

NEGLIGIBLE KINETIC SOLVENT INTERACTIONS FOR THE RATE OF PHOTOBROMINATION OF TOLUENES WHERE THE BROMINE ATOM IS A PRINCIPAL CHAIN CARRIER*

SUNG SOO KIM, † CHANG SOO LEE, CHONG CHAN KIM AND HEE JIN KIM

Department of Chemistry, Inha University, Incheon 402-751, South Korea

The bromine atom is a major chain carrier in the photobromination of toluenes by *N*-bromosuccinimide. Only an uncomplexed bromine atom can abstract hydrogen atoms from toluenes. The nature of the polar transition state is entirely different from that of solvolytic reactions and the solvent polarity therefore cannot influence the rates of the bromination.

INTRODUCTION

The bromine atom has generally been regarded as a major chain carrier for the bromination of toluenes by *N*-bromosuccinimide (NBS).²⁻⁶ Recently, we⁶ and others⁷ have recognized the entropy control of reactivities for these brominations, where ρ^+ can be variable, becoming less negative at lower temperatures, thus approaching an isokinetic point,⁸ a phenomenon indicating the importance of entropy with regard to the rates. We should also point out that conjugation⁹ of aromatic π -electrons on the phenyl ring with the incipient p-orbital of the atom transferring hydrogen can be another¹⁰ factor affecting the polarization of the transition state (TS). The dispersion of positive charge into the phenyl ring cannot occur with hydrogen abstraction from aliphatic hydrocarbons,¹¹ which can reduce the role of activation energy with a corresponding increase in the entropic contribution to the reaction rates. Interestingly, we have observed that the bromination of toluenes⁶ shows a negative $\alpha = -1.30$ for $\Delta\Delta H^\ddagger = \alpha(\Delta\Delta H) + \beta$,¹² which we may term an 'anti-Evans-Polanyi relationship'.¹³ Another peculiarity, as mentioned by Walling, is the decrease in selectivity with reduction in temperature, which has been thoroughly addressed also by Giese.¹⁴ We can fortunately observe the same trends for ρ^+ and the selectivities in hydrogen abstraction from phenols by *tert*-butoxy radicals,¹⁵

where ρ^+ can be calculated from Table 3 in Ref. 15 to be -0.82 (22 °C), -0.68 (0 °C), -0.62 (-30 °C) and -0.48 (-60 °C). The meaning of selectivity changes with variation in temperature may be different between enthalpy-¹¹ and entropy-dominating reactions.^{6,7,14,15} We report here our findings on the role of the solvent during bromination.

RESULTS AND DISCUSSION

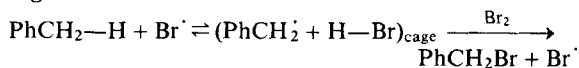
Photobromination by $\text{Br}_2\text{-K}_2\text{CO}_3$ or NBS in various solvents

With $\text{Br}_2\text{-K}_2\text{CO}_3$ as the brominating agent under irradiation, the bromine atom must abstract benzylic hydrogen and then K_2CO_3 neutralizes HBr to prevent the reverse of the abstraction. Comparison of brominations by NBS and $\text{Br}_2\text{-K}_2\text{CO}_3$ with respect to temperature and solvent may clarify previous findings regarding the bromine atom being the chain carrier derived from NBS.²⁻⁶ Pairs of toluenes, that is, substituted toluene-toluene, were photobrominated by $\text{Br}_2\text{-K}_2\text{CO}_3$ or NBS in numerous media to observe the effect of the solvent on the reaction rates, which were determined as described previously⁶ and are given in the Table 1. Although the rates (k_Y/k_H) at 40, 60, and 80 °C with $\text{Br}_2\text{-K}_2\text{CO}_3$ (entries 2-4, 6 and 8 in Table 1) are sometimes slightly lower than those with NBS, both the rates and ρ^+ seem to be generally unaffected by changes in the solvents and brominating agents. The almost identical kinetic data for brominations with $\text{Br}_2\text{-K}_2\text{CO}_3$ and NBS strongly suggest the bromine atom as the main chain carrier in these reactions.²⁻⁶

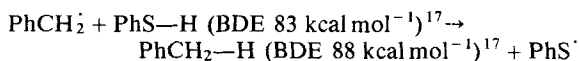
* Dedicated to Professor Ikchoon Lee on the occasion of his 60th birthday. Preliminary results of this work have been presented earlier.¹

† Author for correspondence.

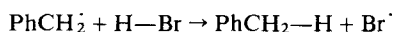
Validity of reversible hydrogen abstraction in the cage¹⁶



A benzyl radical may abstract hydrogen from H—Br (bond dissociation energy, BDE 87 kcal mol⁻¹)¹⁷ in the cage or diffuse out of it to react with Br—Br (BDE 46 kcal mol⁻¹),¹⁷ the latter reaction involving almost zero activation energy, E_a .¹⁸ The activation energy for



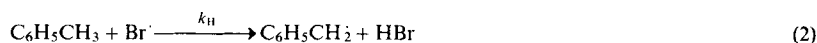
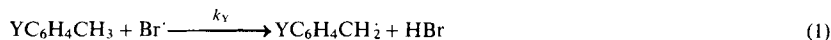
has been reported to be $E_a = 3.8$ kcal mol⁻¹.¹⁹ Since the H—Br bond is 4 kcal mol⁻¹ stronger than the PhS—H bond and the benzylic radical is fairly resonance stabilized, the activation energy should be $E_a \gg 3.8$ kcal mol⁻¹ (Ref. 18) for



Such an energy barrier can render the out-of-cage bromine abstraction dominant over the geminal hydro-

gen transfer. Cage reactions are well established for radical recombinations with $E_a = 0$,²⁰ but not for the reactions requiring substantial activation energies. Another complication with *in situ* bromination of toluenes with Br₂, viz. reactions in sealed degassed ampoules,¹⁶ can be due to equilibration, $\text{Br}^\cdot + \text{Br}_2 \rightleftharpoons \text{Br}_3^\cdot$, with the formation of another hydrogen abstractor.²¹ To avoid such duality in our brominations, we added dilute (0.05–0.1 M) Br₂–CCl₄ solutions slowly to toluenes using a syringe pump. The previous brominations^{2,4} were devised effectively to minimize out-of-cage reversal and the reverse reaction could thus have occurred only in the cage, which can be controlled by the viscosity¹⁷ of the solvents, i.e. 0.329 cP for C₆H₆² and 0.468 cP for CCl₄⁴ at 80 °C. The virtual invariance of ρ^+ for the brominations^{2,4} with change in solvents with different viscosities may indicate that the cage reversal may not occur at all or be too modest to affect the kinetics offering such excellent Hammett correlations. This trend becomes conspicuous in the present brominations, where ρ^+ is a function of temperature only (see Table 1).

Table 1. Relative reactivities of substituted toluenes toward bromine atom and Hammett correlations



No.	Solvent	Brominating agent	Temperature (°C)	k_Y/k_H^a							ρ^{+c}	
				<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>m</i> -CH ₃	<i>p</i> -F	H ^b	<i>p</i> -Cl	<i>m</i> -F		<i>m</i> -Cl
1	CCl ₄ ^d	NBS	10	9.00 ⁱ	1.82	0.93	0.88	1	0.55	0.46	0.33	-1.17
2	CH ₃ CN	Br ₂ –K ₂ CO ₃	40	8.68	2.01	0.98 ^d	0.82	1	0.62	0.35 ^e	0.27 ^e	-1.24
3	CS ₂	Br ₂ –K ₂ CO ₃	40	8.68	2.01	0.98 ^d	0.82	1	0.63	0.35 ^e	0.27 ^e	-1.24
4	CCl ₄	Br ₂ –K ₂ CO ₃	40	8.75	2.00	0.98 ^d	0.82	1	0.63	0.35	0.27	-1.24
5	CCl ₄	NBS	40	9.78	2.15	0.98	0.91	1	0.62	0.40	0.28	-1.26
6	CCl ₄	Br ₂ –K ₂ CO ₃	60	9.32	2.26	1.07 ^d	0.95	1	0.66	0.31	0.24	-1.32
7	CCl ₄ ^d	NBS	60	10.60	2.31	1.07	0.95	1	0.65	0.36	0.26	-1.33
8	CCl ₄	Br ₂ –K ₂ CO ₃	80	9.92	2.33	1.12 ^d	0.84	1	0.70	0.23	0.22 ^d	-1.41
9	CH ₃ CN ^f	NBS	80	11.78	2.55	1.18	0.96	1	0.77	0.29	0.22	-1.43
10	CH ₂ Cl ₂ ^{d,f}	NBS	80	11.78	2.55	1.21	0.97	1	0.72	0.33	0.22	-1.41
11	CCl ₄ ^d	NBS	80	11.78	2.57	1.12	0.99	1	0.72	0.33	0.22	-1.41
12	CCl ₄ ^g	NBS	80	11.70	2.56	1.52	0.58	1	0.80	—	—	-1.38
13	C ₆ H ₆ ^h	NBS	80	12.40	2.62	—	—	1	0.72	—	—	-1.46
14	CS ₂	NBS	80	11.50	2.58	—	0.98	1	0.71	0.32	0.23	-1.40

^a Error limits are less than 3%, being average deviations of more than three runs.

^b Standard.

^c The Hammett correlations are always better with σ^+ taken from ref. 22.

^d Taken from Ref. 6.

^e Values taken from the brominations in CCl₄, i.e. entry 4.

^f Reactions without light showed no disappearance of *p*-methylanisole and *p*-xylene, thus excluding ionic ring brominations.

^g Taken from Ref. 4.

^h Taken from Ref. 2.

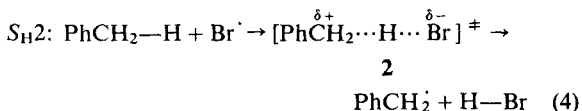
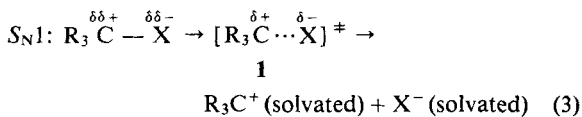
ⁱ The brominations with Br₂–K₂CO₃ show lower selectivities than those with NBS, which are even conspicuous with *p*-OCH₃ and *p*-CH₃. The trend of the selectivities with temperature change can be valid only with the same brominating agent. The selectivity with Br₂–K₂CO₃ at 10 °C should then show a lower value than 8.68.

Complexation of bromine atom with a corresponding decrease in reactivity

Although the bromine atom is less electrophilic than chlorine, both can form charge-transfer complexes^{23,24} with benzene to reduce their reactivities. Such a solvent effect by electron-rich molecules, including CS₂ was originally reported by Russell²⁵ for the chlorination of 2,3-dimethylbutane and confirmed later Walling²⁷ and Mayahi and Walling.²⁶ Recently, Bunce *et al.*²⁸ proposed the equilibration $\text{Cl}^+ + \text{solvent} \rightleftharpoons (\text{Cl} \cdots \text{solvent})^+$, where both species more or less competitively abstract hydrogens from the butane. Similar studies on the halogenation of toluenes appear to be inconclusive with regard to the role of the solvent.²⁹ In the present brominations, a bromine atom, like chlorine, may undergo solvation²⁴ and equilibration, $\text{Br}^+ + \text{solvent} \rightleftharpoons (\text{Br} \cdots \text{solvent})^+$, where the complexed atom, however, can no longer abstract hydrogen from toluenes, thus leaving the 'free' bromine atom as the sole abstractor. The solvation of the halogen atoms may lead to reactivities^{28,30} in the order $\text{Cl}^+ >$ complexed chlorine atom $\gg \text{Br}^+ \gg \gg$ complexed bromine atom. We may thus understand the invariable relative rate constants with change in solvent from CCl₄ to C₆H₆ and CS₂ (see Table 1).

Comparatively small polar solvent effect on reaction rates

The effect of polar solvents on reaction rates is well understood in terms of nucleophilic substitutions.³¹ S_N1³¹ and S_H2³² reactions may proceed via polar TS, each of which can assume mechanistically distinct features as follows:



Solvents can provoke 'stepwise' interactions for formation of the carbocation. The ionizing power may first begin to ionize a 'polar covalent' C—X bond via electron-pair-donor/electron-pair-acceptor (EPD/EPA) interactions³³ to give 1, which can then be subject to dipolar alignment with dipoles of solvent molecules, the former dominantly controlling the rates.³³ Hydrogen abstraction from toluenes by a bromine atom, on the other hand, may proceed through activation of a 'covalent' C—H bond with intervention of 2, whose polarity cannot be attained at all by the action of solvents as in solvolysis, but rather by complex interactions of various factors related with the abstractions.⁹ The only

plausible polar interactions of 2 with its surroundings might be dipole-dipole interactions which were only a minor source of stabilization for 1. The 'dipolar lifetime' of 2 can be even shorter than that of 1 judging from the polarities of the products derived therefrom [see equations (3) and (4)]. The lifetime of 2 could be too short for solvent molecules to orient with it for stabilization. It is therefore not surprising that hardly any variations in the rates and ρ^+ are observed on changing polarity from CCl₄ to CH₂Cl₂ and CH₃CN (see Table 1). The ambiguous effect of the solvents on the rates can be distinguished from the substituent effect leading to the Hammett relationship, and the difference may lie between the inter- and intra-molecular interactions, the former being definitely much less effective.

CONCLUSION

Entropy control of reactivities can exhibit peculiar behaviour, e.g. negative α for the Evans-Polanyi relationship¹² and lower selectivity with decrease in temperatures. The cage reversal¹⁶ can be too modest to influence the present brominations. The rates of the brominations should be immune to solvent properties such as basicity (or nucleophilicity) and polarity, while the bromine atom remains as a major chain carrier.

EXPERIMENTAL

Materials. These were essentially the same as those in previous work⁶ unless indicated otherwise. 1,2-Epoxybutane (purity > 99%) was of Gold Label grade from Aldrich.

Photobromination by NBS. The experimental details were the same as in previous work.⁶

Photobromination by Br₂-K₂CO₃. A 50-ml, three-necked flask with a water-jacket was equipped with a dry-ice-acetone-cooled condenser, a 125-ml Hershberg dropping funnel wrapped with aluminium foil and a nitrogen inlet tube that extended to just over the solution. Nitrogen was not bubbled into the solution so as not to entrain toluenes, thus giving false substrate concentrations. Reaction temperatures were monitored by passing water through the jacket from a constant-temperature bath. In the flask were placed toluene (2–6 mmol), substituted toluene (2–3 mmol), internal standard (chlorobenzene, 2 mmol) and K₂CO₃ (5-fold excess of Br₂ added), which were diluted with the appropriate solvent (CCl₄, etc.) to make a total volume of 10 ml. Dry-ice and acetone were placed in the condenser and Br₂ (1.2 mmol)–CCl₄ (12 ml) in the dropping funnel. While passing water at the desired temperature through the jacket and irradiating with a sun-lamp, 0.1–0.05 M bromine solution was added using a syringe pump over a period of ca. 1–2 h under

a nitrogen atmosphere. The irradiation was normally completed when the starch-potassium iodide test showed no coloration. Chlorotoluene-toluene pairs have been brominated by others⁷ using 1,2-epoxybutane as an HBr scavenger. We tried this method but could not obtain consistent results, especially with the reactions of the *p*-xylene-toluene pair, i.e. *p*-xylene showed much less reactivity than expected, for some unknown reason.

Analytical procedure. The photolysed solutions were analysed on 13 ft. × 1/8 in. stainless-steel column packed with 10% diisodecyl phthalate on Chromosorb W with Varian Vista 4600 with a thermal conductivity detector and a CDS 401 data system.

Relative rates were calculated using the equation⁶

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

where *Y* and *H* indicate molar concentrations of substituted toluene and toluene, respectively, and the subscripts *f* and *i* represent final and initial concentration, respectively.

ACKNOWLEDGEMENTS

We thank the Korea Science and Engineering Foundation for financial assistance and are indebted to Professor Cheves Walling for enlightening comments during the course of this work. We are also very grateful to the Inha University and Dr Chwang Siek Pak at the Korea Research Institute of Chemical Technology for generous support.

REFERENCES

1. S. S. Kim, C. S. Lee, C. C. Kim and H. J. Kim, paper presented at the 190th National Meeting of American Chemical Society, Chicago, September 8-13, 1985; Abstract Orgn. No. 229.
2. R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.* **85**, 354 and 3142 (1963).
3. G. A. Russell, C. DeBoer and K. M. Desmond, *J. Am. Chem. Soc.* **85**, 365 (1963).
4. C. Walling, A. L. Rieger and D. D. Tanner, *J. Am. Chem. Soc.* **85**, 3129 (1963).
5. J. G. Traynham and Y. S. Lee, *J. Am. Chem. Soc.* **95**, 3590 (1974).
6. S. S. Kim, S. Y. Choi and C. H. Kang, *J. Am. Chem. Soc.* **107**, 4234 (1985).
7. R. D. Gilliom and J. G. Wright, *J. Am. Chem. Soc.* **108**, 2340 (1986).
8. J. E. Leffler, *J. Org. Chem.* **20**, 1202 (1955).
9. S. S. Kim, J. S. Seo and M. H. Yoon, *J. Org. Chem.* **52**, 3691 (1987).
10. G. A. Russell, *J. Org. Chem.* **23**, 1407 (1958).
11. J. M. Tedder, *Tetrahedron* **38**, 313 (1982).
12. M. G. Evans and M. Polanyi, *Trans. Faraday Soc.* **34**, 11 (1938).
13. submitted for publication.
14. B. Giese, *Acc. Chem. Res.* **17**, 438 (1984).
15. P. K. Das, M. V. Encinas, S. Steenken and J. C. Scaiano, *J. Am. Chem. Soc.* **103**, 4162 (1981).
16. D. D. Tanner and N. H. Nam., *J. Org. Chem.* **52**, 4685 (1987).
17. R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, 1st student ed. CRC Press, Boca Raton, FL (1987).
18. H. R. Anderson, Jr, H. A. Scheraga and E. R. VanArtsdalen, *J. Chem. Phys.* **21**, 1258 (1953).
19. J. A. Franz, N. K. Suleman and M. S. Alnajjar, *J. Org. Chem.* **51**, 19 (1986).
20. T. Koenig and H. Fischer, in *Free Radicals*, edited by J. K. Kochi, Vol. 1, Chapt. 4. Wiley, New York (1973).
21. W. A. Thaler, in *Methods in Free-Radical Chemistry*, edited by E. Huysen, Vol. 2, p. 156.
22. C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.* **2**, 334 (1964).
23. R. E. Bühler, *Helv. Chim. Acta* **51**, 1588 (1968).
24. N. Yamamoto, T. Kajikawa, H. Sato and H. Tsubomura, *J. Am. Chem. Soc.* **91**, 265 (1969).
25. G. A. Russell, *J. Am. Chem. Soc.* **79**, 2997 (1957); **80**, 4987 and 4997 (1958).
26. C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.* **81**, 1485 (1959).
27. C. Walling, *J. Org. Chem.* **53**, 305 (1988).
28. N. J. Bunce, K. U. Ingold, J. P. Landers, J. Luszyk and J. C. Scaiano, *J. Am. Chem. Soc.* **107**, 5464 (1985).
29. J. Hradil and V. Chvalovsky, *Collect. Czech. Chem. Commun.* **33**, 2029 (1968).
30. J. A. Kerr and S. J. Moss, *CRC Handbook of Bimolecular and Termolecular Gas Reactions*, Vol. 1. CRC Press, Boca Raton, FL (1981).
31. A. Streitwieser, Jr, *Solvolytic Displacement Reactions*, McGraw-Hill, New York (1962).
32. K. U. Ingold, in *Free Radicals*, edited by J. K. Kochi, Vol. 1, Chapt. 2. Wiley, New York (1973).
33. C. Reichardt, *Solvent Effects in Organic Chemistry*, Verlag Chemie, Weinheim, New York (1979).