

iodide was mixed with powdered inactive sodium fluoride and the reflexion spectrum measured. The spectrum of pure red mercuric iodide (Fig. 1, curve *d*) so obtained is similar to the spectrum of the red form on alumina in all important details. The reflexion spectra of mercuric iodide on alumina are therefore not modified significantly by the active adsorbent.

Energy required for the conversion of the stable to the metastable form is apparently derived from the heat liberated by the adsorption of mercuric iodide on alumina. Our experimental findings are in agreement with the theory advanced by Tovbin and Baram⁵ concerning the catalytic conversion of a stable to a less-stable form through heat of adsorption.

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Solution of Iodine in Phosphorus(III) Isocyanate

DURING an investigation of the solvent properties of phosphorus(III) isocyanate¹ it was observed that iodine dissolved to give a reddish-brown solution. It is well known that such coloured solutions of iodine in 'active' solvents indicate some sort of solvent-solute interaction².

Previously³, it had been noted that iodine dissolved in phosphorus trichloride to give a violet solution with an absorption maximum at 5000–5200 Å. Since —NCO can be looked upon as a pseudo-halide, it might be expected that phosphorus isocyanate and phosphorus trichloride would behave similarly in so far as reaction with iodine is concerned.

Iodine dissolves slowly in phosphorus isocyanate with little heat of solution. The resulting solution is red-brown and shows an absorption maximum at 3300 Å. If an excess of iodine is added to phosphorus isocyanate a solid results. Removal of unreacted iodine with carbon tetrachloride yields an orange powder containing one half mole of iodine per mole of phosphorus isocyanate. This adduct reacts violently with water, a property commonly associated with the species phosphorus(III). In contrast, chlorine reacts vigorously with phosphorus isocyanate, sufficient heat being generated to boil the solution. The resulting yellow oil solidifies on contact with carbon tetrachloride to give a yellow crystalline solid, presumably $P(NCO)_3Cl_2$. The latter shows no evidence of phosphorus(III) formation after hydrolysis in water, thus indicating pentavalent phosphorus with chlorine bonded to phosphorus.

The colour of the solutions of iodine in phosphorus trichloride and in phosphorus isocyanate may be a result of the inability of iodine to co-ordinate to phosphorus in the former (due to the electron-withdrawing power of chlorine) and the enhanced co-ordination in the latter (due to the electron donation of isocyanate). Steric effects may also be involved

in the case of iodine and phosphorus trichloride since no PCl_2I_2 has been confirmed, although such a compound has been reported⁴.

The adducts $P(NCO)_3I$, as observed in this work, and PCl_2I ⁴ are similar in stoichiometry and would seem worthy of further investigation.

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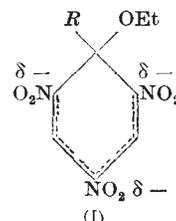
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Interaction of 1,3,5-Trinitrobenzene with Ethoxide Ion

WHEN a dilute solution of 1,3,5-trinitrobenzene in ethanol is treated with sodium ethoxide, a yellow solution is formed. A similar colour is produced when sodium ethoxide is added to 2,4,6-trinitroanisole. The rates of development of the colours have been studied by Ainscough and Caldin¹, who found that there are two colour-producing reactions: (i) a 'fast' reaction the product of which they suggest is a charge-transfer complex, and (ii) a 'slow' reaction, which probably produces an addition compound where OEt is covalently bonded to the nucleus, as was suggested by Meisenheimer² for the solid obtained in this reaction ($I, R = OCH_3$). With 1,3,5-trinitrobenzene and sodium ethoxide only one reaction was observed, and on the basis of similar rates of reaction and similar effects of acid on the two systems, Ainscough and Caldin suggested that the product is a charge-transfer complex analogous to the 'fast' reaction with 2,4,6-trinitroanisole. The absorption spectra of the trinitrobenzene + sodium ethoxide obtained by them did not resemble that of trinitroanisole + sodium ethoxide.



The absorption spectrum of 2,4,6-trinitroanisole in ethanol in the visible region in the presence of an excess of potassium ethoxide has been re-measured and compared with that of 1,3,5-trinitrobenzene under the same conditions. If measured within an hour of mixing at room temperature, the two spectra, expressed in terms of the formal molar extinction coefficient (optical density/molarity of nitrocompound) do resemble one another closely. Both solutions obey Beer's law and both bear a close resemblance to Meisenheimer's compound in acetone³. After a day, the spectrum of 1,3,5-trinitrobenzene in excess potassium ethoxide resembles that obtained by Ainscough and Caldin. Similar results were obtained using sodium ethoxide. This suggests that 1,3,5-tri-