

Quantitative Generalization of Solvent Effect on Radical Halogenation of Hydrocarbons

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Abstract—The dependences of the isomer ratio in photochemical chlorination of 2,3-dimethylbutane and of the selectivity in photochemical bromination of a mixture of cyclopropylbenzene and toluene may be described by linear multiparameter equations. In the first case, the determining factors are the nonspecific solvation power and molar volume of the solvent, and in the second, the molar volume and cohesion energy density.

Effects of the medium on homolytic reactions have received much less attention, as compared to heterolytic reactions. The reasons are relatively narrow range of variation of the rates of homolytic reactions, depending on the solvent properties, and some experimental difficulties originating from the ability of highly active radical species to react with a number of solvents. The more so, quantitative studies on the relations between the rate constants of radical processes and physical parameters of the medium are strongly limited. In fact, only decomposition of peroxy compounds [1, 2] and azo compounds [3] and some oxidation reactions [4] were treated in terms of the known Koppel'–Pal'm multiparameter equation [5] or its modifications taking into consideration possible cage effect via introduction of the Hildebrand solubility parameter (which is proportional to the cohesion energy of the medium). As a rule, the obtained correlations fairly satisfactorily described the available experimental data.

Insofar as homolytic reactions are very important in organic chemistry, it seems reasonable to extend the above approach to other radical processes, primarily halogenation reactions. Russel [6] reported on the selectivity of photochemical chlorination of 2,3-dimethylbutane in various solvents, which was represented as the ratio (Q) of the yields of tertiary 2-chloro-2,3-dimethylbutane and primary halogen derivative, 1-chloro-2,3-dimethylbutane. In fact, this ratio is determined by the relative rates of the corresponding processes. We used the results obtained in [6] as

experimental data set. From the statistical viewpoint, the ratio Q should be 1:6; however, due to higher reactivity of hydrogen at the tertiary carbon atom, the experimental Q value ranges from ~4:1 in aliphatic solvents to (20–30):1 in aromatic media. Russel [6] interpreted these data in terms of intermediate formation of a charge-transfer complex (π complex) between chlorine atom and aromatic ring; the reactivity of such species is lower than that of free chlorine atom, and the selectivity of the process increases.

As shown in [6], variation of the substrate concentration may appreciably affect the selectivity Q . Insofar as 2,3-dimethylbutane was taken in a considerable excess with respect to chlorine, almost no dichloro derivatives were obtained. On the other hand, some solvents were found to be capable of reacting with chlorine. Obviously, partial consumption of chlorine in side reactions should also affect the apparent Q value, thus reducing the reliability of the given data. It should also be noted that the selectivity Q also depends on the temperature: it decreases as the temperature rises.

A linear relation was found between the selectivity logarithm ($\log Q$) and basicity of aromatic solvents; the latter parameter was defined as logarithm of the equilibrium constant of complex formation between the hydrocarbon and gaseous hydrogen chloride at -78.5°C [7]; also, a linear relation was observed between $\log Q$ and Hammett constants σ , which was explained by increase in stability of the π complex with increase in electron density in the ring. However,

Table 1. Experimental (Q_{exp}) [6] and calculated [by Eq. (3)] selectivities (Q_{calc}) of photochemical chlorination of 2,3-dimethylbutane and the corresponding differences (ΔQ)

No.	Solvent	Q_{exp}	Q_{calc}	ΔQ
1	Nitromethane	3.30	2.5216	-0.7784
2	Methyl acetate	4.30	0.6912	-3.6088
3	Butyric acid	4.10	6.2539	2.1539
4	Cyclohexene	3.60	9.5359	5.9359
5	Propionitrile	4.00	1.7652	-2.2348
6	Butyronitrile	4.00	5.4232	1.4232
7	<i>tert</i> -Butyl alcohol	4.80	6.1643	1.3643
8	1,4-Dioxane	5.60	5.5424	-0.0576
9	Dibutyl ether	7.20	11.4424	4.2424
10	Dimethylformamide	9.10	10.1980	1.0980
11	Fluorobenzene	16.20	13.6861	-2.5139
12	Benzene	14.60	14.2072	-0.3928
13	Toluene	15.40	15.8051	0.4051
14	<i>o</i> -Xylene	15.00	18.2436	3.2436
15	Ethylbenzene	16.30	16.8521	0.5521
16	Anisol	18.40	20.2103	1.8103
17	<i>p</i> -Xylene	18.60	16.9757	-1.6243
18	Cumene	20.30	18.1112	-2.1888
19	<i>m</i> -Xylene	22.40	22.6902	0.2902
20	<i>tert</i> -Butylbenzene	24.00	19.5608	-4.4392
21	Mesitylene	25.00	18.6547	-6.3453
22	Iodobenzene	31.00	31.1138	0.1138
23	1-Chloronaphthalene	33.00	34.5510	1.5510
24	Carbon tetrachloride ^a	3.50	11.3189	7.8189
25	Trichloroethylene ^a	3.60	13.4168	9.8168
26	Chlorobenzene ^a	10.20	20.8410	10.6410
27	Methyl benzoate ^a	10.20	22.7262	12.5262
28	Nitrobenzene ^a	4.90	25.5753	20.6753

^a The data were not included in the calculation by Eq. (3).

the above correlations were obtained only for 10–15 aromatic solvents, including mainly alkyl- and halo-benzenes, while aliphatic solvents were not covered. Other attempts to obtain a general dependence for the whole set of data given in [6] were unsuccessful. Pytela [8] tried to generalize these results using multi-parameter equations; it was found that the selectivity is determined mainly by the polarizability parameter, but the four-parameter Koppel–Pal'm equation for 15 solvents was characterized by very low multiple correlation coefficient, $R = 0.620$. Therefore, we made an attempt to analyze the data of [6] using Eq. (1) which,

apart from solvation parameters, takes into consideration the squared Hildebrand solubility parameter δ^2 and molar volume V_m . The latter parameters reflect structural specificity of the medium.

$$Q = a_0 + a_1(n^2 - 1)/(n^2 + 2) + a_2(\epsilon - 1)/(2\epsilon + 1) + a_3B + a_4E_T + a_5\delta^2 + a_6V_m \quad (1)$$

Here, n is the refractive index, ϵ is the dielectric constant, B is the basicity according to Pal'm, and E_T is the Reichardt electrophilicity parameter. The first two parameters determine the polarizability and polarity of a solvent; i.e., they are responsible for nonspecific solvation. The parameters B and E_T characterize acid–base properties of a solvent, i.e., its ability for specific solvation. The solvent parameters were taken from [9, 10], and the calculations were performed according to the recommendations given in [11].

Table 1 contains values of Q [6] obtained at 55°C and a substrate concentration of 4 M in 28 solvents for which all required parameters are available. The multiple correlation coefficient calculated for the whole data set is low, $R = 0.827$. In keeping with [11], the most deviating Q values were successively excluded until $R > 0.95$. As a result, the data for five solvents were excluded: nitrobenzene ($R = 0.880$), methyl benzoate ($R = 0.908$), chlorobenzene ($R = 0.927$), trichloroethylene ($R = 0.945$), and carbon tetrachloride ($R = 0.961$). We thus obtained six-parameter Eq. (2) which describes solvent effects on the reaction selectivity with a sufficient accuracy:

$$Q = -49.21 + (182.75 \pm 22.91)f(n^2) + (21.12 \pm 9.91)f(\epsilon) + (18.58 \pm 8.88) \times 10^{-3}B - (0.18 \pm 0.21)E_T + (8.96 \pm 11.70) \times 10^{-3}\delta^2 + (0.10 \pm 0.03)V_m; \\ R = 0.962, s = 2.53. \quad (2)$$

The pair correlation coefficients r with particular parameters were 0.887, 0.294, 0.378, 0.430, 0.256, and 0.739, respectively. These values indicate that the determining factors are the polarizability and molar volume and that specific solvation and cohesion energy density are in fact insignificant, which is consistent with large standard deviations of the corresponding regression coefficients. Exclusion of the specific solvation and cohesion terms leads to insignificant reduction in R for the resulting equations containing a smaller number of terms: exclusion of δ^2 gives $R = 0.961$, exclusion of E_T leads to $R = 0.960$, and exclusion of B gives $R = 0.953$. Thus the selectivity Q in photochemical chlorination of 2,3-dimethyl-

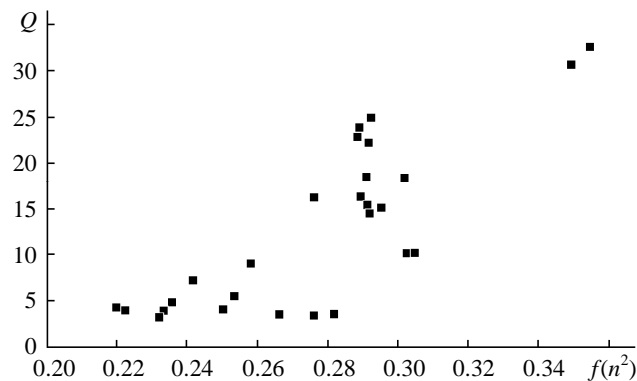
butane at 55°C is described with an acceptable accuracy by three-parameter Eq. (3):

$$Q = -61.00 + (216.03 \pm 19.07)f(n^2) + (17.80 \pm 7.88)f(\epsilon) + (0.088 \pm 0.024)B_m; \\ R = 0.953, s = 6.35. \quad (3)$$

The principal term in Eq. (3) is $f(n^2)$; exclusion of this term destroys the correlation ($R = 0.610$), while exclusion of any other term impairs the correlation to a lesser extent: after exclusion of $f(\epsilon)$ or V_m , R becomes equal to 0.942 or 0.923, respectively.

The plot of Q versus $f(n^2)$ (see figure) shows a fairly uncertain pattern. We can clearly distinguish two groups of solvents. The first of these includes aliphatic solvents and nitrobenzene; despite a considerably wide range of variation in their polarizability, the selectivity changes within a narrow range, $Q \approx 3$ –5. The second group includes aromatic solvents (primarily hydrocarbons) which are characterized by almost similar polarizabilities, $f(n^2) \approx 0.290$ – 0.295 , whereas the selectivity changes strongly, from $Q \approx 10$ for methyl benzoate to $Q \approx 25$ for mesitylene. The Q values for 1-chloronaphthalene and iodobenzene (whose polarizability is even greater) stay apart. On the whole, some parallelism is observed between Q and $f(n^2)$, in keeping with Eqs. (2) and (3); nevertheless, a number of solvents, especially halogen-containing ones, deviate from the presumed linear relation, indicating a complex multifactor character of the process. No relation between Q and the Koppel–Pal'm basicity parameter B could be revealed [5], which is consistent with insignificant contribution of that factor to correlations (2) and (3). However, this fact contradicts the linear relation found in [6] between $\log Q$ and the basicity of aromatic solvents. A probable reason is the use of different basicity scales: according to [6], the basicity was determined by the ability of a solvent to form a complex with gaseous hydrogen chloride, while Eqs. (1)–(3) imply the basicity estimated [5] from the shift of the O–H absorption band in the IR spectrum of phenol in the presence of the corresponding solvent.

Attention should also be given to insignificance of the δ^2 parameter; this means that in our case, unlike other radical reactions, the selectivity of the process does not depend on the cage effect, presumably owing to high reactivity of Cl^\cdot radical. Increase in polarity and molar volume of the solvent changes the selectivity toward formation of tertiary halogen derivatives, but the apparent Q value is determined by overall



Correlation between the selectivity Q of photochemical chlorination of 2,3-dimethylbutane at positions 1 and 3 and the parameter $f(n^2) = (n^2 - 1)/(n^2 + 2)$.

contribution of all significant factors, primarily by the ability for nonspecific solvation.

Table 1 contains Q values calculated by Eq. (3) and their deviations from the experimental values. The deviations do not exceed 25%, except for the data for five excluded solvents (see above), cyclohexene (which is likely to take up chlorine at the double bond), and dibutyl ether.

It should be noted that a correlation with $\log Q$ is also possible; however, the results are appreciably worse. Although the multiple correlation coefficient is almost the same as in the correlation with Q ($R = 0.821$ for all 28 solvents), an acceptable value of R (≥ 0.95) is reached only after exclusion of six solvents, and this value is appreciably lower ($R = 0.952$) than in the correlation with Q ($R = 0.962$). It is more important that all parameters of the resulting equation are significant: exclusion of the δ^2 term reduces R to 0.946, whereas exclusion of any other term destroys the correlation (R decreases to 0.74–0.91).

It was interesting to compare the efficiency of the proposed approach as applied to radical chlorination and bromination. Tanko *et al.* [12] studied photochemical bromination at 25°C of mixtures of cyclopropylbenzene with toluene or *p*-chlorotoluene, which involved cleavage of the cyclopropyl ring in the first case (C–C reactivity) or formation of benzyl bromide in the second case (C–H reactivity). The data obtained in [12] strongly differed from those given in [6]: the reactions were performed mainly in halogenated hydrocarbons in which specific interactions cannot occur and hence π complexes cannot be formed. The results were treated in terms of the internal pressure concept (Table 2). No distinct relation were found between the selectivity $Q = k_C/k_H$, on the one hand, and

Table 2. Experimental [12] and calculated [by Eq. (5)] selectivities Q of photochemical bromination of a mixture of cyclopropylbenzene and toluene

No.	Solvent	Q_{exp}	Q_{calc}	ΔQ
1	Pentane	0.570	0.5948	0.0248
2	1,2-Dibromomethane	4.300	5.3066	1.0066
3	Methylene chloride	3.900	2.9950	-0.9050
4	Chloroform	3.300	2.4179	-0.8821
5	Carbon tetrachloride	1.800	2.2276	0.4276
6	1,2-Dichloroethane	4.200	3.4733	-0.7267
7	Benzene	2.900	2.8121	-0.0879
8	Chlorobenzene	3.600	4.3440	0.7440
9	Bromobenzene	4.000	5.6131	1.6131
10	1-Bromonaphthalene	9.700	8.3180	-1.3820
11	Carbon disulfide	2.900	3.0675	0.1675

viscosity and Kirkwood function of solvents, on the other. Although in both cases some parallelism was observed, the correlation coefficients were poor, 0.79 (for 17 solvents) and 0.8 (for 14 solvents). Much better correlation was found between Q and δ^2 : $r \approx 0.95$ (15 solvents). Even stronger relation was observed with the internal pressure parameter; however, the latter is available only for nine of the examined solvents.

Insofar as parameters necessary for generalization of the data given in [12] according to Eq. (1) were unknown for some solvents (primarily, for fluorochlorohydrocarbons), only 11 solvents were involved (Table 2). We obtained six-parameter Eq. (4) which was characterized by a high correlation coefficient

Table 3. Experimental [12] and calculated [by Eq. (8)] selectivities Q of photochemical bromination of a mixture of cyclopropylbenzene and *p*-chlorotoluene

No.	Solvent	Q_{exp}	Q_{calc}	ΔQ
1	Pentane	–	–	–
2	1,2-Dibromomethane	7.200	7.5913	0.3913
3	Methylene chloride	7.700	6.7131	-0.9869
4	Chloroform	5.900	5.7276	-0.1724
5	Carbon tetrachloride	3.000	2.9129	-0.0871
6	1,2-Dichloroethane	7.600	7.6667	0.0667
7	Benzene	4.300	4.0872	-0.2128
8	Chlorobenzene	5.200	6.6401	1.4401
9	Bromobenzene	6.600	7.6082	1.0082
10	1-Bromonaphthalene	11.000	9.8510	-1.1490
11	Carbon disulfide	3.600	3.4692	-0.1308

($R = 0.978$). However, in keeping with the data of [12], the selectivity is determined mainly by the cohesion energy density; the pair correlation coefficient r for Q and δ^2 is equal to 0.728. Unlike the chlorination process, in this case the polarizability factor turned out to be insignificant; presumably, this is the result of specific choice of the solvents: nine of the eleven solvents are halogen-substituted compounds characterized by enhanced polarizability. Exclusion of the polarizability term only slightly impairs the coefficient R [see Eq. (4)]:

$$Q = -38.62 - (34.28 \pm 9.61)f(\epsilon) - (38.11 \pm 9.24) \times 10^{-3} B + (0.92 \pm 0.22)E_T + (36.70 \pm 9.24) \times 10^{-3} \delta^2 + (7.64 \pm 0.81) \times 10^{-2} V_m; \\ R = 0.976, s = 0.491. \quad (4)$$

Subsequent exclusion of any term from Eq. (4) reduces R to an undesirably low value (<0.95). It should be emphasized that the basicity term in Eq. (4) has a negative sign. It is known that halogenated hydrocarbons are capable of forming π complexes with aromatic hydrocarbons [13, 14], the latter acting as electron donors. Increase in basicity of a halogenated hydrocarbon implies weakening of its π -electron-acceptor power, i.e., the complex formation constant should decrease. According to Eq. (3), the selectivity Q , i.e., the ratio $k_{\text{cyclopropylbenzene}}/k_{\text{toluene}}$ or the relative rate of bromination of cyclopropylbenzene as compared to toluene, decreases as the basicity of the acceptor rises. This suggests that bromine radicals preferentially react with solvated substrate (π complex with the halogenated solvent) rather than with the free hydrocarbon. However, by analogy with the chlorination process, the basicity and electrophilicity factors responsible for specific solvation exert a relatively weak effect on the selectivity, and the relation between Q and solvent properties may be described by two-parameter Eq. (5), though with a poor accuracy:

$$Q = -11.28 + (26.15 \pm 4.16) \times 10^{-3} \delta^2 + (5.57 \pm 1.28) \times 10^{-2} V_m; \\ R = 0.915, s = 0.918. \quad (5)$$

We can conclude that the selectivity of photochemical bromination is determined not only by cohesion energy density and structural parameters of solvents but also by their solvation ability. Presumably, the reason is the larger size of bromine atom as compared to chlorine. Table 2 contains the values of Q calculated by two-parameter Eq. (5) and their deviations from the experimental data; as might be

expected, these deviations are considerably larger than those found for the chlorination process.

We also analyzed in a similar way the data given in [12] on the selectivity of bromination of a cyclopropylbenzene-*p*-chlorotoluene mixture (Table 3). In this case, the corresponding Q values are greater by a factor of 1.5 to 2, i.e., the rate of bromination of the methyl group in *p*-chlorotoluene is lower than the rate of bromination of the methyl group in toluene. Obviously, electron-acceptor character of chlorine in *p*-chlorotoluene reduces its electron-donor power.

$$Q = -29.85 - (37.16 \pm 6.46)f(n^2) - (28.82 \pm 4.46)f(\epsilon) - (32.48 \pm 4.27) \times 10^{-3}B + (0.78 \pm 0.12)E_T + (57.18 \pm 4.81) \times 10^{-3}\delta^2 + (7.10 \pm 0.39) \times 10^{-2}V_m; \\ R = 0.996, s = 0.226. \quad (6)$$

The signs at particular terms in Eq. (6) are the same as in the preceding case, which indicates similar mechanisms of halogenation of toluene and *p*-chlorotoluene. Likewise, the contribution of the polarizability factor $f(n^2)$ is insignificant. As above, the selectivity is determined mainly by cohesion and molar volume of the medium.

$$Q = -21.22 + (0.41 \pm 0.09)E_T + (19.50 \pm 4.26) \times 10^{-3}\delta^2 + (0.048 \pm 0.011) \times 10^{-2}V_m; \\ R = 0.959, s = 0.753. \quad (7)$$

However, unlike photochemical chlorination of 2,3-dimethylbutane, the data for photochemical bromination of both aromatic hydrocarbons are even better described by equations including $\log Q$ rather than Q as selectivity parameter. The data in Table 2 for bromination of a cyclopropylbenzene-toluene mixture give rise to a six-parameter correlation with $R = 0.985$, the cohesion energy density being the determining factor; the pair correlation coefficient r between $\log Q$ and δ^2 is equal to 0.920. An acceptable quality is achieved through three-parameter Eq. (8):

$$\log Q = -1.84 + (0.021 \pm 0.010)E_T + (3.44 \pm 0.48) \times 10^{-3}\delta^2 + (2.97 \pm 1.22) \times 10^{-3}V_m; \\ R = 0.959, s = 0.086. \quad (8)$$

Even better correlation is obtained from the data given in Table 3. The correlation coefficient for the corresponding six-parameter equation is equal to 0.993, the pair correlation coefficient for δ^2 being 0.879. The same three factors as in Eq. (8) are significant [see Eq. (9)]:

$$\log Q = -1.62 + (0.037 \pm 0.006)E_T + (2.06 \pm 0.28) \times 10^{-3}\delta^2 + (2.20 \pm 0.71) \times 10^{-3}V_m; \\ R = 0.979, s = 0.050. \quad (9)$$

It should be noted that exclusion of the V_m term also leads to an acceptable correlation with $R = 0.959$ [Eq. (10)].

$$\log Q = -1.30 + (0.034 \pm 0.008)E_T + (2.04 \pm 0.40) \times 10^{-3}\delta^2; \\ R = 0.959, s = 0.070. \quad (10)$$

Thus, the use of multiparameter equations like (1) makes it possible to generalize experimental data on radical halogenation of hydrocarbons and draw some conclusions concerning the mechanism of these reactions.

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