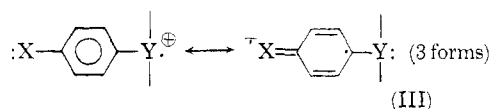


fact that forms such as II are expected to be more important than I^{6,7} accounts for the relative magnitudes of the effects noted above. The above oxidation reaction series indicates that *enhanced resonance effects of meta -R substituents will become increasingly important the greater the radical 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).



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 procedure⁸ for determining ρ ($= \rho_1$).^{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}

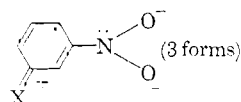
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(6) Cf., for example, I. R. Fox, P. L. Levins and R. W. Taft, Jr., *Tetrahedron Letters*, **7**, 249 (1961).

(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



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 ION¹

Sir:

The recent suggestion² 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 $-2.303RT \cdot [\log(k/k_0) - \sigma^0\rho]$: OCH₃, 1.7 kcal./mole; OH, 1.5 kcal./mole; C₆H₅, 0.8 kcal./mole; CH₃, 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 influence⁴ 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 processes³ as: the ionization constants of aqueous pyridinium ions, the rates of bromination of substituted durennes 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).

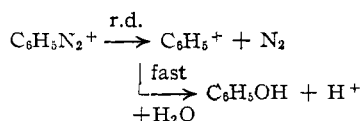
(3) For literature references and values, cf. Table II of R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **81**, 5346 (1959), and H. H. Jaffé and G. O. Doak, *ibid.*, **77**, 4441 (1956). For σ^0 values cf. R. W. Taft, Jr., *J. Phys. Chem.*, **12**, 1805 (1960).

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

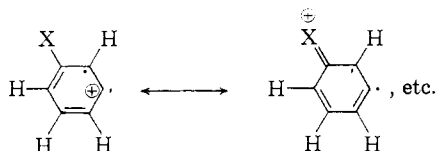
(5) J. F. Bunnett and E. Zahler, *Chem. Revs.*, **49**, 273 (1951); E. S. Lewis and E. B. Miller, *J. Am. Chem. Soc.*, **75**, 429 (1953); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 799-801; D. F. DeTar and T. Kosuge, *J. Am. Chem.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

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

provided that the intermediate phenyl cation is regarded as in a state in which a π electron of the benzene ring has fallen with concerted uncoupling into



the open σ hybrid (sp^2) orbital of the cation (*i.e.*, the orbital occupied by the C-N sigma bond in Ar-N_2^+). This electronic rearrangement presumably gives a more stable structure with an odd number of π -electrons, in which this resonance can occur:



Since uncoupling to give a *triplet* phenyl cation seems necessary, the evidence cited herein appears to indicate that there are rapid rates of spin interconversions in the formation of the phenyl cation and in the reaction of this intermediate with the nucleophile, H_2O . The high reactivity of the intermediate has been established by Lewis⁸ from its small degree of selectivity in reactions with nucleophiles.

The present argument is not inconsistent with the observation that $-R$ *para* substituents strongly retard the rates of decomposition of the phenyl diazonium ion, provided that one regards (as previously^{4,5}) the reaction transition state for such systems as being less stabilized than is the reactant phenyldiazonium ion.

The effects of reaction conditions⁵ on "radical" and "cation" reaction products of the benzenediazonium decomposition, as well as heavy atom catalysis, are in keeping with the expected versatility of reaction of the proposed biradical carbonium ion. The possible role of ground state triplet cation formed in a primary process in many reactions of aromatic diazonium ions bears consideration.

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SEPARATION OF L-VALINE ACCEPTOR "SOLUBLE RIBONUCLEIC ACID" BY SPECIFIC REACTION WITH POLYACRYLIC ACID HYDRAZIDE

Sir:

To achieve the separation of amino acid-specific "soluble ribonucleic acids" (s-RNA), two basically different approaches have been applied in the past: the use of differences in physical properties of the various nucleotide chains¹⁻⁷ and the use of specific

(1) F. Lipmann, W. C. Hülsmann, G. Hartmann, G. H. Boman and G. Acs, *J. Cell. Comp. Physiol.*, **54**, 75 (1959).

chemical reactions involving the ribose part of the adenylic acid end of the s-RNA⁸⁻⁹ or the attached amino acid.¹⁰ The principle of the separation we wish to describe is similar to that introduced by Zamecnik, Stephenson and Scott,⁸ but offers the advantages of much higher yield at a high purification level. Moreover the time required is very short so that possible disruption of the secondary or tertiary structure of the s-RNA is probably minimized. In this procedure s-RNA is freed of all amino acids and then recharged with a single kind of amino acid. Only the remaining unlabelled s-RNA strands then remain available for a specific periodate oxidation to form a dialdehyde grouping on the end of the s-RNA. We found this "dialdehyde end" of the s-RNA to react readily with a specially prepared water-soluble polymer: polyacrylic acid hydrazide (PAAH) prepared according to the procedure of Kern, *et al.*¹¹ The oxidized s-RNA can be removed easily in this manner, leaving behind the single amino acid s-RNA in enriched form.

Yeast s-RNA prepared according to Monier, *et al.*,¹² was freed of amino acids by exposure to pH 10 at 37° for 30 minutes and relabelled with C^{14} -L-valine, using yeast enzyme.³ Then 3 mg. of C^{14} -L-valine s-RNA were incubated for 5 minutes at room temperature with 0.1 M magnesium acetate buffer, pH 3.9, and 0.1 M NaIO_4 in a total volume of 1 ml. Most of the excess periodate was precipitated as the potassium salt by addition of 0.23 ml. 2 M KCl. After standing 5 minutes at 0° the KIO_4 was removed by centrifugation. The resulting solution of oxidized s-RNA was mixed with 4 ml. of polyacrylic acid hydrazide solution (containing 22.6 mg. of PAAH dissolved in 2 ml. of water and 2 ml. of 0.1 M magnesium acetate buffer pH 3.9) and thoroughly shaken at room temperature for 2 minutes. The PAAH s-RNA compound then was precipitated by reaction with 0.2 ml. (2.6 mM.) *n*-butyraldehyde with vigorous stirring and the precipitate was separated under suction on a sintered glass funnel. After removing unreacted traces of *n*-butyraldehyde by extraction with 20 ml. of ether and 10 ml. of ethyl acetate (two extractions with ether, then one with ethyl acetate and a fourth one with ether) the filtrate contained C^{14} -L-valine s-RNA in greatly enriched form. The ratio of absorbances at 280 and 260 $m\mu$ was the same before and after separation,

(2) K. C. Smith, E. Cordes, R. S. Schweet, *Biochim. et Biophys. Acta*, **33**, 286 (1959).

(3) C. L. Cantoni, *Nature*, **88**, 300 (1960).

(4) K. Nishiyama, T. Okamoto, I. Watanabe and M. Takamami, *Biochim. et Biophys. Acta*, **47**, 193 (1961).

(5) G. Hartmann and V. Coy, *ibid.*, **47**, 612 (1961).

(6) G. A. Everett, S. H. Merrill and R. W. Holley, *J. Am. Chem. Soc.*, **82**, 5758 (1960).

(7) R. W. Holley, J. Apgar, B. P. Doctor, J. Farrow, M. A. Marini, S. H. Merrill, *J. Biol. Chem.*, **236**, 200 (1961), and previous papers.

(8) P. C. Zamecnik, M. L. Stephenson and J. F. Scott, *Proc. Natl. Acad. Sci. U. S.*, **46**, 811 (1960).

(9) A. Saponara and R. M. Bock, *Fed. Proc.*, **20**, 356 (1961).

(10) G. L. Brown, A. V. W. Brown and J. Gordon, *Brookhaven Symposium in Biology*, No. 12, 47 (1959).

(11) W. Kern, Th. Hucke, R. Holländer and R. Schneider, *Makromol. Chem.*, **22**, 31 and 39 (1957).

(12) R. Monier, M. L. Stephenson and P. C. Zamecnik, *Biochim. et Biophys. Acta*, **43**, 1 (1960).