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Technical Notes

Observed Acidities of Charcoals, Clays, and Common Laboratory Purification Reagents in Aqueous and Organic Solutions

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Abstract:

In studying the purification and clarification of organic compounds with mixtures of charcoals, clays, and chromatography supports in organic solution, we noted that the observed pH of the resulting slurry was an important factor in determining which of the materials was appropriate. To examine this aspect of these purification methods, we determined the observed acidity of several commercially available reagent-grade clays, decolorizing agents, chromatography supports, and several common laboratory drying reagents in water and in several organic solvents. As expected, we found that clays, decolorizing carbons, and filter aids cannot be assumed to be pH neutral and nonreactive with organic molecules. For the purification of organic compounds with pH-sensitive functionalities, the potential acidity or basicity of a clarification reagent in the chosen solvent should be considered.

In studying the purification and clarification of organic compounds with mixtures of charcoals, clays, and chromatography supports in organic solution, it was observed that the pH of the resulting slurry was an important factor in determining which of the reagents was appropriate. While diatomaceous earths and decolorizing carbons may be equally effective in aqueous, organic, or blended solvents, it is important to consider the compatibility of the clarifying reagent with the functionalities present on the compound to be purified. In one example, we extracted an oxime into aqueous sodium hydroxide solution, and the solution was treated with a Panther Creek 200 clay/decolorizing charcoal mixture and filtered. Upon neutralization of the filtrate and extraction, the oxime was isolated in acceptably pure form, eliminating the need for chromatography.[1] Conversely, a Clarion 550 clay/decolorizing charcoal mixture failed to adsorb any of the impurities in this basic solution, and thus this clay was judged to be ineffective as a clarifying agent for this purification process.[1] We determined the pH of an aqueous slurry of these clays, and found that Panther Creek 200 reagent was basic (pH = 9.5) and apparently unaffected by the basic oxime solution. Conversely, the acidic Clarion clay (pH = 2.7−3.2) was apparently rendered ineffective at the higher pH used in our process.

Table 1. **observed acid strength (H_0) of common laboratory purification reagents as slurries in water and in organic solvents**

	deionized water[n]	ethanol	acetonitrile
Observed Reference pH (Ross Combination Electrode)			
	6.7	6.7	7.0
Clay Supports			
Montmorillonite K-10[a]	2.3 (1.9)	1.9	−1.8
Clarion 470[b]	2.9 (2.7)	4.2	0.9
Engelhard F-24[c]	2.9	3.2	0.9
Engelhard F-105[c]	3.6 (3.0)	4.4	1.3
Clarion 550[b]	3.6 (3.2)	4.5	1.9
Panther Creek 200[b]	9.2 (9.5)	8.3	6.3
Decolorizing Agents			
Darco G-60 charcoal[a]	8.1 (8.2)	5.6	5.6
Nuchar WV-L charcoal[d]	8.2 (7.4)	6.3	6.9
Nuchar WV−H charcoal[d]	8.5 (8.6)	6.4	7.4
Nuchar WV-G charcoal[d]	8.8 (10.0)	6.5	7.5
decolorizing charcoal[e]	10.0 (9.6)	8.3	5.5
Norit RO charcoal[a]	10.5	8.8	6.7
Chromatography Supports			
dextrose[a]	5.0	7.1	6.1
Celite 521 filter agent[a]	5.5 (5.3)	5.6	4.0
silica gel 60 (flash grade)[f]	7.0 (7.4)	8.4	7.1
Celite 545 filter agent[g]	9.2 (10.0)	9.0	9.3
Florisil, 100−200 mesh[h]	9.5	9.4	8.2
activated alumina[i]	9.6 (10.0)	9.0	8.7
Drying/Laboratory Reagents			
sand[a]	6.9	8.2	6.8
Drierite (calcium sulfate)[j]	7.2 (7.3)	5.1	5.9
magnesium sulfate[k]	8.5 (8.0)	6.4	2.1
sodium sulfate[l]	8.9 (8.7)	8.7	9.0
4 Å molecular sieves[h]	10.9 (11.2)	9.5	9.4
potassium carbonate[m]	11.8 (11.9)	13.2	14.2

[a] Purchased from Aldrich Fine Chemicals. [b] Purchased from American Colloid Company. [c] Purchased from Engelhard Corporation. [d] Purchased from Westvaco Chemical Division. [e] Purchased from Acros Organics. [f] Purchased from E. M. Science. [g] Purchased from Krackler Scientific. [h] Purchased from Fisher Scientific. [i] Purchased from Matheson, Coleman & Bell. [j] Purchased from W. A. Hammond, Inc. [k] Purchased from C&P Sales, Inc. [l] Purchased from Surpass Chemical, Inc. [m] Purchased from Van Waters & Rogers, Inc. [n] Values in parentheses were measured by a standard pH electrode from Orion (see Experimental Section).

Along these lines, highly acidic reagents such as Montmorillonite K-10 clay, Nuchar SA charcoal, and some silica gels (vide infra) may be incompatible with acid-sensitive molecular functionalities (acetals, ketals, olefins, etc.). Other functionalities (aldehydes, acids, amine salts, malonates, etc.) may be reactive with basic reagents such as Florisil, Norit RA charcoal and activated alumina (vide infra).

To develop guidelines for our future use of clarification and filtering agents, we systematically determined the acid strengths (H_0) of several commercially available reagent-grade clays, decolorizing agents, chromatography solid

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Table 2. **Observed acid strength (H_0) of common laboratory purification reagents as slurries in other organic solvents**

	toluene	methylene chloride	methyl *tert*-butyl ether	dimethyl sulfoxide
Observed Reference pH(Ross combination electrode)				
	6.8	4.7	5.4	10.7
Clay Supports				
Montmorillonite K-10	3.2	2.4	1.9	4.6
Engelhard F-105	4.2	3.3	4.4	4.9
Decolorizing Agents				
decolorizing charcoal	4.2	5.4	5.0	9.4
Darco G-60 charcoal	4.5	5.0	4.8	5.9
Norit RO charcoal	4.8	4.2	4.4	10.2
Chromatography Supports				
Florisil	4.2	4.3	4.2	12.9
activated alumina	4.2	3.9	4.6	11.1
Silica gel 60 (flash size)	4.5	5.4	6.6	11.0
Celite 545 filter agent	6.1	6.3	5.0	13.2
Drying/Laboratory Reagents				
magnesium sulfate	3.7	6.5	4.7	10.4
sodium sulfate	4.9	3.7	6.2	12.4

supports, and several common laboratory drying reagents in water, 95% ethanol, and acetonitrile. The results of this study are listed in Table 1, in the order of the most acidic compounds to the most basic in each category. This study was then extended to the determination of observed acid strength (H_0) of some of these reagents in toluene, methylene chloride, methyl *tert*-butyl ether, and dimethyl sulfoxide. These results are listed in Table 2.

Experimental Section

For each pH measurement, a 10-g sample of the commercially available reagent was slurried in 100 mL of the indicated HPLC-grade solvent. No effort was made to purify or dry any of these reagents or solvents. The pH measurements were made at 3 and 6 min and results averaged to produce the recorded values. Where possible, our measurements were verified by comparison to published values. In addition, the pH of each solvent was obtained and used as the reference standard against the pH measurement of each reagent mixture in that solvent. Observed acidities (H_0) were measured using an Orion pH meter, Model 230-A, equipped with a Ross combination pH electrode, Model 8102-BN. The electrode was filled with a 3-molar solution of potassium chloride (Ross Internal Filling Solution) and standardized against commercial buffer solutions at pH = 4.00 and 7.00.

As a reference measure, the pH of some of the reagents in deionized water was determined using an Orion pH meter, model 230-A, equipped with an Orion standard pH electrode, model 9157-BN. In these cases, each reagent sample was analyzed as a 20% (weight/weight) slurry in deionized water. For each pH determination, the final pH data was acquired after a 30-min equilibration period was performed. These pH values were then designated as the equilibrated solution acidities, and these numbers are reported in parentheses in Table 1. Where applicable, our observed acidity values were compared with the pH measurements described in the certificate of analysis provided by the vendor of the investigated reagent. The pH meter was standardized before each measurement against pH = 4.00, 7.00, and 10.0 commercial buffer solutions.

Results

The acid strength, H_0, of an organic compound is defined as its proton-donating ability, as described by the Hammett equation. When this acid strength is determined in water as a solvent, this H_0 value is described as the pH. When this measurement is made in an organic solvent, this proton donating ability is described as the effective pK_a range, which is highly solvent dependent.[2] This definition may be extended from hydrogen acids to the acid strength measurement of solid surfaces and Lewis acids.[3] The acid strength of some catalyst surfaces (zeolites,[3] clays,[3] and silica gel[4]) have been reported but were limited to descriptions of observed acidity ranges as determined by the color of adsorbed Hammett indicators in benzene suspensions of these reagents.

In this study, we determined the aqueous acid strengths of several laboratory reagents by direct measurement of the pH of these solid compounds as slurries in deionized water using a pH electrode. We then extended this method to organic solvents, using a methodology developed for the direct pH measurement of soil samples in nonaqueous systems using a combination electrode.[5] These measured acid strength values are described as the "observed" acid strength (H_0) of the reagent in each solvent.

Clay compounds have recently become popular as reagents for organic transformations, either as supports for included metal catalysts[6,7] or as catalysts themselves (montmorillonite, bentonite, and kaolinite).[8,9] They also show potential for the development of environmentally friendly processes.[10] Clays are naturally occurring aluminosilicate minerals which are used commonly in industry as "bleaching earths" for purification purposes. Laszlo[8a] has stated that the Brønsted acidity of clay surfaces is generally very high and

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catalysis is thought to occur in the porous acidic surfaces of these solids. Furthermore, it is important to remember that many of the commercially available clays (such as the montmorillonites K10 and KF and the Engelhard F catalysts) are produced by the treatment of natural clays with strong mineral acids such as HCl or H_2SO_4, further increasing their acidic nature. We observed that most of the commercially available clays were very acidic or slightly acidic in water, in ethanol, and in acetonitrile (Table 1). The exception to this trend was Panther Creek 200, which was found to be close to neutral or basic in these solutions. These observed acidities were in accord with the literature values,[3,7,8] as well as in agreement with pH information reported in vendor certificates of analysis.

Activated carbon has traditionally been used in industrial settings for the partial purification of organic compounds by the decolorization of organic extracts and solutions,[11] or for the decontamination of waste streams.[12] Finely divided carbon has also found a use in organic synthesis in the form of expansive graphite, which has also been used as a catalyst surface.[13] We have found charcoals to be extremely effective as agents to remove polar materials from nonpolar solvents and, conversely, to remove nonpolar materials from polar solvent systems.[1] One should be cautious about using this reagent, as the carbon may actually adsorb small-molecule products as well as impurities. In one case, a team of researchers found that optically active systems may be racemized in the presence of decolorizing carbons.[14] In our investigation of acid strengths, we found that several commercially available charcoals were basic in water and ranged from slightly acidic to slightly basic in ethanol and acetonitrile (Table 1). These observed acidities were in accord with pH information reported in vendor certificates of analysis.

Chromatography supports play a crucial role in the purification of organic compounds. These porous materials possess high surface areas which, as the stationary phase in a moving solvent system, demonstrate the ability to separate materials of different functionality based on principles of polarity. In addition, silica gel[15] and alumina[16] have recently been used as solid catalyst surfaces (as well as for supports for Lewis acids[17]) for some organic transformations. We found that silica gel in water and acetonitrile was approximately neutral in pH but was shown to be slightly basic in ethanol (Table 1). This is contrary to the conventional opinion that silica gel is slightly acidic. Celite 521 filter agent was found to be slightly acidic, whereas Celite 545 was found to be slightly basic. Florisil and alumina were found to be slightly basic in these solvents. These observed acidities were in accord with the literature values,[4,10] as well as in agreement with pH information reported in vendor certificates of analysis.

The acid strengths of some common laboratory reagents were then measured in water, ethanol, and acetonitrile (Table 1). Magnesium sulfate and sodium sulfate, the two most common organic solution drying agents, were found to be moderately acidic and basic, respectively. The exception to this trend was found to be the measurement of magnesium sulfate in water, which was found to be pH $= 8.5$. Upon inspection of several reagent catalogs, it was found that the pH values of sodium sulfate and magnesium sulfate were listed as a range between acidic and slightly basic in water. While our examination was conducted with a single lot of each of these reagents, it should be noted that the observed pH of any reagent is batch-dependent and may vary according to the method of its manufacture. Interestingly, nonactivated 4 Å molecular sieves were found to be slightly basic in these three solvents.

The observed acidities of some of these reagents were then measured in toluene, methylene chloride, methyl *tert*-butyl ether, and dimethyl sulfoxide (Table 2). As reference standards, the acidities of the organic solvents were measured. Toluene, methylene chloride, and methyl *tert*-butyl ether were found by our method to be slightly acidic, whereas dimethyl sulfoxide was observed to be moderately basic. The two clays measured in this experiment were found to be acidic in all solvents, including dimethyl sulfoxide. The three activated charcoal slurries were all found to be acidic, except in dimethyl sulfoxide, where the mixtures were observed to be basic. All of the chromatography supports were found to be acidic in toluene, methylene chloride, and methyl *tert*-butyl ether, and they were found to be basic in dimethyl sulfoxide. Surprisingly, both magnesium sulfate and sodium sulfate were found to be acidic in toluene, methylene chloride, and methyl *tert*-butyl ether. However, both magnesium sulfate and sodium sulfate were found to be basic in dimethyl sulfoxide. Again, these observed acidities were in accord with the literature values (where applicable), as well as in agreement with pH information reported in vendor certificates of analysis.

In conclusion, not all clays, decolorizing carbons, and filter aids are pH neutral and nonreactive with organic molecules. In the purification of organic compounds with pH-sensitive functionalities, the physical parameters of any clarification reagents should be considered for compatibility with those functional groups. Variability in observed acidity, dependent on the clarification reagent and solvent system, may help explain what seems to be anomalous results derived from superficially similar purification procedures.

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