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Correlation Analysis of the Enthalpies of Vaporization of Isomers with the Hammett–Taft Equation

R. G. Makitra and I. P. Polyuzhin

Institute of Geology and Geochemistry of Fossil Fuels, National Academy of Sciences of Ukraine, Lviv, Ukraine

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Abstract — The enthalpies of vaporization of a series of isomeric compounds containing heteroatoms (ketones, alcohols, halo derivatives) are satisfactorily correlated with the Hammett–Taft equation.

Estimation of thermodynamic characteristics of organic compounds, including the enthalpies of vaporization $\Delta_v H^0$, is the subject of numerous papers. However, these quantities depend not only on the molecular weight and composition of substances but also on their structure. Therefore, the calculation scheme should include appropriate empirical increments reflecting the structural features. The corresponding technique for additive calculations has been developed in detail and gives good results for hydrocarbons [1]; for compounds containing heteroatoms, however, it is less developed and leads to significant deviations from the experimental data [2]. One of the probable causes of the poor correlation is the lack of sufficiently large sets of reliable data on $\Delta_v H^0$ of these compounds, which prevents reliable determination of the corresponding increments. The enthalpies of vaporization at 298.15 K were recently reported by Emel'yanenko and Roganov [3] for a large number of isomeric ketones C_5–C_{15}. Based on the experimental data, Emel'yanenko and Roganov [3] suggested a scheme for additive calculation of these quantities. After the exclusion of some $\Delta_v H^0$ values (e.g., for 2- and 3-octanone), they attained excellent agreement between the experimental and calculated values. In this case, as in other cases, the enthalpies are mainly determined by the number and nature of atoms constituting the molecule, but the structural features are also taken into account with empirical increments. Therefore, it seemed appropriate to find a probable correlation between $\Delta_v H^0$ and certain structural characteristics of a substance. As such characteristics we took the substituent constants σ^* and E_S in the Hammett–Taft equation, which is widely used for describing the influence of the electronic and steric features of substituents on the substance reactivity. Considering ketones of the general formula R^1–CO–R^2, we summarized data on $\Delta_v H^0$ for isomeric compounds with the same number of carbon atoms using formula (1):

$$\Delta_v H^0 = a_0 + a_1(\sigma_1^* + \sigma_2^*) + a_2(E_{S1} + E_{S2}). \quad (1)$$

The experimental enthalpies of vaporization of ketones C_5–C_9 from [3, 4] and the constants σ^* and E_S of the hydrocarbon substituents R^1 and R^2 at the carbonyl group [5] are listed in Table 1. In this table, as in the other tables, the enthalpies of vaporization in most of the groups are arranged in the ascending order. The tabulated values of σ^* are taken from [5–7]; however, for some branched radicals such data are lacking. The lacking values of σ^* can be calculated by the additive schemes from [5, 8]. Calculation of E_S is difficult, and we used interpolation schemes based on the known values for other radicals, using the principle of maximal structural similarity.[1]

For one of the most representative groups of ketones ($N = 6$), hexanones (nos. 4–9), we obtained Eq. (2) with a low but acceptable multiple correlation coefficient: R 0.9155.

$$\Delta_v H^0 = 44.66 + 8.2785(\sigma_1^* + \sigma_2^*) + 1.822(E_{S1} + E_{S2}). \quad (2)$$

As seen, both electronic and steric factors lead to a decrease in $\Delta_v H^0$ compared to linear-chain ketones, as the corresponding constants σ^* and E_S appear with negative signs. The quantities $\Delta_v H^0$ calculated by Eq. (2) and their deviations from the experimental values, $\Delta(\Delta_v H^0)$, are given in Table 1. The deviation is maximal, 1.1 kJ mol^{-1}, for branched 3-methyl-2-pentanone (no. 7), for which the calculation by the procedure from [3] also gives a significant deviation, 0.8 kJ mol^{-1}. The other discrepancies between the calculation and experiment are of the same order as in

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[1] A misprint in Table 2 of [3] should be noted: compound no. 29 should be not 3-hexanone but 2,2,4-trimethyl-3-pentanone, which is confirmed by both the text [3, p. 208] and Table 5 from the same paper.

Table 1. Experimental (data from [3]) and calculated enthalpies of vaporization $\Delta_v H^0$ of isomeric ketones C_5–C_9 at 298.15 K and the corresponding Hammett–Taft parameters

Comp. no.	Ketone, R^1–CO–R^2	σ_1^*	σ_2^*	E_{S1}	E_{S2}	$\Delta_v H^0$, kJ mol^{-1}				
						experiment	calculation[a]		deviation from experiment	
							[3]	$F(\sigma^*, E_S)$	[3]	$F(\sigma^*, E_S)$
	n_C = 5, N = 3[b]									
1	3-Methyl-2-butanone, Me–CO–*i*-Pr	0.000	–0.190	0.00	–0.85	36.9	33.8	37.2	3.1	0.3
2	2-Pentanone, Me–CO–Pr	0.000	–0.115	0.00	–0.56	38.2	37.6	38.5	0.6	0.3
3	3-Pentanone, Et–CO–Et	–0.100	–0.100	–0.27	–0.27	38.6	36.7	37.6	1.9	1.0
	n_C = 6, N = 6									
4	3,3-Dimethyl-2-butanone, Me–CO–*t*-Bu	0.000	–0.300	0.00	–2.14	37.9	35.5	38.3	2.4	0.4
5	2-Methyl-3-pentanone, *i*-Pr–CO–Et	–0.190	–0.100	–0.85	–0.27	39.8	39.3	40.2	0.5	0.4
6	4-Methyl-2-pentanone, Me–CO–*i*-Bu	0.000	–0.125	0.00	–1.13	41.0	41.2	41.6	0.2	0.6
7	3-Methyl-2-pentanone, Me–CO–*sec*-Bu	0.000	–0.210	0.00	–1.53	41.2	40.4	40.1	0.8	1.1
8	3-Hexanone, Et–CO–Pr	–0.100	–0.115	–0.27	–0.56	41.9	41.5	41.4	0.4	0.5
9	2-Hexanone, Me–CO–Bu	0.000	–0.130	0.00	–0.59	42.3	42.4	42.5	0.1	0.2
	n_C = 8, N = 4									
10	*4-Octanone*, Pr–CO–Bu	–0.115	–0.130	–0.56	–0.59	37.1	51.5	49.6	–	1.9
11	*3-Octanone*, Et–CO–Pent	–0.100	–0.135	–0.27	–0.60	44.4	51.5	50.3	–	1.2
12	2-Octanone, Me–CO–Hex	0.000	–0.140	0.00	–0.61	51.9	52.4	51.4	0.5	0.5
13	2,2,4-Trimethyl-3-pentanone, *t*-Bu–CO–*i*-Pr	–0.300	–0.190	–2.14	–0.85	43.3	43.6	44.1	0.3	0.8
	n_C = 9, N = 4									
14	2,2,4,4-Tetramethyl-3-pentanone, *t*-Bu–CO–*t*-Bu	–0.300	–0.300	–2.14	–2.14	45.4	45.2	45.2	0.2	0.2
15	2,6-Dimethyl-4-heptanone, *i*-Bu–CO–*i*-Bu	–0.125	–0.125	–1.13	–1.13	50.9	53.7	51.2	2.8	0.3
16	5-Nonanone, Bu–CO–Bu	–0.130	–0.130	–0.59	–0.59	53.3	56.4	54.0	3.1	0.7
17	2-Nonanone, Me–CO–Hept	0.000	–0.145	0.00	–0.62	56.4	57.3	55.7	0.9	0.7
	n_C = 7, N = 14									
18	2-Heptanone, Me–CO–Pent	0.000	–0.130	0.00	–0.60	47.2	47.5	47.4	0.3	0.2
19	3-Heptanone, Et–CO–Bu	–0.100	–0.130	–0.27	–0.59	–	46.6	46.0	–	0.6
20	4-Heptanone, Pr–CO–Pr	–0.115	–0.115	–0.56	–0.56	46.7	46.6	45.4	0.1	1.3
21	3-Methyl-2-hexanone, Me–CO–*sec*-Pent	0.000	–0.210	0.00	–1.53	–	45.2	44.6	–	0.6
22	4-Methyl-2-hexanone, Me–CO–CH_2Bu-*sec*	0.000	–0.125	0.00	–1.13	–	46.1	46.2	–	0.1
23	5-Methyl-2-hexanone, Me–CO–*i*-Pent	0.000	–0.130	0.00	–0.55	–	45.9	47.5	–	1.6
24	2-Methyl-3-hexanone, *i*-Pr–CO–Pr	–0.190	–0.115	–0.85	–0.56	–	44.1	44.2	–	0.1
25	4-Methyl-3-hexanone, Et–CO–*sec*-Bu	–0.100	–0.210	–0.27	–1.53	–	44.2	43.2	–	1.0

Table 1. (Contd.)

Comp. no.	Ketone, R^1–CO–R^2	σ_1^*	σ_2^*	E_{S1}	E_{S2}	$\Delta_v H^0$, kJ mol^{-1}				
						experiment	calculation[a]		deviation from experiment	
							[3]	$F(\sigma^*, E_S)$	[3]	$F(\sigma^*, E_S)$
26	5-Methyl-3-hexanone, Et–CO–*i*-Bu	–0.100	–0.125	–0.27	–1.13	–	45.0	44.8	–	0.2
27	3,3-Dimethyl-2-pentanone, Me–CO–C(Me)2Et	0.000	–0.300	0.00	–2.14	–	42.1	42.5	–	0.4
28	3,4-Dimethyl-2-pentanone, Me–CO–CH(Me)Pr-*i*	0.000	–0.230	0.00	–1.69	–	44.1	44.1	–	0.0
29	4,4-Dimethyl-2-pentanone, Me–CO–CH_2Bu-*t*	0.000	–0.165	0.00	–1.94	–	43.8	44.0	–	0.2
30	2,4-Dimethyl-3-pentanone, *i*-Pr–CO–*i*-Pr	–0.190	–0.190	–0.85	–0.85	41.5	41.9	42.9	0.4	1.4
31	2,2-Dimethyl-3-pentanone, *t*-Bu–CO–Et	–0.300	–0.100	–2.14	–0.27	42.3	40.9	41.2	1.4	1.1

[a] The calculation equation $\Delta_v H^0 = F(\sigma^*, E_S)$ was (10) for C_5, (2) for C_6, (6) for C_7, (11) for C_8, and (3) for C_9 ketones. (n_C) Number of carbon atoms and (N) number of isomers studied; the same for Table 2.

[3], where the discrepancy is still larger for strongly branched 3,3-dimethyl-2-butanone (methyl *tert*-butyl ketone, no. 4), 2.4 kJ mol^{-1}, whereas calculation by Eq. (2) results in appreciably smaller discrepancy, 0.4 kJ mol^{-1}.

Similar results, a decrease in $\Delta_v H^0$ with increasing branching of the compounds and the correlation with the Hammett–Taft constants, were obtained for nonanones (Table 1). For the four isomers of C_9 ketones (nos. 14–17), we obtained Eq. (3) with R 0.9914.

$$\Delta_v H^0 = 57.62 + 2.3953\,(\sigma_1^* + \sigma_2^*) + 2.574(E_{S1} + E_{S2}). \quad (3)$$

Here, as for hexanones, the largest deviations from the experiment are smaller than in the calculation by the scheme suggested in [3], and are observed with ketone nos. 16 and 17 (0.7 kJ mol^{-1}), whereas in [3] the largest deviations, 2.8 and 3.1 kJ mol^{-1}, are observed with the symmetrical ketones: 2,6-dimethyl-4-heptanone (diisobutyl ketone, no. 15) and 5-nonanone (dibutyl ketone, no. 16), respectively.

The correlations for C_5 (nos. 1–3) and C_8 (nos. 10–13) ketones are statistically unreliable, because for these series the experimental $\Delta_v H^0$ values are available for only three (maximum possible number for pentanones) and four isomers, respectively. In the case of octanones, data for two of them, 3- and 4-octanones (printed italic in Table 1), were not included in the calculations in [3], since these data were convincingly shown in [3] to be erroneous. This opinion is also confirmed by our approach, since for the C_5 [Eq. (4)] and C_8 [Eq. (5)] ketones we observe an irregular and inexplicable change in the signs of the coefficients at σ^* and E_S from positive to negative, as well as a jumpwise change in the absolute values of these coefficients:

$$\Delta_v H^0 = 40.81 - 3.4417(\sigma_1^* + \sigma_2^*) + 5.373(E_{S1} + E_{S2}), \quad (4)$$

$$\Delta_v H^0 = 57.52 + 128.3157(\sigma_1^* + \sigma_2^*) - 15.844(E_{S1} + E_{S2}). \quad (5)$$

Furthermore, in the case of octanones, the inclusion of these erroneous experimental data results in complete loss of the correlation (R 0.5961) between the structural characteristics of the substituents and $\Delta_r H^0$. This fact is in conflict with the positive results obtained for C_6 and C_9 ketones (see above). To find the ways for correction of the erroneous data and possible predictions, we also considered data from [3] on $\Delta_v H^0$ for the largest number of isomers (N = 14) of heptanones (nos. 18–31), although, except for 2-heptanone and 4-heptanone, these are not the experimental data but the quantities obtained by an additive calculation following the scheme from [3]. Indeed, correlation of these data with Eq. (6), with a low but acceptable correlation factor (R 0.9268), as for Eq. (2), confirms the general trend toward a decrease in $\Delta_v H^0$ with an increase in the degree of branching of the isomer:

$$\Delta_v H^0 = 49.72 + 7.7714(\sigma_1^* + \sigma_2^*) + 2.264(E_{S1} + E_{S2}). \quad (6)$$

Table 2. Experimental and calculated enthalpies of vaporization Δ_vH^0 of isomeric alcohols C_4–C_6 and the corresponding Hammett–Taft parameters

Comp. no.	Alcohol, ROH	σ^*	E_S	Δ_vH^0, kJ mol^{-1}		
				experiment	calculation and deviation from experiment	
					$F(\sigma^*, E_S)$	$\lvert\Delta(\Delta_vH^0)\rvert$
		n_C = 4, N = 4				
1	2-Methyl-2-propanol, Me_3COH	–0.300	–2.14	46.69	46.91	0.22
2	2-Butanol, MeEtCHOH	–0.210	–1.53	49.72	49.25	0.47
3	2-Methyl-1-propanol, *i*-$PrCH_2OH$	–0.125	–1.13	50.82	50.98	0.16
4	1-Butanol, $PrCH_2OH$	–0.130	–0.59	52.35	52.42	0.07
		n_C = 5, N = 7				
5	2-Methyl-2-butanol, $EtMe_2COH$	–0.300	–2.14	50.17	50.94	0.77
6	3-Methyl-2-butanol, *i*-PrMeCHOH	–0.230	–1.69	53.03	53.05	0.02
7	3-Pentanol, Et_2CHOH	–0.225	–1.98	54.03	53.16	0.87
8	2-Pentanol, PrMeCHOH	–0.210	–1.53	54.23	53.66	0.57
9	2-Methyl-1-butanol, *sec*-$BuCH_2OH$	–0.125	–1.13	55.18	56.21	1.03
10	3-Methyl-1-butanol, *i*-$BuCH_2OH$	–0.130	–0.55	55.63	56.15	0.52
11	1-Pentanol, $BuCH_2OH$	–0.130	–0.60	57.04	56.14	0.90
		n_C = 6, N = 6				
12	2,3-Dimethyl-2-butanol, *i*-$PrMe_2COH$	–0.328	–3.09	54.02	55.18	1.16
13	2-Methyl-2-pentanol, $PrMe_2COH$	–0.332	–2.46	54.82	54.53	0.29
14	3-Methyl-3-pentanol, $MeEt_2COH$	–0.328	–3.67	56.65	55.62	1.03
15	2-Hexanol, MeBuCHOH	–0.234	–2.89	58.47	58.82	0.35
16	4-Methyl-1-pentanol, *i*-$PentCH_2OH$	–0.136	–0.62	60.47	61.03	0.56
17	1-Hexanol, $PentCH_2OH$	–0.140	–0.61	61.61	60.86	0.75

For the majority of compounds, the results obtained by Eq. (6) and by the calculation according to [3] coincide well.

It should be noted here that the absolute term a_0 in Eqs. (2)–(6), as expected, linearly increases with an increase in the number of carbon atoms, i.e., in the molecular weight. Such linear correlations are observed only for a_1 and a_2, except for C_5 and C_8 ketones for which the reliable experimental data were insufficient. These linear dependences of the coefficients a_i (i = 0, 1, 2) on the total number of carbon atoms in the ketone (n_C), which were obtained on the basis of three reliable points, i.e., for hexanones, heptanones, and nonanones, are described by Eqs. (7)–(9) with good correlation factors r_i:

$$a_0 = 4.267n_C + 19.374,\ r_0\ 0.9979, \tag{7}$$

$$a_1 = -2.065n_C + 21.291,\ r_1\ 0.9675, \tag{8}$$

$$a_2 = 0.237n_C + 0.482,\ r_2\ 0.9579. \tag{9}$$

From Eqs. (7)–(9), we obtained the corresponding coefficients a_i for pentanones and octanones [Eqs. (10) and (11), respectively]:

$$\Delta_vH^0 = 40.71 + 10.9666(\sigma_1^* + \sigma_2^*) + 1.667(E_{S1} + E_{S2}), \tag{10}$$

$$\Delta_vH^0 = 53.51 + 4.7718(\sigma_1^* + \sigma_2^*) + 2.378(E_{S1} + E_{S2}). \tag{11}$$

Using Eqs. (10) and (11), we calculated Δ_vH^0 for pentanones and octanones (Table 1).

To check our approach, we performed similar calculations for alcohols and haloalkanes; the substituent bonded to the heteroatom was considered as varied radical. Therefore, the calculations were performed with a simplified equation

$$\Delta_vH^0 = a_0 + a_1\sigma^* + a_2E_S. \tag{12}$$

The initial data on the enthalpies of vaporization at 298.15 K, taken from [5, 6], the σ^* and E_S values, and the calculation results are listed in Table 2.

For butanols (nos. 1–4), there are only four isomers, and for all of them both Δ_vH^0 and the constants σ^* and E_S are known (Table 2). These data show a good correlation (R 0.9913):

$$\Delta_vH^0 = 55.01 + 7.5179\sigma^* + 2.731E_S, \tag{13}$$

Table 3. Experimental and calculated enthalpies of vaporization $\Delta_v H^0$ (kJ mol^{-1}) of isomeric haloalkanes R–X (R = C_4H_9) at 298.15 K and the corresponding Hammett–Taft parameters

R	Hammett–Taft parameters for R		X = Cl			X = Br			X = I		
	$-\sigma^*$	$-E_S$	experiment	calculation by $F(\sigma^*, E_S)$	deviation from experiment	experiment	calculation by $F(\sigma^*, E_S)$	deviation from experiment	experiment	calculation by $F(\sigma^*, E_S)$	deviation from experiment
2-Methyl-2-propyl, Me_3C	0.300	2.14	28.98	29.28	0.30	31.81	32.07	0.26	35.41	35.76	0.35
2-Butyl, MeEtCH	0.210	1.53	31.53	30.91	0.62	34.41	33.87	0.54	38.46	37.75	0.71
2-Methyl-1-propyl, *i*-$PrCH_2$	0.125	1.13	31.67	31.90	0.23	34.82	35.02	0.20	38.83	39.09	0.26
1-Butyl, $PrCH_2$	0.130	0.59	33.51	33.61	0.10	36.64	36.73	0.09	40.63	40.75	0.12

For pentanols, the quantities $\Delta_v H^0$ are known for seven (nos. 5–11) of the existing eight isomers (Table 2). The correlation is acceptable (R 0.9313, N = 7):

$$\Delta_v H^0 = 60.03 + 29.2397\sigma^* + 0.149E_S. \quad (14)$$

For hexanols (nos. 12–17), the quantities $\Delta_v H^0$ are known for only six isomers (Table 2). The correlation is acceptable (R 0.9619, N = 6):

$$\Delta_v H^0 = 66.04 + 40.3727\sigma^* - 0.770E_S. \quad (15)$$

For alcohols, as for ketones, the coefficients a_i (i = 0, 1, 2) linearly correlate with the total number of carbon atoms in the alcohol (n_C) [Eqs. (16)–(18)], with good correlation coefficients r_i:

$$a_0 = 5.515n_C + 32.785,\ r_0\ 0.9987, \quad (16)$$

$$a_1 = 16.427n_C - 56.427,\ r_1\ 0.9831, \quad (17)$$

$$a_2 = -1.751n_C + 9.456,\ r_2\ 0.9644. \quad (18)$$

In correlations (7)–(9) for ketones and (16)–(18) for alcohols, with increasing molecular weight, a_0 tends to increase, whereas a_1 and a_2 vary in opposite directions: for ketones, a_1 decreases and a_2 increases, and for alcohols, vice versa, a_1 increases and a_2 decreases.

For haloalkanes, only for C_4 derivatives available data on $\Delta_v H^0$ are sufficient for calculating a_i (Table 3). The two-parameter correlations (19)–(21) for C_4H_9Cl, C_4H_9Br, and C_4H_9I, respectively, are good:

$$\Delta_v H^0 = 35.05 - 3.2226\sigma^* + 3.147E_S,\ R\ 0.9739, \quad (19)$$

$$\Delta_v H^0 = 38.41 - 1.3957\sigma^* + 3.157E_S,\ R\ 0.9829, \quad (20)$$

$$\Delta_v H^0 = 42.73 + 1.2695\sigma^* + 3.080E_S,\ R\ 0.9746. \quad (21)$$

Here, the following trends should be noted. First, a_0 regularly increases with increasing molecular weight. Second, the coefficient at σ^* changes sign (i.e., for strongly electronegative Cl and Br, electron-donating substituents increase $\Delta_v H^0$, whereas for I the trend is opposite). Third, the steric factor with all the three halogens exerts approximately equal effect.

Thus, the correlation between the enthalpies of vaporization of isomeric organic compounds containing a heteroatom and the Hammett–Taft constants of the corresponding hydrocarbon substituents is acceptable, which allows estimation of the unknown values of $\Delta_v H^0$.

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