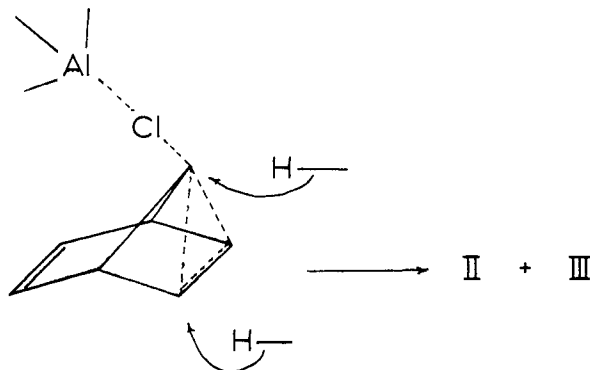coördinates with the chlorine thereby providing impetus to ionization which is strongly assisted by the proper double bond to give a non-classical intermediate. Probably, ionization does not proceed to a great extent before reduction occurs.

The intermediate might be considered as a very tight ion pair. It seems highly unlikely that the reaction proceeds by simple nucleophilic attack on the double bond without some prior ionization, especially since the attack cannot be intramolecular. Support for this position is gained by the preliminary observation that the addition of water increases the rate of reduction but does not change the product ratio. This observation is consistent with that of Eliel[10] who found that yields were materially improved in the lithium aluminum hydride reduction of a chlorohydrin, involving a tertiary chloride, by the addition of water or alcohols. This was attributed to the greater acidity of the oxygen substituted aluminum which was presumed to coördinate with the chlorine.

The chemistry of the tricyclic olefin (III) and the mechanism and scope of the reaction are presently under further investigation.

(10) E. L. Eliel and T. J. Prosser. *J. Am. Chem. Soc.*, **78**, 4045 (1956).

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REGARDING ENHANCED RESONANCE EFFECTS FROM META POSITION IN RADICAL REACTIVITIES[1]

Sir:

A valuable tool for the characterization of the transition state of a radical reaction is provided by a measure of enhanced resonance effects of *meta*-substituents.

The Ar–Y inductive effects of a *meta* methoxy substituent in reactivities of benzene derivatives (in the general formula for such compounds, X–Ar–Y, X refers to the substituent and Y to the reaction center) are precisely described (to a standard error of ± 0.03 sigma unit) by the modified Hammett equation[2]: $\log (k/k_0) = \sigma^0 \rho$. Included are

(1) This work was supported in part by the Office of Naval Research.

(2) (a) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959); (b) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959); (c) R. W. Taft, Jr., *J. Phys. Chem.*, **13**, 1805 (1960).

such pronounced electrophilic reactivities as the rates of solvolysis of *t*-cumyl chlorides, rates of protonolysis of phenyltrimethylsilanes, and rates of bromination of mesitylenes and durenes, as well as such strongly nucleophilic reactivities as the ionization of phenols and thiophenols (for listings of reactions *cf.* Table II, ref. 2a).[3]

In contrast, in three radical reaction series (for which data are available) the *m*-OCH₃ substituent shows enhanced reactivity over that predicted ($\sigma^0 \rho$) for the Ar–Y inductive effect (benzoyl peroxide reaction series F-1, F-3, and F-4 of Table II, ref. 2a), the enhancement (Ar–Y resonance effect) amounting in each case to *0.3 kcal./mole*. While this figure is not impressive in magnitude, it comes from reactions with relatively small ρ values and consequently is clearly discernible in the $\bar{\sigma}$ value.[4] In the radical reactivities listed in Table II of reference 2a, small apparent Ar–Y resonance enhancements in rate are also noted for *m*-alkyl and phenyl substituents.

A much more impressive enhancement (Ar–Y resonance effect) is obtained for the *m*-OCH₃ substituent in the formation of the radical ion by polarographic oxidation of *m*- and *p*-substituted anilines.[5] Here the effect on oxidation potential over that estimated by $\sigma^0 \rho$ amounts to a free energy decrease of *1.1 kcal./mole*. It is further to be noted that an extensive investigation of *m*-substituents has been made and substantial Ar–Y resonance effects are noted for other –R meta substituents (*e.g.*, –NH₂, –NHCOCH₃ and –CH₃). The resonance enhanced effects reach a maximum free energy decrease of *3.0 kcal./mole* for the *m*-NH₂ substituent.

The enhancement of the resonance effect of *meta* substituents may be accounted for in terms of acceptable quinoid isovalent structures,[5a] *e.g.*
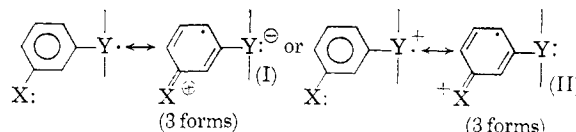
It is well known that the analog interaction structures for –Y:⁻ or –Y⁺ (systems with an even number of π electrons) are not acceptable, in accord with the applicability (noted above) of the modified Hammett equation to such systems. The

(3) Not all -R *meta* substituents are as well behaved as *m*-OCH₃. Effective $\bar{\sigma}$ values for *m*-SCH₃, NH₂ and N(CH₃)₂ are appreciably affected by the polarization from a change in formal charge at the first atom of the side-chain reaction center. In reactivities in which the latter factor is not involved, however, these substituents appear generally to follow the σ^0 scale (*cf.* references 5a and b).
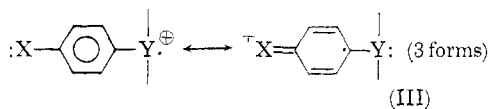
(4) This type of rate enhancement for *para* -R substituents has been well recognized and documented in terms of correlations employing σ^+ values: *cf.* P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960). However, Bartlett and Rüchardt have given an additional reason (besides that considered here for *meta* substituents) for such rate enhancements with *para* substituents. See also, G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); E. S. Hayser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

(5) I. R. Fox, R. W. Taft, Jr., and J. M. Schempf, Abst. of Papers, Am. Chem. Soc. Meeting, Atlantic City, N. J., Sept., 1959.

(5a) NOTE ADDED IN PROOF.--W. N. White, C. D. Slater, and W. K. Fife, *J. Org. Chem.*, **26**, 627 (1961) have similarly noted that enhanced resonance effects of *m*-substituents in the rate of the Claisen rearrangement can be accounted for by the contribution of such structures to the reaction transition state.

fact that forms such as II are expected to be more important than I[6,7] accounts for the relative magnitudes of the effects noted above. The above oxidation reaction series indicates that *enhanced resonance effects of meta −R substituents will become increasingly important the greater the radical cation character of the transition state.*

In each of the reactivity series noted above, the Ar–Y resonance enhanced effects [estimated as log (k^p/k_0) − $\sigma^0\rho$] for *para* substituents are two to three times greater than for the corresponding *meta* substituent. A greater importance of isovalent interaction forms, *e.g.*, III than II for example, is indicated (*cf.* however, footnote 4).

$$:X-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\overset{|}{\underset{|}{Y}}.^{\oplus} \longleftrightarrow \ ^-X=\!\!\left\langle\bigcirc\right\rangle\!\!-\!\overset{|}{Y}: \ \text{(3 forms)}$$

(III)

The pleasing agreement between theory and the results from reactivity analysis may be taken as evidence for the validity of the procedures employed in the analysis (which were deduced quite independent of present considerations). The importance of the reactivity interpretation procedure recommended in reference 2a is emphasized, since all of the effects reported here can be masked to varying degrees of approximation by forced fits to the unmodified Hammett equation. It is apparent that reaction series which involve Ar–Y resonance effects of *meta* substituents present special difficulty in the determination of the reaction constant ρ. The results reported here are based upon the Jaffé and Roberts procedure[8] for determining ρ (= $\rho_{\rm I}$).[2a] In addition to this generally recommended procedure, equivalent results are expected from the judicious limitation of the modified Hammett equation to select substituents.[2,9]

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(6) *Cf.*, for example, I. R. Fox, P. L. Levins and R. W. Taft, Jr., *Tetrahedron Letters*, **7**, 249 (1961).

(7) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961), have determined the half-wave reduction potentials for an extensive series of *m*-substituted nitrobenzenes. The potentials are correlated by σ^0 values with high precision. The relevant interaction structures for the radical anion with a meta -R substituent

(3 forms)
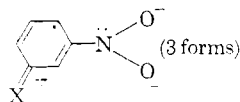
apparently are rendered of little consequence by the long range charge separation and the electron repulsion between oxygen atoms. The importance of the nature of groups X and Y in the general structures I and II is emphasized.

(8) J. L. Roberts and H. H. Jaffé, *J. Am. Chem. Soc.*, **81**, 1635 (1959).

(9) H. Van Bekkum, P. E. Verkade and B. M. Webster, *Rec. Trav. Chim.*, **78**, 815 (1959).

(10) Visiting Associate, California Institute of Technology, Spring, (1961).

EVIDENCE FOR PHENYL CATION WITH AN ODD NUMBER OF π-ELECTRONS FROM THE AQUEOUS THERMAL DECOMPOSITION OF THE DIAZONIUM ION[1]

Sir:

The recent suggestion[2] that substantial enhancements in rate due to −R (conjugatively donor) substituents in the *meta* position of benzene derivatives may be used to characterize the degree of radical cation character of a reaction transition state finds interesting application to the rates of aqueous thermal decomposition of substituted phenyldiazonium salts.

Except for acknowledged radical reactivities, the diazonium decomposition reaction apparently provides the only existing *bona fide* example of a reaction (heretofore regarded as a direct ionic heterolytic cleavage) for which rate enhancements of the above kind are observed.[2a] For the phenyldiazonium ion substituted as indicated in the *meta*-position, these decreases in free energy of activation are estimated from the quantity $-2.303RT\cdot$ [log (k/k_0) − $\sigma^0\rho$]: OCH$_3$, 1.7 kcal./mole; OH, 1.5 kcal./mole; C$_6$H$_5$, 0.8 kcal./mole; CH$_3$, 0.5 kcal./mole; Cl, 0.2 kcal./mole. These figures strongly imply a high degree of radical-cation character for the transition state of the decomposition reaction.

The alternate interpretation that the above rate enhancement figures result from a favorable polarizing influence[4] of the positively charged carbon generated by loss of nitrogen from the diazonium ion appears untenable in the present case in view of the fact that the modified Hammett equation, log (k/k_0) = $\sigma^0\rho$, is followed to high precision (to a standard error of ± 0.03 sigma unit) by the *meta*-methoxy substituent in such "model" non-radical ion processes[3] as: the ionization constants of aqueous pyridinium ions, the rates of bromination of substituted durenes and mesitylenes, the rates of protonolysis of phenyltrimethylsilanes, the rates of diazo coupling of phenyldiazonium ions with 2,6-naphthylaminesulfonic acid, the rates of solvolysis of benzyl tosylates and *tert*-cumyl chlorides.

A transition state with a high degree of radical cation character can be visualized in terms of the generally accepted mechanism[5,6] for the aqueous thermal decomposition of phenyldiazonium ions

(1) This work was supported in part by the Office of Naval Research.

(2) R. W. Taft, Jr., I. R. Fox, and I. C. Lewis, *J. Am. Chem. Soc.*, **83**, 3349 (1961).

(2a) NOTE ADDED IN PROOF.—The rate of the Claisen rearrangement is an additional example, *cf.*, W. N. White, C. D. Slater and W. K. Fife, *J. Org. Chem.*, **26**, 627 (1961).

(3) For literature references and values, *cf.* Table II of R. W. Taft, Jr. and I. C. Lewis, *ibid.*, **81**, 5346 (1959), and H. H. Jaffé and G. O. Doak, *ibid.*, **77**, 4441 (1956). For σ^0 values *cf.* R. W. Taft, Jr., *J. Phys. Chem.*, **12**, 1805 (1960).

(4) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5252 (1959).

(5) J. F. Bunnett and E. Zahler, *Chem. Revs.*, **49**, 273 (1951); E. S. Lewis and E. B. Miller, *J. Am. Chem. Soc.*, **75**, 429 (1953); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 799–801; D. F. DeTar and T. Kosuge, *J. Am. Chem. Soc.*, **80**, 6072 (1958) and earlier references cited therein.

(6) E. S. Lewis, *ibid.*, **80**, 1371 (1958).