

THE THERMAL DECOMPOSITION OF DIAZONIUM SALTS: EVIDENCE FOR THE FORMATION  
OF RADICAL INTERMEDIATES (1,2)

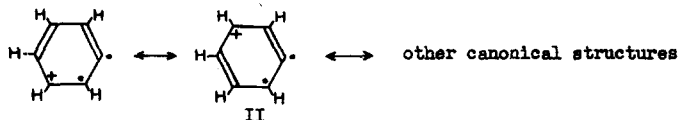
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A considerable body of evidence supports a heterolytic  $S_N1$  mechanism:  
 $C_6H_5-N_2^+ \xrightarrow{r.d.} C_6H_5^+ + N_2$  for the uncatalyzed decomposition of diaz-  
onium salts in both aqueous and non-aqueous solvents (3,4,5). The phenyl  
cation so produced is reported to be highly reactive and unselective (6).  
On the basis of this and other considerations it has been suggested (7)  
that such a cation might attack a nitro-substituted phenyl ring only  
slightly less readily than an unsubstituted phenyl nucleus. We now present  
evidence that the thermal decomposition of diazonium salts involves free  
radical intermediates.

The decomposition of dry benzenediazonium borofluoride (I) in a mix-  
ture of nitrobenzene and benzene under competitive conditions gave mainly  
tars. From the amounts of biphenyl and nitrobiphenyls formed an approxi-  
mate value of the total rate ratio  $\frac{C_6H_5NO_2}{C_6H_6} K \sim 0.40-0.67$  was calculated.  
Contrary to previous reports (5,8) appreciable amounts of *o*-nitrobiphenyl  
were formed ( $f_m/f_o = 2.3-4.4$ ). Both of these results are somewhat unusual  
for an attack by a carbonium ion (which, in this case, would be expected  
to be more stable than an aliphatic one). The competitive phenylation of  
mixtures of toluene and benzene with dry benzenediazonium borofluoride at  
70° in the presence and absence of copper powder (the former involving the  
intermediacy of phenyl radicals (8,9)) was also studied. In both cases

$\frac{\text{C}_6\text{H}_5\text{CH}_3}{\text{C}_6\text{H}_6}\text{K}$  was slightly greater than unity and the ortho-isomer was the main isomer formed in the phenylation of toluene (ca. 60%), the amounts of meta and para isomers being about equal (10).

The above observations may be explained in terms of a diradical cation structure (II) (perhaps in equilibrium with the usual electron-paired structure) for  $\text{C}_6\text{H}_5^+$  (this argument is not affected by the reversibility (11) of the heterolysis step). The participation of such structures in the transition state has already been postulated (12) to explain some aspects of the



thermal decomposition of diazonium salts in aqueous solution.

Evidence for the formation of a radical intermediate in the decompositions reported here has now been obtained. When a suspension of pure dry benzenediazonium borofluoride in dry toluene was heated at 64° an e.s.r. signal was readily detectable (13) at the field close to that corresponding to the free spin value of 2.0023. A symmetrical three line spectrum (the central line being more intense than the other two) was thus observed, the overall width of which was 27 gauss and the hyperfine line width approximately 7 gauss. No signal was given by the individual pure parent compounds at room temperature or by heated toluene. When pure dry benzenediazonium borofluoride was heated in situ within the V-4531 multipurpose cavity at 50° for 5 min. no free radicals were detected. Above 60° the same symmetrical three line spectrum as above appeared and increased in intensity with time; little decrease in intensity was recorded forty-five minutes after cooling the sample to room temperature. The radical is quite stable and is trapped in the solid matrix. When (I) was left exposed to the atmosphere it darkened gradually and the brown sticky solid gave rise to the same e.s.r.

spectrum. Other than that it is aromatic, no definite conclusions can be reached from the above e.s.r. spectrum at this time concerning the nature of the radical produced. No e.s.r. absorption was observed immediately after mixing (I) and pure nitrobenzene at room temperature. When the mixture was heated at 42° for 10 min. a symmetrical e.s.r. spectrum consisting of three equidistant lines of equal intensity was recorded (14). The g factor was again close to the free spin value. The spacing between the lines was 9 gauss and the hyperfine line width approximately 4 gauss. These results would suggest an unpaired electron interaction with a single nitrogen atom (15). There is no doubt, therefore, that a free radical intermediate is formed in these decompositions. The energetically unlikely production of a phenyl radical according to:  $\text{Ph-N}_2^+ \rightarrow \text{Ph}\cdot + \text{N}_2^+$  has already been rejected (16), although evidence has been given for the production of radicals in the photodecomposition of a stabilized diazonium salt (17).

Should the radical produced in the thermal decomposition actually have structure (II), this would explain the small deactivation observed for the substitution of nitrobenzene, and also of pyridine in the Pschorr cyclization (18), as well as the preferred meta orientation in the former case (cf. the preferred  $\beta$ -attack in the o-nitrophenylation of pyridine (19)), since (II) would be expected to behave like a strongly electrophilic free radical in substitution reactions.

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