J. Phys. Chem. A **1999,** *103,* 5978−5982

Application of Hard−Soft Acid−Base Principle To Study Brönsted Acid Sites in Zeolite Clusters: A Quantum Chemical Study

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Received: October 29, 1998; In Final Form: May 11, 1999

The effect of isomorphous substitution of Si by Al, B, and Ga in the tetrahedral sites of a zeolite framework on the properties of Brönsted acid sites is investigated by computational techniques. We used the density functional theory (DFT) based acidity descriptor, "local softness", and a new acidity descriptor, "relative electrophilicity" to predict the acidity sequence of the zeolite clusters. The finite difference approximation is used to calculate local softness. The relative electrophilicity is found to be a suitable descriptor of acidity of zeolite clusters. The trend of acidity derived from local softness values depends on several factors such as basis sets, geometry of zeolite clusters, and different population analyses used to calculate them. The acidity trend derived from the relative electrophilicity follows the experimental trend, and it is not affected by the choice of basis sets or cluster models.

1. Introduction

In recent years, local softness and hardness parameters have been used as descriptors of reactivity. Global hardness, which was defined as the second derivative of energy with respect to the number of particles at constant temperature and external potential, and its inverse, global softness, are related to the stability of the systems.[1] The affinity of two systems to react has been proposed by Pearson,[2] and the principle of maximum hardness (PMH), proposed by Parr and Pearson and rigorously proved by Parr and Chattaraj,[3] relates the stability of the systems at constant chemical potential to chemical hardness. The PMH was tested by several authors using the ab initio, semiempirical, and density functional theoretic level.[4−6] However, to consider reactivity, a local quantity such as the Fukui function was first proposed by Parr and Yang[7] as a measure of reactivity. Local softness, which is related to the Fukui function, through a factor of global softness, is introduced as another measure of reactivity. The local hard−soft acid−base (HSAB) principle based on the polarizability originally proposed by Parr and Yang,[7] and proved by Gazquez and Mendez[8] recently, predicts the reactivity centers of two reactive systems on the basis of equal softness. Krishnamurty et al.[9] have shown the validity of the local HSAB principle in cases of interaction of small gaseous molecules with the zeolite surfaces. Fukui functions and local softness parameters have been used extensively in various studies quite successfully.[10−12] Very recently, a new scheme based on the relative electrophilicity and nucleophilicity has been proposed by Roy et al.[13] to explain the reactivity aspects of some carbonyl compounds such as aldehydes and ketones.

An important development for the design of new zeolites would be the ability to predict the stability of the lattice when substitution of different metals is made in place of silicon and how these modifications would influence the catalytic activity. Theoretical calculations, based on ab initio methods have been found to provide useful information about "structure−reactivity" relations in zeolites.[14−16] While the influence of zeolite composition and structure on acid strength has been studied by several theoretical calculations,[17−22] only a very few of these studies have used the local hardness and softness criteria for this purpose.[19,20] Langenaeker et al.[19] have studied the variation of the Fukui function with electronegativity in the neighborhood of the zeolite acid site. Recently, Geerlings and co-workers[20] investigated the problem of relative acidity of a dimer cluster $H_3Si{-}O(H){-}TH_3$ (where T = Al, Ga or B). The dimer cluster is a model prototype of zeolite (the simplest model for a zeolite unit). Geerlings and co-workers considered condensed local softness for nucleophilic attack at the bridging hydrogen atom, s_H^+, as a reactivity index, and they found that the acidity increases in the order $H_3Si{-}O(H){-}GaH_3 < H_3Si{-}O(H){-}BH_3 < H_3Si{-}O(H){-}AlH_3$. The experimental studies on the acidity or these systems predict that the acidity increases in the order: $H_3Si{-}O(H){-}BH_3 < H_3Si{-}O(H){-}GaH_3 < H_3Si{-}O(H){-}AlH_3$. The less accurate description of the acidity by local softness can be due to the choice of basis set, cluster model, or the population analysis used. In this work we have investigated this problem using local acidity parameters as well as the relative electrophilicity and nucleophilicity, which was proposed by Roy et al.[13] Effects of different cluster models and basis sets are studied. This paper is organized as follows: in section 2, we describe the theoretical aspects of the work. In section 3, we discuss the details of the systems and the computational aspects. In section 4, we present results and a discussion of the results obtained.

2. Theoretical Aspects

The global hardness is defined as the second derivative of the energy with respect to the number of particles for a given external potential.[1]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(\vec{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{\nu(\vec{r})} \qquad (1)$$

where E is the total energy, N is the number of electrons of a chemical species, and μ is the chemical potential. The corre-

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10.1021/jp984267k CCC: $18.00

sponding global softness is expressed in terms of the inverse of global hardness as

$$S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_{\nu(\vec{r})} = \left(\frac{\partial N}{\partial \mu}\right)_{\nu(\vec{r})} \qquad (2)$$

Although these quantities as well as the local quantities to be defined later are derived from density functional theoretical considerations, the finite difference approximation to these quantities are amenable to calculation using wave function based methods. By applying the finite difference approximation, we get well-known operational definitions of hardness and softness, as presented below.[1]

$$\eta = \frac{\mathrm{IP} - \mathrm{EA}}{2} \qquad (3)$$

$$S = \frac{1}{\mathrm{IP} - \mathrm{EA}} \qquad (4)$$

where IP and EA are the first vertical ionization potential and electron affinity of the species. The local softness $s(\vec{r})$ may be defined as

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_{\nu(\vec{r})} \qquad (5)$$

so that $\int s(\vec{r})\, d\vec{r} = S$ is satisfied.

Combining eqs 5 and 2 we can write

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{\nu(\vec{r})} \left(\frac{\partial N}{\partial \mu}\right)_{\nu(\vec{r})} = f(\vec{r}) S = \left(\frac{\partial \mu}{\partial \nu(\vec{r})}\right)_{N} \mathrm{S} \qquad (6)$$

where $f(\vec{r})$ is defined as the Fukui function by Parr and Yang.[7] $f(\vec{r})$ describes the sensitivity of the chemical potential to the local external perturbation at point r. From the definition of the local softness, one can infer that the local softness can also be used as a reactivity measure. A larger local softness indicates a greater reactivity. More recently, Gazquez and Mendez[8] have shown the possible existence of a Local HSAB principle, which states that the two systems react through centers, which have equal local softness.

As seen from eq 6, the definitions of $f(\vec{r})$ and $s(\vec{r})$ involve derivatives of $\rho(\vec{r})$ with respect to the number of electrons. A finite difference scheme can be used to define three different types of local quantities

$$s_k^{+} = [\rho_k(N_{\mathrm{O}} + 1) - \rho_k(N_{\mathrm{O}})]S$$

(suited for studies of nucleophilic attack) (7a)

$$s_k^{-} = [\rho_k(N_{\mathrm{O}}) - \rho_k(N_{\mathrm{O}} - 1)]S$$

(suited for studies of electrophilic attack) (7b)

$$s_k^{\mathrm{O}} = \frac{1}{2}[\rho_k(N_{\mathrm{O}} + 1) - \rho_k(N_{\mathrm{O}} - 1)]S$$

(suited for studies of radical attack) (7c)

where $\rho_k(N_{\mathrm{O}})$, $\rho_k(N_{\mathrm{O}} + 1)$, and $\rho_k(N_{\mathrm{O}} - 1)$ are the number of electrons on atom k for N_{O}, $(N_{\mathrm{O}} + 1)$, and $(N_{\mathrm{O}} - 1)$ electron systems. In ab initio calculations, these numbers are obtained most conventionally by a Mulliken or Löwdin type population analysis.

3. Computational Details

We took the Cartesian coordinates for the atoms in the zeolite model from the crystal structure of ZSM-5 reported by van Koningsveld.[23] There are 12 distinct tetrahedral sites in the asymmetric unit of ZSM-5, and there is no direct evidence to locate the site occupation of Al in this zeolite. However, the theoretical study[17] indicates that Al in zeolites favors sites with longer Si−O bond lengths and smaller Si−O−Si bond angles. Earlier quantum chemical calculations indicated that Si(2) and Si(12) are the likely sites for Al substitution.[24] Here, the Si(12) site is considered as a possible location for Al substitution since the Si(12)−O(24)−Si(12) bridge lies at the intersection of the straight and the zigzag channels, which allows significant interaction between the bridging hydroxyl and adsorbed molecules. Thus, due to the likelihood of it being the catalytically active site, we choose the Si(12) −O(24)−Si(12) bridge. We have terminated the zeolite cluster by hydrogen atoms. The terminating hydrogens are positioned on the vector from the silicon to oxygen. It contains the essential structural elements of several types of zeolites, molecular sieves, and clay materials. To study the change in acidity of bridging hydroxyl groups when Si is isomorphously substituted by various other elements such as Al, B, and Ga, we consider cluster models as described below. We study the properties of a bridging hydroxyl group in aluminosilicate using a cluster model: $H_3Si{-}O(H){-}AlH_3$. The borosilicate and gallosilicates are represented by $H_3Si{-}O(H){-}BH_3$ and $H_3Si{-}O(H){-}GaH_3$, respectively. The zeolite cluster chosen for this study is shown in Figure 1.

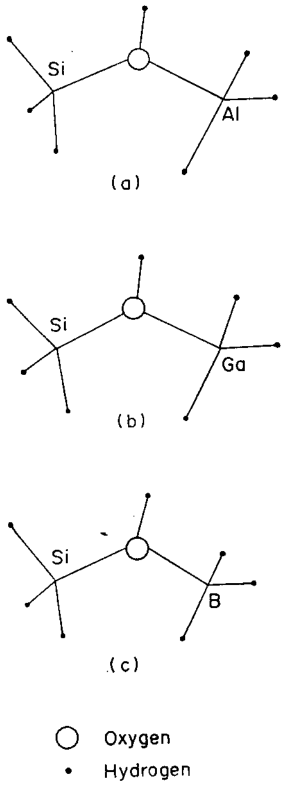

Figure 1. Geometry of the cluster model used to study the influence of chemical composition on the acidic properties. The geometries of these clusters were optimized using 3-21G and DZV basis sets. The properties calculated for optimized clusters are given in Tables 1 and 2. In the rigid cluster models only the central part of the clusters was optimized. The properties calculated for the rigid cluster models are given in Tables 3 and 4.

Initially, we fully optimized each of the cluster models at the Hartree−Fock level with 3-21G and DZV basis sets to determine the dependence of the predicted acidity order on the basis sets. The failure of local softness values calculated using the 3-21G basis set (Table 1) to predict the experimental acidity trend led us to fix some of the geometric parameters. We used

TABLE 1: Calculated Values of the Reactivity Parameters in Atomic Units of the Bridging Hydroxyl Group for the Optimized Models Using the 3-21G Basis Set

		Mulliken				Löwdin			
cluster	r_{OH} (Å)	q_H	$\|q_H q_O\|$	s_H^+	s_H^+/s_H^-	q_H	$\|q_H q_O\|$	s_H^+	s_H^+/s_H^-
(Al, Si)	0.966	0.470 643	0.439 278	0.185 727	3.542 694	0.324 956	0.173 958	0.139 405	3.946 190
(Ga, Si)	0.965	0.469 054	0.434 273	0.164 915	2.926 748	0.322 635	0.172 575	0.132 217	3.432 370
(B, Si)	0.963	0.466 571	0.403 201	0.179 575	2.020 513	0.322 497	0.139 591	0.129 065	2.112 555

TABLE 2: Calculated Values of the Reactivity Parameters in Atomic Units of the Bridging Hydroxyl Group for the Optimized Models Using the DZV Basis Set

		Mulliken				Löwdin			
cluster	r_{OH} (Å)	q_H	$\|q_H q_O\|$	s_H^+	s_H^+/s_H^-	q_H	$\|q_H q_O\|$	s_H^+	s_H^+/s_H^-
(Al, Si)	0.953	0.496 857	0.569 848	0.231 748	3.847 141	0.365 302	0.291 925	0.148 074	4.721 028
(Ga, Si)	0.952	0.489 078	0.543 570	0.206 353	2.918 318	0.362 507	0.285 561	0.136 941	3.634 219
(B, Si)	0.949	0.487 432	0.494 525	0.198 103	2.263 928	0.364 225	0.252 845	0.119 650	2.449 620

the rigid cluster models where we fixed the H−T−H bond angle and H−T−O−H dihedral angle (T = Si, Al, Ga and B) at their crystallographic values. We optimized the H−T and O−H bond distances and the central bridge in the models that include T−O−T and T−O−H bond angles.

As mentioned earlier, all the calculations were performed at the ab initio Hartree−Fock level. Since all the neutral systems considered in this study are closed shell systems, the restricted Hartree−Fock (RHF) method has been used for them. For the anionic and cationic systems we used the restricted open shell Hartree−Fock (ROHF) and calculations were carried out for the optimized geometry obtained for the neutral cluster models in order to satisfy the finite difference approximation. The ab initio calculations were done with the system of computer programs GAMESS.[25] The acidity parameters calculated in this study are charge on the H atom of the bridging hydroxyl group (q_H), O−H bond length (r_{OH}), ionicity of the O−H bond ($|q_O q_H|$), local softness (s_H^+), and the relative electrophilicity (s_H^+/s_H^-).

4. Results and Discussion

Ab initio quantum chemical calculations on zeolite cluster models have a number of problems in representing the zeolite. These include (i) the choice of the cluster, (ii) the termination of the cluster for charge neutrality, and (iii) the relaxation of the cluster models. It has been shown[26] that the proton affinity at the hydroxyl site is sensitive to the size of the clusters. Termination of the cluster with OH groups increased the proton affinity, while termination with SiH_3 decreased the proton affinity. It has also been suggested by natural bond orbitals (NBO) bond dipole analysis[27−29] that the electrostatic potentials of the Si−O−H oxygens are unrealistically large.[26] In this paper we have terminated the zeolite clusters with hydrogen. In general, relaxation of geometry is necessary for an accurate quantitative calculation of acidic properties of zeolites by ab initio methods. However, Sauer has pointed out that the full relaxation of aluminosilicate clusters can lead to structures that do not resemble experimental zeolite geometries.[30] Therefore, considerable care is needed in implementing relaxation of clusters that mimic the zeolite framework. Classical mechanics calculations use force fields and have successfully predicted structures and properties of a variety of silicates and zeolites by means of a lattice-energy minimization scheme.[21,22] In this work, we have compared the results of the cluster models whose geometries are fully optimized with those where the relaxation of the central Si−O(H)−T bridge is carried out but where the locations of peripheral hydrogens are held fixed. The zeolite clusters $H_3Si-O(H)-AlH_3$, $H_3Si-O(H)-GaH_3$, and $H_3Si-O(H)-BH_3$ are denoted by (Al, Si), (Ga, Si), and (B, Si), respectively.

Dependence of Acidity Parameters on Cluster Geometry. *1. Optimized Clusters*. Table 1 contains the acidity parameters of the fully optimized zeolite cluster models calculated using the 3-21G basis set. The local softness values are given only for the bridging H atom obtained through both the Mulliken and Löwdin population analyses. The values of the charge on the bridging H atom, q_H, indicate that the generated sequence of increasing acidity is (Al, Si) > (Ga, Si) > (B, Si). The values of the OH bond length, r_{OH}, the longer value of which is an indicator of a weaker bond, and therefore of a higher acidity of the hydroxyl group, are also in perfect agreement with experimental data.[31] The same conclusions could be arrived by considering $|q_H q_O|$, which is a measure of the ionicity of the O−H bond.

However, local softness (s_H^+) values calculated using the Mulliken population are in the order (Al, Si) > (B, Si) > (Ga, Si), which is not in agreement with the experiment. The disagreement may be due to the use of a smaller basis set. The size and shape of the cluster model also influence the local softness values. It has been shown by Roy et al.[13] that the relative electrophilicity (s_H^+/s_H^-), which is defined as the ratio of local softness for nucleophilic attack to the local softness for electrophilic attack on the system, is a good parameter to locate reactive sites. It is seen from Table 1 that the ratio of s_H^+/s_H^-, which involves two differences of electron densities of systems differing by 1 in the number of electrons at constant nuclear framework, is in excellent agreement with the experimental acidity order. The bridging H atom having the highest s_H^+/s_H^- is the most acidic.[13] The s_H^+/s_H^- value for all the bridging H atoms of the three clusters are presented in Table 1. Comparing the clusters with different T atoms, it is seen that the new parameter, the relative electrophilicity (s_H^+/s_H^-), is a good indicator of acidity. The acidity of a system increases with the increase of s_H^+/s_H^- ratios. All the acidity parameters calculated using Löwdin population are in agreement with the experimental trend.

Since the local softness values calculated using the Mulliken population from 3 to the 21G basis set did not agree with the experimental trend, we calculated all the acidity parameters mentioned above using DZV basis set, and these values are given in Table 2. The calculated O−H, $|q_H q_O|$, s_H^+, and s_H^+/s_H^- are in good agreement with the experimental values. But the q_H values calculated using the Löwdin population did not follow the acidity trend. These results indicate that the acidity sequence derived using local softness or local charge depends on the population analysis used. However, the acidity trend

TABLE 3: Calculated Values of the Reactivity Parameters in Atomic Units of the Bridging Hydroxyl Group for the Rigid Models Using the 3-21G Basis Set

		Mulliken				Löwdin			
cluster	r_{OH} (Å)	q_H	$\|q_Hq_O\|$	s_H^+	s_H^+/s_H^-	q_H	$\|q_Hq_O\|$	s_H^+	s_H^+/s_H^-
(Al, Si)	0.974	0.469 906	0.425 363	0.199 799	5.064 311	0.323 501	0.167 769	0.165 631	6.508 029
(Ga, Si)	0.972	0.470 955	0.423 565	0.176 264	4.310 651	0.322 451	0.166 669	0.156 853	5.764 812
(B, Si)	0.970	0.469 931	0.390 794	0.182 290	2.465 234	0.326 699	0.135 673	0.135 897	2.465 234

TABLE 4: Calculated Values of the Reactivity Parameters in Atomic Units of the Bridging Hydroxyl Group for the Rigid Models Using the DZV Basis Set

		Mulliken				Löwdin			
cluster	r_{OH} (Å)	q_H	$\|q_Hq_O\|$	s_H^+	s_H^+/s_H^-	q_H	$\|q_Hq_O\|$	s_H^+	s_H^+/s_H^-
(Al, Si)	0.955	0.510 619	0.593 253	0.312 512	4.380 090	0.375 091	0.297 357	0.198 565	5.133 553
(Ga, Si)	0.953	0.501 871	0.564 894	0.291 608	4.134 760	0.370 459	0.288 029	0.187 405	4.134 760
(B, Si)	0.950	0.500 703	0.502 754	0.246 822	2.817 605	0.373 028	0.247 513	0.145 073	2.885 920

TABLE 5: Geometry of the Central Si−O(H$_b$)−T (T = Al, Ga, B) Part, the Local Softness, and Relative Electrophilicity Values for the Bridging Hydrogen Atom of the Trimer Cluster

cluster	Si−O(H$_b$) bond length (Å)	T−O(H$_b$) bond length (Å)	O−H$_b$ bond length (Å)	Si−O(H$_b$)−T bond angle (deg)	s_H^+ (au)	s_H^+/s_H^-
(Al, Si)	1.733	1.910	0.968	126.03	0.066 350	1.209 674
(Ga, Si)	1.729	1.934	0.966	123.57	0.064 488	1.084 039
(B, Si)	1.720	1.695	0.964	121.95	0.042 554	0.438 399

TABLE 6: Calculated Values of Local Softness and Relative Electrophilicity in Atomic Units for the Bridging Hydrogen Atom of the (Al, Si) Dimer Cluster at Various Geometries Using the 3-21G Basis Set

local softness parameters	Si−O−Al bond angles (deg)				Si−O bond lengths (Å)				Al−O bond lengths (Å)			
	125	130	135	140	1.735	1.835	1.935	2.035	1.922	2.022	2.122	2.222
s_H^+	0.185 91	0.184 66	0.183 43	0.181 98	0.185 73	0.195 60	0.219 48	0.239 06	0.185 73	0.190 90	0.189 51	0.189 53
s_H^+/s_H^-	3.555 95	4.184 67	5.232 41	7.240 90	3.542 69	3.777 81	3.799 14	3.900 13	3.542 69	3.731 93	4.064 75	4.200 03

derived using the relative electrophilicity values remains unchanged even if we use a different population analysis.

2. Rigid Clusters. Since the fully relaxed, $H_3Si-O(H)-TH_3$ (T = Al, Ga, B) cluster models neither belong to any particular type of zeolite nor reflect the actual experimental situation, we imposed some constraints in the cluster models to mimic the experimental geometry. The acidity parameters for these clusters calculated by 3-21G and DZV basis sets are given in Table 3 and Table 4, respectively. The q_H and the s_H^+ values calculated from the Mulliken population using the 3-21G basis set do not agree with the experimental trend. The q_H values calculated from Löwdin population also do not follow the experimental trend. As an increasing value of s_H^+/s_H^- is an indication for a higher acidity of the bridging hydroxyl group, the following sequence of s_H^+/s_H^- is generated by this property: (Al, Si) > (Ga, Si) > (B, Si), which is in perfect agreement with experimental data. The other acidity parameters (Table 4), q_H and $|q_Hq_O|$, calculated for the same cluster using the DZV basis set and Mulliken population are also in agreement with experimental data. However, q_H values from the Löwdin population do not follow the experimental trend. We have compared the s_H^+ as well as s_H^+/s_H^- with the experimental ν(O−H). The experimental vibrational frequencies of H[Al]-, H[Ga]- and H[B]-ZSM-5 are characterized by well-defined ν(O−H) bands at 3610, 3620, and 3725 cm^{-1} respectively. In each case (Tables 1−4) the trend of s_H^+/s_H^- agrees with the trend of ν(O−H), while the trend of s_H^+ does not agree with the experimental trend of ν(O−H) in the 3-21G basis for both rigid as well as fully optimized cluster models. We have also optimized one unit cell of ZSM-5 zeolite using the lattice energy minimization method[32] and generated a larger cluster model, namely a trimer cluster. As the potential parameters are not available for Ga and B, we optimized the central Si−O$_b$(H)−T part of the cluster by quantum mechanical method using the 3-21G basis set. Table 5 shows the geometry of Si−O$_b$(H)−T units and the calculated local softness values for the bridging hydrogen atom of trimer clusters. It is seen from Table 5 that the local softness values and the relative electrophilicity values for the bridging hydroxyl group agree with the experimental acidity sequence. Thus, the trend of acidity derived from relative electrophilicity (s_H^+/s_H^-) does not change with the cluster size.

These results again indicate that the q_H values are sensitive to the basis set, geometry of the zeolite cluster, and the population analysis used. So, it is difficult to derive an acidity sequence from q_H as well as from s_H^+ values. On the other hand we observed that s_H^+/s_H^- is a good index to obtain the acidity sequence in accord with the experimental data.

3. Variation of Softness Parameters with Local Geometry. To find the relation of local softness parameters with the local geometry, we studied the dimer cluster model $H_3Si-O(H)-AlH_3$. Starting from the fully optimized cluster, we varied the Si−O−Al bond angle and Si−O and Al−O bond distances separately. The results of local softness and relative electrophilicity are presented in Table 6. s_H^+/s_H^-, being a ratio, changes more compared to the s_H^+ values. As the bond angle and the bond lengths are stretched monotonically, the values of s_H^+/s_H^- reflect this monotonic change. However, with respect to the changes of bond angle and Al−O bond length, this pattern is absent for s_H^+ values. We conclude that the ratio, the relative electrophilicity, is a more reliable indicator of a change of local geometry.

5. Conclusion

In this study, we have used the relative electrophilicity of the bridging hydrogen atom of a zeolite dimer cluster as the acidity parameter. Local softness values do not always follow the experimental acidity sequence, as it depends on basis sets, zeolite cluster model, and different population analyses used to calculate them. q_H values are also found to depend on the population analysis used. The relative electrophilicity s_H^+/s_H^- provides the correct experimental acidity sequence, and the acidity trend does not vary from basis set to basis set. These results were confirmed by using a larger cluster model. The relation of local softness parameters with the local geometry was observed.

Acknowledgment. R.C.D. thanks the Council of Scientific and Industrial Research, New Delhi, for financial support in the form of a Senior Research Fellowship.

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