[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

Relative Reactivities of Substituted Toluenes Toward Trichloromethyl Radicals

BY EARL S. HUYSER[1]

RECEIVED JULY 6, 1959

Relative reactivities of substituted toluenes toward attack by a trichloromethyl radical were determined by carrying out competitive brominations using bromotrichloromethane as the brominating agent. Contrary to a previous report, a relatively large polar effect was found. The effect of a nuclear substituent on the reactivity of benzylic hydrogens toward a trichloromethyl radical is dependent on the σ^+-value of the substituent with a ρ-value of -1.46.

Introduction

Nuclear substituents have been observed to effect markedly the reactivity of the benzylic hydrogens of alkyl benzenes toward attack by certain free radicals. Electron-releasing and -withdrawing groups were reported, respectively, to increase and to decrease the reactivity of these hydrogens toward attack by bromine atoms,[2] chlorine atoms,[3] N-succinimidyl radicals[2] and peroxy radicals.[4] In the one study recorded, no polar effect was noted in the reaction of trichloromethyl radicals on benzylic hydrogens.[2]

It was suggested by Kooyman that the polar effects in radical reactions involving the alkyl side-chain were dependent on the electronegativity of the atom in the attacking radical having the unpaired electron. A trichloromethyl radical, in which carbon is the atom bearing the unpaired electron, would not be expected to display a polar effect to the same extent as radicals involving chlorine, bromine or nitrogen atoms carrying the unpaired electron. This conclusion was questioned by Walling and Miller in view of the fact that polar effects are observed in copolymerization and free radical aromatic substitutions, reactions which involve free radicals in which a carbon atom bears the unpaired electron. Walling and Miller postulated that the polar effects depend on the "effective electronegativity" of the free radical which is determined by the substituents on the atom with the unpaired electron. The high degree of substitution by highly electronegative atoms such as chlorine atoms might be expected to alter the "effective electronegativity" of the carbon free radical and reactions of this radical might be subjected to polar effects.

The free radical chain sequence in the photochemically induced bromination of alkylbenzenes with bromotrichloromethane[5] involves the attack of a trichloromethyl radical on an alkyl side-chain and presents an inviting method for investigating the reaction of a trichloromethyl radical with benzylic hydrogens.

$$\cdot CCl_3 + ArCH_3 \longrightarrow HCCl_3 + Ar\dot{C}H_2 \qquad (1)$$

$$Ar\dot{C}H_2 + BrCCl_3 \longrightarrow ArCH_2Br + \cdot CCl_3 \qquad (2)$$

The rather marked effect of nuclear substituents on the reactivity of benzylic hydrogens with trichloromethyl radicals, determined by carrying out competitive brominations of some substituted toluenes using bromotrichloromethane as the brominating agent, is described in this report.

Experimental

Materials and Equipment.—All reagents were commercial materials, fractionally distilled before use. Vapor phase chromatographic analysis of each reagent after distillation showed no detectable impurities. A 10-ft. length of $^1/_4''$ o.d. stainless steel tubing packed with Fluorolube MG 600 (Hooker Chemical Co.) on Celite with helium as the carrier gas was used for the vapor phase chromatographic analysis. The reactions were carried out in 6″ Pyrex test-tubes which were sealed during the course of the reaction by means of a spherical joint and cap. The reactions were run in a constant temperature water bath ($50 \pm 1°$) contained in a Pyrex vessel and initiated by illumination through the side of the water-bath with a General Electric 275-watt sunlamp.

Procedure.—About equivalent quantities (10–20 mmoles) of bromotrichloromethane, toluene and the substituted toluene were accurately weighed out along with about 1–1.5 g. of chlorobenzene. The chlorobenzene, which does not react under these conditions, served as an internal standard for the vapor phase chromatographic analysis. This reaction mixture was chromatographed on the column described above set at 160° with a helium head pressure of 1.35 atm. The areas of toluene and bromotrichloromethane with respect to the area of the internal standard, chlorobenzene, were found with a planar compensating planimeter. The reactants were placed in the reaction tube and illuminated by the sunlamp for 2–4 hours at $50 \pm 1°$, which resulted in about 25–50% reaction of the bromotrichloromethane. The reaction mixture was cooled to room temperature and chromatographed again under the same conditions. The areas of toluene and bromotrichloromethane with respect to chlorobenzene were again determined. Since there is no change in the number of moles of chlorobenzene in the reaction mixture, the areas of toluene and bromotrichloromethane can be corrected to correspond to the same scale as the initial areas. The proportionality between the number of moles of a component and its vapor phase chromatographic area allows for calculation of the number of moles of toluene and bromotrichloromethane remaining in the reaction mixture after illumination. Since essentially all of the bromotrichloromethane which has disappeared resulted in reaction of toluene and the substituted toluene, the difference in the amounts of toluene and bromotrichloromethane which have been consumed is the amount of substituted toluene which has reacted. Thus, the data that are obtained are the concentrations in moles of toluene and substituted toluene after reaction with bromotrichloromethane. Duplicate reactions were carried out for each substituted toluene.

Treatment of Data.—In a competitive bromination with bromotrichloromethane, the rates of disappearance of toluene and substituted toluene are given by

$$-d[X]/dt = k_0[X][\cdot CCl_3] \qquad (3)$$

and

$$-d[S]/dt = k[S][\cdot CCl_3] \qquad (4)$$

where X and S are toluene and the substituted toluene, respectively, and k_0 and k are their respective reaction rate constants with a trichloromethyl radical. Dividing (4) by (3) and rearranging the terms results in a ratio of the two reaction rate constants which is the relative reactivity ratio.

$$k/k_0 = \frac{d[S]/[S]}{d[X]/[X]} \qquad (5)$$

---

[1] Dept. of Chemistry, University of Kansas, Lawrence, Kan.

[2] E. C. Kooyman, R. vanHelden and A. F. Bickel, *Koninkl. Ned. Akad. Wedenschap. Proc.*, **56B**, 75 (1953).

[3] R. vanHelden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954); C. Walling and B. Miller, THIS JOURNAL, **79**, 4181 (1957).

[4] C. Walling and E. A. McElhill, *ibid.*, **73**, 2927 (1951); G. A. Russell, *ibid.*, **78**, 1047 (1956).

[5] E. S. Huyser, *ibid.*, **82**, 391 (1960).

Integrating equation 5, and since (3) and (4) are of the same kinetic order, allowing concentrations to be expressed in moles, results in

$$k/k_0 = \frac{\log S_0/S_{\text{fin}}}{\log X_0/X_{\text{fin}}} \qquad (6)$$

where X_0 and S_0 are the initial number of moles of toluene and substituted toluene, respectively, known from the initial weighing of the reactants, and X_{fin} and S_{fin} are the number of moles remaining after reaction with bromotrichloromethane, determined by the vapor phase chromatographic analysis. Table I presents representative data for *p*-methoxytoluene and *p*-chlorotoluene.

TABLE I

REPRESENTATIVE DATA ON COMPETITIVE REACTIONS OF SUBSTITUTED TOLUENES WITH BROMOTRICHLOROMETHANE AT 50°

Run	S_0	X_0	$BrCCl_{3_0}$ mmoles	S_{fin}	X_{fin}	$BrCCl_{3\text{fin}}$	k/k_0
			p-Methoxytoluene				
1	3.38	11.68	9.25	0.30	10.00	4.49	14.6
2	3.51	11.38	10.12	0.40	9.69	4.80	13.7
			p-Chlorotoluene				
1	18.1	18.8	17.8	14.5	14.0	9.43	0.76
2	15.3	21.6	17.2	12.2	15.7	8.38	0.71

Results and Discussion

Table II contains the relative reactivities of various substituted toluenes toward reaction with a trichloromethyl radical. Examination of these data shows that nuclear substitutents have a definite effect on the reactivity of benzylic hydrogens with a trichloromethyl radical. These results are in contradiction to those reported by Kooyman. The qualitative effect of the nuclear substituent is the same as that reported for other free radicals which possess an electronegative character in that electron-releasing groups increase the reactivity and electron-withdrawing groups decrease the reactivity of the benzylic hydrogens toward reaction with the free radical.

TABLE II

RELATIVE REACTIVITIES OF SUBSTITUTED TOLUENES TOWARD TRICHLOROMETHYL RADICALS AT 50°

Substituent	Expt.	k/k_0	Av. dev.[b]
p-Methyl	3	2.76[a]	0.10
m-Methyl	2	1.58[a]	.15
p-Methoxy	2	14.2	.45
None	..	1.0	..
m-Methoxy	2	0.87	.02
p-Chloro	2	.73	.02
p-Bromo	2	.70	.03
m-Bromo	2	.25	.01

[a] k/k_0 corrected by a statistical factor of two. [b] Average deviation from the mean of individual experiments.

A more quantitative treatment of these data can be obtained in terms of the Hammett equation[6]

$$\log k/k_0 = \rho\sigma$$

where k/k_0 is the reactivity ratio, ρ is a parameter determined by the susceptibility of the particular reaction involved to changes in electron density and σ is a measure of the change in electron density at the reaction site caused by a nuclear substituent. A plot of the log k/k_0 against the σ value for the substituent, illustrated in Fig. 1, shows little quantitative relationship between the reactivity of the benzylic hydrogens with a trichloromethyl radical and the electron-releasing or electron-withdrawing ability of a nuclear substituent which is measured by its σ-value.

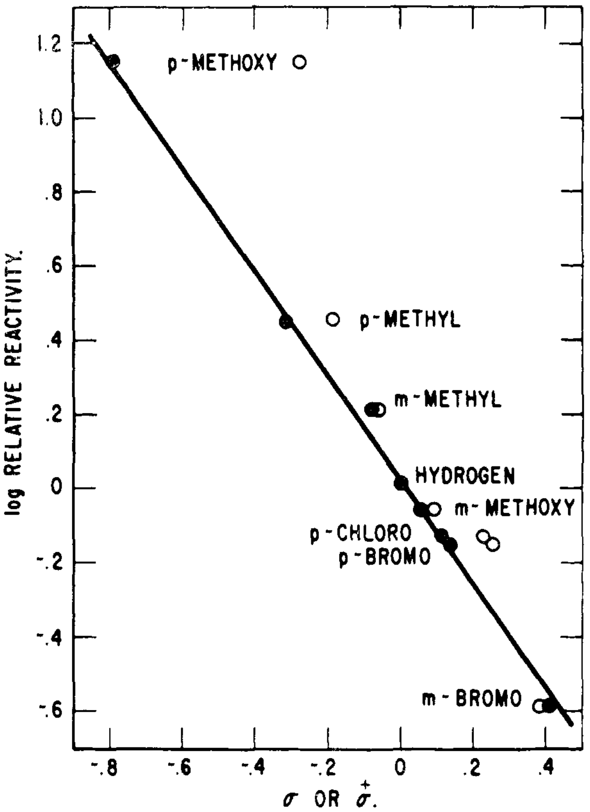
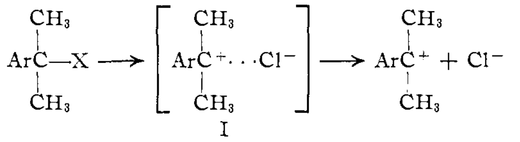


Fig. 1.—Correlation between log k/k_0 and σ- and σ^+-values for substituents; ●, σ^+; ○, σ.

On the other hand, plotting the log k/k_0 against the σ^+-value of the nuclear substituent[7] (Fig. 1) shows a direct correlation between the reactivity and the σ^+-value of the substituent. The σ^+-values of the nuclear substituents used here were determined by Brown and his co-workers from the rates of hydrolysis of phenyldimethylcarbinyl chlorides. The σ^+-value of the aromatic nuclear substituent is a measure of its effect on the ease of formation of the transition state I presumed to be involved in a first-order solvolysis.



$$\mathrm{Ar}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-X} \longrightarrow \underset{\mathrm{I}}{\left[\mathrm{Ar}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}{}^{+}\cdots\mathrm{Cl}^-\right]} \longrightarrow \mathrm{Ar}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}{}^{+} + \mathrm{Cl}^- \qquad (7)$$

Since the effect of the substituent on the reactivity of benzylic hydrogens toward trichloromethyl radicals appears to be the same, a similar transition state (II) might be expected in this reaction.

---

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. VII.

[7] (a) H. C. Brown and Y. Okamoto, THIS JOURNAL, **80**, 4979 (1958); (b) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957); (c) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957); (d) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); (e) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957).

$$ArCH_3 + \cdot CCl_3 \longrightarrow \underset{\text{II}}{[Ar\overset{+}{C}H_2 \ldots \dot{H} \ldots \overset{-}{C}Cl_3]} \longrightarrow Ar\dot{C}H_2 + HCCl_3 \quad (8)$$

The stabilities of both benzyl carbonium ions and a trichlorocarbanion lend support to the existence of such species in the transition state.

In a re-examination of Kooyman's data, Russell pointed out similar correlation between the σ^+-value of a substituent and its effect on reactivity of benzylic hydrogens with bromine atoms and N-succinimidyl radicals.[8] The reactivities of substituted toluenes toward chlorine atoms, however, appear to be dependent on the electron density at the reaction site and consequently are determined by the σ-values of the nuclear substituents. This difference in the effect of nuclear substituents on the reactivity of benzylic hydrogens with chlorine atoms from those with bromine atoms, N-succinimidyl radicals and trichloromethyl radicals suggests differences in halogenation reactions involving chlorine from those involving bromine, N-bromosuccinimide and bromotrichloromethane. The rather striking polar effects noted in the free radical chlorinations of esters, nitriles, alkyl halides, etc., demonstrate the effect of electron density on the site of attack by a chlorine atom, hydrogen abstraction generally occurring at a point of high electron density with considerably less hydrogen abstraction at points of low electron density.[9]

The site of bromination in reactions involving bromine, N-bromosuccinimide and bromotrichloromethane, on the other hand, is largely determined by resonance effects. The relationship between the reactivities of benzylic hydrogens with bromine atoms, N-succinimidyl radicals and trichloromethyl radicals and the σ^+-values of nuclear substituents suggests that resonance stabilization of a carbonium ion may be the important factor in determining the site of attack by such free radicals in certain cases. The bromination of benzylic and allylic positions by such reagents under free radical conditions and the relative ease of formation of benzylic and allylic carbonium ions in numerous ionic reactions tend to support such a conclusion. That resonance stabilization of a carbonium ion rather than a free radical may be important in the transition state in these reactions is also evident from the negative ρ-value for these reactions. In general, electron-releasing groups contribute little to radical stabilization whereas electron-withdrawing groups in the *p*-position tend to stabilize benzyl radicals.[10] If resonance stabilization of the free radical were important in the transition state of these reactions, the order of reactivity of substituted toluenes toward such radicals might be expected to be altered; namely, electron-withdrawing groups increasing the reactivity and electron-releasing groups having little effect on the reactivity.[11]

[8] G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

[9] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 361–365, has several examples and references to these reactions.

[10] See Reference 9, pp. 138–139.

[11] See also footnote 10 of ref. 8.

MIDLAND, MICH.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

Fluorocarbon Nitrogen Compounds. VI.[1] Thio and Nitroso Derivatives of Bis-(trifluoromethyl)-amine[2]

BY JOHN A. YOUNG, SKEVOS N. TSOUKALAS[3] AND RICHARD D. DRESDNER

RECEIVED JUNE 23, 1959

Reaction of sulfur with the mercury derivative of bis-(trifluoromethyl)-amine, $[(CF_3)_2N]_2Hg$, produces HgF_2, HgS, $CF_3N{=}CF_2$, $(CF_3)_2NCF{=}NCF_3$ and both the thio- and dithioamines, $[(CF_3)_2N]_2S$ and $[(CF_3)_2NS]_2$. Vapor phase oxidation of $CF_3N{=}CF_2$ at 380–425° over RbF gives the nitrosamine, $(CF_3)_2N{-}NO$; at higher temperatures only COF_2 and nitrogen oxides result. The nitrosamine can be oxidized by peroxytrifluoroacetic acid to the nitramine, $(CF_3)_2N{-}NO_2$. The nuclear magnetic resonance spectrum of $(CF_3)_2N{-}NO$ shows no double bond character in the N–N bond; because of this fact the compound, in contrast to dialkyl nitrosamines, does not exhibit rotational isomerism and is quite unstable. Infrared assignments are made for bands at 6.12 μ (N–O in $(CF_3)_2N{-}NO$) and 9.80 μ (general for C–N in $(CF_3)_2N$–compounds).

A general paper on the chemistry of $(CF_3)_2NH$ has already appeared.[3] Several compounds related to this amine but not previously described are herein reported.

Thioamines.—The incorporation of sulfur into a fluorocarbon chain has been attained by reaction of C_3F_6 with sulfur[4] and by reaction of fluorocarbon iodides with sulfur[5,6] or mercuric sulfide.[7] Although perfluoro-2-azapropene did not react with sulfur in a manner analogous to that of $CF_3CF{=}CF_2$, an N–S bond derived from $(CF_3)_2NH$ was formed by reaction of the mercury derivative of the amine with sulfur. The products observed indicated the occurrence of two distinct reactions. One set of products, including HgF_2, $CF_3N{=}CF_2$ and $(CF_3)_2NCF{=}NCF_3$, could be ascribed to thermal dissociation of the mercurial, while the other group, consisting of HgS, $(CF_3)_2NSN(CF_3)_2$ and $(CF_3)_2NS_2N(CF)_2$, resulted from its reaction with sulfur. These relationships are shown in eq. 1.

[1] For the preceding paper in this series, see R. D. Dresdner, F. N. Tlumac and J. A. Young, unpublished.

[2] This work was supported by the Office of Naval Research, and reproduction of this paper in whole or in part is permitted for any purposes of the United States Government.

[3] J. A. Young, S. N. Tsoukalas and R. D. Dresdner, THIS JOURNAL, **80**, 3604 (1958).

[4] H. C. Brown, *J. Org. Chem.*, **22**, 715 (1957).

[5] R. N. Haszeldine, *J. Chem. Soc.*, 3219 (1953).

[6] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 5461 (1951).

[7] M. Hauptschein and M. Braid, *ibid.*, **80**, 853 (1958).