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Correlation of the Rates of Solvolyses of Benzhydryl Halides Using an Extended Grunwald-Winstein Equation

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Rates of solvolyses of benzhydryl chloride (Ph$_2$CHCl, **1**) and benzhydryl bromide (Ph$_2$CHBr, **2**) in ethanol, methanol, and aqueous binary mixtures incorporating ethanol, methanol, 2,2,2-trifluoroethanol (TFE) and acetone are reported. Solvolyses were also carried out in TFE-ethanol mixtures. Application of the extended Grunwald-Winstein equation led to *l* value of 1.19 (**1**), 1.29 (**2**) and *m* value of 1.00 (**1**), 0.77 (**2**), correlation coefficient of 0.965 (**1**) and 0.970 (**2**). Sensitivities (*l* = 1.19 (**1**), 1.29 (**2**) and *m* = 1.00 (**1**), 0.77 (**2**)) were similar to those obtained for several previously studied solvolyses, in which an S$_N$2 pathway is proposed for the solvolyses of benzhydryl halides (Ph$_2$CHX, X = Cl or Br).

**Key Words**: Benzhydryl halides, Extended Grunwald-Winstein equation, S$_N$2 pathway

Introduction

Recently there has been considerable interest in reactions of benzylic-type carbocation intermediate, **I**, with nucleophiles. Solvents or added nucleophiles may react with the contact ion pair, the solvent-separated ion pair or the free intermediate, depending on the stability or life time of the carbocation intermediate, **I**.[1] The thermodynamic stability of the carbocation intermediate has been shown to be strongly dependent on the α-substituents, R$_1$ and R$_2$ in **I**.[1h,2]

In contrast, the reactivity of **I** (Y = CH$_3$O) with a solvent composed of TFE and water (1:1) at 25.0 °C is nearly independent of very strong variations in the thermodynamic stability of **I** caused by a wide range of electron-withdrawing or electron-donating power of the α-substituents. R$_1$ and R$_2$.[2] This has been explained by a compensatory reaction between the polar effect of the α-substituents and the resonance effect of the Y-substituent.[3]

I
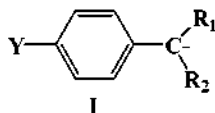
The mechanism of solvolyses of benzhydryl halides, such as of benzhydryl chloride (Ph$_2$CHCl, **1**) and benzhydryl bromide (Ph$_2$CHBr, **2**), have been studied less in spite of their importance as highly reactive chemical intermediates.


1   **2**
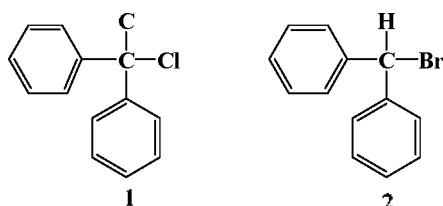
The Grunwald-Winstein equation in its original form[4] correlates the rates of solvolyses of ionization reactions against the solvent ionizing power values.[5] Whereas the Hammett equation involves changes in a remote substituent under otherwise constant conditions, this equation involves changes in the solvent composition under otherwise constant conditions. The Grunwald-Winstein equation can be extended to cover reactions in which the solvent also acts as a nucleophile by the addition of a second term, involving a scale of solvent nucleophilicity.[6] This is the same basic philosophy as in the Taft equation, which extends the Hammett equation by adding a second term involving a scale of steric parameters.

The extended Grunwald-Winstein equation can be expressed as in eq. 1: k and k$_o$ represent the specific rates of solvolysis of a substrate RX in a given solvent and in the standard solvent (80% ethanol), respectively; *l* is the sensitivity of the solvolysis towards changes in solvent nucleophilicity (N$_T$);[6] *m* is the sensitivity of the solvolysis towards changes in solvent ionizing[6] power (Y$_X$, for a leaving group X);[5] and c is a constant (residual) term.[5]

$$\log (k/k_o) = l N_T + m Y_X + c \qquad (1)$$

In this work, we have attempted to investigate the reaction mechanism involved in the solvolyses of benzhydryl chloride (Ph$_2$CHCl, **1**) and benzhydryl bromide (Ph$_2$CHBr, **2**), with a variety of pure and mixed solvents at 35.0 °C, as the following reaction as shown in eq. 2, by determining on the magnitudes of the *l* and *m* of the extended Grunwald-Winstein equation, eq. 1.

$$X = Cl \text{ or } Br \qquad (2)$$
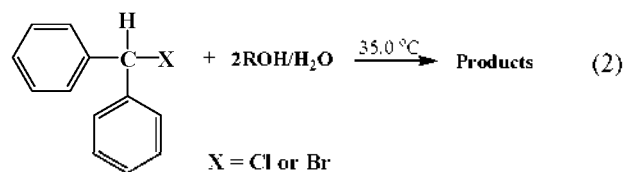
Results and Discussion

Specific rates of solvolyses of **1** and **2** have been determined in 22 and 14 solvents at 35.0 °C, respectively. The

Table 1. Specific rates of solvolysis (k) of benzhydryl chloride (Ph$_2$CHCl, **1**)^a at 35.0 °C and N$_T$ and Y$_{Cl}$ values of the solvents.

Solvent^b	10^3k^c (s^{-1})	N$_T$^{d}	Y$_{Cl}$^{e}
100% EtOH	0.277 ± 0.004	0.37	-2.52
90% EtOH	2.16 ± 0.03	0.16	-0.94
80% EtOH	7.69 ± 0.04	0.0	0.0
70% EtOH	32.2 ± 0.5	-0.20	0.78
60% EtOH	58.7 ± 0.8	-0.38	1.38
50% EtOH	154 ± 4	-0.58	2.02
100% MeOH	2.88 ± 0.04	0.17	-1.17
90% MeOH	22.3 ± 0.5	-0.01	-0.18
80% MeOH	101 ± 3	-0.06	0.67
70% MeOH	529 ± 7	-0.40	1.46
90% Acetone	0.0204 ± 0.0004	-0.35	-2.39
80% Acetone	0.489 ± 0.003	-0.37	-0.83
70% Acetone	19.9 ± 0.3	-0.42	0.17
60% Acetone	81.1 ± 0.6	-0.52	0.95
50% Acetone	330 ± 5	-0.70	1.73
97% TFE^f	15.1 ± 0.3	-3.3	2.83
90% TFE	3.01 ± 0.04	-2.55	2.85
70% TFE	0.708 ± 0.005	-1.98	2.96
80T-20E^g	314 ± 4	-1.76	1.89
60T-40E	52.9 ± 0.6	-0.94	0.63
40T-60E	11.2 ± 0.4	-0.34	-0.48
20T-80E	3.22 ± 0.05	0.08	-1.42

^{a}Unless otherwise indicated, a 10^{-3}M solution of the substrate in the indicated solvent, also containing 0.1% CH$_3$CN within the solvent. ^{b}On a volume-volume basis at 25.0 °C. ^{c}With associated standard deviations. ^{d}Values from ref. 6. ^{e}Values from ref. 5. ^{f}On a weight-weight basis at 25.0 °C. ^{g}T-E indicates 2,2,2-trifluroethanol (TFE)-ethanol mixtures.

Table 2. Specific rates of solvolysis (k) of benzhydryl bromide (Ph$_2$CHBr, **2**)^a at 35.0 °C and N$_T$ and Y$_{Br}$ values of the solvents.

Solvent^b	10k^c (s^{-1})	N$_T$^{d}	Y$_{Br}$^{e}
100% EtOH	0.0506 ± 0.0004	0.37	-2.40
90% EtOH	0.354 ± 0.005	0.16	-0.84
80% EtOH	1.10 ± 0.02	0.0	0.0
70% EtOH	2.92 ± 0.03	-0.20	0.68
100% MeOH	0.566 ± 0.005	0.17	-1.12
90% MeOH	1.92 ± 0.03	-0.01	-0.14
80% MeOH	4.79 ± 0.04	-0.06	0.70
80% Acetone	0.177 ± 0.003	-0.37	-0.70
60% Acetone	1.24 ± 0.03	-0.52	1.03
50% Acetone	4.42 ± 0.04	-0.70	1.74
80T-20E^f	7.43 ± 0.04	-1.76	1.62
60T-40E	2.32 ± 0.05	-0.94	0.31
40T-60E	0.967 ± 0.005	-0.34	-0.57
20T-80E	0.477 ± 0.004	0.08	-1.42

^{a}Unless otherwise indicated, a 10^{-3}M solution of the substrate in the indicated solvent, also containing 0.1% CH$_3$CN within the solvent. ^{b}On a volume-volume basis at 25.0 °C. ^{c}With associated standard deviations. ^{d}Values from ref. 6. ^{e}Values from ref. 5. ^{f}T-E indicates 2,2,2-trifluroethanol (TFE)-ethanol mixtures.

solvents consisted of ethanol, methanol, and binary mixtures of water with ethanol, methanol, acetone, TFE and four binary mixtures of TFE with ethanol. Specific rates of solvolyses are presented in Tables 1 and 2, together with N$_T$^{6} and Y$_X$^{5} values. The specific rates of solvolyses of **1** and **2** were also not found to depend on the initial concentrations of the substrates.

In the present paper, we are concerned with the specific rates of the solvolyses represented in eq. 2. In most solvents, reactions were reasonably fast, and the use of an apparatus allowing a rapid response to changes in conductivity^7 was a convenient way of following the extent of reaction as a function of time. In order to promote a rapid dissolution in the solvent, the substrate was usually added as a small volume of a concentrated stock solution in acetonitrile, such that the reaction solution contained about 0.1% acetonitrile.

A useful tool for quantitatively estimating the rate-controlling influence of nucleophilic participation by solvent during a solvolysis reaction involves the application of the extended Grunwald-Winstein equation, eq. 1,^{8} and compares the l and m values with those previously obtained for other studies.^{6,8} A consideration in terms of the simple Grunwald-Winstein equation [eq. 1 without the lN$_T$ term] to the specific rates of solvolysis of **1** and **2** leads to a poor correlation with value of 0.939 (**1**) and 0.894 (**2**) for the correlation coefficient (R). Meanwhile, analyses of the data (**1** and **2**) using the extend Grundwald-Winstein equation (eq. 1) leads to a good liner correlation with values of 0.965 (**1**) and 0.970 (**2**) for the correlation coefficient (R) (Figures 1 and 2).

Application of eq. 1 to the solvolysis of **1** led to only moderately good correlations, with dispersal for different binary mixtures. For 22 kinds of solvents, values were obtained of 1.21 ± 0.20 for l, 0.94 ± 0.11 for m, and 0.51 for c; the stan-
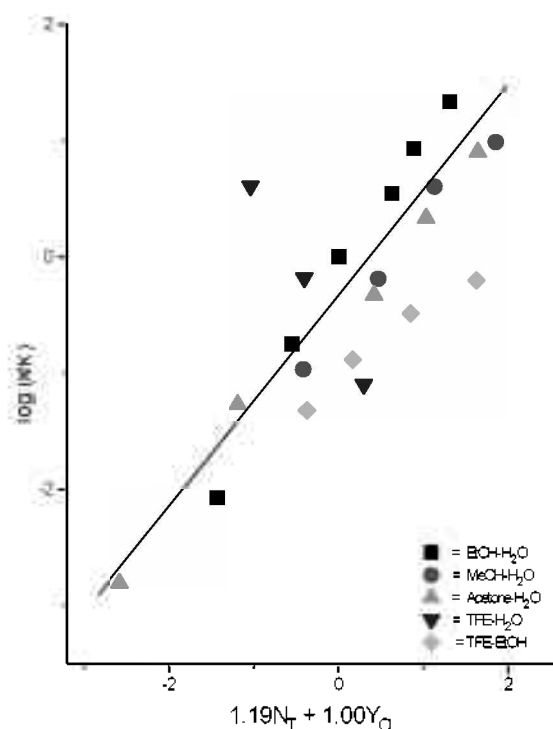

Figure 1. Plot of log(k/k$_0$) against (1.19N$_T$ + 1.00Y$_{Cl}$) for solvolyses of benzhydryl chloride at 35.0 °C

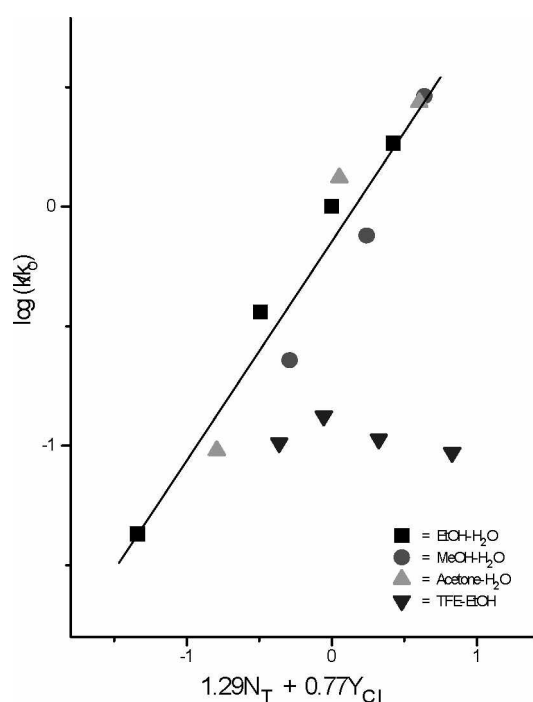380 *Bull. Korean Chem. Soc.* **2009**, Vol. 30, No. 2

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Figure 2. Plot of $\log(k/k_0)$ against $(1.29N_T + 0.77Y_{Cl})$ for solvolyses of benzhydryl chloride at 35.0 °C

dard error of the estimate was 0.14. the R value was 0.884. Inspection of the plot corresponding to this correlation (Figure 1) showed that the three data points for solvolysis in the TFE-H$_2$O mixtures lay cross the best fit line. Also. the four data points for solvolysis in TFE-ethanol mixtures lay below the plot line. Recalculation with omission of these points (TFE-H$_2$O and TFE-ethanol) led to values of 1.19 ± 0.41 for l. of 1.00 ± 0.09 for m. and of 0.39 for c (Figure 1): the standard error of the estimate was 0.12, and R value was 0.965. Inspection of Figure 1 shows a considerable deviation for the four solvolyses in the TFE-ethanol mixtures. In earlier corre-

lations of other reactions of solvolyses, it was found that the data points for these solvent systems usually lay below the correlation line.[9]

The application of eq. 1 to the solvolyses of **2** also led to only moderately good correlations. with dispersal for different binary mixtures. For 14 kinds of solvents, values were obtained of 0.06 ± 0.21 for l. 0.47 ± 0.09 for m. and 0.04 for c: the standard error of the estimate was 0.1. and the R value was 0.897. Inspection of the plot corresponding to this correlation (Figure 2) showed that the four data points for solvolysis in the TFE-ethanol mixtures lay below the correlation line. Recalculation with omission of these points led to values of 1.29 ± 0.32 for l. of 0.77 ± 0.09 for m. and of 0.14 for c (Figure 2): the standard error of the estimate was 0.07. and the R value was 0.970. Inspection of Figure 2 shows a considerable deviation for the four solvolyses in the TFE-ethanol mixtures.

These phenomena are very similar to the solvolysis of 1.[9] The sensitivity values. l and m. are reported in Table 3. together with the corresponding parameters obtained in the analyses of previously studied substrates. where they can be compared with literature values for related substrates.

The extended Grunwald-Winstein equation is a very useful indicator of the extent of nucleophilic participation by the solvent. as expected in the parameter, l, which. in turn, is directly related to whether a substituted reaction is unimolecular or bimolecular pathway. In general, for an ionization reaction without nucleophilic assistance. l will be zero and m close to unity. For a reaction proceeding with extensive nucleophilic assistance. the l value will be in the region of 0.7 to 1.7 and the m value in the region of 0.3 to 0.5. Therefore. determination of these values will be a valuable source of information concerning the structure of the transition state for these solvolyses.[9b,10]

The l and m values for the solvolyses of **1** and **2** obtained are very similar to those recently reported. after an analysis in

Table 3. Coefficients from the extended Grunwld-Winstein correlations of the specific rates of solvolyses of benzhydryl halides (Ph$_2$CHX, X = Cl or Br) at 35.0 °C and a comparison with corresponding values for other solvolytic displacements of halide ion from phosphorus, sulfur, and carbon.

Substrate	Mech.	n[a]	l[b]	m	l/m	c[c]	R[d]
Ph$_2$CHCl	S$_N$2	15	1.19 ± 0.41	1.00 ± 0.09	1.2	0.39 ± 0.12	0.965
Ph$_2$CHBr	S$_N$2	10	1.29 ± 0.32	0.77 ± 0.09	1.7	0.14 ± 0.07	0.970
i-PrSO$_2$Cl[11]	S$_N$2	19	1.28 ± 0.05	0.64 ± 0.03	2.0		0.988
(Me)$_2$NSO$_2$Cl[11]	S$_N$2	32	1.20 ± 0.04	0.72 ± 0.03	1.7	0.11 ± 0.04	0.985
PhCOCH$_2$OTs[12]	S$_N$2	24	1.03 ± 0.04	0.56 ± 0.04	1.8	-0.04 ± 0.12	0.990
(MeO)$_2$PSCl[8a]	S$_N$2	28	1.16 ± 0.08	0.55 ± 0.03	2.0	0.30 ± 0.06	0.966
(Me$_2$N)$_2$POCl[8b]	S$_N$2	31	1.14 ± 0.05	0.63 ± 0.04	1.8	0.17 ± 0.21	0.982
PhOCOCl[17]	A-E	21	1.68 ± 0.10	0.57 ± 0.06	3.0	0.12 ± 0.41	0.973
BzOCOCl[9b]	A-E	15	1.95 ± 0.16	0.57 ± 0.05	3.4	0.16 ± 0.15	0.966
OctOCOF[18]	A-E	23	1.80 ± 0.13	0.79 ± 0.06	2.3	0.13 ± 0.34	0.959
4-NO$_2$BzOCOCl[9b]	A-E	19	1.61 ± 0.09	0.46 ± 0.04	3.5	0.04 ± 0.22	0.975
PhOCSCl[19]	A-E	9	1.88 ± 0.28	0.56 ± 0.15	3.4	0.38 ± 0.15	0.950
EtSCOCl[20]	I	19	0.66 ± 0.08	0.93 ± 0.07	0.7	-0.16 ± 0.31	0.961
BzOCOCl[13a]	I	11	0.25 ± 0.05	0.66 ± 0.06	0.4	-2.05 ± 0.11	0.976
2-AdOCOCl[21]	I	19	~0	0.47 ± 0.03	~0	0.11 ± 0.19	0.970
1-AdOCOCl[22]	I	15	~0	0.47 ± 0.03	~0	0.03 ± 0.05	0.985
Ph$_2$NCOCl[19]	I	33	0.23 ± 0.04	0.58 ± 0.03	0.4	0.08 ± 0.07	0.969

[a]Number of data points. [b]From eq. 1. [c]Standard deviation. [d]Correlation coefficient.

terms of eq. 1, for the specific rates of solvolysis of isopropylsulfonyl chloride (*l* = 1.28 ± 0.05, *m* = 0.64 ± 0.03).[1] *N,N*-dimethylsulfamoyl chloride (*l* = 1.20 ± 0.04, *m* = 0.72 ± 0.03).[11] 2-phenyl-2-ketoethyl tosylate (*l* = 1.03 ± 0.04, *m* = 0.56 ± 0.04).[12] dimethyl thiophosphorochloridate (*l* = 1.16 ± 0.08, *m* = 0.55 ± 0.03),[8a] and *N,N,N',N'*-tetramethyl dimidophosphorochloridate (*l* = 1.14 ± 0.05, *m* = 0.63 ± 0.04).[8b] The *l* values of 1.19 (**1**), 1.29 (**2**) and the *m* values of 1.00 (**1**), 0.77 (**2**) for the solvolyses of **1** and **2**, respectively, were very similar to the previous reported by values for the bimolecular solvolyses of other substrates (Table 3).[8a,b,11,12] They are believed to solvolyze by an S_N2 mechanism involving an attack by the solvent at α-carbon. Solvolysis of **1** and **2**, where bond making (*l* = 1.19 (**1**), 1.29 (**2**)) is more progressed than bond breaking (*m* = 1.00 (**1**), 0.77 (**2**)), is also indicated to proceed by a bimolecular pathway, reflecting nucleophilic assistance from a solvent nucleophile.[9c]

The *l* and *m* ratios have also been suggested as a useful mechanistic criteria and the values (*l/m*) of Table 3 could be divided into three classes with values of 1.2 to 2.0 for those entries postulated to represent bimolecular mechanism (S_N2), values of 2.3 to 3.5 for those believed to represent addition-elimination pathway (A-E), and values below 0.7 for those believed to represent ionization pathway (I).[13] For the solvolyses of **1** and **2**, the values for the ratio (*l/m*) of 1.2 (**1**) and 1.7 (**2**) are very similar to those previously observed for the solvolyses of isopropylsulfonyl chloride,[14] *N,N*-dimethyl-sulfamoyl chloride.[11] 2-phenyl-2-ketoethyl-tosylate.[12] dimethyl thiophosphorochloridate.[8a] and *N,N,N',N'*-tetramethyldiamidophosphorochloridate[8b] which have been shown to solvolyze with the S_N2 mechanism. The higher *m* value for the solvolyses of **1**, relative to **2**, may reflect the need for increased salvation of the developing positive charge on the α- carbon in the presence of the more electronegative chloride attached at the carbon.[13]

A comparison of the *l* and *m* values for the solvolyses of **1** and **2** shows that **2** has a slightly higher *l* value and slightly lower *m* value than **1**. This results would be consistent with the fact that **2** has a slightly tighter transition state.[14]

Conclusions

Application of the extended Grunwald-Winstein equation (eq. 1) led to an *l* values of 1.19 (**1**), 1.29 (**2**) and an *m* values of 1.00 (**1**), 0.77 (**2**), correlation coefficients of 0.965 (**1**) and 0.970 (**2**). These values are shown (Table 3) to be similar to previously determined values for nucleophilic attack by solvent at carbon, sulfur and phosphorus (V). They are also very close

(X = Cl or Br)
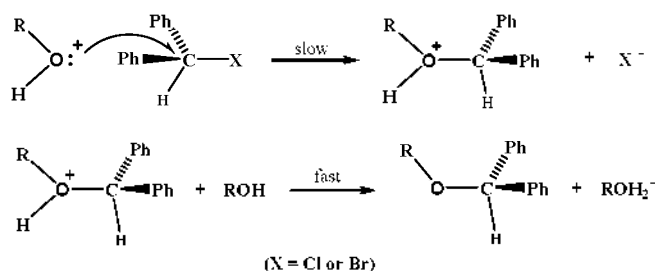
Scheme 1

to the previously studied solvolyses of isopropylsulfonyl chloride.[11] *N,N*-dimethylsulfamoyl chloride.[11] 2-phenyl-2-ketoethyl tosylate,[12] dimethyl thiophosphorochloridate.[8a] and *N,N,N'N'*-tetramethyl diamidophosphorochloridate.[8b] The *l* value of 1.19 (**1**), 1.29 (**2**) and the *m* value of 1.00 (**1**), 0.77 (**2**) for the solvolyses of **1** and **2** were very similar to previously reported values for bimolecular solvolyses of other substrates (Table 3) which is believed to solvolyze by an S_N2 mechanism involving an attack by solvent at α-carbon. Scheme 1.

Experimental

The purification of acetone, methanol, and ethanol were carried out as previous work described.[15] The purification of 2,2,2-trifluoroethanol (TFE) was also carried out by use of previously reported procedures.[16] Water was used after distillation. Benzhydryl chloride and benzhydryl bromide were commercially available. The substrates did not react with the pure acetonitrile within the stock solution.

Kinetic runs were performed with 10 μL of the stock solution of substrate (1 M) and 5ml of the reaction solvent. All kinetic runs were performed, at least, in duplicate. The reaction cell was washed with water and acetone several times and dried prior to each run. A 5 mL portion of solvent was added to the reaction cell and allowed to sit for a few minutes until it reached a temperature equilibrium with the temperature bath. A 10 μL portion of the stock solution was then added and the reaction cell was shaken vigorously. The change of the conductance in the reaction with time was saved in the computer as a data file.

Rates were measured conductimetrically at 35.0 °C. All kinetic measurements were carried out in a constant temperature bath maintained within ± 0.05 °C. The conductivity bridge used in this work was a self-made computer automatic A/D converter conductivity bridge. First-order solvolysis rate coefficients (k_{obs}), with the solvent in large excess, were determined by a curve fitting analysis of the computer data with a modified version of the Origin Program, which fits conductance vs. time data to the equation. $A = A_\infty + (A_o - A_\infty) \exp(-k_{obs} \cdot t)$, where A is the observed conductivity and A_∞, $A_o - A_\infty$, and k_{obs} are iteratively optimized to achieve the best possible least-squares fit.

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