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PYRIDINIUM ION REACTIVITIES: SUBSTITUENT EFFECT ON THE REVERSE MENSCHUTKIN REACTION OF 1-METHYLPYRIDINIUM CATIONS WITH IODIDE ANION

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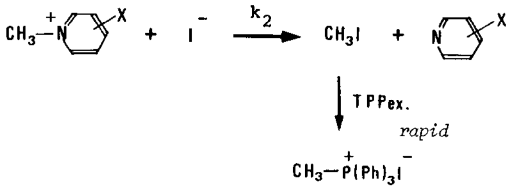
Abstract: Substituent effect on the reverse Menschutkin reaction of 1-methylpyridinium cations with iodide anion can be described in terms of the LArSR equation with ρ=3.60 which provides evidence against very late transition state of the nitrogen-to-iodine transmethylation.

Studies of aliphatic nucleophilic substitution reactions involving pyridines as nucleophiles or leaving groups have been extended in the field of physical organic chemistry.1,2) Among them, Arnett et al. importantly pointed out absence of selectivity-reactivity relationship in the Menschutkin-type reactivities of substituted pyridines with various alkylating agents, such as alkyl iodides or alkyl sulfonates.1) The observation has attracted much attention especially to pyridine and/or pyridinium ion reactivities.3) There are, however, very few systematic substituent effect studies on pyridinium ion reactivities until today;4) almost all of existing data are based on pyridine reactivities.5)

Here, the reverse Menschutkin reaction of 1-methylpyridinium cations with iodide anion in acetonitrile was chosen as a typical system for pyridinium ion reactivities to be investigated. In this paper, we describe the substituent effect on the reverse Menschutkin reaction which allows to estimate that on the equilibrium by their combination between the reverse and the corresponding forward rate systems,1) and then to characterize the nature of the transition state of the system in question.1,3)



The reverse Menschutkin reaction could be successfully followed by using the procedure of Metzger et al.,4) where excess triphenylphosphine (TPP) was added in the system as a trap reagent towards CH_3I. The second order rate constants (k_2) were determined by means of ^{31}P NMR quantitative measurements for the product, $CH_3TPP^+I^-$.6) Confirmation of the data set (Table 1) was achieved as follows. (1) Reproducibility for rate measurements was ca. ±3%. (2) Generally, rate constant for reaction between a cation and an anion depends on the ionic strength of the solution. Observed dependence of k_2 on ionic strengths was closely parallel to that for the reaction of 1-benzyl-2,4,6-triphenylpyridinium cation with iodide anion reported by Katritzky et al. (UV method).7) (3) Activation parameters were nearly equal to the literature values.1) (4) Increase of TPP concentration showed no appreciable change of k_2 at least for the parent (H) or more electron attracting substituent.

Table 1. Kinetic Data for the Reverse Menschutkin Reaction of Substituted 1-Methylpyridinium Cations with Iodide Anion in Acetonitrile

Subst	μ^a M	$[PyI]_0$ M	$[TPP]_0$ M	Temp °C	$10^3 k_2$ $s^{-1}M^{-1}$	ΔH* kcal/mol	ΔS* e.u.
3-Cl	0.025	0.025	0.035∿0.125	130	3.75 ± 0.05^b		
	0.040	0.040	0.160∿0.200	130	3.13 ± 0.01^b		
	0.050	0.050	0.125	130	2.42 ± 0.07^c	33.2^d	11.2^d
	0.050	0.050	0.125	115	0.470		
	0.100	0.050	0.158	130	1.30		
H	0.025	0.025	0.150∿0.250	130	0.153 ± 0.001^b		
	0.040	0.040	0.250	130	0.118		
$3,5-Cl_2$	0.025	0.025	0.125	115	15.1 ± 0.3^b	29.7^e	9.1^e
	0.025	0.025	0.125	100	3.09		

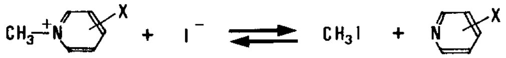
a) Ionic strength. b) Average of 2 different determinations. c) Standard deviation from 8 determinations. d) [ΔH*;ΔS*]=[33.2;10.2].1) e) [ΔH*;ΔS*]=[30.4;7.8].1)

The substituent effect on the reverse Menschutkin reaction is summarized in Table 2. The pyridinium ion reactivity set including meta substituents and para pi-acceptor ones can be successfully described by the LArSR equation (Fig. 1).[8)]

$$\log(k/k_o) = 3.60\ (\ \sigma^o - 0.59\Delta\bar{\sigma}_R^-\ ) \qquad [r=0.996, s=\pm 0.09, n=9]$$

The large ρ value is identical with the ρ_m (=3.63) and the negative r^- value is consistent with the suppressed resonance contribution from para pi-acceptor substituents in the system which is quite similar to that observed in the dissociation of pyridinium ions.[9)]

By the combination with the ρ^f for the corresponding forward Menschutkin reaction under the same conditions (ρ_m^f=-2.54 at 25 °C, $\rho_m^f \simeq$-2.13 at 130 °C),[1)] the substituent effect (ρ^K) on the equilibrium (1) is estimated to be 5.7 (at 130 °C).[12)]


(1)

This just corresponds to the ρ for the carbon-basicity of pyridines which must be compared with that for the proton-basicity of pyridines (ρ=6.2).[9)] Accordingly, the Brønsted α value is obtained to be 0.63,[13)] indicating that the reverse Menschutkin reaction proceeds through very normal S_N2 transition state, not very late one,[1)] that is, ca. 60% C-N bond breaking, as far as the

Table 2. Substituent Effect on the Reverse Menschutkin Reaction of Substituted 1-Methylpyridinium Cations with Iodide Anion[a]

Subst	Followed[b] %	10^3k_2 $s^{-1}M^{-1}$	$\log(k/k_o)$	σ^o [c]	$\Delta\bar{\sigma}_R^-$ [c]
4-C_6H_5	60	0.0997	-0.186	0.04	0.16
H	50	0.153	0.000	0.00	0.00
4-COC_6H_5	50	0.825	0.732	0.47	0.39
4-$COCH_3$	70	0.872	0.756	0.40	0.36
3-$COCH_3$	55	1.16	0.880	0.28[d]	0.00
3-Cl	75	3.75	1.389	0.37	0.00
4-CN	85	6.62	1.636	0.63	0.31
3-CN	75	17.2	2.051	0.58	0.00
3,5-Cl_2	80	65.7[e]	2.633	0.73	0.00

a) In acetonitrile at 130±0.03 °C; under the constant ionic strength of 0.025 M; $[PyI]_o$=0.025 M; $[TPP]_o$=0.125 M. b) % Completion of the reaction followed. c) Aprotic solvent modified values, Ref. 10. d) From Ref. 11. e) Extraporated (Table 1).

substituent effects on the rates and the equilibrium are concerned.

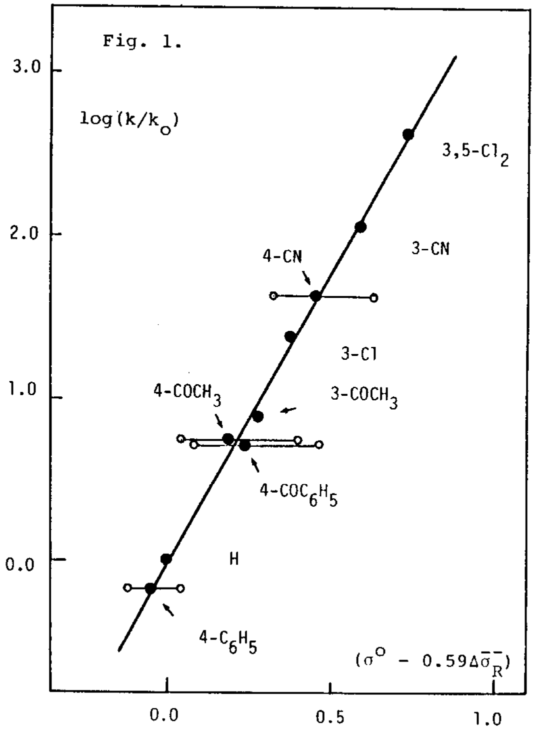


Fig. 1.

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12) $\rho^K = \rho^r - \rho^f = 3.60 - (-2.13) = 5.7$.
13) Brønsted $\alpha = 3.60/5.7 = 0.63$.

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