

A Quantum Chemical Interpretation of the Enhanced Acidity of Halogenated Silica Gel

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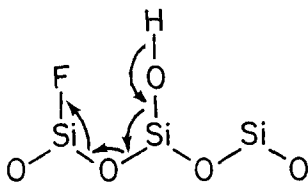
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An electronic state in halogenated silica gel was quantum chemically investigated to elucidate the mechanism of the enhancement of acidity. A semi-empirical SCF-MO calculation was carried out by using the parametrization of CNDO type proposed by Höjer and Meza [*Acta Chem. Scand.* 26, 3723 (1972)]. $(\text{OH})_3\text{Si}-\text{O}-\text{Si}(\text{OH})_2\text{X}$ ($\text{X} = \text{OH}, \text{F}, \text{Cl}, \text{and Br}$) (I) was used as a model of halogenated silica. Electron density of hydrogen and covalent bonding energy ($E_{\text{OH}}^{\text{CO}}$) of a hydroxyl group was calculated for (I) and also the compounds which were coordinated by ammonia (II). The above quantities decreased in the order $\text{X} = \text{OH} > \text{F} > \text{Br} \gtrsim \text{Cl}$, and this trend was consistent with the experimental acidity trend and more clear in (II) than (I). Bond orders between hydrogen and halogen, and $E_{\text{HX}}^{\text{CO}}$ showed the presence of a bonding interaction between hydrogen and halogen. The extent of the interaction in (II) increased in the order $\text{OH} \lesssim \text{F} < \text{Br} < \text{Cl}$. These results indicated that the bonding interaction between the hydrogen of the OH group and halogen was essential to the enhancement of acidity by halogenation of silica gel.

INTRODUCTION

Silica gel shows very weak acidity, but partial exchange of hydroxy groups on a silica surface with halogen remarkably enhances acidity. Chapman (1) proposed a mechanism for the generation of the strong acidity in which an electron shift in the neighboring atoms, induced by the large electronegativity of fluorine, contributed to weakening the OH bond and to an increase in the surface acidity.



We had investigated the acidity of halogenated silica gels which were prepared by treatment with ammonium halides

$(\text{NH}_4\text{X}, \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I})$. Figure 1 shows the regional acidity in a given region of acid strength (2). If we define an average acid strength by an equation:

$$p\bar{K}_a = \frac{\sum n_i pK_{a_i}}{\sum n_i}, \quad (5)$$

where n_i is the number of acid sites (mmole/g) with acid strength of pK_{a_i} , the following values for $p\bar{K}_a$ are obtained; ~ 3 (OH), 1.1 (F), 0.58 (I), -0.95 (Br), -1.8 (Cl). This order of the acid strength is not consistent with that expected from the electronegativities of the halogens. This result suggested that the most important factor for enhancement of acidity is a direct interaction between halogen atoms and hydrogen atoms of silanol groups (3). In this work, a semi-empirical SCF-MO calculation has been carried out to elucidate

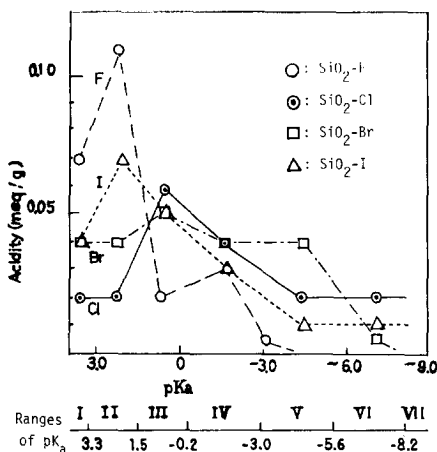


FIG. 1. Regional acidity of halogenated silica gels. Each point shows the number of acid sites (mmole/g) with an acid strength in the region which is given above abscissa.

the mechanism of the enhancement of acidity in halogenated silica gel.

METHOD OF CALCULATION

Nonempirical SCF-MO method is desirable in principle, but as the order of approximation in modeling of silica gel is very high, as mentioned later, a semi-empirical SCF-MO method, CNDO type, is suitable for the present cases. The CNDO method is only applicable to molecules containing first and second row atoms (4), but recently Höjer and Meza (5) proposed parameters necessary for calculation of molecules containing third row atoms by the CNDO method. This modified CNDO method gives satisfactory results for binding energies, dipole moments and ionization potentials of many molecules. In this work, we used the modified CNDO method.

RESULTS

Applicability of the Modified CNDO Method for Silanol Compounds

For the purpose of examining the applicability of the CNDO method, MO calculations were carried out with *p*-X-phenyl dimethyl silanols (X = H, F, Cl, Br).

Atom configurations in the silanol molecules were determined from the data compiled by Sutton (6).

Electron density at the hydrogen atom on a silanol group (P_H), bond order of the OH bond (q_{OH}) and two more indices (E_{OH} , E_{OH}^{CO}) defined by Eq. (2) were calculated.

$$\begin{aligned}
 E_{AB} &= \sum_s^A \sum_t^B \{P_{ss}P_{tt}\gamma_{AB}^{st} \\
 &\quad - (P_{ss}n_{Bt} + P_{tt}n_{As})\gamma_{AB}^{st}\} + \frac{Z_A Z_B}{R_{AB}} \\
 &\quad + \sum_{\mu}^A \sum_{\nu}^B (2P_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2\gamma_{AB}), \quad (2)
 \end{aligned}$$

$$E_{AB}^{CO}$$

$$= \sum_{\mu}^A \sum_{\nu}^B (2P_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2\gamma_{AB}),$$

AB stands for OH.

E_{OH} is an index which manifests the contribution of the OH pair to total

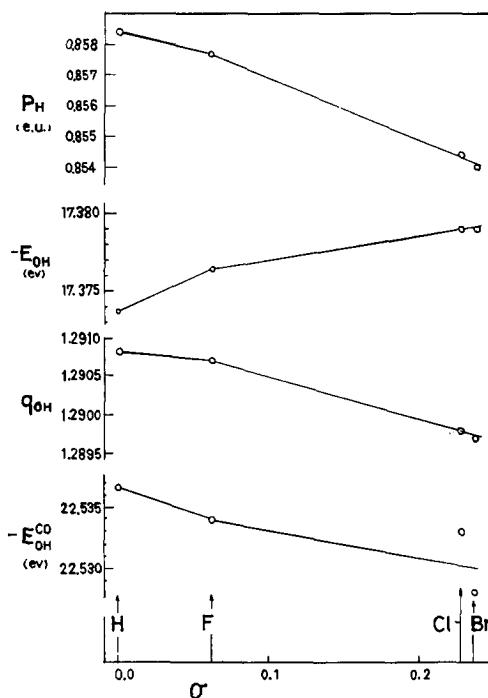


FIG. 2. Indices of silanols.

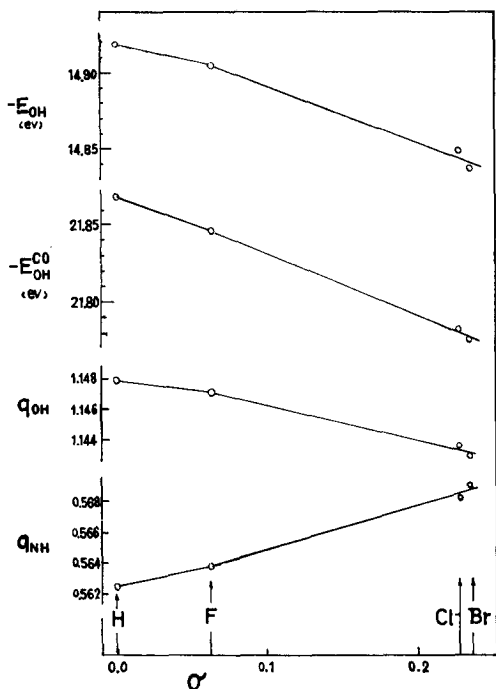


FIG. 3. Indices of silanols coordinated by NH_3 .

electron energy. E_{OH}^{CO} is the last term in Eq. (2) and can be regarded as a measure of the covalent bonding energy of OH bond (7). As shown in Fig. 2, the calculated indices (P_H , q_{OH} , E_{OH}^{CO}) other than E_{OH} decreased with increasing Hammett σ constant. These correlations of P_H , q_{OH} and E_{OH}^{CO} with σ were consistent with the experimental results that pK_a of these silanols decreased linearly with increasing σ of the substituent groups (8).

Next, similar indices were calculated for a complex in which an ammonia molecule coordinated to the silanol group. The complex can be regarded as a model of a silanol compound in a basic solvent. The

calculated results are shown in Fig. 3. q_{NH} stands for the bond order between the N atom of NH_3 and the H atom of an OH group.

That the coordination of ammonia to the H atom of an OH group results in the considerable decrease in the covalent bonding energy of the OH group, was reflected in q_{OH} , q_{NH} , E_{OH}^{CO} and also E_{OH} in this case.

From the above results, we think that the CNDO method modified by Höjer and Meza is useful for the investigation of the acid nature of silanol compounds and that E_{OH}^{CO} is the most appropriate index to estimate the acid strength.

Acidity of Halogenated Silica Gel

A surface OH group of silica gel is influenced by all other atoms in the gigantic molecule, but it is impossible to take up all atoms in a CNDO calculation. As the aim of this work is an investigation of interaction between adjacent silanol groups, we think the essential feature of the interaction could be inferred by the calculation for a small part of silica gel. Models in Fig. 4 were adopted for the purpose. The relative configuration of silicon and oxygen atoms was determined from the crystal structure of α -quartz ($R_{Si-O} = 1.61 \text{ \AA}$, $\angle Si-O-Si = 142^\circ$, $\angle O-Si-O = 110^\circ$). Internuclear distances between silicon and substituent X_s were 1.61 \AA for O, 1.59 \AA for F, 2.01 \AA for Cl and 2.16 \AA for Br. In the surface silanol group represented by $Si^1-O^5-H^6$ in Fig. 4, the bond angle ($\angle Si-O-H = 104^\circ 27'$) was estimated as the same as $\angle H-O-H$ in H_2O , while the bond distance ($R_{OH} = 1.181 \text{ \AA}$) was adopted because R_{OH}

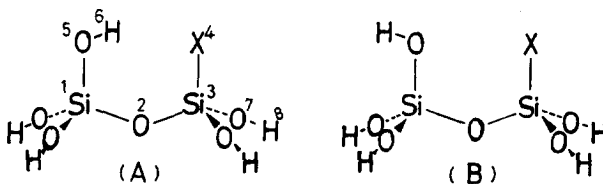


FIG. 4. The models of halogenated silica gel.

$= 0.97 \text{ \AA}$ (bond distance in H_2O) brought about the divergence in the SCF calculations in some cases. It was ascertained that this small difference in R_{OH} had little effect on total electron energy. Hydrogen atoms such as H^8 were introduced for the remainder of the rest of the silica gel. This technique has been found as a good approximation in the case of the V_2O_5 crystal (9).

SCF-MO calculations were carried out for models A and B with $\text{X} = \text{OH}, \text{F}, \text{Cl}$ and Br . In model B, H^6 was rotated by 180° to the Si-O axis. Electron densities at H^6 and X^4 , $E_{\text{OH}}^{\text{CO}}$ of surface OH group and $E_{\text{HX}}^{\text{CO}}$ between H^6 and X^4 were calculated. These values were plotted to average acid strength $p\bar{K}_a$ which is defined by Eq. (1) (Fig. 5). The calculated values of $E_{\text{HX}}^{\text{CO}}$ (less than 0.03 eV for all X_s) indicated clearly that a direct interaction between surface OH and X is small enough to be neglected. Acidity indices, P_{H^6} and $-E_{\text{O}^5\text{H}^6}^{\text{CO}}$, decreased in the order $\text{OH} > \text{F} > \text{Br} > \text{Cl}$, but the difference was very small. On the other hand, $-E_{\text{H}^6\text{X}^4}^{\text{CO}}$ values were 0.54–1.63 for the model A, and the change of the acidity indices by X is obvious. It should be noted that a large difference of indices was obtained between F and Br (or Cl), which was consistent with the experimental results in Fig. 1.

Electron density P_{X} can be a measure of electron shift effects. The value decreased in the order $\text{Cl} > \text{Br} > \text{F} > \text{OH}$ in both models, and configuration of H^6 had little effect on it.

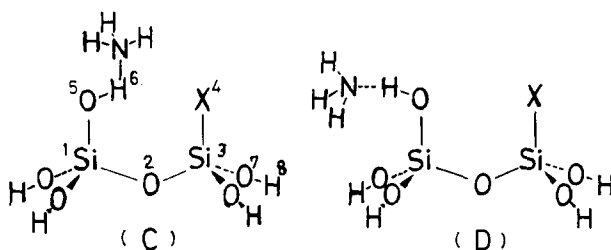


FIG. 6. The models of halogenated silica gel coordinated by NH_3 .

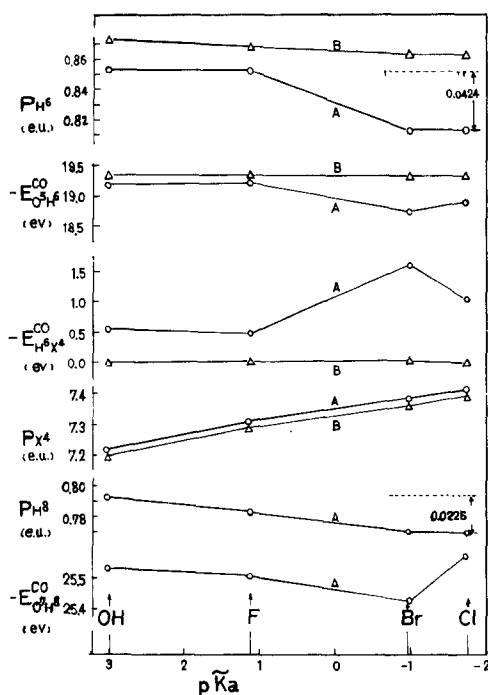


FIG. 5. Acidity indices of halogenated silica gels. A and B show the calculated values for the models A and B, respectively.

Influence by Coordination of Ammonia

Solid acidity has been usually measured by a titration method. A titrant such as *n*-butylamine is adsorbed on the surface, and the color of an indicator changes at the neutral point. Therefore, A and B models are not relevant for models absorbing basic compounds. In fact, change of acidity indices of *p*-substituted halo-phenyl dimethyl silanols by halogens became more

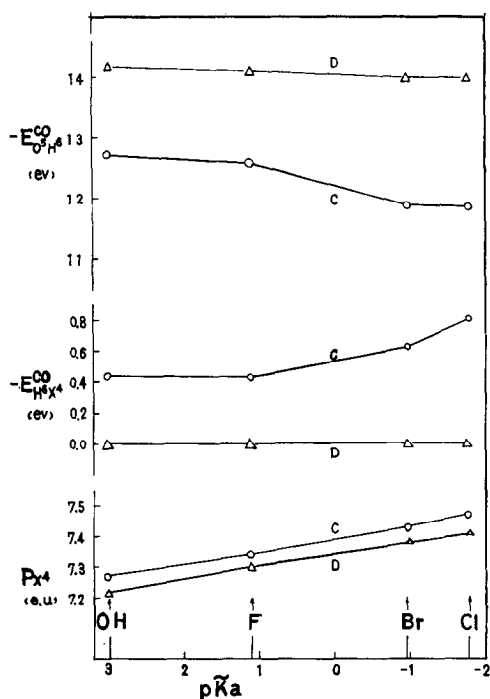


FIG. 7. Acidity indices of silica gels coordinated by NH_3 . C and D show the calculated values for the models C and D, respectively.

clear by coordination of ammonia. A similar effect is expected in the case of halogenated silica gels.

In the models in Fig. 6, an ammonia molecule is attached to a silanol group, and the distance between H and N was taken as same as in an NH_4^+ ion. The calculated results for this model are shown in Fig. 7. In this case the hydrogen atom of the OH group interacts with NH_3 as in NH_4^+ ion, an electron density at the hydrogen atom can not be an index of

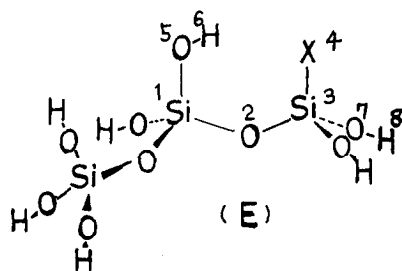


FIG. 8. The modified model of halogenated silica gel.

TABLE I
Comparison of Model A and Model E

Indices	Atom or atom pair	Model A	Model E
E_{AB} (eV)	$\text{O}^5\text{-H}^6$	-16.499	-16.485
	$\text{O}^7\text{-H}^8$	-18.543	-18.543
	$\text{H}^6\text{-F}$	-0.695	-0.683
Bond order	$\text{O}^5\text{-H}^6$	1.406	1.411
	$\text{H}^6\text{-F}$	0.157	0.156
Electron density (e.u.)	F	7.306	7.306
	H^6	0.856	0.856
	$\text{O}^7 + \text{H}^8$	7.274	7.275

acidity. $E_{\text{OH}}^{\text{CO}}$, on the other hand, is a measure of bonding energy and can be used as an index of acidity. As expected, the extent of the change of $E_{\text{OH}}^{\text{CO}}$ is much more clear than that in Fig. 5. Covalent bonding energy between H and X, $E_{\text{HX}}^{\text{CO}}$, was similar as in Fig. 5 and varied in the same order as acid strength ($\text{OH} < \text{F} < \text{Br} < \text{Cl}$) in the case of model C. Electron density at X showed the same trend as in Fig. 5.

DISCUSSION

Models

The calculation method proposed by Höjer and Meza was found to be useful to explain the acid nature of silanol molecules, but there is no theoretical background to support its applicability to silica gels. The present results, that the calculation reproduced the experimental tendency in the change of Brønsted acidity by halogen substitution, indicates that the method is also applicable to silica gel. Models shown in Figs. 4 and 6 are very simple because these contain only two silicon atoms, and the other part of crystal is replaced by four hydrogen atoms. The possibility that the simplification in models exerts an essential influence on the acid nature was not confirmed by a calculation for a model which contained three silicon atoms. The model E in Fig. 8 is obtained by replace-

ment of a hydrogen atom in model A with a Si(OH)₃ group. In the case of X = F, the calculated values of indices are compared with those for model A in Table 1. It is obvious that electron densities, E_{AB} values and bond orders for the parts concerned with solid acidity are almost the same in both models, and no significant influence can be observed by the addition of Si(OH)₃ group. Hence, the simple models A, B, C and D can be regarded as adequate for discussion of the solid acidity.

Electron Shift Effect

On the basis of the hypothesis proposed by Chapman (1), it is expected that acid strength changes parallel to electron density at X. In our calculations, the electron density at X changed in the order OH < F < Br < Cl, as shown in Figs. 5 and 7, which is the same order as acid strength, supporting the Chapman's hypothesis. However, the difference in electron densities at X between model A and B, or between model C and D, was considerably smaller than that of acidity indices. Furthermore, change of acidity indices by X in models B and D was small.

Further, in our models, hydrogen atoms (e.g., H⁸) are placed for a approximate representation of the other part of crystal. This kind of OH group on silicon atom to which a halogen atom attaches may exist in a peculiar region such as crystal edge and behave as acid points. As the OH groups locate near X, the electron shift effect is expected to be significant, but the results in Fig. 5 indicate that in model B changes in electron density at H⁸ (P_{H^8}) and covalent bonding energy ($E_{O^*H^8CO}$) by X are smaller than those in P_{H^6} and $E_{O^*H^6CO}$. These results suggests that the electron shift effect is not a predominant factor for generating strong acidity.

Mechanism of Generation of Strong Acidity

The difference between models A and B, or between model C and D, is that a surface

OH group is rotated by 180° to the Si-O axis and there is little interaction between the hydrogen atom and X in models B and D. E_{HX}^{CO} can be regarded as a measure of the interaction, as was shown in Figs. 5 and 7. A close correlation was observed between E_{HX}^{CO} and acidity indices especially in compounds coordinated by ammonia. $E_{H^8X}^{CO}$ is less than 0.03 eV in all cases, and hence acidity change at H⁸ can not be the result of the interaction between H⁸ and X⁴.

The results obtained here support our previous hypothesis that the generation of strong acidity in halogenated silica gel is resulted of the interaction of surface OH groups and halogens adjacent to them. Electron shift effects should be included as a minor factor.

ACKNOWLEDGMENTS

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