NOTES

ORGANIC REACTIONS IN CLAY-MINERAL MATRICES: MASS-SPECTROMETRIC STUDY OF THE CONVERSION OF TRIPHENYLAMINE TO N,N,N',N'-TETRAPHENYLBENZIDINE

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In the course of a programme of study aimed at the elucidation of the nature of the initial and subsequent reactions of organic molecules with or within montmorillonoid sheet silicates, we have found mass spectrometry to be of great advantage. For example pyrolysis of diprotonated 4,4'-diaminostilbene montmorillonite intercalate, which results in the production of aniline, can be readily explored by mass spectrometry (Tennakoon *et al.,* 1974). Here we report upon the interaction of triphenylamine with montmorillonite. Alcohol solutions of triphenylamine react with suspensions of montmorillonite to produce a green material which becomes deep red on drying. X-ray powder diffraction patterns of the montmorillonite before and after interaction with triphenylamine were identical thus demonstrating that the triphenylamine was not intercalated under the preparative conditions used.

Small samples of the triphenylamine–montmorillonite complex when heated in the temperature range 40–150°C in a vacuum of approximately 10^{-7} torr in an AEI MS30 double-focusing mass spectrometer revealed (see Figure and Table) a cracking pattern totally different from that of triphenylamine itself. Fragments having m-equiv. values greater than 245 the mass:charge ratio of the molecular ion of triphenylamine, are observed in this pattern. The largest fragment has a m-equiv. ratio of 488 and this could reasonably correspond to the tetraphenyl derivative of benzidine.

Moreover the observed cracking pattern is in good agreement with that of pure N,N,N',N'-tetraphenylbenzidine alone (see Table 1). This observation taken together with the u.v. and visible spectroscopic evidence of Hasegawa (1962) (who examined benzene solutions of triphenylamine in contact with aqueous colloidal suspensions of bentonite) for the production of this species, allows us to conclude that the fragment of mass 488, observed in this work, is that of the tetraphenyl derivative of benzidine.

Plausible mechanisms for the production of tetraphenyl benzidine may be formulated based on the initial production of triphenylamine radical cations at Lewis acid sites at the external clay surfaces (for a review of Lewis acid sites at clay surfaces see Theng (1971)).

$$Ph_3N \xrightarrow[\text{Site}]{\text{Lewis Acid}} (Ph_3N\cdot)^+$$
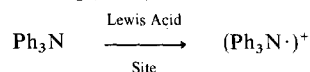
Two reaction pathways may be postulated for the formation of tetraphenylbenzidine: (1) dimerisation resulting in the formation of N–N bonds

$$2(Ph_3N\cdot)^+ \longrightarrow (Ph_3N\text{–}N\,Ph_3)^{2+}$$

followed by deprotonation and the benzidine rearrangment

$$(Ph_3N\text{-}NPh_3)^{2+} \rightarrow 2H^+ + Ph_2N\text{–}\bigcirc\text{–}\bigcirc\text{–}NPh_2$$
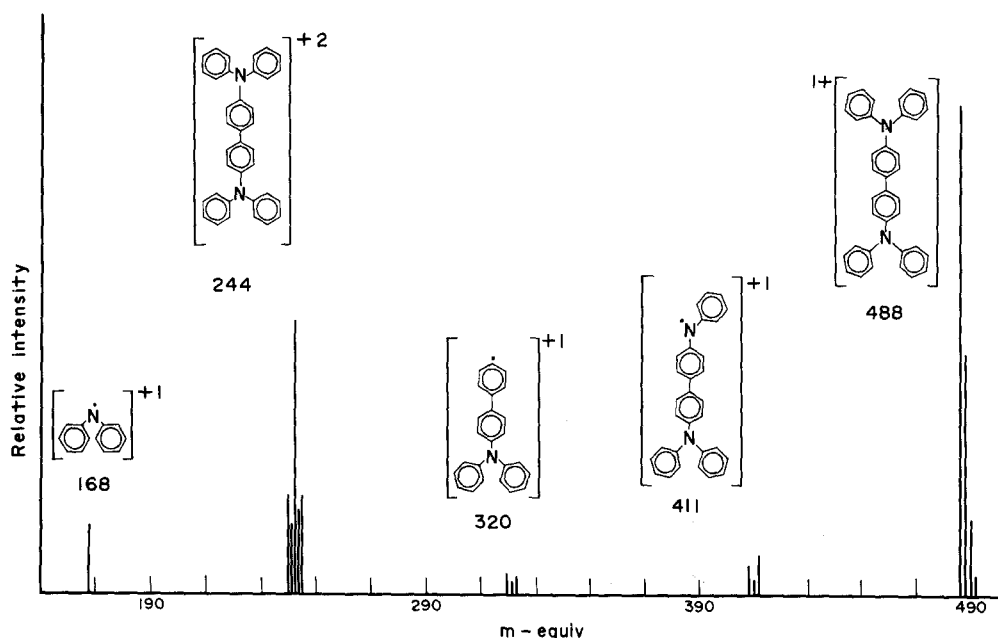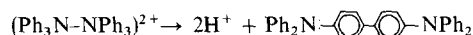

Fig. 1. Salient features of the mass spectrometric cracking pattern of the triphenylamine–montmorillonite complex. Note large fragment having a m-equiv. ratio of 488 corresponding to the molecular ion of tetraphenylbenzidine.

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Table 1. Salient features of the mass spectrometric cracking pattern of tetraphenylbenzidine and of the volatile product produced by heating the montmorillonite triphenylamine complex at 40°C in a vacuum better than 10^{-7} torr. The m-equiv. ratios, the empirical formula of the fragments and relative intensity ratios are tabulated for the significant peaks

| | | Relative intensities | |
m-equiv.		Tetraphenylbenzidine	Volatile products from montmorillonite–triphenylamine complex
490	$[(Ph_2NC_6H_4)_2H_2]^+$	40	40
489	$[(Ph_2NC_6H_4)_2H]^+$	170	130
488	$[(Ph_2NC_6H_4)_2]^+$	420	310
487	$[(PH_2NC_6H_4NPhC_6H_4]^+$	8	9
245	$[(Ph_2NC_6H_4)_2H_2]^{2+}$	64	45
244.5	$[(Ph_2NC_6H_4)_2H]^{2+}$	38	39
244	$[(Ph_2NC_6H_4)_2]^{2+}$	105	100
168	$[Ph_2N]^+$	13	21
167	$[PhNC_6H_4]^+$	20	38
166	$[(C_2H_4)_2N]^+$	7	19

or: (2) a direct coupling between the para positions of the benzene rings of two triphenylamine radical cations followed by elimination of two protons.

We further note that the production of tetraphenylbenzidine is almost quantitative as evidenced by the similarity of the intensity of fragments having a m-equiv. ratio less than 245 in the cracking patterns of the pure organic and of the volatile product from the clay–organic complex.

Other reactions, the study of which is facilitated by mass spectrometry, will be reported in more detail elsewhere.

Experimental

Suspensions of Wyoming montmorillonite in alcohol (sedimented fraction of < 0·02 μm equivalent spherical diameter of Ward's standard clay mineral No. 48W 1250) were allowed to react with an alcohol solution of triphenylamine for one week. The resulting green material thoroughly washed in alcohol, separated and dried over calcium chloride in a vacuum desiccator, to yield a reddish purple product. The N,N,N′,N′-tetraphenylbenzidine was prepared by a method described by Wieland (1913).

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QUANTITATIVE MINERALOGICAL ANALYSIS OF SOIL CLAYS CONTAINING AMORPHOUS MATERIALS: A MODIFICATION OF THE ALEXIADES AND JACKSON PROCEDURE

The scheme for quantitative mineralogical analysis of the clays of soils and sediments based on physico-chemical determinations as proposed by Alexiades and Jackson (1966) can be applied successfully to the analysis of clays which are chiefly composed of crystalline minerals. Cation exchange capacity (CEC) and potassium fixation capacity analyses are used for quantitative determination of the smectite and vermiculite components. In the calculations (Alexiades and Jackson, 1966, equation 2) amorphous material, determined separately, is assigned a CEC value of 110 m-equiv./100 g only if its SiO_2/R_2O_3 molar ratio is greater than 3·0. Amorphous inorganic constituents having a ratio less than 3·0 are assumed to have no CEC. A further assumption that amorphous minerals do not fix potassium on drying is implicit in the calculation for vermiculite (Alexiades and Jackson, 1966, equation 1).

Recent studies (Raman and Mortland, 1970; De Villiers, 1971) have indicated that soil amorphous aluminosilicates with varying SiO_2/R_2O_3 molar ratios lower than 3·0 also have considerable CEC. Similarly, amorphous components have been reported by van Reeuwijk and De Villiers (1968) and Raman and Mortland (1970) to have considerable K^+-fixation capacity. The assumptions made in the Alexiades and Jackson procedure might, therefore, lead to considerable error in the determination of smectite and vermiculite in soil clays containing large amounts of amorphous material. However, Briner and Jackson (1970) assumed a CEC value of 20–160 m-equiv./100 g for allophanes (from basaltic soils of Australia) with SiO_2/Al_2O_3 molar ratios ranging from 2·4–4·0 for quantitative clay mineral analysis. It is difficult to assign CEC and K^+-fixation capacity values to amorphous minerals for eliminating such errors unless a