The alkali metals and singly charged alkaline earth metal ions are one electron systems, e.g. the valence orbital contains just one electron. The ionisation potentials of these one electron systems (1st IP for the alkali metals and 2nd IP for the alkaline earths) agree with the experimental values very closely; the difference being smaller for the higher members.  

In Table 1 are given the first ionisation potentials of the alkaline earth metals obtained through these calculations. It is observed that these values are much lower than the experimental ionisation potentials. For the above calculation we have evaluated the valence electron repulsion integrals using Eq. (4):

$$\phi_1(1) \phi_2(2) = f(q) = \text{constant,}$$

$$\phi_\alpha$$ in Eq. (4) is given by Eq. (3) and $$f(q) = 0.388021$$ for $$q = 1$$.

The results of this calculation show that more elaborate two electron problems should be carried out to achieve more accurate results. Here we propose an alternative simple way of arriving at quite satisfactory results. The electron repulsion terms, in Eq. (4), indicate that for a particular value of $$q$$, these integrals are directly proportional to the respective orbital exponents and the proportionality constant, $$f(q)$$ being the same for a particular periodic group. Thus instead of using the exact value of $$f$$ in Eq. (4), we suggest to treat it as a parameter. So the proposed scheme is to fix the value of this parameter for any one metal in the group and use that value of $$f(q)$$ for all the other metals in the same group to calculate the valence orbital energies and hence ionisation potentials. For the alkaline earth metals, the value of $$f(q$$) has been set to 0.24835. This is the best value of the parameter $$f(q)$$ exactly reproducing the experimental energy of the doubly occupied valence orbital of Be. The use of this value of $$f(q)$$ in the calculation of first ionisation potentials of other alkaline earth metals improves the results substantially, as is observed from Table 1.

**NOTES**

The interaction between vanadyl fluoride and alkaline earth metal fluorides in aqueous hydrofluoric acid medium results in the formation of $$K_2VOF_4$$ and the more complex salts $$Na_2VOF_4$$ and $$K_2VOF_4$$. From the mixture MF-VOF$_2$-H$_2$O (where $$M = K$$, Na or Rb) Pausweng$^4$ prepared $M_2VOF_4$ (where $$M = K$$ or Rb) and $Na_2VOF_4$. The present report includes the results of the phase equilibria study of $MF-VOF_2$-H$_2$O system, where $$M = Na$$ or K at 35$^\circ$.

$$K_2VOF_4$$3H$_2$O was prepared by the reduction of vanadium pentoxide by ethanol in presence of hydrofluoric acid (40%) on a water-bath followed by its evaporation to a viscous liquid and then drying in vacuo over sulphuric acid.

For the estimation of vanadium and fluorine, the compound was fused with sodium carbonate and the fused mass extracted with water. Vanadium was then estimated by standard titrimetric method using Mohr's salt solution and potassium dichromate. From a separate fusion of the compound fluorine was estimated gravimetrically as PbClF after separating vanadium as silver vanadate and excess of silver as silver chloride. Potassium was estimated as $K_2SO_4$ after separating vanadium as above.

Magnetic susceptibility was measured by Guoy method and the diamagnetic correction was applied as described by Figgis and Lewis$^5$. The TGA of the compound was carried out using a manually operated apparatus. The rate of heating was maintained at $\sim 2^\circ$ per min. The IR spectra were recorded with a Perkin-Elmer instrument in KBr in the region 400-4000 cm$^{-1}$.

For the phase equilibria study a series of mixtures were prepared containing different ratios (wt%) of vanadyl fluoride, water and anhydrous alkali metal fluoride in polythene bottles. The volume of water was adjusted in such a way that there always existed a solid phase and a liquid phase in equilibrium. After keeping the bottles for a month in a thermostat at 35$^\circ$, both the solid and liquid phases of each bottle were analysed for vanadium and fluorine and the contents of MF ($M = Na$ or K) and VOF$_2$ present in each phase determined. The results show the formation of $K_2V_3O_9F_8$ (Fig. 1) and $Na_2VOF_4$.

Potassium dioxyfluorodivanadate(IV), $K_2V_3O_9F_8$, was prepared by adding an aqueous solution (20 ml) of potassium fluoride (0.20 mole) dropwise with constant stirring to an aqueous solution (50 ml) of vanadyl fluoride trihydrate (0.05 mole). Immediately a blue crystalline compound separated out which was filtered by suction, washed several times with water and dried in air [Found: K, 39.40; V, 20.70; F, 33.32]. $K_2V_3O_9F_8$ requires: K 38.50; V, 20.40; F, 34.20%.

The potassium compound is sparingly soluble in water and its aqueous solution decomposes on keeping. Thermogravimetric study of $K_2V_3O_9F_8$ in air shows that the compound remains stable upto 300$^\circ$.
Spectroscopic Studies on the Electron Donor-Acceptor Interaction between Tetrachlorophthalic Anhydride & Aromatic Hydrocarbons

P. C. Dwivedi* & Anil K. Banga

Department of Chemistry, Harcourt Butler Technological Institute, Kanpur 208 002

Received 29 March 1979; revised 14 June 1979; accepted 28 June 1979

The electron donor-acceptor interaction between tetrachlorophthalic anhydride and a number of aromatic hydrocarbons has been examined by spectroscopic method. The spectroscopic and thermodynamic parameters of the complexes formed are reported. The \( h\text{CT} \) -ionisation potential plot is found to be linear. The enthalpies of formation range between 0 and 7.0 kcal/mole. Among all the aromatic hydrocarbons studied, hexamethylbenzene appears to be the strongest electron donor towards tetrachlorophthalic anhydride.

Formation of electron donor-acceptor (EDA) complexes has been extensively studied in the last few years. Despite the large number of compounds studied as electron acceptors little is known about the electron accepting properties of tetrachlorophthalic anhydride (TCPA). Electron affinity of TCPA (1.8 eV) is comparable to that of 1,3,5-trinitrobenzene (1.86 eV) which is known to be a good electron acceptor. Therefore, TCPA is expected to form EDA complexes with a variety of electron donors. Stable molecular complexes of TCPA with aromatic hydrocarbons and aza-aromatics are known. Charge-transfer bands in TCPA-aza-aromatic systems have been reported by Chakrabarti. Chowdhury and Basu have evaluated the formation constants \((K)\) of 1:1 complexes of poly-nuclear aromatic hydrocarbon with TCPA. The plot of charge-transfer interaction energy against \( n \)-ionisation potential for these complexes has been found to be linear. With phenanthrene and stilbene as electron donors, accurate values of \( K \) could not be obtained at the charge-transfer peak due to the appreciable absorbance of these donors. As part of an extended program to study the EDA complexes of TCPA, we have recently investigated the interaction of TCPA with bifenyl, \( \alpha \)-bromonaphthalene, naphthalene, anthracene, phenanthrene,acenaphthene, 2-bromofluorene, hexamethylbenzene, \( m \)-xylene and toluene. Another point of interest was to find out the energies of interaction in these systems as these were not available in the literature. Furthermore, attempts were made to determine accurate \( K \) values by compensating for donor absorption in the reference cell and subtracting acceptor absorption.

All the aromatic hydrocarbons were obtained commercially and purified by crystallisation from fractional distillation. Carbon tetrachloride (BDH, AR) was dried and distilled before use. Tetrachlorophthalic anhydride was repeatedly crystallised from benzene until its absorption spectrum in carbon tetrachloride showed no further change. The spectral measurements were made with Beckman DU spectrometer.

---

**References**