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CHARGE TRANSFER COMPLEXES IN SOLUTION. II. DETERMINATION OF IONIZATION POTENTIALS OF ALCOHOLS[*]

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On the basis of Mulliken's charge transfer theory of molecular complexes (1), it is predicted that an electron donor molecule and an acceptor molecule may interact to form a weak intermolecular complex. It has been observed that the electronic absorption spectra of such systems often show a new absorption band, the charge transfer band (CT-band), due to the presence of the complex (a distinct chemical species).

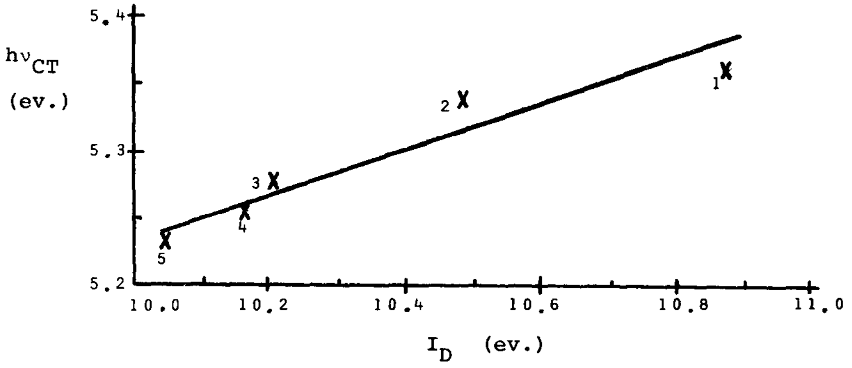
Previous workers have noted (2) that the position of the CT-band maximum is related to the strength of interaction between the components of the complex and that as greater interaction occurs the CT-band maximum undergoes a red shift and appears at lower energy. The strength of interaction in turn, is related to the electron affinity of the acceptor molecule and to the ionization potential of the donor molecule. Thus for a series of systems one may maintain a constant donor molecule to study the effect of acceptor electron affinities or one may maintain a constant acceptor molecule to study the effect of donor ionization potentials. The latter choice was employed for the current study.

By studying the ionization effect one has a means of indirectly studying the inductive effect of the various alkyl groups substituted on the "parent group" common to all the alcohols, the C-OH group. Thus the extent of the observed red shift of the charge transfer band maximum is a measure of the relative inductive effect of the alkyl groups.

It has been empirically observed that a linear relationship exists between the frequency of a charge transfer band, ν_{CT}, and the ionization potential of the donor molecule, I_D (3,4). On the basis of charge transfer theory a non-linear relationship is predicted but the deviations from linearity in the experimentally obtainable limits are quite small (5).

The present study covers a number of aliphatic alcohols as donor molecules in complexes with molecular iodine in the inert solvent n-hexane. The purpose was to study the effect on I_D of increasing the number of methyl groups exerting an inductive effect on the lone pair electrons of the oxygen atom in the alcohol. Thus, in the series of methyl, ethyl, isopropyl and tert-butyl alcohols the number of methyl groups on the "parent" C-O-H group increases from zero to three. A second complicating factor of steric hindrance also has to be considered in this series. From the normal inductive effect of a methyl group it was predicted that I_D should decrease on passing from methyl alcohol to tert-butyl alcohol. This is what has been reported for a number of alcohols (6).

FIG. 1 Relationship between alcohol ionization potential and charge transfer band energy in n-hexane at 26.5°C for alcohol-I_2 complexes. (Numbers refer to alcohols listed in Table 1.)



By the use of a series of five alcohols whose I_D values were known from the literature (6) a linear relationship between h ν_{CT} (in ev.) and I_D (in ev.) was obtained: $h\,\nu_{CT} = 0.197\,I_D + 3.25$ (ev.). This relationship was found for the following alcohols, methyl, ethyl, n-propyl, i-propyl, n-butyl. These results are shown in Figure 1.

From the relationship obtained using the alcohols of known I_D a number of other values for alcohol ionization potentials were made under the assumption that the empirical relationship would hold providing the donor molecule was chemically similar to those employed to obtain the fit. It has been observed (5, 7) that structurally dissimilar molecules can yield quite different relationships for similar correlations. The values of the ionization potentials one can estimate the order of increasing inductive effects as: (Me) < (Et) $\lesssim$ (Me,Me) < (Pr) < (Me,Et) $\sim$ (Me,Me,Me) < (Me,Et,Et) < (Et,Et,Et)

<u>TABLE 1</u> Alcohol Ionization Potentials and Charge Transfer Band Maxima of their Iodine Complexes

	Alcohol	λ_{max} (mμ)	I_D (ev)*
1	methyl	231.0	10.85
2	ethyl	232.5	10.48
3	n-propyl	235.5	10.20
4	i-propyl	236.0	10.16
5	n-butyl	237.0	10.04
6	sec-butyl	238.0	9.93
7	t-butyl	238.0	9.93
8	3-methyl 3-pentyl	239.0	9.82
9	3-ethyl, 3-pentyl	242.0	9.50

* I_D for #1-5 from reference 6, estimated to ±0.02 ev.; #6-9 obtained from this study.

From the observations reported here it is seen that addition of the first methyl or ethyl group exerts a larger inductive effect than does a subsequent one. From I_D values for alcohols #1-3 (see Table 1) it is seen that a single methyl group lowers I_D by 0.37 ev. and a single ethyl group by 0.65 ev. From #7 and #9 it is seen that this is not an additive relationship but that as steric interactions increase the effectiveness of a group in lowering the ionization potential is reduced. Substitution of both a methyl and an ethyl group on the "parent group" (i.e. #6) does not produce as large an effect as the additive relationship suggests, but the effect is reduced by about 0.10 ev. as a result of the steric effect.

Experimental

All spectra were run in a solution of the alcohol and spectroquality n-hexane. All alcohols were either spectroquality or reagent grade chemicals and were used as obtained. Gas chromatography showed detectable impurities present to no greater than one quarter per cent total. In each system the iodine concentration was constant while alcohol concentrations were varied over a five-fold (or greater) range. Ethanol was purified by the method of Smith (8). Mutual insolubility of ethanol in n-hexane and of 3-ethyl, 3-pentanol in n-hexane prevented their study in the usual manner. Spectral bands for these systems were obtained from systems of extremely high alcohol concentration with only a slight trace of hexane.

Spectral measurements were obtained by use of a Beckman DU spectrophotometer thermostatted at 26.5°C. Data were recorded from 200-360 mμ. For methyl, n-propyl, i-propyl and n-butyl alchols the spectral absorbance was negligible and a reference of an iodine - n-hexane solution was employed. For all other alcohols the reference contained an equivalent amount of alcohol and the iodine absorbance was mathematically subtracted by use of the separately determined molar absorptivity at each wavelength. Accuracy of band maxima is estimated to be ±0.5 mμ. This is thought to be the source of scatter in Figure 1.

References

1. R. S. Mulliken, J. Am. Chem. Soc., **72**, 600 (1950); **74**, 811 (1952); J. Phys. Chem., **56**, 801 (1952).
2. L. J. Andrews and R. M. Keefer, Molecular Complexes in Organic Chemistry, Holden Day, Inc., (1964).
3. H. McConnell, J. Ham and J. R. Platt, J. Chem. Phys., **21**, 66(1953).
4. R. Foster, Tetrahedron, **10**, 96 (1960).
5. R. S. Mulliken and W. B. Person, Ann. Rev. Phys. Chem., **13**, 107 (1962).
6. K. Watanabe, T. Nakayama and J. Mottl, Final Report on Ionization Potentials of Molecules by a Photoionization Method, O.T.S.-U.S.D.C. Report #158317, Dec. 1959.
7. H. Yada, J. Tanaka and S. Nagakura, Bull. Chem. Soc. Japan, **33**, 1660 (1960).
8. A. I. Vogel, A Textbook of Practical Organic Chemistry, 3rd ed., p. 168, John Wiley and Sons, Inc., New York (1956).

* Part I of this series, J. Am. Chem. Soc. **86**, 3217 (1964).

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