Analogous isomers where $L = P(C_6H_5)Cl_2$, $P(C_4H_9)_3$, and $P(OC_4H_9)_3$ have been prepared and identified by their infra-red spectra. The *cis*-$Mn(CO)_3py_2Br$ was found not to isomerize to the *trans* form, nor did the aniline complexes. On the other hand, $P(C_6H_5)_3$ formed no disubstituted *cis* product, but at higher temperatures yielded the *trans* compound. The ligand, $P(OCH_2)_3CCH_3$ (ref. 6), forms the disubstituted *cis* compound which isomerizes at 50° only to the extent of 20 per cent, whereas the above isomerizations go essentially to completion. This suggests the importance of steric factors in the isomerization.

The kinetics of the *cis* to *trans* isomerizations have been studied in *s*-tetrachloroethane from 50° to 70°. The rates are first order in complex and independent of added ligand, *L*. The activation energies increase with changing *L* in the following order :

$$P(C_6H_5)Cl_2 < P(C_4H_9)_3 < P(OC_6H_5)_3 < P(OC_4H_9)_3$$

The $P(C_4H_9)_3$ isomerization was measured in $P(C_4H_9)_3$ solvent due to decomposition in tetrachloroethane ; however, solvent effects are very small. The *cis*-isomer, $Mn(CO)_3[P(OC_6H_5)_3]_2Br$, in tetrachloroethane at 60° reacts with $P(OC_4H_9)_3$ at about ten times the rate of its isomerization to give *cis*-$Mn(CO)_3[P(OC_4H_9)_3]_2Br$ probably via the mixed *cis*-$Mn(CO)_3[P(OC_6H_5)_3][P(PC_4H_9)_3]Br$. This suggests a dissociative mechanism for the isomerization involving the formation of a five co-ordinated intermediate which reacts with free phosphine to reform the *cis*-isomer with an activation energy roughly 1 kcal/mole less than that for formation of the *trans*-isomer.

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Hydrogen Bonding and Charge-Transfer Complexes

If equal amounts of trinitrobenzene and a polycyclic aromatic hydrocarbon are dissolved in chloroform and the solution is dried off on to filter paper, a colour often appears due to the formation of a charge-transfer complex. The new absorption bears no relation to that of either of the components separately, and may be almost anywhere in the spectrum depending on the hydrocarbon. It is generally believed that negative charge is transferred from the hydrocarbon, acting as donor, to the trinitrobenzene, acting as acceptor. Other kinds of donor and acceptor are known[1], and a theory of such complexes, base on molecular orbitals, has been given by Mulliken[2].

Interaction under similar conditions but of a different kind was reported by Szent-Gyorgyi between donor-type compounds and acridine[3]. In this case a yellow colour was observed, particularly with the carcinogens. As he pointed out, there could have been no charge-transfer complex since the colour was always the same, and in any event acridine has negligible acceptor properties in this context. There may have been a weak chemical link between the acridine nitrogen and some unsaturated centre in the other molecule, giving the yellow acridinium cation on one side of the associated system. A possible bond of this kind should be contrasted with the delocalized electron interaction found in charge-transfer complexes.

We have now found that if a weak acid such as acetic acid is applied to the acridine/donor system a new colour appears which is dependent on the nature of the second component. Mineral acid, on the other hand, merely intensifies the yellow colour. It seems that a charge-transfer complex can be formed between 'acridine acetate' and donor-type compounds, and tests with each of seventy such compounds showed that the depth of colour produced was similar to that which they produced with 2-methyl naphthoquinone. This means that 'acridine acetate' has an electron affinity similar to that of the strongest known biological acceptors. With mineral acid there is presumably complete ionization of the acridine, and the absence of any charge-transfer colour under these conditions indicates that the interaction is still essentially non-ionic and would take place in the lipid rather than the aqueous phase.

One-electron transfer is believed to play an essential part in metabolism, and some water-soluble Krebs-cycle intermediates have recently been shown to have a high affinity for thermal electrons[4]. Lipid-soluble acceptors important in metabolism are not so easy to find. Some of the ubiquinones were tested for charge-transfer complex formation and found to be rather weak acceptors compared with 2-methyl naphthoquinone. The present observations suggest that suitable compounds can become strong electron acceptors by forming a weak reversible chemical link, such as a hydrogen bond, with a carboxylic acid or other compound containing active hydrogen. In support of this view, it was found that hexyl resorcinol was able to induce what appeared to be a charge-transfer complex between acridine and the strong donor *N*,*N*′ tetramethyl-*p*-phenylenediamine. Trichloroacetic acid was likewise able to induce a colour change in a mixture of dibenzylidene-acetone and the above-mentioned amine. Indolyl-3-acetic acid gave a brown colour with acridine alone, as did indole and acetic acid applied as separate compounds. One may speculate that the plant-growth hormone is not only a good electron donor but also carries, in the acetic acid moiety, a means of inducing certain molecules to accept an electron.

Szent-Gyorgyi's aqueous FMN-serotonin system[5] also seems to be activated by acid, though it is not known yet whether the mechanisms are related.

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