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Surface Acidity of Trisodium Hydrogen Disulfate

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The surface acidity of trisodium hydrogen disulfate is measured by titration with butylamine vapor at −78°C. Titration at low temperature overcomes the problem of diffusion and reaction within the bulk material. Trisodium hydrogen disulfate is not hygroscopic, unlike sodium hydrogen sulfate, and is more readily prepared with a higher specific area than the single salt.

Solid sodium hydrogen sulfate, which is hygroscopic, has some industrial use as an acid catalyst. The double salt, trisodium hydrogen disulfate (*1*), is not hygroscopic (*2*), and is more readily handled. Its acidity was therefore investigated.

The surface acidity of solids is generally estimated by the methods of Johnson (*3*) or Benesi (*4*). There have been few attempts to measure the acidity of hydrogen sulfates.

Titration of supported sodium hydrogen sulfate (*3*), using *p*-dimethylaminoazobenzene, pK = 3.3, as indicator showed good agreement with the bulk acidity. In this case it is not clear whether the sodium hydrogen sulfate was dispersed almost monomolecularly, or whether the base has reacted within the bulk of the sodium hydrogen sulfate crystallites.

The acidity of compressed potassium hydrogen sulfate has also been investigated (*5*). The material was prepared by grinding and the acidity was determined by Benesi's method (*4*). With an indicator of pK = 4.0, the acidity of uncompressed samples was found to be 10.6 mmol g^{-1}. The calculated bulk acidity is only 7.4 mmol g^{-1}.

EXPERIMENTAL METHODS

Materials

Trisodium hydrogen disulfate (*1*), was prepared by the action of ethanol on sodium hydrogen sulfate.

AnalaR anhydrous sodium hydrogen sulfate was used after heating and grinding.

Butylamine was distilled before use.

Titrations

Liquid phase. The indicators were 4-phenylazo-1-naphthylamine, pK = 4.0, and benzeneazodiphenylamine, pK = 1.5. The indicator in dry benzene was equilibrated with the prepared solid hydrogen sulfate. A solution of butylamine in dry benzene was added slowly to the hydrogen sulfate till the acid color on the solid disappeared.

Vapor phase. After equilibration with the indicator, the hydrogen sulfate was dried and transferred to the vacuum apparatus. Butylamine vapor was admitted to the titration vessel in increments. Each increment was left for 15 min to equilibrate. The pressure of the vapor, before and after addition to the solid acid, was monitored by a diaphragm gauge, range 300 N m^{-2}. The end point was taken as the change in color of the indicator to that of the basic form as in the liquid phase titration. The butylamine titer was calculated by summation of the added amounts, corrected for any residual pressure after equilibrium. The residual pressure was zero, i.e., < 3 N m^{-2}, the maximum sensitivity of the gauge, except at the end point. It was assumed that physical adsorption of butylamine would only take place after chemical reaction was complete. This was borne out by the results.

Low temperature runs were carried out with the titration tube cooled in an acetone–solid CO_2 mixture. No data could be found for the vapor pressure of butylamine at low temperatures. Extrapolation of high temperature results for the liquid (*6*) gave a vapor pressure of 5 N m^{-2} at −78°C. As the solid butylamine will have an even lower vapor pressure, the measurement of the pressure after equilibrium would be outside the sensitivity of our instrument. However, if the vapor is added in increments until the indicator changes color, the maximum error will be the magnitude of the last increment, if sufficient time is allowed for the system to equilibrate. The error due to the lack of the final pressure measurement was no more than 5%.

Areas

The BET areas of the samples were obtained with a Perkin-Elmer sorptometer.

RESULTS AND DISCUSSION

Anhydrous sodium hydrogen sulfate was investigated prior to the examination of the double salt. The areas of several ground sodium hydrogen sulfate samples were ca. 0.1 m^2 g^{-1}. Titration of the samples with butylamine in benezene and an indicator of $pK = 1.5$, gave values corresponding to the bulk acidity. This suggests that the reported acidity of supported sodium hydrogen sulfate (*3*) corresponds to the bulk acidity.

Titration of the sodium hydrogen sulfate with an indicator of $pK = 4.0$ gave an even greater value than expected from the bulk acidity; 1.3 butylamine molecules were required/sodium hydrogen sulfate molecule, which compares with the reported value of 1.4 butylamine molecules/potassium hydrogen sulfate (*5*) molecule for this indicator. The excess butylamine, necessary to change the $pK = 4.0$ indicator, does not strongly interact with the acid solid, as was shown by the following. The titer was repeated and the mixture was filtered. The filtrate was extracted with ethanol–water and the extract was back-titrated with HCl. The total titer was 1.3 mol butylamine/mol sodium hydrogen sulfate. The back titration was 0.3 mol butylamine. Therefore 1 mol butylamine combines with 1 mol sodium hydrogen sulfate.

Titration of trisodium hydrogen disulfate with butylamine in benzene also gave values corresponding to the bulk acidity. The surface areas of the samples were, however, only 1–2 m^2 g^{-1}. It is therefore apparent that with liquid phase titrations at 20°C, butylamine diffuses into the bulk of the crystallites of hydrogen sulfates.

In an attempt to achieve greater control over the diffusion of butylamine into the bulk, titrations were carried out by a vapor phase technique (see above). Tests showed that though the indicator could not be displaced from the solid surface by base, as in the liquid phase titrations, an end point could be observed in the vapor phase titrations, corresponding to the indicator changing to the basic form on the solid. The method was shown to be feasible by titrating heat-treated magnesium sulfate (*7*) by both liquid and vapor phase methods. Table 1, runs 1–3, shows the results for both methods, at 20°C, for indicator $pK = 4.0$. The reproducibility of the liquid phase method is ±5% (*3*). The error in the liquid phase titrations will be slightly greater than ±5% because of individual

TABLE 1
ACIDITY OF HEAT-TREATED MAGNESIUM SULFATE (mmol g^{-1})

Sample	Liquid phase	Vapor phase	
	20°C	20°C	−78°C
1	0.045	0.052	—
2	0.070	0.058	—
3	0.096	0.089	—
4	—	0.042	0.042
5	—	0.032	0.044

judgment in deciding the end point. The vapor phase titrations at 20°C agree with the liquid phase ones if the error in the vapor phase titrations is 21% or less. This estimate is probably high as no account is taken of the error in the liquid phase titrations. The agreement is satisfactory as the vapor phase method involves cumulative measurements, and additional calibration of pressure and volume.

Titrations of trisodium hydrogen disulfate with butylamine in the vapor phase at 20°C gave values corresponding again to the bulk acidity. It was noted, however, that if the titration chamber was cooled, addition of butylamine vapor to the acid solid gave initially the basic color of the indicator. After a time, the acid color of the indicator returned. The rate of diffusion of butylamine into the bulk could, therefore, be reduced by cooling, though the acid–base reaction still proceeded. A temperature of −78°C was necessary before the rate of diffusion was reduced to an extent which precluded reversion to the acidic indicator color for an appreciable time (1 hr), after addition of base.

The low temperature technique was tried initially with the magnesium sulfate. Table 1, runs 4–5, shows that the values obtained at −78°C were in agreement with the values at 20°C, if the error in vapor phase titrations at −78°C is at maximum 27%. In view of the difficulties of the low temperature method, this agreement is satisfactory.

Before the acidity of the trisodium hydrogen disulfate may be evaluated, the area occupied by one molecule must be found. No structural data are available for trisodium hydrogen disulfate, or sodium hydrogen sulfate. It is therefore necessary to estimate the area occupied by the sodium hydrogen sulfate moiety. The average volume occupied by a sodium hydrogen sulfate molecule may be calculated from the density of anhydrous sodium hydrogen sulfate. If, as a first approximation the molecule is assumed to occupy a cube, the exposed area (one face) of the molecule may be deduced. For a density of 2.44 g cm^{-3}, the area is ~ 18 Å^2.

Titration of samples of trisodium hydrogen disulfate at −78°C gave the results shown in Table 2. The molecular area of the sodium hydrogen sulfate moiety was taken as the same as in anhydrous sodium hydrogen sulfate. The BET areas, accurate to probably ±10%, are also given. The fraction of acidic molecules at the surface of the trisodium hydrogen disulfate can vary from zero to one, depending on the crystal faces exposed. Considering the numerous crystallite facets exposed in a given sample, on average half the surface molecules may be expected to be acidic. Table 2 (runs 1–3) shows that the area obtained for the acidic portion of the trisodium hydrogen disulfate is less than the

TABLE 2
AREA OF SODIUM HYDROGEN SULFATE IN TRISODIUM HYDROGEN DISULFATE AND IN ANHYDROUS SODIUM HYDROGEN SULFATE (m^2 g^{-1})

Sample	Titration	BET
1. Trisodium hydrogen disulfate	0.7	1.1
2. Trisodium hydrogen disulfate	0.9	1.6
3. Trisodium hydrogen disulfate	1.2	2.3
4. Sodium hydrogen sulfate	0.7	0.9

BET area in all cases. The estimated average area of the sodium hydrogen sulfate molecule cannot be in error by more than a factor of two, as the bulky sulfate ion must necessarily be accommodated. The acidities measured are therefore most probably surface acidities. The results are consistent with half the exposed molecules being acidic. However, the exact fraction of exposed molecules which are acidic is strongly dependent on the estimated area of the sodium hydrogen sulfate moiety.

Anhydrous sodium hydrogen sulfate samples have generally very low areas (< 0.1 m^2 g^{-1}). One exceptional sample, had a BET area of 0.9 m^2 g^{-1}. Titration of this sample at -78°C (Table 2, run 4) gave an area which agreed with the BET area within the accuracies specified. This result provides further support for the estimated area of the sodium hydrogen sulfate molecule, and for the applicability of the method for measurement of surface acidities of anhydrous hydrogen sulfates, which cannot be examined by conventional techniques due to diffusion of base into the bulk material.

REFERENCES

1. Butler, G. S., and Dunnicliff, H. B., *J. Chem. Soc., London* 649 (1920).
2. Vil'nyanskii, Y. E., and Persits, Z. L., *Zh. Obshch, Khim.* **16,** 1997 (1946).
3. Johnson, O., *J. Phys. Chem.* **59,** 827 (1955).
4. Benesi, H. A., *J. Phys. Chem.* **61,** 970 (1957).
5. Ogino, Y., and Kawakami, T., *Bull. Chem. Soc. Jap.* **38,** 972 (1965); Ogino, Y., Kawakami, T., and Tsurumi, K., *Bull. Chem. Soc. Jap.* **39,** 639 (1966).
6. Copley, M. J., Ginsberg, E., Zellhoefer, G. F., and Marvel, C. S., *J. Amer. Chem. Soc.* **63,** 254 (1941).
7. Tanabe, K., and Takeshita, T., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 17, p. 315. Academic Press, 1967.