

Polar Radicals. VII. Reversible Hydrogen Abstraction in the Mechanism of the Bromination Reactions of Bromotrichloromethane. Polar Effects in the Abstraction Reactions of the Trichloromethyl Free Radical¹

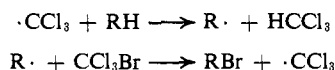
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Abstract: The relative rates of the photoinitiated bromination of substituted toluenes with bromotrichloromethane have been reinvestigated. A Hammett correlation gives a ρ (σ^+) of -1.24 (previously reported -1.46). Under the conditions used for these competitive brominations, mixtures of toluene- α - d_3 and toluene undergo extensive exchange of protium and deuterium during the brominations. The exchange reaction can be ascribed to the presence of hydrogen bromide formed during the reaction. When powdered potassium carbonate or ethylene oxide was added to the reaction mixtures the exchange was dramatically decreased or eliminated completely. Under conditions necessary to completely eliminate the exchange reaction (20% added ethylene oxide) a new ρ (σ^+) of -0.69 was assigned for the trichloromethyl radical abstraction of hydrogen from the substituted toluenes. Since reversible transfer of benzylic radicals with hydrogen bromide has been shown to lower the ρ values for brominations with molecular bromine, the mechanism for the bromotrichloromethane brominations, without additives, can be assigned to a bromine atom chain involving reversible abstraction. The implications, to the understanding of polar interactions in radical reactions, of the new value of ρ assigned for hydrogen atom abstraction by the trichloromethyl radical are discussed.

A mechanism for the bromination reaction of bromotrichloromethane has been proposed⁴ by analogy to the mechanism established for the halogenation reactions of other polyhalomethanes⁵ (Scheme I).

Scheme I

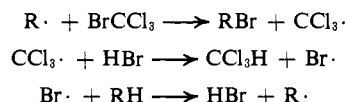


The reaction has been shown to be preparatively useful for the side chain halogenation of alkyl aromatics^{5,6} and its reactions have been used as examples of those governed by the abstraction reactions of the trichloromethyl free radical.⁶⁻¹⁴

In the original study of the mechanism of bromotrichloromethane bromination of arenes Huyser noted that accompanying the very good yield of benzylic bromide and chloroform, small amounts of hydrogen bromide and hexachloroethane were formed.⁵ The presence of small amounts of hydrogen bromide in the reaction mixture suggests the possibility of yet another

chain sequence to explain the bromination behavior of bromotrichloromethane. The alternative mechanism, first suggested by Russell⁷ (Scheme II), was eliminated

Scheme II



as the possible reaction sequence in the bromination since a comparison between the bromination of a number of arenes with molecular bromine and with bromotrichloromethane showed the two reagents to have different relative reactivities toward primary, secondary, and tertiary benzylic hydrogens. Contradictory results have been reported on the reactivity of trichloromethyl.^{15,16} Kooyman^{15,16} while examining the ability of aralkyl hydrocarbons to inhibit the peroxide catalyzed telomerization of 1-hexadecene and carbon tetrachloride concluded that the trichloromethyl free radical was less selective than has subsequently been reported and that its polar interactions, also subsequently reported as extremely high,⁶ were also negligible.

Our present interest in the effects of reversible hydrogen abstraction on the kinetics of a number of free radical reactions involving hydrogen chloride,¹⁷⁻¹⁹ mercaptans,²⁰ and hydrogen bromide²¹ have led us to reconsider and reinterpret the results obtained from the

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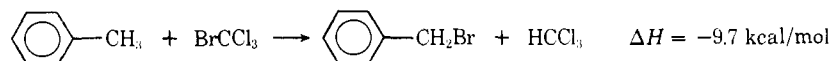
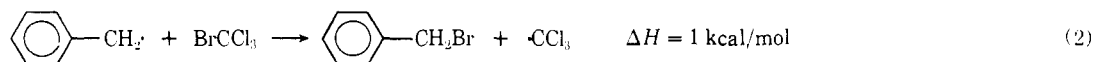
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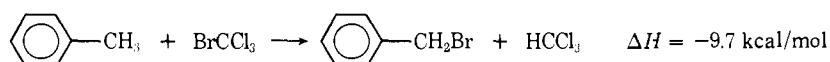
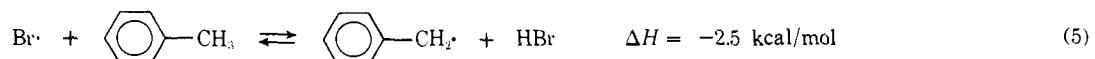
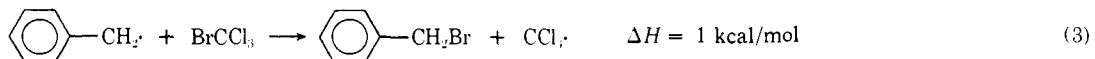
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Scheme III
Scheme I



Scheme II



study of trichloromethyl radicals generated by the photolysis of bromotrichloromethane.

A comparison of the energetics of the chain propagation steps in the two mechanisms considered for the bromination of arenes with bromotrichloromethane shows little predictable preference for either scheme (see Scheme III).²²

Reactions 4 and 5 have both been shown to be reversible^{25,26} during the bromination reactions of chloroform and toluene.

The result of extensive reversible abstraction (eq 5) by the bromine atom would be to mask the true kinetic distribution of radicals produced during the substitution reactions. The usual inequality in the differences of the activation energies of the forward and the reverse reactions for two similar exothermic reactions, $E_{-2} - E_{-1} > E_2 - E_1$, would enable one to predict that the most stable radical in the system would undergo the least reversal. From an analysis of the product distribution (or the relative ratio of reaction in a competitive reaction) from such a reaction, the most stable radical in the system would appear to have been formed in an even higher ratio relative to the comparable less stable radical. The abstracting species, therefore, would appear to be more selective than it in fact was. Possibly the abnormally high selectivities reported for the bromination reactions of bromotrichloromethane (primary:secondary:tertiary benzylic hydrogen, 1:50:250) could be explained by extensive reversal.

The sensitivity, of the side chain brominations of arenes by bromotrichloromethane, to polar substituents has been reported to be abnormally high for a free radical substitution reaction ($\rho = -1.46^6$ for toluenes,

-0.94 for neopentylbenzenes,^{11c} -0.67 for cumenes,^{11b} and -0.39 (σ^+ , -0.58) for allylbenzenes^{11a} and -0.53 for ethylbenzenes.^{12a} The polar interactions observed have been found to correlate more closely with σ^+ constants (except in the case of allylbenzenes) than with σ constants. An analysis of the effects of extensive reversible abstraction with hydrogen bromide on the relative rates of bromination of substituted toluenes is a bit more complicated. Empirically, however, it has been shown that the absolute value of ρ is lowered when the substitution reactions are carried out in the presence of hydrogen bromide. Kooyman²⁷ reported a ρ value of -1.05 (80°) for the photobromination (molecular bromine) of substituted toluenes when the reactions were run under conditions favoring high concentrations of hydrogen bromide. Pearson and Martin²⁸ subsequently demonstrated that under conditions where the ratio of Br_2/HBr is large the ρ value (σ^+ correlation) was -1.36 (80°). If reversible abstraction is used to explain the apparent high selectivities for the bromotrichloromethane brominations then the anomalously high ρ values reported for the reagent are unreasonable, since lower reaction constants would have been observed. A possible mechanistic explanation which accommodates more closely all of the anomalies is the operation of the bromine atom chain (Scheme II). This mechanism predicts, if accompanied by extensive reversal, high selectivities, and ρ values (bromine atom abstraction), although somewhat diminished, of from -1.38^9 to $-1.46.^{28}$ Furthermore, it is reasonable that in the presence of hydrogen bromide transfer of a radical with this transfer agent should be more prevalent in the case of bromotrichloromethane brominations than in brominations using molecular bromine, since transfer with this latter reagent is much faster than with the halomethane.

(22) Values for the bond dissociation energies for $\text{D}(\text{CCl}_3\text{-Br})$ and $\text{D}(\text{HBr})$ were taken from ref 23; values for $\text{D}(\text{CCl}_3\text{-H})$, $\text{D}(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$ and $\text{D}(\text{C}_6\text{H}_5\text{CH}_2\text{-Br})$ were taken from ref 24.

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(28) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 3142 (1963).

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Results and Discussion

The relative rates of the photoinitiated bromination of substituted toluenes with bromotrichloromethane have previously been reported by Huyser.⁶ A reinvestigation of these results showed a reasonable comparison between the relative rate values obtained in both laboratories; see Table I.

Table I. Relative Reactivities of Substituted Toluenes toward Bromotrichloromethane at 50°

Substituent	k/k_0 (this work) ^{a,b}	k/k_0 (ref 6) ^b
<i>p</i> -Methyl	2.39 ± 0.07 (2) ^c	2.76 ± 0.10 ^c
<i>m</i> -Methyl	1.48 ± 0.08 (3) ^c	1.58 ± 0.15 ^c
<i>p</i> -Methoxy	8.75 ± 0.17 (4) ^d	14.2 ± 0.45
None (H)	1.00	1.00
<i>m</i> -Methoxy	0.83 ± 0.05 (3)	0.87 ± 0.02
<i>p</i> -Chloro	0.74 ± 0.03 (2)	0.73 ± 0.02
<i>p</i> -Bromo	0.63 ± 0.03 (2)	0.70 ± 0.03
<i>m</i> -Bromo	0.31 ± 0.02 (3)	0.25 ± 0.01
<i>p</i> - <i>tert</i> -Butyl	2.47 ± 0.32 (2)	

^a Values in parentheses correspond to the number of individual experiments. ^b Errors correspond to average deviation from the mean of individual experiments. ^c k/k_0 corrected by a statistical factor of 2. ^d *p*-Methoxy values of k/k_0 were calculated indirectly from the product of $(k_{p-MeO}/k_{p-Me})(k_{p-Me}/k_H)$; $(3.66 ± 0.5) · (2.39 ± 0.07)$. The value k_{p-MeO}/k_{p-Me} was determined from four independent experiments.

The deviation between the results for *p*-methoxytoluene *vs.* toluene possibly arises from the difficulty of directly obtaining relative rates of disappearance of substrates from competitive reactions which have such large differences in their rates. A further complication arises in the method of calculation used by the two groups. The method used in this work is based on determining the concentration of both substrates before and after the reaction while the previous authors have, assuming that all of the bromotrichloromethane reacted resulted in the monobromination of toluenes, calculated the concentration of the substituted toluene after the reaction from the concentration of the toluene, and the bromotrichloromethane that had reacted. Since detectable amounts of hexachloroethane are formed during the reaction,⁶ and since a direct determination of these values is experimentally difficult, the method of determining the relative rates used in this work is preferred.

Both sets of data give excellent ($r > 0.99$)³⁰ linear free energy correlations with Hammett σ^+ substituent constants and the differences found in the ρ values in the two laboratories are probably not significant.

$$\rho = -1.45, s = 0.0265, r = -0.998 \text{ (calculated from data ref 6)}$$

$$\rho = -1.24, s = 0.0105, r = -0.996 \text{ (this work)}$$

A 1:1 mixture of toluene- α - d_3 and toluene was brominated with bromotrichloromethane under the same conditions used to determine the relative rates of reaction for ring-substituted toluenes. The mixture of un-brominated toluenes was isolated by preparative glpc. The mixture of toluenes was subjected to mass spectral analysis (12 eV) and a comparison of the analysis of the mixture before and after reaction with bromotrichloro-

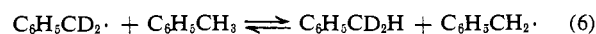
Table II. Isotopic Composition of the Parent Ions from Toluene and Toluene- α - d_3 Before and After the Reaction with Bromotrichloromethane

Additive	% conversion of BrCCl ₂	M ⁺ % ^a					E/C ^d
		<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃		
	0	48.5	0.0	0.9	50.6		
None	59	15.3	32.8	33.9	18.0	3.19	
None	58	13.6	31.4	35.2	19.8	3.24	
None	49	14.3	29.2	33.6	22.9	3.38	
Ethylene oxide ^b	6.7	47.8	0.0	0.9	51.3	0.00	
Ethylene oxide ^b	6.5	47.8	0.0	0.9	51.3	0.00	
Ethylene oxide ^b	96	42.5	0.0	2.0	55.5	0.07	
Ethylene oxide ^b	96	42.5	0.0	2.0	55.5	0.07	
K ₂ CO ₃ ^c	58	37.6	3.2	3.5	55.7	0.14	

^a Values reported are corrected for ¹³C natural abundance. ^b 20% of bromotrichloromethane. ^c 10% of bromotrichloromethane. ^d Lower limits on the number of exchanges (*E*) to the number of molecules of bromotrichloromethane (*C*) reacted.

methane is given in Table II. It can be calculated for reactions carried out to partial completion that more than 76% of the benzyl radicals formed return to give scrambled material before proceeding to side chain brominated product (see Table II). This value, 76%, is a minimum value and is calculated assuming that neither protium nor deuterium returns to a substrate from which it was originally incorporated; these exchanges, which undoubtedly occur, are masked from observation by the analytical method.

Several mechanistic possibilities can be considered to account for the scrambling which occurred during the brominations. The occurrence of a hydrogen bromide catalyzed exchange of protium and deuterium was ruled out by allowing a mixture of toluene, chloroform, and a large amount (20% of the toluene) of deuterium bromide to stand in the absence of light at 50° for several days. Isolation of the toluene from the mixture and its subsequent mass spectral analysis showed that no deuterium had been incorporated into the reisolated toluene. The identity reaction has been eliminated as an important reaction during the bromination of arenes with molecular bromine,²⁴ eq 6 and 7; however,

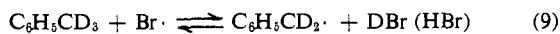
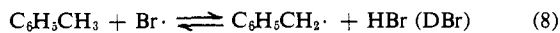


it was necessary to rule out its occurrence in the absence of as facile a transfer agent as molecular bromine. When a mixture of *tert*-butyl peroxy-pivalate, toluene, and toluene- α - d_3 was heated at 60° until the peroxide had decomposed the analysis of the recovered toluenes showed that no exchange had occurred, thus tentatively ruling out eq 6 and 7 as possible pathways leading to scrambling. The unimportance of the identity reaction to the exchange process was further substantiated since under conditions where its occurrence would not be hampered, no exchange was observed (see reaction run with added carbonate and ethylene oxide). Another conceivable path for scrambling is the transfer of a benzylic radical with chloroform or deuteriochloroform, eq 1 and its reverse reaction. The former process is possible since it must only have an activation energy in excess of 10.7 kcal/mol. The process could be completely ruled out by carrying out the bromotrichloromethane brominations in the pre-

(30) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

sence of a large amount of added deuteriochloroform. The unreacted toluene upon isolation and analysis by mass spectroscopy showed no incorporation of deuterium into the recovered toluenes.

The most reasonable mechanistic pathway for the exchange involves the near thermoneutral process of benzyl radical transfer with hydrogen bromide or deuterium bromide (eq 8 and 9).



It was found that the hydrogen bromide produced in the photobrominations of toluene could be scavenged by carrying out the reactions with added powdered potassium carbonate or by, using the method introduced by Huyser³¹ to scavenge hydrogen bromide, the addition of ethylene oxide to the reaction mixture. Qualitatively the reactions run in the presence of an added suspension of potassium carbonate proceeded at a very much slower rate than the reactions without this additive, possibly due to the defraction of the light by the suspended particles. It was found, however, that when a series of reactions was run with and without added ethylene oxide, under conditions where the irradiation of both sets of reactions was constant, that the reactions with added ethylene oxide were approximately eight times slower than those without the additive. The reduction in the rate of the reaction with added ethylene oxide indicates that the mechanism with and without hydrogen bromide was not proceeding by the same pathway.

When 1:1 mixtures of toluene and toluene- α - d_3 were subjected to the photoinitiated bromination reaction with bromotrichloromethane, in the presence of added solid potassium carbonate, the scrambling reaction of deuterium and protium was markedly reduced, while with added ethylene oxide (20 mol %) the reisolated substrates were found to be almost completely free of scrambling; see Table II. The amount of detectable scrambling was found to be dependent upon the percentage reaction and at lower percentage reaction it could be eliminated completely; see Table II. Glpc analyses of the reaction mixtures containing additives were identical with those without additives, with the exception that after reaction, the reactions with added ethylene oxide contained unreacted ethylene oxide and β -bromoethanol, the reaction product of the oxide with hydrogen bromide. An excellent material balance (>90%) was obtained with added epoxide.

The relative rates of reaction for several substrates were determined with added potassium carbonate or with ethylene oxide. A comparison of the values obtained with and without these additives is given in Table III. Significant differences in the values of the relative reactivities were observed with and without the additives. It can be seen from the values listed that under the conditions where reversible abstraction with hydrogen bromide is reduced the sensitivity to polar substituents of the abstracting species in the bromotrichloromethane bromination reactions is apparently very much diminished.

The competitive brominations of the previously investigated substituted toluenes were repeated under conditions where an undetectable amount of scrambling

Table III. A Comparison of the Relative Reactivities of Several Substituted Toluenes with and without Potassium Carbonate or Ethylene Oxide

Substituent	Additive	$k/k_0^{a,b}$
<i>p</i> -Methoxy	None	$8.75 \pm 0.17 (4)^d$
	K_2CO_3	$4.50 \pm 0.35 (3)$
	Ethylene oxide (20%)	$3.59 \pm 0.03 (3)$
<i>p</i> -Methyl ^c	None	$2.39 \pm 0.07 (2)$
	K_2CO_3	$2.05 \pm 0.14 (3)$
	Ethylene oxide (20%)	$1.71 \pm 0.01 (3)$
<i>m</i> -Bromo	None	$0.31 \pm 0.02 (3)$
	K_2CO_3	$0.35 \pm 0.02 (2)$
	Ethylene oxide (20%)	$0.57 \pm 0.02 (3)$

^a Values in parentheses correspond to the number of independent experiments. ^b Errors correspond to average deviation from the mean of individual experiments. ^c k/k_0 corrected by a statistical factor of 2. ^d Value taken from Table I.

would occur (20 mol % added ethylene oxide, 50–60% conversion of bromotrichloromethane). The relative rates determined from an analysis of these reactions are listed in Table IV. The values of the relative rates of

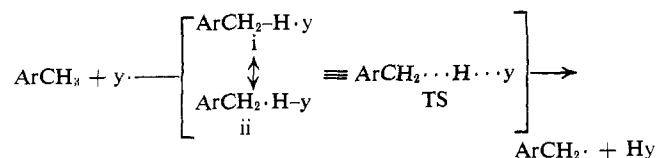
Table IV. Relative Reactivities of Substituted Toluenes toward Bromotrichloromethane with Added Ethylene Oxide at 50°

Substituent	$k/k_0^{a,b}$	Substituent	$k/k_0^{a,b}$
<i>p</i> -Methyl ^c	1.71 ± 0.01	<i>m</i> -Methoxy	0.97 ± 0.08
<i>m</i> -Methyl ^c	1.23 ± 0.02	<i>p</i> -Chloro	0.92 ± 0.02
<i>p</i> - <i>tert</i> -Butyl	1.82 ± 0.06	<i>p</i> -Bromo	0.75 ± 0.03
<i>p</i> -Methoxy	3.59 ± 0.03	<i>m</i> -Bromo	0.57 ± 0.02
None (H)	1.00		

^a Values correspond to average values determined from three independent experiments. ^b Errors correspond to average deviations from the mean of the individual experiments. ^c k/k_0 corrected by a statistical factor of 2.

bromination of the substituted toluenes with added ethylene oxide when compared with the values obtained for the same reactions without ethylene oxide (Table I) all indicate a marked decrease in sensitivity of the abstracting species to the polar effects of the substituent. This observation, made upon comparison of these two sets of data, can be quantitated by carrying out a Hammett correlation upon the values listed. An excellent correlation is obtained ($r = 0.993$); see Figure 1 using σ^+ constants, and the ρ value -0.69 constitutes a new reaction constant for the bromination of toluenes with bromotrichloromethane carried out in the absence of the effect of hydrogen bromide on the relative rates of reaction.

Polar Effects. The origin of the polar interactions in free radical abstraction reactions can be attributed to the effect of dipole-dipole interactions upon the energy of the transition state of the particular reaction.³² For abstractions from toluene or its ring-substituted analogs the energetics of hydrogen transfer can be analyzed by considering the importance of the canonical forms (i and ii) which contribute to the tran-



(31) E. S. Huyser and R. H. C. Feng, *J. Org. Chem.*, **36**, 731 (1971).

(32) J. M. Tedder, *Quart. Rev., Chem. Soc.*, **14**, 336 (1960).

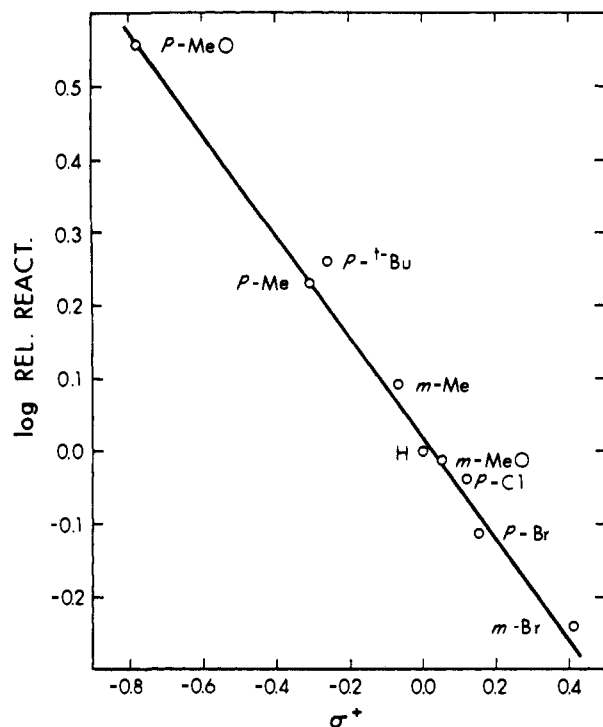


Figure 1. Hammett ρ - σ correlation for bromotrichloromethane bromination of substituted toluenes with added ethylene oxide: σ^+ correlation, $\rho = -0.694$, $r = 0.993$, $s = 0.026$.

sition state (TS). Dipole-dipole interactions contribute to the energy of TS by attractive (lower energy) or repulsive (higher energy) forces. In reactions where y is an atom or a symmetric nonpolar species, as is the trichloromethyl radical, the polar interactions would be determined almost entirely by their effect on ii , since i could not make a dipole-dipole contribution to the energy of the transition state. Any polar interaction attributable to i would be a second-order effect, dipole-induced dipole, and should be an order of magnitude smaller than the interactions present in structure ii . The importance of the dipole-dipole interaction on the overall energy of TS for such a reaction would be determined by the degree of bond breaking in the transition state and the magnitude of the dipoles of the new radical and the polar molecule formed in the reaction. If one compares the energy profile of the two reactions, the abstraction of hydrogen from toluene by a bromine atom ($\Delta H = -2.5$ kcal/mol) or by the trichloromethyl radical ($\Delta H = -10.7$ kcal/mol), the transition state for the more exothermic of the two processes will have the most bond breaking in the transition state and resemble more closely structure ii than the nonpolar structure i . Since the magnitudes of the dipole moments for chloroform (1.01 D) and for hydrogen bromide (0.80 D) are similar, one would predict that the polar interactions for trichloromethyl radicals would be more important than for bromine atom abstraction. The new value which we have assigned to ρ for trichloromethyl radical abstraction seems not to agree with this prediction.

Recently Zavitsas and Pinto³³ have put forward a different rationalization to explain the observation that the relative reactivities of a large number of radical abstraction reactions correlate well with polar substituent

(33) A. A. Zavitsas and J. A. Pinto, *J. Amer. Chem. Soc.*, **94**, 7390 (1972).

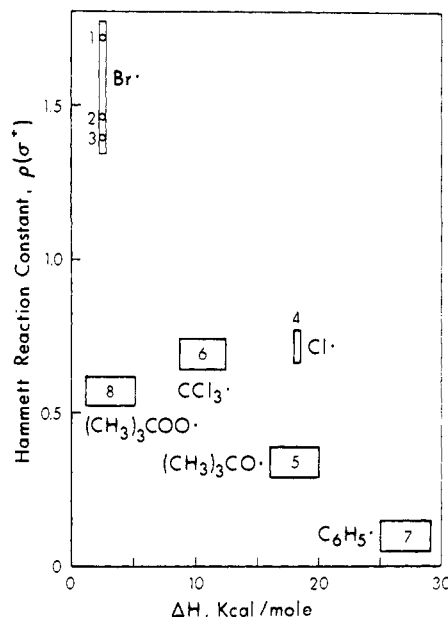


Figure 2. Plot of the values of $\rho(\sigma^+)$ vs. ΔH for abstraction reactions from toluene. Points 1-4 and 7 taken from ref 33. Point 5 was plotted using $\rho(\sigma^+) = -0.35^{23}$ and $D[(CH_3)_3CO-H] = 103 \pm 2$.²⁴ Point 6 was plotted using the new ρ value, -0.69 , obtained for trichloromethyl, and $D(CCl_3-H) = 95.7 \pm 2$ kcal/mol (S. W. Benson, *J. Chem. Phys.*, **43**, 2044 (1965)). Point 8 was plotted using $\rho(\sigma^+) = -0.56$ and $D[(CH_3)_3CO-H] = 88 \pm 2$ kcal/mol.³⁴ Uncertainties in bond dissociation energies are indicated by the size of the points plotted, and errors in ρ were set arbitrarily at ± 0.05 .

constants. These authors have proposed that ρ reflects not polar effects but differences in the bond dissociation energies of the substituted toluenes, and that its magnitude is a measure of the sensitivity of the abstracting radical to these differences. To substantiate this proposal a plot of ρ for the abstraction from toluenes by a number of radicals vs. ΔH for these reactions was shown to be linear. Five radicals (bromine, chlorine, *tert*-butoxy, phenyl, and trichloromethyl) were used in this correlation. The new value of ρ which we have determined for the trichloromethyl radical does not fit the correlation, see Figure 2, and any conclusions drawn from the former correlation must be reexamined. Furthermore, since the completion of this work another piece of data has been reported which also effects the linear correlation reported by Zavitsas.³³ Howard³⁴ by determining a ρ for tertiary butyl peroxy radicals of -0.56 has added another point (see Figure 2) to the plot of ρ vs. ΔH , which does not fit the proposed correlation. Since the argument put forward by the authors³¹ is now based on such limited and contradictory data, a rationalization for the polar effects based solely on the bond strengths of the bonds made and broken does not seem to be warranted.

Experimental Section

Reagents. All reagents were commercially available and were distilled or recrystallized before using. Gpc analyses showed all materials to be >99 mol % pure. Toluene- α - d_3 ($>99.9\%$) and deuterium bromide were obtained from Merck Sharp & Dohme of Canada Ltd.

(34) J. A. Howard and J. H. B. Chenier, *J. Amer. Chem. Soc.*, **95**, 3055 (1973).

Glpc Analysis. Analytical determinations were carried out using an Aerograph Model 202 gas chromatograph equipped with a thermal conductivity detector and fitted with a 20 ft \times $\frac{1}{8}$ in. stainless steel column packed with 5% DEGS on acid-washed Chromosorb W. Standard calibration curves were constructed to correct for the molar sensitivity of Freon 112, chloroform, bromotrichloromethane, and toluene in order to determine the percentage reaction, or the percentage formation of these materials.

An Aerograph Model 1520 gas chromatograph equipped with a thermal conductivity detector and fitted with a 10 ft \times 0.25 in. glass column packed with 10% DEGS on acid-washed Chromosorb W was employed for collection and purification of products.

Mass Spectral Analysis. An A.E.I. Model MS 9 mass spectrometer was used throughout the study. All the spectra of toluene and/or deuterated toluene were obtained at an electron beam energy of 11.0–12.2 eV to avoid the fragmentation of toluenes into tropilium cation radicals. Using this range of electron beam energy it was found that the peaks P – 1 and P – 2 were negligibly small and allowed quantitative analyses in scrambling studies of the toluenes.

Competitive Brominations. Competitive reactions were carried out by placing aliquot solutions of the two substrates (1.5 M, 1.5 M), the standard Freon 112 (1.3 M) and bromotrichloromethane (1.7 M), in Pyrex ampoules. The ampoules were degassed by the freeze-thaw method and sealed. The reaction tubes were placed in a merry-go-round apparatus, thermostated at $50.0 \pm 0.1^\circ$ in a Pyrex water bath, and irradiated using a Hanovia 140-W utility lamp. The ampoules were removed after varying lengths of time (36–48 hr), frozen in liquid nitrogen, and opened, and the contents were analyzed by glpc (20 ft \times $\frac{1}{8}$ in. 5% DEGS, 55–150 $^\circ$). The conversion of the unsubstituted or the substituted toluene was always more than 10% in each reaction analyzed.

The relative reactivities were calculated in the usual manner²⁷ from a determination of the relative amounts of the two substrates that had undergone reaction.

The competitive reactions carried out with added ethylene oxide when irradiated under comparable conditions to those used for the reactions without additives gave a negligible (<5%) reaction. Direct irradiation (lamp distance fixed, 5 in. from the thermostated sample) gave sufficient reaction in 120–190 hr.

The competitive reactions carried out with added finely ground anhydrous potassium carbonate (20 mol %) were carried out as were the reactions without additives except that the finely ground solid, which had been freshly ground in the air, was added to the reaction tubes and the sealed, degassed, ampoules were shaken during the entire irradiation. The solid potassium carbonate remained suspended throughout the solution during the reaction.

Material Balance in the Reaction of Bromotrichloromethane with Toluene in the Presence of Ethylene Oxide. A mixture of bromotrichloromethane (1.51 mmol), toluene (2.01 mmol), Freon 112 (9.0 mmol), and ethylene oxide (0.32 mmol) was placed in a degassed and sealed Pyrex ampoule and was irradiated at 40.0 $^\circ$ for 10 days. After the irradiation a known amount of Freon 112 was added as an internal standard (3.01 mmol) and the mixture was analyzed by glpc (DEGS, 55–180 $^\circ$). Chloroform (0.49 mmol), benzyl bromide (0.65 mmol), β -bromoethanol (0.22 mmol), and hexachloroethane (0.20 mmol) were found as products and bromotrichloromethane (0.52 mmol), toluene (1.43 mmol), and ethylene oxide (N.d.) were found as remaining starting materials. No other products were found in the glpc analysis. Material balance (duplicate reactions) for the benzyl group, trichloromethyl group, and bromine was 102 ± 1 , 91 ± 2 , and $89 \pm 1\%$, respectively.

Bromotrichloromethane Brominations of Toluene and Toluene- α - d_3 . Mixtures of toluene, toluene- α - d_3 , bromotrichloromethane, and Freon 112 placed in sealed, degassed ampoules were allowed to react under the same conditions as those used for the competitive brominations. The ampoules were frozen in liquid nitrogen and broken open under 30–50 ml of water in stoppered flasks. A small amount (0.6–0.7%) of hydrogen bromide was detected and quantitatively determined by the iodometric titration of the iodine liberated after addition of excess potassium iodide and potassium iodate.³⁵ The organic layer was separated and dried over anhydrous sodium sulfate, and aliquots of the solutions were analyzed by glpc (DEGS, 55–150 $^\circ$). Chloroform (46–48%), benzyl bromide (48–54%), and a small amount of hexachloroethane were observed as products. The material balance was >90%. Preparative glpc (DEGS, 100 $^\circ$) of the reaction mixture allowed the isolation of the unbrominated toluenes. The results from the mass spectral analyses of the recovered materials are listed in Table II.

Reactions carried out with added ethylene oxide gave after 48-hr irradiation 6.5 and 6.7% conversion and gave no detectable hydrogen bromide. Reactions carried out to 96% conversion, 16 days, showed no formation of hydrogen bromide. Mass spectral analysis of the recovered toluenes showed no appreciable exchange had taken place (see Table II).

Experiments carried out with added ground potassium carbonate (10 mol %) showed, after 8-days irradiation, a 58% conversion of the bromotrichloromethane. Mass spectral analysis of the recovered toluenes showed that only a small amount of H–D exchange had taken place (see Table II).

A degassed solution of a 1:1:0.2:1 mixture of toluene–toluene- α - d_3 –*tert*-butyl peroxyprivalate–Freon 112 was heated to $60.0 \pm 0.3^\circ$ for 48 hr. Glpc analysis showed that 2% of the initial toluene could be accounted for as bibenzyl. Mass spectral analysis of the recovered toluenes showed that no H–D scrambling had occurred.

Bromotrichloromethane Bromination of Toluene with Added Deuteriochloroform. A degassed solution of a 1:0.5:0.5:1 mixture of toluene–deuteriochloroform–bromotrichloromethane–Freon 112 in a Pyrex ampoule was irradiated at 50.0 $^\circ$ for 48 hr. The conversion of bromotrichloromethane was found to be 68% by glpc analysis. The mass spectral analysis on the recovered toluene showed no incorporation of deuterium had taken place.

Attempted Reactions of Deuterium Bromide and Toluene. A solution of a 1:1.3:1:0.2 molar mixture of toluene–chloroform–Freon 112–deuterium bromide in a degassed sealed ampoule was heated to $50.0 \pm 0.3^\circ$ for 30 hr. The reaction mixture was washed successively with water, 5% sodium carbonate solution, and water and then dried over anhydrous sodium sulfate. Preparative glpc (DEGS, 100 $^\circ$) of the reaction mixture permitted the isolation of the toluene. Mass spectral analysis of the toluene showed no incorporation of deuterium into either the aromatic ring or its side chain.

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(35) G. H. Cady, *Inorg. Syn.*, **5**, 156 (1957).