

Kinetics and Mechanism of the Aminolysis of Benzenesulfonyl, Benzoyl and Benzyl Halides

Byung Choon Lee, Dong Sook Sohn, Ji Hyun Yoon, Sun Mo Yang, and Ikchoon Lee[†]

Department of Chemistry, Choongbuk National University, Chongju 360-763

[†]Department of Chemistry, Inha University, Incheon 402-751. Received May 21, 1993

Kinetic studies are conducted for the reactions of *Y*-benzoyl, *Y*-benzenesulfonyl and *Y*-benzyl halides with *X*-anilines in acetonitrile, and the transition state (TS) structures and their variations with substituents *X* and *Y* are discussed. The magnitude of the cross-interaction constants, ρ_{XY} , is the largest and the inverse secondary kinetic isotope effect (SKIE), $k_H/k_D < 1.0$, with deuterated aniline nucleophiles is the smallest for benzoyl fluoride reflecting the tightest TS for this compound. The SKIEs for sulfonyl halides are relatively large due to a relatively large, diffuse nature of the reaction center, S, causing weaker steric hindrance to the vibrations of the two N-H(D) bonds. For benzoyl and sulfonyl halides, the trends in k_H/k_D and $|r_X|$ variations with σ_Y contradict each other, which is rationalized by the negative charge accumulation on the reaction center, CO and SO₂, causing inefficient charge transfer for the substrate with an electron donating substituent.

Introduction

In a series of work on the application of cross-interaction constants, ρ_{ij} in Eq. 1 where $i, j = X, Y$ or Z , as a measure of the transition state (TS) structure, we have shown the S_N2 TS

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (1)$$

structures and their variations with the substituents in the nucleophile *X*, substrate *Y* or leaving group (LG), *Z*, (Scheme 1) can be assessed based on the sign and magnitude of ρ_{ij} .¹ For example, the magnitude of ρ_{XY} is an indicative of the degree of bond formation in the TS, and the sign of ρ_{XZ} , Eq. 2, can be used to characterize the type of reaction. A negative ρ_{XZ} indicates that a stronger nucleophile

$$\rho_{XZ} = \frac{\partial^2 \log k_{XZ}}{\partial \sigma_X \cdot \partial \sigma_Z} = \frac{\partial \rho_Z}{\partial \sigma_X} = \frac{\partial \rho_X}{\partial \sigma_Z} \quad (2)$$

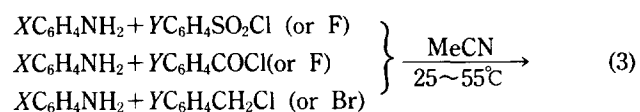
with a more electron-donating substituent (EDS) ($\delta\sigma_X < 0$) leads to a greater degree of bond cleavage with a greater positive ρ_Z ($\delta\rho_Z > 0$). Likewise a stronger nucleofuge (or a better LG) with a more positive σ_Z ($\delta\sigma_Z > 0$) leads to a greater negative ρ_X ($\delta\rho_X < 0$) so that a greater degree of bond-making in the TS is expected. In effect the negative ρ_{XZ} value predicts a "later" TS for a strong nucleophile and/or a strong nucleofuge, which is what we would expect from the quantum-mechanical (QM) model for predictions of TS variation.²

Conversely if ρ_{XZ} is positive, a stronger nucleophile and/or

a stronger nucleofuge lead to an "earlier" TS with a lower degree of bond-making and -breaking. In this case the TS variation conforms to predictions based on the potential energy surface (PES) model.³ The TS variation is dominated by intrinsic effects when ρ_{XZ} is negative, while it is controlled by thermodynamic effects when ρ_{XZ} is positive.¹

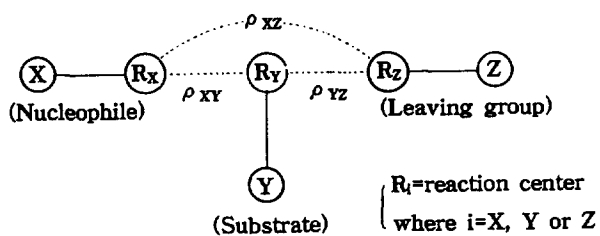
On the other hand, it has also been shown that much useful information on the TS structure can be obtained from secondary (deuterium) kinetic isotope effect, SKIE = k_H/k_D , using deuterated aniline nucleophiles, $XC_6H_4ND_2$.⁴ Normally the stretching and bending vibrations of the two N-H(N-D) bonds in anilines are sterically hindered in the bond-making process so that the vibrational frequencies increase in the TS resulting in an inverse SKIE, $k_H/k_D < 1.0$.⁵ The closer the nucleophile approaches to the substrate, the smaller is the value of k_H/k_D (< 1.0).

In this work, we carried out kinetic studies and determined the cross-interaction constants, ρ_{XY} , and KSIE, k_H/k_D , with deuterated anilines in order to investigate the TS structures and their variations with the substituents in the nucleophile (*X*) and substrate (*Y*) for the reactions of benzenesulfonyl halides, benzoyl halides and benzyl halides with anilines in acetonitrile, Eq. 3.



Results and Discussion

The second-order rate constants, k_2 , and the secondary deuterium kinetic isotope effects, k_H/k_D , are summarized in Tables 1-6. Comparison of the rates for chlorides indicate that the rates are the fastest for benzoyl (-CO-), the slowest for benzyl (-CH₂-) and the intermediate for sulfonyl (-SO₂-) chlorides. The rate increases with a stronger nucleophile in all cases. However the rate is greater with an electron-withdrawing substituent (EWS) in the substrate ($Y = p\text{-Cl}$) for the benzoyl (-CO-) and sulfonyl (-SO₂-) in contrast to



Scheme 1.

Table 1. Second Order Rate Constants, $k_2(\times 10^3 \text{ M}^{-1}\text{s}^{-1})$, k_H/k_D Values and Hammett Reaction Constants for the Reactions of *Y*-Benzenesulfonyl Fluorides with *X*-Anilines and Deuterated *X*-Anilines in Acetonitrile at 55.0°C
$$\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2) + \text{YC}_6\text{H}_4\text{SO}_2\text{F} \xrightarrow[55.0^\circ\text{C}]{\text{MeCN}}$$

<i>X</i>	<i>Y</i>	<i>p</i> -CH ₃	H	<i>p</i> -Cl	ρ_Y^d
<i>p</i> -CH ₃	H ^a	1.27 (0.99) ^f	2.17 (0.98) ₁	4.13 (0.98) ₃	1.24
	D ^b	1.30	2.21	4.20	
H	H	0.748 (0.97) ₂	2.26 (0.97) ₆	2.10 (0.98) ₁	1.10
	D	0.769	2.29	2.14	
<i>m</i> -Cl	H	0.301 (0.96) ₁	0.392 (0.96) ₃	0.561 (0.96) ₈	0.67
	D	0.313	0.407	0.580	
ρ_X^d		-1.17	-1.37	-1.59	

^aWith $\text{XC}_6\text{H}_4\text{NH}_2$. ^bWith $\text{XC}_6\text{H}_4\text{ND}_2$. ^cThe k_H/k_D values are in parenthesis. The standard errors = $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$ were less than ± 0.007 in all cases. ^d ρ_X and ρ_Y values are for reactions with $\text{XC}_6\text{H}_4\text{NH}_2$; those for reactions with $\text{XC}_6\text{H}_4\text{ND}_2$ are very similar to these values. Correlation coefficients were better than 0.996 in all cases.

Table 2. Second Order Rate Constants, $k_2(\times \text{M}^{-1}\text{s}^{-1})$, k_H/k_D Values and Hammett Reaction Constants for the Reactions of *Y*-Benzenesulfonyl Chlorides with *X*-Anilines and Deuterated *X*-Anilines in Acetonitrile at 35.0°C
$$\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2) + \text{YC}_6\text{H}_4\text{SO}_2\text{Cl} \xrightarrow[35.0^\circ\text{C}]{\text{MeCN}}$$

<i>X</i>	<i>Y</i>	<i>p</i> -CH ₃	H	<i>p</i> -Cl	ρ_Y^d
<i>p</i> -CH ₃	H ^a	3.23 (0.99) ^f	4.79 (0.99) ₃	8.62 (0.99) ₆	1.06
	D ^b	3.25	4.83	8.66	
H	H	1.33 (0.97) ₈	2.39 (0.97) ₄	3.18 (0.98) ₄	0.92
	D	1.36	2.44	3.23	
<i>m</i> -Cl	H	0.219 (0.96) ₆	0.309 (0.96) ₈	0.460 (0.97) ₈	0.79
	D	0.229	0.320	0.473	
ρ_X^d		-2.15	-2.23	-2.34	

^aWith $\text{XC}_6\text{H}_4\text{NH}_2$. ^bWith $\text{XC}_6\text{H}_4\text{ND}_2$. ^cThe k_H/k_D values are in parenthesis. The standard errors = $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$ were less than ± 0.010 in all cases. ^d ρ_X and ρ_Y values are for reactions with $\text{XC}_6\text{H}_4\text{NH}_2$; those for reactions with $\text{XC}_6\text{H}_4\text{ND}_2$ are very similar to these values. Correlation coefficients were better than 0.998 in all cases.

a faster rate with an EDS ($Y = p\text{-CH}_3$) for benzyl ($-\text{CH}_2-$) halides. This suggests that for the benzoyl and sulfonyl series the reaction center becomes negatively charged whereas for the benzyl system it is positively charged in the TS, which in turn implies that bond-making is more advanced than bond cleavage in a tight TS for the former two ($-\text{CO}-$ and $-\text{SO}_2-$) halides, whereas bond cleavage is more advanced than bond-making in a loose TS for the latter ($-\text{CH}_2-$). This is

Table 3. Second Order Rate Constants, $k_2(\times 10^3 \text{ M}^{-1}\text{s}^{-1})$, k_H/k_D Values and Hammett Reaction Constants for the Reactions of *Y*-Benzoyl Fluorides with *X*-Anilines and Deuterated *X*-Anilines in Acetonitrile at 55.0°C
$$\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2) + \text{YC}_6\text{H}_4\text{CO}_2\text{F} \xrightarrow[55.0^\circ\text{C}]{\text{MeCN}}$$

<i>X</i>	<i>Y</i>	<i>p</i> -CH ₃	H	<i>p</i> -Cl	ρ_Y^d
<i>p</i> -CH ₃	H ^a	5.72 (0.86) ^f	16.2 (0.86) ₄	52.0 (0.86) ₈	2.38
	D ^b	6.65	18.8	59.9	
H	H	2.29 (0.85) ₄	5.09 (0.85) ₆	14.5 (0.85) ₉	1.92
	D	2.91	5.94	16.9	
<i>m</i> -Cl	H	0.328 (0.84) ₈	0.689 (0.85) ₂	1.62 (0.85) ₇	1.75
	D	0.421	0.799	1.89	
ρ_X^d		-2.31	-2.36	-2.62	

^aWith $\text{XC}_6\text{H}_4\text{NH}_2$. ^bWith $\text{XC}_6\text{H}_4\text{ND}_2$. ^cThe k_H/k_D values are in parenthesis. The standard errors = $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$ were less than ± 0.010 in all cases. ^d ρ_X and ρ_Y values are for reactions with $\text{XC}_6\text{H}_4\text{NH}_2$; those for reactions with $\text{XC}_6\text{H}_4\text{ND}_2$ are very similar to these values. Correlation coefficients were better than 0.995 in all cases.

Table 4. Second Order Rate Constants, $k_2(\times \text{M}^{-1}\text{s}^{-1})$, k_H/k_D Values and Hammett Reaction Constants for the Reactions of *Y*-Benzoyl Chlorides with *X*-Anilines and Deuterated *X*-Anilines in Acetonitrile at 25.0°C
$$\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2) + \text{YC}_6\text{H}_4\text{COCl} \xrightarrow[25.0^\circ\text{C}]{\text{MeCN}}$$

<i>X</i>	<i>Y</i>	<i>p</i> -CH ₃	H	<i>p</i> -Cl	ρ_Y^d
<i>p</i> -CH ₃	H ^a	15.2 (0.90) ^f	38.8 (0.90) ₅	109 (0.91) ₆	2.12
	D ^b	16.9	42.9	119	
H	H	6.00 (0.90) ₆	14.1 (0.90) ₄	34.5 (0.90) ₇	1.89
	D	6.66	15.6	38.1	
<i>m</i> -Cl	H	1.08 (0.89) ₆	2.37 (0.89) ₇	5.12 (0.90) ₁	1.68
	D	1.21	2.64	5.68	
ρ^d		-2.10	-2.21	-2.42	

^aWith $\text{XC}_6\text{H}_4\text{NH}_2$. ^bWith $\text{XC}_6\text{H}_4\text{ND}_2$. ^cThe k_H/k_D values are in parenthesis. The standard errors = $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$ were less than ± 0.008 in all cases. ^d ρ_X and ρ_Y values are for reactions with $\text{XC}_6\text{H}_4\text{NH}_2$; those for reactions with $\text{XC}_6\text{H}_4\text{ND}_2$ are very similar to these values. Correlation coefficients were better than 0.996 in all cases.

supported by a large magnitude of k_H/k_D for benzyl relative to the other two halides; for the chlorides at a common temperature of 55°C, the k_H/k_D values are 0.91₂, 0.98₀ and 0.98₆ for benzoyl, sulfonyl and benzyl, respectively. The relatively large value for the sulfonyl may well be due to a large size of the diffuse sulfur reaction center causing a lesser steric hindrance to the two approaching N-H bonds.⁶ For the benzoyl fluorides, the k_H/k_D values are considerably small-

Table 5. Second Order Rate Constants, k_2 ($\times 10^4$ M $^{-1}$ s $^{-1}$), k_H/k_D Values and Hammett Reaction Constants for the Reactions of *Y*-Benzyl Chlorides with *X*-Anilines and Deuterated *X*-Anilines in Acetonitrile at 55.0°C
$$XC_6H_4NH_2(D_2) + YC_6H_4CH_2Cl \xrightarrow[55.0^\circ C]{MeCN}$$

<i>X</i>	<i>Y</i>	<i>p</i> -CH ₃	H	<i>p</i> -NO ₂	ρ_Y^d
<i>p</i> -CH ₃	H ^a	5.58	3.52	1.75	-0.47
	D ^b	5.69 (0.98 ₈) ^c	3.61 (0.97 ₅)	1.80 (0.97 ₀)	
H	H	2.16 (0.98 ₇)	1.06 (0.98 ₆)	0.520 (0.98 ₃)	-0.57
	D	2.19	1.07	0.531	
<i>m</i> -Cl	H	0.962 (0.99 ₄)	0.453 (0.99 ₂)	0.190 (0.99 ₀)	-0.66
	D	0.969	0.456	0.191	
ρ^d		-1.14	-1.37	-1.48	

^aWith $XC_6H_4NH_2$. ^bWith $XC_6H_4ND_2$. ^cThe k_H/k_D values are in parenthesis. The standard errors = $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$ were less than ± 0.007 in all cases. ^d ρ_X and ρ_Y values are for reactions with $XC_6H_4NH_2$; those for reactions with $XC_6H_4ND_2$ are very similar to these values. Correlation coefficients were better than 0.950 in all cases.

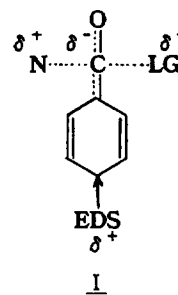
Table 6. Second Order Rate Constants, k_2 ($\times 10^3$ M $^{-1}$ s $^{-1}$), k_H/k_D Values and Hammett Reaction Constants for the Reactions of *Y*-Benzyl Bromides with *X*-Anilines and Deuterated *X*-Anilines in Acetonitrile at 35.0°C
$$XC_6H_4NH_2(D_2) + YC_6H_4CH_2Br \xrightarrow[35.0^\circ C]{MeCN}$$

<i>X</i>	<i>Y</i>	<i>p</i> -CH ₃	H	<i>p</i> -Cl	ρ_Y^d
<i>p</i> -CH ₃	H ^a	7.24	3.62	2.58	-0.38
	D ^b	7.56 (0.95 ₈) ^c	3.79 (0.95 ₅)	2.71 (0.95 ₂)	
H	H	2.33 (0.96 ₆)	1.09 (0.96 ₃)	0.664 (0.96 ₀)	-0.48
	D	2.41	1.13	0.691	
<i>m</i> -Cl	H	1.34 (0.97 ₆)	0.558 (0.97 ₄)	0.267 (0.97 ₁)	-0.63
	D	1.37	0.573	0.275	
ρ^d		-1.11	-1.23	-1.50	

^aWith $XC_6H_4NH_2$. ^bWith $XC_6H_4ND_2$. ^cThe k_H/k_D values are in parenthesis. The standard errors = $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$ were less than ± 0.009 in all cases. ^d ρ_X and ρ_Y values are for reactions with $XC_6H_4NH_2$; those for reactions with $XC_6H_4ND_2$ are very similar to these values. Correlation coefficients were better than 0.948 in all cases.

ler compared to those for other halides indicating that the benzoyl fluorides react with a very tight TS. For benzoyl and sulfonyl halides, the k_H/k_D (< 1.0) values increase with an EDS in the nucleophile ($X = p\text{-CH}_3$). This means that an EDS in the nucleophile leads to a less tight TS with a lesser degree of bond formation. As we have noted in the introduction this is an indication that for benzoyl and sulfonyl halides ρ_{XZ} is positive, since a strong nucleophile leads to an earlier

TS.¹ In contrast, for benzyl halides the trends are opposite; a stronger nucleophile ($X = p\text{-CH}_3\text{O}$) exhibits a smaller k_H/k_D value, indicating that a stronger nucleophile leads to a later TS, *i.e.*, this reaction belongs to the type with a negative ρ_{XZ} ($= -0.10$).¹ The variation of k_H/k_D with substituent in the substrate (σ_Y) indicates that for benzoyl and sulfonyl halides the TS is tighter (SKIE is smaller) for $Y = \text{EDS}$ than for $Y = \text{EWS}$, while in contrast for benzyl halides the TS is tighter for $Y = \text{EWS}$ than for $Y = \text{EDS}$. However the magnitude of the negative ρ_X values increases, and hence positive charge development on the nucleophile in the TS increases, uniformly from $Y = \text{EDS}$ to $Y = \text{EWS}$ for all compounds, which appears to suggest that, the degree of bond formation increases from $Y = \text{EDS}$ to $Y = \text{EWS}$ for all compounds. Thus the trends in the k_H/k_D and ρ_X variations with σ_Y contradict each other for benzoyl and sulfonyl halides, *i.e.*, the variation of k_H/k_D indicates that the TS is tighter for $Y = \text{EDS}$ whereas $|\rho_X|$ suggests that the TS is tighter for $Y = \text{EWS}$. This discrepancy between the trends in the two selectivity parameters can be rationalized as follows: For benzoyl and sulfonyl halides the TS is relatively tight (this is also supported by the large ρ_{XY} values, *vide infra*) with negative charge development ($\rho_Y > 0$), and charge transfer from N in aniline may be inefficient ($|\rho_X|$ is smaller) for $Y = \text{EDS}$ due to a greater negative charge accumulation in the CO (and SO₂) moiety, in the TS **I**. On the other hand, an EDS in the substrate raises the antibonding lowest unoccupied MO, σ_{C-LG}^* , so that a later TS (a greater degree of bond-making) is required.⁸ Thus positive charge development is smaller ($|\rho_X|$ is smaller) due to inefficient charge transfer although the degree of bond formation is greater (k_H/k_D is smaller) for $Y = \text{EDS}$ than for $Y = \text{EWS}$. For $Y = \text{EWS}$ the situation will be exactly the



opposite to that for $Y = \text{EDS}$; positive charge development is greater ($|\rho_X|$ is greater) but the degree of bond-making in the TS will be smaller ($k_H/k_D < 1.0$ is greater). For benzyl system, there is no strong acceptor atoms attached to the C_a center so that no such discrepancy between the trends in $|\rho_X|$ and k_H/k_D arises. We therefore conclude that **the magnitude of ρ_X can not serve in general as a measure of the degree of bond formation.** The decrease in ρ_Y with a more EWS in the nucleophile for the benzoyl and sulfonyl series most probably results from a greater degree of bond cleavage for $X = \text{EWS}$ since the degree of bond-making is greater ($k_H/k_D < 1.0$ is smaller) for $X = \text{EWS}$ in a push-pull type S_N2 TS.

The rate data in Table 1-6 are subjected to multiple regression analysis using Eq. 1 with $i, j = X, Y$. The results are summarized in Table 7. Examination of this table reveals that the magnitude of ρ_{XY} is the largest and hence the degree of bond formation is the greatest for the reactions of benzoyl

Table 7. The Hammett (ρ_X and ρ_Y) and Cross-Interaction Constants (ρ_{XY}) for Nucleophile Substitution Reactions

Reactions	ρ_X	ρ_Y	ρ_{XY}	r^a
$XC_6H_4NH_2 + YC_6H_4SO_2F \xrightarrow[55.0^\circ C]{MeCN}$	-1.34	1.10	-1.13	0.999
$XC_6H_4ND_2 + YC_6H_4SO_2F \xrightarrow[55.0^\circ C]{MeCN}$	-1.32	1.10	-1.13	0.999
$XC_6H_4NH_2 + YC_6H_4SO_2Cl \xrightarrow[35.0^\circ C]{MeCN}$	-2.22	0.97	-0.47	0.999
$XC_6H_4ND_2 + YC_6H_4SO_2Cl \xrightarrow[35.0^\circ C]{MeCN}$	-2.20	0.96	-0.50	0.999
$XC_6H_4NH_2 + YC_6H_4COF \xrightarrow[55.0^\circ C]{MeCN}$	-2.48	2.13	-1.14	0.999
$XC_6H_4ND_2 + YC_6H_4COF \xrightarrow[55.0^\circ C]{MeCN}$	-2.46	2.08	-1.28	0.999
$XC_6H_4NH_2 + YC_6H_4COCl \xrightarrow[25.0^\circ C]{MeCN}$	-2.22	1.97	-0.79	0.998
$XC_6H_4ND_2 + YC_6H_4COCl \xrightarrow[25.0^\circ C]{MeCN}$	-2.22	1.95	-0.78	0.998
$XC_6H_4NH_2 + YC_6H_4CH_2Cl \xrightarrow[55.0^\circ C]{MeCN}$	-1.29	-0.57	-0.27	0.975
$XC_6H_4ND_2 + YC_6H_4CH_2Cl \xrightarrow[55.0^\circ C]{MeCN}$	-1.30	-0.56	-0.28	0.975
$XC_6H_4NH_2 + YC_6H_4CH_2Br \xrightarrow[35.0^\circ C]{MeCN}$	-1.20	-0.49	-0.40	0.947
$XC_6H_4ND_2 + YC_6H_4CH_2Br \xrightarrow[35.0^\circ C]{MeCN}$	-1.22	-0.49	-0.40	0.948

^aCorrelation coefficients.

fluoride. This is in agreement with the smallest value of $k_H/k_D < 1.0$ observed for this compound in Table 3. The magnitude of ρ_{XY} is also large for the reactions of benzenesulfonyl fluorides, which is in contrast, however, with the relatively large k_H/k_D values for sulfonyl fluorides. As we pointed out above, this inconsistency between the large ρ_{XY} value (indicative of tight bond-making) and the large $k_H/k_D < 1.0$ value (suggesting a lesser degree of hindrance to the N-H(D) vibrations) may result from a large and diffuse nature of the sulfur atom in sulfonyl compounds.⁶ Bond energies of the sulfur-halide bonds (45.6 and 56.6 kcal mol⁻¹ for the S-F and S-Cl bonds)⁹ indicate that the S-halide bonds are easier to break than the C-halide bonds (bond energies are 75.8 and 69.6 kcal·mol⁻¹ for C-F and C-Cl bonds.⁹ This means that the S-halide bonds are weaker than the C-halide bonds so that a later TS with a tighter nucleophile-substrate bond is expected in the TS for benzoyl halides in accordance with the Bell-Evans-Polanyi (BEP) principle.¹⁰

An interesting aspect regarding the relative size of SKIE for the two, -CO- and -SO₂-, series is that the size of SKIE differs considerably between fluoride and chloride for benzoyl series in contrast to a similar size for fluoride and chloride of sulfonyl series. For the benzoyl series, bond energy is greater for fluoride and hence tighter bond formation is expected for fluoride than for chloride (BEP principle).¹⁰ In contrast for sulfonyl series, however, bond energy is greater for chloride than for fluoride so that energetically tighter bond formation is expected for chloride than for fluoride.

This is, however, counteracted by a stronger electron accepting ability of the S-F bond relative to the S-Cl bond, which should lead to a greater degree of bond formation for fluoride.¹⁰ In reality, however, the degree of bond formation is larger for fluoride than for chloride as indicated by a larger $|\rho_{XY}|$ for fluoride in Table 7. The relatively large $k_H/k_D < 1.0$ values for both halides with small difference between them result merely from large size of the sulfur atom,⁶ as noted above. Benzoyl derivatives show the greatest magnitude of ρ_{XY} values and the benzyl derivatives the least. This is in accord with the trends found for the size of SKIE discussed above; the tightest TS is formed with benzoyl whereas the loosest TS is formed with benzyl derivatives. On the other hand the two ρ_{XY} values for $XC_6H_4NH_2$ and $XC_6H_4ND_2$ agree well in most cases indicating that the isotopic substitution of NH₂ to ND₂ does not cause significant TS variation.

Experimental

Materials. Baker GR acetonitrile was dehydrated with KOH and distilled three times over P₂O₅ (bp. 82°C). Substituted benzoyl and benzenesulfonyl fluorides were prepared from the corresponding chlorides.¹¹ All other substrates used were Aldrich GR grade. Physical and spectroscopic data are as follows; *p*-CH₃C₆H₄SO₂F: mp. 41-43°C, *R_f* 0.49, ν_{max} (KBr) 1410 (SO₂, asm, str), 1215 and 1205 (SO₂, sym, str), 1090 (S-O, sym, str) and 760 (O₂S-F, sym, str); C₆H₅SO₂F: bp. 88-89°C at 13 mmHg, *R_f* 0.52, ν_{max} (neat) 1410 (SO₂, asym, str), 1210 (SO₂, sym, str) and 1740 (O₂S-F, sym, str); *p*-ClC₆H₄SO₂F: mp. 36-37°C, *R_f* 0.46, ν_{max} (KBr) 1405 (SO₂, asym, str), 1210 (SO₂, sym, str), 1085 (S-O, sym, str), 900 (C₆H₅-Cl, sym, str) and 740 (O₂S-F, sym, str); *p*-CH₃C₆H₄COF: bp. 67-68°C/10 mmHg, ν_{max} (neat) 1750 (C=O, sym, str), 1300 (C₆H₅-CH₃), 1050 (C-F, str), ¹H-NMR (60 MHz, CDCl₃), 7.0-7.3 (2H), 7.8-8.0 (2H), 2.4 (3H, CH₃), Found (calcd) C, 69.41 (69.57) H, 5.07 (5.11); C₆H₅COF: bp. 43-45°C/mmHg, ν_{max} 1750 (C=O), 1010 (C-F, str), ¹H-NMR (CDCl₃) 7.2-8.2 (4H, ring), Found (calcd) C, 67.73 (67.70), H, 4.01 (4.06); *p*-ClC₆H₄COF: bp. 63-65°C/10 mmHg, ν_{max} (neat) 1750 (C=C, str), 1070 (C-F, str), ¹H-NMR (CDCl₃) 7.3-8.2 (4H, ring), Found (calcd) C, 52.99 (53.04), H, 2.61 (2.54).

Kinetic Procedure. The rates were measured by conductometric method and rate constants are obtained with at least four aniline concentrations as described previously.⁴ The secondary kinetic isotope effects using deuterated aniline nucleophiles were determined as reported previously.⁴

Acknowledgement. This work was supported by a Non Directed Research Fund of the Korea Research Foundation.

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Chemistry of Ruthenium Hydridonitrosyl Complexes Containing Chelating Triphosphines IV-Reactions between RuH(NO)(Cytpp) and Alkynes (Cytpp: Bis(dicyclohexylphosphino-propyl)phenylphosphine)

Ik-Mo Lee*, Ook-Jae Cho, Chan-Yong Kim, and Devon W. Meek^{†,‡}

Department of Chemistry, Inha University, #253 Yonghyun-dong, Nam-ku, Incheon 402-715

[†]Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio 43210, U.S.A.

[‡]deceased on December 7, 1988. Received May 22, 1993

The types of the products of the reactions between RuH(NO)(Cytpp) and alkynes are sensitive to the nature of alkynes. Terminal, nonactivated alkynes (HC≡CR, R=Ph, hexyl and CH₂OH) produce acetylide complexes and terminal (HC≡CR, R=C(O)Me, COOEt) or internal activated ones (RC≡CR, R=COOMe) lead to form alkenyl complexes. On the other hand, internal nonactivated alkynes (RC≡CR, R=Ph) do not show reactivity toward RuH(NO)(Cytpp). These products can be rationalized by the *cis*-concerted mechanism but the radical pathway appears to work in the reaction of propargyl chloride. From the spectroscopic data, the trigonal bipyramidal structure with a linear NO group is proposed for these products.

Introduction

The reactions between alkynes and transition metal complexes have drawn attention due to their implication in the catalytic processes such as hydrogenation, oligomerization, and polymerization. There are several important reactions in this field; substitution, isomerization to vinylidenes, metallocyclization with other acetylene molecules or small molecules (CO and RNC), and the insertion reactions of alkynes to metal hydride or alkyl bonds. These reactions and catalytic reactions are well reviewed several places in the literature.¹⁻⁷ One of the interesting parts in these reactions is that the products of the reactions between metal hydrides and alkynes are closely related with the nature of metal hydrides and alkynes. In other words, various types of products such as acetylides and alkenyl complexes were reported depending upon the nature of the reactants and many mechanisms have been proposed to explain these products. These mechanisms are mainly proposed to explain the geometry of the alkenyl products but investigation on the kinetic data^{8,9} and solvent effect is scarce. This has been partly attributed to easy or fast isomerization of the products. Important mechanisms proposed are concerted mechanism (*cis*^{10,11} and *trans*¹²), stepwise ionic mechanism^{10,13}, and radical mechanism.^{14,15} Therefore, at this point, as Herberich *et al.*¹⁶ pointed out, it is difficult to predict the type of the products. In

this paper, the reactions between alkynes and ruthenium hydridonitrosyl complexes including insertion reactions were investigated to clarify the mechanism of these reactions.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk techniques unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Reagent grade chemicals were purchased from Aldrich Chemical Co., Inc. and used without further purification unless stated otherwise. Ruthenium trichloride hydrate was loaned from Johnson Matthey, Inc. and RuH(NO)(PPh₃)₃¹⁷ and RuH(NO)(Cytpp)¹⁸ were prepared by modified literature methods. The ³¹P{¹H}, ¹H and ¹³C{¹H}-NMR spectra were recorded by using 5 mm tube on a Bruker AM-250 FT NMR spectrometer operating at 101.256 MHz, 250.133 MHz, and 62.896 MHz, respectively. These spectra were referenced to 85% H₃PO₄ and residual deuterium solvent peaks. Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Mass spectra were collected by Dr. David Chang of the Ohio State University on VG 720-250S double focussing mass spectrometer using FAB (Fast Atom Bombardment) method. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Az., U.S.A. or Oneida Research Services, Inc., Whitesboro, N.