o −15°. A mixture of nitric acid (d. 1.42) (10 ml.) and sulfuric acid (10 ml.) was added dropwise, the temperature being kept below −5°. Stirring was continued for 30 minutes and the mixture poured on ice. The solid material was filtered, washed with water and twice with ethanol and recrystallized from methanol or ethanol; yellow rods of m.p. 95–96°, yield 8.8 g. (66%).

p-**Fluorophenylglyoxal (VI).**—To a solution of selenious acid (43 g.) in dioxane (200 ml.), warmed to 60°, *p*-fluoroacetophenone[6a,b] (46 g.) was added slowly. After 5 minutes, a red precipitate formed. The solution was refluxed for 4 hours and left overnight. It was then decanted from the red precipitate and fractionated. At 105–115° (30–35 mm.) a thick, yellow oil went over which showed no tendency to crystallize; yield 35 g. (78%). The oil was dissolved in benzene and a few drops of water added. This resulted in the formation of a white powder. Recrystallization from water gave the hydrate of VI as glistening, white leaflets, m.p. 80°.

Anal. Calcd. for $C_8H_5O_2F\cdot H_2O$: C, 56.5; H, 4.1. Found: C, 56.9; H, 4.3.

The bis-2,4-dinitrophenylhydrazone crystallized from pyridine–*n*-butyl acetate, decomposition point 296°.

Grignard Reaction with 2,4,ω-Trifluoroacetophenone (III).—To a Grignard solution, prepared from bromobenzene (4.7 g.) and magnesium (0.7 g.) in ether, was added slowly an ethereal solution of 2,4,ω-trifluoroacetophenone (4.5 g.) during 15 minutes. The mixture was refluxed for 2 hours and then left overnight. It was decomposed with ammonium chloride and worked up in the usual way. Fractional distillation gave 5.2 g. of a yellow oil of b.p. 135–138° (4 mm.).

Anal. Calcd. for $C_{14}H_{10}OF_2$: C, 72.4; H, 4.3. Found: C, 72.0; H, 4.7.

The 2,4-dinitrophenylhydrazone crystallized from isopropyl alcohol in pointed plates of m.p. 165–167°.

Anal. Calcd. for $C_{20}H_{14}O_4N_4F_2$: N, 13.6. Found: N, 13.4.

The authors wish to thank Prof. E. Alexander, Department of Physics, for the X-ray spectra and Mrs. Hanna Feilchenfeld, Department of Organic Chemistry, for the infrared measurements used for identification of *p*,ω-difluoroacetophenone.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Relative Reactivities of Substituted Toluenes toward Chlorine Atoms[1]

BY CHEVES WALLING AND BERNARD MILLER[2]

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Competitive halogenations of a series of substituted toluenes have been carried out and relative reactivities determined by the precise deuterium tracer technique of Russell and Brown.[7] For photochlorination the results yield a ρ value for attack of chlorine atoms of −0.76, appreciably smaller than the value of −1.5 reported by Kooyman.[15] Identical relative reactivities and k_H/k_D ratios are observed in photochlorination and in reaction with SO_2Cl_2, giving no evidence for different chain carriers in this system. However, some variation in relative reactivity is observed for reactions run in primarily aromatic media and in carbon tetrachloride. Data on photobromination are also presented, together with a discussion of the importance of polar effects in free radical halogenation.

The reaction of chlorine with aliphatic hydrocarbons and the side-chains of alkyl-aromatics is well established[3] as a radical chain process involving the chain carrying steps.

$$Cl\cdot + RH \longrightarrow HCl + R\cdot \qquad (1)$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \qquad (2)$$

With hydrocarbons containing more than one type of C–H bond (or in mixtures of hydrocarbons) the products formed evidently will depend upon the relative rates of reactions of type (1) of chlorine atoms with the different sorts of C–H bond available. The work of Hass, McBee and Weber[4] has shown clearly that, with aliphatic hydrocarbons, the case of hydrogen displacement lies in the order primary < secondary < tertiary, the selectivity being somewhat greater in the vapor than in the liquid phase and decreasing with increasing temperature. Recently Pritchard, Pyke and Trotman-Dickenson[5] have studied the competitive chlorination of a number of simple hydrocarbons with results leading to similar conclusions, and have actually determined rate constants for hydrogen abstraction by carrying out competitions with the process

$$Cl\cdot + H_2 \longrightarrow HCl + Cl\cdot \qquad (3)$$

for which the rate constant is known over a wide temperature range.[6] Since C–H bond dissociation energies lie in the order primary > secondary > tertiary, decreasing approximately 4 kcal. with each substitution, this weakening, presumably due to resonance stabilization of the resulting radicals, has commonly been given as the explanation of the observed order of chlorine atom substitution.

Unfortunately for this simple picture, more complex molecules do not yield results which indicate a simple parallel between C–H bond strength and ease of attack by chlorine atoms. Competitive chlorination of toluene and *t*-butylbenzene shows[7] that the C–H bonds of the former are only slightly more reactive in spite of the great resonance stabilization (∼ 25 kcal.) of the benzyl radical. More strikingly, the C–H bonds of cyclohexane prove to be ***more*** reactive than those of toluene by a factor of 2.7.[7,8] Still more anomalous results are observed in the chlorination of molecules containing other

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[1] Taken from a portion of a dissertation submitted by Bernard Miller in 1955 to the Graduate Faculties of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy; a preliminary report of this work was made at the 126th meeting of the American Chemical Society, New York, September, 1954.

[2] University Fellow, Columbia University, 1954–1955.

[3] Extensive experimental evidence is reviewed by E. W. R. Steacie. "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1954, Chapter X.

[4] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

[5] H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, THIS JOURNAL, **77**, 2629 (1955).

[6] P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953).

[7] G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4578 (1955).

[8] H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952).

substituent atoms. Brown and Ash[9] have recently summarized data on the chlorination of 1-chlorobutanes and related compounds which show plainly that the presence of a chlorine atom decreases the ease of further chlorine substitution at the same and adjacent carbons, in spite of the fact that the C–H bonds are weakened.[10] In a number of cases the chlorinating agent was actually SO_2Cl_2; see below. Similarly, radical chlorination of aliphatic acids and their derivatives (acid chlorides, esters and nitriles)[9,11] gives predominantly substitution along the chain with little α-attack in spite of the expected resonance stabilization of the resulting $-\dot{C}H-CO-$ radical, and the known fact that alkyl radicals preferentially attack acid derivatives in the α-position.[12]

In 1950 Mayo and Walling[13] suggested that the anomalous results in the chlorination of alkyl halides and aliphatic acid derivatives might be explained on the basis of the importance of polar contributions to the transition state of the radical displacement, an idea which may be restated by saying that structures such as

$$Cl\cdot\ H-R \longleftrightarrow Cl^{-}H\ \overset{+}{R} \qquad (4)$$

can aid in lowering the activation energy in the attack of chlorine atoms on hydrocarbons but would be relatively unimportant in the presence of strongly electron-withdrawing groups. Brown and Ash[9] have interpreted the situation similarly but less specifically in terms of the inductive effect of –Cl and –COR groups in decreasing electron availability at the adjacent C–H bonds.

One of the most effective techniques for separating such polar effects from others arising from steric and related factors is by studying the effect of *m*- and *p*-substituents on the side-chain reactions of benzene, and treating the results in terms of the Hammett equation

$$\log k/k_0 = \rho\sigma \qquad (5)$$

in which k and k_0 are rate (or equilibrium) constants for reaction of substituted and unsubstituted benzenes, respectively, and ρ and σ are parameters determined, respectively, by the particular reaction under investigation and the substituent involved.[14] Accordingly, we have undertaken a study of the effects of *m*- and *p*-substituents on the liquid-phase, side-chain photochlorination of toluenes, employing a competitive technique, since, as noted above, this method gives directly the relative rates of hydrogen abstraction from different molecules by chlorine atoms, without involving the complicated over-all kinetics of the long-chain processes involved.

Shortly after this work was initiated, Kooyman published a similar study of the side-chain bromination of toluene,[15a] and has subsequently extended his work to the sulfuryl chloride chlorination,[15b] finding that, in both cases, substitution is facilitated by electron supplying and retarded by electron withdrawing groups. Qualitatively, the results of the study reported here are in agreement with Kooyman's sulfuryl chloride data. However, we have employed a more extensive series of derivatives and a more precise analytical method, and have arrived at a somewhat different interpretation which we believe makes a detailed report desirable.

Experimental

Materials

Substituted toluenes—except as indicated—were commercial materials, fractionally distilled (and dried if necessary) before use. **p-t-Butyltoluene** was prepared by the alkylation of toluene with isobutyl alcohol in the presence of H_2SO_4.[16] ***m*-Phenyltoluene** was prepared by treating *m*-tolylmagnesium bromide with cyclohexanone, dehydrating the resulting alcohol by heating with $KHSO_4$, and dehydrogenating the 1-(*m*-tolyl)-cyclohexene over 10% Pd on charcoal at 280–300° in an over-all yield of 56.5%, b.p. 148–152° (20 mm.), $n^{20}D$ 1.6002. *Anal.* Calcd. for $C_{13}H_{12}$: C, 92.86; H, 7.14. Found: C, 92.87; H, 7.12. ***p*-Phenyltoluene** was prepared similarly from *p*-bromotoluene and recrystallized from petroleum ether. m.p. 46–47°; lit.[17] 47–48°, over-all yield, 44%. **Toluene-α-d_1** was prepared in 76% yield from benzylmagnesium bromide and DCl by the method of Russell and Brown.[7] The reaction product was twice distilled from sodium through a 10-plate helix packed column, b.p. 110–110.5°, $n^{20}D$ 1.4947. The toluene-α-d_1 was combined with its volume of pure toluene for use, and, after completion of a series of runs, combined reaction mixtures were fractionated and combined with fresh toluene-α-d_1 and toluene. All these mixtures are referred to below as *deuterotoluene*.

Solvents.—**Carbon tetrachloride** was washed three times with a 50% aqueous ethanol solution of KOH, with water, and dried over $CaSO_4$. It was then treated for 15 hours with chlorine and light, dried over $MgSO_4$ and fractionated through a 10-plate column, b.p. 76°. **Thiophene-free benzene** was washed with sulfuric acid and water, dried, distilled from sodium, and fractionally crystallized, m.p. 5.2°, $n^{25}D$ 1.4494. ***o*-Dichlorobenzene** was dried over P_2O_5 and fractionally distilled through a 10-plate column, b.p. 179–180°, $n^{25}D$ 1.5501.

Halogenating Agents.—**Chlorine** was commercial material, distilled through sulfuric acid before use. **Bromine** was distilled from P_2O_5, and **sulfuryl chloride** was a colorless middle cut obtained by fractionating commercial material. It was stored in an aluminum foil covered flask until used.

Halogenations

Our technique in general involved the halogenation of mixtures of toluene-α-d_1 and substituted toluenes and determining relative reactivities by analysis of the DCl–HCl mixture evolved. This method, which was used by Brown and Russell,[7,8] is capable of high precision, but was checked in several cases by fractional distillation of our reaction mixtures.

Photochlorinations were carried out in the apparatus shown in Fig. 1. With stopcock A open and C closed, chlorine was condensed in B by chilling with a Dry Ice-bath. Trap B was graduated to permit measurement of the volume of chlorine condensed (1.5–2.5 ml.) at its boiling point. With the stirrer, F, running, a gentle stream of prepurified nitrogen was next passed through C, the mixing bulb D, and the rest of the apparatus to remove traces of

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[9] H. C. Brown and A. B. Ash, THIS JOURNAL, **77**, 4019 (1955); *cf.* also A. B. Ash and H. C. Brown, *Rec. of Chem. Progr.*, **9**, 81 (1948).

[10] The value of $D(CCl_3-H)$ is 89 kcal. compared with $D(CH_3-H)$ of 102 kcal., T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954.

[11] A. Bruylants, M. Tits and R. Danby, *Bull. soc. chim. Belg.*, **58**, 310 (1949); A. Bruylants, M. Tits, C. Dieu and R. Gautier, *ibid.*, **61**, 366 (1952).

[12] M. S. Kharasch and M. Gladstone, THIS JOURNAL, **65**, 15 (1943); C. C. Price and H. Morita, *ibid.*, **75**, 3686 (1953).

[13] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[14] L. P. Hammett, THIS JOURNAL, **59**, 96 (1937); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184–207. A recent review of the validity of this equation is given by H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[15] (a) E. C. Kooyman, R. van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B56**, 75 (1953); (b) R. van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954).

[16] H. Meyer and K. Bernbaum, *Monatsh.*, **53**, 730 (1926).

[17] A. Gattermann, *Ann.*, **347**, 381 (1906).

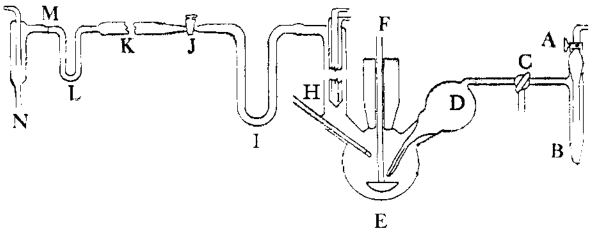

Fig. 1.—Apparatus for competitive liquid-phase halogenation of toluenes.

air. With A closed, and C turned so that all three tubes were connected, the bath around B was lowered and chlorine swept by the nitrogen stream into the reaction flask E which was illuminated by a 200-watt incandescent bulb at the distance of one inch. Both reaction flask and bulb are submerged in a thermostat kept at 69.5 ± 0.5°.

The gases generated passed through an efficient condenser H and Dry Ice trap I where any organic vapors are condensed. They next reached the tube K, packed at both ends with glass wool, and containing a 2-mole excess of tightly packed silver oxide, where the DCl–HCl was converted to D_2O–H_2O. Since this reaction is strongly exothermic, K was cooled and kept from light by a wet towel. Prior to reaction, the entire system beyond J was carefully dried by pumping on a vacuum pump for a half-hour. After all the chlorine had been introduced the stream of nitrogen was continued for 15 minutes to sweep out residual DCl–HCl. The stopcock J was then closed, and the water drawn by a vacuum pump connected to the end of the system into the U-tube L, containing more silver oxide, and cooled by Dry Ice. Next the pump was stopped, the bath lowered, and the water, after melting, shaken with silver oxide. It was then distilled under vacuum through the sintered plate M into the final Dry-Ice trap N where it was weighed and a drop withdrawn and tested for halide with silver nitrate. The water was finally pipetted into a centrifuge tube, centrifuged to remove air bubbles, and the deuterium content measured.

In typical experiments, 0.25–0.35 mole of mixed toluenes was treated with 0.035–0.045 mole of chlorine and E had a volume of 100 ml. In runs using solvents, 100 cc. of solvent and a larger 250-ml. reaction flask were employed, and an additional trap, immersed in an ice-salt bath, was interposed between H and I.

Photobrominations.—A similar apparatus was employed and bromine was pipetted into B, which was maintained at 50° by a water-bath during the reaction.

Sulfuryl Chloride Reactions.—Here the apparatus for halogen introduction was replaced by a pressure equalized dropping funnel, and benzoyl peroxide, rather than light, was used as an initiator. Three ml. of sulfuryl chloride was placed in the funnel, and the system flushed with nitrogen. Next, 0.5 ml. of sulfuryl chloride was dropped into E, and after vigorous reaction began (5–15 min.) the balance introduced over two hours. In operation it was found that the SO_2 and most of the HCl produced condensed in the Dry Ice trap I, so it was necessary to close off the system between H and I by an additional stopcock, and distil the HCl–DCl into K under reduced pressure. The rest of the procedure was similar to that used in photochlorination.

Vapor Phase Reactions.—A mixture of toluene and toluene-α-d_1 was photochlorinated in the vapor phase in order to determine the magnitude of the isotope effect under these conditions. The apparatus used is shown in Fig. 2. In operation, deuterotoluene was placed in B, and chlorine condensed in A by means of a Dry Ice trap. The receiver E was cooled with Dry Ice, while B and the reaction coil D were maintained at 69.5° by a thermostat. During reaction, the pressure in the system was maintained at 85 mm. by a vacuum pump at the end of the usual absorption and conversion train attached at F, and the toluene mixture continually distilled from B through coil D, which was illuminated by a 200-watt incandescent lamp at a distance of one inch, passed into E, and was recycled. Chlorine slowly was introduced by lowering the cooling bath around A, the whole reaction taking 2–3 hours, and the toluene recycling about once every 20 minutes. The absorption of the DCl–HCl mixture and conversion to D_2O–H_2O was accomplished in the same manner as in the liquid-phase experiments.

In addition, we also investigated the competitive chlorination of toluene and cyclohexane in the vapor phase. Here, because of the difference in volatility of the two components, it was not possible to use a recycling system. Accordingly, in place of the flask B, an apparatus was attached consisting of a vaporizer maintained at 100–120° and a coil immersed in the thermostat and intended to bring the vaporized hydrocarbon mixture to thermal equilibrium with the system. The toluene–cyclohexane mixture was dripped slowly into the vaporizer from a pressure-equalized dropping funnel. Considerable difficulty was encountered with this set-up, and only two satisfactory runs were achieved. Accordingly, we have some reservations about the accuracy of our results.

Analytical Methods

Deuterium Determinations.—Measurement of the deuterium content of water was done by the falling drop method[18] in which water density is effectively measured from the time required for uniform droplets to sink a predetermined distance in a carefully thermostated column of *o*-fluorotoluene. A standard curve for sinking time was constructed using known mixtures of D_2O–H_2O, and frequently rechecked. Three or more drops were timed for each sample, the reproducibility being ±0.01% D_2O.

Deuterium analysis in our deuterotoluene was done by burning samples in a conventional apparatus for C–H determination, and collecting the water in a Dry Ice trap protected by a soda-lime tube. On completion of the combustion, the water was distilled into a second trap, and redistillation from a crystal of $KMnO_4$ showed no measurable change in deuterium content.

Total Halogen.—A 2-ml. sample of reaction mixture was refluxed 2–3 hours with xylene and sodium according to the method of Landis and Wichmann.[19] The xylene was distilled from sodium before use and butyl alcohol was used to activate the reaction since commercial amyl alcohol was found to contain significant halogen. The resulting chloride ion was determined by Mohr titration.

Benzyl Halogen.—A 2-ml. sample of reaction mixture was refluxed 2 hr. with 10 ml. of 0.487 *N* NaOH and 30 ml. of ethanol. After neutralization with dilute nitric acid, chloride ion was determined by Mohr titration.

The difference between the two analyses presumably represents non-side-chain substitution, and amounted to 1–4% of the total halogen. Our deuterium concentrations were corrected accordingly, and with chloro- and cyanotoluenes where the method was inapplicable, a correction of 1.5% was used.

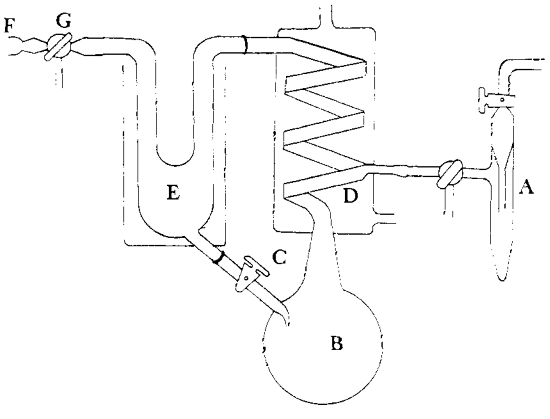

Fig. 2.—Apparatus for vapor-phase halogenation.

Treatment of Data

Isotope Effects.—In a "deuterotoluene" (toluene-α-d_1–toluene mixture) the rate of reaction of halogen with

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(18) A. S. Keston, D. Rittenberg and R. Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1937); A. P. Wolf, Ph.D. Thesis, Columbia University, 1952, p. 90.

(19) Q. Landis and H. T. Wichmann, *Ind. Eng. Chem., Anal. Ed.*, **2**, 394 (1930).

replaceable hydrogen and deuterium is given by

$$d[\mathrm{HCl}]/dt = -d[\mathrm{H}]/dt = k_\mathrm{H}\ [\mathrm{Cl}\cdot][\mathrm{H}] \qquad (6a)$$

$$d[\mathrm{DCl}]/dt = -d[\mathrm{D}]/dt = k_\mathrm{D}\ [\mathrm{Cl}\cdot][\mathrm{D}] \qquad (6b)$$

where [Cl·] represents the concentration of halogen atoms and [H] and [D] of replaceable hydrogen and deuterium, respectively. Division of (6*a*) by (6*b*) gives

$$d[\mathrm{H}]/d[\mathrm{D}] = (k_\mathrm{H}/k_\mathrm{D})[\mathrm{H}]/[\mathrm{D}] \qquad (7)$$

Equation 7 is integrated readily, and, since (6*a*) and (6*b*) are of the same kinetic order, concentrations may be expressed as total moles of material present

$$\frac{k_\mathrm{H}}{k_\mathrm{D}} = \frac{\log (H_0 - H_r)/H_0}{\log (D_0 - D_r)/D_0} \qquad (8)$$

where H_0 and D_0, respectively, represent moles of replaceable hydrogen and deuterium originally present, and H_r and D_r moles reacted. The foregoing derivation assumes that only one hydrogen is substituted in each toluene molecule reacted, a circumstance assured by using an approximately ten-fold excess of deuterotoluene.

The quantities in (8) are related to the analytically determined deuterium concentrations by the relations

$$\begin{array}{ll} H_0 = 3S_c - D_0 & H_r = T(100 - D_s) \\ D_0 = 8D_c\,S_0/100 & D_r = TD_s/100 \end{array} \qquad (9)$$

where S_0 and T represent initial moles of deuterotoluene and halogen employed and D_c and D_s, respectively, the per cent. D_2O in the water obtained on combustion of the particular sample of deuterotoluene and on conversion of the DCl–HCl evolved to D_2O–H_2O.

Table I lists three runs which illustrate the reproducibility of our data treated in this way.

TABLE I

ISOTOPE EFFECT IN THE PHOTOCHLORINATION OF TOLUENE D_c (4 DETERMINATIONS) 2.30, 2.30, 2.31, 2.31, Av. 2.305

T	S_0	D_s	$k_\mathrm{H}/k_\mathrm{D}$
0.041	0.271	3.45	2.05
.037	.316	3.40	2.11
.039	.312	3.39	2.08

Determination of Relative Reactivities.—In a similar manner to that above, the rates of halogenation of deuterated toluene and a substituted toluene are given by

$$-d[\mathrm{S}]/dt = k'\ [\mathrm{S}][\mathrm{Cl}\cdot] \qquad (10)$$

$$-d[\mathrm{X}]/dt = k\ [\mathrm{X}][\mathrm{Cl}\cdot] \qquad (11)$$

where [S] and [X] are concentrations of deuterotoluene and substituted toluene, respectively. Accordingly

$$\frac{k}{k'} = \frac{\log (X_0 - X_r)/X_0}{\log (S_0 - S_r)/S_0} \qquad (12)$$

where S_0 and X_0 are the moles of deuterotoluene and substituted toluene initially present, and S_r and x_r the amounts reacted. Again, these quantities may be related to D_x, the per cent. D_2O in the water obtained from evolved DCl–HCl, *via* the relations

$$T = S_r + X_r,\ D_x/D_s = S_r/(S_r + X_r) \qquad (13)$$

giving finally

$$\frac{k}{k'} = \frac{\log (D_sX_0 - D_sT + D_xT)/(D_sX_0)}{\log (D_sS_0 - D_xT)/(D_sS_0)} \qquad (14)$$

However, for comparing relative reactivities with *undeuterated* toluene, it should be noted that, because of the isotope effect, k' is not identical with k_0, the rate constant for reaction of halogen atoms with undeuterated toluene. The ratio k'/k_0, however, may be obtained by applying an equation similar to (14) to mixtures of a deuterotoluene and undeuterated toluene, or calculated from the $k_\mathrm{H}/k_\mathrm{D}$ ratio *via* the relation

$$\frac{k'}{k_0} = 1 - \frac{F}{3}\left(1 - \frac{k_\mathrm{D}}{k_\mathrm{H}}\right) \qquad (15)$$

where F represents the mole fraction of toluene-α-d_1 in the deuterotoluene, determined by combustion. Table II presents typical data for *p*-xylene and *p*-chlorotoluene.

TABLE II

REPRESENTATIVE DATA ON PHOTOCHLORINATION OF SUBSTITUTED TOLUENES AT 70°

X_0	S_0	T	H_2O–D_2O obtained	D_x	% ring subst.	k/k'	k/k_0[b]
			p-Xylene[a]				
0.2102	0.0839	0.0390	0.0192	0.70	2.87	1.85	1.69
.1535	.1455	.0335	.0169	1.55	2.06	1.66	1.54
.1058	.1648	.0369	.0174	2.11	1.94	1.78	1.64
			p-Chlorotoluene				
.1139	.1213	.0330	.0169	3.76	..	0.79	0.725
.0846	.1790	.0350	.0176	4.71	..	80	.73
.1810	.0679	.0337	.0170	2.13	..	75	.69

[a] k ratios corrected by a statistical factor of 2. [b] k'/k_0 = 0.92 for this sample of deuteroluene.

Our technique of determining relative reactivities was also checked for the toluene–*p*-chlorotoluene system by carrying out several larger scale runs using ordinary toluene, and determining the unreacted toluenes by fractional distillation. Data from one experiment appear in Table III, the composition of intermediate fractions being estimated by index of refraction. Three similar experiments, the last two carried out in benzene solution, gave k/k_0 = 0.63, 0.72 and 0.73, average 0.69, which appears within experimental error of the more precise deuterium technique.

TABLE III

FRACTIONATION OF PRODUCT FROM PHOTOCHLORINATION OF 0.386 MOLE TOLUENE, AND 0.3575 MOLE *p*-CHLOROTOLUENE WITH 0.212 MOLE CHLORINE

B.p., °C.	Wt., g.	$n^{25}\mathrm{D}$	Moles C_7H_8	Moles C_7H_7Cl
109–112	20.0	1.4943	0.217	....
113–158.5	6.1	1.5049	.031	0.0257
159–163	25.9	1.5191	...	.206
164–177.5	8.6	1.5271	...	.032
			.248	.263

(Moles not recovered) − (Chlorine used) = 0.021
k/k_0 = 0.69

Results and Discussion

Our data on relative reactivities of substituted toluenes are summarized in Table IV, and in Fig. 3 our values of log k/k_0 are plotted against Hammett ρ values of substituents, taken from Jaffe's review.[18] A straight line, drawn by the method of least squares through all points with the exception of the phenyl substituents (which are discussed further below) fits the equation log k/k_0 = −0.76 + 0.03, whence ρ = −0.76. Our results are thus in qualitative agreement with those of Kooyman (who reports ρ = −1.5) in that electron supplying groups facilitate, and electron withdrawing groups retard, the attack of chlorine atoms on toluene. This observation we also consider to be a polar effect perhaps best interpreted in terms of resonance structures of the sort indicated in eq. 4. However, before discussing this matter further we should consider the quantitative differences between the two sets of results.

Kooyman's study[15] differs from ours in that he employed sulfuryl chloride as his chlorinating agent, operated in a solvent (benzene), used a different analytical method (competitions were run against *t*-butylbenzene and products analyzed by separation or by differential rates of alkaline hydrolysis) and a somewhat different method of treating his data. Consideration of each of these

TABLE IV

RELATIVE REACTIVITIES OF SUBSTITUTED TOLUENES TOWARD RADICAL HALOGENATING AGENTS AT 70°

Substituent	Solvent	No. expts.	k/k_0	Av. dev.[b]	Lit.
		Photochlorination			
p-Methyl	.....	3	1.62[a]	0.05	
p-Phenyl	.....	3	1.59	.03	
m-Methyl	.....	3	1.33[a]	.022	
m-Phenyl	.....	3	1.12	.05	
None	.....	3	1.0	.02	
p-Chloro	.....	3	0.72	.017	
p-Chloro	Benzene	2	.69	.01	
p-Chloro	CCl_4	2	.465	.015	
m-Chloro	.....	3	.54	.017	
p-Cyano	.....	3	.38	.015	
m-Cyano	.....	3	.36	.015	
Cyclohexane[c]	Vapor	2	2.12	.03	
		Photobromination			
p-t-Butyl	.....	1	1.6	...	1.5[14]
m-Bromo	.....	1	0.37	...	0.37[15]
p-Cyano	.....	1	0.28	...	0.22[15]
		SO_2Cl_2			
p-Chloro	.....	2	0.69	.01	0.35[15]
m-Cyano	.....	2	0.33	.01	0.16[15]

[a] A statistical factor of two was used in calculating k/k_0. [b] Average deviation from the mean of individual experiments. [c] This experiment was a competitive vapor-phase chlorination of toluene and cyclohexane, and a statistical factor of 4 was used in computing k/k_0.

points in turn provides a convenient basis for presenting some of the conclusions of this work.

Since discovery of the reaction by Kharasch and Brown in 1939,[20] the radical initiated chlorination of hydrocarbons by sulfuryl chloride has generally been considered as a chain process involving chlorine atoms as the chain carriers, and hence it should be identical in selectivity to photochlorination. However, Russell and Brown[21] have recently reported a significantly higher selectivity for tertiary *vs.* primary C–H bonds in the sulfuryl chloride reaction. They have suggested that, at least under some conditions, the $\cdot SO_2Cl$ radical may be the attacking species,[22] and have used the discrepancy between the preliminary report of our work[11] and that of Kooyman to support this interpretation. However, as shown in Table IV, competitive experiments with p-chloro- and m-cyanotoluene, in our hands, yield results indistinguishable from our photochlorinations. Chlorine and sulfuryl chloride also give indistinguishable k_H/k_D ratios, so we conclude that our substituted toluene experiments give no evidence for different carrier species in the two reactions.

On the other hand, Russell and Brown[7] have reported a k/k_0 value in the competitive chlorination of toluene and cyclohexane of 3.5 at 80°, compared with 2.8 for photochlorination. We have carried out the photochlorination in the vapor phase, obtaining $k/k_0 = 2.12$, which may be within experimental error of the liquid phase reaction, but certainly differs significantly from the SO_2Cl_2 result, particularly since, as observed by Hass,[3] chlorine atom selectivity is generally greater in the vapor than in the liquid phase.

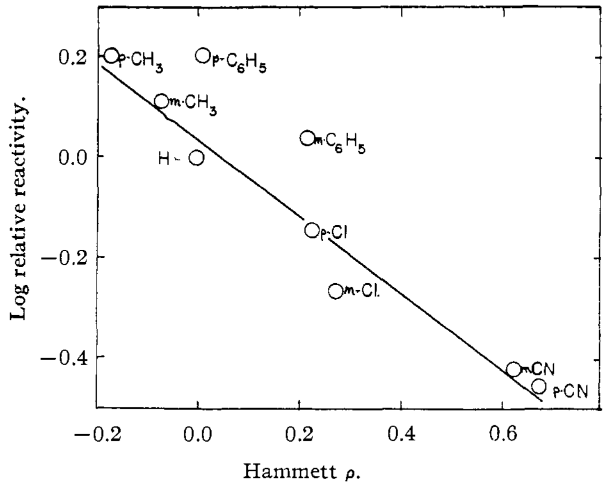

Fig. 3.—Relative reactivities of substituted toluenes toward chlorine atoms *vs.* Hammett ρ values for substituents.

To see if change of solvent plays any role in our systems, we have determined the relative reactivity of p-chlorotoluene in benzene and carbon tetrachloride, the systems being approximately 3 M in mixed toluenes. In benzene (the solvent used by Kooyman) no significant change occurs, but in carbon tetrachloride selectivity is increased about 50%, a result which has been checked by fractionation of larger runs (two experiments give $k/k_0 = 0.49$, 0.43, in excellent agreement with the isotope method). This then appears to be one of the very few examples of a significant variation in the relative rates of two radical reactions with change of medium and we are unable to afford any convincing explanation, although there also appears to be a significant change in k_H/k_D, see below. Direct interference of the solvent by interaction with the chain carrying radicals by processes such as

$$Cl\cdot + CCl_4 \longrightarrow Cl_2 + \cdot CCl_3 \qquad (16)$$

$$\text{or} \quad R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3 \qquad (17)$$

seems unlikely since the reverse of (16) should occur with great ease, and neither should compete well with the very fast chain carrying reactions.[23]

Conceivably, the properties of a chlorine atom in a primarily aromatic solvent are significantly altered from those in carbon tetrachloride, so that, in the bulk of our measurements, we are studying the properties of a complexed radical. Such a suggestion has been made by Russell and Brown,[21] and the possibility of such complexes of peroxy radicals (with more strongly electron donating aromatic systems) has been advanced by Boozer,

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(20) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

(21) G. A. Russell and H. C. Brown, *ibid.*, **77**, 4031 (1955).

(22) M. S. Kharasch and A. F. Zavist, *ibid.*, **73**, 964 (1951), have also suggested the participation of $\cdot SO_2Cl$ radicals in SO_2Cl_2–olefin reactions to account for the formation of β-chlorosulfones when terminal olefins are employed.

(23) Reaction 16 would compete with hydrogen abstraction which has a rate constant of $>10^{10.5}$ while the rate constant for (17) may be estimated as <1 from values of chain-transfer with CCl_4 and chain propagation in styrene polymerization where a similar radical is involved.

Hammond, *et al.*,[24] to account for their observations on the inhibition of autoxidation. The possible existence of a type of chlorine atom–aromatic complex is discussed further in the following paper.[25] If such is the case, one might anticipate that a complexed radical would show a decreased sensitivity to a polar effect (since polarization in the same direction is involved in the complex) as is observed, and a decrease in selectivity when polarization is not important (since a complexed atom would be somewhat stabilized and less reactive). There is evidence for the latter in our discussion of isotope effects below.

Although our results on photochlorinations and sulfuryl chloride reactions are in good agreement, except for the results in carbon tetrachloride just discussed, neither check well with Kooyman's results on the same compounds, and evidently the major source of difference is experimental error. Although Kooyman has used a plausible experimental technique, with the exception of *p*-chlorotoluene (run in duplicate with an experimental error given as 14%) his data represent single experiments. Accordingly, in view of our excellent reproducibility and the good check given by fractionation of reaction mixtures, we believe our results give, at present, the best measure of relative reactivity of substituted toluenes toward chlorine atoms. Actually, it should be pointed out that part of the difference lies in the manner of treatment of data. Kooyman has determined ρ by a "best line" passing through the origin (toluene point), and the resulting slope is heavily influenced by the point for *p*-nitrotoluene for which the "usual" value of 0.778 was employed. In some other radical reactions, better Hammett plots have been obtained by using 1.27, the value for polar reactions involving anilines and phenols.[26] If the larger value is used (or if the *p*-nitrotoluene point is disregarded) and the toluene point is not given special weight, a value of $\rho \cong -1.0$ is obtained.

The negative sign of ρ in our series again points to the importance of polar effects in halogen atom reactions, particularly since any contribution to the transition state due to radical stabilization should produce an effect in the opposite direction.[12] However, our value now indicates a lower selectivity and smaller effect of polar contributions to the transition-state in chlorination than in bromination. For photobromination, Kooyman has reported $\rho = -1.05$, and, from Table IV, our results on three substituted toluenes are in good agreement with his. Actually, there is some uncertainty as to the significance of bromination data due to the reversibility of hydrogen abstraction, but deferring this point for the moment, the difference appears in a reasonable direction. Hydrogen abstraction from toluene by chlorine atoms occurs at a rate comparable to attack on ordinary secondary aliphatic C–H bonds,[8] and, from Pritchard, Pyke and Trotman-Dickenson's work,[5] the latter reaction (in the gas phase, at least) has an activation energy of ~ 1 kcal. In contrast, the bromine atom reaction has a reported[27] activation energy of 7 kcal. One would anticipate that, other things being equal, a low-activation energy process would show less sensitivity to a polar, or any other sort of, effect due to structural variation of the reactants.

Kooyman[15a] has suggested a simple correlation between ρ in radical reactions involving the toluene side-chain and the electronegativity[28] of the attacking atom, based on data involving chlorine and bromine atoms and $\cdot CCl_3$ and succinimide radicals. Our results with photochlorination indicate that the correlation was fortuitous, and it seems implausible to use an electronegativity value for a simple atom for highly substituted species such as the $\cdot CCl_3$ and succinimide radicals, particularly since copolymerization results[13] and recent data on aromatic substitution[29] show plainly that polar effects in the selectivity of carbon radicals vary markedly with the radical structure. Rather, it appears to us that the magnitude of polar effects depends upon an "effective electronegativity" of a radical, markedly influenced by substituents, and the size of the energy barrier to the reaction involved.

As is evident from Fig. 3, our data on phenyl-substituted toluenes indicate anomalously high reactivities. Berliner[30] has reviewed evidence for the value of the *p*-phenyl group, and suggests that at least two different sigma values should be assigned since ". . . effects are much greater where strong resonance interaction of the substituent group is possible, or where it can be enhanced in the transition state." Apparently participation of the *p*-phenyl group in resonance structures of type (4) here represents such a case. The value for *m*-phenyl was given originally on the basis of a single reaction,[14] and has been recalculated by Lichtin and Leftin,[31] from the ionization of *m*-phenylbenzoic acid, as 0.06 ± 0.03, a result which is in better agreement with our data. Thus nei-

TABLE V

ISOTOPE EFFECTS IN THE RADICAL HALOGENATION OF TOLUENE

Reagent	Solvent	No. expts.	k_H/k_D	Av. dev.[a]
Cl_2, light	......	3	2.08	0.03
Cl_2, light	Benzene	3	2.09	.01
Cl_2, light	*o*-Dichlorobenzene	3	2.09	.03
Cl_2, light	CCl_4	4	1.99	.02
Cl_2, light	Vapor phase	3	2.08	.03
SO_2Cl_2	......	4	2.105	.012
Br_2, light	......	3	(3.08)	(.02)

[a] Average deviation from the mean of individual experiments.

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[24] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3238 (1955).

[25] B. Miller and C. Walling, *ibid.*, **79**, 4187 (1957).

[26] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, *ibid.*, **70**, 1537 (1948). *Cf.* also ref. 13 which discusses further the justification for this choice.

[27] H. R. Anderson, H. A. Scheraga and E. R. Van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953); there are, however, some unexplained peculiarities in this study, since it yields a value of $D(C_6H_5CH_2–H)$ significantly higher than the generally accepted value.

[28] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1946, pp. 58–88.

[29] R. L. Dannley and E. C. Gregg, Jr., THIS JOURNAL, **76**, 2997 (1954); J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1425 (1955).

[30] E. Berliner and L. L. Liu, THIS JOURNAL, **75**, 2417 (1953).

[31] N. N. Lichtin and H. P. Leftin, *ibid.*, **74**, 4207 (1952).

ther of our phenyl results appear particularly inconsistent with our picture.

Finally, a series of k_H/k_D ratios for halogen atom attack on toluene are collected in Table V. Results for photochlorination in no solvent, vapor, benzene and *o*-dichlorobenzene are experimentally indistinguishable from each other and from the sulfuryl chloride reaction, in accord with our other data on relative reactivities, but the value in CCl_4 is significantly lower, further evidence for some difference in this solvent.

Our value of 3.08 for photobromination is larger than for chlorination, as might be anticipated for a process of higher activation energy,[32] but is actually too low,[33] since photobromination is significantly reversible. Accordingly, the measurement actually involves the complex process

$$RH + Br\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\cdot + HBr \xrightarrow[k_2]{Br_2} RBr + \cdot Br \quad (18)$$

in which k_2 and k_{-1} have roughly comparable values.[27] A similar complication necessarily attends Kooyman's[15a] and our studies of competitive brominations, so, in spite of the good agreement, it may well be that both sets of data here represent values which are slightly different from, and probably smaller than, the actual ratios of k_2's.

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(32) An admirable review of the relation between reaction properties and isotope effects is given by K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955); *cf.* also G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(33) K. B. Wiberg, private communication, the actual value (in the absence of HBr) is 4.6–4.9.

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The Displacement of Aromatic Substituents by Halogen Atoms[1]

BY BERNARD MILLER[2] AND CHEVES WALLING

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The reaction of chlorine with bromobenzene to give chlorobenzene and bromine is apparently a radical chain process on the basis of the following evidence: (1) the reaction is light catalyzed; (2) the analogous reaction using sulfuryl chloride is accelerated by benzoyl peroxide; (3) the reaction is inhibited by nitro-, azo- and azoxybenzene; (4) reactions run in competition with the side-chain chlorination of toluene yield comparable ratios of products in light and dark. Similar reactions of substituted bromobenzenes have been studied and competitive experiments show that the displacement is retarded by electron withdrawing groups. Benzenesulfonyl chloride and diphenylsulfone also undergo ready photochemical reaction with chlorine to give chlorobenzene and SO_2, and the photochemical exchange of bromobenzene and Br_2^{82} has been demonstrated. Radical chain sequences are proposed, and the critical step, $Cl\cdot + C_6H_5Br \rightarrow C_6H_5Cl + Br\cdot$, is suggested as possibly involving the rearrangement of an intermediate radical–substrate "pi complex."

The difficulty with which aromatic halogen is replaced by polar reagents is well known[3] and chlorination of bromobenzene in the presence of ferric or aluminum chloride proceeds smoothly to give chiefly *o*- and *p*-chlorobromobenzene.[4] However, in 1903 Eibner[5] reported that bromobenzene, on standing with chlorine at room temperature in the absence of catalysts, gave 50% chlorobenzene, together with polyhalogenated products. Molecular bromine was produced, and the reaction was stated to be favored by moisture and direct light.

Similar displacements have been reported in attempts to chlorinate bromotoluenes. Although the successful preparation of *ortho-*,[6] *meta-*[7] and *para*-bromobenzyl chlorides[8] by this route have all been claimed, in 1890 Srpek[9] reported that room temperature chlorination of *p*-bromotoluene gives an inseparable mixture of products with chlorine and bromine in both ring and side-chain. These reactions have been reinvestigated by Asinger,[10] who found that extensive nuclear substitution of chlorine for bromine occurred in all cases.

More recently, Goerner and Nametz reported similar nuclear displacement of bromine during the reaction of bromotoluenes with sulfuryl chloride and benzoyl peroxide at 93°.[11]

While our work was in progress, Voegtli, Muhr and Langer[12] have also described similar displacements on substituted bromobenzenes during photochlorination in refluxing carbon tetrachloride, the three isomeric chlorobromobenzenes giving 82–90% of the corresponding dichlorobenzenes. *p*-Fluorobromobenzene gave *p*-fluorochlorobenzene in similar yield, but under these conditions bromobenzene yielded only 68% chlorobenzene together with a dark residue.

Interestingly, iodine apparently is not replaced as is bromine, chlorination of iodobenzene producing only iodobenzene dichloride,[13] and similar dichlorides are reported from *p*-bromoiodobenzene and *sym*-tribromoiodobenzene.

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(1) Taken from a portion of a dissertation submitted by Bernard Miller in 1955 to the Graduate Faculties of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) University Fellow, Columbia University, 1954–1955.

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XV; thus nucleophilic displacements occur with ease only in the presence of strongly electron withdrawing substituents as in 2,4-dinitrochlorobenzene.

(4) M. A. F. Holleman and T. Van der Linden, *Rec. trav. chim.*, **30**, 253 (1911).

(5) A. Eibner, *Ber.*, **36**, 1229 (1903).

(6) W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **20**, 665 (1915).

(7) H. Berger, *J. prakt. Chem.*, **2**, 241, 346 (1932).

(8) M. J. Boeseken, *Rec. trav. chim.* **23**, 99(1904).

(9) O. Srpek, *Monatsh.*, 11, 431 (1890).

(10) F. Asinger, *ibid.*, **64**, 153 (1934).

(11) G. L. Goerner and R. C. Nametz, THIS JOURNAL, **73**, 2940 (1951). A similar observation was made by C. W. in 1946 in an attempt to prepare *m*-bromobenzal chloride.

(12) W. Voegtli, H. Muhr and P. Langer, *Helv. Chim. Acta*, **37**, 1627 (1954)

(13) C. Willgerodt, *J. prakt. Chem.*, **2**, 33, 154 (1886).