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Development of a group contribution method to predict the aqueous-phase reactivities of hydrated electrons with organic compounds

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ABSTRACT

Hydrated electrons produced in aqueous-phase advanced reduction processes (ARPs) effectively destroy oxidized forms of environmentally relevant organic contaminants, including alkyl halides. Although the rate constants of hydrated electrons with various organic compounds have been experimentally measured and compiled in the literature, no mechanistic prediction tools have been developed. Given that numerous organic compounds are used in commercial production, a prediction tool for the fate of organic compounds in the aqueous-phase ARPs will be useful. This study focused on developing a group contribution method for hydrated electrons (GCMe) to predict the second-order rate constants with aliphatic and aromatic compounds. The GCMe includes 262 organic compounds undergoing four major reaction mechanisms. The GCMe fragments the structure of a given functional group of an organic compound based on the base structure that represent the major reaction with hydrated electrons and the neighboring functional group(s) that impact the main reaction. A total of 37 group rate constants and 69 group contribution factors were calibrated with 189 experimentally determined rate constants of single functional group compounds. Then, the parameters were validated with 73 multiple functional group compounds. Overall, the accuracy of GCMe in predicting the rate constants is within a difference of a factor of two from the experimental values. This predictive tool requiring only structural information of compounds can be used to screen hundreds of compounds in the prior assessment for experimental investigation in ARPs.

1. Introduction

Advanced reduction processes (ARPs) that generate reactive radicals (e.g., superoxide anion radicals [1]) and electrons in homogeneous solution [2] and heterogeneous electrochemical [3,4] or catalytic [5] processes are effective in degrading the oxidized forms of organic and inorganic contaminants [6,7]. In particular, homogeneous, electrochemical, or a combination of both ARPs has been successfully applied to degrade conventional and emerging groups of organic pollutants, such as alkyl halides [3,4], and per- and polyfluorinated alkyl substances (PFASs) [8].

While the second-order rate constants, k_{exp}, of the hydrated electrons, e_{aq}^-, for various conventional organic compounds and a limited number of fluorinated compounds were measured and compiled in the NIST dataset [9], few studies have established prediction tools for the k_{exp} values. Quantitative structure–activity relationships (QSARs) have been developed based on molecular descriptors [10,11]; however, such QSARs are highly empirical and molecular descriptors are not readily available. Therefore, if a large number of datasets are available in the literature, the group contribution method (GCM) is an attractive and promising approach for developing a computational tool to estimate the rate constant [12–16]. GCM fragments the structure of a given compound based on the reactivities with $e_{aq}^-$and impacts of neighboring functional groups. The benefit of GCM is that it requires only structural information that may hold the physical chemical properties of functional groups to determine correlations with the k_{exp} values.

Three major reaction mechanisms of e_{aq}^- with aliphatic organic compounds include (1) association with the π bond of a double bond [17]; (2) concerted dissociative cleavage of a carbon halogen (C–X, where X = F, Cl, Br, or I) bond of haloalkanes [18] or a carbon–nitrogen (C–N) bond [17]; and (3) stepwise cleavage of a C–X bond of haloalkanes and haloalkenes, a sulfur–sulfur (S–S) bond, or a carbon–sulfur (C–S) bond of sulfides or disulfides [17]. In our previous study, the calculation of aqueous-phase one-electron reduction potentials of all possible reactive sites of 250 aliphatic organic compounds revealed the possible attacking site by e_{aq}^- in the structure of a given molecule [19]. Furthermore, the functional groups present in the molecular structure were found to significantly impact the reactivity of e_{aq}^-. By taking advantage of

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GCM's nature, including the only use of structural information over previously developed QSARs, a mechanistic tool is needed to predict the k_{exp} values for a wide variety of organic compounds including aromatic compounds as our previous study did not investigate these compounds.

In this study, we develop a GCM for e_{aq}^- (GCMe) by fragmenting structures of a wide variety of organic compounds based on the mechanistic understanding of e_{aq}^- reactivities with those of organic compounds. We calibrate the parameters representing the reactivities with base structure and the impact from the neighboring functional group for single functional group compounds with the k_{exp} values. Then, the parameters are validated by comparing the estimated k values for multiple functional group compounds. An MS Excel spreadsheet that can be used to calculate the k values of hydrated electrons as supporting material is also provided. Such computational tools with inputs of only structural information will be useful to screen hundreds of organic compounds to prioritize the important group of compounds for degradation in an aqueous phase ARP. The tool can also be used to study the fate of a targeted compound degradation induced by e_{aq}^- for the prior design and assessment of treatment feasibility.

2. Methods

2.1. Critical data evaluation

Experimentally measured k_{exp} with e_{aq}^- for 262 structurally diverse aliphatic and aromatic compounds were obtained from the NIST database [20]. All k_{exp} values were critically evaluated based on the experimental conditions used in the original study, as described below. Deprotonated compounds measured at pH less than their *p*Ka values and vice versa were removed from the calibration due to experimental inaccuracies. All k_{exp} values were corrected to an ionic strength of 0 M to ensure uniform experimental conditions [21]. When multiple k_{exp} values were reported for a given compound, the statistical average of k_{exp} values was adopted. The k_{exp} for the chemical reaction was calculated for each compound to eliminate the impact of diffusion, as described in our previous study [19].

2.2. Group contribution method for hydrated electrons

The basis of GCMe is that the overall rate constant of a compound reacting with e_{aq}^- is the sum of partial rate constants that can be estimated based on the Arrhenius kinetic theory [22,23]. The Arrhenius activation energy, E_a, for each elementary reaction is the sum of the base E_a, which is attributed to e_{aq}^- interacting with the reactive site and the E_a of the neighboring functional group(s) that contributes to the reactivity at the reactive site. Four major mechanisms of e_{aq}^- with aliphatic compounds were included in the GCMe, which were (1) association with a carbon–oxygen double bond (C=O) [17], (2) concerted or stepwise cleavage of a carbon–halogen bond (C–X, where X = F, Cl, Br, and I) [18], (3) association with a carbon–carbon double bond (C=C) [17], and (4) interaction with sulfur (*S*)- or nitrogen (N)-atom-containing functional groups, including association and cleavage of a carbon–sulfur (C–S), a sulfur-sulfur (S-S), or a carbon–nitrogen (C–N) bond [17]. As for aromatic compounds, aforementioned four major reaction mechanisms occur on the side chain of a benzene ring (see the details below). The partial rate constant for each reaction mechanism was denoted as $k_{aso\text{-}CO}$, k_{clv}, $k_{aso\text{-}CC}$, $k_{int\text{-}SN}$, and k_{arm} for association with C=O, cleavage of a C-X bond, association with C=C, interaction with S or N, and interaction with the side chain of aromatic compounds, respectively. The overall reaction rate of an organic compound, $k_{overall}$, can be written in an additive manner based on Benson's additivity of thermodynamics [24], as shown in Eq. (1). If the reaction mechanism does not occur due to the lack of structure in a given molecule, the corresponding partial rate constant would be zero.

$$k_{overall} = k_{aso-CO} + k_{clv} + k_{aso-CC} + k_{int-SN} + k_{arm} \quad (1)$$

The methods for determining each partial rate constant are described in the following sections.

2.2.1. Associative mechanism

The high electron density in the orbitals above and below the π-bond of C=O, C=C, and the functional group(s) as well as the polarity caused by the electronegative oxygen create an electron deficiency in the carbon atoms, which is the association site of e_{aq}^-. Organic compounds containing –CO–NH_2– or –CO–OR– (where R is the functional group) showed lower reactivity with e_{aq}^- due to the mesomeric effect [25], creating new electrophilic centers. Nevertheless, to avoid the increase in the number of calibration parameters, we accounted one unified association mechanism for C=O among carboxylates, carboxylic acids, ester and amides. The neighboring functional group(s) increases or decreases the E_a at the reactive site due to electron-withdrawing or -donating ability. Consequently, k_{aso} can be written as follows:

$$k_{aso-(structure)} = A_{(structure)} e^{-\left[E^0_{a,(structure)} + E^{R_i}_{a,aso-(structure)}\right] / RT} \quad (2)$$

where the structure is the base structure of CO, CC, or SN, A is the Arrhenius frequency factor that is constant under the same reaction mechanism in each base structure, R_i is the functional group of *i*, R is the gas constant and T is the absolute temperature. For example, for the base structure of CO, using the rate constant of k_{CO} and the group contribution factor, X_{Ri}, of R_i functional group, the partial rate constant for association with C=O can be written as

$$k_{aso-CO} = k_{CO} X_{Ri} \quad (3)$$

where

$$k_{CO} = A_{CO} e^{-E^0_{a,CO}/RT} \quad (4)$$

$$X_{R_i} = e^{-\left(E^{R_i}_{a,aso-CO}/RT\right)} \quad (5)$$

2.2.2. Concerted or stepwise cleavage of a C–X bond

When a C–X bond is present in a molecular structure, the bond is split by e_{aq}^- through the concerted or stepwise mechanism [3,4]. The neighboring functional group(s) of the C–X bond impacts the cleavage by donating or withdrawing the electrons to the targeted C–X bond. Consequently, the rate constant for the cleavage of a C—Cl bond (i.e., X=Cl) with functional group R_i in the neighboring position can be written as follows:

$$k_{clv} = k_{C-Cl} Y_{R_i} \quad (6)$$

where

$$k_{C-Cl} = A_{C-Cl}\, e^{-E^0_{a,C-Cl}/RT} \quad (7)$$

$$Y_{R_i} = e^{-\left(E^{R_i}_{a,C-Cl}/RT\right)} \quad (8)$$

2.2.3. Interaction with S- or N-atom-containing compounds through the association or cleavage of a C–S bond or a C–N bond

Compounds containing S- or N-atom undergo concerted dissociative cleavage or stepwise cleavage mechanisms [17]. The C–N bond of an alkyl ammonium functional group and the C–S bond of a thiol functional group undergo concerted cleavage due to a lack of antibonding σ* orbitals. The S–S or C–S bond initially elongates, resulting in a decrease of energy of the antibonding σ* orbital that localizes over the elongated S–S or C–S bond [26]. This antibonding orbital temporarily holds the e_{aq}^- for more than one vibration, creating a three-electron bonded radical anion intermediate, $CSSC^{\bullet-}$ or C-centered radical [27,28]. From these mechanisms, the group rate constants were defined based on the structure of their reactive sites (e.g., –C≡N, $-NH_3^+$, $-NO_2$, NO, >C=N,

–SO_3^-, -S=O, –S–, –S–S–, –SH, –S^-, and –C=S). The impacts of neighboring functional groups on the reactive site were not considered in the calibration for two reasons: (1) limited number of data available for calibration and (2) insignificant impact observed by neighboring functional groups on the k_{exp} values with the exception of a group of ammonium compounds. Consequently, the rate constant for the interaction with S- or N-atom-containing compounds k_{SN} can be written as follows:

$$k_{int-SN} = A_{SN} e^{-E_{a,SN}/RT} \tag{9}$$

where the A_{SN} and $E_{a,SN}$ is the Arrhenius A and E_a for the interaction with S- or N-atom-containing functional group. For example, for a -S=O bond, the partial rate constant of k_{SO} can be written as below,

$$k_{int-SN} = k_{SO} \tag{10}$$

where

$$k_{SO} = A_{SO} e^{-E^0_{a,SO}/RT} \tag{11}$$

2.2.4. Aromatic compounds

As the reactivity of e^-_{aq} with benzene is low (i.e., $k_{exp} = 7.2 \times 10^6$) [29–32], the presence of a functional group significantly impacts the reactivity (e.g., $k_{exp} = 10^9$–10^{10} M^{-1} s^{-1} for bromobenzene or nitrobenzene and $k_{exp} = 2.28 \times 10^7$ M^{-1} s^{-1} for C_6H_5OH [33–35]), indicating the negligible reactivity with the aromatic ring. Consequently, the reaction of e^-_{aq} with the benzene ring was not included. This treatment can also be justified according to the experimentally observed reaction mechanisms with halo- and nitrobenzene (i.e., nucleophilic substitution to form a negatively charged carbanion) [36–39]. Moreover, the localized reactions of e^-_{aq} with aromatic compounds support the major reaction occurring on the functional groups. Thus, only group rate constants on the alkyl side chain on the benzene ring were factored. For the di- and trifunctional groups on the benzene ring, the formation of a localized electron-deficient center is impacted by the functional groups and their locations [17]. Thus, isomers (i.e., the position of the functional group on the ring relative to a targeted bond) were accounted for using different group contribution factors. 27 group contribution factors were determined for isomers containing the nine branched functional groups: – CH_3, –OH, –O^-, –COO^-, –F, –Cl, –Br, –I, and –NH_2. Eq. (12) represents the general equation for calculating k.

$$k_{arm} = A'_{R_i} e^{-\left[E^0_{a,arm} + E^{R_i}_{a,arm}\right]/RT} \tag{12}$$

For mono-substituted benzene, only group rate constant represents the partial rate constant as below

$$k_{arm} = A'_{R_i} e^{-E^0_{a,arm}/RT} \tag{13}$$

By assigning the group rate constant for the side chain reactive site and the group contribution factor of functional group at the position relative to the reactive site,

$$k'_{(base)} = A'_{(base)} e^{-E^0_{a,arm(base)}/RT} \tag{14}$$

$$\sum_i Z_i = e^{-\left(\sum E^{R_i}_{a,arm(position)}/RT\right)} \tag{15}$$

For example, for a C—Cl bond cleavage on the alkyl side chain of dichlorobenzene, the rate constant can be shown for 1,2-, 1,3-, and 1,4-dichlorobenzene (C—Cl bond at one position is cleaved and another Cl functional group at ortho, meta, or para position impact the C—Cl bond cleavage), respectively as below

$$k_{arm} = k'_{C-Cl} Z_{Cl(o)} \tag{16}$$

$$k_{arm} = k'_{C-Cl} Z_{Cl(m)} \tag{17}$$

$$k_{arm} = k'_{C-Cl} Z_{Cl(p)} \tag{18}$$

For the cleavage of a C—Cl bond of 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,4-trichlorobenzene (C—Cl bond at one position is cleaved and other two Cl functional groups at ortho, meta, or ortho and para positions impact the C—Cl bond cleavage) can be written as

$$k_{arm} = k'_{C-Cl} Z_{Cl(o)} Z_{Cl(o)} \tag{19}$$

$$k_{arm} = k'_{C-Cl} Z_{Cl(m)} Z_{Cl(m)} \tag{20}$$

$$k_{arm} = k'_{C-Cl} Z_{Cl(o)} Z_{Cl(p)} \tag{21}$$

2.2.5. Datasets

A total of 262 structurally diverse aqueous organic compounds, including 181 aliphatic and 81 aromatic compounds are selected. While the NIST datasets [20] contained 3 alkanes and 13 aliphatic amines, the k_{exp} values were between 10^5 and 10^7 M^{-1} s^{-1}, and the k_{exp} values did not vary significantly regardless the changes in the alkyl chain lengths and positions. More importantly, nucleophilic e^-_{aq} does not react with alkyl and amine functional groups; thus, these k_{exp} values in the GCMe development are not included. All group rate constants and group contribution factors in the GCMe were determined by minimizing the objective function (OF) using the genetic algorithms [40,41] in Eq. (22).

$$OF = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left[\left(k_{exp,i} - k_{calc,i}\right)/k_{exp,i}\right]^2} \tag{22}$$

where $k_{exp,i}$ and $k_{calc,i}$ are the experimentally determined and GCMe-calculated k values of a compound i, respectively, and N is the total number of compounds. The error goal (EG) of the calibration and validation were set to a difference of a factor of 2 and 5, respectively, to account for the experiment error of measurements by pulse radiolysis [20,42] and the uncertainties due to the variabilities of ages and equipment used by different groups of researchers. The EG was previously adapted upon the development of a GCM for hydroxyl radicals [43].

3. Results and discussion

3.1. Overall results

Fig. 1 plots the k_{calc} values of 262 aliphatic and aromatic compounds against k_{exp} values from both calibration and validation. Through calibration, 106 parameters, including 37 group rate constants and 69 group contribution factors, were determined with a total of 189 k_{exp} values. Tables 1–5 show all the group rate constants and group contribution factors. Tables S1 and S2 in the supplemental material (SM) contain all the values used in calibration and validation. It was found that 79% (150 compounds) and 92% (174 compounds) of the k_{calc} values were within a difference of a factor of 2 and 5 from k_{exp} values, respectively, from calibration (Table 6). The OF value determined in Eq. (22) represents sample deviation (SD) [44], in which the number of fitted data is distributed within one standard deviation from the mean value under the assumption of the normal sample distribution. The SD value weighs all k_{calc} values equally; hence, the outweighed data point does not significantly impact the overall correlation. The least-square fit determines a correlation coefficient of r^2 as 0.86. Although the approach is significantly different from our GCMe, the overall correlation of our GCMe appeared to be superior to those that were reported by QSARs, with an r^2 of 0.75 for aliphatic compounds ($n = 100$) and r^2 of 0.70 for aromatic compounds ($n = 147$) [10,11].

Next, using the calibrated group rate constants and group contribution factors, a total of 73 k_{exp} values for multifunctional group compounds were calculated for validation. The SD value was 0.653 with

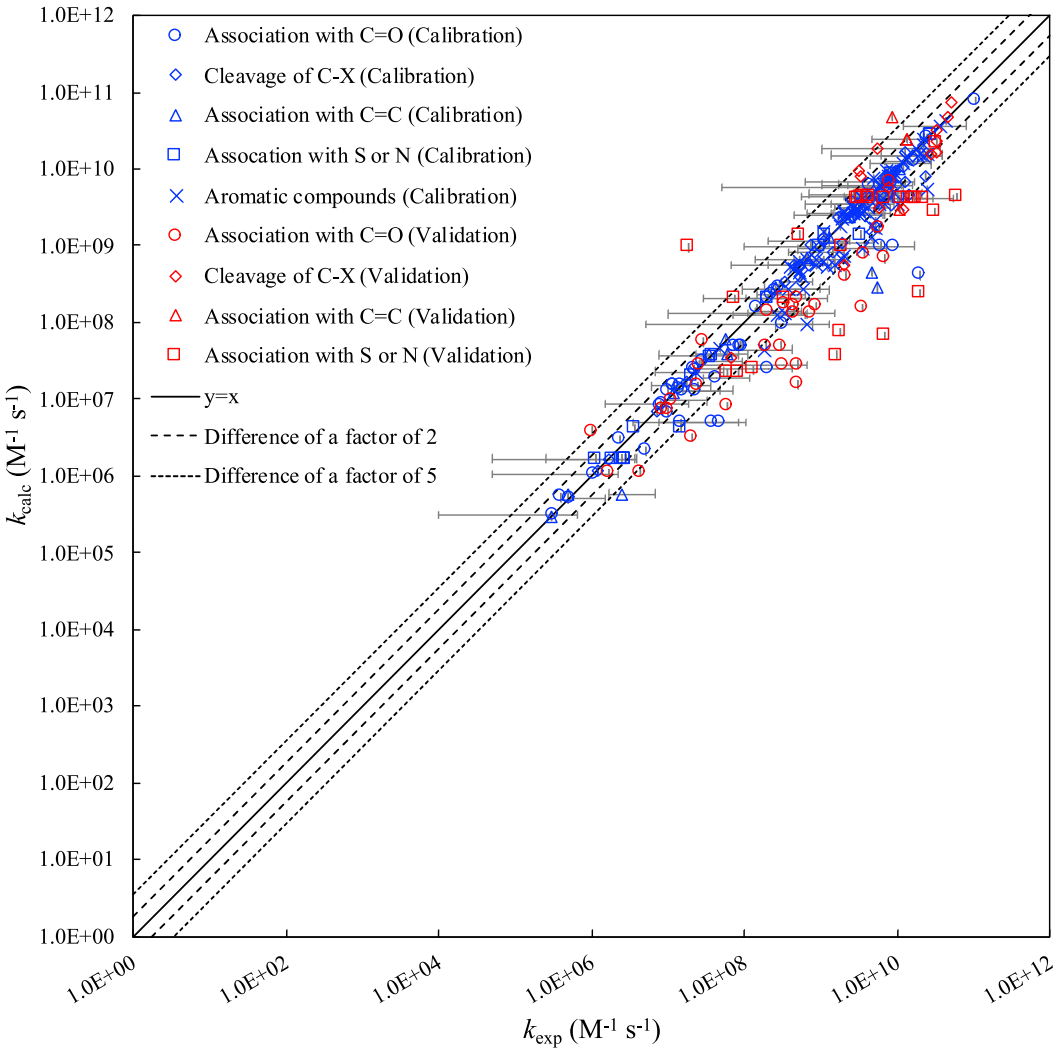

Fig. 1. Calculated k_{calc} obtained through calibration and validation against the experimentally measured k_{exp} for 262 compounds with e^-_{aq}. Horizontal error bars indicate the range of the reported experimental rate constants for a given compound.

Table 1
Group rate constants and group contribution factors for compounds undergoing association with C=O/O.

C=O Association	
Group rate constant ($\times 10^8$ M^{-1} s^{-1})	
$k_{C=O}$	1.64
$k_{C=O(II)}$	400.10
k_O	0.03
Group contribution factor	
-O^-	0.040
-COO^-, -CH_2COO^-, -$CH_2CH_2COO^-$	0.990
-CH_2, -CH_3, –CH_2CH_2, –CH_2CH_3, -$C(CH_3)_3$	0.170
-OH	0.810
-COOH	100.003
-CH_2CH_2COOH	1.001
-CH_2COOH	11.424
-CHOH, -CH_2OH	1.000
–OCH_3, -OCH_2CH_3, -$OC(CH_3)_3$	1.000
-NH_2, -NH	0.300
-$NHCH_2$, -$NHCH_3$	0.110
-CH_2NH_2	1.000
-NHC=O, -CH_2C=O, -CH_2CH_2C=O	1.000
-$N(CH_3)_2$	0.517
-$NHC(CH_3)_3$	0.433
-$N(CH_2CH_3)_2$	0.300

Table 2
Group rate constants and group contribution factors for compounds undergoing concerted or stepwise cleavage of C-X.

Cleavage of C-X bond	
Group rate constant ($\times 10^8$ M^{-1} s^{-1})	
k_{C-Br}	63.00
k_{C-I}	135.31
k_{C-Cl}	14.54
$k_{C-F(I)}$	1.80
$k_{C-F(II)}$	0.001
Group contribution factor	
-CH, -CH_2, –CH_2CH_3	0.380
-CH_3	0.721
–CH_2CH_2	0.235
-Cl	2.210
-COOH	6.587
-COO^-	0.790
-C=O	5.400
-F	2.103
-CF_2, -CF_3	2.490
-CF_2*, [a]	74.752

[a] -CF_2* is only used in the association component (C=O or O) of the overall rate equations for fluorinated compounds.

Table 3
Group rate constants and group contribution factors for compounds undergoing association with C=C.

C=C Association	
Group rate constant ($\times 10^9\ M^{-1}\ s^{-1}$)	
$k_{HH>C=C<HH}$	0.0001
$k_{HH>C=C<H}$	0.28
$k_{>C=C<HH}$, $k_{H>C=C<H(trans)}$	4.89
$k_{H>C=C<H(cis)}$	14.08
$k_{>C=C<H}$	82.49
k_{SO3-}	1.72
Group contribution factor	
-C=O	9.922
$-COO^-$	0.989
$-CH_3$	0.091
-Cl	1.024
$-CH_2$, $-CH_2CH_2$, $-CH_2NH_2$	0.043
$-SO_3^-$	2.191
$-CH_2OH$, -CHOH	0.135
$-CH_2CH_2OH$, $-CH_2CHOH$	0.003
$-CONH_2$	9.995

Table 4
Group rate constants and group contribution factors for compounds interacting with S or N-containing compounds.

Interaction with S or N	
Group rate constant ($\times 10^7\ M^{-1}\ s^{-1}$)	
$k_{C=N}$	3.74
k_{NH3+}	3.92
k_{SO3-}	3.50
$k_{S=O}$	0.42
k_{-S-}	2.00
k_{-S-S-}	434.87
k_{SH}	408.02
k_{S-}	95.51
$k_{C=S}$	138.00
k_{NO2}	2699.59
$k_{N=O}$	826.24
$k_{C=N}$	20.20
Group contribution factor	
$-CH_3$, $-CH_2CH_3$, $-CH_2CH_2$, $-C(CH_3)_3$	0.043

53% (39 compounds) of the k_{calc} values were within a difference of a factor of 5 from k_{exp} values. Table 6 summarizes the statistical results from calibration and validation. It appears that the validation results do not show strong correlations, indicating the limitation of our GCMe to the application for the multifunctional group compounds. Detailed discussions on the limitation are given in subsections below.

3.2. Association with a C=O bond

For the association mechanism with a C=O bond, 43 compounds, including 5 carboxylates, 6 carboxylic acids, 4 alcohols, 5 esters, 3 ketones, 2 aldehydes, and 18 amides, were used to calibrate 3 group rate constants and 18 group contribution factors. The SD value of the calibration was 0.435, with 74% (32 compounds) and 86% (37 compounds) of the datapoints falling within a difference of a factor of 2 and 5, respectively. Three group rate constants were considered: (1) $k_{C=O}$ for carboxylates, carboxylic acids, esters, and acetamides, (2) k_O for alcohols, and (3) $k_{C=O(II)}$ for ketones and aldehydes owing to significantly higher reactivities than $k_{C=O}$ [9]. The group rate constant of $k_{C=O(II)}$ was also used in esters and amides that contain multiple carbonyl groups (such as dimethyl oxalate, malonamide, and biuret) because of the significantly larger k_{exp} values due to the presence of a second C=O functional group [9]. The alkyl functional group(s) in the medium position of dicarboxylate did not appear to impact the overall k_{exp} values for oxalate, malonate, and succinate. Thus, one group contribution factor was assigned for COO^-, CH_2COO^-, and $(CH_2)_2COO^-$. In contrast,

Table 5
Group rate constants and group contribution factors for compounds undergoing addition to an aromatic compound.

Addition to aromatic	
Group rate constant ($\times 10^9\ M^{-1}\ s^{-1}$)	
k_{C-O}	15.00
k_{C-Br}	6.00
k_{C-Cl}	0.64
k_{C-F}	0.30
k_O	0.02
k_{S-}	0.05
k_{C-N}	18.00
k_{NO2}	36.60
$k_{N=O}$	43.00
k_{SO3-}	2.60
k_{C-I}	0.47
Group contribution factor, Monosubstituted	
-OH	0.773
$-O^-$	0.229
-Cl	2.085
-F	1.423
$-NH_2$	1.000
Group contribution factor, Di and tri substituted	
$-CH_3$(o)	1.000
-Cl(o)	1.008
-OH(o)	1.000
$-NH_2$(o)	0.643
$-O^-$(o)	0.435
$-COO^-$(o)	0.380
-Br(o)	1.174
-F(o)	0.883
-I(o)	1.287
$-CH_3$(m)	0.900
-Cl(m)	1.364
-OH(m)	1.000
$-NH_2$(m)	0.999
$-O^-$(m)	0.419
$-COO^-$(m)	0.060
-Br(m)	1.997
-F(m)	1.002
-I(m)	3.801
$-CH_3$(p)	0.800
-Cl(p)	1.658
-OH(p)	0.800
$-NH_2$(p)	0.687
$-O^-$(p)	0.150
$-COO^-$(p)	1.000
-Br(p)	2.303
-F(p)	1.259
-I(p)	2.516

the number of CH_2 alkyl functional groups in the medium position of dicarboxylic acid considerably impacted the k_{exp} values, affording k_{exp} in the range of 10^8 – $10^{10}\ M^{-1}\ s^{-1}$ [9]. Thus, three separate group contribution factors were determined for COOH, CH_2COOH, and $(CH_2)_2COOH$, respectively. Similar to the carboxylate functional groups, other functional groups that exhibited a similar impact on the overall k_{exp} values were combined into a single group contribution factor to reduce the total number of parameters for calibration (e.g., alkyl functional groups of CH_2, CH_3, CH_2CH_2, CH_2CH_3, and $C(CH_3)_3$, alcohol functional groups of CHOH and CH_2OH, ether functional group of OCH_3, OCH_2CH_3, and $OC(CH_3)_3$, amine functional groups of NH and NH_2, alkyl amine functional groups of $NHCH_2$, $NHCH_3$, and amide, and carbonyl functional groups of NHC=O, CH_2C=O, and CH_2CH_2C=O).

The group contribution factors of O^- in formate and NH_2 in urea were determined using compound-specific group contribution factors as the k_{exp} values were significantly smaller (i.e., $10^5\ M^{-1}\ s^{-1}$ [25]) than those that were determined for other compounds (10^7–$10^8\ M^{-1}\ s^{-1}$) because of the lack of any well-defined electrophilic center [45]. As GCMe determines the O^- and NH_2 from longer chain functional groups, it is not able to account for those appeared in the smallest chain. This is a common issue in the GCM application for small molecular weight compounds observed for hydroxyl radicals as well [43].

Table 6
Summary of experimental data, parameters, and statistical results.

	Total	Calibration					Validation	
	# of k_{exp}	# of k_{calc}	# of group rate constants	# of group contribution factors	Number and (%) of data within EG Factor of 2	Factor of 5	# of k_{calc}	Number and (%) of data within EG Factor of 5
Overall	**262**	**189**	**37**	**69**	**150 (79%)**	**174 (92%)**	**73**	**39 (53%)**
Association with C=O	72	43	3	18	32 (74%)	37 (86%)	29	13 (45%)
Concerted or stepwise C-X cleavage	43	29	5	9	25 (86%)	29 (100%)	14	11 (79%)
Association with C=C	20	16	6	9	13 (81%)	13 (81%)	4	2 (50%)
Association with S- or N-containing functional groups; cleavage of C-S or C-N	46	20	12	1	17 (85%)	19 (95%)	26	13 (50%)
Aromatic compounds	81	81	11	32	63 (78%)	76 (94%)	0	–

The validation process was conducted using the calibrated group rate and contribution factors for 29 multifunctional compounds, including 8 carboxylates, 3 carboxylic acids, 6 esters, 1 ketone, 3 amines, and 8 amides. The SD value was 0.69, and 45% (13 compounds) of the datapoints were within a difference of a factor of 5. Methyl trifluoroacetate (CF_3COOCH_3) was included as a validation compound in a group for association with C=O even though it undergoes two types of mechanisms: stepwise cleavage of the C–F bond and association with C=O. Our previous study confirmed the associative mechanism based on potential energy surface, spin density, and lowest unoccupied molecular orbital investigations [19]. Inferior estimation of the overall k_{exp} values for validation to those for calibration appears to result from the underestimation of the overall k_{exp} values for multifunctional compounds, indicating the enhancement of the overall reactivities due to the contribution of second CO-containing functional group. While this is the significant limitation of current GCMe, due to the limited availability of k_{exp} values for multifunctional compounds we calibrated the parameters only with k_{exp} values of single functional compounds.

3.3. Concerted or stepwise cleavage of a C–X halogen bond

For the cleavage mechanism of a C–X halogen bond, a total of 29 compounds, including 10 haloalkanes, 5 halooxygens, 11 halocarboxylates, and 3 fluorinated compounds, were used to calibrate five group rate constants and nine group contribution factors. The SD value was 0.296, and 86% (25 compounds) and 100% (29 compounds) of k_{calc} values were within a difference of a factor of 2 and 5 from k_{exp} values, respectively. The calibration only used chlorinated haloalkanes because the k_{exp} values for all brominated and iodinated alkanes significantly exceeded the diffusion limit rate constants [19]. However, the group rate constants and group contribution factors of bromine- or iodine-containing compounds were calibrated from halooxygens and halocarboxylates. The compounds in the halooxygen and halocarboxylate groups contained two possible reactive sites undergoing: (1) cleavage of a C–X bond and (2) association with a C=O bond. For these compounds, group rate constants for the association previously determined were used to calibrate only the parameters for the cleavage mechanism.

The group rate constants for each of the four halogen atoms: $k_{C\text{-}F}$, $k_{C\text{-}Cl}$, $k_{C\text{-}Br}$, and $k_{C\text{-}I}$ (1.80×10^8, 1.45×10^9, 6.30×10^9, and 1.35×10^{10} M^{-1} s^{-1}, respectively) were found to follow the trend with the bond dissociation energy of each C–X bond [46], indicating the consistency with the general physical–chemical properties of calibrated group rate constants. The k_{exp} values of trifluoroacetate, perfluorobutanoic acid, and perfluorooctanoic acid were included in the calibration. However, the k_{exp} values were significantly smaller than those of other fluorinated compounds (e.g., fluoroacetone, methoxyflurane, and enflurane) due to the presence of long-chain alkyl groups and other functional groups [47]. Therefore, another group rate constant, $k_{C\text{-}F(II)}$, was determined (9.52×10^4 M^{-1} s^{-1}) for the group of longer chain fluorinated compounds. It should be noted that halogenated compounds with strong electron-withdrawing functional groups may undergo a stepwise mechanism where e^-_{aq} associates with the electron-withdrawing functional group (e.g., C=O) and elongates the C–F bond, followed by the cleavage of the C–F bond [3,4]. Hence, to avoid this complication, current GCMe adapts only cleavage of any C–X bond regardless of the concerted or stepwise mechanism. While this simplification of a C–X bond cleavage did not appear to reflect the embedded reaction mechanism, calibrated group rate constants and group contribution factors seemed to follow the general chemical and physical properties. A total of 14 multifunctional compounds, including 7 haloalkanes and 7 halooxygens, were used for the validation. The SD value was 0.53, and 79% (11 compounds) of k_{calc} values were within a difference of a factor of 5 from the k_{exp} values.

3.4. Association with a C=C bond

For the association with a C=C bond, 16 alkenes were used to calibrate six group rate constants and nine group contribution factors. The SD value was 0.407, and 81% (13 compounds) of k_{calc} values were within a difference of a factor of 2 from k_{exp} values. Six group rate constants were accounted for, including $k_{H2C=CH2}$, $k_{H2C=CH}$, $k_{C=CH2}$, $k_{HC=CH(cis)}$, $k_{HC=CH(trans)}$, and $k_{C=CH}$, to ensure the structural impact from isomers and the number of functional groups to the reactivities with e^-_{aq}. The determined group rate constants were found to increase with a smaller number of hydrogens on unsaturated carbon(s) (i.e., $k_{H2C=CH2} = 1.50 \times 10^5$ M^{-1} s^{-1} vs. $k_{C=CH} = 8.25 \times 10^{10}$ M^{-1} s^{-1}), indicating that the functional group(s) significantly enhances the reactivity for association with a C=C bond. Our previous study determined that chlorinated alkenes (e.g., vinyl chloride (CH_2═$CHCl$) and trans-1,2-dichloroethylene (ClCH═CHCl)) were reduced solely through the association with a π-bond that is impacted by the presence of chlorine atoms [19]. Due to the limited number of available k_{exp} values, the nearest functional group on the side chain of a C=C bond and the next nearest functional group were integrated to be one group contribution factor. For example, CH_2, CH_2CH_2, and CH_2NH_2 were integrated into one group contribution factor, including CH_2OH and CHOH for one, and CH_2CH_2OH and CH_2CHOH for one. A total of four alkenes were used for validation. The SD value was 0.74, and 50% (2 compounds) of the k_{calc} values were within a difference of a factor of 5 from k_{exp} values. It should be noted that even though the contribution of diffusion from k_{exp} values were subtracted, the k_{exp} values in this group for association with a C=C bond were significantly larger than 2.00×10^{10} M^{-1} s^{-1}, which provides uncertainties about the k_{exp} values.

3.5. Interaction with S- or N-atom-containing compounds

For the association with S=S and NO_2 or cleavage of a C–S or C–N

bond, 20 compounds, including one cyanide, 5 ammonia, one sulfate, 2 sulfoxide, 2 thiol, 1 sulfide, 1 disulfide, 1 S-, 2 CS, 3 nitro, and 1 imine were used to calibrate 12 group rate constants and one group contribution factor that represents alkyl functional groups (i.e., CH_3, CH_2CH_3, CH_2CH_2, and $C(CH_3)_3$). The diversity in the structures of the reactive sites afforded the calibrated group rate constants ranging from 4.2×10^6 (i.e., $k_{S=O}$) to 2.7×10^{10} (i.e., k_{NO2}). Most compounds used in the calibration contained only one S- or N-atom-containing functional group, which reduced the degree of freedom to 8 and identical calibrated k_{calc} values regardless of the length of the alkyl chain. For example, thiourea ($k_{exp} = 3.3 \times 10^9$) [48] and thiosemicarbazide (1.2×10^9) [48] have identical k_{calc} values of 1.38×10^9 because only one group rate constant, k_{CS}, was calibrated for these compounds. Unfortunately, this is one limitation of the current GCMe. However, due to data scarcity, this approach was accepted for calibration and validation (see below). The SD value was 0.316, and 95% (19 compounds) of the k_{calc} values were within a difference of a factor of 5 from the k_{exp} values.

A total of 26 multifunctional S- or N-atom-containing compounds were used for validation, including 1 sulfoxide, 3 cyanides, 1 ammonia, 2 hydrogen sulfides, 6 thiols, 6 sulfides/disulfides, 2 S-, 2 CS, and 3 imines. Using only one group rate constant for the same group of compounds, the k_{calc} values for validation indicate identical values. Regardless of this limitation, the SD value was 0.706, and 50% (13 compounds) of the k_{calc} was within a difference of a factor of 5 from the k_{exp} values.

3.6. Aromatic compounds

For aromatic compounds with single- and multifunctional groups, 81 compounds, including 14 mono-, 58 di-, and 9 trisubstituted benzenes, were used to calibrate 11 group rate constants and 32 group contribution factors. First, only k_{exp} values for monosubstituted benzenes were used to determine the group rate constants of 11 aliphatic functional groups on the benzene side chain. The group rate constants for di- and trisubstituted benzenes and group contribution factors using those calibrated group rate constants were determined. While there are common functional groups under the same reaction mechanisms between aliphatic and aromatic compounds (note: aliphatic side chains on a benzene ring), the impact of aromatic structure is in the localization of electron density of a benzene ring to form an electron-deficient center and the reaction on the side chain through association and cleavage of a C-X bond [44]. Thus, we determined the group rate constants and contribution factors separately for aromatic compounds. The SD was 0.348, and 78% (63 compounds) and 94% (76 compounds) of the k_{calc} values were within a difference of a factor of 2 and 5 from the k_{exp} values, respectively. Due to limited data availability, we could not conduct the validation.

3.7. Relationships between the group contribution factors and Taft constants

Fig. 2 shows the relationship between calibrated group contribution factors and the Taft constant [49]. The Taft constant was used to determine the impact of neighboring functional group(s) on the main mechanisms in aliphatic compounds. In general, the reactivities of nucleophilic e^-_{aq} were enhanced by the presence of electron-withdrawing functional groups and reduced by the electron-donating ones. The positive slope of an overall correlation supports the general trend; functional groups with larger group contribution factors (i.e., more electron-withdrawing groups) correlate with the larger Taft constant. A group of greater electron-withdrawing functional groups (i.e., halogenated ones) appears with larger group contribution factors, followed

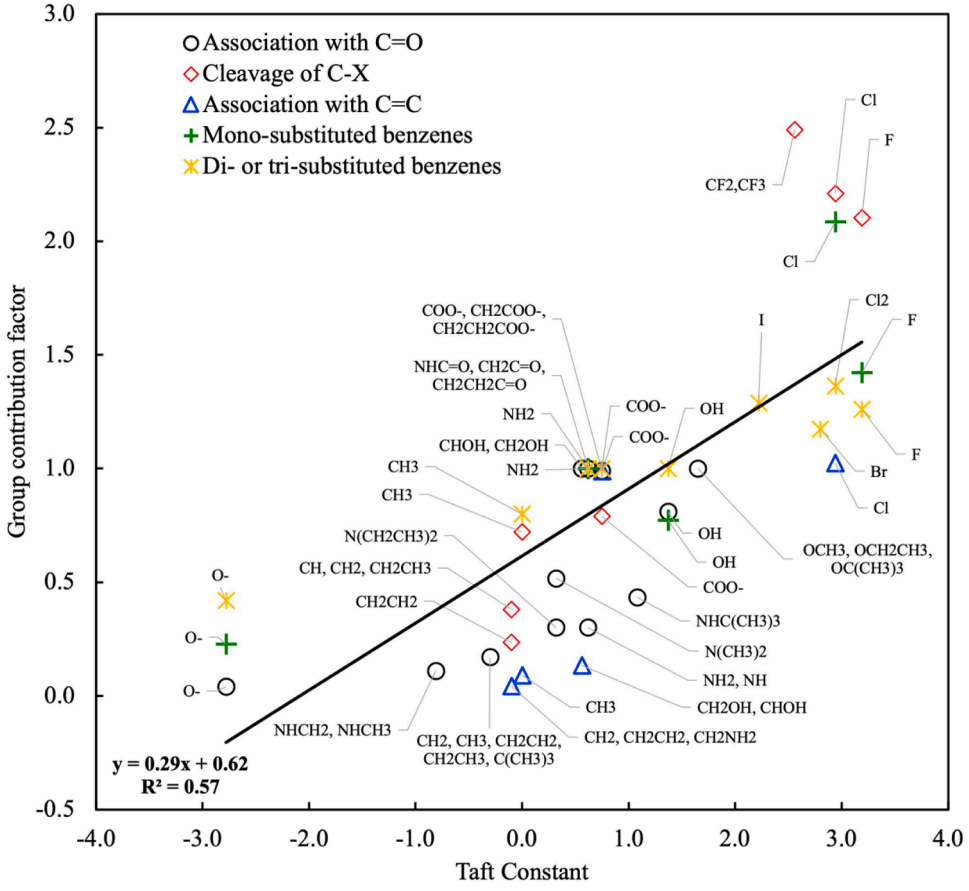

Fig. 2. Relationship between calibrated group contribution factors and the Taft constants.

by a group of oxygenated groups (i.e., carboxylate, carbonyl, and alcohols) and a group of amines and alkyl functional groups. The positive correlation verifies the physical–chemical properties of calibrated group contribution factors.

The significant e_{aq}^- reactions with aromatic compounds occurred on the branched aliphatic chain of the benzene ring; thus, the Taft constants were also used to investigate the impact of these functional groups. Previously, a linear correlation was observed between the Hammet constants at para-position and the relative reactivity of various monosubstituted benzenes to benzene, implying the reactivity of e_{aq}^- with electrophilic centers [44]. Anbar and Hart discussed the limitation of Hammet constants and the additivity of the parameters, and concluded that the reaction of e_{aq}^- may be rather localized, being impacted by the overall π-electron density of the monosubstituted functional group and the formation of the localized electron-deficient center by multifunctional groups [35]. For multifunctional compounds, the electron-donating functional groups at para-position reduced the overall reactivities with e_{aq}^- the most compared to those at ortho- and meta-position due to the notable increases in the π-electron density of the ring by resonance effect. The electron-withdrawing functional groups at the para-position enhance the overall reactivities with e_{aq}^- the most compared to those at ortho- and meta-positions due to induction's exceptional electron withdrawing effects. The observations here are consistent with the experimentally determined reactivities with multiple functional compounds on a ring.

4. Limitation of GCMe and engineering implications

One of the limitations of GCMe is that it cannot predict the rate constants for the reactions close to the diffusion-control limit because it is based on the group additivity of the rate constants. Additionally, the rate constant expression based on the thermochemical additivity may not thoroughly reflect the reaction mechanisms in the aqueous phase because of the unknown reaction mechanisms. In addition, there are insufficient experimental datasets. As a result, the group contribution factors with the electron-donating and -withdrawing abilities, i.e., the Taft constant, did not exhibit a strong correlation. The observed inconsistencies in the experimental data may have resulted from the difference in experimental protocols, such as the differences in the analytical approach. For these groups, additional experimental studies are required to obtain better calibration.

Although the GCMe used only experimentally reported rate constants based on the thermochemical additivity of the activation energies, the group contribution factors linearly correlated with the general inductive constants for most cases. In addition, the rate constants for the compounds with multifunctional groups were validated and compared with the experimental rate constants. The GCMe can be used to predict most of the rate constants within a difference of a factor of 2 to 5 from the experimental values. Therefore, the GCMe can be used to predict the rate constants for many compounds with any type of functional groups for which we have sufficient data to calibrate the group rate constants and group contribution factors. Furthermore, the GCMe does not account for the effect of solvation or steric hindrance resulting from specific functional group(s), although these impacts are implicitly accounted in the group rate constants and contribution factors. Overall, the GCMe can be used to predict the rate constants within the EG, and this may be acceptable for the design of ARPs, depending on how sensitive the model is to the rate constants.

Supplemental materials

Additional information for 2 tables: group rate constants and contribution factors, summary of experimental and predicted data for calibration and validation. MS excel spreadsheet is provided as a supplemental material for any users to calculate the *k* values for hydrated electrons.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Supplementary materials

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