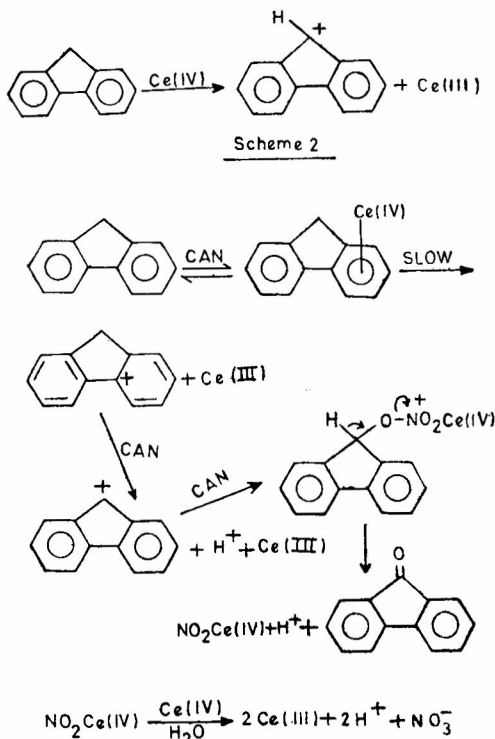Fig. 1 — (A) log $(k/k_H)_{65°}$ versus log $(k/k_H)_{50°}$ in the case of oxidation of fluorenes by ceric ammonium nitrate. (B) log $(k/k_H)_{65°}$ versus log $(k/k_H)_{50°}$ in the case of oxidation of fluorenes by ammonium metavandate. (C) log $(k/k_H)_{65°}$ for V(V) series versus log $(k/k_H)_{65°}$ for Ce(IV) series. [(1) 2-Nitrofluorene, (2) 2-chlorofluorene, (3) 2-bromofluorene, (4) 2-iodofluorene and (5) 1-methylfluorene]

Scheme 2

Scheme 3

enabling CAN to abstract selectively an electron, resulting in the formation of a cation-radical.

Curiously, a plot of log $|(k/k_H)_{CeIV}$ versus $log(k/k_H)_{V(V)}$ at 65° gives a very good correlation, indicating similar transition state in both the oxidation series.

One of the authors (S.N.) thanks the CSIR, New Delhi, for financial assistance.

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Effect of Structure on Activation Parameters

S. NARASIMHAN & N. VENKATASUBRAMANIAN

Department of Chemistry, Vivekananda College
Madras 600004

The effect of substituents on the activation parameters has been discussed. The trend observed is explained on the basis of energies of the ground state and activated complex.

IN the oxidation of fluorenes by ammonium metavanadate, a good linear free energy relationship as evidenced by a satisfactory Hammett plot was obtained[1]. But a plot of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (the isokinetic plot) showed a marked deviation for the 2-nitrofluorene molecule. In view of a recent communication[2] on the nature of variations of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ with σ, we have analysed our results in a similar fashion and the results are reported in this note.

The rate constants for the V(V) oxidation of the 2-substituted fluorenes and the derived activation parameters are presented in Tables 1 and 2.

The enthalpy of activation of the reaction increases with decrease in the electron density at the reaction centre as revealed by σ values of the 2-substituents. These data do not have a linear

TABLE 1 — TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS

[[V(V)] = 0·004M; [substrate] = 0·024M; μ = 3·5; [H₂SO₄] = 1·0M; solvent: 80% HOAc-20% H₂O (v/v)]

Substrate	$k_2 \times 10^2$ (litre mole⁻¹ sec⁻¹) at		
	50°	57·5°	65°
1-Methylfluorene	2·98	4·98	9·97
Fluorene	2·38	4·26	8·02
2-Iodofluorene	0·88	1·57	3·21
2-Chlorofluorene	0·33	0·74	1·56
2-Bromofluorene	0·39	0·75	1·65
2-Nitrofluorene	0·017	0·038	0·077
2-Ethylfluorene	74·12	46·00*	27·23†

*At 40°. †At 30°.

TABLE 2 — ACTIVATION PARAMETERS FOR THE
OXIDATION OF SUBSTITUTED FLUORENES BY
AMMONIUM METAVANADATE

Substate	E_a kcal	$\Delta H^{\ddagger}$ kcal	$-T\Delta S^{\ddagger}$ kcal	$\Delta G^{\ddagger}$ kcal
2-Ethylfluorene	10·23	9·58	9·04	18·62
1-Methylfluorene	16·38	15·73	4·99	21·28
Fluorene	16·57	15·92	5·55	21·47
2-Iodofluorene	18·96	18·31	3·20	21·51
2-Bromofluorene	20·42	19·77	2·27	22·04
2-Chlorofluorene	21·05	20·40	1·75	22·15
2-Nitrofluorene	21·93	21·28	3·29	24·57

relationship, but tend to fall on the branches of a hyperbola (Fig. 1A) correlated by expression (1).

$$\Delta H^{\ddagger} = 26 \cdot 8 \left[\frac{\sigma_p + 0 \cdot 4776}{\sigma_p + 0 \cdot 8042} \right] \qquad \ldots(1)$$

It is curious that $T\Delta S^{\ddagger}$ also varies in a similar fashion with σ_p (Fig. 1B). The curve is best represented by the hyperbola correlated by expression (2).

$$T\Delta S^{\ddagger} = -5 \cdot 0176 \sigma_p - 21 \cdot 469 + 26 \cdot 8 \left[\frac{\sigma_p + 0 \cdot 4776}{\sigma_p + 0 \cdot 8042} \right] \ldots(2)$$

(at 323°K)

However, it is interesting to note that $\Delta G^{\ddagger}$ varies linearly with σ_p (Fig. 1C). The fact that
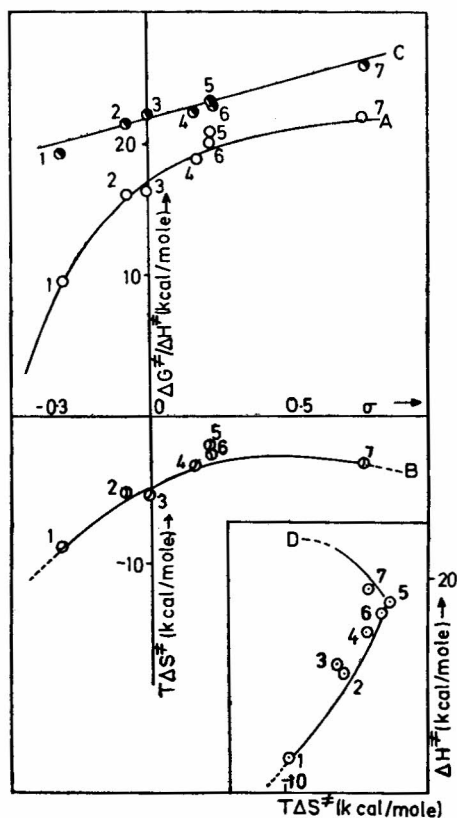

Fig. 1 — (A) Variation of $\Delta H^{\ddagger}$ with σ_p, (B) variation of $T\Delta S^{\ddagger}$ with σ_p, (C) variation of $\Delta G^{\ddagger}$ with σ_p, (D) variation of $\Delta H^{\ddagger}$ with $T\Delta S^{\ddagger}$ [(1) 2-Ethylfluorene, (2) 1-methylfluorene, (3) fluorene, (4) 2-iodofluorene, (5) 2-chlorofluorene, (6) 2-bromofluorene, (7) 2-nitrofluorene. The curves drawn correspond to the respective theoretical expressions (1), (2) and (5)]

$\Delta G^{\ddagger}$ is a linear function of σ and $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ are not, indicates that a common function between $T\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ exists, i.e.

$$\Delta H^{\ddagger} = A_1\sigma + B_1 + f(\sigma) \qquad \ldots(3)$$

$$T\Delta S^{\ddagger} = A_2\sigma + B_2 + f(\sigma) \qquad \ldots(4)$$

Since $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ a linear relationship between $\Delta G^{\ddagger}$ and σ can be derived, which is of the form

$$\Delta G^{\ddagger} = 5 \cdot 0176 \sigma_p + 21 \cdot 469 \qquad \ldots(5)$$

This is in good agreement with the least square analysis of $\Delta G^{\ddagger}_{\text{exptl}}$ given by Eq. (6).

$$\Delta G^{\ddagger}_{\text{exptl}} = 5 \cdot 126 \ \sigma_p + 20 \cdot 808 \qquad \ldots(6)$$

Fig. 1D represents the curve for the plot of $\Delta H_{\text{Calc.}}$ and $T\Delta S^{\ddagger}_{\text{Calc.}}$ from Eqs. (1) and (2). This curve accounts for the experimental points.

The theoretical curves from expressions (1) and (2) are in excellent agreement with the rate data. This indicates that the empirical relationships for $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ are valid for the substituted fluorenes studied. Thus the nonlinear variation of $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ with σ_p explains the observed deviation in the isokinetic plot. Also, the existence of a common function between $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ indicates a linear variation of $\Delta G^{\ddagger}$ with σ_p which is actually obtained.

It is interesting to study the variation of $\Delta H^{\ddagger}$ versus σ_p and $T\Delta S^{\ddagger}$ versus σ_p obtained in the present case. The concave downward curve indicates that the enthalpy of activation increases with increasing σ. However, a steep decrease in $\Delta H^{\ddagger}$ is observed with electron releasing substituents. This can be explained by considering the energy of the ground state and the activated complex.

It is known that the methylene group in fluorene (I) can interact with the rings by hyperconjugation[3].

Such an interaction is facilitated by electron withdrawing groups in the 2-position, thus stabilizing the ground state of the molecule to a great extent. This increases, obviously, the enthalpy of activation. On the contrary, electron releasing groups at the 2-position destabilize the structure (II) by opposing the hyperconjugative effect. The ground state is therefore not stabilized. The activated complexes envisaged in the reaction is the cation radical of the type[1] (III).

Hence the activated complex is stabilized by hyperconjugation both by the ethyl substituent and by the methylene group. This decreases largely the enthalpy of activation. An interesting extrapolation is the value of σ_p when $\Delta H^{\ddagger} = 0$. When $\sigma_p^+ = -0 \cdot 4776$, $\Delta H^{\ddagger}$ becomes zero, and the reaction is instantaneous. Thus 2-methoxyfluorene reacts instantaneously under the experimental conditions.
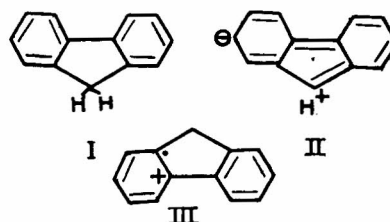
The trend observed in $T\Delta S^\ddagger$ versus σ curve can be explained by considering the solvation of the activated complex. The activated complex is more polar in the case of 2-ethylfluorene resulting in a large decrease in entropy. The electron withdrawing substituents render the molecule a dipole resulting in the solvation of the ground state. Thus, a smaller change in $\Delta S^\ddagger$ is effected.

One of the authors (S.N.) thanks the CSIR, New Delhi for financial assistance.

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Oxopentafluoroniobates(V)

A. K. SENGUPTA & N. G. MANDAL

Department of Chemistry, Kalyani University
Kalyani 741235

The oxopentafluoroniobates (V) of the type [(CH$_3$)$_4$N] [HNbOF$_5$] and [M(py)$_4$][NbOF$_5$], where M = Cu, Ni, Zn, Cd, Co and py = pyridine, have been prepared. The IR spectra and TGA data for the above compounds are reported.

A LARGE number of oxopentafluoroniobates[1,2] are known. In the present paper several new oxopentafluoroniobates of $(CH_3)_4N^+$ and [M(py)$_4$]$^{2+}$, where M=Cu, Ni, Zn, Cd, Co, and py=pyridine, are reported. The compounds are studied through thermogravimetry and infrared spectroscopy.

Niobium pentoxide (purity about 99·9%) obtained from the BARC was utilized in the present work. Methods for determining Nb, F and N in the compounds were as before[3]. For estimating niobium in the fluoroniobates containing Ni^{2+}, Cu^{2+} or Co^{2+} ion the sample was fumed with H$_2$SO$_4$, diluted and tartaric acid added. From the solution Ni^{2+}, Cu^{2+} or Co^{2+} were precipitated by standard methods and estimated, whilst from the filtrate niobium was precipitated as its cupferronate and estimated as Nb$_2$O$_5$. The presence of Zn and Cd along with Nb does not interfere in the precipitation of niobium as its cupferronate from the acidic oxalate solution. For determining fluorine as PbClF it was separated from Nb and the other metals by fusing the samples with K$_2$CO$_3$ and extracting with water.

Preparation of oxopentafluoroniobates — Tetramethylammonium compound was prepared as follows: Nb O$_5$ (2 g) was dissolved in minimum volume of HF (40%) and to it [(CH$_3$)$_4$N]OH (1·4 g) acidified with HF (10%) was added. The mixture was evaporated on a water-bath to crystallization. The colourless crystals were filtered, pressed between filter papers and dried to constant weight *in vacuo* over H$_2$SO$_4$ and KOH and analysed. The compound was highly soluble in water and hydrolyse on boiling. The pH of its aqueous solution is ca. 3. The molar conductivity of its aqueous solution at different dilutions also indicate progressive dissociation of the complex ion with dilution.

Tetrapyridinemetal(II) *oxopentafluoroniobates* — Copper compound was prepared as follows: Nb$_2$O$_5$ (2 g) was dissolved in a minimum amount of HF (40%) and then excess pyridine was added to it. Copper carbonate (1·9 g) was suspended in pyridine (5 g) and HF (3M) was added till copper carbonate dissolved almost completely. The solution was filtered and then added to the niobium solution with stirring when immediately deep blue precipitate appeared. The precipitate was filtered, washed with water, filter-pressed and dried *in vacuo* over fused CaCl$_2$; yield 7·3 g.

Light blue nickel compound was prepared as above starting from its carbonate (1·8 g), Nb$_2$O$_5$ (2 g), pyridine and HF; yield 6·6 g. The cadmium compound (white polyhedra) was obtained as above by adding a solution of tetrapyridinecadmium nitrate [prepared by dissolving cadmium carbonate (2·6 g) in minimum amount of HNO$_3$(2N), and adding pyridine (5 g)] to a solution prepared by dissolving Nb$_2$O$_5$ (2 g) in HF (10%) and then neutralizing with pyridine. The zinc and cobalt compounds were prepared in a similar manner as the cadmium compound starting from their respective carbonates.

The analytical data are given in Table 1. The above compounds hydrolyse in water with the generation of pyridine and are insoluble in common organic solvents.

The strong bands for Nb=O in the IR spectra were found to occur at 892-952, 918, 930-960, 935-958, and 918 cm^{-1} for the Cu, Ni, Zn, Cd and Co compounds respectively. Thus it is observed that νNb=O appears in the region, as observed[2] in the case of M^{II}NbOF$_5$, nH$_2$O (M=Cu^{2+}, Mn^{2+}, etc.). The data suggest that in the above tetrapyridinemetal compounds the NbOF$_5^{2-}$ anion remains unaltered. Due to the limitations of the instrument bands below 700 cm^{-1} could not be recorded. In

TABLE 1 — ANALYTICAL DATA OF OXOPENTAFLUORONIOBATES

Compound	Found (%)				Calc. (%)			
	M(II)	N	Nb	F	M(II)	N	Nb	F
[(CH$_3$)$_4$N][HNbOF$_5$]		4·96	33·92	34·86		5·02	33·32	34·06
[Cu(py)$_4$][NbOF$_5$]	10·75	9·51	16·18	16·36	10·89	9·6	15·92	16·29
[Ni(py)$_4$][NbOF$_5$]	9·66	9·78	16·38	16·55	10·15	9·68	16·05	16·42
[Zn(py)$_4$][NbOF$_5$]	---	9·33	16·09	15·80	—	9·57	15·87	16·23
[Cd(py)$_4$][NbOF$_5$]	—	8·81	14·94	15·45	—	8·86	14·69	15·05
[Co(py)$_4$][NbOF$_5$]	10·32	9·62	16·39	16·17	10·18	9·68	16·05	16·42