

## Base-Strength Distribution Studies of Solid-Base Surfaces

JUN-ICHIRO TAKE, NOBUJI KIKUCHI,\* AND YUKIO YONEDA

*Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo,  
Bunkyo-ku, Tokyo, Japan*

Received June 9, 1970

A method has been developed for the determination of the base-strength distribution of solid surfaces. The present method consists of the titration of solids suspended in cyclohexane with benzoic acid, using a series of  $H_-$  indicators. The base-strength distribution of solid surfaces has been measured by this method for alkaline-earth oxides and some other solid bases. Alkaline-earth oxides increased remarkably in base strength upon heat treatment in vacuum. The base strength of these oxides proved to decrease in the order  $SrO(H_- \geq 26.5) \approx CaO(H_- \geq 26.5) > MgO(H_- = 18.4 \text{ to } 26.5)$ , in accordance with the observation by Krylov *et al.* and also with the order expected from the partial negative charge of combined oxygen anions in these oxide surfaces. A distinct distribution of base strength was observed on these oxide surfaces. No basic sites having an  $H_-$  equal to or higher than 12.2 were observed on the surfaces of  $ZnO$ ,  $ZrO_2$ ,  $ThO_2$ , or  $Na_2CO_3$ . The catalytic activity and selectivity of alkaline-earth oxides in the elimination of hydrogen chloride from 1,1,2-trichloroethane were quantitatively interpreted from the observed base-strength distribution.

### INTRODUCTION

A number of researchers have measured the acid strength and acid content of solid-acid surfaces in order to interpret the catalytic properties of solid acids. However, little attention has been devoted to the measurement of either the base content or the base strength of solid-base surfaces. The base contents of magnesia, calcium oxide, and some other solid bases were determined by the titration of the solids suspended in benzene with benzoic acid, using bromothymol blue as the indicator (1), as well as from the amount of adsorption of phenol vapor on the solids (2). The base strength of silica gels impregnated with sodium hydroxide (3) and of magnesia (4) were determined from the color changes of phenolphthalein and bromothymol blue adsorbed on the solids in a nonpolar sol-

vent. The relative base strength of solid bases such as magnesia and calcium oxide was also qualitatively determined from the adsorption power of the solids for phenol vapor (2). However, these measurements are not satisfactory from the viewpoint of base-strength distribution because of the scantiness of the indicators employed.

Quantitative information on the base-strength distribution of solid-base surfaces are essential for studies of solid-base catalysis. The present study was undertaken in order to obtain such information.

According to the Brönsted concept, the base strength of a solid surface is defined as its proton-accepting ability and is quantitatively expressed by the Hammett and Deyrup  $H_-$  function (5) after the analogy of acid strength by the  $H_0$  function:

$$BH = B^- + H^+ \quad (1)$$

$$H_- = -\log a_{H^+} f_{B^-} / f_{BH} \\ = pK_{BH} - \log C_{BH} / C_{B^-} \quad (2)$$

where  $a_{H^+}$  is the activity of the proton ad-

\* Present address: Central Research Laboratory, Mitsubishi Chemical Industry, Kawasaki, Kanagawa, Japan.

sorbed on the surface and  $f$  and  $C$  are the activity coefficient and the concentration of an adsorbed indicator, respectively. Equation (2) means that the base strength of solid surfaces increases with an increase in  $H_-$ . The  $H_-$  values of a variety of basic solutions and the  $pK_{BH}$  values of  $H_-$  indicators have been reviewed recently by Bowden (6) and Rochester (7).

As the first step, the base strength of a variety of basic solids was measured from the color changes of a series of  $H_-$  indicators adsorbed on the solids. Next, the base-strength distribution of alkaline-earth oxides and some other solid bases was measured by the titration of above materials suspended in cyclohexane with benzoic acid, using a series of  $H_-$  indicators. The use of a series of  $H_-$  indicators extended the range of measurable base strength of the solid surfaces and consequently the measurement of base contents over a wide range of base strengths became possible. On the basis of the results of both measurements, the nature of basic sites on basic-oxide surfaces and also some correlation between catalytic activity and basicity of alkaline-earth oxides will be discussed.

## EXPERIMENTAL

### Indicators

The  $H_-$  indicators used in this study are listed in Table 1, together with their colors and  $pK_{BH}$  values. These indicators were commercial reagents purified by recryst-

allization. Each indicator was dissolved in benzene for the preparation of a 0.1 wt% solution, because of its poor solubility in cyclohexane.

### Solvent and Titrant

Cyclohexane was chosen as the nonpolar solvent for all the experiments described below. It was passed through two chromatographic columns (100 cm long, 3 cm in diameter), in each of which several layers of activated silica gel alternated with those of activated alumina, in order to remove water and other impurities. Benzoic acid (GR grade) was dissolved in purified cyclohexane for the preparation of a 0.05 mole/liter solution as the titrant.

### Solid Bases

Magnesia, calcium oxide, and strontium oxide were prepared by the calcination of basic magnesium carbonate at 600°C for 20 hr, of calcium carbonate at 900°C for 20 hr, and of hydrated strontium hydroxide at 850°C for 20 hr, respectively. All the starting materials were of GR grade. The ignition losses were as follows: 66.7% (calcd for  $Mg(OH)_2 \cdot 4 MgCO_3 \cdot 5 H_2O$ , 58.4%), 45.6% (calcd for  $CaCO_3$ , 44.0%) and 62.7% (calcd for  $Sr(OH)_2 \cdot 8 H_2O$ , 61.0%). The powder of 100 to 200 mesh was taken for the measurement.

Zinc oxide, zirconium oxide, thorium oxide and anhydrous sodium carbonate were all GR grade reagents and were used without further treatment. Commercial

TABLE 1  
INDICATORS

	Indicator	$pK_{BH}^a$	Color	
			Neutral (BH)	Basic (B <sup>-</sup> )
I	2,4,6-trinitroaniline	12.2	Yellow	Redish orange
II	2,4-dinitroaniline	15.0	Yellow	Purple
III	4-chloro-2-nitroaniline	17.2	Yellow	Orange
IV	4-nitroaniline	18.4	Yellow	Yellowish orange
V	4-chloroaniline	26.5 <sup>b</sup>	Colorless	Pink <sup>c</sup>

<sup>a</sup> Determined by Stewart and O'Donnell (8).

<sup>b</sup> Estimated value, see text.

<sup>c</sup> O' served only on strong solid-base surfaces.

soda lime and sodium hydroxide were quickly ground in air before use.

#### *Base-Strength Measurement*

The method of measurement corresponded to Walling's method (9) for measurement of the acid strength of solids. The color of the indicator adsorbed on the solid was visually observed after the addition of about 5 ml of purified cyclohexane and one drop of a certain indicator solution to roughly 0.1 g of a solid in a 30-ml conical flask equipped with a ground glass stopper.

#### *Base-Strength Distribution Measurement*

The method corresponded to the *n*-butylamine titration method (10) for measurement of the acid-strength distribution on solids. The procedure given below was devised so as to exclude traces of moisture, which may affect titration results.

Samples of 0.15 g each were weighed into separate glass sample tubes (40 to 50 mm long, 10 mm in diameter) stoppered with quartz wool at either end. A large glass tube containing 8 to 25 sample tubes was carefully evacuated to  $10^{-3}$  mm Hg at 450°C overnight, cooled to room temperature and then filled with dry nitrogen. To avoid direct contact of the samples with moisture, all the sample tubes were covered with purified cyclohexane in a stream of dry nitrogen after the seal of the large glass tube had been cut off.

The desired amount of benzoic acid solution was added from a microburette to each sample, which had been transferred from the sample tube into a glass-stoppered 30-ml conical flask containing purified cyclohexane (5–10 ml). The amount of benzoic acid added might differ among samples in steps of 0.01 to 0.1 meq/g sample, depending on the expected base-strength distribution. After vigorous shaking at room temperature for at least 4 hr, each sample was subdivided into five 30-ml conical flasks, and into them two drops of each indicator solution were added separately. From the resultant color changes of indicators after one day, the end point of ti-

tration, where basic colors just disappear, was determined visually.

An increase in the period of vigorous shaking from 4 to 12 hr had no effect on the titration results.

## RESULTS

### *Colors of Indicators*

The indicators, other than 4-chloroaniline, when adsorbed on sufficiently basic solids, exhibited the same color changes as observed in a variety of aqueous dimethylsulfoxide solutions containing tetramethylammonium hydroxide of 0.011 mole/liter (8, 11). These basic colors turned yellow, the neutral color, when the surfaces were neutralized with benzoic acid. With regard to 4-chloroaniline, which is so weakly acidic, no such basic solutions as may convert it to its conjugate base have been available. This indicator changed from colorless, the neutral color, to pink only on strongly basic solids such as CaO and SrO, and this color returned colorless when the surfaces were neutralized. This color, therefore, may be ascribed to the conjugate base of 4-chloroaniline. Table 1 summarizes the results of above observation.

The  $pK_{BH}$  of 4-chloroaniline, though it has not been determined, is estimated to be 26.5 from the linear correlations of acidities of substituted anilines ( $pK_{BH}$ ) with either their basicities ( $pK_{BH^+}$ ) (11) or acidities of similarly substituted phenols (12).

### *Base Strength of Solids*

The effect of heat treatment on the base strength of solids was examined. Some of the results are summarized in Table 2. On ZnO, ZrO<sub>2</sub>, ThO<sub>2</sub> or Na<sub>2</sub>CO<sub>3</sub>, even when evacuated at 450°C for 2 hr, no color changes were observed for any indicators. This fact demonstrates that these solids possess no basic sites having an  $H_-$  equal to or higher than 12.2. These solids, therefore, have not been used in the following experiments.

TABLE 2  
EFFECTS OF PRETREATMENTS ON BASE STRENGTH

Pretreatment	Base Strength ( $H_-$ range)		
	MgO	CaO	SrO
Untreated	12.2 to 15.0	$\leq 12.2$	$\leq 12.2$
Calcined at 450°C for 2 hr in air	15.0 to 17.2	15.0 to 17.2	—
Calcined at 450°C and $10^{-3}$ mm Hg for 2 hr	18.4 to 26.5	18.4 to 26.5	—
Calcined at 450°C and $10^{-3}$ mm Hg overnight	18.4 to 26.5	$\geq 26.5$	$\geq 26.5$

### Base-Strength Distribution

The titers of benzoic acid are plotted as a function of base strength in Figs. 1 and 2. These titers are equal to the number of basic sites (in meq/g sample) having an  $H_-$  equal to or higher than the  $pK_{BH}$  value of the indicator used. The actual base content in a given  $H_-$  range is obtained as the difference in titer with the two indicators bracketing that  $H_-$  range. Table 3 shows the base content in each range of base strength and also the total base content, which equals to the titer at the lowest  $H_-$  value.

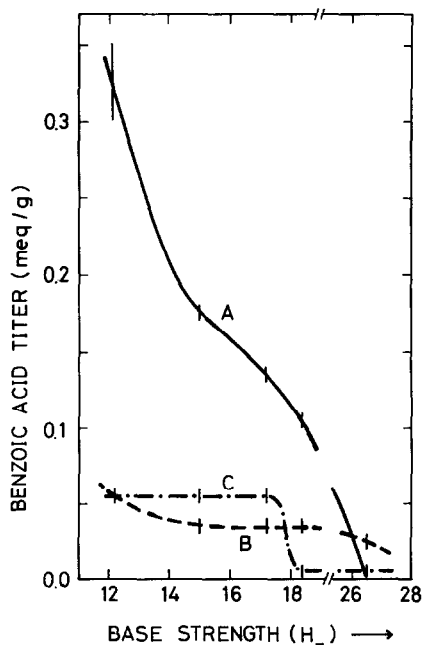


FIG. 1. Benzoic acid titer vs base strength of (A) MgO, (B) CaO, and (C) SrO.

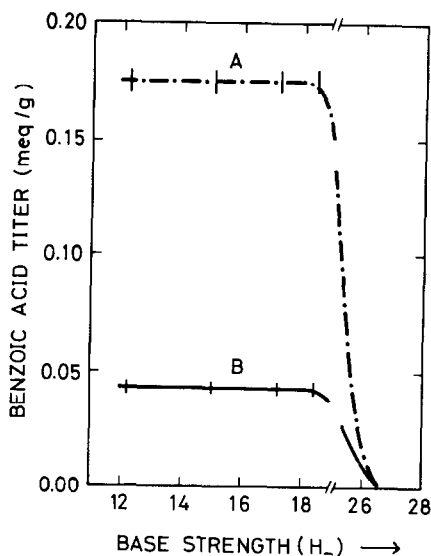


FIG. 2. Benzoic acid titer vs base strength of (A) NaOH and (B) Soda lime.

### DISCUSSION

#### Color Changes on Solid Bases

Obviously, the base strength embodied by Eqs. (1) and (2) is justified only if the color change of an adsorbed indicator results from its proton loss, and the  $f_{B^-}/f_{BH}$  ratio for an adsorbed indicator is independent of the indicator used.

With regard to the first requirement, it is known that two modes usually are possible for the ionization of nitroanilines in basic solutions; namely, (1) the loss of a proton from the amino group and (2) the addition of a base group to the ring carbon atom, forming a "Meisenheimer" 1:1 complex (13). Recent studies have presented

TABLE 3  
 BASE STRENGTH DISTRIBUTION

Solid base	Benzoic acid titer (meq/g) in the $H_-$ range					Total
	12.2 to 15.0	15.0 to 17.2	17.2 to 18.4	18.4 to 26.5	$\geq 26.5$	
MgO <sup>a</sup>	0.16	0.04	0.03	0.10	0.0	0.33 <sup>b</sup>
CaO <sup>a</sup>	0.020	0.0	0.0	0.01	0.025	0.055 <sup>c</sup>
SrO <sup>a</sup>	0.0	0.0	0.05	0.0	0.005	0.055 <sup>c</sup>
NaOH <sup>d</sup>	0.0	0.0	0.0	1.75	0.0	1.75 <sup>e</sup>
Soda lime <sup>a</sup>	0.0	0.0	0.0	0.43	0.0	0.43 <sup>b</sup>

<sup>a</sup> Calcined overnight at 450° and 10<sup>-3</sup> mm Hg.

<sup>b</sup> Titer uncertainty is  $\pm 0.02$  meq/g.

<sup>c</sup> Titer uncertainty is  $\pm 0.005$  meq/g.

<sup>d</sup> Evacuated overnight at room temperature and 10<sup>-3</sup> mm Hg.

<sup>e</sup> Titer uncertainty is  $\pm 0.05$  meq/g.

both direct (13) and indirect (8b, 12) evidence that several nitroanilines such as 2,4-dinitroaniline and 2,4,6-trinitroaniline lose preferentially a proton from the amino groups in basic solutions such as an alcoholic dimethylsulfoxide containing sodium or potassium alkoxide and an aqueous dimethylsulfoxide containing tetramethylammonium hydroxide. Therefore, the identity of the colors of indicators on the solid bases with those in the aqueous dimethylsulfoxide solutions suggests that the proton loss takes place on these solid-base surfaces.

In regard to the second requirement, it should be noted that the experimental points lie on a one-valued function curve as shown in Figs. 1 and 2; viz., that the entire series of indicators used in this study exhibit self-consistent color changes on the solid base surfaces. This means that the  $f_B/f_{BH}$  ratio is either independent of the indicator used or varies in a regular manner with increasing indicator acidity, as pointed out by Benesi in the case of  $H_0$  indicators (14). This indicates also that the estimation of the  $pK_{BH}$  value for 4-chloroaniline and the assignment of its basic color are reasonable.

#### Base Strength and Its Distribution

A recent study (1) showed that magnesia and calcium oxide increased in base content upon heat treatment in atmosphere although the former decreased slightly in

base content upon severe heat treatment. In addition to this, the base strength of alkaline-earth oxides increased considerably upon heat treatment in atmosphere, especially in vacuum (Table 2). These results are reasonable in the scope of acid-base interaction. Since water is amphoteric and carbon dioxide is acidic, fresh basic oxides may adsorb them when they are left out in the atmosphere, forming surface carbonates and hydroxides. The heat treatment of such solid bases may result in a gradual but progressive elimination of adsorbed water and carbon dioxide. This elimination, of course, involves a reappearance of basic sites with an inherent base strength of the solid. Further evidence for this explanation is provided by the fact that the extent of such poisoning, the difference in base strength between an untreated solid and the evacuated, appears to increase with an increase in base strength of solid-base surfaces. Evidently, the use of a series of  $H_-$  indicators has extended the range of measurable base strength of solid surfaces.

Table 3 shows that the alkaline-earth oxides examined possess a distinct distribution of base strength and decrease in base strength in the order of SrO (the highest  $H_-$  range,  $\geq 26.5$ )  $\approx$  CaO ( $\geq 26.5$ )  $>$  MgO (18.4–26.5). This sequence is in accordance with the observation by Krylov and Fokina (2) and also with that expected from the

decomposition temperatures of the corresponding carbonates, where carbon dioxide is liberated.

Generally speaking, a combined oxygen anion in an oxide surface can act as an electron donor and its capacity is expected to be related to the effective negative charge on the oxygen atom (15): the higher the negative charge, the stronger the donor or base property. The partial negative charge on a combined oxygen anion has been estimated from the electronegativity equalization principle (15) as  $-0.59$ ,  $-0.57$ , and  $-0.50$  for SrO, CaO, and MgO, respectively. Accordingly, the base strength of alkaline-earth oxides is expected to decrease in the order of SrO, CaO, and MgO. A good agreement in the order of base strength between the observed and the expected strongly suggests that the combined oxygen anion acts really as a basic site on these oxide surfaces. Kortum (16) holds the same view on a basic site on magnesia.

If the surface of a basic oxide has a regular structure, the base strength would be uniform. However, actual basic oxides have irregular surface structures possessing many kinds of defects, which would be produced more easily in oxides of high melting points than in those of low melting points, and foreign groups such as surface hydroxyl groups. Combined oxygen anions in such irregular surfaces are expected to have a nonuniform negative charge depending on their environment; for instance, the oxygen anion would be more negative in a metal cation-deficient environment and, on the other hand, less negative in a metal cation-sufficient one. Thus, the distribution of base strength of an alkaline-earth oxide may be explained in terms of the extent of polarization of the combined surface oxygen anion. According to this model, combined metal cations in such oxide surfaces would act as the Lewis acid. Experimental evidence for such a possibility (17) has been presented.

Both sodium hydroxide and soda lime possess a uniform base strength in contrast with alkaline-earth oxides, as Table 3 shows. In addition, these solids are the

same in base strength. These findings suggest that a basic property of soda lime, such as its ability for adsorbing carbon dioxide, is not due to that of calcium oxide (one component) but exclusively due to that of sodium hydroxide (the other). The observed uniformity in base strength seems reasonable in view of the low melting point of sodium hydroxide.

#### *Correlation of Basicity with Catalytic Activity and Selectivity*

In a previous paper (18) it has been concluded that an  $\alpha,\beta$ -elimination of hydrogen chloride from chloroethanes proceeds through the stepwise E 2 mechanism on solid-base catalysts, where the abstraction of an either  $\alpha$ - or  $\beta$ -proton is rate determining. According to this mechanism, some close correlation of catalytic activities of solid bases with their base strength and base content is expected.

In the catalytic hydrogen chloride-elimination, 1,1,2-trichloroethane,  $\text{Cl}_2\text{HC}(\alpha)-\text{C}(\beta)\text{H}_2\text{Cl}$ , yields 1,1-dichloroethylene (I) and 1,2-dichloroethylene (II). This selectivity has been explained in terms of the reactivity of the proton to be abstracted in the rate-determining step: that is, the abstraction of a more reactive  $\alpha$ -proton in this molecule may lead to the formation of I and that of a less reactive  $\beta$ -proton, on the other hand, to the formation of II. Accordingly, it seems acceptable to think that I forms even on weakly basic sites, whereas II only on strongly basic sites. It is now supposed that basic sites having an  $H_-$  equal to or higher than 12.2 are equally active for the formation of I and those having an  $H_-$  equal to or higher than 18.4 for the formation of II. The relative activities of alkaline-earth oxide catalysts would thus be given in the ratios of 1(SrO):1(CaO):6(MgO) for the formation of I and of 1:7:20 for the formation of II, as expected from their base-strength distributions in Table 3. According to the results in the previous experiment (18), where the catalysts were taken from the same batch as that used in the present study, the relative catalytic activities were 1:1.3:4.2 for the

formation of **I** and 1:2.7:27 for the formation of **II**. These agreements are satisfactory, if the simplicity of the above assumption and the inaccuracy unavoidable in the visual determination of base strength distribution are taken into account. The selectivity to **I**-formation over **II**-formation, which increases with increasing base strength of catalysts, can also be explained from the same point of view. These satisfactory interpretations demonstrate that information on the base-strength distribution of catalyst surfaces will be essentially important for quantitative investigations of solid-base catalysis.

#### ACKNOWLEDGMENT

The authors wish to express their thanks to Dr. Y. Saito for his helpful discussion.

#### REFERENCES

1. TANABE, K., AND YAMAGUCHI, T., *J. Res. Inst. Catal., Hokkaido Univ.* **11**, 179 (1964).
2. KRYLOV, O. V., AND FOKINA, E. A., *Probl. Kinet. Katal., Akad. Nauk, S.S.S.R.* **8**, 248 (1955).
3. MALINOWSKY, S., AND SZCZEPANSKA, S., *J. Catal.* **2**, 310 (1963).
4. MALINOWSKY, S., SZCZEPANSKA, S., BIELANSKI, A., AND SLOCZYNSKY, J., *J. Catal.* **4**, 324 (1965).
5. HAMMETT, L. P., AND DEYRUP, A. J., *J. Amer. Chem. Soc.* **54**, 2721 (1932); HAMMETT, L. P., "Physical Organic Chemistry," p. 269, McGraw-Hill, New York, 1940; PAUL, M. A., AND LONG, F. A., *Chem. Rev.* **57**, 1 (1957).
6. BOWDEN, K., *Chem. Rev.* **66**, 119 (1966).
7. ROCHESTER, C. H., *Quart. Rev.* **20**, 511 (1966).
8. (a) STEWART, R., AND O'DONNELL, J. P., *J. Amer. Chem. Soc.* **84**, 493 (1962); (b) *Can. J. Chem.* **42**, 1681 (1964).
9. WALLING, C., *J. Amer. Chem. Soc.* **72**, 1164 (1950).
10. BENESI, H. A., *J. Phys. Chem.* **61**, 970 (1957).
11. STEWART, R., AND DOLMAN, D., *Can. J. Chem.* **45**, 911 (1967).
12. STEWART, R., AND DOLMAN, D., *Can. J. Chem.* **45**, 925 (1967).
13. CRAMPTON, M. R., AND GOLD, V., *Proc. Chem. Soc.* 298 (1964); *Chem. Commun.* 256 (1965); *J. Chem. Soc. (B)*, 893 (1966).
14. BENESI, H. A., *J. Amer. Chem. Soc.* **78**, 5490 (1956).
15. SANDERSON, R. T., "Chemical Periodicity." Chap. 6, Reinhold, New York, 1960.
16. KORTUM, G., *Angew. Chem.* **70**, 651 (1958).
17. ZEITLIN, H., KONDO, N., AND JORDAN, W., *J. Phys. Chem. Solids* **25**, 641 (1964); ZEITLIN, H., FREI, R., AND McCARTER, M., *J. Catal.* **4**, 77 (1965).
18. MOCHIDA, I., TAKE, J., SAITO, Y., AND YONEDA, Y., *J. Org. Chem.* **32**, 3894 (1967).