New Colored Chlorinated Hydrocarbon-Clay Complexes*

by R. HAQUE and DEAN HANSEN
Department of Agricultural Chemistry
Environmental Health Sciences Center
Oregon State University
Corvallis, Ore. 97331

Introduction

Chlorinated hydrocarbons such as insecticides of the DDT class and the polychlorinated biphenyls (PCB's) are widely distributed in the environment. Most of these compounds are practically insoluble in water, and show a tendency to be sorbed on particulate matter, especially on soils and bio-colloids. This sorption property is a major factor influencing the distribution of these chemicals in the biosphere, although little is known about their mechanism of interaction. In this report we present evidence of the formation of colored complexes between chlorinated hydrocarbons and sodium saturated montmorillonite clay. These complexes show a strong electron spin resonance (e.s.r.) signal, indicating their free-radical nature. Since chlorinated hydrocarbons persist in soils for years (NASH and WOOLSON, 1967), these findings may have significance in determining the fate of chlorinated hydrocarbons in soils.

Experimental

The montmorillonite clay used was Wyoming bentonite furnished by Baroid Division of National Lead Company. This clay was ion exchanged with sodium, centrifuged, and spray dried. The chlorinated hydrocarbons and related compounds used in this study are listed in Table 1, and were 99+% pure. The complexes were prepared by refluxing the chlorinated-hydrocarbon and the montmorillonite clay (normally 0.5g of chemical per g of clay) in cyclohexane for 20 hours. A Dean-Stark condenser was used to collect any water which was released; however, no water was collected. As the reaction progressed, the color of the clay changed. The color was highly dependent upon the nature of the chlorinated hydrocarbon. All complexes showed e.s.r. signal around $g=2.0$. The e.s.r. measurements were carried out on a Varian E-4 spectrometer. Samples were run in a quartz tube at room temperature. The experiments as a function of pH and humidity were carried out by controlling the pH and humidity of the clay before the reaction was started.

Results and Discussion

Montmorillonite itself gives an e.s.r. signal (WAUCHOPE and HAQUE, 1971) around $g=2.0$ i.e., the free electron value, which in most cases was enhanced in the complexes. This indicates either

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an increase in the concentration of the original free radical in the clay or formation of a new free-radical in the complex. Since the intensity of the e.s.r. signal and the color of the complex (Table 1) are strongly dependent upon the chemical, it is more likely that the increase in the signal intensity is due to a chlorinated hydrocarbon free-radical on the clay surface.

The e.s.r. signal observed in the present investigation may be explained on the basis of a free radical of the chlorinated hydrocarbon in the interlamellar layer of the clay. Apparently the formation of the free radical may be due to the catalytic activity of acidity on the clay surface. Such a catalytical reaction has been reported by ROONEY and PINK (1961) for the free-radical formation with aromatic hydrocarbon on a silica-alumina surface.

MORTLAND and co-workers (1969, 1971) have shown that aromatic hydrocarbons can interact with copper saturated montmorillonite and may form colored complexes and that the color of the complex is due to the π bonding between the aromatic molecule and the copper ion. RUPERT (1973) has recently reported that the aromatic hydrocarbon-copper saturated montmorillonite clay complex gives an e.s.r. signal around g=2.0 and has explained that the e.s.r. signal arises because of loss of aromaticity in the complex. However, our findings show that the sodium-montmorillonite clay which is considered less reactive can also form colored complexes. This also suggests that the color of the complex is not necessarily due to metal binding as reported earlier (DONER and MORTLAND, 1969; MORTLAND and PINNAVAIA, 1971; RUPERT, 1973). Furthermore, these findings also suggest that chlorinated hydrocarbons, which are quite different than simple aromatic hydrocarbons could also form colored complexes.

The color of the complex and the intensity of the e.s.r. signal was dependent upon the humidity and pH of the clay. The signal intensity increased up to 30% humidity, with a further increase in the humidity the intensity of the signal decreased. At very low humidity (23%) the clay platelets are collapsed making it impossible for the DDT molecules to penetrate between the layers. As the humidity increases (>30%) more water is sorbed on the clay. At this point due to the low affinity of chlorinated hydrocarbons to water, the extent of the reaction decreases, causing a decrease in the signal intensity. At pH 7.0 the intensity of the DDT-clay complex (brown-moss green) was 100 whereas at pH 3-4 the intensity of the e.s.r. signal increased to 500 with the change in the color of the complex (dark brown to black). No reaction occurred in alkaline solution. Upon exposing the complex to air for few hours, the color changed from brown or moss green to blue gray, and the e.s.r. signal of the blue gray complex showed three additional peaks. MORTLAND and PINNAVAIA (1971) also observed a color change upon the addition of water to a benzene-copper-montmorillonite complex. The addition peaks may be attributed either to the physical adsorbed species or anisotropy caused by the hydration. Upon heating the blue gray complex at 110°C for an hour, the complex reverted to its original color and the additional e.s.r. signals disappeared.

Methoxychlor; *p,p'*-DDT; dicofol; *p,p'*-DDD and the PCB 4,4'-dichlorobiphenyl produce strong signals. Whereas dieldrin, 4,4-dichlorobenzophenone, and *o,p'*-DDT show small increases in the e.s.r. signal. Finally *p,p'*-DDE, *p,p*-DDA, and lindane produce no enhancement in the e.s.r. signal. It is interesting to note that *p,p'*-DDE and *p,p'*-DDA are relatively non-toxic and their complexes show no enhancement in the e.s.r signals. The observation of no enhancement in the e.s.r. signal in lindane-complex may be due to the absence of a benzene ring in the complex.

At present, with limited data it is difficult to elucidate the precise mechanism of the free radical formation. Nevertheless, these results are important in many respects and their environmental significance may be speculated. Some of the chlorinated hydrocarbons used in the present investigation are persisent compounds and spend considerable time in soils (NASH and WOOLSON, 1967). The formation of these complexes in soils and biosphere could be visualized in a rather extreme condition. The colored complexes reported in this paper are new and their possible presence in the biosphere may represent an additional factor in describing the persistence and behavior of chlorinated hydrocarbons in the environment.

References

DONER, H.E., and M.M. MORTLAND: Science 166, 1406 (1969).

MORTLAND, M.M., and T.J. PINNAVAIA: Nature (London) 229, 75 (1971).

NASH, R.G., and E.A. WOOLSON: Science 157, 924 (1967).

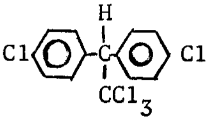
ROONEY, J.J., and R.C. PINK: Proc. Chem. Soc. 142 (1961).

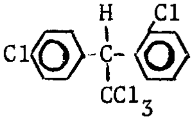
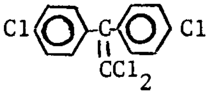
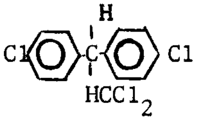
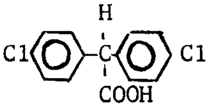
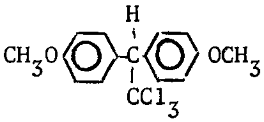
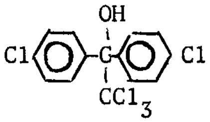
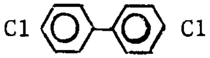
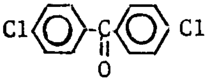
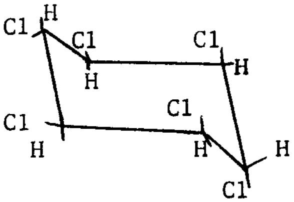
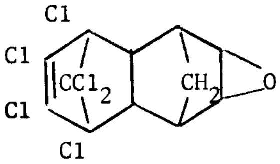
RUPERT, J.P.: J. Phys. Chem. 77, 784 (1973).

WAUCHOPE, R.D., and R. HAQUE: Nature (London) Phys. Sci. 233, 141 (1971).

TABLE 1

CHARACTERISTICS OF THE CHLORINATED HYDROCARBON-MONTMORILLONITE CLAY COMPLEXES

Compound	Structure	Color of the complex	E.S.R. signal height (arbitrary unit)	Signal width Hz
Clay alone		Light tan	21	16
p,p'-DDT		Brown to moss green	103	13

o,p'-DDT		Brown	36	12
p,p'-DDE		Light tan	25	6
p,p'-DDD		Brown	103	13
p,p'-DDA		Light tan	27	8
Methoxychlor		Brown	290	7
Dicofol		Brown	110	8
PCB		Brown	107	6
4,4'-Dichlorobenzophenone		Light tan	45	11
Lindane (γ-hexachlorophene)		Light tan	24	7
Dieldrin		Light tan	42	9