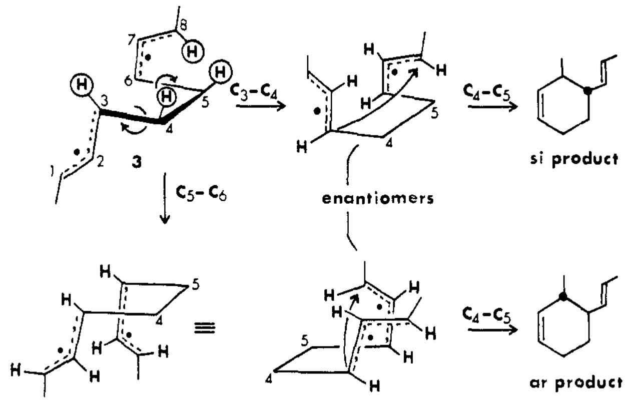
that *trans*-1,2-divinylcyclobutane (tDV) gives 4-vinylcyclohexene with 54% inversion (si + ai) and 46% retention (sr + ar) of configuration (8% net inversion, 92% racemization). In the case of tDV, where the four-pathway analysis cannot be achieved for lack of a stereochemical label to distinguish antarafacial from suprafacial migration, the gross inversion:retention ratio might suggest a small inversion component superimposed upon a largely stereorandom, chirality-destroying process passing through planar or rapidly rotating diradical intermediates. The present results show that for tTT and tCT (and by analogy, for tDV), this is not the case. Although the gross inversion: retention ratios (51.6:48.4 and 49.5:50.5) again might suggest near-randomization of stereochemistry, this would require the formation of substantial amounts of antarafacial products. Table I shows that not more than 12% of the tTT and 5.5% of the tCT 1,3 rearrangements can involve a rapidly rotating diradical intermediate.

In one interpretation of the present results (Scheme II), tTT gives a diradical intermediate **3**. All four pathways from **3** require bond rotation about C_1–C_5 to permit juncture of the migrating carbon (C_3) to the terminus (C_8). Pathway sr (not shown), a shearing motion of the two allylic units past each other, requires no additional rotations. Pathways si and ar each require one (or an odd number) of additional rotations, si about C_3–C_4, and ar about C_5–C_6. Pathway ai (not shown) requires an odd number of additional rotations about each of C_3–C_4 and C_5–C_6.

Scheme II



If the C_3–C_1 and C_5–C_6 rotational barriers were identical and the ring-closure rates to products **1** and **2** were not very different, the relative rates through each of the pathways would be controlled largely by probability and would rank sr > si = ar > ai. The experimental order (Table I) is si > sr ≫ ar > ai from both tTT and tCT. It seems unlikely that product stabilities make any significant contribution to the ordering, and in two cases, si ≫ ar, and sr ≫ ai, this factor is ruled out rigorously because the pairs of products are enantiomeric.

Since the magnitudes of rotational barriers in diradicals are imperfectly known, it is conceivable that, perhaps because of differences in steric interactions between the circled hydrogens, the rotational rate ratios $(C_3\text{–}C_4)/(C_5\text{–}C_6)$ could be as large as the values (9.4 from tTT and 18.4 from tCT) needed to fit the observed si/ar ratios. On the other hand, the diradical mechanism offers no obvious explanation for the observations that in the suprafacial mode, inversion is preferred over retention, but the reverse is true in the antarafacial mode. At the least, the present results provide an experimental basis for refinement of the diradical theory.

For the present, a simpler and hence preferable interpretation would describe the major reactions si and sr as concerted processes, si allowed,[7] but only slightly preferred over sr, which is forbidden.[8] Both antarafacial reactions are slow because of the difficulty of migration through the π-nodal plane.

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[7] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 114.

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[9] National Institute of General Medical Sciences Predoctoral Fellow (No. 5-FO1-GM-40662), 1968–1971.

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A Criticism of the Use of the Hammett Equation in Structure–Reactivity Correlations

Sir:

The theoretical interpretation of σ, σ^+, and σ^- values derived from the Hammett equation as indices of measurement of substituent-ring electronic interactions receives abundant acceptance. The significance of ρ is also assumed, in numerous publications, diagnostic of the extent of charge development in the transition state of a kinetic process. However legitimate such concepts may or may not be, it is essential that the reasoning should be consistent; *if* it is accepted that the (entirely empirical) Hammett equation as applied to the effect of a perturbation in a benzene ring on rate of reaction of a side chain or nuclear position can be "explained" in this way, *then it inevitably follows*, despite many reports implying the contrary, that it is entirely inconsistent to use ρ as indicative of the ability of other ring systems to transmit substituent effects, or to substantiate selectivity–reactivity relationships in accordance with the Hammond postulate.[1]

We illustrate the point with three examples taken from recent work on the application of Hammett equations to areas of major mechanistic interest.

Electrophilic Substitution in Heteroaromatic Systems. Consistent σ^+ values have been attached to the effect produced by replacement of CH═CH in the benzene ring system by S and O, so that the α and β reactivity of thiophene and furan toward electrophiles follows the Stock–Brown "extended selectivity relationship" very closely.[2,3] The observation that apparent ρ values evaluated from substituent effects on the reactivity of such rings are different from those of the substituted benzenoid compounds indicates only that the effects of substituent and heteroatom are not additive; it cannot indicate different transition state structures.[4–6] Thus, the ρ value for the chlorination (CH_3COOH, 25°) of the

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[3] G. Marino, *Advan. Heterocycl. Chem.*, **13**, 235 (1971).

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[5] S. Clementi and G. Marino, *J. Chem. Soc. B*, 71 (1972).

[6] A. R. Butler and J. B. Hendry, *ibid.*, 848 (1970).

thiophene ring has been reported as -6.5 and for the benzene ring as -10.0, explicable at first sight by the Hammond postulate in that thiophene reacts some 10^7 times faster than benzene, and therefore has less positive charge on it in the transition state.[6] The fallacy in this argument is readily seen, however, when it is noted that the reactivity of the para position of anisole is 10^4 times greater than that of the α position of 2-carboethoxythiophene. In general, ρ values should be the same in the two systems, as noted by one set of authors[6,7] (although disputed by others[3,5]).

Aromatic Nucleophilic Substitution. The ρ values of 3.6 and 8.5 for the reaction of 4-substituted 1-chloro-2-nitro- and 1-chlorobenzene, respectively, with methoxide anions in methanol at 50° are taken to arise from the increased negative charge on the transition state of the latter molecules, the slower reaction yielding the less reactant-like transition state.[8] 4-Nitro-1-chlorobenzene, however, will react at a speed similar to that of 1-chloro-2-nitrobenzene; a uniform steric effect in the substituted 1-chloro-2-nitrobenzenes altering the transition state structure relative to that of the 1-chlorobenzenes is the only interpretation in accordance with Hammett equation theory. This explanation is borne out by the observation that the reaction of substituted anilines with 1-chloro-2,4-dinitrobenzene and 1,4-dichloro-2-nitrobenzene (80% aqueous dioxane, 65°) give identical ρ values even though the reactivity of the latter system is 10^5 times smaller than that of the former.[9]

Electrophilic Substitution in Benzenoid Systems. Olah has examined Friedel-Crafts benzylation and benzoylation reactions in which the rate of reaction with aromatics is varied by substituent alteration in the benzyl or benzoyl chlorides.[10-12] Data taken from Olah's results are shown in Table I, where the ρ values have been calculated as

$$\rho = \log [(k_{\text{toluene}}/k_{\text{benzene}})(\%\ \text{para}/100)(6)]/-0.31 \quad (1)$$

Table I

	$k_{\text{toluene}}/k_{\text{benzene}}$	% para substitution in toluene	ρ
$NO_2C_6H_4CH_2Cl$	2.5	34.2	-2.3
$CH_3OC_6H_4CH_2Cl$	97.0	69.9	-8.4
$NO_2C_6H_4COCl$	52	89.3	-7.9
$CH_3OC_6H_4COCl$	233	83.6	-9.9

The low selectivity of the more electrophilic reagents is taken to indicate an early transition state, and the high selectivity of the less electrophilic reagents a late transition state. The flaw in this argument is that if the reaction with a weaker electrophile is characterized by a large negative value of ρ, *i.e.*, by high selectivity supposedly denoting a late transition state, and the reaction with a more reactive electrophile by a smaller negative value of ρ, *i.e.*, by low selectivity supposedly denoting an early transition state, then a point inevitably arises where reaction with the less reactive electrophile would become faster than the reaction with the more reactive one. The value of σ^+ at which this changeover would occur and two electrophiles (a and b) react at the same rate is

$$\sigma^+ = \frac{(\log k_{\text{benzene}})_{\text{b}} - (\log k_{\text{benzene}})_{\text{a}}}{\rho_{\text{a}} - \rho_{\text{b}}} \quad (2)$$

Thus, if the electrophile from $CH_3OC_6H_4CH_2Cl$ were to react 100 times more slowly with benzene than did that from $O_2NC_6H_4CH_2Cl$, then σ^+ would be -0.33, so that the para position of toluene would be almost of the the same reactivity toward each of the two electrophiles, while on the one hand the difference for the meta position of chlorobenzene would be a factor between 10^4 and 10^5, and on the other hand the reactivities of the two reagents toward the para position of anisole would be reversed by a factor of greater than 100. It has been contended[10] that the rates of reaction of the ostensibly more reactive electrophile should be correlated by σ, but this yields from eq 1 a value of $\rho = -4.0$, similar to that for the reaction defining σ^+ values. Moreover, however theoretically desirable equations of the Yukawa–Tsuno type[13] may be in correlating reactions involving development of positive charge, in practise they rarely give a theoretically significant improvement over the simple Stock–Brown version of the Hammett equation.[14,15]

As regards Olah's results we do not comment on the physical significance of the region of reactivity where reversal of reactivities would appear to be required to occur, but would point out that for many electrophilic substitutions absolute rates of reaction cannot be found since the concentration of the true electrophile is generally not known and that, in any case, the reaction of the electrophile with the aromatic is not necessarily the rate limiting step in the overall reaction. The apparently widely differing selectivities reported by Olah may well be produced by increasing inexactitude of competitive experiments with increasing speed of reaction.[12]

The available evidence suggests that generally, for the reactions of a series of reagents whose reactivity is altered by substituents removed from steric interaction with the reaction site, operating under the same conditions, values of ρ, properly observed, should not differ greatly. Examples are to be found in the results of Kirsch, Clewell, and Simon on ester hydrolysis,[16] where an alternative form of eq 2 is given, in those of Norman previously cited,[10] and in work on diazo coupling with $XC_6H_4 \cdot N_2^+$,[17] where, in particular, reaction with 1-naphthol and 1-naphtholate gives rates differing by 10^9, but similar ρ values, 4.8 and 4.2, respectively.

As a general conclusion, we emphasize that at this

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(16) J. F. Kirsch, W. Clewell, and A. Simon, *J. Org. Chem.*, **33**, 127 (1968), and references quoted therein.

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stage we are not commiting ourselves to an acceptance of any particular viewpoint—we merely demonstrate that the generally accepted significance of ρ values is quite contrary to the Hammond postulate and note that in general such interpretation of *linear* free energy relationships is by definition incompatible with structure–reactivity correlations invoking variable transition states.[18]

[18] See, *e.g.*, remarks on the Brønsted equation: F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, **94**, 3910 (1972).

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Nuclear Magnetic Relaxation Rates of Thallium(I)-205 in Aqueous Solution with Respect to Complexing of Molecular Oxygen

Sir:

The nmr relaxation rates of spin half ($^1/_2$) nuclei have not been widely investigated. Information is available for hydrogen, fluorine-19, carbon-13, and silicon-29.[1-3] Recently, a study of spin-lattice relaxation rates of ^{205}Tl, in the presence of the enzyme pyruvate kinase, has been reported in an attempt to indicate the binding site of the monovalent metal activator.[4,5] The only other study of ^{205}Tl(I) spin relaxation was aimed at the nature of bonding in aqueous solution between paramagnetic $Fe(CN)_6^{3-}$ and free Tl(I) ion.[6] A study of ^{205}Tl(I) nuclear spin relaxation is reported here for the aqueous ion and selected results are listed in Table I. No dependence of R_1 on the Tl(I) concentration is observed between 0.03 and 3.5 *M* and furthermore the anion dependence of R_1 is also negligible for the ions acetate, fluoride, sulfate, and nitrate. The most striking feature of the data is the sensitivity of R_1 and R_2 to dissolved oxygen, which at atmospheric partial pressure has a solubility of 4.8×10^{-6} mole fraction in pure water at 25°.[7] The relaxation times of ^{205}Tl(I) solutions cited by Reuben and Kayne[5,6] are included in Table I and clearly reflect the presence of dissolved oxygen. The conclusions of these authors, regarding distances between monovalent and bivalent binding sites estimated from relaxation rates of ^{205}Tl(I), are quite suspect since both R_1 and R_2 are strongly dependent on oxygen concentration.

The results in this study indicate a relaxation mechanism, in oxygenated solutions, which is dominated by electron-nuclear dipole–dipole interaction. A contact hyperfine interaction seems unlikely because R_2 is not appreciably greater than R_1.[8] The dipole–dipole mechanism is very short range with an r^{-6} dependence, so oxygen must penetrate the loose solvation sphere[9] of Tl(I) to form a weak "complex" through interaction with the thallous ion, *via* the (6s) "lone pair" electrons. Work is in progress to discover the nature of this metal ion–molecular oxygen complex. The rapid reversibility and reproducibility of the relaxation data with oxygen pressure are a strong argument in favor of an ion–molecule complex. It is known that ^{23}Na(I) and ^{7}Li(I) in aqueous solution do not relax appreciably faster with molecular oxygen in solution.[10,11] The effect is almost two orders of magnitude smaller. The relaxation rate of ^{19}F in aqueous fluoride ion is affected, to about the same extent as ^{205}Tl(I) in this study, by addition of aqueous Cu(II) which forms a paramagnetic complex CuF^+.[12,13] Cu(II) and ferricyanide also enhance the relaxation rate of ^{205}Tl(I) (see Table I). The preferential increase in R_2 indicates a significant hyperfine transverse relaxation which is not completely averaged by exchange.

Table I. Relaxation Rates of Aqueous Solutions of Tl^+

Solute	Solvent	Concn, mol l.$^{-1}$	R_1,[a] sec^{-1}	R_2,[b] sec^{-1}
$TlNO_3$	$H_2O(N_2)$[c]	0.0803	0.54	0.83
	H_2O(air)[d]		8.3	9.6
	$H_2O(O_2)$[e]		38.0	
	f	*f*	5.8[f]	17.5[f]
	$D_2O(N_2)$[c]	0.0839	0.44	0.8
	D_2O(air)[d]		8.3	*g*
	$D_2O(O_2)$[e]		41.0	*g*
	$H_2O(N_2)$[c] 8×10^{-5} *M* $Fe(CN)_6^{3-}$	0.080	15.3	13
	$H_2O(N_2)$[c] 7×10^{-3} *M* Cu^{2+}	0.15	9.9	19

[a] $R_1 = 1/T_1$, the longitudinal relaxation rate, measured from plots of log of free-induction decay amplitude *vs.* pulse spacing (ref 13), from standard 180 to 90° pulse sequences. Estimated precision ±4%. [b] $R_2 = 1/T_2$, the transverse relaxation rate, measured from standard Carr-Purcell spin-echo sequences (ref 13). Estimated precision ±8%. A Fabritek (Nicolet) 1074 signal averager was used to enhance repetitive signals in both R_1 and R_2 measurements. Probe temperature 26.0°. [c] The sample was thoroughly purged with N_2, and less than 10^{-6} mol of $N_2H_4 \cdot H_2O$ was added to reduce any remaining O_2. [d] The sample was saturated with air. [e] The sample was saturated with O_2 at 1 atm. [f] From Table IV of ref 5. The sample consisted of 0.10 *M* $TlNO_3$ and 0.05 *M* cacodylate buffer. [g] Measurements of R_2 in D_2O in the presence of dissolved oxygen indicate that the relaxation rate is independent of the isotopic composition of the solvent. The enhancement of the relaxation rate follows that in H_2O.

The relaxation mechanism in the absence of oxygen or paramagnetic substances is somewhat problematical because in uncontaminated water the relaxation times of ^{205}Tl are almost independent of isotope substitution of deuterium in the water. The relaxation mechanism, if dominated by nuclear dipole–dipole coupling (correlation times for tumbling assumed equal), should give R_1 and R_2 approximately in the ratio $\gamma_H{}^2/\gamma_D{}^2 \simeq 42$ when H_2O is changed to D_2O as solvent. An order of magnitude calculation for the dipole–dipole contribu-

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