Registry No.—**1**, 6159-17-7; 1 oxime (*Z*), 53369-67-8; 1 oxime (*E*), 53403-31-9; **2**, 53369-68-9; 2 hydrochloride, 53403-32-0; **3**, 10289-77-7; **4**, 53369-69-0; **5**, 53403-33-1; **6**, 53403-34-2; **7**, 53369-70-3; 2,2-dimethyl-3-dimethylaminopropanal, 15451-14-6; hydroxylamine hydrochloride, 5470-11-1; 2,2-dimethyl-3-dimethylaminopropanal oxime, 7405-24-5; 2,2-dimethyl-3-dimethylaminopropylamine, 53369-71-4; 2-(dimethylaminomethyl)cyclohexanone oxime, 53369-72-5; *cis*-2-(dimethylaminomethyl)cyclohexylamine, 53369-73-6; *trans*-2-(dimethylaminomethyl)cyclohexylamine, 53369-74-7; 2-methyl-3-dimethylaminopropylamine, 6105-72-2; 4-methyl-3,4-diazatricyclo$[5.2.1.0^{2,6}]$-2-decene, 53369-75-8; 3-methylene-2-norbornanone, 5597-27-3; methylhydrazine, 60-34-4; *o*-(dimethylaminomethyl)benzonitrile, 53369-76-9; *o*-cyanobenzyl bromide, 22115-41-9; dimethylamine, 124-40-3; *o*-(dimethylaminomethyl)benzylamine, 53369-77-0; *o*-(dimethylaminomethyl)benzylamine hydrochloride, 53369-78-1; *N,N,N′,N′*,2,2-hexamethyl-1,3-propanediamine, 53369-79-2; *o*-bis(dimethylaminomethyl)benzene, 53369-80-5; *o*-bis(dimethylaminomethyl)benzene monoperchlorate, 53369-81-6.

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The Intrinsic Hydrophilic Character of Organic Compounds. Correlations in Terms of Structural Contributions[1]

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Log γ, where $\gamma = c_w/c_g$, with c_w being the concentration of a compound in dilute aqueous solution at 25° and c_g the concentration in the gas phase in equilibrium with the aqueous solution (both in moles per liter), is defined as the intrinsic hydrophilicity of a compound. Values for 292 compounds are listed, and parameters for a bond contribution correlation and a group contribution correlation are determined. Major deviations from the correlations arising from distant polar interactions (interactions between halogen, oxygen, nitrogen, or sulfur substituents separated by more than one carbon atom) are observed. The significance of such deviations and of the relative magnitudes of the group contributions is discussed.

The hydrophilic and hydrophobic character of compounds[2,3] is commonly discussed in terms of data on systems involving an aqueous phase and some other liquid phase. Such data, which include water solubilities and distribution coefficients between water and some other solvent,[4,5] have been quite useful. They depend on differences in free energy (or of enthalpy or some other property) of the molecules of a compound when they are surrounded by water molecules and when they are surrounded by molecules of the other solvent. Hence they depend not only on the nature of the compound in question and on the nature of water but also on the nature of the other solvent in the system in question. The interpretation of data may be simplified somewhat if we consider the difference in free energy of molecules of a given compound when they are surrounded by water and when they are surrounded by nothing, that is, when they are in the gas phase. We shall consider the tendency of a molecule to go from the gas phase to dilute aqueous solution to be a measure of its *intrinsic hydrophilic character*.

In order to discuss the relationship between molecular structure and the intrinsic hydrophilic character of compounds in quantitative terms we have carried out correlations in terms of structural additivity schemes. Such schemes have been used in correlations of enthalpies of formation, entropies, and other thermodynamic properties.[6-8] These correlations have been largely restricted to the properties of compounds in the gas phase. They would be more useful if they were extended to the common solvents in which most reactions are run. Such extensions would consist of correlations concerning transfer processes between the gas phase and the solvents of interest. Butler and coworkers pointed out long ago that the free energy of transfer of organic compounds from the gas phase to aqueous solution is an approximately additive function of the groups present in the compounds.[9-11] Pierotti, Deal, and Derr treated about 340 cases, including 71 in which water was the solvent, by an empirical equation that may be applied to any compound in any solvent (when the appropriate parameters have been determined).[12] Although this equation is reasonably economical with parameters in its application to solvents, in general it is less so when applied to any one solvent. The 15 homologous series of compounds whose activity coefficients in water were correlated required 30 disposable parameters. A group contribution scheme of the Benson type[6,8] would cover all these compounds and many more with only 24 parameters. For this reason and because of the increased number of reliable data that have become available in recent years, we have correlated activity coefficients in the gas phase relative to aqueous solution using both a bond contribution and a group contribution scheme. Not only will such correlations aid in understanding hydrophobic bonding[2,3] and in predicting equilibrium constants for chemical reactions, they will also be useful in studies of the loss of flavor components from largely aqueous foods,[13] the transfer of pesticides and other compounds between various bodies of water and the atmosphere, and in other ways. In addition, when either the vapor pressure or the water solubility of a difficultly soluble organic compound is known, the other may be estimated from such correlations.

Results

We have tried to correlate values of log γ for various compounds, where γ is the activity coefficient in the ideal gas phase relative to infinitely dilute aqueous solution. As shown in eq 1, γ is taken to be equal to the concentration of

$$\gamma = c_w/c_g \qquad (1)$$

the compound in a dilute aqueous solution divided by its concentration in the gas phase that is in equilibrium with that solution. When the compound and water are not very soluble in each other, c_w may be taken as the water solubility and c_g as the vapor pressure of the compound. We have made γ dimensionless by expressing c_w and c_g in moles per liter. Data at 25° were used and water solubilities were used only for compounds whose water solubility is 1.0 *M* or less, except for ethyl formate (1.2 *M*).

The values of log γ, log c_w, log c_g, and P (where P is the vapor pressure in millimeters; log c_g = log P − 4.269) we used and the appropriate literature references are listed in Table IV.[14] The values of γ cover a range of about 10^{10}.

The bond contribution scheme used is similar to that of Benson and Buss, in which certain groups such as cyano, nitro, and carbonyl are treated as atoms. Thus the contribution of the C-CN bond includes implicitly the contribution of the carbon–nitrogen triple bond of the cyano group, and the H-CO bond contribution includes half the contribution of the carbon–oxygen double bond. Olefinic, acetylenic, and aromatic carbon are denoted C_d, C_t, and C_{ar}, respectively. The contribution for a C_d–H bond (or for any C_d–X bond) includes one-fourth of the contribution for the carbon–carbon double bond, and any C_t–X contribution contains half the triple bond contribution. However, the C_{ar}–H contribution does not include a $C_{ar}{=\!=}C_{ar}$ contribution. The latter was kept separate so as to simplify the treatment of data on nonbenzenoid aromatic compounds. For example, log γ for naphthalene is equal to eight times the C_{ar}–H contribution plus 11 times the $C_{ar}{=\!=}C_{ar}$ contribution, and log γ for pyridine is equal to five times the C_{ar}–H contribution plus four times the $C_{ar}{=\!=}C_{ar}$ and two times the $C_{ar}{=\!=}N_{ar}$ contribution. The 34 bond contributions obtained by least-squares treatment of data on 263 compounds are listed in Table I. The 263 values of log γ calculated from these contributions, which are listed in Table IV,[14] differed from the experimental values with a standard deviation of 0.41. The deviations from about 40 additional values of log γ, some of which had not been located when the parameters listed in Table I were calculated but some of which had been left out of the least-squares treatment because of their highly deviant nature, tended to be larger than this. Most of the larger deviations were of the types that will be rationalized in our discussion of the group contribution correlation.

Table I
Bond Contributions to the Logarithms of Activity Coefficients in the Gas Phase Referred to Aqueous Solution[a]

Bond[b]	Contribution	Bond	Contribution
C–H	−0.11	C_{ar}–Br	0.21
C–F	−0.50	C_{ar}–NO_2[c]	1.83
C–Cl	0.30	C_{ar}–O	−0.74
C–Br	0.87	C_{ar}–S	0.53
C–I	1.03	C_{ar}–CO[d]	1.14
C–CN[c]	3.28	$C_{ar}{=\!=}C_{ar}$[e]	0.33
C–NO_2[c]	3.10	$C_{ar}{=\!=}N_{ar}$[e]	1.64
C–O	1.00	C_d–H	−0.15[f]
C–S	1.11	C_d–Cl	0.16[f]
C–N	1.35	C_d–C_d	0.48[f]
C–C	0.04	C_d–CO[d]	2.42[f]
C–CO[d]	1.78	C_t–H[g]	0.00
C–C_d	0.15[f]	CO–H[d]	1.19
C–C_t[g]	0.64	CO–O[d]	0.28
C–C_{ar}	0.11	O–H	3.21
C_{ar}–H	−0.21	S–H	0.23
C_{ar}–Cl	−0.14	N–H	1.34

[a] At 25°. [b] C without a subscript refers to a carbon atom bound by single bonds to four other atoms except in CN. [c] The cyano and nitro groups are treated as univalent atoms. [d] The CO group is treated as a divalent atom. [e] The bond denoted $=\!=$ is the $\sigma^+ + \pi$ bond in an aromatic ring. [f] This contribution includes one-fourth the contribution of the carbon–carbon double bond(s). [g] This contribution includes one-half the contribution of the carbon–carbon triple bond.

The group contribution scheme we used is similar to that of Benson and coworkers.[6,8] In most cases a group is taken to contain one polyvalent atom and the monovalent atoms bonded to it, but the group is *characterized* by the nature of the atoms to which it is attached as well as those it contains. Thus a methylene group attached to two oxygen atoms is different from one attached to a carbon and an oxygen atom. Our notation for group contributions, which is $[CH_2(O)_2]$ and $[CH_2(C)(O)]$ for the two groups just referred to, for example, differs from that of Benson and coworkers in that the atoms contained in the group are not parenthesized. We feel that the notation $[C(H)_2(O)_2]$ makes it less obvious that additional contributions are required for the oxygen atoms but not for the hydrogen atoms. The value of log γ for methyl ethyl ether, for example, is taken to be the sum of the four contributions $[CH_3(O)]$, $[O(C)_2]$, $[CH_2(C)(O)]$, and $[CH_3(O)]$. Instead of the symbol C_B for benzenoid carbon[6,8] we have used C_{ar} to include the carbon atoms in the rings of polynuclear aromatic and certain hetaromatic compounds as well. For example, log γ for pyridine is set equal to $3[C_{ar}H(C_{ar})_2] + 2[C_{ar}H(C_{ar})(N_{ar})] + [N_{ar}(C_{ar})_2]$. As in the case of the bond contribution scheme, C_d and C_t refer to olefinic and acetylenic carbon, respectively. Since any C_d must be attached to another C_d and any C_t to another C_t, the C_d or C_t at the other end of the multiple bond is not included in the nota-

Table II Group Contributions to the Logarithms of Activity Coefficients in the Gas Phase Referred to Aqueous Solution[a]

Group	Contribution	Group	Contribution
$CH_3(X)$[b]	−0.62	$C(C)_3(O)$	0.78
$CH_2(C)_2$	−0.15	$CH_2(O)_2$	−2.54
$CH(C)_3$	0.24	$CH(C)(O)_2$	−1.35[c]
$C(C)_4$	0.71	$CH_2(C_d)(O)$	−0.57[c]
$CH_2(C)(C_{ar})$	−0.19	$CH_2(C)(CO)$	−0.15
$CH(C)_2(C_{ar})$	0.29	$C_{ar}(O)(C_{ar})_2$	−0.43
$C(C)_3(C_{ar})$	0.93	$C_{ar}(CO)(C_{ar})_2$	−0.84[c]
$CH_2(C)(C_d)$	−0.23	$C_dH(CO)$	0.28
$CH_2(C_d)_2$	−0.31[c]	$CHO(Y)$[f]	3.23
$CH_2(C)(C_t)$	−0.29[d]	$CO(C)_2$	4.03
C_dH_2	−0.41	$CO(C)(C_{ar})$	4.26[c]
$C_dH(C)$	0.22	$CO(C)(O)$	4.09
$C_d(C)_2$	0.67	$CO(C_{ar})(O)$	4.57[c]
$C_dH(C_d)$	0.18	$CH_2(C)(S)$	−0.02
$C_d(C)(C_d)$	0.86	$C_{ar}(S)(C_{ar})_2$	−0.25[c]
C_tH	0.00[d]	$CH_2(C)(N)$	−0.08
$C_t(C)$	0.96[d]	$CH_2CN(C)$[g]	3.43
$C_{ar}H(C_{ar})_2$	0.11	$CH_2NO_2(C)$[g]	3.27
$C_{ar}(C)(C_{ar})_2$	0.70	$CHNO_2(C)_2$[g]	3.53[c]
$C_{ar}(C_{ar})_3$[e]	0.47	$C_{ar}H(C_{ar})(N_{ar})$	0.11[h]
$CHF_2(C)$	0.70[c]	$C_{ar}(C)(C_{ar})(N_{ar})$	0.59
$CH_2Cl(C)$	1.05	$C_{ar}NO_2(C_{ar})_2$[g]	2.19
$CHCl_2(C)$	1.33	$OH(C)$	4.45
$CCl_3(C)$	0.80[c]	$OH(C_{ar})$	4.45[i]
$CHCl(C)_2$	1.46	$O(C)_2$	2.93
$CH_2Cl(C_d)$	0.61[c]	$O(C)(C_{ar})$	1.25[c]
C_dHCl	0.05[c]	$O(C)(CO)$	−0.53
$C_{ar}Cl(C_{ar})_2$	0.18[c]	$SH(C)$	1.56
$CH_2Br(C)$	1.10	$SH(C_{ar})$	1.56[j]
$CHBr(C)_2$	1.58[c]	$S(C)_2$	2.35
$C_{ar}Br(C_{ar})_2$	0.49	$S(C)(C_{ar})$	2.30[c]
$CH_2I(C)$	1.14	$NH_2(C)$	4.15
$CHI(C)_2$	1.57[c]	$NH(C)_2$	4.37
$CH_2(C)(O)$	−0.13	$N(C)_3$	4.14
$CH(C)_2(O)$	0.12	$N_{ar}(C_{ar})_2$	3.06

[a] At 25°. [b] X is C, O, N, CO, C_d, C_{ar}, C_t, or S. [c] Based on only one log γ value. [d] This is one of a set of contributions whose sum was determined by a considerably larger set of log γ values but for which only the minimum number of log γ values required for separation into individual contributions was available. [e] This refers to a carbon atom common to two fused aromatic rings, such as C-9 in naphthalene. It may not be applicable to the carbon atoms joined by single bonds in biphenyl, for example. [f] Y is C, O, C_d, or C_{ar}. [g] Nitro and cyano groups are treated as univalent atoms. [h] Assigned the same value as $[C_{ar}H(C_{ar})_2]$. [i] Assigned the same value as [OH(C)]. [j] Assigned the same value as [SH(C)].

Table III Distant Polar Interactions in Various Types of Compounds[a]

Compound(s)	Interaction	Compound	Interaction
Pyrazines	−2.26	*cis*-$CHCl{=}CHCl$	0.76
$RO{-}\overset{\vert}{\underset{\vert}{C}}{-}\overset{\vert}{\underset{\vert}{C}}{-}OR$	−1.58	$ClCH_2CH_2Br$	−0.72
$HOCH_2CH(OH)CH_2OH$	−7.05	$BrCH_2CH_2Br$	−0.66
$HOCH_2CH_2OH$	−3.02	$MeCHBrCH_2Br$	−0.65
$(ClCH_2CH_2)_2S$	−1.53	$BrCH_2CH_2CH_2Br$	−0.61
p-$HOC_6H_4NO_2$	1.12	$ClCH_2CH_2CH_2Cl$	−0.57
Cl_3CCHCl_2	−1.12	Cl_3CCCl_3	−0.56
$H_2NCH_2CH_2NH_2$	−1.00	*trans*-$CHCl{=}CHCl$	0.46
$MeCHClCH_2Cl$	−0.98	*p*-$C_6H_4Br_2$	0.27
Cl_2CHCH_2Cl	−0.95	*p*-HOC_6H_4Br	0.26
$Cl_2CHCHCl_2$	−0.92	*o*-$C_6H_4Cl_2$	0.19
p-HOC_6H_4CHO	0.83	*m*-$C_6H_4Cl_2$	−0.09
$ClCH_2CH_2Cl$	−0.83	*p*-$C_6H_4Cl_2$	−0.07

[a] Values of $(\log \gamma)_{obsd} - (\log \gamma)_{calcd}$, with the latter being obtained from the group contribution scheme.

tion for the group contribution. Thus the contribution of an olefinic methylene group is written $[C_dH_2]$ rather than $[C_dH_2(C_d)]$.

The values of certain group contributions must be assigned arbitrarily.[6,8] Most such assignments were made in the same way used by Benson and coworkers; *e.g.*, $[CH_3(O)]$, $[CH_3(CO)]$, $[CH_3(N)]$, etc., were all assigned the same value as $[CH_3(C)]$. We also followed their practice of treating certain groups, such as cyano, nitro, and carbonyl, as if they were atoms.

Many of the deviations observed in the bond contribution correlation may be thought of as arising from interactions between polar bonds. When the polar bonds involve a common atom, such interactions are included automatically in a group contribution. The interaction between the two carbon–oxygen bonds involving the central carbon atom of methylal, for example, is included in the $[CH_2(O)_2]$ group contribution. However, early regression analyses convinced us that interactions between more widely separated polar bonds were producing marked deviations from our group contribution correlation. To ignore such interactions would reduce the quality of our correlation and make the values of the parameters depend significantly on the particular set of compounds for which log γ values were available. We therefore decided to obtain contributions for such distant polar interactions or to neglect data upon which such interactions might have a significant effect. Most distant polar interactions of a given type appeared in only one of the 292 compounds for which we had log γ values. Also, a number of group contributions appeared in sets of compounds no larger than the number of parameters to be determined. Compounds of either of these types were deleted from the set before the regression analysis because the analysis would be trivial in such cases. Analysis of the remaining 212 log γ values gave two distant interaction parameters and 49 group contributions (not counting some assigned arbitrarily). From these parameters the log γ values may be calculated with a standard deviation of 0.12, which may not be very much larger than the average experimental uncertainty. The 49 group contributions are listed in Table II with the contributions assigned arbitrarily and 20 additional contributions calculated from data that had not been included in the least-squares treatment. Since these latter contributions are based on small sets of log γ values of the same size as the set of contributions being determined (the set size being 1.0 in most cases), they are less reliable than those obtained from the overdetermined system.

The only distant polar interactions (numbers that must be added to the group contributions to obtain log γ values) that appeared in more than one compound, and hence the only ones calculated by a least-squares treatment, were the interaction of the two nitrogen atoms in a pyrazine ring and the interaction of two alkoxy groups attached to adjacent saturated carbon atoms. These are the first two entries in Table III. The other distant polar interactions or sets of distant polar interactions occurred in only one compound each and are therefore listed with the formula of the compound in Table III.

Most of the larger interactions seem qualitatively understandable in terms of the structures of the compounds involved. Glycerol and ethylene glycol are internally hydrogen bonded in the gas phase. Hence their hydroxy groups do not gain as much hydrogen bonding on going into aqueous solution and their log γ values are smaller than would be expected from [OH(C)] and [CH_2(C)(O)] values derived from data on monohydroxylic alcohols, for which internal hydrogen bonding is impossible. The third largest interaction, that found in pyrazines, may also be explained in terms of hydrogen bonding, which we assume is the main reason that pyridine and most other azines are much more water soluble than benzene. That is, the large positive value of [$N_{ar}(C_{ar})_2$] listed in Table II, which arises from data on pyridine derivatives, is a reflection of the ability of the pyridine nitrogen atom to accept hydrogen bonds from water. The hydrogen-bonding ability of these nitrogen atoms, like that of other basic atoms of a given type, is known to be decreased by electron-withdrawing substituents.[15] The value of log K for hydrogen bonding of 3- and 4-substituted pyridines to *p*-fluorophenol in carbon tetrachloride at 25° decreases by 0.24 for each pK unit by which the basicity in water at 25° decreases.[15] Each nitrogen atom in pyrazine is about 4.8 pK units more weakly basic than the nitrogen atom in pyridine.[16] These numbers seem large enough to make it plausible that weak hydrogen bonding to the two nitrogen atoms of pyrazines (relative to hydrogen bonding to the nitrogen atom of pyridine) accounts for much of the distant polar interaction listed for pyrazines. A qualitatively similar effect would be expected for ethylenediamine, but since the amino groups in ethylenediamine are only about 1.0 pK unit weaker than the one in ethylamine[16] it is not surprising that the distant polar interaction is smaller than for pyrazines. The interactions for β-diethers and for the saturated polyhalides and 2,2′-dichlorodiethyl sulfide may be rationalized qualitatively in the same way. Interpretation of the relative magnitudes of these interactions is probably complicated by the following facts. (1) Some of the halides are probably of such low basicity that they are so little involved in hydrogen bonding with water that further decreases in basicity have little effect. (2) Some of the compounds, such as those with dichloromethyl groups, may be acidic as well as basic participants in hydrogen bonding. (3) The strength of hydrogen bonding depends on the polarity as well as the acidity and basicity of the interacting species. (4) Some of the interactions listed may contain major experimental errors.

The largest positive distant polar interaction, for *p*-nitrophenol, is probably also attributable largely to hydrogen-bonding effects. The nitro group probably interacts with water largely by acting as a base in hydrogen bonding. With the hydroxy group, however, hydrogen bonding to water with the group acting as an acid must be important. The *p*-hydroxy substituent acts as an electron donor and increases the basicity of the nitro group and the *p*-nitro substituent acts as an electron withdrawer and increases the acidity of the hydroxy group. Thus the nitro and hydroxy groups in *p*-nitrophenol may interact more strongly with water than do the nitro and hydroxy groups in nitrobenzene and phenol, respectively. The same argument explains the smaller but still positive interaction observed with *p*-hydroxybenzaldehyde.

We do not understand why the interactions listed for the 1,2-dichloroethylenes are positive (although the value for the more polar cis isomer would be expected to be more positive, as observed).

Intrinsic hydrophilic character is more simply understood in terms of molecular structure than is the hydrophilic character measured by water solubility or distribution coefficients. Since a hydroxy group can participate as both an acid and a base in hydrogen bonding whereas an ethereal oxygen atom can participate only as a base, alcohols should ordinarily be considerably more hydrophilic than isomeric ethers. In agreement with expectation γ for *n*-butyl alcohol is more than 100 times as large as γ for its isomer diethyl ether. In contrast, the solubilities of the two compounds differ by less than 20%; *n*-butyl alcohol is already so strongly hydrogen bonded in the organic phase that it does not gain as much hydrogen bonding on going into aqueous solution as it otherwise would.

Although the relative magnitudes of the group contributions in Table II tend to agree with common notions concerning structural effects on hydrophilic character, with the contributions for oxygen- and nitrogen-containing groups tending to be larger than those for hydrocarbon groups, it should be remembered that some of the numbers are the results of arbitrary assignments. In the following discussion we shall consider only points that are independent of such assignments. Some of the contributions reflect the kind of polar interactions already discussed in connection with Table III. For example, although [CH_2(C)(O)] is essentially equal to [$CH_2(C)_2$], [$CH_2(O)_2$] is more than two units smaller. Each of the two atoms lowers the basicity and, hence, the hydrogen-bonding ability of the other. Neither of the oxygen atoms is *in* the $CH_2(O)_2$ group, as the carbon and hydrogen atoms are, but since the $CH_2(O)_2$ is the only group uniquely characteristic of a compound with two oxygen atoms bonded to the same methylene group, the interaction appears in the [$CH_2(O)_2$] contribution.

The fact that [S(C)(C_{ar})] is about equal to [$S(C)_2$] whereas [O(C)(C_{ar})] is considerably smaller than [$O(C)_2$] reflects the much greater ability of a phenyl group to withdraw electrons, by a resonance interaction, from an oxygen atom to which it is bonded than from a sulfur atom. The fact that [O(C)(CO)] is still smaller than [O(C)(C_{ar})] reflects the greater electron-withdrawing power of a carbonyl group.

In applying the group contributions in Table II to compounds in which significant distant polar interactions seem possible, the magnitudes of such interactions may be estimated from the interactions listed in Table III. Although the group contribution scheme is to be preferred when the required group contributions have been (or can be) determined, the less precise bond contribution scheme presently covers a significantly larger number of possible compounds.

A brief and preliminary account of this investigation will appear in a forthcoming book.[17]

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Table IV. Experimental and Calculated Activity Coefficients in the Gas Phase Referred to Dilute Aqueous Solution at 25°.

Compound	P(mm)[a]	$-\log c_g$[b]	Ref.[c]	$-\log c_w$[d]	Ref.[c]	$\log \gamma$[e]		
						Exptl	Group	Bond
1. Methane	760	1.39		2.82	(1-4)	-1.43	f	-0.43
2. Ethane	760	1.39		2.70	(1-4)	-1.31	-1.23	-0.60
3. Propane	760	1.39		2.85	(1-4)	-1.46	-1.38	-0.78
4. *n*-Butane	760	1.39		2.97	(1-4)	-1.58	-1.52	-0.95
5. 2-Methylpropane	760	1.39		3.07	(1,3)	-1.68	-1.61	-0.95
6. *n*-Pentane	512.5	1.56	(6b,7,21)	3.27	(1-3,5,8)	-1.71	-1.67	-1.13
7. 2,2-Dimethylpropane	760	1.39		3.34	(1,3)	-1.95	-1.76	-1.13
8. Cyclopentane	317.5	1.77	(6a,21)	2.65	(1,3,5)	-0.88	-0.73	-0.87
9. *n*-Hexane	151.3	2.09	(6b,7,21)	3.96	(1-3,5,8)	-1.87	-1.81	-1.30
10. 2-Methylpentane	211.8	1.94	(6b,7,21)	3.79	(1,3,5)	-1.85	-1.90	-1.30
11. 3-Methylpentane	189.8	1.99	(6b,7,21)	3.83	(1,3)	-1.84	-1.90	-1.30
12. Cyclohexane	97.58	2.28	(6a,7,21)	3.18	(1,3,5)	-0.90	-0.87	-1.05
13. Methylcyclopentane	137.5	2.13	(6a,7,21)	3.30	(1)	-1.17	-0.95	-1.05
14. 2,2-Dimethylbutane	319.1	1.77	(6b,7,21)	3.67	(1,3)	-1.90	-1.90	-1.30
15. *n*-Heptane	45.81	2.61	(6b,7,21)	4.53	(1-3,5,8)	-1.92	-1.96	-1.47
16. 2,4-Dimethylpentane	98.40	2.28	(6b,7,21)	4.39	(1,3,5)	-2.11	-2.12	-1.47
17. Methylcyclohexane	46.33	2.60	(6a,7,21)	3.85	(1,3,5)	-1.25	-1.10	-1.22
18. *n*-Octane	14.04	3.12	(6b,7,21)	5.24	(1-3,5,8)	-2.12	-2.10	-1.65
19. 2,2,4-Trimethylpentane	49.34	2.58	(6b,7,21)	4.67	(1)	-2.09	-2.28	-1.65
20. *cis*-1,2-Dimethylcyclohexane	14.47	3.11	(6a,7,21)	4.27	(1)	-1.16	-1.33	-1.40
21. Ethylene	760	1.39		2.33	(1,2)	-0.94	-0.82	-0.59
22. Propylene	760	1.39		2.32	(1-3)	-0.93	-0.81	-0.61
23. 1-Butene	760	1.39		2.40	(1,3)	-1.01	-1.03	-0.79
24. 2-Methylpropene	760	1.39		2.33	(1,3)	-0.94	-0.97	-0.64
25. 1-Pentene	648.8	1.46	(6b,7,21)	2.68	(1,5)	-1.22	-1.18	-0.96
26. *trans*-2-Pentene	505.5	1.56	(6b,7)	2.54	(1,3,5)	-0.98	-1.02	-0.81
27. Cyclopentene	380.2	1.69	(6a)	2.10	(1,5)	-0.41	-0.16	-0.56
28. 2-Methyl-2-butene	466.1	1.60	(6b,7,21)	2.56	(3)	-0.96	-0.95	-0.66
29. 3-Methyl-1-butene	760	1.39		2.73	(1)	-1.34	-1.41	-0.96
30. 1-Hexene	187.2	2.00	(6b,7,21)	3.23	(1,3,5)	-1.23	-1.32	-1.14
31. Cyclohexene	88.83	2.32	(6a,21)	2.59	(1,3,5)	-0.27	-0.30	-0.73
32. 4-Methyl-1-pentene	268	1.84	(6b)	3.24	(5)	-1.40	-1.42	-1.14
33. *trans*-2-Heptene	46.55	2.60	(6b,7,21)	3.82	(1,3,5)	-1.22	-1.31	-1.16
34. 1-Methylcyclohexene	30.61	2.78	(6a)	3.27	(1)	-0.49	-0.48	-0.76
35. 1-Octene	17.38	3.03	(6b,7)	4.62	(1,5)	-1.59	-1.61	-1.48
36. 1,3-Butadiene	760	1.39		1.87	(1,3)	-0.41	-0.46	-0.40
37. 1,4-Pentadiene	734.3	1.40	(6b,7,21)	2.09	(1,5)	-0.69	g	-0.80
38. 2-Methyl-1,3-butadiene	550	1.53	(6b,7)	2.03	(1)	-0.50	-0.40	-0.42
39. 1,5-Hexadiene	208	1.95	(6b,7)	2.69	(1,5)	-0.74	-0.83	-0.97
40. 2,3-Dimethyl-1,3-butadiene	143.8	2.11	(6b)	2.40	(3)	-0.29	-0.34	-0.45
41. Acetylene	760	1.39		1.38	(2,3)	0.01	g	-0.01
42. Propyne	760	1.39		1.04	(1,3)	0.35	g	0.31
43. 1-Butyne	760	1.39		1.27	(1,3)	0.12	0.05	0.14
44. 1-Pentyne	431.4	1.63	(6b)	1.64	(1,5)	-0.01	-0.06	-0.03
45. 1-Hexyne	136.0	2.14	(6b)	2.35	(1,5)	-0.21	-0.23	-0.21
46. 1-Heptyne	52.51	2.55	(6b)	2.99	(1,5)	-0.44	-0.36	-0.39
47. 1-Octyne	15.60	3.14	(6b)	3.66	(1,5)	-0.52	-0.52	-0.56
48. 1-Nonyne	6.26	3.47	(6b)	4.24	(1,5)	-0.77	-0.67	-0.74
49. Benzene	95.18	2.29	(6a,7,21)	1.64	(1-5)	0.65	0.67	0.67
50. Toluene	28.44	2.81	(6a,7,21)	2.25	(1-5)	0.56	0.64	0.68
51. Ethylbenzene	9.57	3.29	(6a,7,21)	2.84	(1-5)	0.45	0.45	0.51
52. *o*-Xylene	6.69	3.44	(6a,7,21)	2.78	(1-3,5)	0.66	0.62	0.69
53. *m*-Xylene	8.36	3.35	(6a,7,21)	2.76	(2,3)	0.59	0.62	0.69
54. *p*-Xylene	8.82	3.32	(6a,7,21)	2.73	(2,3)	0.59	0.62	0.69
55. Propylbenzene	3.43	3.73	(6a,7,21)	3.34	(1-3,5)	0.39	0.31	0.33
56. 2-Propylbenzene	4.65	3.60	(6a,7,21)	3.38	(1-3)	0.22	0.32	0.33
57. 1,2,4-Trimethylbenzene	2.10	3.95	(6a,7,21)	3.32	(1,5)	0.63	0.59	0.70
58. Butylbenzene	1.08	4.23	(6a,7,21)	3.94	(1-3)	0.29	0.16	0.16
59. 2-Butylbenzene	1.88	4.00	(6a,7,21)	3.67	(1-3)	0.33	0.17	0.16
60. *t*-Butylbenzene	2.21	3.92	(6a,7,21)	3.60	(1-3)	0.32	0.34	0.16
61. *t*-Amylbenzene	0.97	4.28	(6a,7)	4.15	(2,3)	0.13	0.20	-0.02
62. Naphthalene	0.084	5.34	(23,6a,7)	3.57	(6a,2,3)	1.77	1.84	1.89
63. Acenaphthene	0.0024	6.89	(24)	4.40	(2)	2.49	2.63	2.16
64. Anthracene		9.49[h]	(23)	6.35	(2,3)	3.14	3.01	3.11
65. Phenanthrene		8.03[h]	(23)	5.05	(2,4)	2.98	3.01	3.11
66. Fluoromethane	760	1.39		1.23	(3,22)	0.16	f	-0.82
67. Trifluoromethane	760	1.39		1.98	(3)	-0.59	f	-1.62
68. Tetrafluoromethane	760	1.39		3.71	(3)	-2.32	f	-2.02
69. Chloromethane	760	1.39		1.00	(3,22)	0.39	f	-0.02
70. Dichloromethane	411.2	1.66	(7,21)	0.63	(2,3)	1.03	f	0.39
71. Trichloromethane	202.8	1.96	(7,21)	1.21	(2,3,5)	0.75[i]	f	0.80
72. Tetrachloromethane	109.6	2.23	(6c,7,21)	2.30	(2,3)	-0.07	f	1.21
73. Bromomethane	760	1.39		0.81	(3,22)	0.58	f	0.55
74. Dibromomethane	44.11	2.62	(7,21)	1.18	(2,3)	1.44	f	1.53
75. Tribromomethane	6.25	3.47	(7,21)	1.91	(2,3)	1.56	f	2.51
76. Iodomethane	405.9	1.65	(6c,7,21)	1.00	(2,3,5,22)	0.65	f	0.71
77. Chlorofluoromethane	760	1.39		0.82	(3)	0.57	f	-0.42
78. Chlorodifluoromethane	760	1.39		1.47	(3)	-0.08	f	-0.61
79. Chlorotrifluoromethane	760	1.39		3.24	(3)	-1.85	f	-1.21
80. Dichlorodifluoromethane	760	1.39		2.63	(3)	-1.24	f	-0.40
81. Bromotrifluoromethane	760	1.39		2.70	(3)	-1.31	f	-0.64
82. 1,1-Difluoroethane	760	1.39		1.31	(3)	0.08	g	-1.40
83. Chloroethane	760	1.39		0.93	(2,3,5)	0.46	0.44	-0.19
84. Bromoethane	474.5	1.39	(7,21)	1.08	(2,3,5)	0.51	0.48	0.38
85. Iodoethane	136.2	2.13	(6c,7,21)	1.60	(2,3,5)	0.53	0.53	0.54
86. 1,1-Dichloroethane	229.8	1.91	(7,21)	1.29	(2,3)	0.62	0.71	0.22
87. 1,2-Dichloroethane	85.52	2.33	(7,21)	1.06	(2,3)	1.27	2.10[j]	0.22
88. 1,2-Dibromoethane	11.40	3.21	(7,21)	1.67	(2,3)	1.54	2.20[j]	1.35
89. 1-Chloro-2-bromoethane	33.1	2.75	(7,21)	1.32	(2,3)	1.43	2.15[j]	0.79
90. 1,1,1-Trichloroethane	120.7	2.19	(6c,7,21)	2.01	(3,2)	0.18	g	0.65
91. 1,1,2-Trichloroethane	24.13	2.89	(6c,7,21)	1.46	(2,3)	1.43	2.38[j]	0.63
92. 1,1,2,2-Tetrachloroethane	5.95	3.49	(6c,7,21)	1.76	(3)	1.73[i]	2.65[j]	1.04[k]
93. Pentachloroethane	4.54	3.61	(7,21)	2.61	(3)	1.00	2.12[j]	1.45
94. Hexachloroethane	0.367	4.70	(7,21)	3.67	(3)	1.03	1.59[j]	1.86
95. 2-Chloro-1,1,1-trifluoroethane	760	1.39		1.43	(3)	-0.04	l	-1.36
96. 1,1,2,2-Tetrachlorodifluoroethane	47.8	2.59	(21)	3.19	(3)	-0.60	l	0.24
97. 1,1,2-Trichlorotrifluoroethane	340	1.74	(21)	3.04	(3)	-1.30	l	-0.56
98. 1,1-Dichlorotetrafluoroethane	760	1.39		3.23	(3)	-1.84	l	-1.37
99. 1,2-Dichlorotetrafluoroethane	760	1.39		3.09	(3)	-1.70	l	-1.37
100. Chloropentafluoroethane	760	1.39		3.49	(3)	-2.10	l	-2.18
101. 1-Chloropropane	348.8	1.72	(7,21)	1.46	(2,3,5)	0.26	0.29	-0.37
102. 2-Chloropropane	482.1	1.59	(7,21)	1.41	(2,3,5)	0.18	0.23	-0.37
103. 1-Bromopropane	143.7	2.11	(7,21)	1.70	(2,3,5)	0.41	0.34	0.20
104. 2-Bromopropane	213.6	1.94	(7,21)	1.59	(2,3,5)	0.35	g	0.20
105. 1-Iodopropane	43.09	2.63	(6c,7,21)	2.20	(2,3,5)	0.43	0.38	0.36
106. 2-Iodopropane	69.01	2.43	(6c,7,21)	2.09	(2,3)	0.34	g	0.35
107. 1,2-Dichloropropane	53.61	2.53	(7,21)	1.61	(2,3)	0.92	1.90[j]	0.04
108. 1,3-Dichloropropane	18.25	3.01	(6c,7,21)	1.62	(2,3,5)	1.39	1.96[j]	0.04
109. 1,2-Dibromopropane	5.16	3.56	(6c,7,21)	2.14	(3)	1.42	2.07[j]	1.18
110. 1,3-Dibromopropane	1.35	4.14	(6c,7,21)	2.70	(5)	1.44	2.05[j]	1.18
111. 1-Chlorobutane	106.3	2.24	(21,7)	2.14	(5)	0.10	0.14	-0.54
112. 1-Bromobutane	41.27	2.66	(6c,7,21)	2.36	(2,3,5)	0.30	0.19	0.03
113. 1-Bromo-2-methylpropane	69.02	2.43	(6c,21)	2.44	(3,2)	0.02	0.11	0.03
114. 1-Iodobutane	13.86	3.13	(6c,7,21)	2.94	(2,3,5)	0.19	0.24	0.19
115. 1,1-Dichlorobutane	22.83	2.91	(6c,21)	2.40	(3)	0.51	0.42	-0.13
116. 1-Chloropentane	31.07	2.78	(6c,21)	2.73	(3)	0.05	0.00	-0.72
117. 2-Chloropentane	48.66	2.58	(6c,21)	2.63	(3)	-0.05	-0.05	-0.72
118. 3-Chloropentane	45.77	2.60	(6c,21)	2.63	(3)	-0.03	-0.05	-0.72
119. 1-Bromo-3-methylbutane	34.62	2.73	(6c,21)	2.88	(3)	-0.15	-0.03	-0.15
120. Chloroethylene	760	1.39		1.75	(3)	-0.36	g	-0.28
121. *cis*-1,2-Dichloroethylene	202.7	1.96	(7,21)	1.10	(3,2)[i]	0.86	0.10[j]	0.02
122. *trans*-1,2-Dichloroethylene	330	1.75	(7,21)	1.19	(3,2)	0.56	0.10[j]	0.02
123. Trichloroethylene	74.31	2.40	(6b,7,21)	2.08	(3,2)	0.32	l	0.32
124. Tetrachloroethylene	18.47	3.00	(6b,7,21)	3.04	(3)	-0.04	l	0.63
125. 3-Chloropropene	366.8	1.70	(6c,21)	1.28	(3)	0.42	g	-0.20
126. Chlorobenzene	12.1	3.18	(7,21)	2.44	(2,3,5)	0.74	g	0.75
127. Bromobenzene	4.18	3.65	(6a,7,21)	2.58	(3,2)	1.07	1.05	1.10
128. 1,2-Dichlorobenzene	1.78	4.01	(7,21)	3.01	(2,3,5)	1.00	0.81[j]	0.82
129. 1,3-Dichlorobenzene	2.92	3.80	(7,21)	3.08	(2,3,5)	0.72	0.81[j]	0.82
130. 1,4-Dichlorobenzene	1.76	4.02	(7,21)	3.28	(2,3,5)	0.74	0.81[j]	0.82
131. 1,4-Dibromobenzene	0.032	5.76	(6a,7,21)	4.07	(3)	1.69	1.42[j]	1.53
132. *p*-Bromotoluene	1.15	4.21	(6a,7,21)	3.19	(3)	1.02	1.02	1.11
133. 1-Bromo-2-ethylbenzene	0.531	4.54	(6a,21)	3.67	(3)	0.87	0.83	0.93
134. *o*-Bromocumene	0.290	4.81	(6a,21)	4.19	(3)	0.62	0.69	0.76
135. Dimethyl ether	760	1.39		0.00	(10,35)	1.39	1.70	1.37
136. Dimethyl sulfide	484.9	1.58	(6c,10,21)	0.45	(10)	1.13	1.11	1.59
137. Dimethoxymethane					(35)	2.15	2.09	3.12[k]
138. 1,3-Dioxolane					(30)	3.00	3.06	3.38[k]
139. Diethyl ether					(31,35)	1.28	1.44	1.02
140. Diethyl sulfide	58.37	2.50	(6c,21)	1.45	(2)	1.05	1.07	1.24
141. Methyl propyl ether	454.6	1.60	(7,21)	0.38	(2,5)	1.22	1.42	1.02
142. Methyl isopropyl ether	570	1.51	(7,15,21)	0.04	(33,2,5)	1.47	1.20	1.02[k]
143. Tetrahydrofuran					(30,31)	2.54	2.38	1.24[k]
144. 1,4-Dioxane					(30)	3.70	3.76	3.20[k]
145. Ethyl propyl ether	178	2.02	(12b,21)	0.69	(12b)	1.33	1.29	0.91[k]
146. Methyl *t*-butyl ether					(33)	1.62	1.24	0.91[k]
147. 2-Methyltetrahydrofuran					(30)	2.42	2.01	1.06[k]
148. Tetrahydropyran					(30)	2.29	2.23	1.05[k]
149. Dipropyl ether	65.0	2.46	(12b,7,21)	1.61	(12b,2,5)	0.85	1.15	0.62
150. Diisopropyl ether	151	2.09	(7,21)	1.70	(10)	0.39	0.71	0.62
151. 1,2-Diethoxyethane	33.73	2.74	(7,21)	0.15	(2)	2.59	2.53	2.64
152. 1,1-Diethoxyethane	34.61	2.73	(7,21)	0.33	(2)	2.40	g	2.64
153. Di-*n*-butyl ether					(35,7)	0.61	0.83[k]	0.26[k]
154. Anisole	4.16	3.54	(10,21)	2.88	(10)	0.76	g	0.84
155. Thioanisole	0.76	4.39	(10)	2.39	(10)	2.00	g	2.22
156. 2,2'-Dichlorodiethyl sulfide	0.105	5.24	(7,21)	2.37	(5)	2.87	4.40[j]	2.05
157. Methanol					(10,35)	3.72	3.83	3.89
158. Methanethiol	760	1.39		0.48	(10)	0.91	0.94	1.02
159. Ethanol					(10,35)	3.59	3.70	3.72
160. Ethanethiol	527.3	1.59	(6c,21)	0.60	(2)	0.95	0.92	0.83[k]
161. 2,2,2-Trifluoroethanol					(29)	3.15	g	2.53[k]
162. Ethylene glycol					(12b)	5.61	8.63[j]	6.02[k]
163. 1-Propanol					(12a,35)	3.56	3.55	3.54
164. 2-Propanol					(12a,35)	3.48	3.33	3.54
165. Allyl alcohol					(35,34)	3.69	g	3.69[k]
166. 1,1,1-Trifluoro-2-propanol					(29)	3.05	l	2.35[k]
167. 2,2,3,3-Tetrafluoropropanol					(29)	3.59	l	1.95[k]
168. 2,2,3,3,3-Pentafluoropropanol					(29)	3.04	l	1.57[k]
169. Hexafluoro-2-propanol					(29)	2.76	l	1.18[k]
170. Glycerol					(12b)	6.15	13.20[j]	12.10[k]
171. 1-Butanol					(12a,35)	3.46	3.41	3.37
172. 2-Butanol					(12a,35)	3.38	3.19	3.37
173. *t*-Butyl alcohol					(12a,35)	3.31	3.37	3.37
174. 2-Methyl-1-propanol					(12a)	3.31	3.33	3.37
175. 1-Pentanol					(12a)	3.29	3.26	3.19
176. 2-Pentanol					(12a)	3.22	3.04	3.19
177. 2-Methyl-1-butanol					(12a)	3.24	3.18	3.19
178. 2-Methyl-2-butanol					(12a)	3.25	3.23	3.19
179. 1-Hexanol	0.719	4.41	(12a,7,21)	1.21	(12a)	3.20	3.12	3.02
180. 3-Hexanol	4.88	3.58	(21,7)	0.80	(5)	2.70	2.90	3.02
181. Cyclohexanol	1.66	4.05	(7,21)	0.42	(5)	3.63	3.84	3.87
182. 2,3-Dimethylbutanol	10.55	3.24	(7)	0.37	(5)	2.87	3.00	3.02
183. 2-Methyl-3-pentanol	5.13	3.55	(7)	0.70	(5)	2.85	2.82	3.02
184. 4-Methyl-2-pentanol	5.45	3.53	(7,21)	0.79	(5)	2.74	2.82	3.02
185. 2-Methyl-2-pentanol	7.87	3.37	(7,21)	0.49	(5)	2.88	3.08	3.02
186. 1-Heptanol	0.224	4.92	(12a,21)	1.80	(12a,5)	3.12	2.97	2.84
187. 1-Octanol	0.083	5.35	(12a,21)	2.34	(12a,5,35)	3.01	2.83	2.67
188. Phenol					(26,10)	4.79	4.58	3.35
189. 4-Bromophenol					(26)	5.21	4.95[j]	3.78[k]
190. 4-Nitrophenol					(26)	7.77	6.65[j]	5.40[k]
191. Thiophenol	1.92	3.99	(10)	2.12	(10)	1.87	g	1.65[k]
192. 2-Cresol					(25)	4.30	4.55	3.36[k]
193. 4-Cresol					(25)	4.49	4.55	3.36[k]
194. 4-Hydroxybenzaldehyde					(26)	7.68	6.85[j]	5.91[k]
195. 4-*t*-Butylphenol					(25)	4.34	4.25	2.82[k]
196. Acetaldehyde					(11,35)	2.57	2.62	2.66
197. Propanal					(11,35)	2.52	2.47	2.48
198. Butanal					(11,35)	2.33	2.33	2.31
199. Pentanal					(11)	2.22	2.18	2.13
200. Hexanal					(11)	2.08	2.03	1.96
201. Heptanal					(11)	1.96	1.89	1.76
202. Octanal					(11)	1.68	1.74	1.61
203. Nonanal					(11)	1.52	1.60	1.43

Table IV (Continued)

	Compound	P(mm)	$-\log c_g$	Ref.	$-\log c_w$	Ref.	Exptl	Group	Bond
204.	trans-2-Butenal					(28,35)	3.10	3.12	3.13^k
205.	trans-2-Hexenal					(28)	2.70	2.75	2.77^k
206.	trans-2-Octenal					(28)	2.52	2.46	2.41^k
207.	trans,trans-2,4-Hexadienal					(28)	3.40	3.27	3.31^k
208.	Benzaldehyde	1.306	4.16	(20)	1.21	(9)	2.95	g	3.22^k
209.	Acetone					(11,35)	2.79	2.80	2.93
210.	2-Butanone					(11,35)	2.72	2.65	2.75
211.	2-Pentanone					(11)	2.58	2.51	2.58
212.	2-Heptanone					(11)	2.23	2.22	2.23
213.	2-Octanone					(11)	2.11	2.07	2.06
214.	2-Nonanone					(11)	1.82	1.93	1.88
215.	2-Undecanone					(11)	1.58	1.64	1.53
216.	Acetophenone	0.372	4.70	(6a,7,21)	1.34	(2,14,17)	3.36	g	3.50
217.	Acetic acid						4.91	4.92	4.94
218.	Propionic acid						4.74	4.77	4.76
219.	Butyric acid						4.66	4.62	4.58
220.	Methyl formate					(18)	2.04	2.09	2.14
221.	Ethyl formate	255.4	1.86	(7,21)	-0.08	(5)	1.94	1.96	1.98
222.	Methyl acetate					(12b)	2.43	2.33	2.43
223.	Propyl formate	85.8	2.33	(7,21)	0.51	(2,5)	1.82	1.81	1.81
224.	Isopropyl formate	142.6	2.11	(7,21)	0.63	(2)	1.48	1.59	1.81
225.	Ethyl acetate					(12b)	2.26	2.20	2.25
226.	Methyl propionate	87.0	2.33	(7,21)	0.15	(2,5)	2.18	2.19	2.25
227.	Isobutyl formate	43.3	2.68	(7,21)	1.00	(2)	1.63	1.55	1.63
228.	Propyl acetate	33.0	2.75	(12b,21)	0.66	(12b,2,5)	2.09	2.05	2.08
229.	Isopropyl acetate	61.1	2.48	(7,21)	0.54	(2,5)	1.94	1.83	2.08
230.	Ethyl propionate	37.5	2.69	(7,21)	0.64	(2)	2.05	2.06	2.08
231.	Methyl butyrate					(11)	2.06	2.04	2.08
232.	Isoamyl formate	15.3	3.08	(7,21)	1.52	(2)	1.56	1.44	1.46
233.	Butyl acetate	10.8	3.24	(7)	1.37	(2,5)	1.87	1.91	1.90
234.	Isobutyl acetate	18.11	3.01	(7,21)	1.28	(2,5)	1.73	1.83	1.90
235.	Propyl propionate	13.58	3.14	(7,21)	1.34	(2,5)	1.80	1.91	1.90
236.	Isopropyl propionate	22.53	2.92	(7)	1.29	(2,5)	1.63	1.69	1.90
237.	Ethyl butyrate	15.9	3.06	(7,21)	1.23	(2,5)	1.83	1.91	1.90
238.	Methyl pentanoate					(11)	1.86	1.90	1.90
239.	Amyl acetate	4.1	3.66	(7)	1.86	(2)	1.80	1.77	1.73
240.	Isoamyl acetate	5.5	3.53	(7,21)	1.91	(2)	1.62	1.65	1.73
241.	Propyl butyrate	4.8	3.59	(7,21)	1.92	(2,5)	1.67	1.76	1.73
242.	Ethyl pentanoate	4.8	3.59	(7)	1.74	(2,5)	1.85	1.76	1.73
243.	Methyl hexanoate					(11)	1.82	1.75	1.73
244.	Hexyl acetate	3.62	3.71	(7)	2.05	(2)	1.66	1.62	1.55
245.	Amyl propionate	3.6	3.71	(7)	2.25	(2)	1.46	1.62	1.55
246.	Methyl octanoate					(11)	1.50	1.46	1.38
247.	Ethyl heptanoate	0.68	4.43	(7)	2.74	(2,5)	1.69	1.47	1.38
248.	Methyl benzoate	0.394	4.67	(6a,7)	1.53	(2)	3.14	g	3.00
249.	Ethylamine					(12b)	3.38	3.46	3.53
250.	Propylamine					(12b)	3.30	3.32	3.27
251.	Butylamine					(12b)	3.21	3.17	3.17
252.	Pentylamine					(27)	3.00	3.02	2.99
253.	Hexylamine					(27)	2.96	2.86	2.81
254.	Dimethylamine					(27)	3.14	3.14	3.38

Table IV (Continued)

	Compound	P(mm)	$-\log c_g$	Ref.	$-\log c_w$	Ref.	Exptl	Group	Bond
255.	Diethylamine					(27)	2.98	2.99	3.02
256.	Pyrrolidine					(32)	4.01	3.93	3.28
257.	Piperidine					(32)	3.74	3.78	3.10
258.	Dipropylamine					(27)	2.68	2.70	2.66
259.	Hexamethylenimine					(32)	3.60	3.64	2.92
260.	Dibutylamine					(27)	2.43	2.41	2.30
261.	Trimethylamine					(27)	2.37	2.29	3.06
262.	Triethylamine					(27)	2.22	2.06	2.52
263.	n-Methylpyrrolidine					(32)	2.91	3.08	2.96
264.	n-Methylpiperidine					(32)	2.85	2.93	2.78
265.	Ethylenediamine					(19)	7.15	6.15^j	7.67
266.	Acetonitrile					(10)	2.85	f	2.95
267.	Propionitrile					(12b)	2.82	2.82	2.78
268.	Butyronitrile					(12b)	2.67	2.67	2.61
269.	Nitroethane	21.07	2.96	(7,21)	0.24	(2)	2.72	2.66	2.61
270.	1-Nitropropane	10.20	3.26	(7,21)	0.81	(2)	2.45	2.51	2.43
271.	2-Nitropropane	17.41	3.03	(7,21)	0.73	(2)	2.30	g	2.43
272.	Nitrobenzene	0.284	4.82	(6a,7,21)	1.80	(2,5)	3.02	2.74	2.72
273.	2-Nitrotoluene	0.21^h	4.95	(21,7)	2.32	(2)	2.63	2.72	2.73
274.	3-Nitrotoluene	0.20^h	4.97	(21,7)	2.44	(2)	2.53	2.72	2.73
275.	Pyridine					(13)	3.44	3.62	3.51
276.	2-Methylpyridine					(13)	3.39	3.48	3.52
277.	3-Methylpyridine					(13)	3.50	3.59	3.52
278.	4-Methylpyridine					(13)	3.61	3.59	3.52
279.	2-Ethylpyridine					(13)	3.17	3.29	3.35
280.	3-Ethylpyridine					(13)	3.37	3.40	3.35
281.	4-Ethylpyridine					(13)	3.46	3.40	3.35
282.	2,3-Dimethylpyridine					(13)	3.53	3.46	3.53
283.	2,4-Dimethylpyridine					(13)	3.56	3.46	3.53
284.	2,5-Dimethylpyridine					(13)	3.45	3.46	3.53
285.	2,6-Dimethylpyridine					(13)	3.37	3.35	3.53
286.	3,4-Dimethylpyridine					(13)	3.62	3.56	3.53
287.	3,5-Dimethylpyridine					(13)	3.55	3.56	3.53
288.	2-Methylpyrazine					(28)	4.04	4.16	6.34^k
289.	2-Ethylpyrazine					(28)	4.00	3.97	6.16^k
290.	2-Isobutylpyrazine					(28)	3.70	3.60	5.80^k
291.	2-Ethyl-3-methoxy-pyrazine					(28)	3.22	l	6.31^k
292.	2-Isobutyl-3-methoxy-pyrazine					(28)	2.70	l	5.95^k

[a] Vapor pressure of pure solute (mm Hg) at 25°. [b] c_g is the concentration in the gas phase in moles per liter. [c] The first reference cited was used in calculations. [d] c_w is the water solubility (M). [e] $\gamma = c_w/c_g$, the activity coefficient referred to dilute aqueous solution. [f] Since this is the only possible compound that could contain the required group, its inclusion in the regression analysis would have been trivial. [g] Since this is one of a set of compounds whose log γ values were used to calculate a set of group contributions of the same size, the calculated value is identical to the experimental one. [h] Extrapolated from data at higher temperatures. [i] Data cited in other references differ significantly from this. [j] Omitted from the regression analysis because of a distant polar interaction. [k] Not included in the regression analysis. [l] This compound contained a group present only in compounds with distant polar interactions. Hence neither the interaction nor the group contribution could be calculated.

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Appendix

Table IV is arranged in the order: hydrocarbons, halohydrocarbons, ethers and sulfides, alcohols and mercaptans, phenols and thiophenols, aldehydes, ketones, carboxylic acids, esters, amines, nitriles, nitro compounds, pyridines, and pyrazines. The regression analyses were carried out using a computer program (BMDX 85).[16] In cases where there are no entries under P, $\log c_g$, and $\log c_w$, the values of $\log \gamma$ were obtained from data in the reference cited first.[1-15,17-35] In most cases the units had to be changed to obtain the values listed. Data on aldehydes in aqueous solution were not corrected to allow for the amount present as hydrate (1,1-diol). To permit a direct comparison of the correlating abilities of the group and bond contribution schemes, the latter was applied to the same 212 values of $\log \gamma$ that had been used for the group contribution correlation. The resulting standard deviation, 0.42, was essentially the same as that obtained in the bond correlation of 263 compounds that yielded the parameters in Table I and the calculated values of $\log \gamma$ in the last column of Table IV.

To help in assessing the quality of the correlations, a plot of $\log \gamma_{\mathrm{bond}}$ *vs.* $\log \gamma_{\mathrm{exptl}}$ is shown in Figure 1. The quality of the group contribution correlation may be inferred from the fact that the standard deviation was only 29% as large as that in the bond contribution correlation.

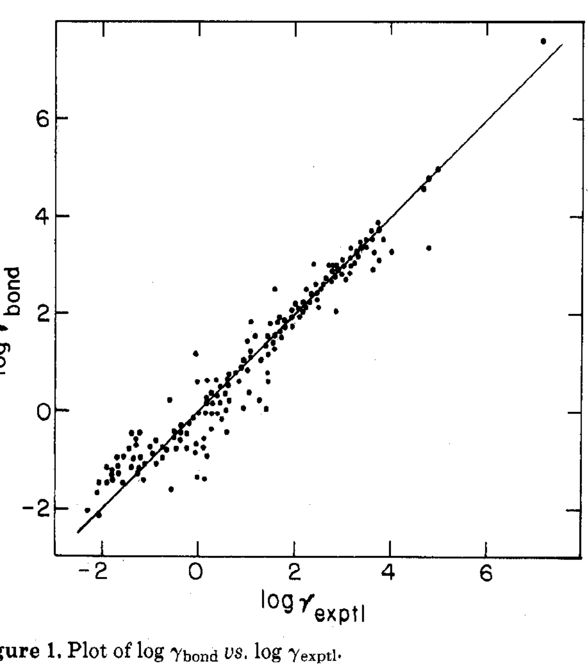

Figure 1. Plot of $\log \gamma_{\mathrm{bond}}$ *vs.* $\log \gamma_{\mathrm{exptl}}$.

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Ranking Strong Acids *via* a Selectivity Parameter. I

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The relative facility of an acid in catalyzing the isomerization of methylpentanes to 2,2-dimethylbutane and *n*-hexane and the simultaneous deprotonation of carbonium ion intermediates is used to define a selectivity parameter, $k_{iso}/k_{ex} \equiv I/E$, characteristic of the medium. I/E is used to rank Lewis acids in HBr, HCl, HF, HSO_3F, and CF_3SO_3H. Data for two I/E scales, one for exchange with isopentane and the other for exchange with methylcyclopentane, are reported.

The choice of an acid catalyst for a hydrocarbon reaction is to a large extent governed by qualitative observations rather than quantitative information about existing possibilities. This situation exists because the relative acid strength of important acids is often unknown and because firm information about the stability of ionic intermediates in most acids is virtually unavailable.

To help clarify the issues recent work, notably that of Professor R. J. Gillespie and his colleagues, has aimed at determining Hammett acidity function values, H_0, for systems employing SbF_5 as a Lewis acid.[1-3] Using nitro aromatics as indicators, he has shown that some acids have about 10^8 times the protonating ability of 100% H_2SO_4. Acids in this range are generally useful for paraffin–olefin alkylation, paraffin isomerization, and certain types of cracking reactions. Using similar techniques we are in the process of extending Gillespie's measurements to other acids, but of added importance, we have developed a new procedure to classify acids according to the manner in which they stabilize or interact with alkyl carbonium ions.

Our procedure is aimed at giving us quantitative information about the nucleophilicity of a given acid solution. Specifically it tells us if an alkyl cation can rearrange with or without deprotonating during its lifetime in the acid. It should be noted that the nucleophilicity of an acid system is not necessarily directly related to its acidity as a Brønsted acid, a property more properly evaluated by an H_0 type measurement.

This information is acquired by simultaneously reacting a hydrocarbon which contains an essentially uniform distribution of tritium around its skeleton with another molecular weight but unlabeled hydrocarbon over any acid catalyst. A "perfect" acid will allow all isomerizations to occur without hydrogen exchange while a "poor" acid, which is unable to stabilize the ion, will tend to induce faster exchange than isomerization. The ratio of isomerization to exchange rate constants, k_{iso}/k_{ex} or I/E, is defined as a selectivity parameter which permits the ranking of all strong acids. This parameter should be useful until alternate exchange mechanisms become important. At very high acidities direct protonation and displacement may become significant but it is not a serious factor through 2 *M* SbF_5–HSO_3F solutions which have H_0 values > -18.

Strategical Approach to the Problem

In order to obtain the selectivity parameter, it is first necessary to prepare a suitably labeled hydrocarbon. This was done by contacting 2- or 3-methylpentane with 98% H_2SO_4 containing tracer quantities of T_2O (1 mCi/ml) for several days. In this acid, the methylpentanes isomerize without undergoing chain branching rearrangements and exchange all protons except the tertiary hydrogen.[4-13] The labeled methylpentanes were diluted with unlabeled methylpentanes and mixed with isopentane (mixture 1) or methylcyclopentane (mixture 2).

Since it is known that during the isomerization of methylpentanes to an equilibrium mixture of all isomers there is a rapid equilibration of 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane which is followed by a slower conversion of this mixture to 2,2-dimethylbutane and *n*-hexane[4,14,15] we choose the rate of the latter process, k_{iso}, as a measure of the isomerization activity of the acid.

We also measure the rate of depletion of radioactivity in the total hexane fraction. The isomerization and overall exchange processes are both assumed to follow first-order kinetics and the rate constants are obtained from log concentration or radioactivity *vs.* time plots. In the more reactive acid systems there is substantial uncertainty in the rate