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OXIDATION OF BENZIDINE ON LOW-IRON SMECTITES: A PROPOSED MECHANISM

Key Words—Benzidine, Cation exchange, Iron, Oxidation, Smectite, Tetramethylbenzidine.

Benzidine (BZ) and its derivative compounds, such as 3,3′,5,5′-tetramethylbenzidine (TMBZ), adsorb instantly on smectites at low pH by cation exchange (McBride, 1979, 1985). For smectites which possess octahedral Fe^{3+} in significant quantities (such as Upton, Wyoming, montmorillonite), an immediate electron transfer between adsorbed BZ or TMBZ and structural Fe occurs, with the oxidation of the BZ and TMBZ molecules to form a blue charge-transfer complex (McBride, 1985). This reaction consumes little or no molecular oxygen from solution at least initially, although evidence exists for a small O_2 consumption after long equilibration times, which may reflect a slow reoxidation of structural Fe^{2+} by O_2 (unpublished data). The rapid kinetics of the oxidation of BZ and TMBZ by structural Fe^{3+} compared with oxidation by O_2 in solution is probably due in part to concentration of the reactants on the surface (by ion exchange), and the close proximity of the electron donor to the acceptor. Thus, the probability of reaction is greatly improved on the clay surface.

For hectorite, however, the immediate oxidation of BZ and TMBZ is limited by the low level of structural Fe^{3+} (McBride, 1979). If dissolved molecular oxygen is removed from the hectorite suspension, very little oxidation occurs over a period of days. In the presence of air, oxidation of adsorbed BZ and TMBZ by O_2 in clay suspensions is slow, but much more rapid than in aqueous solution. No evidence exists for O_2 consumption by the reaction in hectorite suspensions, even after long-term equilibrations. Measurement of the oxidation potential of TMBZ-hectorite suspensions by a Pt electrode shows the potential to be lower (less positive) than that of the analogous TMBZ-montmorillonite at all stages of reaction (unpublished data). The lower potential may be a consequence of the low Fe^{3+} content of hectorite and could account for the relatively slow oxidation on hectorite. Nevertheless, the presence of hectorite does promote oxidation of TMBZ when compared with oxidation in solution. This paper offers an explanation for the accelerated rate of oxidation on hectorite. The proposed mechanism may explain the modified behavior of numerous reactive molecules on layer silicates.

PROPOSED MECHANISM

Several possible reasons can be proposed for an enhanced oxidation rate at a low-Fe clay surface:

1. The oxidation of the diamine (BZ and TMBZ) to the charge-transfer complex (one-electron oxidation product) or diimine (two-electron oxidation product) generates protons. The clay exchange sites can adsorb these protons, maintaining a less acidic environment favorable to oxidation. Inasmuch as TMBZ is insoluble in water at high pH, and low pH is less favorable to solution oxidation, oxidation in aerated solutions is slow. An explanation for rapid oxidation on clays based on buffering, however, is not convincing because the acidification of Na^+-hectorite suspension to pH 3.5 does not appear to slow the rate of oxidation of adsorbed TMBZ (unpublished data).

2. The oxidized product may have a stronger bonding energy to the surface then the unoxidized cationic molecule. Thus, the equilibrium would shift in favor of oxidation (Feldkamp and White, 1979); however, the fact that TMBZ and BZ adsorb almost completely from solution *prior* to oxidation on low-Fe^{3+} smectites suggests that bonding energy is not the controlling factor.

3. Adsorption of the TMBZ and BZ cations at the planar smectite surface may favor a flattened configuration of the molecule as opposed to the twisted configuration expected in solution (Figure 1). X-ray powder diffraction of moist hectorite films after equilibration with aqueous acid TMBZ solution has revealed both collapsed (12.6 Å) and expanded (19.1 Å) interlayer spacings (McBride, 1985). Electrostatic and van der Waals attractive forces combined with the motional restrictions imposed by narrow interlayer spacings may overcome the energy barrier (several kilocalories/mole) to a planar configuration. Bipyridinium ions, which are structurally similar to the benzidine compounds, also adopt a flattened orientation on wet montmorillonite (Hayes *et al.*, 1978). In fact, the adsorption process appears to be less exothermic if the molecule is forced to flatten in the collapsing interlayer (Hayes *et al.*, 1978). The end result is a higher energy state for the adsorbed molecule, attained by sacrificing part of the adsorption energy.

Calculations of molecular orbital energies of benzidine by extended Hückel theory for different tilt angles between the aromatic rings predict that the planar molecular configuration (tilt angle = 0°) destabilizes the highest energy occupied molecular orbital (HOMO) of BZ or TMBZ (Figure 2), thereby making the electron transfer from BZ or TMBZ to the lowest-energy un-

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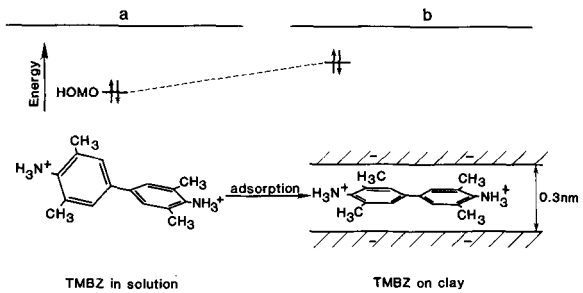


Figure 1. Diagram showing the twisted (a) and planar (b) configurations of tetramethyl-benzidine (TMBZ) in solution and in a clay interlayer, respectively. Corresponding relative energy levels of the highest occupied molecular orbital (HOMO) are also depicted.

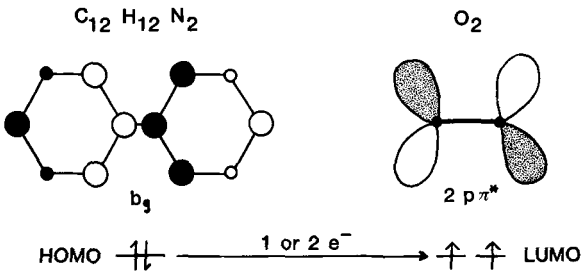


Figure 3. Molecular orbitals involved in the oxidation of benzidine ($C_{12}H_{12}N_{12}$) by O_2. Electron density is unequally distributed in the highest occupied molecular orbital of benzidine, indicated by the unequal size of the circles.

occupied molecular orbital (LUMO) of O_2 (or to structural Fe^{3+}) energetically more favorable, as demonstrated diagrammatically in Figure 3. The products of both the one-electron and two-electron oxidation steps are planar because the radical cation and diimine oxidation products are both conjugated ring structures having double bond character associated with the interring C–C bond (Hester and Williams, 1981). Therefore, based upon orbital symmetry and energy arguments, the planar configuration of the benzidine molecule should facilitate oxidation relative to the nonplanar configuration.

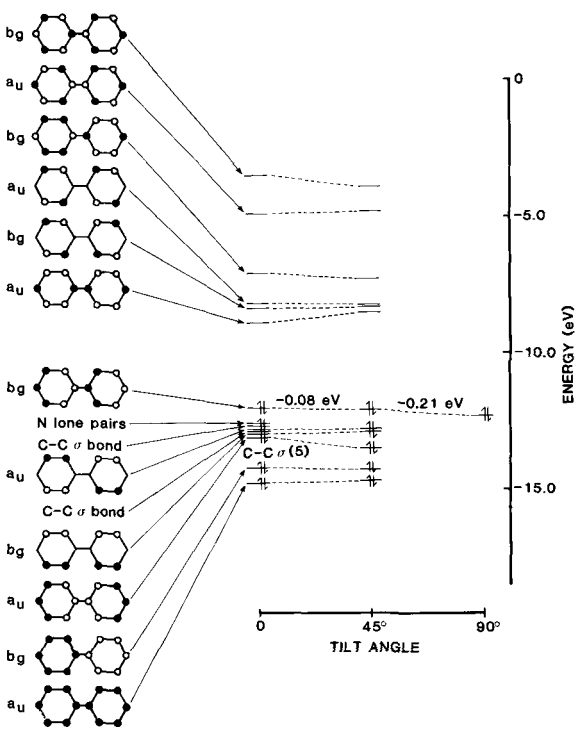


Figure 2. Symmetries and calculated energies of the molecular orbitals of benzidine according to Hückel theory. Signs (positive or negative) of the coefficients for the orbitals are demarked by open and closed circles. Symmetry designations for the orbitals are listed to the left of the molecular orbital diagrams.

Although the energy level of the HOMO is of most concern (because it is this orbital that donates one or two electron(s) in the oxidation process), the calculated energy levels and symmetry of the other molecular orbitals of benzidine are depicted in Figure 2. The effect of ring-tilt angle on energy is shown for selected orbitals. In particular, flattening the molecule from the 90°-twisted to the 0°-planar configuration generates a predicted increase of 0.29 eV (6.7 kcal/mole) in the energy of the HOMO. (The absolute energies of the orbitals calculated from extended Hückel theory are not highly accurate, but energy changes as a function of molecular configuration are reliably predicted.)

A test of the hypothesis that the planar molecular configuration of BZ on smectites promotes oxidation could be based upon the behavior of a chemically similar compound, such as aniline, which is not stereochemically modified by adsorption. Aniline adsorbs on smectites as a cation, but shows no evidence of immediate oxidation, unlike BZ (Furukawa and Brindley, 1973). Polarography, however, indicates that aniline oxidizes as readily as BZ in acid aqueous solution. Oxidation potentials for aniline and BZ under the same experimental conditions are +0.42 V and +0.47 V (relative to the standard calomel electrode), respectively (Meites and Zuman, 1977). Therefore, promotion of oxidation is not wholly explained by the chemical environment of the surface or the tendency of the surface to adsorb the oxidation product more strongly, inasmuch as both BZ and aniline are subject to these influences.

The results of chemical pretreatments of Na^+-hectorite designed to modify the availability and character of surface adsorption sites or eliminate potential electron acceptors support the hypothesis of surface-promoted oxidation of BZ and its derivatives by molecular oxygen. Addition of hydroquinone, an electron donor,

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to the clay does not prevent the surface oxidation of subsequently added TMBZ. Pretreatment of the clay with solutions of hydroquinone or hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in an attempt to reduce any Mn oxide impurities does not prevent subsequent oxidation of TMBZ, indicating that such impurities in the hectorite could not have acted as a catalyst or electron acceptor for the oxidation process (unpublished data). This possibility has to be considered in clay systems because of the effectiveness of manganese oxides in oxidizing benzidine and related compounds. Preliminary experiments in our laboratory indicate rapid oxidation of TMBZ by synthetic hausmannite (Mn_3O_4) to generate soluble Mn^{2+}, with little or no consumption of O_2.

Saturation of the exchange sites with hexadecyltrimethyl-ammonium ($HDTMA^+$) cations prior to the addition of TMBZ to hectorite prevents the oxidation reaction. Saturation of the exchange sites with tetramethylammonium cations (TMA^+) does not prevent oxidation, but visibly alters the reaction in favor of the yellow free radical and/or diimine over the blue charge-transfer complex. These results can be rationalized if it is realized that the $HDTMA^+$-saturated hectorite, despite a basal spacing of 19.2 Å, has little interlayer surface available for the adsorption and oxidation of TMBZ because of the large size of the $HDTMA^+$ cations (McBride *et al.,* 1977). In contrast, the TMA^+-saturated clay has a large interlayer surface (>200 m^2/g), despite a low basal spacing (13.6 Å). The site dimensions, determined by the interlayer width and the distances among TMA^+ cations, may be too small to accommodate pairs of TMBZ molecules necessary to form the charge-transfer complex. Instead, the planar free radical or diimine monomer is generated by a one- or two-electron oxidation, respectively. Either of these species, if aligned flat on the surface, can be accommodated in the narrow interlayer of TMA^+-hectorite. This explanation of results based on site geometry is not the only possibility, inasmuch as the suppression of formation of charge-transfer complexes can also be explained by strong competition of TMA^+ for exchange sites, thereby preventing a high surface loading of TMBZ. McBride (1985) noted that low adsorption densities of TMBZ on hectorite tend to inhibit the formation of the charge-transfer complex.

The planar layer silicate surface appears to offer a unique chemical environment for adsorption of benzidine and its derivatives, promoting oxidation to products which can be predetermined to some degree by clay surface modification. The proposed mechanism for oxidation, if correct, implies that layer silicates may catalyze oxidation of numerous compounds for which adsorption changes the most favorable stereochemical arrangement of the molecule.

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