

**Table I.** Enthalpies of Solution in MeOH and DMF and Enthalpies of Transfer at 25°<sup>a</sup>

Compound	$\Delta H_s$ (MeOH), kcal/ mol	$\Delta H_s$ (DMF), kcal/mol	$\Delta\Delta H_s$ (MeOH →DMF), kcal/mol	$\Delta\Delta H_s$ calcd, kcal/mol
Benzene	0.36	0.04	-0.3	
Biphenyl	4.3	3.7	-0.6	-0.6
<i>o</i> -Terphenyl	4.6	3.6	-1.0	-0.9
Naphthalene	4.5	3.9	-0.6	
Acetophenone	1.2	-0.1	-1.3	
Chlorobenzene	0.17	-0.25	-0.4	
<i>o</i> -Dichlorobenzene	0.34	-0.13	-0.5	-0.5
Nitrobenzene	1.0	-0.2	-1.2	
<i>p</i> -Nitrobiphenyl	5.6	4.2	-1.4	-1.4
<i>p,p'</i> -Dinitrobiphenyl	6.1	4.1	-2.0	-2.2
1-Nitronaphthalene	5.3	3.9	-1.4	-1.4
1-Chloronaphthalene	0.55	-0.19	-0.7	-0.7
<i>o</i> -Nitrochlorobenzene	4.7	3.6	-1.1	-1.2
<i>m</i> -Nitrochlorobenzene	5.6	4.4	-1.2	-1.2
<i>p</i> -Nitrochlorobenzene	4.2	3.0	-1.2	-1.2
2,4-Dinitrochlorobenzene	5.5	3.6	-1.9	-2.0
<i>o</i> -Nitroacetophenone	1.7	-0.6	-2.3	-2.1
<i>m</i> -Nitroacetophenone	6.6	4.5	-2.1	-2.1
<i>p</i> -Nitroacetophenone	6.4	4.2	-2.2	-2.1
<i>p</i> -Chloroacetophenone	1.13	-0.25	-1.4	-1.4

<sup>a</sup> All calorimetric values  $\pm 0.1$  kcal/mol.

From the enthalpies of transfer of the neutral molecules the enthalpy of transfer for the various functional groups may be calculated in the following manner

$$\Delta\Delta H_s(\text{NO}_2) = \Delta\Delta H_s(\text{nitrobenzene}) - \Delta\Delta H_s(\text{benzene})$$

$$\Delta\Delta H_s(\text{Cl}) = \Delta\Delta H_s(1\text{-chloronaphthalene}) - \Delta\Delta H_s(\text{naphthalene})$$

$$\Delta\Delta H_s(\text{COCH}_3) = \Delta\Delta H_s(\text{acetophenone}) - \Delta\Delta H_s(\text{benzene})$$

$$\Delta\Delta H_s(\text{C}_6\text{H}_5) = \Delta\Delta H_s(\text{benzene}) = \frac{1}{2}\Delta\Delta H_s(\text{biphenyl}), \text{ etc.}$$

The average values for the functional groups in kcal/g group wt are as follows:  $\Delta\Delta H_s(\text{NO}_2) = -0.8$ ,  $\Delta\Delta H_s(\text{Cl}) = -0.1$ ,  $\Delta\Delta H_s(\text{COCH}_3) = -1.0$ ,  $\Delta\Delta H_s(\text{C}_6\text{H}_5) = -0.3$ .

Surprisingly, substituent  $\Delta\Delta H_s$  values are not dependent on the overall molecular dipole moment. This is exemplified by the three nitrochlorobenzene isomers which have (within experimental error) the same enthalpy of transfer, but quite different dipole moments. The solvents appear to interact with each functional group individually without interference from ortho substituents, which results in additive values of  $\Delta\Delta H_s$ .

Group enthalpies of transfer will have a variety of applications when enough data are available, including the following. (1) Calculation of  $\Delta\Delta H_s$  values of molecules without resorting to direct calorimetric measurements. Suppose, for example, one wished to calculate  $\Delta\Delta H_s$  (2,4-dinitrochlorobenzene)

$$\begin{aligned} \Delta\Delta H_s^{\text{calcd}}(2,4\text{-dinitrochlorobenzene}) = & \\ & -1.6 \text{ (two nitro groups)} + \\ & -0.1 \text{ (chloro group)} + \\ & -0.3 \text{ (phenyl group)} = \\ & -2.0 \text{ kcal/mol} \end{aligned}$$

The observed value of  $\Delta\Delta H_s$  (2,4-dinitrochlorobenzene) is  $-1.9$  kcal/mol. Values obtained in this manner would be a convenience in transition-state  $\Delta\Delta H$  studies, and would provide an approach to  $\Delta\Delta H_s$  values of unstable molecules and molecules which rapidly solvolyze in the solvents of interest. (2) Studies of the interactions between individual functional groups and various types of solvents. (3) Observation of specific interactions between the functional group and the rest of the molecule which alter electron distribution and affect the additivity of  $\Delta\Delta H_s$  (for example, a strong direct resonance interaction between  $-\text{NH}_2$  and  $-\text{NO}_2$  in *p*-nitroaniline).

We currently are investigating other functional groups using both aromatic and aliphatic models.

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## Additions and Corrections

**The Proton Magnetic Resonance Spectra of Olefins. V. 3-Chloro- and 3-Methoxypropenes** [*J. Amer. Chem. Soc.*, **88**, 2466 (1966)]. By AKSEL A.B. OTHNER-BY,\* S. CASTELLANO, S. J. EBERSOLE, and H. GÜNTHER, Mellon Institute, Pittsburgh, Pennsylvania 15213.

Linda Tomsyck and Professor R. Scott Pyron of Furman University have kindly pointed out to us that the values of  $\Delta H$ ,  $J^g$ , and  $J^t$  given for allyl chloride and allyl methyl ether are incorrect as a result of some computational error. We concur and confirm their findings that the best parameters are as follows ( $J$  in Hz and  $\Delta H$  in cal).  $\text{CH}_2=\text{CHCH}_2\text{Cl}$ :  $J^g$ , 2.4;  $J^t$ , 11.6;  $J^c$ , 5.5;  $\Delta H$ , 958.  $\text{CH}_2=\text{CHCH}_2\text{OCH}_3$ :  $J^g$ , 2.3;  $J^t$ , 12.4;  $J^c$ , 5.7;  $\Delta H$ , -160.

**Oxygen-17 Nuclear Magnetic Resonance Studies of Aqueous Nickel Ion** [*J. Amer. Chem. Soc.*, **94**, 3419 (1972)]. By JAMES W. NEELY and ROBERT E. CONNICK,\* Department of Chemistry, University of California, and the Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California 94720.

The rounded off value of  $\Delta S^\ddagger$  in Table III should be 9 eu. The kinetic parameters obtained in the least-squares fit were 13.88 kcal and 8.7 eu for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , respectively.

**Neopentyl Displacement Reactions without Rearrangements** [*J. Amer. Chem. Soc.*, **94**, 4184 (1972)]. By BETTY