# Rates of the Reactions of Substituted Phenyl Radicals with Hydrogen Donors[1,2]

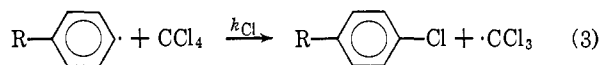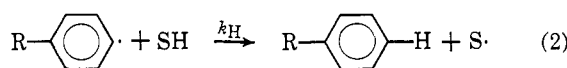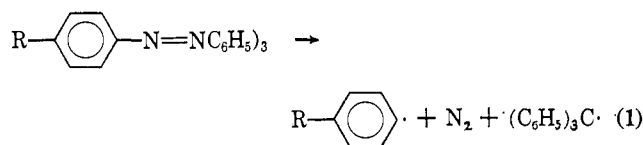William A. Pryor, J. T. Echols, Jr.,[3] and Kennedy Smith

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received September 27, 1965

Abstract: The relative reactivities of a series of hydrogen donors SH and carbon tetrachloride were measured toward *p*-tolyl, phenyl, *p*-bromophenyl, and *p*-nitrophenyl radicals, generated from the appropriate arylazotriphenylmethane at 60°. The data are expressed as k_H/k_{Cl} values (see reactions 2 and 3). For all the hydrogen donors studied, the values of k_H/k_{Cl} increase in the order *p*-tolyl < phenyl < *p*-bromophenyl < *p*-nitrophenyl. The ρ values in the Hammett equations for hydrogen abstraction from substituted toluenes by these radicals also become increasingly larger negative numbers in this order. These effects are explained by postulating polar resonance structures for the transition states for the reactions. The *p*-tolyl and the phenyl radicals show very little sensitivity to polar factors, whereas the *p*-nitrophenyl radical is significantly electrophilic; in hydrogen abstraction from ring-substituted toluenes it gives $\rho = -0.6$, nearly the same value that is obtained for the reaction of chlorine atoms with substituted toluenes. The selectivity of the radicals also increases in the same order, with *p*-nitrophenyl being the most discriminating radical in selecting between primary, secondary, and tertiary benzylic hydrogen atoms, between hydrogen and deuterium in deuterioacetone, and responding most to the electronic nature of substituents in the hydrogen donor. The technique for calculation of k_H/k_{Cl} values from experimental data is discussed in some detail, and it is concluded that yields of products should be extrapolated to infinite dilution in the radical source. When this is done, the sum of the yields of ArH and ArCl from decomposition of $ArN=NC(C_6H_5)_3$ in SH–CCl₄ mixtures approaches 100% for aliphatic solvents. However, for aromatic and olefinic solvents the yield remains less than 100% even at infinite dilution. If it is assumed that "each missing" Ar radical has added to (or arylated) one solvent molecule, values of k_{ad}/k_{Cl} can be calculated. These values also increase in the order of *p*-tolyl < *p*-nitrophenyl for any given unsaturated solvent.

The relative reactivities of radicals most often have been compared by measuring their rates in abstracting hydrogen atoms from a variety of hydrogen donors SH.[4] Phenyl radicals generated from phenyl-

$$R\cdot + SH \longrightarrow RH + S\cdot$$
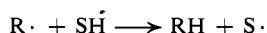
azotriphenylmethane (PAT) recently have been studied extensively in this way.[5] PAT is an excellent source of phenyl radicals since it yields 95–98% free phenyl radicals in most solvents, and since the triphenylmethyl (trityl) radical reacts with secondary radical products and reduces kinetic complications. We have now extended the study of radical reactivity to include reactions of ring-substituted phenyl radicals produced from substituted PAT-type compounds. Our technique has been the usual one[5] of generating radicals in a mixture of hydrogen donor solvent SH and CCl₄ and comparing the amounts of hydrogen abstraction from SH with chlorine abstraction from carbon tetrachloride. Radicals were generated at 60° from the decomposition of the substituted azo compound, and the solutions were analyzed at the completion of the reaction for ArH and ArCl using gas phase chromatography (gpc). This technique requires that reactions 2 and 3 be of the

(1) Reactions of Radicals, Part XII. Some of this material was presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) This work was supported in part by a Public Health Service research grant from the National Institutes of Health.

(3) A Postdoctoral student supported by the National Institutes of Health.

(4) For reviews see: A. F. Trotman-Dickenson, "Free Radicals: An Introduction," John Wiley and Sons, Inc., New York, N. Y., 1959, pp 61–91; W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapter 12.

(5) (a) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963); (b) W. A. Pryor and H. Guard, *ibid.*, **86**, 1150 (1964); (c) M. V. Bazilevskii and Kh. S. Bagdasar'yan, *Kinetics Catalysis* (USSR) (Engl. Transl.) **5**, 189 (1964); M. V. Vazilevskii, *Russ. J. Phys. Chem.* (Engl. Transl.), **38**, 122 (1964).

$$R-\!\!\!\bigcirc\!\!\!-N=NC_6H_5)_3 \longrightarrow$$

$$R-\!\!\!\bigcirc\!\!\!\cdot + N_2 + (C_6H_5)_3C\cdot \quad (1)$$

$$R-\!\!\!\bigcirc\!\!\!\cdot + SH \xrightarrow{k_H} R-\!\!\!\bigcirc\!\!\!-H + S\cdot \quad (2)$$

$$R-\!\!\!\bigcirc\!\!\!\cdot + CCl_4 \xrightarrow{k_{Cl}} R-\!\!\!\bigcirc\!\!\!-Cl + \cdot CCl_3 \quad (3)$$

same order in Ar radicals; this was demonstrated by showing that variations in the ratio of SH to CCl₄ and of the concentration of the azo compound had little or no influence on the k_H/k_{Cl} values. Bridger and Russell[5a] and ourselves[5b] have previously concluded that PAT satisfied this requirement.

The technique also requires that reactions 2 and 3 be the only sources of ArH and ArCl. This is not strictly true since some ArH is formed even when these initiators are allowed to decompose in pure carbon tetrachloride. We believe this amount of ArH arises from the reaction of Ar· with trityl radicals in a reaction which occurs both in the cage and in the free solution. We have solved this problem by extrapolating all yields of products back to zero molarity of the radical source and subtracting the amount of ArH formed in the reaction between Ar· and trityl in the cage from the total yield of ArH. Our values of k_H/k_{Cl} therefore are calculated as

$$\frac{k_H}{k_{Cl}} = \frac{[(ArH)_0 - (ArH)_{cage}]}{(ArCl)_0}R \quad (4)$$

where R is the mole ratio of CCl₄ to the SH solvent used and is constant in any run, $(ArH)_0$ and $(ArCl)_0$
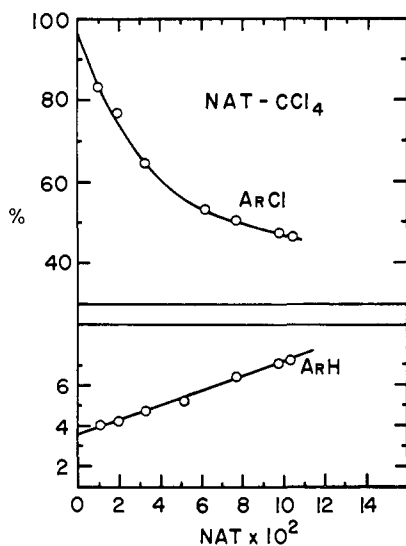
Figure 1. Per cent yield of nitrobenzene and p-chloronitrobenzene vs. the molarity of NAT in pure carbon tetrachloride at 60°.

are the yields of ArH and ArCl extrapolated to zero concentration of the azo compound, and $(ArH)_{cage}$ is taken as the amount of ArH formed in the decomposition of the azo compound in pure carbon tetrachloride, again extrapolated to infinite dilution. This procedure is discussed and justified later. The azo compounds studied are listed in Table I.

Table I

Ar in ArN=NC(C₆H₅)₃	Abbreviation
Phenyl	PAT
p-Bromophenyl	BrAT
p-Nitrophenyl	NAT
p-Methylphenyl (p-tolyl)	TAT

Experimental Section

Azo compounds were synthesized using modifications of methods reported in the literature.[6] They were checked for absence of hydrazo compounds or other possible hydrogen-donor impurities by analyzing the reaction mixtures resulting from the decomposition of 0.1 M solutions of the azo compound in pure carbon tetrachloride. If the yield of ArH was higher than the minimum value, precipitation of the hydrochloride salt of the hydrazo compound from an ether solution of the azo compound,[5a] reoxidation, or recrystallization were used to reduce it to this minimum value.

Chemicals. Carbon tetrachloride was spectral grade and was further purified by passing through a column packed with silica gel. Liquid solvents were examined directly by gpc and solvents which are solids at room temperature were examined as carbon tetrachloride solutions; impurities were generally less than 1%, and the absence of ArH and ArCl was demonstrated. Most solvents were Eastman Kodak, Fisher, Aldrich, Baker, or Mallinckrodt. Acetone-d_6 was supplied by the Nuclear Research Chemicals Corp. and was 99.5% isotopically pure. Hexane was Amsco Hi purity, and p-phenoxy- and p-methoxytoluene were supplied by the Research Organic Chemicals Co.

Chromatography Technique. Solvent mixtures were prepared by weight or volume and were added to known weights of azo compounds in volumetric flasks and transferred to ampoules using long syringe needles, and the ampoules were de-aired in the usual manner.

(6) (a) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953); (b) We have recently developed a synthesis using ArN₂⁺BF₄⁻ and trityllithium. Our modifications of the older method, therefore, are not given.

(The azo compound occupies an appreciable volume and solutions could not be prepared by measuring in one solvent and then diluting to a known volume with carbon tetrachloride.) The ampoules were placed in a light-proof oil bath at 60.0 ± 0.01° and held there for 10 half-lives of the azo compound. Analyses were performed on a MicroTek Model 2000R gas chromatograph with dual columns, temperature programming, and flame-ionization detectors. A Westronics recorder with DiscChart Integrator was used. A calibration graph giving peak area vs. molarity was prepared for each compound by analyzing a standard volume of known solutions in carbon tetrachloride. Analysis of unknown solutions was always preceded and followed by the known standards. Reproducibility was better than about 1.0%. Chromatographic columns and conditions are given in Table II.
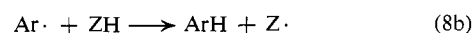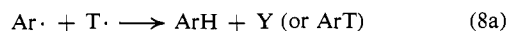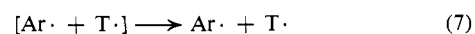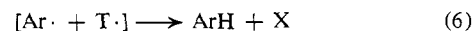
Table II. Chromatography Conditions

Azo compd	Column length, ft	Packing[a]	Column temp, °C[b]	Relative retention times[c]
NAT	6	B-DIP-1	115	25:31
BrAT	8	CW	140	8.5:18.5
TAT	12	B-DIP-2	d	2.5:6.0
PAT	12	B-DIP-1	e	1.7:4.2

[a] Columns were 0.125-in. stainless tubing. B-DIP is 5% Bentone-34 and diisodecyl phthalate on (1) 80–90 Chromport XXX or (2) 80–100 Chromport XXX; CW is 20% Carbowax 20M on 60–80 Chromport XXX. [b] Injector temperature was 200°, detector was 235°, and the nitrogen gas flow was 30 cc/min throughout. [c] Retention times for ArH and ArCl, respectively, relative to that of CCl₄ as 1.0. [d] Column held at 70° until toluene elutes and then raised to 100° at 10°/min. [e] Column held at 50° until benzene elutes and then raised to 100° at 10°/min.

Results and Discussion

Cage Processes. The general features of these azo compound reactions can be discussed using NAT as a specific example. The decomposition of a 0.1 M solution of NAT in pure carbon tetrachloride produces a 46% yield of p-chloronitrobenzene (ArCl) and a 7% yield of nitrobenzene (ArH). As shown in Figure 1, the yields of ArCl increase rapidly as the initial NAT concentration is reduced and the yields of ArH decrease linearly until at infinite dilution yields are 3.5% ArH and about 96% ArCl.

We suggest the following mechanism for the formation of ArH in nonhydrogen donor solvents such as carbon tetrachloride

$$\text{NAT} \longrightarrow [\text{Ar·} + \text{T·}] + \text{N}_2 \qquad (5)$$

$$[\text{Ar·} + \text{T·}] \longrightarrow \text{ArH} + \text{X} \qquad (6)$$

$$[\text{Ar·} + \text{T·}] \longrightarrow \text{Ar·} + \text{T·} \qquad (7)$$

$$\text{Ar·} + \text{T·} \longrightarrow \text{ArH} + \text{Y (or ArT)} \qquad (8a)$$

$$\text{Ar·} + \text{ZH} \longrightarrow \text{ArH} + \text{Z·} \qquad (8b)$$
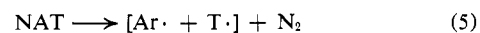
where T is the trityl radical, square brackets represent caged radicals, X and Y are unknown molecular products, and ZH is a product formed by reaction of any of the species present. (For example, products such as X or Y may act as hydrogen donors in subsequent reactions.)

Reaction of radicals in the cage to produce ArH competes with diffusion from the cage, and reaction 6 produces a constant amount of ArH from a geminate process regardless of the concentration of NAT. As the NAT concentration increases, a reaction which is first order in NAT (see Figure 1) contributes an additional amount of NAT. This reaction yielding ArH in the free solution in carbon tetrachloride could be the re-
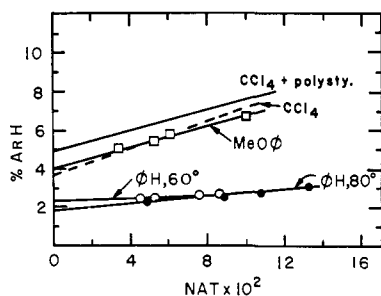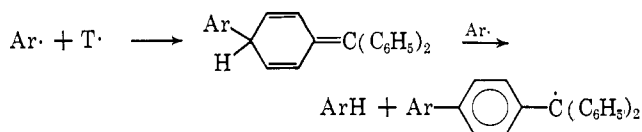
Figure 2. Per cent yields of nitrobenzene vs. NAT molarity in several solvents which are very poor hydrogen donors.
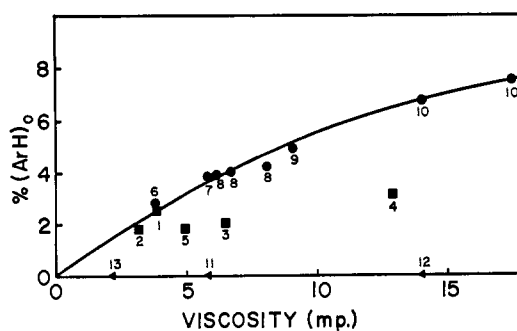

Figure 3. Yields of ArH at infinite dilution for NAT at 60° vs. the viscosity of the solvent (in millipoises): 1, benzene; 2, benzene (80°); 3, benzene plus polystyrene; 4, benzene plus Dow Silicone 710; 5, chlorobenzene; 6, carbon tetrachloride (100°); 7, carbon tetrachloride; 8, carbon tetrachloride plus varying amounts of Dow Silicone 710; 9, carbon tetrachloride plus polystyrene; 10, carbon tetrachloride plus varying amounts of Dow Silicone 200; 11, carbon tetrachloride plus iodine (0.19 M); 12, carbon tetrachloride plus Dow Silicone 200 plus iodine (0.18 M); 13, carbon disulfide.
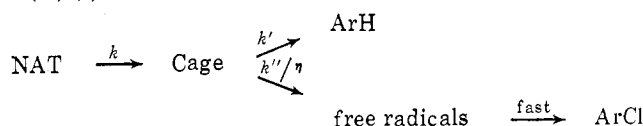
action of Ar· with (1) NAT, (2) Ar·, (3) trityl radicals, or (4) some reaction product ZH.

(1) The process leading to ArH in solution is *probably not* the reaction of free Ar radicals with NAT since that reaction would not be first order in NAT and since PAT and NAT show no evidence of induced decompositions. (2) The reaction of Ar· with itself to produce ArH is also unlikely since the concentration of Ar· is much too small for this to be probable. (3) Some of the ArH formed in the free solution probably arises from the same reaction which leads to ArH in the cage, namely, the reaction of Ar· with trityl. The concentration of trityl radicals is sufficiently high so that they could become an important scavenger for Ar· radicals. Furthermore, some products which could be of the X and Y type have been isolated from PAT experiments.[7,8] (4) There is also some evidence that primary reaction products can react with Ar radicals to produce ArH (reaction 8b). One possibility of this type which has been demonstrated to occur is shown below.[7g] However, since the

$$Ar· + T· \longrightarrow \underset{H}{Ar}\diagdown\diagup=C(C_6H_5)_2 \xrightarrow{Ar·}$$

$$ArH + Ar\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup\dot{C}(C_6H_5)_2$$

extrapolated yields of ArH plus ArCl are 100%, this reaction, and others like it which consume Ar radicals, do not occur at infinite dilution. Figure 1 shows that the total yield decreases sharply as the NAT concentration is increased above 0.01 M, and reactions like this may become significant sources of ArH at finite concentrations.

Figure 2 shows the yield of ArH from NAT in a number of solvents which are such poor hydrogen donors that ArH from reaction 2 can be neglected.[9]

(7) (a) D. H. Hey and M. J. Perkins, *Tetrahedron Letters*, 445 (1963); (b) D. H. Hey and R. Tewfik, *J. Chem. Soc.*, 2402 (1965); (c) D. H. Hey and J. Peters, *ibid.*, 79 (1960); (d) D. H. Hey, M. J. Perkins, and G. H. Williams, *ibid.*, 110 (1965); (e) E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Letters*, 749 (1962); (f) J. F. Garst and R. S. Cole, *ibid.*, 679 (1963); (g) Professor J. A. Kampmeier, and R. P. Geer, Ph.D. Thesis, University of Rochester, 1964; (h) M. J. Perkins, *J. Chem. Soc.*, 5932 (1964); (i) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Inc., New York, N. Y., 1960.

(8) (a) An obvious possibility for X is 9-phenylfluorene, but there is no simple mechanism which could produce this product directly. (b) In benzene and p-xylene, products are found which result from the addition of Ar to the solvent followed by reaction with trityl radicals. See ref 7c,d. Reactions of these types lead to potential hydrogen donors, but not in nonaromatic solvents.

(9) Notice that the lines in Figure 2 for these poor hydrogen donors all slope upward to the right; lines for solvents in which reaction (2) provides a source of ArH slope downward. (For example, compare Figure 2 with Figures 4, 5, and 6.)

The lines can be extrapolated to zero molarity of NAT to give a value of (ArH)₀. Figure 3 shows that these values of (ArH)₀ are proportional to the viscosity of the solvents. This is strong evidence that this amount of ArH is produced in a cage reaction; the lifetime of the cage, and consequently the yield of product from reaction 6, should increase in proportion to the viscosity of the solvent.[10a] The line in Figure 3 is drawn through the origin since the yield of cage products is zero at zero viscosity (as in the gas phase).

In Figure 3, the points for aromatic solvents and for solvents containing appreciable concentrations of the scavenger iodine lie well below the line which joins the carbon tetrachloride data. Clearly, viscosity is not the only factor which determines the yield of ArH at infinite dilution. We currently hypothesize that the

Table III

	(ArH)₀, %	k_6/k_7
TAT	3.5	0.036
PAT	3.4	0.035
BrAT	3.7	0.038
NAT	3.7	0.038

(10) (a) For the scheme

$$NAT \xrightarrow{k} Cage \overset{k'}{\underset{k''/\eta}{\diagup\diagdown}} \begin{array}{l} ArH \\ \\ free\ radicals \xrightarrow{fast} ArCl \end{array}$$

at the steady state in cage concentrations and assuming that $k' < k''/\eta$, $d(ArH)/dt = (kk'\eta/k'')$ (NAT). For two solvents of slightly different viscosities and small extents of cage reactions such that k, k', and k'' are independent of viscosity

$$\frac{d(ArH)_1}{d(ArH)_2} = \frac{\eta_1(NAT)_1}{\eta_2(NAT)_2} = \frac{\eta_1}{\eta_2}$$

where the subscripts refer to the two solvents. This simple proportionality will fail if the cage product becomes appreciable so that $k' \approx k''/\eta$, or if the cage reverts to starting material so that $d(NAT)/-dt$ itself depends on the viscosity. For a more complex case, see W. Braun, L. Rajenbach, and F. R. Eirich, *J. Phys. Chem.*, 66, 1591 (1962); (b) H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 1911 (1964). (c) It should be pointed out that special solvent mixtures were used for the experiments shown in Figure 3; these mixtures had much higher viscosities than did any of the SH–CCl₄ mixtures used in hydrogen abstraction studies. The uncertainty in (ArH)₀ in calculations of k_H/k_{Cl} values is far less than the range of (ArH)₀ values shown in Figure 3.

Table IV. Products from the Reaction of TAT, PAT, BrAT, and NAT in Various Solvents at 60°[a]

Hydrogen donor, SH	$(CCl_4)/(SH)$	$(Azo) \times 10^2$	% ArH	% ArCl	k_H/k_{Cl}	k_{ad}/k_{Cl}
p-Tolylazotriphenylmethane (TAT)						
Carbon tetrachloride	. . .	11.1	8.2	75.6		
Carbon tetrachloride	. . .	9.00	7.3	77.5		
Carbon tetrachloride	. . .	6.60	5.7	. . .		
Carbon tetrachloride	. . .	6.00	5.8	. . .		
Carbon tetrachloride	. . .	4.40	5.4	83.0		
Carbon tetrachloride	. . .	0	3.5	. . .	. . .	. . .
Acetone (3)	0.76	0	18.4	80.0	0.14	0.07
Acetone-*d₆* (4)	0.095	0	19.7	40.8	0.040	. . .
Cyclohexene (4)	3.15	0	38.4	15.4	7.1	9.4
Methyl acetate (1)	0.274	5.00	17.8	42.2	0.075	. . .
Hexane (1)	1.35	5.00	30.5	37.1	0.89	. . .
p-Methoxytoluene (3)	1.30	0	20.4	63.0	0.35	0.34
m-Xylene (3)	1.27	0	30.1	5.28	0.64	0.41
m-Bromotoluene (3)	1.26	0	19.2	66.6	0.29	0.27
p-Bromotoluene (3)	1.27	0	15.8	55.2	0.28	0.67
p-Fluorotoluene (3)	1.14	0	21.0	66.6	0.30	0.21
p-Nitrotoluene (3)	3.08	0	9.6	72.0	0.26	0.57
Thiophenol (3)	10.6	0	97.0	2.2	450	. . .
Thiophenol (3)	31.9	0	76.5	5.1	420	. . .
Phenylazotriphenylmethane (PAT)						
Toluene	0.552	2.52	. . .	37.0		
Toluene	0.552	9.20	. . .	29.1		
Toluene	0.552	4.10	. . .	35.0		
Toluene	0.552	6.00	23.5	33.1		
Toluene	0.552	3.33	27.5	36.1		
Toluene	0.552	10.9	20.2	26.0		
Toluene	0.552	0	26.7	40.2	0.36	0.41
p-Methoxytoluene (3)	2.60	0	19.4	73.6	0.57	0.25
p-Methoxytoluene (3)	1.30	0	24.8	50.4	0.56	0.64
p-Xylene (3)	3.84	0	21.6	66.7	1.02	0.67
Mesitylene (3)	1.45	0	29.5	33.1	1.14	1.6
m-Bromotoluene (3)	1.26	0	15.3	56.7	0.26	0.62
Thiophenol (4)	34.4	0	94.0	6.0	518	
p-Bromophenyltriphenylmethane (BrAT)						
Carbon tetrachloride	. . .	9.83	7.8	. . .		
Carbon tetrachloride	. . .	8.24	7.1	. . .		
Carbon tetrachloride	. . .	6.70	6.4	. . .		
Carbon tetrachloride	. . .	5.03	6.0	. . .		
Carbon tetrachloride	. . .	3.35	4.8	. . .		
Carbon tetrachloride	. . .	0	3.7	. . .	. . .	. . .
Acetone (3)	0.76	1.81	21.9	40.0	0.35	0.72
Acetone-*d₆* (3)	0.095	0	33.0	33.0	0.084	. . .
Cyclohexane (1)	1.12	5.00	53.6	15.3	3.54	. . .
Cyclohexene (3)	5.25	0	49.0	15.9	14.9	11.6
Methyl acetate (1)	0.823	5.00	17.5	48.8	0.22	. . .
Hexane (1)	1.35	5.00	45.0	19.4	2.76	. . .
Toluene	1.11	4.60	19.8	23.0		
Toluene	1.11	2.46	20.0	27.2		
Toluene	1.11	1.40	20.0	28.6		
Toluene	1.11	0	20.3	23.8	0.77	2.6
Toluene	0.370	7.68	22.1	8.3		
Toluene	0.370	5.25	22.6	8.6		
Toluene	0.370	3.72	23.0	8.6		
Toluene	0.370	0	24.0	9.3	0.80	2.7
Ethylbenzene	1.27	0	33.0	14.9	2.49	8.7
Cumene	1.45	0	35.8	12.4	3.75	6.1
n-Propylbenzene	1.45	0	32.8	20.0	2.11	3.4
t-Butylbenzene	0.536	0	12.0	22.5	0.19	1.6
p-Methoxytoluene	1.29	0	25.8	22.2	1.28	3.0
p-Xylene	1.28	0	36.8	19.6	2.16	2.8
m-Xylene	1.27	0	32.0	21.6	1.66	2.7
Mesitylene	1.45	0	22.6	9.7	2.85	10.0
p-Fluorotoluene	1.14	0	19.6	29.4	0.61	2.0
p-Nitrotoluene	3.08	0	14.3	52.0	0.62	2.0
p-Nitrotoluene	1.11	0	13.2	19.2	0.54	3.9
Thiophenol	34.4	0	94.2	5.7	569	
p-Nitrophenylazotriphenylmethane (NAT)						
Carbon tetrachloride	. . .	10.4	7.2	46.4		
Carbon tetrachloride	. . .	9.80	7.0	47.3		
Carbon tetrachloride	. . .	7.70	6.7	50.6		
Carbon tetrachloride	. . .	5.20	5.2	53.0		
Carbon tetrachloride	. . .	3.33	4.9	64.5		
Carbon tetrachloride	. . .	1.02	4.0	83.0		
Carbon tetrachloride	. . .	0	3.7	96	. . .	. . .
Anisole (5)	. . .	0	4.0	. . .	. . .	. . .

Table IV (*Continued*)

Hydrogen donor, SH	$(CCl_4)/(SH)$	$(Azo) \times 10^2$	% ArH	% ArCl	k_H/k_{Cl}	k_{ad}/k_{Cl}
Benzene	...	10.1	2.6	...		
Benzene	...	8.60	2.6	...		
Benzene	...	7.60	2.5	...		
Benzene	...	5.30	2.4	...		
Benzene	...	4.56	2.4	...		
Benzene	...	3.25	1.8	...		
Benzene	...	0	2.0	...	...	...
Benzene (80°)	...	0	1.9	...	...	...
n-Hexane	...	0	99.8	...		
Cyclohexane	...	3.90	70.6	...		
Cyclohexane	...	2.03	79.0	...		
Cyclohexane	...	1.11	91.2	...		
Cyclohexane	...	0	97.5	...	...	...
p-Methoxytoluene	...	0	15.2	...	...	...
Toluene	...	5.93	13.1	...		
Toluene	...	3.94	12.9	...		
Toluene	...	2.23	13.6	...		
Toluene	...	1.06	14.2	...		
Toluene	...	0	14.5	...	...	...
m-Chlorotoluene	...	0	10.1	...	...	...
Acetone (3)	2.90	0	16.0	57.8	0.613	1.31
Acetone (7)	0.760	0	28.1	31.0	0.600	1.01
Acetone (5)	0.095	0	55.1	8.0	0.610	0.44
Acetone-d_6 (3)	0.095	0	21.7	13.9	0.123	...
Cyclohexane (5)	1.53	0	86.0	14.0	9.0	...
Cyclohexane (6)	4.0	0	72.5	27.5	10.0	...
Cyclohexane (4)	6.72	0	58.5	41.0	9.0	...
Cyclohexane (4)	11.2	0	47.0	53.0	9.2	...
Cyclohexane (5)	61.6	0	17.5	82.5	10.3	...
Cyclohexane (3)	12.6	0	37.9	13.4	33.0	46.0
Cyclohexane (3)	8.40	0	34.6	8.6	30.5	55.5
Hexane (5)	4.05	0	66.0	34.0	7.50	...
Heptane	3.20	9.50	57.0	15.4	11.1	...
1-Bromohexane	1.44	9.80	46.5	11.5	5.4	...
Ethylbenzene	2.55	8.41	13.8	4.0		
Ethylbenzene	2.55	4.14	14.2	4.2		
Ethylbenzene	2.55	2.22	14.3	3.9		
Ethylbenzene	2.55	0	14.5	4.3	7.0	48
Cumene	4.33	10.8	18.8	6.4		
Cumene	4.33	7.10	22.4	7.2		
Cumene	4.33	3.49	26.9	7.5		
Cumene	4.33	0	30.0	8.0	14.6	33
n-Propylbenzene (3)	5.78	0	22.2	7.4	14.4	58
t-Butylbenzene (3)	0.806	0	4.9	4.8	0.21	20
Toluene	3.33	10.2	9.8	13.1		
Toluene	3.33	7.70	10.0	13.8		
Toluene	3.33	5.90	10.4	14.2		
Toluene	3.33	4.70	10.6	14.2		
Toluene	3.33	2.02	10.8	14.5		
Toluene	3.33	1.21	10.9	14.7		
Toluene	3.33	0	11.2	15.0	1.67	16.4
Toluene	1.11	14.1	16.2	7.8		
Toluene	1.11	10.2	16.9	8.4		
Toluene	1.11	10.0	16.6	8.4		
Toluene	1.11	9.70	16.9	8.8		
Toluene	1.11	8.10	17.1	9.5		
Toluene	1.11	5.00	17.4	9.7		
Toluene	1.11	2.54	18.8	10.0		
Toluene	1.11	0	19.4	10.4	1.67	7.5
p-Methoxytoluene	3.05	10.1	11.7	7.3		
p-Methoxytoluene	3.05	6.60	11.9	7.5		
p-Methoxytoluene	3.05	4.05	12.5	8.3		
p-Methoxytoluene	3.05	0	12.9	9.2	3.05	25.5
p-Methoxytoluene	1.94	11.3	14.5	5.6		
p-Methoxytoluene	1.94	7.90	15.9	7.1		
p-Methoxytoluene	1.94	5.70	15.9	7.2		
p-Methoxytoluene	1.94	0	16.9	8.8	2.91	16.4
p-Phenoxytoluene	4.88	5.05	7.9	11.8		
p-Phenoxytoluene	4.88	2.83	8.2	13.0		
p-Phenoxytoluene	4.88	1.72	8.6	14.1		
p-Phenoxytoluene	4.88	0	9.2	15.0	1.79	24.6
p-Xylene	4.53	10.8	20.9	16.1		
p-Xylene	4.53	7.60	22.6	16.7		
p-Xylene	4.53	4.70	23.7	18.3		
p-Xylene	4.53	0	25.6	20.2	4.85	12.2
p-Xylene	1.94	9.60	25.4	9.0		
p-Xylene	1.94	7.10	26.2	9.5		

Table IV *(Continued)*

Hydrogen donor, SH	(CCl$_4$)/(SH)	(Azo) $\times 10^2$	% ArH	% ArCl	k_H/k_{Cl}	k_{ad}/k_{Cl}
p-Xylene	1.94	4.60	26.5	9.7		
p-Xylene	1.94	0	28.8	10.2	4.80	11.7
p-Xylene	1.16	10.3	22.5	4.7		
p-Xylene	1.16	9.70	23.1	4.8		
p-Xylene	1.16	6.90	25.6	5.0		
p-Xylene	1.16	4.35	25.7	5.2		
p-Xylene	1.16	0	28.0	5.7	4.94	13.5
m-Xylene	3.80	9.70	13.8	10.9		
m-Xylene	3.80	6.10	14.2	11.4		
m-Xylene	3.80	4.30	14.7	12.1		
m-Xylene	3.80	0	15.8	12.5	3.66	21.0
m-Xylene	1.91	9.00	17.4	6.7		
m-Xylene	1.91	6.90	17.4	6.7		
m-Xylene	1.91	5.80	17.5	7.0		
m-Xylene	1.91	4.60	17.6	7.6		
m-Xylene	1.91	0	17.8	7.2	3.72	19.8
Mesitylene (4)	7.18	0	9.6	7.2	5.90	82.5
p-Bromotoluene (3)	1.16	0	14.3	9.8	1.33	7.8
m-Bromotoluene (4)	1.26	0	12.6	10.5	1.06	9.2
p-Chlorotoluene (2)	3.67	0	10.7	20.0	1.28	12.7
m-Chlorotoluene (4)	1.13	0	11.7	9.3	0.972	9.6
p-Fluorotoluene (4)	1.12	0	18.6	13.3	1.24	5.8
p-Nitrotoluene (3)	2.52	0	8.7	18.5	0.68	21.0
Thiophenol (3)	42.5	0	95.5	4.5	869	
Anisole (4)	1.13	0	4.5	6.9	0.13	15.1
Anisole (3)	0.755	0	4.0	4.9	0.14	14.1
Anisole (3)	0.483	0	5.9	3.6	0.16	12.2

[a] The values of per cent ArH and per cent ArCl listed for 0 M azo compound are the extrapolated values at infinite dilution using graphs analogous to Figures 4 and 5; however, to conserve space, only the extrapolate value is shown for the majority of solvents. See footnote 11.

low values in Figure 3 result from scavenging of radicals by reactive species (such as benzene, carbon disulfide, or iodine) before geminate combination can occur.[10b] The system is not simple, however. For example, in benzene plus iodine, 97% yields of ArI are obtained,[7f] but the yield of ArH is 0 rather than the expected 3%. In carbon tetrachloride plus iodine the products are roughly 97% ArI and 3% ArCl (unpublished experiments of Dr. J. Schreck). It appears that iodine blocks reaction 6. We are currently studying these cage reactions by more direct methods.[10c]

Relative Rates of Reactions 6 and 7. The ratios of the rate constants for diffusion from the cage k_7 and reaction with trityl radicals in the cage k_6 can be calculated for each of the phenyl radicals studied. In carbon tetrachloride at infinite dilution, assuming a steady state in Ar radicals, and using the fact that $(\text{ArCl})_0 = 1 - (\text{ArH})_0$

$$\frac{d(\text{ArH})}{d(\text{ArCl})} = \frac{k_6(\text{cage})}{k_7(\text{cage})}$$

and

$$\frac{(\text{ArH})_0}{1 - (\text{ArH})_0} = \frac{k_6}{k_7}$$

This equation gives the values listed in Table III. Thus, all the radicals are similar and diffuse from the cage about 30 times faster than they react with trityl radicals in the cage.

Method Used to Calculate k_H/k_{Cl} Values. The total amount of ArH formed at any given concentration of NAT in a hydrogen-donor solvent SH must be corrected for the amount of ArH which is formed from reactions 6 and 8. In the older method of making this correction,[5] the yield of ArH at 0.1 M NAT in carbon tetrachloride is taken as the yield of ArH from reactions

6 and 8 in all solvents at this molarity of azo compound, and this amount is subtracted from the observed yield of ArH. *Note, however, that the slopes of the lines in Figure 2 vary.* In benzene the slope is almost zero; apparently benzene scavenges free Ar radicals before they can react with a trityl radical. Since the yields of ArH differ in different solvents, the older method of making the correction for ArH will be in error. Figure 2 shows that this procedure could overestimate the amount of ArH at 0.1 M NAT by threefold in an aromatic solvent. Thus, even if the total yield of ArH is as large as 50%, the derived k_H/k_{Cl} could be in error by as much as 10%. Should the total ArH be as low as 20%, as it usually is, the k_H/k_{Cl} value would be in error by about 20%.

If the yields of products are extrapolated to zero molarity of azo compound, reaction 8 no longer contributes any ArH and only the ArH from reaction 6 need be corrected for. The most exact way of correcting for this amount of ArH formed in the cage would be to measure the viscosity of the particular solvent mixture used and subtract the amount of $(\text{ArH})_0$ interpolated from Figure 3.[10c] We have used a simpler and slightly less exact method which gives a good approximation of this; since most of the solvents used have viscosities which are very close to that of carbon tetrachloride, and since the solvent mixtures usually consist mainly of carbon tetrachloride, the value of $(\text{ArH})_0$ obtained in carbon tetrachloride can be taken as an excellent approximation of the amount of cage product which would be formed in any of the solvent mixtures used. Figure 2 shows that this procedure should give a value of $(\text{ArH})_0$ which is within $\pm 1\%$ of the value for most of the solvent mixtures. Values of k_H/k_{Cl}, therefore, were calculated using eq 4.
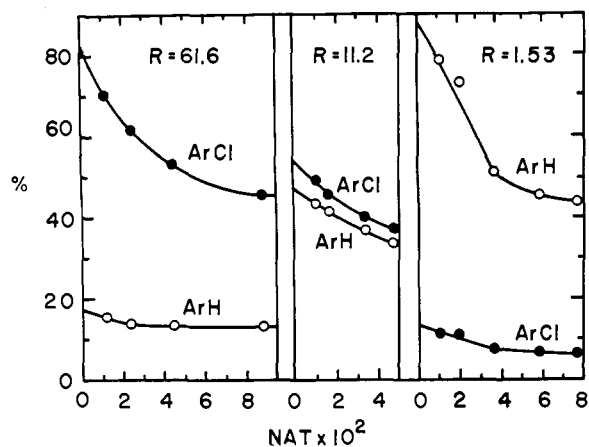
The constancy of k_H/k_{Cl} as the solvent ratio R is

Figure 4. Per cent yields of ArH and ArCl vs. NAT molarity in three mixtures of cyclohexane and carbon tetrachloride.

Figure 5. Per cent yields of ArH and ArCl vs. NAT molarity in two mixtures of toluene and carbon tetrachloride.

varied is an indication of the correctness of the scheme used. Particular attention can be called to the NAT data for these solvents: for acetone, $R = 2.90$, 0.760, and 0.095 gives $k_H/k_{Cl} = 0.613, 0.610$, and 0.600; for p-xylene, $R = 4.53$, 1.94, and 1.16 gives $k_H/k_{Cl} = 4.85$, 4.80, and 4.94; for m-xylene, $R = 3.80$ and 1.91 gives $k_H/k_{Cl} = 3.66$ and 3.72; and for p-methoxytoluene, $R = 3.05$ and 1.94 gives $k_H/k_{Cl} = 3.05$ and 2.91.

Table IV gives the values of ArH and ArCl at infinite dilution for all of the experiments which were done and gives the complete data on which extrapolations are based for selected runs.[11] Figures 4 and 5 show typical graphs of the yield of ArH and ArCl vs. azo concentration used in the extrapolation procedure. Figure 4 shows the data for NAT in cyclohexane–carbon tetrachloride mixtures and Figure 5 gives similar data for toluene. The precision of the data and the effect of varying the CCl$_4$/SH ratio can be judged from the figures. These two graphs show a striking difference: in cyclohexane the total yield extrapolates to nearly 100% at infinite dilution, whereas in toluene the yields change very little with increasing dilution, and the total yield is only 26% at $R = 3.33$, and 29% at $R = 1.11$ even at infinite dilution. This difference is most reasonably ascribed to the fact that toluene is arylated by the p-nitrophenyl radicals, and some biphenyl and complex polyaromatic materials are formed even at high dilution.[7]

The difference in using eq 4 rather than the older equation can be illustrated using these two solvents. At 0.1 M NAT, the yield of ArH in carbon tetrachloride is 7.2%, and at 0.05 M it is 5.5% (see Figure 1). Therefore, at these two concentrations of NAT the older method gives eq 9a and 9b.

$$k_H/k_{Cl} = R[(ArH) - 0.072]/(ArCl) \text{ at } 0.1 \ M \quad (9a)$$

$$k_H/k_{Cl} = R[(ArH) - 0.055]/(ArCl) \text{ at } 0.05 \ M \quad (9b)$$

(11) In order to conserve space, most of the data are omitted for the runs shown in Table IV. The complete data are given for carbon tetrachloride and toluene as solvents for all of the azo compounds and selected data are given for NAT in several pure solvents and in mixtures of carbon tetrachloride with several aromatic solvents. For the remainder of the experiments, only the values of ArH and ArCl extrapolated to infinite dilution are shown. These values were obtained from graphs similar to Figures 4 and 5, and the number of experiments used for the extrapolation is given in parentheses following the name of the solvent. A mimeographed copy of the complete data for the 350 experiments represented in Table IV can be obtained by writing to the senior author.
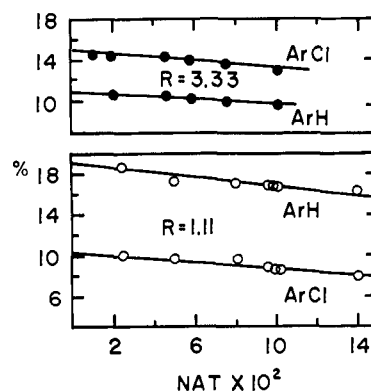
For cyclohexane, eq 4 and 9 give the results listed in Table V. Thus, for this aliphatic solvent, the two methods agree within 6% and have about the same precision. (The data for hexane in Table IV support this conclusion.) However, for toluene, eq 4 and 9 give the results listed in Table VI. Thus, in the case of toluene it is important to extrapolate to infinite dilution. In fact, if this is not done the values of k_H/k_{Cl} which are obtained are not independent of R, the solvent ratio. (The data for p-xylene in Table IV support this.)

Table V

R		k_H/k_{Cl}	
		0.05 M	Infinite dilution
61.1		8.9	9.0
11.2		8.4	10.0
6.72		7.7	9.0
4.00		9.7	9.2
1.53		9.7	10.3
	Av	8.9	Av. 9.5

Table VI

R	k_H/k_{Cl}	
	0.1 M NAT	Infinite dilution
3.33	0.69	1.68
1.11	1.24	1.67

The difficulty with the application of the older method to aromatic solvents is that the correction factor is too large. In aromatic solvents, the solvent scavenges Ar radicals and keeps reaction 8 from contributing as much ArH as it would in carbon tetrachloride. In fact, a better approximation than eq 9 for aromatic solvents is to *always* use a correction factor of 3.7% (*i.e.*, the amount of ArH formed at infinite dilution in carbon tetrachloride) regardless of the NAT concentration which was used. If this is done, the toluene data give 1.55 and 1.71 for the two values of k_H/k_{Cl} at R of 3.33 and 1.11, considerably closer to the value obtained by the extrapolation method at infinite dilution.
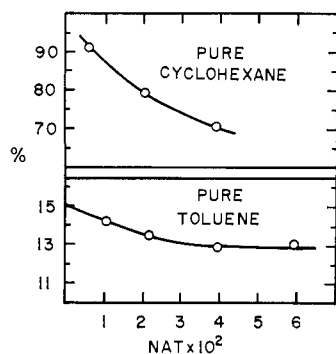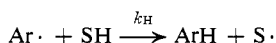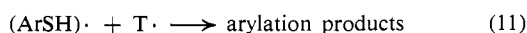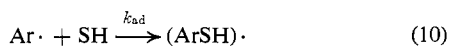
Figure 6. Per cent yield of nitrobenzene from NAT in pure cyclohexane (upper curve) and pure toluene (lower curve).

Arylation Rates. As has been pointed out, mixtures of aromatic solvents and carbon tetrachloride lead to less than 100% total yields even at infinite dilution, and these data can be used to calculate arylation rate constants. Although the purpose of this research was to measure hydrogen abstraction reactions and not addition reactions, and although our data for the latter process is probably only of semiquantitative significance, it is more convenient to discuss the data on addition reactions at this point and to turn to the more extensive and accurate data on hydrogen abstractions in the following section.

The difference between aromatic and aliphatic solvents is illustrated dramatically by runs in pure solvents. Table IV gives data for a number of such systems, and Figure 6 illustrates the data for cyclohexane and toluene with NAT. In cyclohexane, the yield of ArH can be extrapolated to give approximately 100% at infinite dilution, whereas in toluene the data extrapolate to give only 14.5% ArH a infinite dilution.[12] Data such as these can be used to calculate a rate constant for arylation by p-nitrophenyl radicals if it is assumed that at infinite dilution each of the missing Ar radicals has produced the arylation of one solvent molecule.[13] The arylation mechanism can then be given as

$$\text{Ar·} + \text{SH} \xrightarrow{k_{ad}} (\text{ArSH})· \qquad (10)$$

$$(\text{ArSH})· + \text{T·} \longrightarrow \text{arylation products} \qquad (11)$$

$$\text{Ar·} + \text{SH} \xrightarrow{k_H} \text{ArH} + \text{S·}$$

where SH is an aromatic solvent such as toluene. Arylation rates can then be calculated both in pure solvents and in solvent mixtures. We can illustrate both methods for the case of NAT and toluene: in pure toluene k_{ad}/k_H can be calculated if it is assumed that

(12) The data in Table IV for NAT in hexane also show that (ArH)₀ is 100%; in this case more points were obtained at very low concentrations, and the data can be extrapolated to 100% with considerable confidence. One of the strongest indications that the extrapolation procedure is correct is the fact that if yields are not extrapolated, all solvents (including carbon tetrachloride, hexane, etc.) appear to undergo an addition with Ar radicals. If yields are extrapolated only aromatic solvents and those which contain unsaturation (including cyclohexene and acetone) appear to add radicals.

(13) In particular, it is assumed that at infinite dilution, the radical Q in the equation below is never Ar. It probably is most often the

$$\text{Ar·} + \text{SH} \longrightarrow (\text{ArSH})· \xrightarrow{Q·} \text{ArS} + \text{QH} + \text{ArSHQ}$$
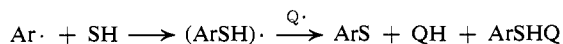
trityl radical; see ref 7d,h. If ArH were produced from this process, k_H/k_{Cl} values would not be expected to be independent of R.

about 2.5% ArH is formed in the cage reaction (*i.e.*, the value of (ArH)₀ in pure benzene). Then

$$\frac{k_{ad}}{k_H} = \frac{100 - (\%\ \text{ArH})_0}{(\%\ \text{ArH})_0 - 2.5} \qquad (12)$$

and from Figure 6, k_{ad}/k_H for toluene is 6.8. Then, since

$$\frac{k_{ad}}{k_H}\frac{k_H}{k_{Cl}} = \frac{k_{ad}}{k_{Cl}} \qquad (13)$$

and taking k_H/k_{Cl} for toluene as 1.67 from Table IV, $k_{ad}/k_{Cl} = 11.4$. This value of k_{ad}/k_{Cl} is the rate constant for arylation of toluene in *pure toluene* relative to the rate constant for abstraction of a chlorine atom in *toluene–carbon tetrachloride mixtures*. This method of calculation using eq 12 and 13 can be termed the indirect method. In contrast to this method, the value of k_{ad}/k_{Cl} can be calculated directly for toluene–carbon tetrahloride solvent mixtures, again assuming that each Ar radical which disappears represents one arylation reaction. For these solvent mixtures

$$\frac{k_{ad}}{k_{Cl}} = \frac{100 - [(\text{ArH})_0 + (\text{ArCl})_0]}{(\text{ArCl})_0}R \qquad (14)$$

Applying eq 14 to the data for toluene in Table IV gives these results: at $R = 3.33$, $k_{ad}/k_{Cl} = 7.5$; at $R = 1.11$, $k_{ad}/k_{Cl} = 16.2$. The agreement between these three values of k_{ad}/k_{Cl} (11.4, 7.5, and 16.2) is poor, but the other solvents studied give values of k_{ad}/k_{Cl} which are less dependent on the solvent mixture. Table VII gives value of k_{ad}/k_{Cl} for solvents where

Table VII. Ratios of the Rate Constant for Addition to the Solvent k_{ad} Relative to k_{Cl} for the p-Nitrophenyl Radical

Solvent	R	k_{ad}/k_{Cl}	Av
Toluene	0[a]	11.8	
	1.11	16.4	
	3.33	7.5	11.9
p-Xylene	1.16	13.5	
	1.94	11.7	
	4.53	12.2	12.4
p-Chlorotoluene	0[a]	11.5	
	1.13	9.6	10.5
p-Methoxytoluene	0[a]	19.7	
	1.94	16.4	
	3.05	25.5	20.9
m-Xylene	1.91	19.8	
	3.80	21.0	20.4
Anisole	0[a]	7.9	
	0.483	12.2	
	0.755	14.1	
	1.13	15.1	12.3
Acetone	0.095	0.44	
	0.760	1.01	
	2.90	1.31	0.92
Cyclohexene	8.40	55.5	
	12.6	46.0	51

[a] Pure aromatic solvent; the indirect method of calculation using eq 12 and 13 was used.

several solvent ratios were studied. Although these rate constant ratios are not as independent of R as are the values of k_H/k_{Cl}, they appear to show only random scatter. Since arylation products were not measured directly and rate constants for addition were calculated from the "missing" Ar radicals, values of k_{ad}/k_{Cl} cannot be expected to be more precise; however, we believe

Table VIII. Values of k_{ad}/k_{Cl}

	TAT	PAT	BrAT	NAT
Toluene	...	0.41	2.6	16
Ethylbenzene	...	...	8.7	48
Cumene	...	...	6.1	33
t-Butylbenzene	...	...	1.6	20
p-Methoxytoluene	0.34	0.44	3.0	21
p-Methyltoluene	...	0.67	2.8	12
m-Methyltoluene	0.41	...	2.7	21
Mesitylene	...	1.6	10	82
p-Bromotoluene	0.67	0.62	...	7.8
p-Fluorotoluene	0.21	...	2.0	6
p-Nitrotoluene	0.57	...	2.8	21
Anisole	...	...	...	12.3
Acetone	0.07	0.72	0.72	0.92
Cyclohexene	9.4	...	11.6	51

these constants indicate qualitative trends. Values of k_{ad}/k_{Cl} calculated from eq 14 are given in Table VIII.

The most probable mechanism for arylation by low concentrations of PAT-type compounds is shown.[7]
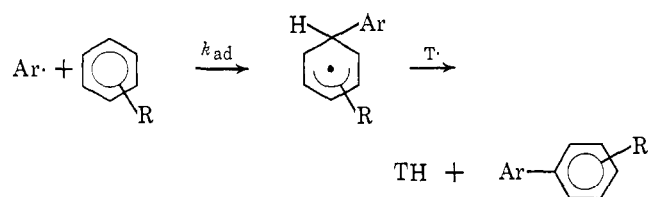
The rate constant k_{ad} should reflect both the electron density of the ring and the stability of the intermediate cyclohexadienyl radical.[14] The influence of the former factor is indicated by the relative rate pattern for NAT; in general, the p-nitrophenyl radical attacks aromatic compounds faster if they contain electron-donating substituents. However, p-nitrotoluene gives a value of k_{ad}/k_{Cl} for NAT which is some tenfold larger than expected from a Hammett equation graph, and this would appear to be due to the exceptional stability of the intermediate radical.[15]

In all cases where k_{ad}/k_{Cl} was determined for three or four initiators, the values increase moving from TAT to NAT; for example, examine the data in Table VIII for toluene, p-methoxytoluene, mesitylene, p-bromotoluene, and p-fluorotoluene. Thus, aromatic radicals increasingly favor attack on benzene rings relative to attack on carbon tetrachloride as the radicals become increasingly more electrophilic, regardless of whether

the ring being attacked contains an electron-withdrawing or -donating substituent. This reflects polar influences on the reaction and is consistent with a mechanism in which the attacking radical is an electrophilic species.

One final comment should be made on the values of k_{ad}/k_{Cl} reported here. Our values of k_{ad} represent the rate constant for the loss of Ar fragments from volatile products, and we have proposed that this is a good approximation for the total rate at which Ar radicals attack unsaturated solvents. It should be pointed out, however, that this is not necessarily identical with the rate constant for formation of arylated products. It is frequently observed that all of the cyclohexadienyl radical intermediates do not go on to form biphenyl products. Therefore, the total number of Ar radicals which attack aromatic solvents may be greater than the number which finally appear as biphenyls and the rate constant for the two processes may be different. In general, it is the rate of formation of biphenyl products which is usually termed the rate of arylation.[15,16]

Rates of Hydrogen Abstraction by Substituted Phenyl Radicals.

We now turn to a consideration of the most important aspect of this work, namely, the effects on the rates of hydrogen abstraction reactions of electronic substituents in either the radical or the substrate undergoing attack. Table IX summarizes the majority of the $k_H k_{Cl}$ values for the four radicals studied. The data on the phenyl radical are partly from Table IV and partly from the extensive data of Bridger and Russell.[5a] (Data from their study are marked with a superscript a.) Our data were extrapolated to infinite dilution whereas theirs were not, and it is encouraging to see the agreement in the two sets of data for the aliphatic substrates where this difference should not be significant. For example, the data for hexane, acetone, methyl acetate, and acetone-d_6 are all in excellent agreement. The aromatic solvents do not agree well, however, because of the difference in the method of calculation, and this must be recognized when comparisons are made to PAT data in the table.

All of the values of k_H/k_{Cl} increase in going across Table IX from TAT to NAT. This is an example of the polar effect on radical reactions. In each case, the competition is that shown below
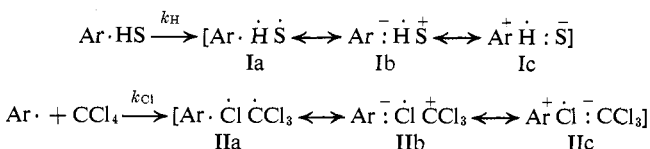
In the attack on carbon tetrachloride, resonance structure IIc is more important than IIb because of the stability of the trichloromethyl anion. Therefore, transition state II includes an appreciable contribution from a resonance structure in which a partial positive charge is placed on the aromatic radical, and this structure is stabilized by electron-donor groups. For attack on most hydrogen donors by the p-nitrophenyl radical, structure Ib might be expected to be more significant than Ic, and the substantial negative value of ρ for the reaction of NAT with substituted toluenes supports this

(14) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Butterworth and Co. (Publishers) Ltd., London, 1959, p 262 ff.
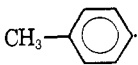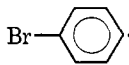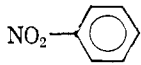
(15) After this manuscript had been submitted, the article appeared by R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, 21, 955 (1965). These authors measured the partial rate factors for arylation of substituted benzenes by Ar radicals from nitrosoacetanilides, and they are able to dissect substituent effects in more detail than can be done using only total rates of arylation. They find that arylation *meta* to a substituent follows the Hammett equation. (The ρ for *meta* arylation is 0.05 by phenyl radicals and −0.8 by p-nitrophenyl radicals.) Reaction occurs faster at the *ortho* and *para* positions than the correlation based on the *meta* positions would predict because of the direct conjugation of the substituent with the odd electron in the cyclohexadienyl radical intermediate. The nitro substituent is particularly effective regardless of the nature of the arylating radical. The substituents in the radicals affect the rate mainly by an inductive effect. It must be cautioned, however, that Simamura, *et al.*, calculate rates of arylation from the isolated (by isotopic dilution) yields of biaryls, whereas we count every missing Ar radical as one arylation reaction, regardless of whether the Ar ultimately becomes part of a biaryl or of another of the many polynuclear or dihydroaromatic type products which can be formed in these systems. It is noteworthy that the exceptional ability of the nitro group to conjugate with radical centers is also observed in the dissociation of hexaarylethanes.

(16) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1665 (1957); A. L. J. Beckwith, *ibid.*, 2248 (1962); E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, 82, 2936 (1960). Also see ref 7.

Table IX. Summary of k_H/k_{Cl} Values for TAT, PAT, BrAT, and NAT at 60°

Hydrogen donor	CH_3—⟨◯⟩·	⟨◯⟩·	Br—⟨◯⟩·	NO_2—⟨◯⟩·
Hexane	0.89	0.80, 0.80[a]	2.76	7.5
Octane	...	1.15[a]	5.1	11.0
2,4-Dimethylpentane	...	0.67[a]	4.1	9.7
2,2,4-Trimethylpentane	...	0.34[a]	0.82	2.1
2,2-Dimethylbutane	...	0.31[a]	0.64	2.2
Cyclohexane	1.11	1.08[a]	3.5	9.3
Acetone	0.14	0.17, 0.17[a]	0.35	0.607
Methyl acetate	0.075	0.086, 0.086[a]	0.22	...
Thiophenol	438	518	569	869
Cyclohexene	7.1	4.4[a]	14.9	31.8
Toluene	...	0.36, 0.27[a]	0.79	1.67
Ethylbenzene	...	0.84[a]	2.49	7.0
Cumene	...	0.93[a]	3.75	14.6
t-Butylbenzene	...	0.11[a]	0.21	0.19
p-Methoxytoluene	0.35	0.57	1.28	2.98
p-Xylene	...	1.02	2.16	4.86
Mesitylene	...	1.14, 0.85[a]	2.84	5.90
p-Fluorotoluene	0.30	...	0.61	1.24
p-Nitrotoluene	0.26	0.22[a]	0.54	0.68
ρ vs. σ	−0.1	−0.4, −0.1[a]	−0.32, −0.93[b]	−0.59
ρ vs. σ^-	−0.1	−0.3	−0.25, −0.32[b]	−0.44
k_H/k_D for acetone	3.5	4.2, 4.2[a]	4.2	4.9

[a] Data of Bridger and Russell (not extrapolated to infinite dilution). [b] Excludes the point for p-nitrotoluene.

expectation (see below). The p-tolyl and phenyl radicals will be less sensitive to polar influences, and structures Ib and Ic may play equal but minor roles in determining their reactivity. Even for these radicals however, structure Ib will be more important that IIb for most hydrogen donors.

These considerations lead to the prediction that as radicals become more electrophilic they will attack SH by increasingly large margins relative to the rate at which they attack carbon tetrachloride. In accord with this, all the values of k_H/k_{Cl} increase in going from TAT to NAT. The spread in the k_H k_{Cl} values depends on the structure of the substrate SH. For example, k_H/k_{Cl} increases ninefold for p-methoxytoluene and only 2.6-fold for p-nitrotoluene in going from TAT to NAT. Structure Ib makes a more significant contribution in the transition state for reactions with p-methoxytoluene, and the electrophilicity of the radical plays a greater role in this case (see further discussion in the following section).

Hammett Equation Correlations. The importance of the polar nature of the attacking radical is shown by the values of ρ for their reaction with substituted toluenes. The values become more negative going from TAT to NAT, indicating the increasing importance of resonance structure Ib. For TAT and PAT either σ or σ^+ could be used to correlate the data; the value of ρ is very small and the fit is not sensitive to which parameter is used. This is also true for BrAT; interestingly, however, in the correlation using σ the point for p-nitrotoluene is far off the line, whereas σ^+ correlates all the data. For BrAT ρ is about −0.3 using σ and about −0.2 using σ^+. For NAT, the least-square treatment gives

$$\log k/k_0 = -0.589\sigma + 0.0028 \quad \text{std error } 0.053$$

$$\log k/k_0 = -0.437\sigma^+ + 0.00034 \quad \text{std error } 0.058$$

Again, the fit is not sensitive to whether σ or σ^+ is used, but σ is slightly superior.
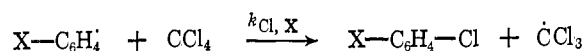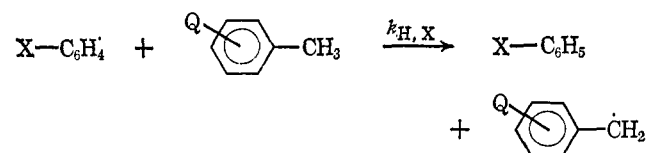
Selectivity. The selectivity of the radicals as measured by k_H/k_D values in acetone and acetone-d_6 increases in going from TAT to NAT, but the change is small. The data are consistent with a slightly higher activation energy for reaction by the p-nitrophenyl radical.

This pattern is borne out by data on toluene-ethyl-benzene-cumene-t-butylbenzene as well. The values of the relative reactivity of the four types of hydrogens in these four substrates are given in Table X. Thus, the p-nitrophenyl radical is more selective, again suggesting that higher activation energies are associated with its hydrogen abstraction reactions.

Table X

	PAT	BrAT	NAT
Primary benzyl hydrogens	(1)	(1)	(1)
Secondary benzyl hydrogens	4.6	4.7	6.2
Tertiary benzyl hydrogens	9.7	13.8	26.0
Primary hydrogens β to phenyl	0.13	0.081	0.041

A "Two-Way" Hammett Equation Graph. Figure 7 summarizes the data for the Hammett equation graphs in which X, the substituent in the radical, is varied (while Q held constant) in the following equations.

$$X-C_6H_4 + \text{Q}-⟨◯⟩-CH_3 \xrightarrow{k_{H,X}} X-C_6H_5$$

$$+ \text{Q}-⟨◯⟩-\dot{C}H_2$$

$$X-C_6H_4 + CCl_4 \xrightarrow{k_{Cl,X}} X-C_6H_4-Cl + \dot{C}Cl_3$$

All of the values of ρ are positive, but the values are significantly more positive when Q is p-methoxy than

when it is p-nitro. The fit of the data to these lines is quite poor, since k_H and k_{Cl} respond to the electronic influence of X differently. Nevertheless, the figure gives a capsule view of the electronic influences at work. For example, consider the case where the hydrogen donor is p-methoxytoluene. Resonance form Ib will be important, and electron-withdrawing X groups in the radical will stabilize this form still more. Thus, k_H would be expected to increase in going from TAT to NAT. Since k_{Cl} decreases from TAT to NAT, k_H/k_{Cl} should increase significantly in going from TAT to NAT. In agreement with this prediction, ρ is $+1$ (*i.e.*, the slope of the upper line in Figure 7 is $+1$).

When the hydrogen donor is p-nitrotoluene, both k_H and k_{Cl} would be expected to decrease in going from TAT to NAT. It is reasonable, however, to expect k_{Cl} to decrease more than does k_H (IIc is more important than is Ic), and the net effect is that k_H/k_{Cl} increases slightly in going from TAT to NAT. Figure 7 shows that ρ is 0.4 in this case.

A Limitation on k_H/k_{Cl} Values. One limitation which is implicit in the discussion in the preceding paragraph may warrant clarification. Values of k_H are relative only in a single vertical column in Table IX. For clarity, consider two radicals with two different ratios, k_H/k_{Cl} and k_H'/k_{Cl}'. To compare k_H and k_H' directly, the ratio of k_{Cl} to k_{Cl}' must be known. These data could be obtained by either measuring the ratio k_{Cl}/k_{Cl}' or by obtaining the absolute rate constants for chlorine abstraction for each of the radicals by some technique. Relative k_{Cl}/k_{Cl}' values cannot be obtained by studies of the type done here. If two different PAT-type initiators are allowed to decompose in the same solution in the presence of carbon tetra-
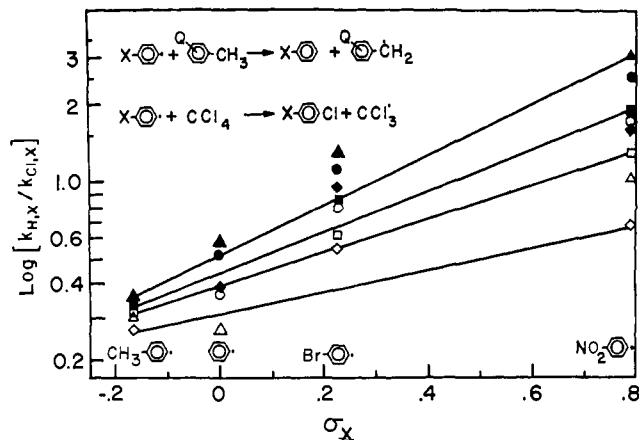

Figure 7. The effect of the electronic substituent in the phenyl radical on the rate of hydrogen abstraction from toluene and substituted toluenes. The log of the relative rate of abstraction of hydrogen is plotted on the vertical axis and the Hammett σ constant of the *substituent in the radical* on the horizontal axis. The points indicate the substituent in the hydrogen donors, coded as follows: O, toluene; ▲, p-methoxytoluene; ■, m-xylene; △, m-bromotoluene; ●, p-bromotoluene; ▢, p-fluorotoluene; ◆, mesitylene; ◇, p-nitrotoluene.

chloride, their different rates of reaction result in different steady-state concentrations of radicals, and k_{Cl}/k_{Cl}' cannot be obtained.

Hydrogen Secondary Isotope Effects on the Radical Polymerization of Styrene[1,2]

William A. Pryor, Richard W. Henderson,[3a] Robert A. Patsiga,[3b] and N. Carroll[3c]

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received October 18, 1965

Abstract: It has generally been assumed that radical and ionic reactions will lead to similar hydrogen secondary isotope effects, but this assumption has not been tested in any detail, since very few studies on radical reactions have been reported. This paper reports isotope effects on the propagation step in the polymerization of styrene. The following substituted styrenes were studied: α-d, β-d_2, ring-d_5, α-t, and *trans*-β-t. All these isotopically substituted styrenes react faster than does normal styrene, *i.e.*, the isotope effects are all inverse. Table I gives values which approximate k_p/k_p' (*i.e.*, the isotope effect k_H/k_D on the propagation step) and Table III gives values of k_p/k_p'' (k_H/k_T for the propagation step).

Secondary hydrogen isotope effects are of theoretical interest and a large number of examples have now been reported.[4] These effects are divided into two

types: those of the "first kind," in which the deuterium or tritium atom is substituted on an atom which undergoes a spatial (or hybridization) change during the

(1) This research was supported in part by a grant from the Air Force Office of Scientific Research.

(2) Reactions of Radicals. Part XIII. Most of these data were presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(3) (a) An Undergraduate Research Participant; (b) a postdoctoral student on a National Science Foundation Summer Research Participation Program; (c) a postdoctoral student supported by a grant from the Air Force Office of Scientific Research.

(4) Reviews are given by (a) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963); (b) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960; (c) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, 1, 15 (1958); (d) R. E. Weston, Jr., *Ann. Rev. Nucl. Sci.*, 11, 439 (1961); (e) F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961); (f) K. B. Wiberg, *ibid.*, 55, 713 (1955); (g) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 351 ff.