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Mechanistic Significances of the Reactivity-Selectivity Principle

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The relationship between the signs of $\rho_{X(i)}$, $\rho_{Y(i)}$ and ρ_{ij} and validity of the reactivity-selectivity principle (RSP) has been derived: RSP is valid when $W = \rho_{X(i)} \cdot \rho_{X(i)} / \rho_{ij}$ is negative. The analysis of 100 reaction series indicated that for normal S_N2 reactions involving variations of substituents in the nucleophile (X) and in the substrate (Y) RSP is valid only for a dissociative type for which $\rho_{Y(i)}$ is negative, whereas for the acyl transfer reactions with rate-limiting breakdown of the tetrahedral intermediate RSP is valid in general for all substituent changes, X, Y and/or Z (substituent on the leaving group). The trends in the validity of RSP for certain types of reaction can be useful in supplementing the mechanistic criteria based on the signs of $\rho_{X(i)}$, $\rho_{Y(i)}$ and ρ_{ij} .

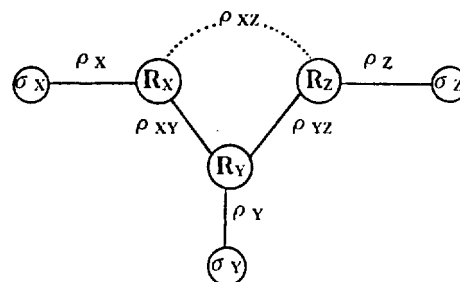
Introduction

Increasing reactivity of a reagent is often accompanied by decreasing selectivity. This so-called Reactivity-Selectivity Principle (RSP)¹ has attracted considerable interests of experimental organic chemists. However, usefulness of RSP as a general rule has been questioned, because there are so many experimental examples of invalid cases.² Recently, Exner³ has shown in his work involving statistical examination of RSP with 100 reaction series that RSP is valid only in half (50%) of the cases studied. He concluded, however, that although RSP is not evidently a general rule "investigations of selectivity and its relation to reactivity should be continued and used possibly to characterize a certain type of reaction or a certain mechanism".

For the past several years we have been developing the cross-interaction constants, ρ_{ij} in eq. 1,⁴ as a mechanistic tool for organic reactions in solution.

$$\log(k_{ij}/k_{00}) = \rho_{X(i)}\sigma_i + \rho_{Y(i)}\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (1)$$

For a typical S_N2 TS, Scheme 1, $i, j = X, Y$ or Z where X, Y and Z represent the nucleophile, substrate and leaving group,



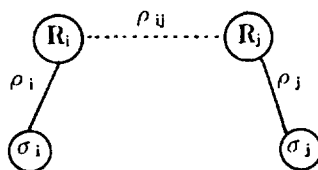
Scheme 1.

respectively. $\rho_{X(i)}$ (or $\rho_{Y(i)}$) denotes the Hammett ρ value for variation of σ_i (or σ_j) with $\sigma_i = 0$ (or $\sigma_j = 0$).

In this work, we examine the relationship between the signs of $\rho_{X(i)}$, $\rho_{Y(i)}$ and ρ_{ij} and the validity of RSP, which can be used to characterize a certain type of reaction or mechanism, as Exner has suggested in his paper.

Derivation of the Relationship

Let us consider a simple reaction system consisting of



Scheme 2.

reactants i and j , Scheme 2, where R and σ are reaction center and substituent respectively.

For example, the change of substituent in the reactant i ($\delta\sigma_i$) will result in a Hammett reaction constant ρ_i . The ρ_i value will, however, depend on σ_j so that $\rho_{i(j)}$ and $\rho_{i(0)}$ represent the ρ_i values for $\sigma_j \neq 0$ and $\sigma_j = 0$ respectively. Here we emphasize that i and j represent X, Y or Z in Scheme 1. On the other hand, eq. 1 can be transformed into eq. 2.

$$\begin{aligned} \log(k_{ij}/k_{00}) &= \rho_{i(j)}\sigma_j + (\rho_{i(0)} + \rho_{ij}\sigma_j)\sigma_i \\ &= \rho_{i(j)}\sigma_j + \rho_{i(0)}\sigma_i \\ &= \rho_{i(j)}\hat{\sigma}_j = -\frac{\rho_{i(0)}\rho_{ij}}{\rho_{ij}} = -W \end{aligned} \quad (2)$$

where $\rho_{i(0)} + \rho_{ij}\sigma_j = \rho_{i(j)}$ (3)

$$\hat{\sigma}_j = -\frac{\rho_{i(0)}}{\rho_{ij}} (= \text{Non-interaction point})^5 \quad (4)$$

and $W = -\frac{\rho_{i(0)}\rho_{ij}}{\rho_{ij}} = \text{constant}$ (5)

Eq. 5 is, of course, strictly valid only for nonzero ρ_{ij} . Now let us consider changes in reactivity, $\delta R_{i(j)}$, and selectivity $\delta S_{i(j)}$, which are defined as eqs. 6 and 7. Eq. 6, i.e., $\delta R_{i(j)}$, represents the change of reactivity by substituting $\sigma_j (\neq 0)$

$$\delta R_{i(j)} = \log k_{i(j)} - \log k_{00} = \log \left(\frac{k_{i(j)}}{k_{00}} \right) = \rho_{i(j)}\sigma_j \quad (6)$$

$$\delta S_{i(j)} = \frac{\rho_{i(j)}}{\rho_{i(0)}} - \frac{\rho_{i(0)}}{\rho_{i(0)}} = \frac{\rho_{i(j)} - \rho_{i(0)}}{\rho_{i(0)}} \quad (7)$$

for $\sigma_j = 0$ when σ_i is kept constant to $\sigma_i = 0$ and likewise, eq. 7, $\delta S_{i(j)}$, represents the change of selectivity by substituting $\sigma_j (\neq 0)$ for $\sigma_j = 0$. Here division by $\rho_{i(0)}$ assures that we are comparing two relative selectivities, which are the magnitude of ρ irrespective of the sign; we are tacitly assuming that there is no sign change of ρ within the set of substituents $j(\sigma_j)$ considered⁵ (vide infra). Substitution of eq. 3 into eq. 7 leads to eq. 8. On final correlation is obtained by substituting eq. 6 into eq. 8.

$$\delta S_{i(j)} = \frac{\rho_{ij}\sigma_j}{\rho_{i(0)}} \quad (8)$$

$$\delta S_{i(j)} = \frac{\rho_{ij}}{\rho_{i(0)} \cdot \rho_{j(0)}} \delta R_{j(0)} \quad (9)$$

or alternatively,

$$\delta R_{i(j)} = \frac{\rho_{i(0)}\rho_{j(0)}}{\rho_{ij}} \delta S_{i(j)} = W \cdot \delta S_{i(j)} \quad (10)$$

It is clear from eq. 10 that increasing reactivity of reactant

j leads to decreasing selectivity only when W is negative, i.e., RSP is valid only when $W < 0$. The fact that the sign of W determines the sign relationship between changes $\delta R_{i(j)}$ and $\delta S_{i(j)}$ is evident from eqs. 6 and 8; the sign of $\delta R_{i(j)}$ is determined by $\rho_{i(j)}$ (eq. 6) whereas that of $\delta S_{i(j)}$ is determined by $\rho_{i(0)}/\rho_{ij}$ (eq. 8), and hence the combination of the two by eliminating σ_j from the two equations, i.e., W , represents the sign correlation of two changes.

Eq. 2 shows that at a noninteractive point⁵ (or magic point),³ $\hat{\sigma}_j$, the reaction becomes isokinetic (irrespective of the substituent i) and the sign of ρ_i reverses. This means that the validity of RSP can also reverse at this point.

Results and Discussion

We can use the combination of the signs of three Hammett type coefficients, $\rho_{i(0)}$, $\rho_{j(0)}$ and ρ_{ij} , to examine how RSP is related to mechanism for certain types of reactions.

For normal S_N2 reactions, i.e., for concerted and backside attack S_N2 processes, the signs of $\rho_X(\rho_{nuc})$ and $\rho_Z(\rho_g)$ are always negative and positive respectively; $\rho_X < 0$ and $\rho_Z > 0$.⁴ However the sign of ρ_Y can be either negative or positive. In a dissociative type of S_N2 reaction it is negative ($\rho_Y < 0$), whereas in an associative S_N2 reaction it is positive ($\rho_Y > 0$). On the other hand the signs of cross-interaction constants for the normal S_N2 reactions are: $\rho_{XY} < 0$, $\rho_{YZ} > 0$ and $\rho_{XZ} < 0$.^{4,6} For a dissociative type S_N2 mechanism, the sign of ρ_{XZ} is often found to be negative ($\rho_{XZ} < 0$), whereas for an associative S_N2 reaction ρ_{XZ} is normally positive ($\rho_{XZ} > 0$) in which case the transition state (TS) variation is controlled thermodynamically.⁴ These signs of $\rho_{i(0)}$, $\rho_{j(0)}$ and ρ_{ij} where $i, j = X, Y$ or Z involved in the nucleophilic substitution reactions can be correlated to validity of RSP as shown in Table 1. For example, the signs of $\rho_{X(0)} (< 0)$, $\rho_{Z(0)} (> 0)$, $\rho_{XY} (< 0)$ and $\rho_{YZ} (> 0)$ are fixed for the normal S_N2 reactions and hence the sign of W involving X and Y and/or Y and Z is determined by $\rho_{Y(0)}$ alone. Thus the negative sign of W is obtained only when $\rho_{Y(0)}$ is negative, in which case the S_N2 reaction proceeds through a loose TS, i.e., RSP is valid only for dissociative S_N2 reactions involving X and Y and/or Y and Z. When ρ_{XZ} is positive, RSP is valid between X and Z in all cases.⁴

A remarkable result in Table 1 is that for rate-limiting breakdown of the tetrahedral intermediate involved in the nucleophilic substitution of carbonyl compounds the sign of W is always (i.e., for all combinations of i and j ; for X and Y, Y and Z, and X and Z) negative and hence RSP holds in general. For this type of mechanism the signs of $\rho_{Y(0)}$ and ρ_{XZ} are invariably positive, in addition to the fixed signs of other constants, i.e., $\rho_{X(0)} < 0$, $\rho_{Z(0)} > 0$, $\rho_{XY} > 0$ and $\rho_{YZ} < 0$.⁶ We note that the acyl transfer with rate-limiting formation of the tetrahedral intermediate is kinetically indistinguishable from an S_N2 process with positive $\rho_{Y(0)}$.

We have carried out analysis for validity of RSP based on the signs of $\rho_{i(0)}$, $\rho_{j(0)}$ and ρ_{ij} (i.e., the sign of W in eq. 5) using 100 reaction series as shown in Table 2. In some cases, more than two substituents are varied so that the number of validity test for RSP exceeds that of the reaction series used. Nucleophiles are in most cases neutral molecules such as anilines, benzylamines, N,N-dimethylanilines and methanol, however anionic nucleophiles, e.g., $\text{XC}_6\text{H}_4\text{S}^-$, XC_6H_4

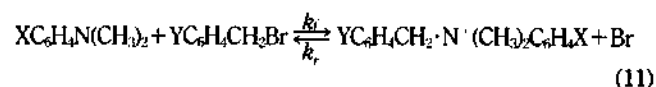
Table 1. The signs of $\rho_{i(i)}$, $\rho_{j(i)}$ and ρ_{ij} where $i, j = X, Y$ or Z and validity of the reactivity-selectivity principle for nucleophilic substitution reactions

	sign				RSP ^a
	$\rho_{i(i)}$	$\rho_{j(i)}$	ρ_{ij}	$W = \rho_{i(i)}\rho_{j(i)}/\rho_{ij}$	
S_N2	$\rho_{X(i)} < 0$	$\rho_{Y(i)} < 0$	$\rho_{XY} < 0$	-	○
		$\rho_{Y(i)} > 0$		+	×
	$\rho_{Z(i)} > 0$	$\rho_{Y(i)} < 0$	$\rho_{YZ} > 0$	-	○
	$\rho_{Y(i)} > 0$	+		×	
	$\rho_{X(i)} < 0$	$\rho_{Z(i)} > 0$	$\rho_{XZ} > 0$	-	○
				$\rho_{XZ} < 0$	+
Carbonyl Add-Elim:					
(i) Rate-limiting	$\rho_{X(i)} < 0$	$\rho_{Y(i)} > 0$	$\rho_{XY} < 0$	+	×
Add.	$\rho_{Z(i)} > 0$	$\rho_{Y(i)} > 0$	$\rho_{YZ} > 0$	+	×
	$\rho_{X(i)} < 0$	$\rho_{Z(i)} > 0$	$\rho_{XZ} > 0$	-	○
				$\rho_{XZ} < 0$	+
(ii) Rate-limiting	$\rho_{X(i)} < 0$	$\rho_{Y(i)} > 0$	$\rho_{XY} > 0$	-	○
Elim.	$\rho_{Z(i)} > 0$	$\rho_{Y(i)} > 0$	$\rho_{YZ} < 0$	-	○
	$\rho_{X(i)} < 0$	$\rho_{Z(i)} > 0$	$\rho_{XZ} > 0$	-	○

^aThe circle and cross symbols stand for *valid* and *invalid* cases, respectively.

COO⁻ etc. are also included. Reactions in classes A and C proceed mostly by a dissociative type S_N2 mechanism so that $\rho_{Y(i)}$ is negative and hence RSP is valid (Table 1). On the other hand class B reactions are associative S_N2 type with $\rho_{Y(i)} > 0$ so that RSP does not hold. There are two distinct type of mechanism for carbonyl compounds: Class I reactions are either associative S_N2 or rate-limiting addition type for which the sign of ρ_{XY} is negative and hence RSP is invalid. In contrast, however, the reactions of carbonyl compounds in class J are reported to proceed by a rate-limiting elimination mechanism so that RSP holds in general. As we have pointed out previously, the reactions of phenacyl compounds (class K) behave like those of class J and the similar mechanism, *i.e.*, two-step mechanism with rate-limiting elimination, can not be ruled out entirely for the phenacyl compounds.⁶ On the whole, the signs of $\rho_{i(i)}$, $\rho_{j(i)}$ and ρ_{ij} for a specific type of reaction agreed well with those listed in Table 1, practically no exception was found. Of course if there is any special mechanistic changes from the typical ones listed in Table 1, the signs can differ from those expected from Table 1.

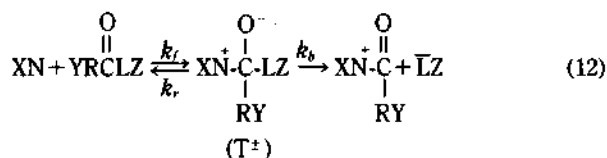
One interesting example (reaction series 10) is the reversible reactions of benzyl bromides with *N,N*-dimethylanilines, eq. 11.⁷ For the forward reaction,


Table 2. Results of analysis for validity of RSP based on the signs of $\rho_{i(i)}$, $\rho_{j(i)}$ and ρ_{ij} (*i.e.*, the sign of W in eq. 5)

Class	Reaction types ^a	Number of Reaction Series	Substituents (i-j)	RSP		Remarks
				(○)	(×)	
A	Benzyl halides	10	X-Y	8	2	Dissoc. S_N2
B	Benzenesulfonyl halides	7	X-Y	0	7	Assoc. S_N2
C	Benzylbenzenesulfonates	16	X-Y	13	0	} Dissoc. S_N2
			Y-Z	6	7	
			X-Z	3	7	
D	Benzylsulfonyl halides	4	X-Y	0	4	
E	α -Substituted benzyl Chlorides	4	X-Y	1	3	
F	Alkyl benzenesulfonates	10	X-Z	10	0	$\rho_{XZ} > 0$
G	Identity exchanges	3	X-Z	0	3	$\rho_{XZ} < 0$
H	Primary and secondary benzenesulfonates	28	X-Y	1	0	} $\rho_{XZ} > 0$
			Y-Z	1	1	
			X-Z	23	3	
I	Benzoyl halides	4	X-Y	0	4	Assoc. S_N2 or Rate-limit Add.
J	Benzoyl benzoates ^b	8	X-Y	8	0	} Rate-limit Elim.
			Y-Z	3	0	
			X-Z	5	0	
K	Phenacyl compounds	6	X-Y	5	1	
			Y-Z	3	0	
			X-Z	3	0	
Total		100		93	42	

^aNucleophiles are mostly neutral molecules, *e.g.*, methanol, anilines, benzylamines and *N,N*-dimethylanilines, but include also some anionic nucleophiles such as $\text{XC}_6\text{H}_4\text{S}^-$, $\text{XC}_6\text{H}_4\text{COO}^-$ etc. ^bInclude cinnamoyl chlorides. ^cThe circle (○) and cross (×) symbols stand for valid and invalid cases, respectively.

k_f , the signs were $\rho'_{X(O)} < 0$, $\rho'_{Y(O)} < 0$ and $\rho'_{XY} < 0$, but for the reverse reaction, k_r , they were $\rho'_{X(O)} > 0$, $\rho'_{Y(O)} < 0$ and $\rho'_{XY} > 0$. The reverse process corresponds to rate-limiting breakdown of the adduct between X and Y. It is quite interesting to compare this reversible process, eq. 11, with aminolysis of a carbonyl compound (reaction series 88-92) involving rate-limiting breakdown of a tetrahedral intermediate, T^\pm , eq. 12.



For eq. 11, the equilibrium $\rho_{X(O)}$ and ρ_{XY} values, i.e., $\rho'_{X(O)}$ and ρ'_{XY} , become large negative since $K = k_f/k_r$, and hence the values for the forward and reverse processes contribute additively.

$$\rho'_{X(O)} = \rho'_{X(O)} - \rho'_{X(O)} = (-) - (+) < 0 \quad (13a)$$

$$\rho'_{XY} = \rho'_{XY} - \rho'_{XY} = (-) - (+) < 0 \quad (13b)$$

However for the acyl transfer with rate-limiting breakdown of T^+ ,

$$k_{\text{obsd}} = Kk_b \text{ where } K = k_f/k_r \quad (14)$$

$$\text{Thus } \rho_{X(\text{obsd})} = \frac{\partial \log k_{\text{obsd}}}{\partial \sigma_X} = \frac{\partial \log k_f}{\partial \sigma_X} - \frac{\partial \log k_r}{\partial \sigma_X} + \frac{\partial \log k_b}{\partial \sigma_X} \\ = (-) - (+) + (-) < 0 \quad (15)$$

$$\text{whereas, } \rho'_{XY(T^\pm)} = \frac{\partial^2 \log k_{\text{obsd}}}{\partial \sigma_X \partial \sigma_Y} = \frac{\partial^2 \log K}{\partial \sigma_X \partial \sigma_Y} > 0^{\delta} \quad (16)$$

(since $\frac{\partial^2 \log k_b}{\partial \sigma_X \partial \sigma_Y} \cong 0$)

This comparison shows that for the normal S_N2 reactions, eq. 11, both $\rho'_{X(O)}$ and ρ'_{XY} are large negative, whereas for the acyl transfers with rate-limiting breakdown of T^\pm , eq. 12, $\rho_{X(\text{obsd})}$ is also large negative but ρ'_{XY} is positive. The sign reversal of ρ'_{XY} is an important difference between the two mechanisms. Despite this sign reversal RSP holds in both cases because of the different signs of $\rho_{Y(O)}$, which is negative in the former but is positive for the latter.

We found two interesting cases in the literature: (i) In the first example, RSP trend correctly reflects the two different mechanisms of acyl transfer i.e., rate-limiting breakdown (RSP valid) and rate-limiting formation (RSP invalid) of T^\pm . For the reactions of substituted pyridines (X) with acetyl chloride and methyl chloroformate (Y) in aqueous solution,⁸ the former had higher reactivity with lower selectivity ($\beta_X = 0.80$) (valid RSP) than the latter ($\beta_X = 0.93$) in the lower pK_a region of pyridines, for which the reaction proceeds with rate-limiting breakdown of T^+ (corresponding to $\rho_{XY} > 0$); this is however reversed to higher selectivity ($\beta_X = 0.24$) with higher reactivity (invalid RSP) for the former than the latter ($\beta_X = 0.15$) in the higher pK_a region of pyridines where the reaction proceeds concertedly or by rate-limiting formation of T^+ (corresponding to $\rho_{XY} < 0$); (ii) In the second example RSP trend fails to predict correct mechanism. For the reactions of substituted phenolate anions (X) with *m*-nitrophenyl, *p*-nitrophenyl and 3,4-dinitrophenyl formates and acetates

(Y),⁹ acetates have lower reactivity with higher selectivity and the sign of ρ_{XY} corresponds to positive. Thus the correct sign of ρ_{XY} ($\rho_{XY} > 0$) and valid RSP for these two series of reactions suggest that the reactions should proceed by rate-limiting breakdown of the anionic tetrahedral intermediate, T^- . However, the authors concluded that the reactions proceed by a concerted mechanism,⁹ for which a negative ρ_{XY} and invalid RSP are predicted (Table 1). Theoretical studies indicated that partially the reactions of *m*- and *p*-nitrophenyl compounds should proceed by rate-limiting breakdown of T^- in the gas-phase;¹⁰ solvation of transition states, however, favors the concerted mechanism as experimentally predicted. These two examples illustrate that the mechanistic criteria based on the signs of $\rho_{i(O)}$, $\rho_{j(O)}$ and ρ_{ij} and validity of RSP provide only necessary conditions.

Eq. 2 indicates that when RSP holds k_{ij} is greater than k_{oo} since W is negative. Thus the noninteractive (or magic) point ($\hat{\sigma}_j$) is situated on the higher reactivity side. Conversely when RSP fails, i.e., $W > 0$, the noninteractive point is located on the side of lower reactivity ($k_{ij} < k_{oo}$). Both examples were indeed experimentally observed.⁵

The results of our analysis can be summarized as follows.

(i) For the normal S_N2 reactions involving X and Y and/or Y and Z RSP is valid only for dissociative type of processes, for which $\rho_{Y(O)}$ is negative; RSP fails for associative S_N2 reactions, for which $\rho_{Y(O)}$ is positive.

(ii) For the acyl-transfer reactions, RSP involving X and Y and/or Y and Z is valid only for rate-limiting breakdown of the tetrahedral intermediate; RSP does not hold for rate-limiting formation of intermediate.

(iii) For all nucleophilic substitution reactions including acyl-transfer, RSP involving X and Z is valid only when ρ_{XZ} is positive, in which case the TS variation is thermodynamically controlled.

(iv) For the acyl-transfer reactions with rate-limiting breakdown of the tetrahedral intermediate, RSP is valid in general.

(v) The mechanistic prediction based on the validity of RSP and the signs of $\rho_{i(O)}$, $\rho_{j(O)}$ and ρ_{ij} is not always definitive, as it is true for all the experimentally based mechanistic criteria.

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Visible Emission Spectra of *o*-Xylyl Radical

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The visible emission spectra of the *o*-xylyl radical in the gas phase have been obtained using a Fourier transform spectrometer coupled with a technique of supersonic expansion. The *o*-xylyl radical was generated in a jet by expansion with an inert buffer gas He from a high voltage dc discharge of the precursor *o*-xylene. The spectra were analyzed on the basis of the rotational contours of the vibronic bands as well as the known vibrational frequencies by a matrix isolation method.

Introduction

Alkyl substituted benzyl radicals^{1,2} have less studied as large aromatic radicals, while much attention has been given on the vibronic structure of benzyl radical as a representative of aromatic free radicals.³⁻⁷ The earlier works of the xylyl radical was reported by Schuler *et al.*⁸ and by Walker and Barrow⁹ in the visible region. Bindley *et al.*^{10,11} made tentative assignments of the vibronic bands from the visible emission spectra of xylyl radicals generated by an electric discharge of the corresponding xylenes and alkyl substituted toluene. Leach *et al.*¹² compared the ring vibrational modes and frequencies of the corresponding xylyl radicals with those of xylene species using a matrix isolation method. The existence of the doublet states of the xylyl radicals which lie very closely to each other was identified by Hiratsuka *et al.*¹³ Charlton and Thrush¹⁴ measured the lifetime of radicals using a technique of laser induced fluorescence. Most of earlier works on *o*-xylyl radical are limited to low resolution studies of the vibrational structure of the gas phase¹⁰ and the solid solution emission.^{12,15} For high resolution work, Cossart-Magos *et al.*¹ extended the rotational contour analysis of benzyl radical to that of the *o*-xylyl. From the comparison of calculated with observed spectra, they have determined the direction of the dipole moment of the molecule upon the electronic excitation. Also, there has been suggested that the strength of the electronic interaction between the methyl group and the benzene ring be undoubtedly the second order in *o*-xylyl as compared to the interaction between the methylene group and the ring. Thus, the electronic states of the *o*-xylyl radical should exhibit a close relation to those of the benzyl radical. The identification of the electronic states was carried out by Cossart-Magos *et al.*¹ who concluded that the lowest excited electronic state of *o*-xylyl radical is of ²A₂ symmetry from which the two lowest excited electronic

states are similar to those of the parental benzyl ¹A₂ and ²B₂ states. As shown by Selco and Carrick recently,^{3,7} the accurate frequencies of vibronic bands in emission could be determined from the rotationally cooled but vibronically hot spectra.

In this study, we describe the observation and the analysis of the vibronic bands of the visible electronic emission spectra of *o*-xylyl radical in the gas phase.

Experimental Details

The observation of low resolution visible emission spectra of *o*-xylyl radical has been performed using the experimental setup similar to those described previously.¹⁶⁻¹⁸ The parent compound *o*-xylene of the spectroscopic grade was purchased commercially from Aldrich and used without further purification. The vapors of the compound were expanded with an inert carrier gas He through 0.2 mm diameter of quartz nozzle into the vacuum chamber made by a six-way cross Pyrex glass tube of 5.0 cm in diameter. The concentration of the parent compound in a carrier gas could be controlled by immersing the sample in a temperature-controllable water bath or by adjusting the opening of the bypass valve of the carrier gas. In this experiment, the concentration of the precursor was adjusted for the maximum fluorescence and believed to be about 1% in the gas mixture.

For the nozzle which is similar to that developed by Engelking,¹⁹ a 3 mm thick walled glass tube was flame heated until one end was narrowed to the desired size opening. The *o*-xylyl radical was formed in a green jet by flowing the gas mixture over an electric dc discharge between the anode fixed inside the nozzle and the pump which acts as the cathode. The sharpened stainless steel anode of 2 mm in diameter was connected to a 3000 V dc power supply via a 500 K Ω current limiting ballast resistor. The condition