Mechanistic Implication of "LFER" in the Oxidation of Acetophenones by Vanadium(V)

M. S. Kelkar, R. Shanker, and G. V. Bakore
Chemistry Department, M. B. College Buildings, University of Udaipur, Udaipur, India

(Z. Naturforsch. **31 b**, 140–141 [1976]; received November 11, 1974)

Mechanistic Implication, Acetophones, Vanadium(V)

A linear combination of the effect of substituents on pre-equilibrium and subsequent rate limiting step, K and k respectively, describes the structure reactivity relationship of the form $\log k/k_0 = -2.17\sigma^+ + 3.3\,\sigma$, where former corresponds to V(V)-ketone complex and the latter its rate limiting disproportionation.

Linear free energy relationships, LFER's, like Hammett equation[1] are often used to demonstrate structure-reactivity relationship. The sometimes written but nearly always implied is that the entropy must remain constant or be proportional to the free energy. This latter notion is embodied in the ideas concerning the isokinetic relationship, IKR, and its significance to the validity of LFER. The reactions of acetophenones with semicarbazide[2] follows both LFER and IKR. However, the complexity in the mechanism of semicarbazone series are such that a Hammett plot is not expected under general conditions[3] and a detailed analysis is warranted. We report here our findings on the reaction of acetophenones with vanadium(V) under acid conditions.

Reagents used were either chemically pure (AnalaR) or were purified by standard methods. The reaction was followed spectrophotometrically at 680 and 750 nm using Hilger pattern Biochem absorptiometer. The cell tube was currounded by a metallic block through which water was circulated from a thermostat which maintained the temperature constant to within ± 0.02 °C. The error in the measurement of rate constants is not greater than $\pm 5.0\%$ corresponding to an error of ± 1.5 kcal/mole in the calculated energy of activation and ± 5.0 e.u. in the entropy of activation. Activation parameters were evaluated using Eyring's equation where $(ek/h) = 5.665 \times 10^{10}$ deg.$^{-1}$ sec^{-1}.

Results and Discussion

Effect of substituents on rate of oxidation has been recorded in the Table. A plot of log k_1 against σ^+ or σ, where σ is Hammett substituent constant and σ^+ are modified σ values for para substituents which have a direct resonance interaction with the benzene ring[4], do not show any correlation (*cf.* Fig. 1). However, the trend seems to be a curve which is concave downward. This type of behaviour has been correlated with the change in rate limiting step with otherwise constant mechanism[5] or may be expected if the observed rates are the resultant of substituent effects on the two steps K_{eq} and k. Thus

Table. Rate of oxidation of acetophenones and their activation parameters.

[Ketone]: 1.0 M, [H_2SO_4]: 1.0 M; Temperature: 40 °C

Acetophenones	H	p-NO_2	p-OMe	p-Br	p-Cl	m-NO_2
$k_1 \times 10$ sec^{-1}	2.1	8.1	4.4	3.1	7.5	7.7
ΔE^* kcal/mole	25.6	14.3	14.6	14.5	13.8	20.0
ΔS^* e.u.	+ 4.0	—31.4	—26.0	—30.0	—30.0	— 11.0

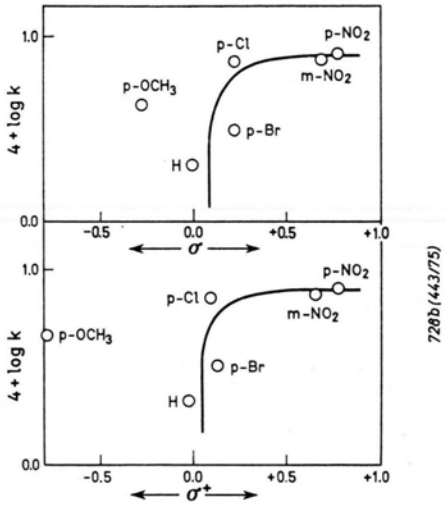

Fig. 1. A Hammett plot.

$$\text{Ketone} + V(V) \underset{}{\overset{K_{eq}}{\rightleftharpoons}} >C{=}O \rightarrow V(V) \xrightarrow[k]{\text{slow}} \text{rpoducts.}$$

The donor characteristic of the carbonyl group in ketones is well known and a substrate-vanadium(V) complex would be greatly stabilised by electron donor para substituents, thus following a log k—σ^+ correlation.

A separation of the two effects can be accomplished by a linear combination of the two – one for pre-equilibrium effect, $\varrho_1\sigma^+$ and the other for the slow step, $\varrho_2\sigma$ reflecting the electronic requirements at the α-C atom (α to C=O). Thus the structure-reactivity relationship can be expressed as:

Requests for reprints should be sent to Prof. G. V. Bakore, Department of Chemistry, Maharana Bhupal College Buildings, *Udaipur*, India.

$$\log k/k_0 = \varrho_1 \sigma^+ + \varrho_2 \sigma \quad (1)$$

This type of treatment is analogous to the one used by YUKAWA and TSUNO[6]. The first value is a measure of resonance interaction of substituents on the donor characteristic of the carbonyl oxygen and can be measured by their basicities. The basicities of acetophenones follow σ^+ with ϱ^+ (here ϱ_1) = —2.17. Assuming this value of ϱ_1 here, we have equation (1) as:

$$\log k/k_0 = -2.17\sigma^+ + \varrho_2 \sigma$$

or

$$\log k/k_0 + 2.17\sigma^+ = \varrho_2 \sigma \quad (2)$$

A plot of $\log k_1 + 2.17\sigma^+$ against σ gives a straight line (Fig. 2) with $\varrho_2 = +3.3$ and correlation coefficient equal to 0.995. A positive value of ϱ_2 is consistent with the hypothesis that H of C–H bond is removed as a proton. Thus the observed curvature (non-validity of Hammett equation) reflects an incomplete cancellation of substituent effects on the two steps rather than a change in the rate limiting step.

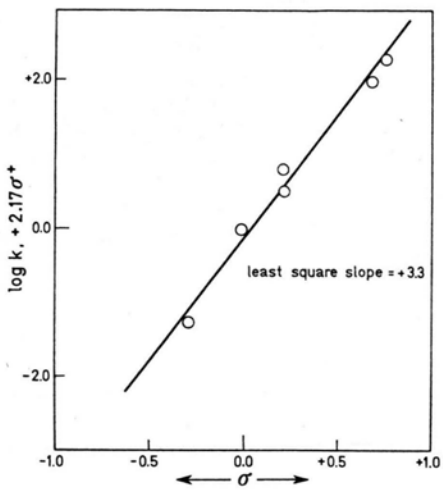

Fig. 2. Structure-reactivity relationship.

A plot of ΔE^* against ΔS^* gives a straight line with slope, β, (isokinetic temperature) = 327 °K. The validity of ΔE^*—ΔS^* plot as a criterion for IKR has recently been questioned[8]. The isokinetic model is better understood if it is formulated as a relation between the reactivities (natural logarithms of the rate constants) of different reactions *i.e.* if these obey the linear Arrhenius equation:

$$\ln k_{ji} = A_i + B_i (1/T_{ji} - 1/T_0) \quad (3)$$

where T is in degrees Kelvin and T_0 an arbitrary fixed temperature. A direct consequence of (3) is that the reactivities at two temperatures T_1 and T_2 be linearly dependent[9]. Thus

$$\ln K_{T_2 i} = a + b \ln k_{T_1 i} \quad (4)$$

The parameters a and b depend only on the choice of T_1 and T_2. A plot of $\log k_{T_1}$ against $\log k_{T_2}$ does not show a linear behaviour at all possible combinations of T_1 and T_2. We, therefore feel that IKR is non-valid here. A perfect ΔE^*—ΔS^* plot seems to be due to equal free energies of the reactions. This series, therefore, does not seem to follow Hammett equation and IKR and the general classification of thermodynamic behaviour[10].

One of us (M.S.K.) is thankful to the Government of M.P. for grant of leave of absence.

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