BASIC FUNCTION OF OXYGEN IN CERTAIN ORGANIC COMPOUNDS

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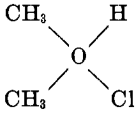
I. INTRODUCTION

Increasing interest has been shown in recent years in the strength of organic oxygen-containing bases, and data on the relative strengths of these bases have been shown to have numerous important applications. The probable course of new and known reactions may be predicted from a knowledge of which of two functional groups or molecules will react preferentially with a proton, a carbonium ion, or some other acid particle. The interpretation of acid-base catalysis, the large changes in reaction rates resulting from changing the solvent medium, and the separation of mixtures by coördinating the more basic components with a suitable acid are but a few of these applications.

Specific interest in the basic function of oxygen in certain organic compounds has emerged from a study of inorganic nonmetallic halide–organic compound systems (50, 51, 60) in which the study of the solubility of hydrogen chloride has revealed several significant features. It now seems timely that some of these features be correlated with the results from widely differing experimental approaches to indicate that some order is observed in the assessment of the basic function of oxygen in certain organic compounds.

No attempt in this paper is made to define the "basicity" or "basic strength" of solvents, for, as has been pointed out in a previous discussion on the subject (124), the disagreement in the interpretation of the results has often been one involving the fundamental definition. Preference is given here to methods which measure definable quantities (e.g., solubility, infrared band shifts), particularly in systems of two components which correlate well with measurements on one-component systems, rather than to procedures which result in the calculation of the less easily defined "basicity constants."

Similarly, the nature of the complexes involving the hydrogen halides with oxygen bases will be only briefly mentioned here. The earliest structure proposed for such complexes was that of the oxane type



involving quadrivalent oxygen (48). This same structure was again proposed, together with others of a similar nature involving an oxygen valency of up to 10, to account for the addition of up to five hydrogen chloride molecules to one molecule of methyl ether, ethyl ether, and propyl alcohol at low temperatures (2). In general the addition of hydrogen halides to alcohols is accepted today as forming the oxonium derivative $ROH_2^+Cl^-$, but for ethers the hydrogen-bonded complex $R_2O\cdots H—Cl$ is preferred. Materials with dielectric constants lying between these two probably form one or the other or both of these types of association.

II. METHODS OF DETERMINING BASIC STRENGTHS

A. INFRARED AND RAMAN SPECTRA

The early infrared and Raman spectra studies were directed towards the elucidation of the complex formed between acceptor molecules, such as chloroform and hydrogen halides, and donor molecules such as alcohols, ethers, and esters. The Raman spectrum of ether containing hydrogen bromide at −40°C. showed band variations compared with that of the pure solvent (14), whereas similar studies with hydrogen chloride (157) failed to indicate retention of the H—Cl band. The dimethyl ether–hydrogen chloride spectrum was interpreted in terms of a single complex with both the hydrogen and the chlorine bonded to the oxygen atom (15). It was also interpreted as a strengthening of the heteropolarity of hydrogen chloride, rendering the H—Cl band forbidden in the Raman spectrum (153). Further work on dimethyl ether was discussed in terms of two complexes involving one or two molecules of hydrogen chloride per molecule of ether (49). Owing to the use of unfiltered exciting light, the complicated spectra obtained in these early investigations make these conclusions very unreliable, as is shown by later work on the complex of dimethyl ether with hydrogen chloride, deuterium chloride, and hydrogen bromide (152). Results are interpreted in support of the designation of the simple 1:1 complex as a hydrogen-bonded structure and the higher complexes as oxonium compounds.

Infrared measurements on alcohols in the 0.8–1.2 μ region showed that both the bands due to associated O—H and unassociated O—H disappeared in the presence of hydrogen chloride, and, remarkably enough, it was concluded that complexing with the alcohol occurred through the $—O\cdots Cl—H$ linkage rather than through the $—O\cdots H—Cl$ linkage (47). Infrared frequency shifts of the hydrogen chloride fundamental band in benzene (121), in nitrobenzene and nitrotoluene (162), and in other nonconducting solutions led to interest in active solvents containing oxygen. No absorption bands were found for hydrogen chloride in ethers and alcohols at 1.7 μ (158), but characteristic bands were found at approximately 4.0 μ for its solutions in ethyl acetate, dioxane, and ethyl ether (72). After extension to *n*-butyl and isopropyl ethers (73), it was shown that the new band was due to a shift to longer wavelengths of the 3.46 μ fundamental H—Cl band. On the basis of the view that the H—Cl bond was not broken but merely modified in the presence of ethers, this was interpreted in terms of hydrogen bonding between the hydrogen chloride and the basic oxygen in the ether. Further work using CH_3OD (74) and D_2O (71) indicated that the strength of the hydrogen bond formed between electron-donor and electron-acceptor atoms was directly proportional to the magnitude of the frequency shift. From the values of the frequency shift a table of basic strengths for a large number of ethers and esters was drawn up. A comparison of the donor properties of saturated cyclic ethers using CH_3OD (134) showed that these were at least as basic as their equivalent open-chain ethers. The ring size was found to be important and the following order of electron donation was indicated: four- > five- > six- > three-membered rings.

The acid strengths of various alcohols were compared by infrared spectroscopy by measuring the O—H band shift using ether (3, 100) and triethylamine (3) as electron donors. The order of increasing acidity was found to be primary > secondary > tertiary. When phenol was used as electron acceptor the reverse order for basic strengths was obtained (100). A slightly different method has been used (20, 21) for comparing the basic strengths of open-chain and cyclic aliphatic alcohols. The integrated intensity of the O—H stretching band was measured for a number of alcohols and was found to decrease as the electron-donating power of the molecule increased. Since no second molecule is involved with the hydroxyl group in these measurements, the method should give an accurate measure of the inherent basic strength of the molecule, i.e., electron density on oxygen. The alcohols fall into the accepted pattern of electron release of the substituent groups to give the following orders of basic strengths: methyl < *n*-propyl < *sec*-butyl < *tert*-butyl; trimethylcarbinol < triethylcarbinol < triisopropylcarbinol.

The effect of chlorine substitution was shown by the large increase in intensity (decrease in basic strength) in 3-chloro-1-propanol and again in 2,2,2-trichloroethanol.

By means of the C—H infrared band shift of chloroform in mixtures, ethers were also investigated (69), but difficulties were encountered owing to overlapping of this band with similar bands for the solvent. These difficulties were overcome by the use of chloroform-*d* (107) and by dilution in carbon tetrachloride (23). From the frequency shifts of the OD band in CH_3OD the relative proton-attracting powers of the solvents were in the following order:

$$(n\text{-}C_4H_9)_2O > (C_2H_5)_2O > 1,4\text{-dioxane} > \text{anisole}$$

Similar investigations in chloroform with alcohols containing a phenyl group indicated the following order for the strengths of the complexes (46):

$$C_6H_5CH_2OH > (C_6H_5)_2CHOH > (C_6H_5)_3COH > C_6H_5OH$$

Raman studies of equimolecular mixtures of chloroform with acetone, ethyl acetate, and ethyl ether (29) showed the occurrence of interaction.

Forty-one organic compounds containing a carbonyl group have been examined in the absence and presence of hydrogen chloride or phenylacetylene and the frequency shift of the H—Cl or C—H band recorded (27). Relationships were obtained between $\nu_{HCl}-\nu_{CH}$, $\nu_{CH}-\nu_{C=O}$ and $\nu_{HCl}-\nu_{C=O}$ (where ν_{HCl}, ν_{CH}, and $\nu_{C=O}$ are frequencies of the HCl band, the C—H band, and the C=O stretching band, respectively). It was found that in the absence of any effect due to ring strain or steric hindrance, the proton-attracting power of the carbonyl group is directly related to the inductive strength and direction of the substituent groups adjacent to the carbonyl group. The carbonyl-stretching frequency itself was shown to be wholly dependent upon the inductive effect of the substituent groups, provided no ring strain or steric hindrance were present (95, 106).

B. REACTION RATES

One of the earliest systematic investigations into the effect of oxygen-containing solvents on the rate of a selected reaction was that of the alkaline dealcoholization of diacetone alcohol at 25°C. (1'). Monohydric and polyhydric alcohols were investigated and the following order of reaction velocities was observed: glycerol < ethylene glycol < methanol ≪ ethanol ≪ 1-propanol ≪ 2-propanol. From studies of the halogenation of alkyl and substituted alkyl ethers (91), the reaction velocity was found to increase with chain length of the alkyl group. This was progressive to the third or fourth carbon atom and thereafter remained practically constant. This follows the expected relative inductive powers of *n*-alkyl groups. Substitution of halogens or phenyl drastically reduced the reaction velocity, although moving the substituent further from the oxygen decreased the effect of the substitution.

Ingold (89) suggested that the rate of ester hydrolysis might be used for evaluating the polarity of substituent groups. Relying on experimental work carried out by a large number of other investigators, Taft used the ratio of the rate constants for the base- and acid-catalyzed hydrolysis of aliphatic esters ($RCOOC_2H_5$) to calculate polar substitution constants σ^* for various R groups relative to the methyl group (139, 140, 141, 142). The values of σ^* for alkyl groups and for halogen- and phenyl-substituted alkyl groups agree with the expected electron attraction or release by the inductive mechanism. The introduction of a methylene group between substituent R and the functional group reduces the value of σ^* by a constant factor of 2.8, i.e., $\sigma^*(R) = 2.8 \times \sigma^*(RCH_2)$. A comparison between the value of σ^* and values obtained by other methods for the same group is given in table 7.

The relative acid strengths of water, alcohols, and glycols were compared by measuring the optical densities of two solutions of an indicator, one as a control and the other containing a certain concentration of the weak acid under observation (86). The value of the equilibrium constant K_e at 27°C. was taken as a measure of the acid strength of the weak acid and the following order was recorded: glycols ≫ methanol > water > ethanol > *n*-butyl alcohol > isobutyl alcohol > *sec*-butyl alcohol > *tert*-butyl alcohol > 2-propanol.

The higher acid strength of methanol than that of water is explained in terms of a modification of the "*B*-strain" hypothesis (17). This hypothesis was originally proposed to explain the reduction in basic strength on substituting methyl groups for hydrogen atoms. It is believed that a strain is set up by mutual repulsion of adjacent substituent groups. The substitution of a methyl group for hydrogen generally produces a decrease in acid strength, as shown by the lower value of K_e obtained for the higher alcohols.

The effect of changes in structure on the basic strength of oxygen-containing compounds was measured by their ability to decrease the rate of the acid-catalyzed self-esterification of benzhydrol and the dehydration of *tert*-butyl alcohol in benzene solution at 80°C. (122). For para-substituted acetophenones and ethyl benzoates the basic strength decreased as the electron-releasing ability of the substituent decreased: $tert\text{-}C_4H_9 > CH_3 > H > Cl > Br > NO_2$.

For chloro esters the basic strength increased as the number of α-chlorine atoms decreased and as successive methylene groups were introduced between the chlorine atom and the carbethoxy group. Similar effects were found for phenyl in "benzyl ethers":

$$C_6H_5CH_2OC_4H_9(n) > C_6H_5CH_2OCH_2C_6H_5 > (C_6H_5)_2CHOC_4H_9(n) > (C_6H_5)_2CHOCH(C_6H_5)_2 > (C_6H_5)_2CHOCH_2C_6H_5$$

$$C_6H_5(CH_2)_3OC_4H_9(n) > C_6H_5(CH_2)_2OC_4H_9(n) > C_6H_5CH_2OC_4H_9(n) > C_6H_5OC_4H_9(n)$$

Observations on the dehydration of *tert*-butyl alcohol showed the following order of basic strengths:

$$CH_3(CH_2)_8CH_2OH > CH_3(CH_2)_2CH_2OH > CH_3(CH_2)_4CHOHCH_3 > C_6H_5CH_2OH$$

In contrast to the prediction of inductive effects, alcohols were found to be more basic than the symmetrical ethers. It was suggested that the increased steric hindrance and alkyl group repulsion in ethers reduced the basicity through internal strains.

Alcohols have also been examined by using the oxidation of decaborane (4, 5) according to the equation:

$$B_{10}H_{14} + 30ROH \rightarrow 10B(OR)_3 + 22H_2$$

The bimolecular rate constants for several alcohols were compared, and generally it was found that the reaction was slower the more acidic the alcohol. Substitution at the fourth carbon atom from the oxygen had little effect on reaction rate. Methyl-substituted 1-butanols reacted faster than 1-butanol and the reverse was found for chlorine substitution.

No review on the directive effect of substituent groups on reaction rates would be complete without reference to the work of H. C. Brown and coworkers. Although most of this work has been concerned with the substitution in aromatic nonoxygen-containing systems, electrophilic substitution constants have been calculated from the ionization of diphenyl- and triphenylcarbinols in aqueous sulfuric acid (36, 37) and from infrared absorption frequency for the carbonyl stretching band (92). These values have been compared with similar values from a large range of reactions for forty-one substituent groups (18).

C. MEASUREMENTS OF GAS SOLUBILITY

The interaction between an acid gas and a series of basic solvents may be expected to yield information on the relative basic strengths of the solvents and a number of such systems may be used for this purpose.

1. *Hydrogen chloride*

Until recently the solubility of hydrogen halides in basic solvents has been a neglected field of investigation and few references are to be found prior to the last five years. Determinations of the solubility of hydrogen chloride in methyl and ethyl alcohols (33, 34), on recalculation into moles of hydrogen chloride per mole of solvent, indicated that the expected order of basic strength (methyl < ethyl) was obtained at all temperatures from 30°C. to −10°C. These solubilities were furthermore considerably greater than the values obtained for water over the same temperature range (127, 128). In correlating these values with structure one must pay due regard to the effect of other factors such as solvent association and solvation, particularly in the case of water.

Diethyl ether, also investigated with hydrogen chloride (133) from 30°C. to −9.2°C., gave values comparable to the values for alcohols at room temperature and are to be found together with those for the alcohols in the *International Critical Tables*.

Measurements of the absorption of hydrogen chloride by a number of alcohols were carried out in order to confirm the formation of a stoichiometric complex, $ROH \cdot HCl$ (98). Values were recorded at one temperature only (usually 3–6°C.) and within a variation of 8 per cent an equimolecular ratio of gas to solvent was obtained. Since no correlation was made between the variation in structure or substituent groups in the alcohols and the deviation from stoichiometry, it must be assumed that all alcohols were believed to possess the same affinity for hydrogen chloride, i.e., the same basic strength. The solubility of hydrogen chloride in 2-propanol, methyl and ethyl acetates, and other solvents was investigated at 25°C. (25), but values for these solvents are not in good agreement with subsequent values.

A preliminary investigation of alcohols using hydrogen chloride indicated (57) that although at room temperature (usually 11°C.) unsubstituted alcohols absorbed approximately one mole of hydrogen chloride per mole of alcohol, the alcohols containing a halogen atom retained considerably less than this ratio at saturation. These results led to a more comprehensive study of alcohols, carboxylic acids, and esters, using hydrogen chloride as solute in the temperature region 0–50°C. and at a total pressure of 1 atm. (52). For each of these series of compounds it was found that the basic strength of the particular compound was directly related to the electron density on the effective oxygen atom, which in turn depended on the inductive strength and direction of the group R adjacent to the oxygen atom in ROH, CH_3COOR, $RCOOC_2H_5$, and RCOOH. For most of the compounds investigated linear relationships between solubility (moles of hydrogen chloride per mole of solvent) and reciprocal absolute temperature were observed and compounds were compared at a fixed temperature (10°C.) which was considered representative of the solvent.

With the exception of neopentyl alcohol, which is known to be peculiar in its interaction with hydrogen chloride (159), the alcohols ROH were found to follow the known inductive strength (90) of the adjacent R group, as indicated by the following comparisons for α- and β-methyl substitutions.

$$\begin{array}{ccccccc} CH_3 & < & C_2H_5 & < & \text{iso-}C_3H_7 & < & \textit{tert}\text{-}C_4H_9 \\ 0.857 & & 0.950 & & 1.030 & & \text{(reacts)} \end{array}$$

$$\begin{array}{ccccccc} C_2H_5 & < & n\text{-}C_3H_7 & < & \text{iso-}C_4H_9 & < & \text{neo-}C_5H_{11} \\ 0.950 & & 0.956 & & 0.973 & & 0.930 \end{array}$$

The decrease in influence of the phenyl group on removing it from the oxygen atom was shown by the values for benzyl alcohol (0.812), 2-phenylethanol (0.831), and 3-phenyl-1-propanol (0.894). In the series of acetates CH_3COOR the solubility values again followed the series of inductive strengths of the group R.

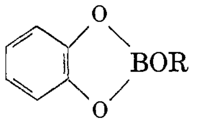
$$\begin{array}{ccccccc} H & < & CH_3 & < & C_2H_5 & < & \text{iso-}C_3H_7 \\ 0.19 & & 0.612 & & 0.633 & & 0.723 \end{array}$$

$$\begin{array}{ccccc} C_2H_5 & < & n\text{-}C_3H_7 & < & \text{iso-}C_4H_9 \\ 0.633 & & 0.665 & & 0.712 \end{array}$$

The inductive effect of chlorine was clearly reflected in the solubilities in the following ethyl esters:

$$\begin{array}{ccccccc} \text{Acetate} & > & \text{chloroacetate} & > & \text{dichloroacetate} & > & \text{trichloroacetate} \\ 0.633 & & 0.273 & & 0.167 & & 0.109 \end{array}$$

For saturated open-chain or cyclic alcohols the change in solubility was shown to bear a quantitative relationship to a change in the structure of the alcohol (53). From the values obtained for solubility changes a relationship between the number and position of carbon–hydrogen bonds present in the molecule and their contribution to the electron density on the oxygen atom was established. This enabled the solubility at 10°C. to be calculated directly from the structural formula; comparison between the calculated and the experimental values was found to be very good, as can be seen from table 1.

Calculations for halogen-substituted alcohols gave a similar agreement with experimental values (table 1); more recently (55) this type of correlation has been extended to the results for the following: acetates, CH_3COOR (52); carbonates, $(RO)_2CO$; silanes, $Si(OR)_4$; borates, $B(OR)_3$; and  (58, 59).

From the extension of solubility measurements to low temperatures, it has been found that the solubility–structure relationships are maintained to approximately −80°C. (58).

2. Other gases

The substitution of halogens and phenyl groups in alcohols was found to decrease the solubility of hydrogen bromide in such solvents (57, 59) in a similar manner to that observed for hydrogen chloride. The solubility of ammonia in

TABLE 1

Comparison of calculated and observed solubilities of hydrogen chloride in alcohols at 10°C.

Alcohol	Solubility (observed)	Moles HCl / Moles Solvent (calculated)	Alcohol	Solubility (observed)	Moles HCl / Moles Solvent (calculated)
Methanol	0.857	0.857	1-Heptanol	0.973	0.970
Ethanol	0.950	0.943	1-Octanol	0.977	0.971
1-Propanol	0.956	0.957	Cyclohexanol	1.030	1.031
2-Propanol	1.030	1.029	2-Methylcyclohexanol	1.044	1.045
1-Butanol	0.964	0.965	2-Chloroethanol	0.500	0.467
2-Methyl-1-propanol (isobutyl alcohol)	0.973	0.971	2-Bromoethanol	0.490	0.488
2-Butanol	1.048	1.043	1-Chloro-2-propanol	0.553	0.553
1-Pentanol	0.967	0.968	1-Bromo-2-propanol	0.574	0.574
2-Pentanol	1.056	1.057	1,3-Dibromo-2-propanol	0.122	0.119
4-Methyl-2-pentanol	1.052	1.058	2,3-Dibromo-1-propanol	0.304	0.304
1-Hexanol	0.970	0.969			
3,5,5-Trimethyl-1-hexanol	0.979	0.980			

alcohols and water indicated that the affinities for the alkaline gas were in the order water > methanol > ethanol, whereas the acidic sulfur dioxide was found to give the reverse order (33). Later work with sulfur dioxide (35) agreed with these early investigations, but the values obtained for higher alcohols were not in keeping with the inductive strengths, as can be seen by the following: *n*-propyl ether > *n*-butyl ether > 1-pentanol > ethanol > 1-octanol > 1-hexanol > methanol > 1-propanol ≫ water. Using carbon dioxide as solute the expected order of solubilities—i.e., methanol < ethanol < 1-propanol < isobutyl alcohol —was obtained (94, 101).

The stability of the complex between boron trifluoride and an ether was found to be in the reverse order to that expected from the inductive strength of groups adjacent to the oxygen (16).

$$BF_3 \cdot (CH_3)_2O \quad > \quad BF_3 \cdot (C_2H_5)_2O \quad > \quad BF_3 \cdot (\text{iso-}C_3H_7)_2O$$

Steric strain was invoked to account for this reversal of order. Although the protonization of ethers would not be expected to be affected by steric restrictions, on account of the small size of the proton involved, it has been found (56) that the presence of a large group (e.g., isoamyl) does lower the solubility of hydrogen chloride by a steric mechanism. However, in this case it is not a free proton which must become attached, but a molecule of hydrogen chloride. This restriction was not found for cyclic ethers, such as tetrahydrofuran and dioxane, which have high affinities for hydrogen chloride as well as for boron trifluoride (16).

D. VAPOR PRESSURE

Indications of the donor–acceptor type of interaction are often obtained from measurements of vapor pressure in multicomponent systems. A strong negative deviation from ideal behavior, as predicted by Raoult's law, is normally found for systems in which the two components interact.

Hydrogen chloride was found to obey Henry's law in acetic acid at low con-

TABLE 2

Ionization constants of some carboxylic acids at 25°C.

Acid	Ionization Constant	References	Acid	Ionization Constant	References
$HCOOH$	1.77×10^{-4}	(79)	CF_3COOH	0.588	(82, 138)
CH_3COOH	1.753×10^{-5}	(108)	CCl_3COOH	0.2	(79)
C_3H_5COOH	1.343×10^{-5}	(6, 80)	$CH_3CHClCOOH$	1.47×10^{-3}	(79)
n-C_3H_7COOH	1.510×10^{-5}	(6, 81)	$CH_3CHBrCOOH$	1.08×10^{-3}	(79)
iso-C_3H_7COOH	1.5×10^{-5}	(79)	CH_2ClCH_2COOH	8.59×10^{-5}	(79)
n-C_4H_9COOH	1.6×10^{-5}	(79)	CH_2BrCH_2COOH	9.8×10^{-5}	(79)
iso-C_4H_9COOH	1.7×10^{-5}	(79)	CF_3CH_2COOH	9.52×10^{-4}	(82)
CH_2FCOOH	2.2×10^{-3}	(138)	$CH_3CH_2CHClCOOH$	1.4×10^{-3}	(124)
$CH_2ClCOOH$	1.35×10^{-3}	(6)	$CH_3CHClCH_2COOH$	8.8×10^{-5}	(124)
$CH_2BrCOOH$	1.38×10^{-3}	(79)	$CF_3CH_2CH_2COOH$	6.98×10^{-5}	(82)
CHF_2COOH	5.7×10^{-2}	(138)	$CF_3CF_2CF_2COOH$	0.678	(82)
$CHCl_2COOH$	5×10^{-2}	(79)			

centrations but deviated at partial pressures above about 100 mm. of mercury (126). Comparison (118) of the partial pressures of hydrogen chloride from solutions in benzene (130), nitrobenzene, acetic acid (126), ethylene glycol, and water (123) indicated that even at low concentration the latter two compounds had a high degree of complex formation. For solvents such as anisole, phenetole, and β,β'-dichloroethyl ether, Henry's law was found to hold with hydrogen chloride for low concentrations (116, 119), and a relationship between entropy of solution from vapor pressure measurements and frequency shift for the 3.46 μ absorption band of hydrogen chloride in the same solvent (71, 73) was found to be of the form:

$$\Delta S = 10.0\Delta\mu - 21.1$$

A method of measuring the Henry's law constant for hydrogen chloride in dilute solutions of a solvent in heptane, originally used with aromatic hydrocarbons, was adapted to compare the basic strength of a number of ethers (115). The Henry's law constant was calculated for infinite dilution and then compared with other methods of measuring the basic strength (70, 74, 75, 93, 116, 134) with good agreement in all cases. Comparison of results from this method with those from saturated solubility measurements have since been carried out (53, 54).

E. CONDUCTIVITY

Ionization constants, calculated from conductivity data, have been obtained for a large number of carboxylic acids (6, 79, 80, 81, 108), and these values (table 2) have been used as a measure of the relative acid strength. The effect of halogen substitutions was also investigated (6, 79, 82, 108, 138), and the expected order of increase in acid strength of F > Cl > Br was found. Some doubt has been cast on the validity of using ionization constants which have been obtained at a single temperature as a true measure of the relative strength of acids (43, 75). Heats of neutralization (105, 146), taken in conjunction with values of log K_{25} (38, 39, 40), suggested that inversions of acid strength should occur between 15°C. and 45°C. Six cases of inversion were later found (42) from measurements over a range of temperature of E.M.F.'s in cells of the type

$$H_2 \left| \begin{matrix} HA_1 \\ NaA_1 \end{matrix} \quad NaCl \mid KCl \mid NaCl \quad \begin{matrix} HA_2 \\ NaA_2 \end{matrix} \right| H_2$$

where HA_1 and HA_2 are the acids under comparison. A similar phenomenon of inversion was also found in measurements of the solubility of hydrogen chloride (52).

Alcohols have also been similarly measured, in particular the highly fluorinated alcohols. The values given in table 3 for water, methanol (45), and ethanol (30) indicate that the decrease in acidity is in the expected order: water > methanol > ethanol. However, when the dissociation constant obtained from conductivity measurements (31) is used rather than that from E.M.F. measurements for ethanol, the order of the two alcohols is reversed. The expected large increase in acidic strength resulting from the substitution of fluorine for hydrogen in alcohols is indicated by an increase in the order of the ionization constants from 10^{-19} for ethanol to 10^{-12} for 2,2,2-trifluoroethanol. The successive substitution of a methyl group in the α-position of 2,2,2-trifluoroethanol yields a rather erratic change in acid strength which is difficult to explain.

The values (table 4) of the equivalent conductivity at infinite dilution for hydrogen chloride in nonaqueous solvents give a measure of the extent to which the solvent can serve as a proton acceptor (160), the dielectric constant of the medium having lesser effect. The value for ether is very low at this dilution, since the complex with hydrogen chloride is hydrogen-bonded and not an oxonium derivative, as for the alcohols.

TABLE 3

Dissociation constants of some alcohols at 25°C.

Alcohol	Dissociation Constant	Reference	Alcohol	Dissociation Constant	Reference
HOH	1×10^{-16}	(79)	CF_3CH_2OH	4.0×10^{-12}	(83)
CH_3OH	7×10^{-18}	(45)	$CF_3CH(CH_3)OH$	6.3×10^{-12}	(83)
C_2H_5OH	7.28×10^{-20}	(30)	$CF_3C(CH_3)_2OH$	2.5×10^{-12}	(83)
	2.89×10^{-16}	(31)	$HOCH_2CF_2CF_2CH_2OH$	1×10^{-11}	(125)

TABLE 4

Conductivity at infinite dilution of hydrogen chloride in oxygen-containing solvents at 25°C.

Solvent	Equivalent Conductivity	References	Solvent	Equivalent Conductivity	Reference
Methanol	196.7	(66, 88, 143)	3-Methyl-1-butanol	2.15	(8)
Ethanol	84.7	(66, 143)	Formic acid	75.0	(131)
1-Propanol	46.6	(68)	Acetic acid	0.0925	(99)
1-Butanol	28.4	(67)	Diethyl ether	0.00053	(112)
2-Methyl-1-propanol	12.07	(65)			

F. HEATS OF MIXING, FREEZING POINTS, AND VISCOSITY

Studies of the latent heat of evaporation and freezing points of binary mixtures of volatile liquids (147, 148, 164, 165) showed that systems such as methyl alcohol–chloroform, acetone–chloroform, ether–carbon tetrachloride, and ethyl alcohol–benzene exhibited irregularities due to interaction between the two components. It was evident that there were strong attractive forces present in this type of system, and this was confirmed by determinations of viscosity and heats of reaction (9). Further studies (166) on the freezing-point diagram of the ethyl ether–chloroform system showed the existence of three complexes the stabilities of which were in the following order:

$$(C_2H_5)_2O \cdot CHCl_3 > 2(C_2H_5)_2O \cdot CHCl_3 > 3(C_2H_5)_2O \cdot CHCl_3$$

This was independently confirmed (135). The complexes were thought to be due to donation of an electron pair from the oxygen of the ether to the chlorine of the halogen-containing substance. Ethers were considered better donors than ketones. From the heats of reaction at varying temperatures, which gave a maximum at the equimolecular ratio for this system (109), it was calculated that at 15°C. 15–20 per cent of the molecules had formed complexes. A value of 20 per cent at 20°C. was also obtained by calculation from viscosity studies (110). In a slightly more comprehensive study of binary mixtures involving the haloforms the following order of donor strength was obtained (61): diisopropyl ether > diethyl ether > β,β'-dichloroethyl ether; using ether, acetone, and quinoline the following order of acceptors was obtained: chloroform > bromoform > iodoform. From this work came the first suggestion that this complex formation might result from bonding through the hydrogen of the haloform, a suggestion which met with much criticism at the time.

Measurements of solubilities and heats of mixing carried out on more than a hundred ethers, esters, glycols, and ether esters using chloroform (167), dichlorofluoromethane (167, 168), trichlorofluoromethane (28), and dichlorodifluoromethane (28) indicated that cyclic ethers such as 1,4-dioxane were less basic than open-chain ethers, as were halogen-substituted ethers. Esters were almost as basic as ethers, but glycols were found to form complexes only slightly, owing to the high degree and strength of their association. Decrease in basic strength as a result of halogen substitution (28) and phenyl substitution (111) was illustrated by reduction in the heat of solution on mixing. Later work (102) on a few fluorinated ethers $CHClFCF_2OR$ (where $R = CH_3$, C_2H_5, n-C_3H_7, and iso-C_3H_7) gave small positive heats of mixing with chloroform, indicating that the tendency to form hydrogen bonds had been destroyed by reducing the basic character of the oxygen atom of the ether by substitution of fluorine for hydrogen.

G. OTHER METHODS

Abnormalities observed for the dielectric constants of ether–chloroform mixtures (120, 129, 132) and for ether compounds in dioxane and ether (26, 102, 145) were further investigated by measurements of electric polarizations on mixtures of ethyl, isopropyl, and β,β′-dichloroethyl ethers with halogen derivatives of methane (41). The extent of compound formation was calculated for each system, and with chloroform the tendency was found to increase in the series: isopropyl ether > ethyl ether > β,β′-dichloroethyl ether. Similar compound formation was observed for dioxane and, in addition, evidence from dipole moments for an excess of chloroform indicated the formation of a second complex $C_4H_8O_2 \cdot 2CHX_3$, involving coördination of chloroform to both of the oxygen atoms in dioxane. Dipole moments of hydrogen fluoride, hydrogen chloride, and hydrogen bromide measured in dioxane and compared with values obtained in carbon tetrachloride and heptane indicated compound formation of the hydrogen-bonded type, with a small proportion of an oxonium derivative of the type  $O^+H\ Cl^-$ (154). The quantity of oxonium derivative was thought to depend upon the ionic character and bond energy of the H—X bond, since the quantities of this derivative decreased in the order HF > HCl > HBr.

The activity of hydrogen chloride in glacial acetic acid was calculated from measurements using the cell

$$\mathrm{Pt}\left|\begin{matrix}\text{chloranil (satd.)}\\ \text{hydrochloranil (satd.)}\end{matrix}\right.\quad \mathrm{HCl}(m)\quad \mathrm{AgCl(satd.)}\Big|\ \mathrm{Ag}$$

at 25°C. (85), and values were compared with measurements made in water (24), methanol (163), and ethanol (114). The activity of hydrogen chloride at the same concentrations was used to give a relative but inverse measure of the basic strengths of these solvents. The order of basic strength was acetic acid < ethanol < methanol < water.

Cryoscopic studies in sulfuric acid have long been used to investigate the ionization of weak bases. Hantzsch employed the method from 1907 to 1930 to determine the van't Hoff *i* factor; more recently the technique has been improved and results elaborated (77, 113). The basic strengths of ketones and their methyl ethers have recently been studied by comparing the ionization in sulfuric acid with the low-temperature absorption of hydrogen chloride (161).

Although the formation of colored complexes with Lewis acids such as ferric chloride is used to indicate the basic character of ethers, no direct comparison using such methods has been made. However, use has been made of this phenomenon to show the reduction in basic strength by the introduction of fluorine into the ether molecule, particularly when substitution occurs close to the oxygen atom (84). Solution color changes using ferric chloride in conjunction with propyl gallate have been used to compare the relative basic strengths of a number of alcohols and glycols (136). Results are not in very good agreement with other methods, as seen in table 5, and from the order of basic strength of the isomeric butyl alcohols: *sec*-butyl alcohol > *tert*-butyl alcohol > *n*-butyl alcohol > isobutyl alcohol.

Comparisons between carbinols and silanols show that the silanols are markedly stronger as hydrogen-bonding acids, as predicted. Half-neutralization values in potentiometric titration showed that triphenylsilanol is more acidic than phenol

TABLE 5

Comparison of basic strengths of alcohols as determined by various methods

Alcohol	A' [(a)]	$\Delta\nu_{OH}$ [(b)]	Water [(c)]	K_e [(d)]	K [(e)]	Solubility of HCl in Alcohol [(f)]
	1×10^4 mole^{-1} liter cm.$^{-2}$	*cm.$^{-1}$*	*mole per cent*			*moles/mole*
tert-Butyl alcohol	0.34	116	—	0.2	0.09	(1.115)[(g)]
Cyclohexanol	0.38	—	3.4	—	—	1.030
2-Propanol	—	122	—	0.076	2.01	1.030
2-Butanol	0.39	123	—	0.2	3.80	1.048
Cyclopentanol	0.44	—	—	—	3.36	—
2-Methyl-1-propanol (isobutyl alcohol)	—	—	1.5	ca. 0.5	4.79	0.972
1-Hexanol	—	—	2.1	—	—	0.970
1-Butanol	—	135	1.5	ca. 0.6	6.70	0.964
1-Propanol	0.52	—	1.2	ca. 0.5	5.35	0.956
Ethanol	—	133	0.97	0.95	5.20	0.950
Methanol	0.50	136	3.1	4.0	7.27	0.857
Benzyl alcohol	0.54	—	—	3.8	2.86	0.812
3-Chloro-1-propanol	0.63	—	—	—	—	(0.750)[(g)]
2-Chloroethanol	0.60	177	—	—	—	0.500
2,2,2-Trichloroethanol	0.76	—	—	—	—	0.087

(a) Intensity (A') of O—H stretching frequency (20).
(b) Infrared shift of OH band of alcohol in ether (3).
(c) Mole per cent of water required to chelate the indicator (136).
(d) Value of K_e at 27°C. (86).
(e) Specific bimolecular rate constant at 25°C. for reaction of decaborane with the alcohol (4, 5).
(f) Solubility of hydrogen chloride in alcohol at 10°C. (52, 53).
(g) The figures in parentheses represent calculated solubilities, not measured values.

or *p*-methoxyphenol (155), whereas trialkylsilanols, alkylcarbinols, or arylcarbinols were found to be too weak as acids to be measured by this method.

III. COMPARISON OF RESULTS OBTAINED BY DIFFERENT METHODS

Correlations between the methods of individual workers on the basic strengths and hydrogen-bonding properties of organic compounds containing oxygen have been made from time to time, particularly within a particular series of compounds (viz., ethers, alcohols, esters). Infrared work on ethers and esters, using CH_3OD, has been compared with solubilities of dichlorofluoromethane (74), carbon dioxide (74), and hydrogen chloride (54), with Henry's law constants (137), and with partial pressure work on hydrogen chloride (119). In all of these cases good agreement has been found, since all of these methods recorded the hydrogen-bonding property of the solvent. This form of comparison has been extended in tabular form to alcohols and esters in tables 5, 6, and 7, which show comparisons between several methods for these compounds and for ethers. The solvents have been arranged in order of decreasing basic strength, as shown by the more reliable methods of comparison. It can be seen that the solvents generally follow the order predicted by an inductive mechanism alone. Since some of the infrared methods involve only the solvent molecule and give good correlation with methods involving interaction by a second molecule, it would appear that the latter is generally unaffected by steric factors in the cases shown. Disagreement amongst the methods is found mainly for comparisons of straight-

TABLE 6

Comparison of basic strengths of ethers as determined by various methods

Ether	$\Delta\nu_{OD}$ (a)	$\Delta\nu_{HCl}$ (b)	$\Delta\nu_{OD}$ (c)	*k* (d)	Solubility of HCl in Ether (e)
	cm.$^{-1}$	*cm.*$^{-1}$	*cm.*$^{-1}$		*moles/mole*
Tetrahydrofuran	—	—	117	2100	1.38
Tetrahydropyran	—	—	115	2600	—
Dioxane	97	—	111	7500	1.046
Isopropyl ether	123	463	110	—	0.978
Ethyl ether	130	439	96	4000	(0.892)(f)
n-Propyl ether	117	—	—	5200	0.930
n-Amyl ether	110	—	—	—	0.914
n-Butyl ether	110	439	101	5200	0.890
Ethyl butyl ether	117	—	97	—	
Methyl *n*-butyl ether	—	—	95	—	0.788
Dibenzyl ether	114	—	—	10300	0.540
γ,γ'-Dichloropropyl ether	84	—	—	—	0.276
β,β'-Dichloroethyl ether	84	313	—	17300	0.209
Phenetole	57	238	—	—	0.180
Anisole	70	258	—	18500	0.160

(a) Infrared shift of OD band for CH_3OD in ether (74).
(b) Infrared shift of HCl band for hydrogen chloride in ether (71).
(c) Infrared shift of OD band for CH_3OD in ether (134).
(d) Henry's law constant for hydrogen chloride in solvent at infinite dilution (137).
(e) Solubility of hydrogen chloride in ether at 10°C. (56).
(f) Value from reference 133.

TABLE 7

Comparison of basic strengths of some esters as determined by various methods

Ester	$\Delta\nu_{OD}$ (a)	$\Delta\nu_{HCl}$ (b)	σ^* (R) (c)	Solubility of HCl in Ester (d)	*A* (e)
	cm.$^{-1}$	*cm.*$^{-1}$		*moles/mole*	*1 × 10*^{4} *mole*$^{-1}$ *cm.*$^{-2}$
Ethyl isobutyrate	—	—	0.20	0.6	—
n-Amyl acetate	90	—	—	0.678	—
Ethyl acetate	84	313	0.00	0.659	3.45
Ethyl phenylacetate	—	—	0.215	0.492	—
Ethyl benzoate	—	—	0.60	0.450	—
Methyl benzoate	63	286	—	0.445	—
Ethyl formate	—	—	0.49	0.387	—
Benzyl benzoate	63	286	—	0.370	—
Phenyl acetate	—	286	—	0.325	—
Ethyl bromoacetate	—	—	1.00	0.293	2.82
Ethyl chloroacetate	70	—	1.05	0.273	3.84
Ethyl cyanoacetate	49	—	1.3	0.	3.24
Ethyl dichloroacetate	—	—	1.94	0.167	2.74

(a) Infrared shift of OD band for CH_3OD in solvent (74).
(b) Infrared shift of HCl band for hydrogen chloride dissolved in solvent (71).
(c) Polar substitution constant for group R in $RCOOC_2H_5$ (141).
(d) Solubility of hydrogen chloride in ester at 10°C. (52, 56).
(e) Intensity of infrared carbonyl band (19).

chain alkyl groups, where the changes in basic strength involved are very small, and in general this reflects the lack of sensitivity of a number of the methods. Few disagreements are found where halogens or phenyl groups are involved, since the magnitude of the changes in basic strength is much greater.

Whereas reasonable agreement may be found within a series of a particular type of compound, it is a different story when comparisons are made between the different types of compounds. Generally if the compounds are of a similar form, then comparative methods which are not affected by steric factors (i.e., infrared spectroscopy, hydrogen chloride, etc.) will generally clearly distinguish between the two. An example of such a comparison is that between ethers, $R'OCH_2R$, and esters, $R'COOR$, which are clearly separated by infrared measurements (74) and studies of the solubility of hydrogen chloride (52). Similarly alcohols, RCH_2OH, and carboxylic acids, $RCOOH$, present no problems. However, difficulty arises when the hydrogen atoms of water are successively replaced by alkyl groups to form alcohols and ethers. If this change involved only an electron movement towards the oxygen atom, then the order of basic strength would become ethers > alcohols > water, but other properties of the molecules are changed by this substitution. Bond angles on the oxygen atom are altered from 104° 31′ in water (32) to 110° 15′ in methanol (22) to 115° 50′ in dimethyl ether (96) by the increasing mutual repulsion of the groups attached to the oxygen. Even larger repulsions are obtained when these oxygen compounds are protonated, and a value of 110° has been estimated for the unsubstituted oxonium ion (97). Reduction in the number of hydrogen atoms by alkyl substitution decreases the extent of hydrogen bonding in the pure solvent from water to ether and also decreases the stability due to resonance of the oxonium derivatives, until finally in ethers the complex with hydrogen halides is of the hydrogen-bonded rather than the ionic form as found for water and alcohols. Such profound changes in the nature of the solvent and in the derivatives, particularly with hydrogen halides, account to some extent for the disagreement between various methods of comparison. A further factor which has not been considered too carefully in the past in comparisons between types of compounds is the effect of temperature. The solubility of hydrogen chloride, although not the best of comparative methods where solvent changes occur, shows this effect excellently. The temperature at which a comparison is made between water, *n*-butyl alcohol, and *n*-butyl ether determines the order of basic strengths, as indicated by absorption of hydrogen chloride. Above 50°C. the order is alcohol > water > ether; between 50° and 1°C. the order is alcohol > ether > water; below 1°C. the order is ether > alcohol > water (56). Similar effects have been found in other methods of comparison (42), and until the effect of temperature has been more fully investigated there is little hope of an accurate comparison, particularly among water, alcohols, and ethers.

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