

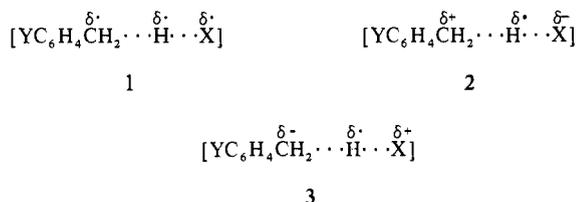
The Reality of Polar Transition States in Photobromination of Toluenes by *N*-Bromosuccinimide (NBS)^{1,2}

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Abstract: Relative reactivities of toluene and substituted toluenes toward NBS have been compared in CCl₄ (heterogeneous phase) and in CH₂Cl₂ (homogeneous phase). Hammett correlations show better fit with σ^+ to give ρ 's as follows, $\rho = -1.41$ (-1.41), -1.33, -1.26, and -1.17 (-1.17) at 80, 60, 40, and 10 °C, respectively, with the values in the parentheses corresponding to the homogeneous reactions. The ρ 's become less negative with decreasing temperature and approach an isokinetic point (-71 °C) but remain unchanged regardless of the solvents. From absolute rate theory, differential enthalpies and entropies of activation in CCl₄ were obtained. The values could reflect variable benzylic C-H cleavages experienced by the toluenes. The degree of bond breakages could be a function of σ^+ of the substituents, which may give the transition state considerable translational degrees of freedom. This entropic contribution to the rates may be important enough to control the reactivities of most of the toluenes, a tendency consistent with the changes of the ρ 's with the temperatures.

The effects of substituents on the rates of hydrogen-atom abstraction from toluenes has been a subject of interest to many during the last 30 years or so.³⁻¹⁰ Substituents on the phenyl ring control the reactivities via a kinetic effect possibly reflected in the transition-state (TS) structures 1-3. A linear free energy



relationship (LFER) (Hammett correlation) has been observed and interpreted as an evidence for a polar TS, which has been widely accepted also for other types of radical reactions¹¹⁻¹³ (polar effect).

Zavitsas,¹⁴ however, proposed that the substituent might also change dissociation energies of the benzylic C-H bonds with the reactivities being thus governed (BDE effect). Only negative ρ values¹⁵⁻²¹ had been reported at the time of his publication and did not contravene the premise.²²

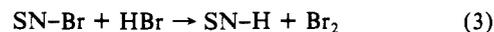
Subsequently, Pryor^{8,9} and Henderson²³ have obtained series of positive ρ 's with alkyl radicals,²⁴ which are not consistent with the prediction of the BDE effect. Besides, other kinetic²⁶ and EPR²⁷ data of para-substituted benzyl radicals do not substantiate the validity of the hypothesis.^{14,22}

Despite these negative aspects on the role of the neutral TS, Pryor⁸ has recently presented limited data showing that substituents could indeed change the strengths of benzylic C-H bonds. He has, further, suggested that electron affinity and heats of reaction could be the factors determining the direction of the substituent effects.

Bromination of toluenes by NBS has been studied at 80 °C only.¹⁶⁻¹⁸ The better Hammett correlation with σ^+ rather than σ has been taken as evidence of a charge-separated dipolar TS 2. We have measured relative rates of photobromination by NBS of substituted toluenes vs. toluene at four temperatures in CCl₄ and at two temperatures in CH₂Cl₂. Differential enthalpies and entropies of activation have been derived from absolute rate theory,²⁸ and Hammett ρ 's were also obtained at the four temperatures. An attempt has been made to elucidate the structure of the TS controlling the reactivities.

Results and Discussion

Determination of Relative Rates, Hammett ρ 's, and Differential Activation Parameters. The competitive photobromination of pairs of toluenes by NBS has been carried out at 10, 40, 60, and 80 °C in CCl₄¹⁸ and 10 and 80 °C in CH₂Cl₂,¹⁷ for which we can write the following reactions.²⁹



(SN-Br = NBS, Y = *p*-OCH₃,
p-CH₃, *m*-CH₃, *p*-F, *p*-Cl, *m*-F, and *m*-Cl)

- (1) This work has been presented at the 187th ACS National Meeting, St. Louis, April 8-13, 1984; Abstract Orgn No. 171.
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(22) Zavitsas postulated, on the basis of the indirect evidence then available, that electron-donating groups weakened the benzylic C-H bond while electron-withdrawing ones operated in the opposite direction. This has been, recently, confirmed for a limited number of substituents by Pryor.⁸ He estimated one unit of σ value is equivalent to a 3 kcal/mol change of the bond energy.

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(24) The validity of the reactions by the alkyl radicals has been seriously questioned by Tanner²⁵ which, in turn, has been defended by the original workers.^{8,9}

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Table I. Relative Reactivities of Substituted Toluenes toward NBS (per H) and the Hammett Rho (ρ) Values at 10, 40, 60, and 80 °C in CCl₄ and CH₂Cl₂

$$\text{YC}_6\text{H}_4\text{CH}_3 + \cdot\text{Br} \xrightarrow{k_Y} \text{YC}_6\text{H}_4\dot{\text{C}}\text{H}_2 + \text{HBr} \quad (1)$$

$$\text{C}_6\text{H}_5\text{CH}_3 + \cdot\text{Br} \xrightarrow{k_H} \text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2 + \text{HBr} \quad (2)$$

temp, °C	solvent	$(k_Y/k_H)^a$								$\sigma^+{}^c$ or σ	ρ^d	r^e
		<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>m</i> -CH ₃	<i>p</i> -F	H ^h	<i>p</i> -Cl ^b	<i>m</i> -F	<i>m</i> -Cl			
10	CCl ₄	9.00	1.82	0.93	0.88	1.00	0.55	0.46	0.33	σ^+	-1.17	0.983
										σ	-1.71	0.898
40	CCl ₄	9.78	2.15	0.98	0.91	1.00	0.62	0.40	0.28	σ^+	-1.26	0.993
										σ	-1.87	0.917
60	CCl ₄	10.6	2.31	1.07	0.95	1.00	0.65	0.36	0.26	σ^+	-1.33	0.996
										σ	-1.98	0.928
80	CCl ₄	11.7 ^g	2.57	1.12	0.99	1.00	0.72	0.33	0.22	σ^+	-1.41	0.996
										σ	-2.12	0.932
10	CH ₂ Cl ₂ ^f	9.04	1.81	0.93	0.87	1.00	0.56	0.46	0.33	σ^+	-1.17	0.982
										σ	-1.70	0.896
80	CH ₂ Cl ₂ ^f	11.7 ^g	2.55	1.21	0.97	1.00	0.72	0.33	0.22	σ^+	-1.41	0.996
										σ	-2.13	0.936

^aError limits are less than 3%, being the average deviations of more than five and two runs for CCl₄ and CH₂Cl₂, respectively. ^bOne of the referees indirectly informed us of a recent study of the temperature dependence of the competitive bromination of toluene and *p*-chlorotoluene by molecular bromine: Gilliom, R. D.; Brewer, R. M.; Miller, K. R. *J. Org. Chem.* **1983**, *48* 3600. Their reactivity pattern conflicts with ours. For discussion, refer to ref 39. ^cRitchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 334. ^dHammett ρ values obtained with σ or σ^+ . ^eCorrelation coefficients. ^fHomogeneous reactions were run with lower substrate concentrations. Refer to experimental part. ^gTaken from ref 18. ^hStandard.

Table II. Differential Activation Parameters of Photobromination of Substituted Toluenes by NBS in CCl₄

differential activation parameters	(YC ₆ H ₄ CH ₃ + ·Br) vs. (C ₆ H ₅ CH ₃ + ·Br)							
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>m</i> -CH ₃	<i>p</i> -F	H	<i>p</i> -Cl	<i>m</i> -F	<i>m</i> -Cl
$\Delta\Delta H^*_{Y-H}{}^a$	0.73 ± 0.04	0.96 ± 0.06	0.54 ± 0.02	0.33 ± 0.01	0	0.73 ± 0.04	-0.95 ± 0.06	-1.09 ± 0.08
$\Delta\Delta S^*_{Y-H}{}^{b,c}$	6.90 ± 0.35	4.57 ± 0.27	1.74 ± 0.07	0.90 ± 0.02	0	1.39 ± 0.07	-4.87 ± 0.29	-6.04 ± 0.42

^a $\Delta\Delta H^*_{Y-H} = \Delta H^*_Y - \Delta H^*_H$, in which ΔH^*_Y and ΔH^*_H are enthalpies of activation of the substituted and unsubstituted toluene, respectively. Unit: kcal/mol. ^b $\Delta\Delta S^*_{Y-H} = \Delta S^*_Y - \Delta S^*_H$, in which ΔS^*_Y and ΔS^*_H are entropies of activation of the substituted and unsubstituted toluene, respectively. Units: eu. ^cFrom a private communication with Professor Walling; he has pointed out the rather striking changes of the entropies. A similar drastic variation as well as an excellent isokinetic relation had been reported during thermolysis of *tert*-butyl perbenzoate by Blomquist and Berstein (*J. Am. Chem. Soc.* **1951**, *73*, 5546).

Two control experiments were designed for the homogeneous reaction in CH₂Cl₂, ruling out ring brominations and other side reactions by NBS during gas-liquid chromatographic (GLC) analyses. The concentrations of the substrates and relative rates would be related to the following manner, where Y and H indicate concentrations of substituted toluene and toluene, respectively, the subscripts f meaning final and i initial concentrations. The

$$k_Y/k_H = \frac{\log(Y_f/Y_i)}{\log(H_f/H_i)} \quad (4)$$

reaction conditions were so arranged that the consumption of the substrates would fall within the range of (30 ± 10)% to minimize side reactions. Analyses were made by GLC, using internal standards.

Relative rates were measured via eq 4 and were plotted against Hammett σ and σ^+ values at each temperature. The resulting ρ values are listed in Table I. Logarithms of the relative rates (k_Y/k_H) measured in CCl₄ were plotted against 1000/*T* to fit excellently the Eyring equation²⁸ as shown in Figure 1; differential activation parameters thereby derived are listed in Table II.

Hammett Correlation and the ρ 's. All the ρ 's in Table I are much better correlated with σ^+ than with σ , and the value at 80 °C ($\rho = -1.41$) is virtually identical with the previously reported values: i.e., Walling's $\rho = -1.38$ in CCl₄,¹⁸ Martin's $\rho = -1.46$ in C₆H₆.¹⁶ The ρ of the bromine atom ($\rho = -1.26$ at 40 °C) is

much more negative than those of the chlorine atom ($\rho = -0.66$ at 40 °C)¹⁵ and *tert*-butoxy radical ($\rho = -0.35$ at 45 °C).²¹ The TS for the bromine atom may, accordingly, assume more polar character involving much greater C···H bond breakage with far less H···Br bond formation,³ which could be the S_N1-like TS with "much the longer distance" between the ion pair. The extensive bond breaking is also consistent with the result of kinetic isotope effect³¹ and the Hammond postulate.³²

The ρ 's become less negative at lower temperature, indicating that the reactions are above the isokinetic temperature and accordingly controlled by the entropies.³³ The unsymmetrical bond breaking/formation and "the longer separation" of the pair could render the TS "quasi three isolated bodies", which should, then, attain considerable translational degrees of freedom with a large entropy increase.³⁴

The ρ value in benzene¹⁶ is little different from that in CCl₄, indicating that aromatic complexation of the bromine atom³⁵ is of little significance. The chlorine atom³⁶ and *tert*-butoxy radical³⁷ have been known to form complexes with reasonable reactivities. Although the polarity and such solubility of NBS in CCl₄ and CH₂Cl₂ are quite different, identical ρ values were measured in

(29) NBS bromination of toluenes and alkanes has been suggested to involve different hydrogen atom abstracting species, i.e., the former with the bromine atom and the latter with the succinimidyl radical.³⁰

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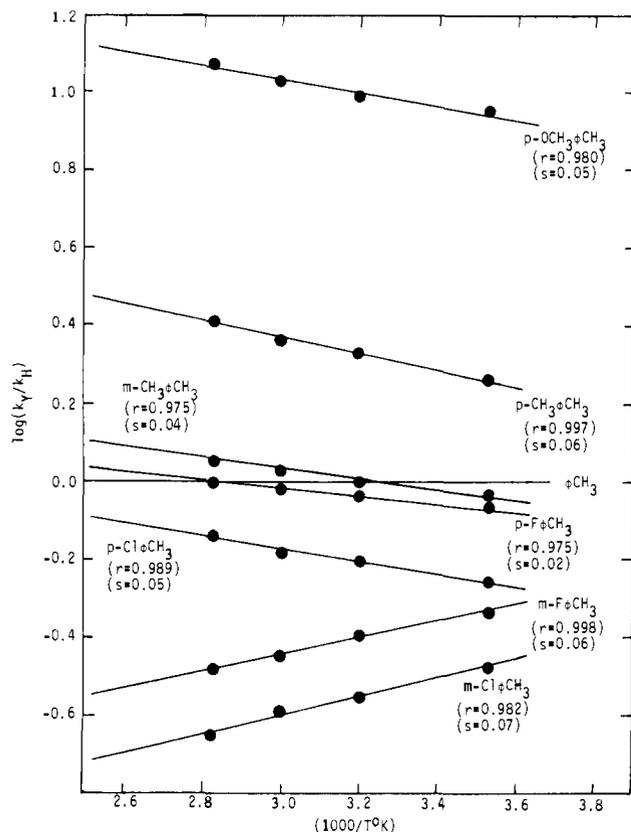


Figure 1. $\log(k_V/k_H)$ vs. $1000/T$ (r = correlation coefficient, s = standard deviation).

the two solvents. In CH_2Cl_2 , dissolved NBS would be an efficient HBr scavenger inhibiting reversal of the hydrogen-transfer reactions. Since identical results were obtained in CCl_4 (heterogeneous), it appears that reversal in this system is also not important. The invariance of ρ 's with solvent polarity could be interpreted as a sign of negligible polar interaction between the TS and the solvent. Sakurai and Hosomi²¹ also observed little solvent dependence of ρ values for the reactions of toluenes with the *tert*-butoxy radical. It is conceivable that the charge transfer is controlled not by the ionizing power of the solvent but by the electron affinities^{3,8} and heats of reaction.⁸

The minor solvent role, whether complexing or polar, on the reactivity thus suggests that the entropy of activation would be mostly controlled by structural changes in the TS involved.

Differential Activation Parameters and Isokinetic Relationship. The better fit with σ^+ has been taken as an evidence of TS 2, which partially assumes the character of benzylic cation stabilized by conjugation with the phenyl ring. The degree of benzylic C...H cleavage leading to the formation of the fractional carbonium ion may, therefore, be a function of the σ^+ of the corresponding substituent. This relative reactivity against toluene is reflected in the values of the differential activation parameters of Table II.

Since very little H...Br formation may occur,³ the enthalpy of activation may be mainly governed by the degree of C...H breaking which the toluenes undergo (factor *a*) and partly modified by the stability of the developing carbonium ion (factor *b*). Excluding *p*-chloro- and *p*-methoxytoluenes, the other toluenes could be more influenced by factor *a* to exhibit appropriate positive or negative differential enthalpies of activation depending on the values of σ^+ with a negative value of σ^+ leading to a positive differential enthalpy of activation. Since *p*-Cl has $\sigma^+ > 0$, this toluene ($\Delta\Delta H^* = 0.73$ kcal/mol) may experience less but comparable bond cleavage to that of toluene with factor *b* coming into operation to cause the positive differential. Although *p*-methoxytoluene ($\Delta\Delta H^* = 0.73$ kcal/mol) would suffer more cleavage than *p*-xylene ($\Delta\Delta H^* = 0.96$ kcal/mol), the resulting cation could be far better stabilized by the methoxy group (factor *b*) so as to

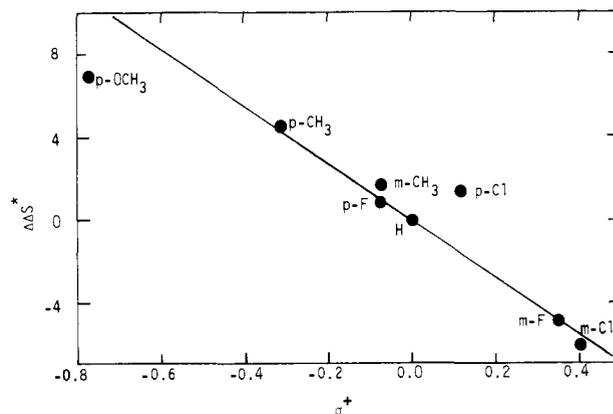


Figure 2. Plot of $\Delta\Delta S^*$ vs. σ^+ .

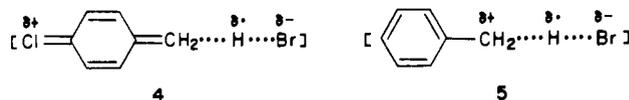
require smaller enthalpy of activation.

Entropy of activation would be closely related to the differences in number and character of the degrees of freedom between transition state and reactant.³⁴ On going from reactant to activated complex in the bromination, we may envision following three changes controlling the entropy of the system.

First, the vibration of the benzylic C-H bond is replaced by a translational mode²⁸ which should be partitioned to the aforementioned "quasi three bodies." This bond breaking could apparently give rise to a large entropy increase³⁴ (factor *c*). The increase may be, however, reduced by the attraction between the ion pair (factor *d*) which is minimized by the relatively long distance between Br and carbon. Another negative entropy effect could be expected from the conjugation of the benzylic cation which should, inevitably, freeze the rotation of the phenyl ring with respect to the methylene group (factor *e*).

Since the order of contribution to entropy is translation \gg rotation \gg vibration,³⁴ factor *c* may prevail over the latter two factors to become the controlling factor in determining the entropies of activation of most of the reactions. The differential entropies may, thus, be the result of C...H breaking for the substituted toluenes being less than for toluene itself. The relation has been well illustrated by plotting the $\Delta\Delta S^*$ against σ^+ in Figure 2.

The positive deviation of the *p*-chlorotoluene could be explained by the additional contribution of canonical structure 4, which decreases the ion-pair attraction (factor *d*) occurring in 5. The weakening of this attraction may also counteract the entropy reduction due to factor *e*. *p*-Chlorotoluene could, accordingly,



enjoy more degrees of freedom and a less tight TS than toluene itself. *p*-Methoxytoluene has undergone most extensive bond cleavage forming the greatest amount of charge-transfer structure in which factor *d* could become important with a large entropy reduction to give the negative deviation.

The differential activation parameters have been utilized in justifying the polar TS 2, previously supported by a Hammett correlation. The σ^+ value of the toluene should thus be related to the degree of C...H breaking, which, in turn, may influence both $\Delta\Delta H^*$ and $\Delta\Delta S^*$,³⁸ i.e., more cleavage makes both terms larger. Furthermore, the parallelism is linearly related so as to give the excellent isokinetic relation of Figure 3, which measures the isokinetic point to be $\beta = -71$ °C.³³ *p*-Chloro- and *p*-

(38) The values of $\Delta\Delta H^*$ are quite small (less than 1 kcal/mol), which could be the result of two opposing effects of the factors *a* and *b* with comparable magnitudes. Since the increase of the entropy by factor *c* is much larger than the reduction by factors *d* and *e*, the values of $\Delta\Delta S^*$ become rather large.

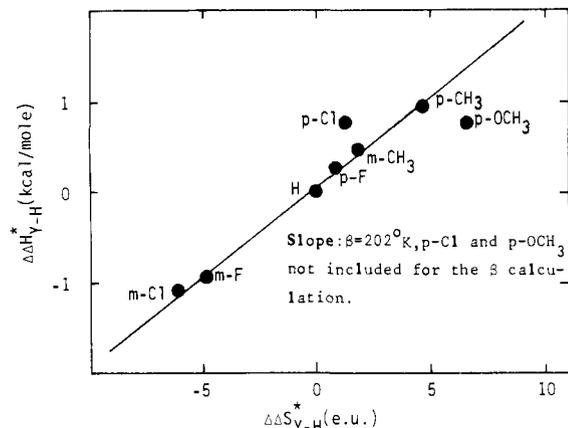


Figure 3. Isokinetic relationship by the enthalpy-entropy compensation effect.

methoxytoluenes have shown significant deviation from the relation, suggesting again somewhat different activation processes are involved. The points on the isokinetic line are arrayed in the order of the values of the σ^+ and reiterate, on the whole, the entropy-driven reactivities.

Conclusion

The evaluation of Hammett ρ 's and of activation parameters consistently supports the role of a polar TS **2**. This could be a very "loose" S_N1 -like TS, thereby preserving a good portion of the translational degrees of freedom derived from the benzylic C-H cleavage. The translation may contribute to the entropy to such an extent that the reaction is entropy controlled. The minor role of ionizing power of the medium might be responsible for the small polar solvent effect, which will be further explored in the near future.

Experimental Section

Materials. All the reagents are commercial materials which were checked by GLC for purity and fractionally distilled, if necessary, only

(39) In connection with the different reactivity patterns of the *p*-chlorotoluene, we wish to include following arguments. (a) N_2 bubbling could not efficiently prevent the reverse of the hydrogen transfer reaction occurring in the solvent cage,⁴⁰ which should become important with lower temperature, i.e., with increasing solvent viscosity. The lower temperature could also increase the solubility of HBr. Pearson and Martin¹⁶ reported different ρ values at 19 °C with different bromine concentration and suggested that the slow addition of Br_2 with N_2 bubbling could not eliminate the reversal. (b) Our control experiment (at 25 °C with water-cooled condenser) confirmed that the bubbling could also entrain the toluenes to give the erratic concentrations of the substrates. To avoid this, Wiberg and Slauch³¹ used a dry ice-acetone-cooled condenser instead of the water-cooled one. (c) When fitting their data into the Arrhenius equation, the relative reactivity of *p*-chlorotoluene at 80 °C has been calculated to be $k_Y/k_H = 0.57$, which is different from our $k_Y/k_H = 0.72$ as well as Martin's $k_Y/k_H = 0.72$ ¹⁶ and Walling's $k_Y/k_H = 0.8$.¹⁸ The value of 0.72 corresponds to the relative reactivity at 44 °C in their reactivity scale.

(40) Tanner, D. D.; Ochiai, T.; Paće, T. *J. Am. Chem. Soc.* **1975**, *97*, 6162.

the center cut being collected. NBS was rapidly recrystallized from boiling distilled water and dried in a dark vacuum oven for 3 days at ambient temperature (purity 99.8% by iodometric titration).¹⁸

Competitive Photobromination.¹⁸ All the experiments were carried out in either hetero- or homogeneous systems consisting of toluene, substituted toluene, NBS, internal standards (chlorobenzene or benzene) and either CCl_4 or CH_2Cl_2 as solvent, which were placed together in sealed degassed Pyrex ampules prepared by the freeze-pump-thaw method.

Typical reaction mixtures were as follows. In CCl_4 , 1–4 mmol of each toluene and 1 mmol of internal standard were dissolved in CCl_4 to give 3 mL of solution. This and 3 mmol of NBS were placed in the ampules for the brominations at 10, 40, 60, and 80 °C. In CH_2Cl_2 , 0.2–0.8 mmol of each toluene, 0.2–0.6 mmol of internal standard, and 1 mmol of NBS were dissolved in CH_2Cl_2 to make 3 mL of homogeneous solutions, which were placed in the tubes for the reactions of 10 and 80 °C. The light source was a 250-W incandescent lamp, and the intensities could be adjusted by changing voltage at each temperature. Relative concentrations of the two toluenes, light intensities, and reaction time were so arranged that the consumption of the substrates fell within the range of $(30 \pm 10)\%$.

After reaction, the tubes were quenched by cooling in the dark, opened, and, for heterogeneous reactions, additionally worked up by filtering the liquid from the residual insolubles. The solutions, then, were stored in small vials wrapped with foil for GLC analyses.

Control Experiments. The homogeneous solutions in sealed, degassed, Pyrex ampules were held at 10 °C in the dark for a prolonged time and analyzed by GLC. The results showed no disappearance of the substrates (*p*-xylene and toluene), thus excluding ionic ring bromination.

Before being irradiated the CH_2Cl_2 solutions were analyzed by GLC to indicate again no change in the concentrations of the two toluenes. NBS remaining in the CH_2Cl_2 did not cause any appreciable side reactions during the GLC analyses (injection port, 150 °C).

Analytical Procedure. The photolyzed solutions were analyzed on a 7 ft. \times $1/8$ in. stainless steel column packed with bentone 34 + dinonyl phthalate, (5 + 5)% on uniport KA with Hitachi 063 gas chromatography with TCD and temperature programming from 50 to 140 °C. A fraction of the homogeneous reactions in CH_2Cl_2 was analyzed on a 13 ft. \times $1/8$ in. stainless steel column packed with 10% diisodecyl phthalate on Chromosorb W with Varian Vista 4600 with TCD and CDS 401 data system.

Analytical Method.¹⁸ Relative rates were calculated via eq 4 which requires knowledge of the initial and final quantities of the toluenes.

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Registry No. *p*- $CH_3OC_6H_4CH_3$, 104-93-8; *p*- $CH_3C_6H_4CH_3$, 106-42-3; *m*- $CH_3C_6H_4CH_3$, 108-38-3; *p*- $FC_6H_4CH_3$, 352-32-9; $C_6H_5CH_3$, 108-88-3; *p*- $ClC_6H_4CH_3$, 106-43-4; *m*- $FC_6H_4CH_3$, 352-70-5; *m*- $ClC_6H_4CH_3$, 108-41-8; NBS, 128-08-5.