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REACTIVITY OF PHENYL RADICALS TOWARD AROMATIC SOLVENTS. ON "CAGE" PHENYLATION BY PHENYLAZOTRIPHENYLMETHANE.

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THE MECHANISM of aromatic phenylation has been an object of considerable interest over the past 25 years.[2] Most authors presently seem to accept the view that the process involves two, separate stages. When benzoyl peroxide is the source

$$\mathrm{Ph\cdot} + \mathrm{ArH} \longrightarrow \mathrm{PhArH\cdot} \qquad (1)$$

$$\mathrm{PhArH\cdot} + \mathrm{R\cdot} \longrightarrow \mathrm{PhAr} + \mathrm{RH} \qquad (2)$$

of phenyl radicals, R· has been identified as the phenylcyclohexadienyl radical (PhArH·), at least, in relatively dilute solutions.[3,4] Eliel, Eberhardt, Simamura, and Meyerson[5] have recently presented evidence that phenylation proceeds through different paths when phenylazotriphenylmethane (PAT) or N-nitrosoacetanilide (NNA) is used instead of benzoyl peroxide as the source of phenyl radicals. They suggested that phenylation by the former reagents proceeds through the attack of geminately formed radical pairs on nearby solvent molecules. It was recognized that this mechanism implies a very short

$$\mathrm{Ph{-}N_2{-}R} \longrightarrow \overline{\mathrm{Ph\cdot} + \mathrm{R\cdot} + \mathrm{N_2}} \qquad (3)$$

$$\mathrm{ArH} + \overline{\mathrm{Ph\cdot} + \mathrm{R\cdot} + \mathrm{N_2}} \longrightarrow \mathrm{PhAr} + \mathrm{RH} + \mathrm{N_2} \qquad (4)$$

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[1] National Science Foundation Predoctoral Cooperative Fellow, 1962-3.

[2] Leading references are given in citations 3 and 4.

[3] E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.* **82**, 2936 (1960). Also, M. Eberhardt and E. L. Eliel, *J. Org. Chem.* **27**, 2289 (1962).

[4] D. F. DeTar and R. A. J. Long, *J. Am. Chem. Soc.* **80**, 4742 (1958).

[5] E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Letters* 749 (1962).

lifetime for the phenyl radicals, and that there is some difficulty in reconciling the mechanism with scavenging experiments,[6,7] but it was pointed out that scavengers in sufficient concentrations might compete successfully for the phenyl radicals with the "cage" reaction.

We report the results of two kinds of studies which yield results bearing on the lifetime of phenyl radicals produced from PAT in aromatic solvents. First, we have studied the effects of moderate concentrations of a pair of reactive scavengers, iodine and carbon tetrabromide. Second, we have measured the amounts of benzene produced when PAT is decomposed in toluene and chlorobenzene. Table 1 contains the relevant data.

Consider first the implications of the data for added scavengers. Iodine in concentrations down to 3×10^{-2} $\underline{M}$ clearly captures phenyl radicals with 90% efficiency or better. Carbon tetrabromide is not much less efficient.

Reactions 5 and 6, whether the phenyl radicals represented therein be "caged" or "free", must be in direct competition with those reactions which ordinarily lead to substitution. Since there is very little increase in the

$$Ph\cdot + I_2 \longrightarrow PhI + I\cdot \qquad (5)$$

$$Ph\cdot + CBr_4 \longrightarrow PhBr + \cdot CBr_3 \qquad (6)$$

yield of iodobenzene accompanying a four-fold increase in the iodine concentration in toluene, it is difficult to conclude other than that the scavenging process is near its maximum efficiency even in the lowest concentrations of iodine.

In a detailed theoretical treatment of the kinetics of reactions of reactive species produced in pairs, Noyes has defined three modes of reaction of such pairs.[8] Primary recombination refers to the mutual destruction of geminate pairs before the partners have separated at all. Secondary

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[6] R. Huisgen and H. Nakaten, Ann. 586, 70 (1954).

[7] G. L. Davies, D. H. Hey, and G. H. Williams, J. Chem. Soc. 4397 (1956).

[8] R. M. Noyes, J. Chem. Phys. 22, 1349 (1953); J. Am. Chem. Soc. 77, 2042 (1955); J. Phys. Chem. 65, 763 (1961); "Progress in Reaction Kinetics," edited by G. Porter, Permagon Press, London, England, 1961.

Table 1

Decomposition of PAT in Toluene

T(°C)	S(scavenger)	$[S]_0$[a]	$[PAT]_0$[b]	PhH[c]	PhBr[c]	PhI[c]
50[d]	I_2	12.0	6.0	1		96
		8.0	4.0	1		94
		4.0	2.0	1		89
	none		4.0	33		
	none[e]		4.0	<2		
70	I_2	12.0	6.0			95
		11.7	6.0	2		94
		8.0	4.0			94
		6.0	3.0	3		93
		4.0	2.0			90
		3.0	1.4	6		91
	CBr_4	36.2	34.4	4	97	
		6.3	5.9	13	84	
		3.0	2.9	17	78	
		1.9	5.7	26	52	
		2.0	11.5	30	37	
	none		1.4	49		
			3.0	54		
			5.9	49		
	none[e]		4.0	<3		

[a,b] Initial concentrations (m/l) of scavenger and PAT times 10^2.

[c] Percent of phenyl radicals produced yielding indicated product. Analyses were by vapor phase chromatography.

[d] Experiments in benzene at this temperature gave very similar results.

[e] Solvent: chlorobenzene.

recombination refers to the similar self-destruction of geminate pairs which at some time achieved a separation of at least one step of diffusive displacement. Geminate pairs which have reached the latter stage of separation may also proceed (reaction 7) to kinetically independent species, "free"

$$\overline{Ph\cdot + R\cdot + N_2} \longrightarrow Ph\cdot + R\cdot + N_2 \qquad (7)$$

radicals, which then suffer independent destructive reactions. Since the radicals from PAT (and other azo compounds) are likely initially separated by an inert nitrogen molecule, it is probable that all geminate pairs should be considered to suffer either secondary recombination or diffusive separation.

Application of the equations of Noyes to a solution of a scavenger which reacts with radicals at a diffusion controlled rate leads to the estimates that no more than about 9% of the radicals which would otherwise undergo secondary recombination would be intercepted by the scavenger at 3×10^{-2} $\underline{M}$, and that a scavenger concentration near 1 $\underline{M}$ is necessary to capture 90% of such radicals. The results of Hammond and Waits indicate that concentrations of bromine in chlorobenzene approaching 2 $\underline{M}$ are necessary to suppress as much as 90% of the geminate recombination in the decomposition of 1,1'-azocyanocyclohexane.[9] Unless the latter data are inapplicable and the Noyes theory incorrect by two orders of magnitude, the iodine results show that most of the phenyl radicals produced escape geminate reactions.

The second consideration relative to geminate reaction of radicals from PAT depends on the fact that decomposition of PAT in toluene at 70° yields about 50% benzene, while decomposition in chlorobenzene yields very little benzene (3% or less). We presume that in toluene most of the benzene results from attack of phenyl at the methyl group. In view of the

$$Ph\cdot + PhCH_3 \longrightarrow PhH + PhCH_2\cdot \qquad (8)$$

facts that similar abstraction reactions are often encountered in free radical chemistry, but that there appears to be no evidence suggesting that these proceed through the cooperative action of two or more radicals, we further assume that reaction 8 is not assisted by a second radical.

Unless reaction 8 is sufficiently rapid to compete with diffusive separation of geminate pairs, at least 50% of the phenyl radicals formed at 70° must escape geminate reactions. A semiquantitative argumant makes the former possibility appear highly unlikely.

The rate of the hydrogen abstraction reaction can be estimated by reference to data on gas phase reactions. Rate constants for the abstraction of hydrogen by gaseous methyl radicals are less than 10^4 $l\text{-}mol^{-1}\text{-}sec^{-1}$ for a number of such

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[9] G. S. Hammond and H. P. Waits, private communication. The data show no indication of scavenging of more than one kind of geminate reaction.

reactions.[10] It is unlikely that phenyl radicals have widely dissimilar reactivities, certainly not by orders of magnitude. The pseudo first order rate constant for reaction 8 in toluene solution (solvent concentration ca. 10 M) is estimated in this manner to be about 10^5 sec.$^{-1}$.

Noyes estimates the maximum lifetime of the geminate pair as about 10^{-9} sec. Geminate reactions must therefore occur with a first order rate constant of 10^9 sec^{-1} or greater.

In order for reaction 8 to compete successfully with a geminate reaction, the above estimates would have to be incorrect by about 4 orders of magnitude. The fact that 50% of the phenyl radicals produced from PAT in toluene yield benzene, in the absence of added scavenger, therefore implies that at least 50% of the phenyl radicals produced escape their geminate partners. Furthermore, unless one is willing to accept the highly unlikely postulate (consider the products from benzoyl peroxide in toluene) that all "free" phenyl radicals abstract hydrogen, the results demand that the number of radical pairs which dissociate be substantially greater than 50% (33% at 50°).

In summary, two kinds of evidence have been presented, both of which strongly indicate that most of the radicals produced from PAT in aromatic solvents escape geminate reactions. We therefore conclude that such processes cannot be a principal source of aromatic phenylation products.

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[10] A large number of rate parameters relating to reactions of this type are tabulated by A. F. Trotman-Dickenson, "Gas Kinetics," Buttersworth Scientific Publications, London, 1955, pp. 199-202.