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Chemical Reactions on Clays

PIERRE LASZLO

Layer aluminosilicates catalyze reactions in numerous ways. They stabilize high-energy intermediates. They can store energy in their lattice structures and can release it in the form of chemical energy. They can catalyze redox reactions and can serve as photocatalytic devices. They often exhibit high surface acidity. Organic reactions that are catalyzed by the agency of clays are reviewed. The role of clays in prebiotic chemistry is also examined.

THE SYNTHETIC CHEMIST RARELY BORROWS ACCESSORIES for the laboratory from the vast stockroom of nature. We resist scooping some dust into a reaction flask. Yet elegant chemistry can be performed if clays are used as supports or catalysts. The design of intercalated clay catalysts has been reviewed recently (*1*). Clays, long used as catalysts for cracking hydrocarbons, are also crucial to soil chemistry (*2*). Clay-related chemistry has burgeoned in recent years. This article will document some of the applications of acidic clays to carbocationic reactions and condensations, of clay surfaces to cycloadditions and rearrangements and to redox reactions; and it will consider the possible involvement of clays in biogenesis.

The Structure of Clays

Examination with a microscope shows that clay particles are organized, often into parallel plates stacked one upon another: kaolinite, for example, displays hexagonal flakes. Dehydrated clays, such as potter's clay, can reabsorb water. The class of clay minerals known as smectites share this property. Water molecules insert between the stacked plates. These planar arrays gain lateral mobility in hydrated clays, accounting for the plasticity of these materials.

The distance between these layers, or the basal distance, is revealed by x-ray diffraction. For smectites, this basal distance varies from about 10 Å in totally dehydrated clays, collapsed to such an extent that adjacent layers come into van der Waals contact, to as much as 20 to 50 Å, depending upon the number of intercalated water layers within the gap (known as the interstitial or the interlamellar space).

The primary structure of a smectite is lamellar, with parallel layers of tetrahedral silicate and of octahedral aluminate sheets. The secondary structure, that is, the constitution of the clay, stems from the valence deficiencies that occur in a not altogether random manner (if one considers the whole family of clay minerals). For example, Al(III) or Fe(II) can replace Si(IV) in the tetrahedral layer. The tertiary structure is a consequence of the secondary structure. This is a result of the effect of interstitial cations (such as Na^+, K^+, and Ca^{2+}, . . .) that are trapped as freely moving ions between the negatively charged planes.

Clays are aluminosilicates. The aluminum(III) cations are bonded to an octahedral arrangement of oxygen anions. Repetition of these AlO_6 units in two dimensions forms an octahedral layer. Likewise, a tetrahedral layer is formed from SiO_4 silicate units.

Clays are classified (*3*) according to the relative number of tetrahedral and octahedral layers. Montmorillonite clays, which have been used in organic chemical applications, have an octahedral layer sandwiched between two tetrahedral layers. The basal distance is

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that between the tetrahedral layer at the bottom of a 2 : 1 sandwich and the tetrahedral layer at the bottom of the next 2 : 1 sandwich in the stack.

The diversity of clays arises from deviations with respect to this idealized description. Aluminum can be substituted for silicon in the tetrahedral layer, to a maximum of 15%. Phosphorus can also replace silicon. A number of metallic cations, usually divalent, such as Mg(II), Fe(II), Zn(II), and Ni(II), but also Li(I), substitute for Al(III) in the octahedral layer. In the ideal representation of a montmorillonite (a dioctahedral phyllosilicate), two out of three positions in the octahedral layer are occupied by Al(III) (*3*). Three Mg(II) ions can replace two Al(III) ions, which fills all the available octahedral positions in trioctahedral phyllosilicates. Total replacement of aluminum by magnesium is found in the mineral saponite. Similarly, replacement by iron gives nontronite, by chromium, volkhonskoite, and by zinc, sauconite (*3*). Calculations have been performed at the extended Hückel level and they match the experimental energy sequence for such substitutions [from lowest potential energy up: Al(III), Fe(III), Mg(II), Fe(II), Ca(II) ≈ Na(I), K(I) (*4*)].

Such isomorphous substitution produces additional chemical diversity: replacement of the tetravalent silicon with Al^{3+} or of the trivalent aluminum with a divalent metal cation results in a net negative charge. In order to maintain electroneutrality, exchangeable cations come to the interlamellar space. In natural clays these are typically Na^+, K^+, Ca^{2+}, Mg^{2+}, and similar ions but these can be exchanged with other ions (such as quaternary ammonium ions with long hydrocarbon chains, in "organophilic" clays), which makes these materials more versatile for the chemist.

Surface Properties of Clays

A remarkable property of clays is their surface proper. With overall dimensions below 2 μm, clay particles show large specific surfaces, as measured with adsorption of dinitrogen in the standard Brunauer-Emmett-Teller (BET) method. Specific areas are 15 to 20 m^2/g for kaolinite, a 1 : 1 phyllosilicate; they are 80 to 90 m^2/g for illite. Montmorillonites have specific areas of the order of 500 m^2/g, sometimes as high as 760 m^2/g. By comparison, alumina has a specific area of 70 to 200 m^2/g, while values range between 400 and 600 m^2/g for silica gel.

In montmorillonites and micas, the excess negative charge is smeared over all the superficial oxygens on a tetrahedral or octahedral sheet. The negatively charged aluminosilicate sheets are conjugate bases of (usually strong) oxyacids, extending indefinitely in two dimensions. Like inorganic oxyacids, clay surfaces can be highly acidic. The Brønsted acidity stems from the terminal hydroxyl groups and from the bridging oxygens. High acidity is due especially to the latter. It is measured using a standard set of dye indicators by the Hammett H_0 acidity function (*5*). This surface acidity for natural clays with Na^+ or NH_4^+ as interstitial cations ranges from +1.5 to −3. Washing of the clay with mineral acid, such as HCl, brings H_0 down to −6 to −8, which is between that for concentrated nitric acid ($H_0 = -5$) and that for sulfuric acid ($H_0 = -12$) (*6*).

High acidity has been attributed to the presence of exchangeable cations. These cations polarize coordinated water molecules and induce their dissociation. This mechanism explains the decrease in surface acidity as the humidity increases in a clay sample (*7*).

Delocalization of negative charge on the surface oxygens of a layered silicate makes this plane into a polyelectrolyte. An electrical double layer is formed. Counterions, whose overall charge counterbalances the surface charge, accumulate in the diffuse layer extending out several tens of angstroms from the charged surface. Their distribution is determined by both Brownian motion and electrical forces. This distribution is best described by numerical solutions of the Poisson-Boltzmann equation or by Monte Carlo methods: both types of calculations give similar distributions (*8*) (Fig. 1). This electrical double layer is important not only for chemical reactions but also for other phenomena such as liquid transport through clays (*9*).

A useful distinction in the microscopic topography of clay platelets can be made between the edges and the basal surfaces. Basal surfaces are the aluminosilicate sheets which have uniform negative charge density. The edges of these sheets bear hydroxyl groups in a manner similar to a metallic oxide. These will be ionized or not depending on the *p*H of the surface. Hence, basal surfaces have a fixed negative charge, determined by the clay structural type, while the edges have a *p*H-dependent charge.

Reactions Due to Brønsted Acidity

Alkenes are protonated in the interlamellar space of smectites. Since the interlamellar Brønsted acidity of the clay decreases with the charge of the interlamellar cation, it is greatest with trivalent ions such as Cr(III), Al(III), and Fe(III) (*2, 10*). The carbocations generated react with interlayer water to form alcohols and ethers (*11*). Alcohols also add to alkenes, especially if they replaced water in the interlamellar space, to produce ethers (*12, 13*). For example, methanol adds to isobutene to form methyl-*t*-butyl ether in about 60% yield (*13*). The trisubstituted olefin 2-methyl-pent-2-ene adds methanol in 90% yield to give $H_3C–O–C(CH_3)_2–C_3H_7$; it adds also to primary alcohols (C_1 to C_{18}) at 95°C over an aluminum-exchanged montmorillonite (*13*).

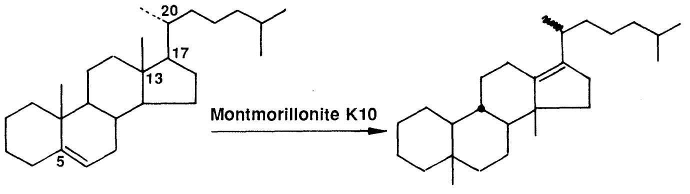
Several other carbocationic reactions are catalyzed by acidic clays (*14*). Acetals add to enol ethers to form precursors of α,β-unsaturated aldehydes (*15*). Esters are produced readily by the direct addition of carboxylic acids to alkenes (an activation energy of 30 to 50 kJ/mol) (*16*).

Such clay-catalyzed reactions differ from analogous solution reactions catalyzed by acids in four attractive ways: (i) the interlamellar reactions are not constrained to highly stable carbocations as intermediates; (ii) they proceed efficiently with terminal alkenes; (iii) they are more selective; and (iv) their work-up is simple. The influence of the water content of the clay is predictable, since the acidity decreases with higher humidity. The effect of humidity has been ascertained with 2-methylpropene as a substrate. Two distinct pathways exist. With a normal interlayer water content of about 12%, the olefin adds either water or methanol. The same clay, if dehydrated and thus made even more acidic, catalyzes oligomerization of 2-methylpropene (*17*).

Clays can be used as solid acids for a number of reactions normally catalyzed by mineral acids in aqueous solutions. Examples include esterifications of carboxylic acids (*18*), lactone formation (*19*), and conversion of ketones into enamines (*20*).

Some natural clays have high Brønsted acidity. An interesting case, due to its relevance to the possible formation of the biomolecules during the prebiotic era, is that of the Japanese acidic clays formed by decomposition of volcanic ash. Industrially modified and acidified clays such as the K10 montmorillonite clay (*21*) also exist. After its humidity has been removed by heating in an oven at 120°C for a few hours, this composite material (*21*) has an H_0 between −5.6 and −5.9. If left in humid air, H_0 for the K10 clay increases to values between −3.7 and −4.3 (*22*).

This clay silicate with exceptionally high acidity is an excellent catalyst for a number of applications. The K10 montmorillonite clay catalyzes the clean backbone rearrangement of cholest-5-ene into cholest-13(17)-enes; the transformation shown is quantitative and can be run on the gram scale (*23*):

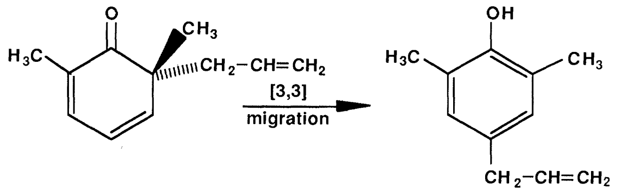


1

2 (20*R* + 20*S*)

The biosynthetic transformation of squalene epoxide into precursors of lanosterol is also acid catalyzed. This synthesis or related reactions could take place in the presence of clays, such as the Japanese acidic clay.

With the finding that interstitial Fe(III) cations increase the Brønsted acidity, it became tempting to apply Fe^{3+}-exchanged K10 montmorillonite to catalysis of the dienone-phenol rearrangement. Cyclohexadienones are highly prone to rearrange (*24*). They follow multiple paths depending on the migrating group (allyl, benzyl, or propargyl) and on the reaction conditions, whether thermal or acidic. Acid conditions are usually provided by codissolution with acetic anhydride and a trace of sulfuric acid (Thiele conditions) (*25*). The cyclohexadienone-phenol rearrangement is an excellent candidate for catalysis by an inorganic solid (*26*). The objectives were to reduce the number of pathways to boost product selectivity, and to decrease the reaction temperature, typically 3 hours of heating above 100°C (*25, 27*). In the presence of the Fe(III)-exchanged K10 clay (*28*), these rearrangements are very easy. They are quantitative at room temperature in a few minutes. This is illustrated by the following example, in which the acceleration with respect to the earlier standard (*27*) is between five and six orders of magnitude (*29*):



Product selectivity is also improved. In general, use of the acidic clay directs predominant product formation to those arising by 1,2-shifts from benzenonium carbocations (*29*).

Diels-Alder cycloadditions are also subject to catalysis by protic acids in certain cases, such as that of 2,4-dimethylpenta-2,4-diene as diene and dienophile (*30*). Such Diels-Alder reactions are facilitated in the presence of an acidic clay system by Brønsted acid catalysis (*31*).

These spectacular rate enhancements with solid as opposed to solution acids are due in part to the lamellar nature of the solid. Adsorption onto the surfaces of a layered mineral reduces the dimensionality of reaction space from three to two. This constraint translates into vastly increased encounter rates (*26, 32, 33*).

Reactions Due to Lewis Acidity

The secondary and tertiary structures of a clay are responsible for the presence of Lewis acidic sites. The operational distinction between Brønsted and Lewis acidic sites is simple. A base (for example, ammonia, an aliphatic amine, or pyridine) is adsorbed. Infrared spectra show absorptions that can be assigned to either the metal-ion-coordinated base or the protonated base, or both. For example, absorptions at about 1440 and 1465 cm^{-1} are seen for coordinated pyridine, whereas the pyridinium ion has an absorption at 1545 cm^{-1} (*6*).

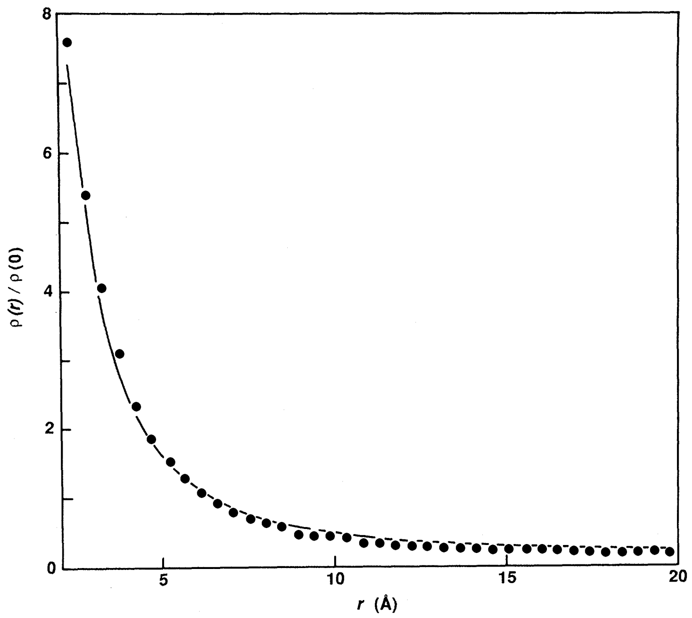


Fig. 1. Comparison between distributions of univalent counterions as a function of the distance to a plane with uniform charge density as calculated by numerically solving a Poisson-Boltzmann equation (solid line), or by a Monte Carlo simulation, in which two charged planes are parallel 20 Å apart (filled circles) (*8*).

A number of Diels-Alder cycloadditions are catalyzed by Lewis acids and are susceptible to catalysis by clay systems. We have devised an efficient procedure for the difficult Diels-Alder reactions of furans. Rather than resort to high pressure (*34*), one can catalyze the cycloaddition by the Fe(III)-exchanged K10 montmorillonite (*35*). Since the cycloreversion is also subject to catalysis by Lewis acids, the only precaution is quick neutralization of the reaction mixture and work-up after product formation (*35*).

Another organic reaction of practical importance is the Lewis acid–catalyzed Friedel-Crafts reaction (*36*). Ordinarily, the halide RX or an acid halide RCOX is the starting material for the arene ring substitution in the presence of a Lewis acid such as AlCl$_3$ (*37*). Since clays contain Lewis acid sites and can be doped easily with additional Lewis acid sites, this effect can be combined successfully with the effects of reduced dimensionality. Using adamantane as the probe substrate and a K10-FeCl$_3$ system under strongly dehydrating conditions (a reverse Dean-Stark trap) as the Lewis acid catalyst, we induced Friedel-Crafts substitution of the aromatic solvent directly from the hydrocarbon. It is likely that this reaction involves the tertiary adamantane carbocation as the intermediate and as the agent responsible for efficient hydride transfer (*38*); substitution occurs only at the tertiary positions (*39*). However, the intermolecular selectivity characteristic of Friedel-Crafts reactions in solution, which favors toluene over benzene by a factor of 2 to 20 depending upon conditions (*37*), vanishes altogether (*39*).

Reactions subject to catalysis by Lewis acids will also be catalyzed by Lewis acidic clays, with the attendant accelerations stemming from reduction in dimensionality, and will have the practical advantage of simplification of work-up (a simple filtration). For example, acetals and carbonyl compounds are allylated in a few minutes under mild conditions by allylic silanes in the presence of catalytic quantities of the K10 montmorillonite (*40*).

Redox Reactions on Clays

A clay surface with the accompanying counterions in the electrical double layer is the equivalent of a cathode immersed in an electrolytic solution, except for the continuous electric current. Hence redox reactions should occur readily on clay surfaces, provided that energy be made available. This energy can come from reorganization of the clay lattice with an overall decrease in the potential energy.

One of the simplest cases is oxidation of aromatic molecules to the radical cation by phyllosilicates containing transition metal cations. The systems that have been investigated most are Cu(II) and Fe(III) smectites. Single electron transfer from the aromatic donor to the metal center occurs readily under mild reaction conditions (*41–45*). Formation of the radical cations is detected by electron spin resonance. In some cases radical coupling products (biphenyls, *p*-polyphenyl polymers) have been obtained (*42, 44*).

Important applications of such reactions exist, such as the detoxification of dioxin. Dibenzo-*p*-dioxin forms a radical cation and polymerizes under mild reaction conditions on Cu(II)-smectites (*46*). Water photocleavage shows considerable promise. Montmorillonite is completely exchanged by methyl viologen in the interlamellar space using one out of three $\mathrm{Ru(bipy)}_3^{2+}$ (bipy = bipyridyl) dications on the surface. Triethanolamine acts as a sacrificial donor at *p*H 7.0 to produce hydrogen by irradiation by visible light (*47*). In these experiments, the ruthenium bipyridinium dication is the photosensitizer, and reduction of the methyl viologen by an electron relay mechanism (Fig. 2) on the clay surface completes the redox cycle (*48*).

Facile oxidation of aromatic molecules by clay surfaces into the corresponding radical cations (*41–45*) has opened a new route for their nitration. After similar suggestions had been made by Soviet scientists (*49*), Perrin proposed formation of a radical cation as the initial step in electrophilic aromatic nitrations. This cation would couple with the NO_2 radical to form the classic Wheland intermediate (*50*). This mechanism also solves the paradox of the observed regioselectivity in a diffusion-controlled reaction. The NO_2 radical bonds to centers of maximum unpaired electron density in a single molecular orbital.

The ability of clays to produce radical cations from aromatic rings and the Perrin mechanism of aromatic nitrations can be combined if an abundant and inexpensive source of NO_2 radicals is provided. Covalent metallic nitrates are a useful source, because their potential as oxidants has been demonstrated (*51*). Liberation of NO_2 is a favorable pathway for their decomposition (*51*).

Another important area is the activation of inorganic salts through partial or total dehydration. The resulting coordinative unsaturation causes the metal center to be highly reactive. For example, dehydration of an acetone solution of ferric nitrate nonahydrate gives an oil so reactive that it oxidizes nujol.

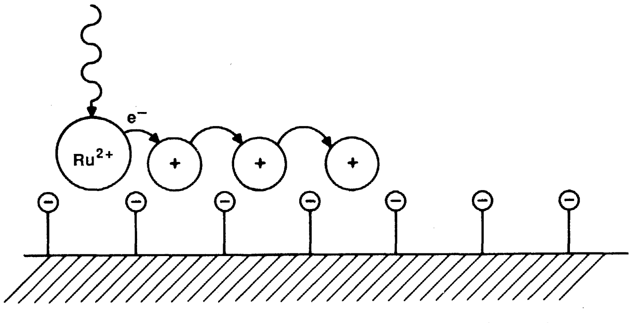


Fig. 2. Electron relay mechanism for electron transfer, subsequent to photochemical excitation, from $\mathrm{Ru(bipy_3^{2+})}$ (shown as $\mathrm{Ru^{2+}}$) to methyl viologen $\mathrm{MV^{2+}}$ (shown as +) on the polyanionic sheet formed by the surface of a montmorillonite.

Deposition of anhydrous ferric nitrate on the K10 montmorillonite provides a reagent known as "clayfen" (*28*) that effects nitration of phenols with superior results (*22, 52, 53*). An analogous reagent, which is made from cupric nitrate ("claycop") (*28*) in the presence of acetic anhydride, nitrates aromatic hydrocarbons with high regioselectivities (*54*), in agreement with the Perrin mechanism (*50*).

The Bauld group has catalyzed the slow Diels-Alder addition of unactivated dienes and dienophiles (such as 1,3-cyclohexadiene adding to itself) with triarylaminium radical cations (*55*). The postulated radical cationic intermediate in phenol nitration may play a similar role. These radical cations catalyze the Diels-Alder cycloaddition of 1,3-cyclohexadiene, presumably through a radical chain mechanism (*56*). The $\mathrm{Fe^{3+}}$-doped K10 clay also catalyzes this type of Diels-Alder reaction (*57*).

Prebiotic Synthesis over Clays?

The diversity of organic reactions catalyzed by clay systems is impressive. It is tempting to consider clays as possible chemical microreactors in prebiotic syntheses. The working hypothesis is that montmorillonite clays could have served as supports and as catalysts for the emergence of the first biomolecules. A number of points must be addressed. Can clays oligomerize simple molecules into biomolecules? Can the required dehydration reactions occur in an aqueous environment? Can clays protect their reaction products from photodecomposition under intense irradiation from sunlight? Can clays store energy and release it transformed into chemical energy to operate these condensation reactions? Can clays distinguish stereoisomers to form certain products selectively?

Before giving the answers to these questions (and most of them are affirmative), note that the assumed importance of clays for the origin of life can be traced to J. Desmond Bernal. In the late 1940's, he gave a series of lectures that were reprinted as a book, *The Physical Basis of Life* (*58*).

The Bernal hypothesis was seminal. Many prebiotic scenarios invoking clays have been written, and likewise many prebiotic experiments have used clays. Clays have been variously postulated as buffers, as adsorbants, and as catalysts and templates (*59*). A number of prebiotic simulations have used clay surfaces (*2, 60, 61*). Many experiments have used clays as catalysts for the formation of biomolecules (*61*) such as porphyrins (*62*). In Coyne's words "essentially all of the biologically significant monomers have been produced on clay surfaces, as have a number of oligomeric chains of these monomers" (*63*).

Weiss has suggested that clays may have served as templates for the first self-replicating systems on this planet. He claimed that the irregularities (that is, the information content) in an aluminosilicate sheet are transferred to the replica layers during an intercalating synthesis (*64*). Cairns-Smith's genetic takeover scenario holds that clays could very well have served as "low-tech" precursors to the self-replicating biomolecules as we now know them (*65*). Oligomers of glycine have been formed in the presence of clays subjected to cycles of wetting and drying simulating natural cycles (*66*).

Coyne has addressed the question of conversion of energy through the agency of clays. Ionizing radiation from radioactivity or the energy due to mechanical stress could be stored within the lattice as trapped holes, and released in the form of additional acidic catalytic sites (*67*). Luminescence can be induced by dehydration of a clay and mechanical stress can translate into triboluminescence (*68*). In short, clays can store energy from the environment and release it in various forms (*63*).

Future Directions

Iron-rich clays exhibit impressive and varied activity. Two avenues for research are prospection of the properties of clays doped with other transition metal cations and of modes of activation that will disorganize the crystalline lattice of smectite clays. A third and complementary approach is the study of energy storage, redistribution, conversion, and release by clays. Much of clay chemistry is driven by lattice energies, through reorganization of the perturbed system to a lower potential energy and use of a small fraction of the energy thus released. Such studies should reveal not only other applications for clay chemistry, but also new insight into the mechanisms of these reactions.

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