BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 546—550 (1973)

Solvent Effect on the Free Radical Phenylation with Phenylazotriphenylmethane

Michio Kobayashi, Hiroshi Minato, and Nobuko Watanabe
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya, Tokyo

(Received June 1, 1972)

The effect of solvent on free radical phenylation of arenes was studied by using phenylazotriphenylmethane as the source of phenyl radical. Mixtures of two arenes were phenylated in a solvent (CCl_4, CH_3CN, DMSO, or cyclohexane), and isomer distributions of diaryls produced were determined. The effect of salts ($NaNO_2$, KNO_2, $NaClO_4$) was also studied in DMSO. Both the solvent effect and salt effect suggest the contribution of polar structure in the transition states for the formation of phenylcyclohexadienyl radicals.

Decomposition of phenylazotriphenylmethane (PAT) yields phenyl radical and triphenylmethyl radical.[1] An investigation on the effect of solvents on the rate of the homolysis of PAT showed that the solvent effect is not too great, and an isokinetic relationship holds.[2] The isomer distributions and partial rate factors in phenylations of arenes with PAT were reported in a previous paper.[3]

Although phenylations of arenes have been investigated with various phenyl radical sources (benzoyl peroxide, *N*-nitrosoacetanilide, the Gomberg reaction, *etc.*),[4] their experimental conditions vary considerably and little evidence has been given which warrants the arguments based on the comparison of these data. It has recently been established that free radical phenylation with phenylazo *p*-tolyl sulfone is very little affected by changes in temperature.[5] The effect of solvents on free radical phenylation has not been reported in the literature. Although solvent effects on free radical reactions are believed to be small, a considerable solvent effect was reported on photo-chlorination of

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[1] W. A. Pryor, J. T. Echols, Jr., and K. Smith, *J. Amer. Chem. Soc.*, **88**, 1189 (1966); M. Harada, R. Ito, T. Migita, and O. Simamura, *Kogyo Kagaku Zasshi*, **69**, 962 (1966).

[2] W. G. Bentrude and A. K. McKnight, *Tetrahedron Lett.*, 3147 (1966).

[3] M. Kobayashi, H. Minato, N. Watanabe, and N. Kobori, This Bulletin, **43**, 258 (1970).

[4] G. H. Williams, "Homolytic Aromatic Substitutions," Pergamon Press, Oxford (1960).

[5] M. Kobayashi, H. Minato, M. Kojima, and N. Kamigata, This Bulletin, **44**, 2501 (1971).

substituted toluenes by Russell and Williamson, Jr.[6]

When isomer distributions and partial rate factors in phenylation of arenes are determined, usually a phenyl-radical generator is dissolved in an equimolar mixture of benzene and an arene, and thermally or photochemically decomposed; the amounts of diaryls produced are determined by use of glc, IR, or the isotope dilution method. In these methods, the reacting substrates themselves are the solvents. Thus, what is really determined is the results of reactions of different substrates in different media (solvents). These methods are based on an assumption that solvent effect is negligible in these free radical reactions. However, no one can say *a priori* that the stability of a substituted cyclohexadienyl radical in nitrobenzene is the same as that in anisole. For accurate comparison, aromatic substrates should be phenylated in a large amount of a common inert solvent.

PAT is an effective phenyl radical generator, and its rate of decomposition is very little affected by solvent. In order to investigate the effect of solvent on the free radical phenylation of arenes, arenes have been phenylated with PAT in a large amount of a solvent (CCl_4, CH_3CN, DMSO, or cyclohexane). The effect of added salts ($NaNO_2$, KNO_2, or $NaClO_4$) has also been investigated in DMSO. Results of these investigations are given in this paper.

Experimental

Materials. Solvents and aromatic substrates were purified according to the methods described in "Organic Solvents."[7]

Analyses of Phenylation Products. *(a) In DMSO*: Nitrogen was bubbled through a mixture of PAT (5 mmol), two arenes (0.125 mol each) and DMSO (0.50 mol) for one hr for removal of oxygen, and then the mixture was heated at 60°C till evolution of nitrogen ceased. After an internal standard for glc determination was added, the mixture was washed with water in order to remove DMSO, and concentrated under reduced pressure. The residual oil was analyzed by glc (10% Apiezon L-Chromosorb column, 2 m or 5 m; a Hitachi K53 Gas Chromatograph).

(b) In CH_3CN: A mixture of PAT (5 mmol), two arenes (0.125 mmol each) and CH_3CN (1.0 mol) was treated in a manner similar to that described above for the experiment with DMSO.

(c) In CCl_4: A mixture of PAT (5 mmol), two arenes (0.125 mol each) and CCl_4 (1.0 mol) was also similarly treated. Because of the occurrence of reactions with CCl_4, yields of diphenyls were less, and much 1,1,1-triphenyl-2,2,2-trichloroethane and some benzophenone were found.

(d) In Cyclohexane: Because of smaller solubility of PAT in this solvent, 5 mmol of PAT was dissolved in 1.25 mol of cyclohexane and 0.125 mol each of two arenes. In this solvent, much cyclohexylation of arenes by cyclohexyl radical took place, and glc determination of diaryls and cyclohexylarenes was possible only in a few cases. Thus, the data in cyclohexane should be evaluated with some reservation.

Calculation of Partial Rate Factors. Partial rate factors for PhCN, PhCl, and PhEt were obtained from the isomer distributions of diaryls produced by the decomposition of PAT in mixtures of benzene, an arene and a solvent. In the experiments with PhOMe and $PhNO_2$, removal of these high-boiling arenes requires high temperature, and some non-substituted diphenyl is lost during concentration. The partial rate factors for PhOMe and $PhNO_2$ were therefore calculated from the partial rate factors of chlorobenzene and the isomer distributions of diaryls produced by the decomposition of PAT in mixtures of chlorobenzene, an arene, and a solvent.

Rates of Decomposition of PAT. Rates of decomposition of PAT were determined by measureing the rates of evolution of nitrogen.

Results and Discussion

The rates of decomposition of PAT were found to be of first order. As shown in Table 1, the rate constants vary to some extent in different media, but not too greatly.

TABLE 1. FIRST ORDER RATE CONSTANTS OF DECOMPOSITION OF PAT IN VARIOUS MEDIA AT 60°C[a]

Solvent	PhH	$(CH_2)_6$	MeCN	DMSO	CCl_4
$10^4k_1(\mathrm{sec}^{-1})$	4.66	4.62	3.80	3.10	2.60
Solvent	PhH–PhEt	PhCl–$PhNO_2$	PhCl–PhOMe	PhH–PhCl	
$10^4k_1(\mathrm{sec}^{-1})$	4.67	4.36	3.97	3.64	
Solvent	DMSO–PhMe–PhCl	DMSO–PhCl–$PhNO_2$	DMSO–PhCl–PhOMe		
$10^4k_1(\mathrm{sec}^{-1})$	4.42	3.58	3.40		
Solvent	DMSO–PhH–PhEt	DMSO–PhCl–PhH	DMSO–PhCl–PhEt		
$10^4k_1(\mathrm{sec}^{-1})$	2.96	2.74	2.33		
Solvent	CCl_4–PhCl–PhOMe	CCl_4–PhCl–$PhNO_2$	CCl_4–PhH–PhEt		
$10^4k_1(\mathrm{sec}^{-1})$	3.00	2.90	2.50		
Solvent	CCl_4–PhH–PhCN	CCl_4–PhH–PhCl	$(CH_2)_6$–PhH–PhCl		
$10^4k_1(\mathrm{sec}^{-1})$	2.40	2.30	3.72		
Solvent	DMSO–KNO_2–PhCl–$PhNO_2$	DMSO–KNO_2–PhCl–PhOMe			
$10^4k_1(\mathrm{sec}^{-1})$	3.93	3.64			
Solvent	DMSO–$NaNO_2$–PhCl–PhOMe	DMSO–$NaNO_2$–PhCl–$PhNO_2$			
$10^4k_1(\mathrm{sec}^{-1})$	3.11	3.00			

a) Error range was usually ±3%.

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[6] G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

[7] J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd Edition, Interscience Publishers, New York (1955).

Phenylation of several arenes was carried out in various media using PAT as the phenyl radical source. Atkinson, Perkins, and Ward recently reported that when PAT was decomposed in chlorobenzene the *ortho*-phenylated cyclohexadienyl radical was trapped by trityl radical, and 2-chloro-1,4-dihydro-4-trityldiphenyl was formed.[8] In our experiments, the residual oil obtained by concentration of the reaction mixture was fed directly to the injection port of the gas chromatograph, and any coupling products formed must have been thermolyzed to diaryl and triphenylmethane; therefore the normal diaryl distribution was observed.

Table 2. Isomer distributions of diaryls formed from PAT at 60°C[a)]

Arene		Solvents				
		None	CCl_4	MeCN	DMSO	$(CH_2)_6$
PhOMe	*o*-	67.0	55.7	63.7	75.2	59.7%
	m-	22.5	24.8	21.9	17.6	28.3
	p-	10.5	19.5	14.4	7.2	12.0
PhEt	*o*-	50.1	62.5	48.1	58.4	(b)
	m-	34.1	24.5	35.8	26.2	(b)
	p-	15.8	13.0	16.1	15.5	(b)
PhCl	*o*-	59.9	(b)	61.3	74.5	83.9
	m-	22.6	(b)	22.1	15.6	9.7
	p-	17.5	(b)	16.6	9.9	6.5
PhCN	*o*-	67.6	(b)	68.1	63.6	(b)
	m-	10.1	(b)	10.2	12.3	(b)
	p-	22.4	(b)	21.6	24.1	(b)
$PhNO_2$	*o*-	78.4	66.4	61.4	76.2	(b)
	m-	9.2	8.9	10.6	7.9	(b)
	p-	12.4	24.7	28.0	16.9	(b)

a) Experimental error was ±5%.

b) Determination by glc was not possible due to the presence of by-products.

Table 3. Partial rate factors in phenylation of arenes with PAT in various media at 60°C

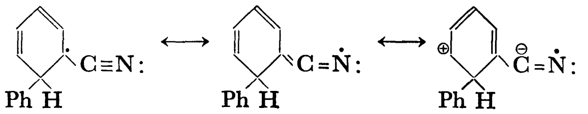
Arene		None	Solvents			
			CCl	MeCN	DMSO	$(CH_2)_6$
PhOMe	*o*-	4.16	1.57	3.38	3.27	2.03
	m-	1.44	0.69	1.14	0.87	1.22
	p-	1.32[a)]	1.07	1.56	0.70	1.29
PhEt	*o*-	1.98	2.96	1.72	1.62	—
	m-	1.50	1.16	1.29	0.73	—
	p-	1.28	1.23	1.16	0.86	—
PhCl	*o*-	3.83	4.23	3.51	3.80	(2.16)
	m-	1.45	1.26	1.24	0.82	—
	p-	2.32	—	1.86	0.93	—
PhCN	*o*-	6.83	—	8.94	8.86	—
	m-	1.03	0.84	1.35	1.72	—
	p-	4.55	4.98	5.69	6.71	—
$PhNO_2$	*o*-	9.58	9.69	7.26	10.99	—
	m-	1.14	1.29	1.26	0.95	—
	p-	3.04	7.18	6.63	4.62	—

a) The value 1.32 should replace the value 2.6 given in our previous paper by mistake.[3)] The correct ρ value for the left half of the V-shaped line for phenylation in aromatic solvents is, therefore, −0.460 instead of −1.51.

Isomer distributions and partial rate factors are shown in Tables 1 and 3. It is clear that variations in isomer distribution and partial rate factors are greater than experimental error. The variations in isomer distributions in particular are fairly great. In general, when the amount of an *o*-isomer increases, the amount of the corresponding *p*-isomer decreases.

When the logarithms of *meta* and *para* partial rate factors are plotted against σ values, *meta* partial rate factors do not vary much with σ values, whereas the plots for *para* partial rate factors usually form V-shaped lines. The ρ value in the right half region is +1.06 in acetonitrile and +0.93 in DMSO; these values differ from the corresponding value for benzoyl peroxide in aromatic solvents (+1.15), that for *N*-nitrosoacetanilide in aromatic solvents (+1.27), and that for phenylazo *p*-tolyl sulfone in aromatic solvents (1.38). The data indicate that the reactivities of arenes with phenyl radical depend on the type of phenyl radical source and also of the solvents used.

The partial rate factors for anisole and benzonitrile are greater in the solvents of greater polarity. This can be rationalized in terms of the stabilization of the transition states by solvation with polar solvents; there must be contribution of a polar structure to the transition states for formation of cyclohexadienyl radicals (a substituted cyclohexadienyl radical form is shown below for the sake of convenience).



When anisole is used as a substrate, the partial rate factors in anisole alone are greater than those in CCl_4 or cyclohexane. This can be ascribed to the fact that anisole itself is a polar solvent.

With ethylbenzene the partial rate factors in polar solvents are smaller than those in CCl_4. This is probably because the contribution of polar structure to transition state is very little when an ethyl group is a substituent.

Since the partial rate factors are the ratios of the reactivities of arenes with that of benzene (or chlorobenzene), the solvent effects observed on partial rate factors should be understood as the difference between the solvent effects on the reactivities of arenes and those on benzene (or chlorobenzene). The solvent effects on the partial rate factor for the *ortho* position of chlorobenzene are very small as shown in Table 3, and we can assume that the solvent effects on partial rate factors represent the solvent effects on the reactivities of arenes. In fact, when phenylation of an equimolar mixture of anisole and benzene was compared with that of an equimolar mixture of anisole and chlorobenzene, the results were the same within experimental error.

The solvent effects on the partial rate factors of nitrobenzene are fairly large, but it is difficult to give an adequate explanation. It might have something to do with the fact that nitrobenzene itself is a polar solvent.

Effect of Temperature on Partial Rate Factors and Isomer

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[8] D. J. Atkinson, M. J. Perkins, and P. Ward, *J. Chem. Soc. C*, **1971**, 3240.

Table 4. Isomer distributions and partial rate factors in phenylations at different temperatures

Arene		Isomer distribution		Partial rate factor	
		60°C	80°C	60°C	80°C
PhOMe	*o*-	75.2	68.7	3.27	2.40
	m-	17.6	19.7	0.87	0.69
	p-	7.2	10.0	0.70	0.72
PhCl	*o*-	74.5	78.5	3.80	2.33
	m-	15.6	13.5	0.82	0.41
	p-	9.9	8.0	0.93	0.49
PhNO	*o*-	76.3	76.9	10.99	9.57
	m-	7.9	7.7	0.95	0.96
	p-	16.9	15.3	4.62	3.82

Table 5. Effect of salts on isomer distributions at 60°C[a)]

Arene		No Salt	$[\mathrm{NaClO_4}]=0.70$	$[\mathrm{NaNO_2}]=0.45$	$[\mathrm{NaNO_2}]=0.84$	$[\mathrm{NaNO_2}]=0.66$
PhOMe	*o*-	75.2	73.1	70.8	71.6	
	m-	17.6	19.3	18.4	18.4	
	p-	7.2	7.7	10.9	9.9	
PhEt	*o*-	58.4	54.2			
	m-	26.2	32.6			
	p-	15.5	13.2			
PhCl	*o*-	74.5	64.4			62.6
	m-	15.6	20.6			19.5
	p-	9.9	15.0			17.4
PhCN	*o*-	63.6	63.5			
	m-	12.3	11.4			
	p-	24.1	25.2			
$\mathrm{PhNO_2}$	*o*-	76.2	55.1		68.0	
	m-	7.9	11.0		6.5	
	p-	33.9	33.9		25.6	

a) In DMSO. [PAT]=0.12 M.

Table 6. Effect of salts on partial rate factors at 60°C[a)]

Arene		No Salt	$[\mathrm{NaClO_4}]=0.70$	$[\mathrm{NaNO_2}]=0.45$	$[\mathrm{NaNO_2}]=0.66$	$[\mathrm{NaNO_2}]=0.84$
PhOMe	*o*-	3.27	4.10	3.03		3.00
	m-	0.87	1.08	0.80		0.77
	p-	0.70	0.86	0.95		0.84
PhEt	*o*-	1.62	2.62			
	m-	0.73	1.58			
	p-	0.86	1.28			
PhCl	*o*-	3.80	4.23		3.51	
	m-	0.82	1.35		1.11	
	p-	0.93	1.97		2.06	
PhCN	*o*-	8.86	11.85			
	m-	1.72	2.10			
	p-	6.71	9.35			
$\mathrm{PhNO_2}$	*o*-	10.99	6.67			6.95
	m-	0.95	1.33			0.66
	p-	4.62	8.24			5.23

a) In DMSO. [PAT]=0.12M.

Distribuitons. The partial rate factors in phenylation of arenes with phenylazo *p*-tolyl sulfone change very little with temperature.[5)] Table 4 compares the isomer distributions and the partial rate factors in phenylation with PAT at 60 and 80°C. It is clear that they change very little with temperature in this case too. Since partial rate factors are always smaller at higher temperatures, the activation energy for phenylation of benzene must be a little greater than those for phenylation of substituted benzenes.

Effect of Salts on Partial Rate Factors and Isomer Distributions. If the solvent effect is due to the contribution of polar structures to transition state, addition of salts to the medium is expected to result in change in partial rate factors and isomer distributions. Arenes were phenylated in the media containing sodium perchlorate and sodium nitrite. The results are summarized in Tables 5 and 6. The effect of added salts is fairly great in chlorobenzene and nitrobenzene; in both cases the amount of the *ortho* isomer decreases and that of the *para* isomer increases upon addition of salt. In the case of nitrobenzene, the presence of $NaClO_4$ and $NaNO_2$ in about the same concentration results in different isomer distributions. Thus, not only the ionic strength but also the kind of anion probably influence the stabilization of transition state. Since DMSO solvates cations strongly but solvates anions very little, the anions added are more free than the counter cations, thus directly contributing to the stabilization of transition state.

Decrease in the amount of *ortho* isomers and increase in that of *para* isomers could arise either from the decrease of *ortho* partial rate factors or from the increase of *para* partial rate factors. Table 6 shows that, in general, partial rate factors increase upon addition of salts and the increase of *para* partial rate factors are especially great. Only one exception is the case of nitrobenzene, in which the *ortho* partial rate factor decreased upon addition of salts. Thus both the solvent effect and the salt effect are irregular in the case of nitrobenzene.

Although more detailed investigations are required for understanding the salt effect in phenylation, the fact that all the partial rate factors (except for that of the *ortho* position of nitrobenzene) increase upon addition of salts suggests that the contribution of polar structure in the transition state is greater for the addition of phenyl radical to substituted benzenes than that of phenyl radical to benzene itself; increase in ionic strength should stabilize the transition state for the addition of phenyl radical to substituted benzenes.

In conclusion, both the solvent effect and salt effect suggest the contribution of polar structure in the transition state for the addition of phenyl radical to arenes.