that I(7) and I(8) can each rearrange to a single product by either a semibenzilic or a cyclopropanone intermediate shows a delicate balance between the two mechanisms and suggests the possibility that the semibenzilic mechanism may be operating with other α-halo ketones bearing α'-hydrogen atoms, either in preference to or concomitant with a cyclopropanone mechanism. Operation of the semibenzilic path might even be involved in the explanation for the puzzling variation of inversion and retention found in certain Favorskii rearrangements.[4c,e,i]

During cyclopropanone formation from I(7), it is difficult to visualize the bromine atom in any conformation other than equatorial with respect to the cyclohexanone ring. Perhaps there do exist two routes to a cyclopropanone,[11] one being a concerted 1,3 elimination with loss of equatorial α' hydrogen and α bromine in the case of I(7),[12] and the other involving loss of axial halogen from an enolate anion.[4l] Finally, if it is accepted that a cyclopropanone is the intermediate in reactions 5 and 7,[4k] then the exclusive formation of *cis*-II(7) and *cis*-II(8) provides additional evidence for the stereochemistry of cleavage of cyclopropanones, *i.e.*, with complete retention of configuration in the solvents used.[13,14]

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(9) Conformational equilibration and symmetrical solvation of the intermediate are assumed.

(10) Authentic samples of *cis*-II(6), -II(7), and -II(8) and *trans*-II(7) and -II(8), R = H, have been prepared and their methyl esters compared with product methyl ester by gas–liquid partition chromatography. The isomers are readily distinguished in each case.

(11) H. O. House and F. A. Richey, *J. Org. Chem.*, **32**, 2151 (1967).

(12) *Cf.* A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 3915 (1967).

(13) W. Reusch and P. Mattison, *Tetrahedron*, **23**, 1953 (1967).

(14) Thus, cleavage of three-membered cyclic ketones takes the same stereochemical course as fission of cyclopentanones; *cf.* nortricyclanone, P. G. Gassman and F. V. Zalar, *Tetrahedron Letters*, 3251 (1964).

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The Formation of the Pentafluorosilicate Anion in Dehydrofluorination Reactions

Sir:

The pentafluorosilicate anion has very recently been reported[1,2] in salts of the Ph_4As^+, Et_4N^+, and *trans*-$(Et_3P)_2PtCl(CO)^+$ cations. We wish to report our evidence[3,4] for the formation of this anion in dehydrofluorination reactions.

The reactions of silicon tetrafluoride were included in a general study of the dehydrofluorination of pri-

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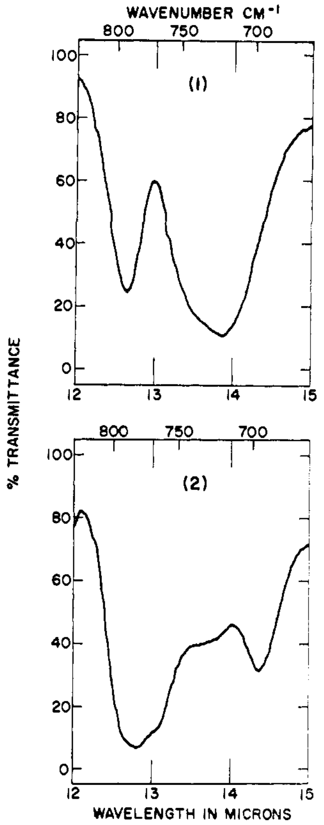

Figure 1. Infrared absorption of (1) $(Me_3NH^+)_2SiF_6^{2-}$ and (2) $Me_3NH^+SiF_5^-$.

mary amines and metalloid fluorides or of alcohols and metalloid fluorides. Dehydrofluorination in our studies was usually effected by the reaction of an adduct of a tertiary amine with the metalloid fluoride with resulting formation of the tertiary amine fluorometalate salt. Thus when the dehydrofluorination of silicon tetrafluoride systems was studied, tertiary amine hexafluorosilicate salts were expected as illustrated in eq 1 for the dehydrofluorination of primary amines and silicon tetrafluoride or eq 2 for the dehydrofluorination of phenol and silicon tetrafluoride.

$$nRNH_2 + 2nSiF_4 + 2nR_3N \longrightarrow (RNSiF_2)_n + n(R_3NH^+)_2SiF_6^{2-} \quad (1)$$

$$4PhOH + 3SiF_4 + 4R_3N \longrightarrow (PhO)_4Si + 2(R_3NH^+)_2SiF_6^{2-} \quad (2)$$

The expected hexafluorosilicate salt formed when triethylamine was used, but neither the reaction stoichiometry nor the properties of the salt precipitated from the reaction when trimethylamine was used were consistent with eq 1 or 2. For example, 1.80 moles of phenol and 1.79 moles of trimethylamine reacted with 2.42 moles of silicon tetrafluoride. The stoichiometry is consistent with reaction 3, which requires 2.25 moles

$$4PhOH + 5SiF_4 + 4Me_3N \rightarrow (PhO)_4Si + 4Me_3NH^+SiF_5^- \quad (3)$$

of silicon tetrafluoride, rather than reaction 2, which requires 1.35 moles of silicon tetrafluoride.

The insoluble salt isolated, postulated to be trimethylammonium pentafluorosilicate, formed trimethyammonium hexafluorosilicate according to eq 4 or 5.

$$2Me_3NH^+SiF_5^- \xrightarrow{1\text{ mm, }100\text{–}140^\circ} (Me_3NH^+)_2SiF_6^{2-} + SiF_4 \quad (4)$$

$$2Me_3NH^+SiF_5 \xrightarrow{H_2O\text{ (air)}} (Me_3NH^+)_2SiF_6^{2-} + SiO_2 + 4HF \quad (5)$$

Thus 4.3 g (0.0234 mole) of the salt postulated to be trimethylammonium pentafluorosilicate sublimed at reduced pressure at 100–140° to give 3.00 g (0.0115 mole) of trimethylammonium hexafluorosilicate. Leaving 4.5 g (0.0246 mole) of trimethylammonium pentafluorosilicate in air for 24 hr followed by sublimation gave 3.12 g (0.0120 mole) of trimethylammonium hexafluorosilicate sublimate and 0.95 g of silica residue. The salt did not decompose under vacuum at room temperature.

Nujol or halocarbon mulls prepared for infrared analysis in the drybox gave the spectrum of the postulated salt, trimethylammonium pentafluorosilicate, while mulls prepared in air gave the infrared spectrum of trimethylammonium hexafluorosilicate containing silica. The infrared spectra of the postulated trimethylammonium pentafluorosilicate and of trimethylammonium hexafluorosilicate are shown in Figure 1 from 830 to 660 cm^{-1}. This is the only region in the infrared from 5000 to 650 cm^{-1} for which they differ. The very strong absorption at 721 cm^{-1} in the region characteristic of the hexafluorosilicate anion[5] has been replaced by a very strong absorption at 779 cm^{-1} and a weaker absorption at 697 cm^{-1}. The recently reported tetraphenylarsonium pentafluorosilicate salt has strong infrared absorptions at 790 and 770 cm^{-1}. It was not possible to obtain F^{19} nmr spectra because the trimethylammonium pentafluorosilicate salt was not soluble without decomposition.

Because of the relatively poor stability of the salt, satisfactory analyses were not obtained. Analytical data indicated an atomic ratio of $NSiF_{4.4}$. Thus the salt had the 1:1 nitrogen to silicon ratio required for trimethylammonium pentafluorosilicate rather than the 2:1 ratio required for the hexafluorosilicate salt. The fluorine analysis is somewhat low. If some decomposition of the sample in transit occurred, loss of fluorine as the volatile HF would be expected while silicon would be retained.

The results reported above indicate the formation of a relatively unstable anion of either SiF_5^- or $Si_2F_{10}^{2-}$ (the latter formed by the sharing of an octahedral edge by SiF_6^{2-} and SiF_4, *i.e.*, the addition of silicon tetrafluoride to the hexafluorosilicate anion). The latter possibility is in accordance with the previously reported[6] solutions of composition $H_2SiF_6\cdot SiF_4$.

We believe that the infrared spectrum is more indicative of the SiF_5^- anion than of $Si_2F_{10}^{2-}$. An increase in infrared absorption frequency was found experimentally, as would be expected for the pentafluorosilicate anion as compared to the hexafluorosilicate anion (ref 5, p 2766). Very little difference in absorption frequency would be expected between the hexafluorosilicate anion and $Si_2F_{10}^{2-}$ since each species contains silicon–fluorine octaheda (ref 5, p 2763).

Although we do not favor the anion being formulated as $Si_2F_{10}^{2-}$, the formation of complex anions from the hexafluorosilicate anion deserves more attention in light of the recently reported complex anions $(BF_4\cdot BF_3)^-$[7,8] and $(SbF_6\cdot nSbF_5)^-$.[9,10] Thus from the re-

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sults reported with the tetrafluoroborate anion, hexafluorosilicate salts of large cations such as Bu_4N^+ might absorb silicon tetrafluoride to give complex fluorosilicate anions.

Further details of the dehydrofluorination reactions will be reported in subsequent articles.

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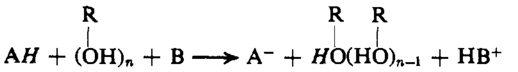
Higher-than-Termolecular Proton Transfer in Aqueous Solutions of Imidazole[1]

Sir:

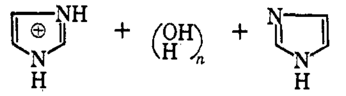
Three mechanisms for proton transfer are commonly recognized: direct bimolecular reaction of an acid with a base; termolecular reaction in which an acid donates a proton to a substrate while a base abstracts a (different) proton from the substrate; and, in hydroxylic solvents, acid–base reaction by a Grotthus mechanism such as (1), in which n solvent molecules participate.



$$AH + (\overset{R}{\overset{|}{O}}H)_n + B \longrightarrow A^- + H\overset{R}{\overset{|}{O}}(H\overset{R}{\overset{|}{O}})_{n-1} + HB^+$$ (1)

By means of nuclear magnetic resonance, it is possible to measure the rates of proton exchange resulting from (1) independently for the acid and the solvent, and thus to obtain directly the number, n, of solvent molecules.[2,3] This experiment has been tried on a number of systems. Examples are phenol (HA) and methoxide ion (B) in methanol (ROH); Me_3NH^+ and Me_3N in water; benzoic acid and benzoate ion in methanol; and phenol and phenoxide ion in water and methanol.[2–4] Up to now, all such *direct* measurements have led to the result that $n = 1$; that is, the reaction is termolecular.

At the same time, there is strong *indirect* evidence from reaction diameters and proton-exchange kinetics that certain very fast reactions, such as that of H_3O^+ with OH^- or Me_3N, or that of $H_2PO_4^-$ with HPO_4^{2-}, in water involve two or more water molecules.[5–7] We now wish to report a *direct measurement* in which $n > 1$. The reaction is that of imidazolium ion ([ImH+], HA in eq 1) with imidazole ([Im], B in eq 1) in water.



(2)

Rates (R_{NH}) of exchange of NH protons of imidazolium ion with OH protons of water were measured by nuclear magnetic spin–echo techniques, as described previously.[8] Rates (R_{OH}) of proton exchange of water molecules were measured in O^{17}-enriched water, as described by Luz and Meiboom.[3] The resulting rate laws are stated in eq 3–5. Results and standard errors

$$R_{NH} = k_2[ImH^+][Im] + 5.9 \times 10^3[ImH^+]$$
$$(pH\ 5.44\text{–}3.74,\ 25.0°,\ [ImH^+] = 0.07\ M) \quad (3)$$

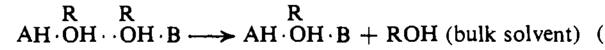
$$R_{OH} = k_2'[ImH^+][Im] + 3.3 \times 10^{11}[OH^-] + 3.3 \times 10^{11}[H^+] \quad (pH\ 6.587,\ 25.0°,\ [ImH^+] < 0.26\ M) \quad (4)$$

$$k_2' = nk_2 \quad (5)$$

at 25° are $k_2' = (1.52 \pm 0.15) \times 10^8\ sec^{-1}\ M^{-1}$; $k_2 = (1.07 \pm 0.11) \times 10^8\ sec^{-1}\ M^{-1}$; $n = 1.42 \pm 0.19$.[9]

The number, $n = 1.42$, must be interpreted as an *average*. Since direct bimolecular proton transfer contributes neither to R_{OH} nor to R_{OH}, the smallest value that n can take is unity. Hence, in (2), somewhat more than half of the individual events are termolecular, while the others are quadrimolecular or higher. If we arbitrarily rule out $n > 2$, then the fraction of $n = 1$ is 0.58 and that of $n = 2$ is 0.42.

We believe that the average value for n in reactions of the general type 1 is closely related to the strength of the hydrogen-bonded solvation complexes. Consider the conversion of the quadrimolecular to the termolecular encounter complex (eq 6). Of the two



$$AH\cdot\overset{R}{O}H\cdot\cdot\overset{R}{O}H\cdot B \longrightarrow AH\cdot\overset{R}{O}H\cdot B + ROH\ (\text{bulk solvent})$$ (6)

ROH molecules on the left, the one forming the weaker hydrogen bonds will diffuse out more rapidly, so that the rate of eq 6 will reflect largely the properties of that molecule. If the binding is strong, the rate is probably slower than that for diffusion of ROH in bulk solvent. At the same time, the strong binding will probably enhance the Boltzmann factors of those configurations that permit multiple proton transfers.

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[9] The following facts suggest that these standard errors are estimated conservatively. (a) In 11.47 mole % *t*-butyl alcohol–88.53 mole % water, an analogous set of experiments results in $n = 1.01 \pm 0.15$, showing that our method is capable of detecting a value of unity. (b) In eq 4, the contributions to R_{OH} from [OH−] and [H+] are in very good agreement with previous reports: S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961); A. Loewenstein and A. Szöke, *J. Am. Chem. Soc.*, **84**, 1151 (1962).

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Dielectric Measurements on Triethylamine–Iodine Complex

Sir:

The previous papers of Toyoda and Person[1] and of Kobinata and Nagakura[2] incited us to undertake measurements on triethylamine–iodine mixtures because the values of 11 and 12 D, obtained for the 1:1 complex, are not in good agreement with the values of 4 to 7 D measured on the other amine–iodine complexes.[1–4] Toyoda and others have used dioxane as the solvent because they noticed an instability of the solutions in heptane at the concentration used for dielectric measurements.

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