

Solvolytic of Highly Congested Tertiary Benzylic Halides. A Caution in the Use of the Yukawa-Tsuno Equation

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The Yukawa-Tsuno equation (1)^{1,2} has been widely employed in structure-reactivity correlation analyses for systems involving rate-determining formation of cationic transition states with a direct conjugative interaction of the reaction center with the ring substituent, such as the recent work on the formation of arenosulfonium cations in Friedel-Crafts reactions,³ the nature of the transition state in Michael reactions,⁴ and solvolytic reactivities.⁵

$$\log(k_X/k_H) = \rho[\sigma^o + r(\sigma^+ - \sigma^o)] \quad (1)$$

Despite the occasional argument on its necessity or validity,⁶⁻⁹ many others believe the superiority of eq 1 over the simple form of the Hammett-Brown equation (2).^{5,10}

$$\log(k_X/k_H) = \rho\sigma^+ \quad (2)$$

From the study on the rates of solvolysis for certain sterically congested tertiary halides, we would like to report that the Yukawa-Tsuno equation might yield a better correlation but with a misleading conclusion, and thus should be used with caution.

Results and Discussion

1-Aryl-1-bromo-1-phenyl-2,2,2-trifluoroethanes (1a-d, f-h), 1-aryl-1-chloro-1-coumaranyl-2,2,2-trifluoroethanes (2a, d, e, g, h-j), 1-aryl-1-bromo-1-(4-phenoxyphenyl)-2,2,2-trifluoroethanes (3a, b, d, e, g-j) and 1-aryl-1-chloro-1-(4-phenoxyphenyl)-2,2,2-trifluoroethanes (4a, b, d, e, g-j) were prepared and were solvolyzed in a variety of solvents. The reactivities were monitored by the conductimetric method, and the pertinent rate constants are shown in Table I.

Correlation analyses employing eqs 1 and 2 were carried out. Although no significant difference between the use of the common σ^+ constants¹¹ and the solvent-dependent ones⁵ was realized, the former was the choice because the latter had not been well-tested. Moreover, the number of substrates is sufficient for this purpose. In the correlation analysis for the solvolysis of 2-aryl-1,1,1-trifluoro-2-propyl tosylate,⁸ the results obtained from only eight points were essentially the same ($\rho = -6.269$, $r = 1.433$, and $R = 0.997$ by using the commonly used σ^+ ,¹² or $\rho = -6.296$, $r = 1.393$, and $R = 0.998$ by using the solvent-dependent σ^+) as that

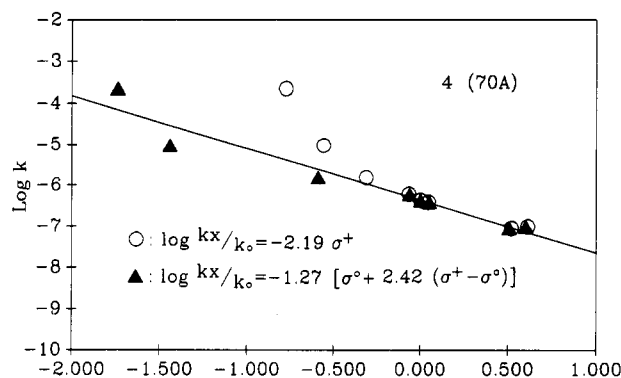
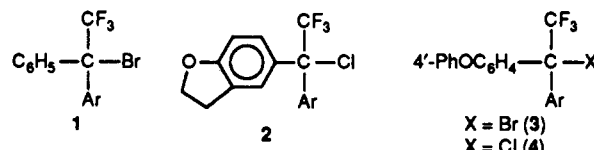


Figure 1. Correlation analysis using Hammett-Brown treatment (O, $R = 0.934$) and Yukawa-Tsuno treatment (Δ , $R = 0.971$) for the solvolysis of 1-aryl-1-chloro-2,2,2-trifluoro-1-(4'-phenoxyphenyl)ethane (4) in 70% acetone.

from 28 points ($\rho = -6.287$, $r = 1.390$, and $R = 0.999$ by using the solvent-dependent σ^+).¹³ The results are listed in Table II.

For 1, the treatment of rate data with both equations resulted in good to excellent linear relationships with ρ values of -5.9 to -7.4 , dependent upon the solvent and the regression method employed. These values are normal for S_N1 solvolysis of tertiary substrates containing an α -CF₃ group.^{8,13,14} Therefore, it demonstrates a significant resonance contribution from the substituted aryl ring in the cationic transition state. The probe for detecting the resonance contribution by measuring the order of reactivity, k_p/k_m , for substrates containing electron-withdrawing substituent¹⁴⁻¹⁶ was not able to be applied in this case because of the low reactivity of 1. The estimated rate constants for 1i and 1j will be on the order of 10^{-12} /s at 25 °C, which have to be measured at 150 °C or higher and will be impractical according to our experience.



a, Ar = 4'-CH₃OC₆H₄; b, Ar = 4'-PhOC₆H₄; c, Ar = 3', 4'-(CH₃)₂C₆H₃.
d, Ar = 4'-CH₃C₆H₄; e, Ar = 3'-CH₃C₆H₄; f, Ar = 4'-FC₆H₄; g, Ar = C₆H₅;
h, Ar = 3'-CH₃OC₆H₄; i, Ar = 3'-CF₃C₆H₄; j, Ar = 4'-CF₃C₆H₄

On the other hand, this probe is applicable to 2-4 because of the higher reactivities. In the presence of a strongly electron donating aryl group, the other α -aryl ring is presumably the one distorted severely from the coplanarity with the incipient cationic center in the transition state, and thus has little contribution to the resonance stabilization.¹⁵ Indeed, inverse orders of reactivities, i.e. $k(p\text{-CF}_3)/k(m\text{-CF}_3) > 1$, have been observed for all three substrates in different solvents (Table I). From Table II, the very small ρ values, -1.2 to -2.6 , and the relatively poor correlation coefficient, $R = 0.93$ - 0.98 , obtained from Hammett-Brown plots support the lack of resonance contribution of the substituted aryl ring. From the Yukawa-Tsuno treatment the ρ values for 2-4, -1.0 to -1.9 , are even smaller, which also suggest the insignificance of resonance. In contradiction, the correlations, $R = 0.97$ - 0.99 , were better. An example is shown in Figure 1. More remarkably, the r parameters for expressing the

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Table I. Pertinent Rate Constants for Solvolysis of Halides 1-4

substrate	$k, \text{s}^{-1} (25^\circ\text{C})^a$				$k_j/k_i(\text{solvent})^b$
	80E ^b	70E ^b	70A ^b	60A ^b	
1a		1.27×10^{-2}		1.40×10^{-2}	
1b ^c		1.28×10^{-4}		1.37×10^{-4}	
1c ^d		1.78×10^{-6}		1.57×10^{-6}	
1d ^d		7.83×10^{-7}		7.03×10^{-7}	
1f ^d		3.79×10^{-8}		3.20×10^{-8}	
1g ^d		1.55×10^{-8}		1.37×10^{-8}	
1h ^d		1.34×10^{-8}		7.19×10^{-9}	
2a	3.05×10^{-2}		1.31×10^{-2}		
2d	3.49×10^{-3}		2.01×10^{-3}		
2e	2.00×10^{-3}		1.27×10^{-3}		
2g	1.83×10^{-3}		1.03×10^{-3}		
2h	1.50×10^{-3}		8.30×10^{-4}		
2i	3.38×10^{-4}		2.57×10^{-4}		1.22 (80E), 1.06 (70A)
2j	4.12×10^{-4}		2.73×10^{-4}		
3a	3.21×10^{-2}		1.76×10^{-2}		
3b	1.70×10^{-3}		7.34×10^{-4}		
3d	2.30×10^{-4}		1.24×10^{-4}		
3e	6.88×10^{-5}		4.56×10^{-5}		
3g ^c	5.38×10^{-5}		3.35×10^{-5}		
3h	4.19×10^{-5}		2.82×10^{-5}		
3i ^d	4.06×10^{-6}		4.27×10^{-6}		1.28 (80E), 1.04 (70A)
3j ^d	5.20×10^{-6}		4.43×10^{-6}		
4a	6.33×10^{-4}		2.23×10^{-4}		
4b	3.19×10^{-5}		9.60×10^{-6}		
4d ^d	4.25×10^{-6}		1.53×10^{-6}		
4e ^d	1.40×10^{-6}		5.97×10^{-7}		
4g ^d	1.14×10^{-6}		4.30×10^{-7}		
4h ^d	8.24×10^{-7}		3.85×10^{-7}		
4i ^d	1.06×10^{-7}		9.08×10^{-8}		1.34 (80E), 1.08 (70A)
4j ^d	1.42×10^{-7}		9.84×10^{-8}		

^a With less than 2% deviation in at least two independent measurements. ^b Volume percent of acetone (A) or ethanol (E) in aqueous solution. ^c 1b and 3g are the same. ^d From data obtained at other temperatures.

Table II. Correlation Analysis for Halides 1-4 in Different Solvents

substrate (solvent) ^a	correlation analysis				
	HB ^b		YT ^c		
	ρ	R^d	ρ	r	R^d
1 (70E)	-7.18	0.986	-5.97	1.25	0.989
(60A)	-7.44	0.988	-6.14	1.26	0.991
2 (80E)	-1.35	0.984	-1.10	1.52	0.993
(70A)	-1.21	0.988	-0.993	1.51	0.996
3 (80E)	-2.59	0.967	-1.89	1.75	0.983
(70A)	-2.37	0.954	-1.65	1.90	0.975
4 (80E)	-2.48	0.958	-1.68	1.93	0.979
(70A)	-2.19	0.934	-1.27	2.42	0.971

^a Volume percent of acetone (A) and ethanol (E) in aqueous solution. ^b Hammett-Brown treatment. ^c Yukawa-Tsuno treatment. ^d Correlation coefficient.

degree of resonance interaction as compared with that in the solvolysis of *tert*-cumyl chloride¹ are surprisingly higher (1.5-2.4), not lower, than in the case of 1 (1.2).

Accordingly, the better correlations obtained from the Yukawa-Tsuno treatment of the solvolytic rate constants for 2-4 are likely due to the statistical preference with two adjustable parameters, instead of only one parameter in eq 2. In other words, the observed superiority in the linear plots might not be the consequence of the reliability of the eq 1 or some kind of inherent structure-reactivity relationship, but might be merely a computational artifact. The present observation from the solvolysis of 2-4 clearly demonstrates that the results obtained from the treatment of rate data by the Yukawa-Tsuno equation (2) might be misleading, and thus should be interpreted cautiously.

Experimental Section

General Remarks. Capillary melting points are uncorrected. NMR spectra were determined on a Varian EM390 spectrometer.

Infrared spectra were measured on a Perkin-Elmer 983G spectrometer. Mass spectra were obtained with a Finigan TSQ-16C instrument at this Department or with a JEOL JMS-D300 instrument at Department of Chemistry, National Taiwan Normal University. Elemental analyses were done using a Perkin-Elmer 240C analyzer in the Microanalytical Laboratory of this Department.

Materials. Solvents for the kinetic studies were spectral grade or reagent grade after being purified according to standard procedures.¹⁷ Anhydrous solvents were freshly distilled before use.

The preparations of 1,1-diaryl-2,2,2-trifluoroethanol were carried out by using Grignard addition of the appropriate aryl-magnesium bromide to trifluoroacetophenones in tetrahydrofuran. The halogenation of tertiary alcohols proceeded with thionyl chloride to give the chlorides (81-97% yield), or with phosphorus tribromide or thionyl bromide to give the bromides (70-92% yield). The completion of the transformation was monitored by TLC (silica gel) or by IR spectroscopy. All of the halides were purified by chromatography over a short column of triethylamine-silica gel. Proton NMR, IR, and mass spectral data are compatible with the assigned structures. With the exception of a few reactive substrates, 1a, 2a, 3a, and 3b, acceptable elemental analyses (C and H) have been obtained for all new halides.

Kinetic Measurements. The rate constants were measured with an automatically PC-XT monitored multichannel conductivity rate measuring system developed in this laboratory. Conductivity cells were placed in the thermostat with a temperature variation of $\pm 0.02^\circ\text{C}$. Solutions of 10^{-4} - 10^{-5} M were employed in this study. For some very reactive halides, such as 1a, 2a, 3a, and 3b, the kinetic measurements were performed using the freshly prepared substrates. In certain cases the addition of a small amount of 2,6-lutidine to the solution was found to be necessary to prevent the formation of curvature of the rate constant plot. All reactions were followed to 2 or more half-lives and gave excellent first-order behavior with correlation coefficients of greater than 0.99. Arrhenius plots of rate data obtained at other

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temperatures were applied to the cases that the k at 25 °C could not be measured directly. The rate constants were determined at least in duplicate, and the deviation was within $\pm 2\%$. The mean values of these data are listed in Table I.

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Preparation of Stable Thioketenes from Diazoalkanes and Carbon Monosulfide

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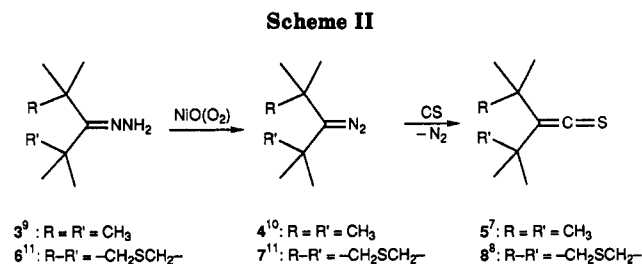
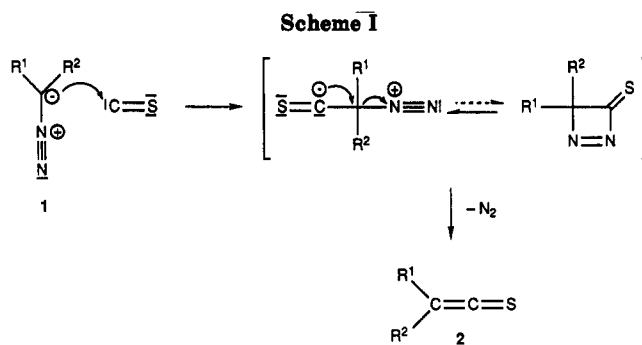
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Thioketenes, which are useful building blocks in the syntheses of heterocycles,³ are generally unstable compounds which tend to dimerize to 1,3-dithietanes or polymerize.⁴ Introduction of bulky or strongly electron withdrawing groups adjacent to the thioketene functionality has a pronounced stabilizing effect, and such thioketene derivatives can often be distilled with little decomposition.^{5,6}

The presently available methods for the syntheses of thioketenes suffer from several drawbacks. Sterically hindered ketenes or acid chlorides can be thionated in good to excellent yields with P_4S_{10} ,^{5,6} but since the reaction conditions are drastic in both cases (reflux in pyridine for up to 25 h), precluding syntheses of less stable thioketenes, and the syntheses of the starting ketenes or acid chlorides⁶ are rather tedious, this method is of limited scope. Other methods⁴ involve high-temperature pyrolyses of various precursors and are less useful for the syntheses of thioketenes on a preparative scale.

As early as 1974, K. J. Klabunde and collaborators⁷ showed that bis(trifluoromethyl)diazomethane (1, $R^1 = R^2 = CF_3$) reacts at -196 °C with codeposited carbon monosulfide (CS) to form, in low yield, bis(trifluoromethyl)thioketene (2, $R^1 = R^2 = CF_3$), which was not isolated but only observed by GLC. It occurred to us that this approach might be elaborated to a versatile thioketene synthesis (Scheme I) with several advantages compared to the above mentioned methods (low reaction temperature, anhydrous and oxygen-free reaction and workup procedures). Since 1984 the use of CS as a synthetic reagent has expanded considerably, and CS can now be prepared and handled in molar quantities as exemplified by reports on



insertion of CS into sulfur-chlorine, nitrogen-hydrogen, and sulfur-hydrogen bonds and cycloaddition of CS to nucleophilic alkenes.^{8,9}

We have now carried out the reactions of the sterically hindered diazo compounds 4^{10} and 7^{11} , with CS (Scheme II) in toluene solution at -78 °C on a preparative scale and were able to obtain the thioketenes 5^5 and 8^6 in 30 and 42% yield (based on 3^{12} and 6^{11}), respectively.

The low reaction temperature (-78 °C) seems to rule out the intermediacy of the corresponding carbene (R^1R^2C) in the formation of 2 and suggests instead interaction between the LUMO of CS and the HOMO of the diazoalkane 1 (Scheme I),^{7,13} There is no a priori reason to assume a ring closure to a highly strained 1,2-diazetidine-3-thione prior to the nitrogen extrusion since the corresponding charged open chain should be equally capable of loss of molecular nitrogen. Interaction of 1 and CS_2 does not lead to thioketene formation.

Attempts to trap unstable 2 [$(R^1, R^2) = (Ph, Ph)$, $(H, COOEt)$], generated according to Scheme I, failed, presumably because of secondary reactions between 2 and diazo compound 1.¹⁴ Resonance stabilized diazoalkanes such as 1 ($R^1 = R^2 = COOC_2H_5$) do not react with CS.¹⁴

Experimental Section

General Procedure for the CS Experiments. Carbon monosulfide was generated in a conventional vacuum line by passing CS_2 vapor through an 8-kV AC discharge. The detailed procedure has been recently described.^{15,16} The gas mixture leaving the discharge tube consisting of approximately 70% CS and 30% CS_2 , together with minor amounts of C_3S_2 and elemental sulfur, was

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