Use of the Tool of Increasing Electron Demand in Determination of the Status of the Yukawa–Tsuno (YT) Equation

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The YT eq 1[2] has been widely used in correlation of reactions in which a positive charge is generated in conjugation with the site of aryl substitution.

$$\log k/k_0 \text{ or } \log K/K_0 = \rho\{\sigma + r(\sigma^+ - \sigma)\} \qquad (1)$$

Deviations of the parameter r from unity arise from three possible effects. (1) The substituted aryl ring is twisted out of full conjugation with the reaction site by steric interaction: a convincing example of this is afforded by the $\mathrm{p}K_R{}^+ - \sigma^+$ correlation for triphenylcarbinols.[3] (2) The overall reaction correlated is of two steps, a preequilibrium and a rate-limiting step, one of which correlates with σ and the other with σ^+. The initial reaction used to elucidate eq 1, the acid-catalyzed decomposition of diazoacetophenones,[4] can be shown[5] to fall into this category. Effects 1 and 2 thus lend themselves in general to clear and unequivocal experimental elucidation. (3) The electronic demand of the reaction site differs from the defining reaction, the S_N1 hydrolysis of substituted phenyldimethylcarbinyl chlorides,[6] a factor which should be reflected in both the ρ and r values of eq 1. This last effect is the one envisaged by Yukawa and Tsuno[2] as responsible for the operation of the YT eq 1 in the cases they considered, and this has received wide support.[7,8]

On the other hand, use of the extended selectivity principle (ESP),[6] in which $\log k_X/k_H$ is plotted against ρ,

$$\log k_X/k_H = \rho\sigma^+ \qquad (2)$$

where X is a strong resonance donor, generally affords reasonable straight lines indicative of an essentially constant σ^+ value. Nevertheless, occasional random deviations from precise agreement with the ESP do occur and therefore, because of the wide range of reaction types and conditions encompassed in the definition of the ρ values, there must be some doubt whether these are due to experimental errors or mechanistic ambiguities, or represent realistic manifestations of the operation of eq 1 due to effects 1, 2, or 3.

A critical, sensitive and unequivocal test of the ESP/YT treatments is therefore urgently required, and this is now amply provided by the tool of increasing electron demand initiated by Gassman and Fentiman[10] and extensively exploited by Brown and co-workers.[11] This is particularly appropriate for the following reasons. First, a standard reaction, the S_N1 hydrolysis of tertiary carbinyl systems, has been studied; the procedure is specifically designed to provide different degrees of stabilization of a carbonium ion attached to an aromatic ring, and thus differing extents of charge formation in the transition state of an S_N1 process as measured by the widely variable and often very large ρ values, *precisely the situation the YT equation was set up to elucidate* and designated here as effect 3. Second, the leaving group, p-nitrobenzoate (OPNB), is kept constant, as are the conditions for solvolysis (80% aqueous acetone at 25 °C). Third, sensitive tests[12,13] exist for detection of steric interactions in the molecules considered, which could lead to deviations from the ESP and values of r in the YT equation differing from unity because of ring twisting (effect 1, although these tests also give indications of steric interactions other than twisting—see below.). Fourth, and obviously most important, the substit-

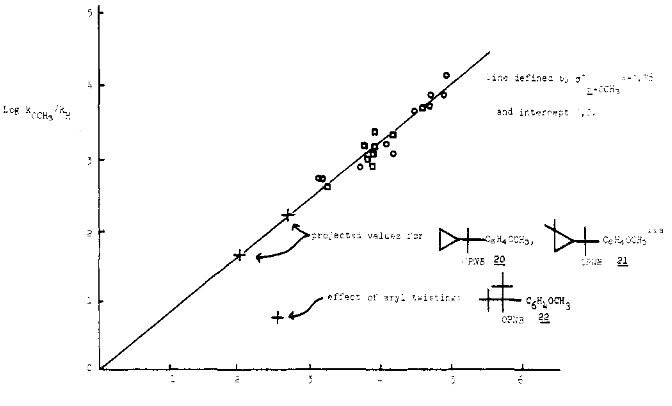
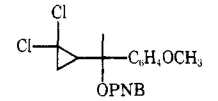
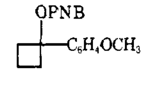


Figure 1. ESP plot: $\log k_{OCH_3}/k_H$ vs. ρ for S_N1 hydrolysis of tertiary carbinyl systems.[11] Full line is drawn with slope −0.78 (σ^+ value for p-OCH_3[6]) and intercept 0,0. ⊙ Substrates for which the p-methoxy compound was measured directly (1–10).



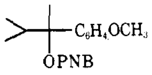
1

(log k_{OCH_3}/k_H 4.11, ρ −4.99)



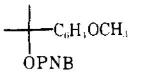
2

(3.89,−4.91)



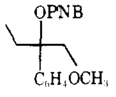
3

(3.84,−4.76)



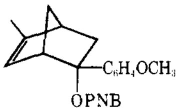
4

(3.71,−4.72)



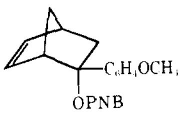
5

(3.61,−4.52)



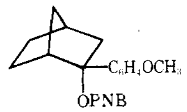
6

(3.07,−4.19)



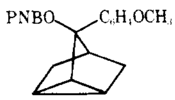
7

(3.13,−4.17)



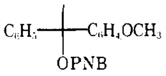
8

(2.88,−3.77)



9

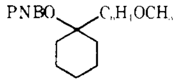
(2.63,−3.27)



10

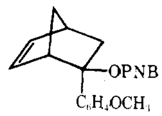
(2.61,−3.23)

▣ Substrates for which the p-methoxy compound was measured as the benzoate and multiplied by 20.8[14] (11–19).



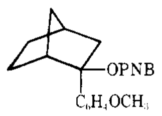
11

(3.66,−4.60)



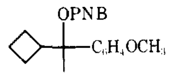
12

(3.31,−4.21)



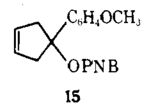
13

(3.18,−3.96)



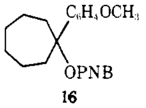
14

(3.06,−3.94)



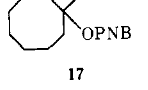
15

(3.35,−3.92)



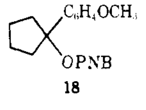
16

(2.89,−3.87)



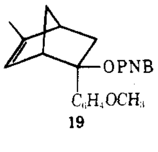
17

(2.94,−3.83)



18

(3.18,−3.82)



19

(2.51,−3.28)

Points	Slope	Intercept	Corr coeff
1–10	−0.828 (±0.065)	−0.174	0.976
1–10 and 0,0	−0.795 (±0.027)	−0.030	0.994
1–19 and 0,0	−0.805 (±0.029)	−0.050	0.988

0022-3263/78/1943-1814$01.00/0

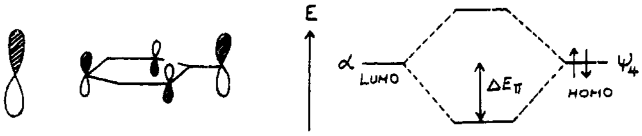


Figure 2. NBMO interaction between vacant carbon p orbital and benzyl anion.

uents measured include p-OCH$_3$, whose σ^+ value (−0.78) differs widely from its σ value (−0.27).

Figure 1 shows the resultant ESP plot of the log k_{OCH_3}/k_H values vs. ρ.[11] The correlation of the experimental values with the line defined by the coordinates (0,0) and the slope −0.78 is excellent. The graph also shows data for systems **11–19** obtained by extrapolation from benzoate hydrolysis, which also closely fit the correlation. This result clearly indicates that effect 3 is not a significant contributor to deviations from the ESP for para-substituted resonance donors. Any such deviations must be sought in the operation of effects 1 or 2, experimental errors or mechanistic complexities, of which effect 2 forms an example. **6, 7,** and **16** have been found previously to have a degree of steric acceleration associated with them;[13] however, this steric effect does not prevent the aryl group from exerting its maximum effect on stabilizing the carbonium ion. Thus, deviations from the line in Figure 1 are indicative *specifically* of resonance loss due to twisting (effect 1). For example, various data[12,13,15,16,17] for solvolysis of aryldi-*tert*-butylcarbinyl p-nitrobenzoate reveal severe restriction of resonance due to aryl twisting (effect 1); the relevant point[15] on Figure 1 is well off the line.

Why should the methoxy substituent, and apparently other resonance donors, yield an invariant σ^+ value rather than the spectrum of values predicted? The qualitative answer may be that the energy levels defining the through conjugation responsible for adherence to σ^+ are either present or absent; the quantum theory does not permit infinite gradation. The interaction of such substituents with the carbonium ion type transition state can be pictured as a LUMO(carbonium ion)–HOMO(substituent) interaction. This leads to an interaction energy $\Delta E\pi$ of the form

$$\Delta E\pi = (C_H C_L \beta)^2/(E_L - E_H) \qquad (3)$$

where $\Delta E\pi$ is the stabilization energy resulting from interaction of the substituent with the positive center, C_H and C_L are the coefficients of the HOMO and LUMO, respectively, at the point of union, and E_H and E_L are their energies. This treatment has, however, been used to argue both for variable[18] *and* constant[19] σ^+ values. In its simplest (but possibly still relevant) form the interaction may be likened to the union of a vacant carbon p orbital and the HOMO of the benzyl anion, both NBMOs (Figure 2). In this case

$$\Delta E\pi = 2\alpha\beta \qquad (4)$$

where α and β are the NBMO coefficient and resonance integral, respectively.[20] α will thus measure the influence of the substituent; variations in degree of interaction between HOMO and LUMO, i.e., extent of charge development in the transition state, will be given by the β term, which has been shown to reflect variations in ρ.[20–22] It is likely that this partitioning effect may be retained in more sophisticated theoretical treatments.

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Registry No.—**1**, 61971-63-9; **2**, 64822-39-5; **3**, 41327-33-7; **4**, 23852-76-8; **5**, 64822-35-1; **6**, 54265-32-6; **7**, 37776-01-5; **8**, 20547-61-9; **9**, 55408-73-6; **10**, 60921-49-5; **11**, 60174-87-0; **12**, 37776-03-7; **13**, 20550-37-2; **14**, 62861-28-3; **15**, 57955-44-9; **16**, 64822-42-0; **17**, 64822-46-4; **18**, 57955-42-7; **19**, 54265-31-5; **20**, 41327-36-0; **21**, 61971-59-3; **22**, 65275-59-4.

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Hydrophobic Forces in Selective Hydrolyses of Nonionic p-Nitrophenyl Ester and Anionic 3-Nitro-4-acyloxybenzoic Acid Substrates by Hydroxamic Acids

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The elucidation of binding-step mechanism in enzyme reactions is one of the goals in biochemical researches.[1] Recently, hydrophobic (apolar) forces have received considerable attention in the biochemical studies on the hydrolysis of ester substrates by such synthetic enzyme models as poly[4-vinylimidazole],[2] a copolymer of N-methylacrylohydroxamic acid