Estimation of the Heats of Formation of Gaseous Carbonium Ions by the Group Contribution Method

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(Received June 12, 1967)

The data of the heats of formation of gaseous carbonium ions often make it possible to estimate thermochemically the rates and the mechanisms of the reactions in which the carbonium ions are considered to be reaction intermediates. Dealkylation reactions of some alkylbenzenes on the cracking catalysts, for example, were successfully correlated with the heats of carbonium ion formation from paraffins.[1] The heats of formation of unstable species such as carbonium ions, however, may not be always on hand when requested. The method to estimate those of unobserved is thus desirable. The method of group increment,[2] an empirical method to calculate the thermodynamic properties as the sum of a set values or group equivalents characteristic of the various groups that make up the molecule, was extended by Franklin[2a] to the calculation of the heats of formation of gaseous carbonium ions and radicals. However, it is not natural to assume that every methyl group may contribute to the stabilization of the cation to the same extent regardless of its position, neglecting the screening effect of the methylene groups between a methyl group and the methyl cation. It may be causative of comparably large errors in the calculation of some primary carbonium ions as shown in Table 1.

Another estimation method of the heats of formation is the group contribution,[3] by which the substitution position effect can be taken into consideration. Lately, the group contribution concept was used also to understand the ^{31}P chemical shifts of tertiary phosphines.[4]

Results and Discussion

The principle of the group contribution method for carbonium ions is mathematically expressed in Eq. (1) with a methyl cation as the base group,

$$\Delta H_f^\circ(R_1^+) = \Delta H_f^\circ(CH_3^+) + \sum n_i X_i \qquad (1)$$

where $\Delta H_f^\circ(R_1^+)$ and $\Delta H_f^\circ(CH_3^+)$ are the heats of formation of R_1^+ and CH_3^+, respectively, X_i is the stabilization contribution of the methyl substitution, and n_i is the number of the equivalent substitutions; five kinds of substitutions, that is, first primary, second primary, third primary, next-adjacent secondary and ordinary secondary,[5] were considered in this calculation for saturated

1) I. Mochida and Y. Yoneda, *J. Catalysis*, **7**, 386, 393 (1967).
2) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).
2a) J. L. Franklin, *J. Chem. Phys.*, **21**, 2029 (1953).
3) O. A. Hougen, K. M. Watson and R. A. Ragatz, "Chemical Process Principles, Part II," John Wiley & Sons, Inc., New York, N. Y. (1959), p. 1004.
4) S. O. Grim, W. McFarlane and E. F. Davidoff, *J. Org. Chem.*, **32**, 781 (1967).
5) "Primary" means the methyl group that substitutes the hydrogen atoms of the base group (CH_3^+). "Secondary" means the substitution of the hydrogen atoms of methyl groups. Next-adjacent secondary substitution is that of the primary methyl groups.

Table 1. Comparison of measured and calculated heats of formation of alkylcarbonium ions
$\Delta H_f°$, kcal/mol at 298°K

	Meas.[a]	Group contribution	Error[b]	Group increment	Error[b]
CH_3^+	262	262[c]	0	—	—
$CH_3CH_2^+$	224	225	0.4	202	10
$CH_3CH_2CH_2^+$	216	215	−0.4	197	−8.7
$CH_3CH^+CH_3$	190	191	0.5	189	−0.5
$CH_3CH_2CH_2CH_2^+$	207	210	1.5	192	−7.8
$CH_3CH_2CH^+CH_3$	181	181	0	184	1.6
$(CH_3)_3C^+$	166	164	−1.2	165	−0.6
$(CH_3)_2CHCH_2^+$	211	206	−2.4	191	−11
$(CH_3)_3CCH_2^+$	194	196	+1.0	184	−5.5
$(CH_3)_2C^+CH_2CH_3$	152	154	1.3	159	3.2
$(CH_3)_2CHCH^+CH_3$	170	172	1.2	177	4.0
$CH_3CH_2CH_2CH_2CH_2CH^+CH_3$	169	166	−1.8	169	0

a) From Refs. 2a and 6.
b) The relative error, (calc.−meas.)/meas.%.
c) The base group.

hydrocarbon cations. The values of X_i in Table 2 were calculated by the method of the least squares from the known heats of formation listed in Table 1. The values for ordinary secondary substitutions are the same for the stable hydrocarbons given in the monograph.[3]

An example of the calculation is cited for a dimethyl ethyl carbonium ion,

$$\Delta H_f°((CH_3)_2C^+CH_2CH_3)$$
$$=262 - 37.0 - 34.0 - 27.1 - 9.7=154.$$

The calculated values are shown in Table 1 and compared with the observed ones.[6] The agreement is well in all cases and better than that by the method of group increment.[2a]

The values of X_i in Table 2 represent clearly the screening effect of the methylene group; the stabilization contribution of the first primary substitution is the largest and those of secondary decrease in this order.

Table 2. Contribution of substitution groups

	kcal/mol
First primary CH_3	-37.0 ± 2.1[a]
Second primary CH_3	-34.0 ± 2.1[a]
Third primary CH_3	-27.1 ± 2.7[a]
Next-adjacent secondary CH_3	-9.7 ± 1.1[a]
Ordiary secondary CH_3[b]	−5.0
Primary F[c]	−19.7
Primary Cl[c]	+15.0

a) The standard error.
b) This value is taken from Ref. 3.
c) Group contribution replacing a CH_3 group.

6) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y. (1957).

Table 3. Comparison of measured and calculated heats of formation of the halogen substituted carbonium ions
$\Delta H_f°$, kcal/mol at 298°K

	Meas.[a]	Calc.[b]	Error, %
CH_2F^+	197	205	4.1
CHF_2^+	147	152	3.4
CF_3^+	109	105	−3.7
CH_2Cl^+	230	240	4.4
$CHCl_2^+$	215	221	2.8
CCl_3^+	215	209	−2.8

a) From Ref. 7.
b) By the group contribution method.

The calculations were also tried for the cations which contain heteroatoms such as a halogen or an oxygen atom. The contributions of halogen groups substituting the methyl groups are shown in Table 2. The calculation for the substitution other than methyl group was made by the usual group contribution method.[3] Examples are cited for a trichlorocarbonium ion and a difluorocarbonium ion,

$$\Delta H_f°(CCl_3^+)=262-37.0-27.1+3\times15.0=209$$
$$\Delta H_f°(CHF_2^+)=262-37.0-34.0+2\times(-19.7)$$
$$=152.$$

The agreement with the observed values[7] is bearable in the cases of fluorine- and chlorine-substituted ions, as shown in Table 3, whereas it is far from satisfaction as for methoxy- and phenyl-substituted ions, in which the first substitution contributes to the stabilization much more than the second one. This trend is generally

7) R. H. Martin, F. W. Lampe and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 1353 (1966).

observed in other cases, but especially distinct for these cases. This fact may be attributable to that such groups stabilize the carbonium ion not only through the inductive effect, but also somewhat through the resonance effect; the simple additivity principle is not valid for these cases perhaps because of the saturation of the latter effect. This explanation is contradictory to the conclusion of Franklin and Lumpkin[8] that no resonance energy results from the interaction of a π bond and a vacant orbital on an adjacent atom. The stabilization effect of halogen atoms, however, cannot be explained by the inductive effect alone, but some resonance structure of C^{-}-X^{+} should be considered. Besides the above two effects, the steric effect should be dealt with quantitatively for the bulky groups in future. The calculation of the method of the least squares was made on an OKITAC 5090 at the Data Processing Center of our University.

8) J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **19**, 1073 (1951).