

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS, URBANA, ILL.]

The Identity of the Chain-Carrying Species in Brominations with N-Bromosuccinimide: Selectivity of Substituted N-Bromosuccinimides toward Substituted Toluenes

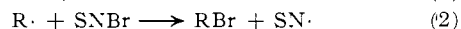
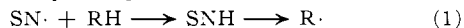
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Molecular bromine, N-bromosuccinimide, N-bromotetrafluorosuccinimide, and N-bromotetramethylsuccinimide show identical selectivities in competitive brominations of mixtures of substituted toluenes. Interpretation of this fact in terms of a chain mechanism involving atomic bromine as the hydrogen abstracting species is reconciled with data in the literature which have previously been rationalized in terms of mechanisms involving succinimidyl radicals in this role.

Since the discovery and development of allylic bromination, and the apparently analogous benzylic bromination, by N-bromosuccinimide² (NBS), considerable controversy has centered about the mechanisms of these reactions. Most discussions have implicitly assumed that both reactions follow the same pathway, although proof of this has not yet been established. Succinimidyl radicals commonly have been assigned to the role of the chain-carrying species in a free radical chain reaction.³ Bromine atoms have also been proposed as serving this function,⁴ and recently evidence has been reported⁵ providing strong support for this possibility. This paper offers a more complete description of evidence indicating the action of bromine atoms as chain carriers and some explanations for the results which hitherto have been accepted as supporting the alternative pathway.

Evidence abounds that replacements of allylic or benzylic hydrogen by bromine from NBS proceed by free radical chain mechanisms.⁶ For some time the involvement of succinimidyl radicals in the chain propagating steps 1 and 2, as proposed by Bloomfield⁷ in 1944, was widely accepted.



SNBr = NBS and RH = hydrocarbon substrate

This scheme provides an appealingly direct route to the observed products of allylic or benzylic bromination, the corresponding bromides plus succinimide. Two kinetic studies⁸ of NBS brominations have been taken as confirmation for the designation of succinimidyl radicals as the hydrogen abstracting species.

(a) The kinetics of the reaction of NBS with cyclohexene have been investigated by Dauben and Youngman.^{8b,c} For the bromination initiated by the decomposition of 2,2'-azobisisobutyronitrile (AIBN), the rate of disappearance of NBS depends upon the concentrations of reactants according to eq. 3.

$$-d(\text{SNBr})/dt = k(\text{RH})^{1/2}(\text{AIBN})^{1/2} \quad (3)$$

(1) (a) R. E. P., from whose Ph.D. Thesis (University of Illinois, 1963) this paper is abstracted, held fellowships from American Cyanamid Co. in 1959 and Standard Oil Co. (Indiana) in 1960; (b) Alfred P. Sloan Foundation Fellow, 1962-1963.

(2) (a) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948); (b) L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).

(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 381 ff.

(4) (a) F. L. J. Sixma and R. H. Riem, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **61B**, 183 (1958); (b) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961); (c) a similar mechanism for chlorination with N-chlorosuccinimide was supported by work of J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature*, **171**, 704 (1953).

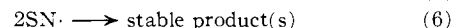
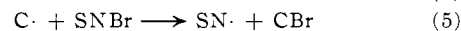
(5) (a) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963); (b) G. A. Russell, C. De Boer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

(6) (a) H. J. Dauben, Jr., and L. L. McCoy, *ibid.*, **81**, 4863 (1959); (b) H. J. Dauben, Jr., and L. L. McCoy, *J. Org. Chem.*, **24**, 1577 (1959); (c) H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).

(7) G. F. Bloomfield, *J. Chem. Soc.*, 14 (1944).

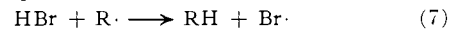
(8) (a) E. C. Kooyman, R. van Helden, and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **56B**, 75 (1953); (b) E. A. Youngman, Ph.D. Thesis, University of Washington, Seattle, Wash., 1952; (c) ref. 6a, footnote 42.

This rate expression corresponds to that derived from Bloomfield's chain-propagating steps plus initiation steps 4 and 5 and termination step 6 below (C· = initiator fragment). While the kinetic work is consistent with this formulation, it does not exclude other



reaction pathways.

(b) The most compelling evidence which has been advanced against the Goldfinger mechanism (involving bromine atoms) for benzylic bromination has come from studies of Kooyman, van Helden, and Bickel^{8a} on selectivities in the brominations of substituted toluenes with bromine and with NBS. Their treatment, involving the calculation of relative rate constants from the product compositions in competitive brominations of mixtures of substituted toluenes, assumes that every benzyl radical which is formed reacts with a bromine atom donor to give a molecule of the corresponding benzyl bromide. The relative rate constants therefore are assumed to refer to the hydrogen abstraction step of the reaction. The rates so obtained were found to be correlated by the Hammett $\rho\sigma$ treatment (using σ^+ rather than σ)⁹ to give values of ρ which differ for bromination with molecular bromine (-1.05 at 80°) and NBS (-1.55 at 80°). These differing ρ -values, if we accept them at face value, indicate differing sensitivities to polar effects in the two bromination reactions and hence demand different hydrogen abstracting species in each case. Since bromine atoms undoubtedly fill this role in the molecular bromine reaction, the succinimidyl radical was suggested as the chain-carrying species in NBS brominations.



An important contribution from reaction 7 would result in an apparent lowering of the selectivity of bromine atoms, since not all benzylic radicals would yield product benzyl bromides. The rates of reaction 7 would be expected to vary with substituents in a manner roughly parallel to the variation in rates of the hydrogen abstraction reaction. The apparent change in selectivity resulting from an incursion of 7 would therefore not necessarily occasion a deterioration of the Hammett correlation but would be reflected in a change of ρ toward zero.

Work by Goldfinger¹⁰ on allylic chlorinations with N-chlorosuccinimide (NCS) has suggested that halogen atoms, rather than succinimidyl radicals, may function as the chain-carrying species. He has developed kinetic arguments to show that low chlorine concentration should favor substitution, rather than addition. The halogen presumably is maintained in a low, constant concentration by an ionic reaction of HCl and NCS.

(9) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

(10) J. Adams, P. A. Gosselain, and P. Goldfinger, *Bull. soc. chim. Belges*, **65**, 523 (1956).

Sixma and Riem^{4a} and McGrath and Tedder^{4b} have pointed up the possibility of an analogous mechanism for NBS brominations by showing that allylic substitution is competitive with addition in reactions of bromine with olefins at low bromine concentration.

Sixma reported^{4b} fragmentary data suggesting that the selectivities NBS and molecular bromine brominations of toluenes are indeed essentially identical. Only two toluenes were brominated in this study, however, and the uncertainties involved are large.

We have shown, in work which we here describe in detail, that when proper safeguards are observed, identical selectivities in the brominations of substituted toluenes are evidenced by NBS, N-bromotetrafluorosuccinimide (NBTFs), N-bromotetramethylsuccinimide (NBTMS), and molecular bromine. These results make it possible to discount some of the evidence which has been interpreted in terms of the succinimidyl radical mechanisms and make the bromine atoms mechanism very attractive indeed. Simultaneously with our presentation of this evidence^{5a} Russell, DeBoer, and Desmond^{5b} present complementary evidence leading to the same conclusion. Their conclusions, based on selectivity studies with NBS and bromine in systems leading to primary, secondary, and tertiary benzyl bromides, are also restricted to the mechanism of benzylic bromination.

Experimental¹¹

Materials.—Benzene and toluenes, all commercially available, were purified by standard methods and ascertained to be free from impurities by examination with gas-liquid phase chromatography. The recrystallization of 2,2'-azobisisobutyronitrile from 50% aqueous ethanol gave material of m.p. 101–102° (reported¹² 102–103°).

N-Bromosuccinimide was recrystallized from hot water and was determined to be 99.7 ± 0.1% pure by titration for active bromine with thiosulfate.

N-Bromotetrafluorosuccinimide (NBTFs) was prepared from the diethyl ester of tetrafluorosuccinic acid by the method of Henne and Zimmer.^{13a} The last step of their procedure, bromination of the imide, was reported^{13a} incorrectly, and a modification of the successful procedure outlined in Zimmer's thesis was utilized.^{13b}

In 100 ml. of trifluoroacetic acid containing 15 ml. of trifluoroacetic anhydride, 14.8 g. (0.064 mole) of silver oxide and 21.76 g. (0.127 mole) of tetrafluorosuccinimide were dissolved, followed by slow addition of an excess of bromine. After removal of silver bromide and solvent, as described by Henne and Zimmer,¹³ the remaining solid was sublimed at 1 mm. at room temperature to give 12.61 g. (40%) of crude N-bromotetrafluorosuccinimide, m.p. 48–53° (reported¹³ 49.5–50.5°). The most effective purification procedure required that all transfers of the bromoimide be performed in a drybox. Sublimation at 60° (15 mm.) produced a white solid, m.p. 51–54°, 96 ± 4% pure by titration.

Anal. Calcd. for C₄BrF₄NO₂: C, 19.22; N, 5.60. Found: C, 19.81, N, 5.76 (loses weight on balance).

Tetramethylsuccinimide.—In 175 ml. of toluene, 43 g. (0.26 mole) of AIBN was heated under reflux for 6 hr. After the solution was cooled and solvent evaporated, 27.8 g. (78%) of crude tetramethylsuccinonitrile was obtained. A portion was recrystallized from ethanol; m.p. 167–169° (reported¹⁴ 170.5–171.5°). The remainder was sublimed at 170°. Tetramethylsuccinimide was prepared utilizing the method of Bickel and Waters¹⁵; m.p. 190–192° (reported¹⁵ 187–188°).

N-Bromotetramethylsuccinimide.—The mild conditions of Brownlee¹⁶ for the bromination of succinimides were utilized. Five grams (0.032 mole) of tetramethylsuccinimide were dissolved with 2.56 g. of sodium bicarbonate in 327 ml. of water to yield a clear solution. The solution was cooled to 3° in an ice bath and a slight excess of bromine was added in small increments

with constant stirring. Collection of the precipitate by filtration gave crude N-bromotetramethylsuccinimide (7.31 g., 97%). Two sublimations at 150° (1 mm.) afforded the bromoimide, 99.5 ± 1.5% pure by titration.

Anal. Calcd. for C₉H₁₂BrNO₂: C, 41.04; H, 5.17. Found: C, 41.14; H, 5.09.

Reaction of Hydrogen Bromide and NBS.—At the temperature of a Dry Ice-acetone bath, anhydrous hydrogen bromide bubbled into a toluene solution of NBS immediately produced the yellow-orange color characteristic of bromine. The color did not deepen in appearance with time.

Competitive Reactions initiated by AIBN.—At 80°, reactions involving the N-bromoimides were run in sealed tubes for 2 hr.; 10 ml. of a benzene solution of the N-bromoimide and a catalytic amount of AIBN were added to the tubes containing the toluenes and, after degassing, sealed under vacuum.

To reduce the importance of undesired side reactions, the brominating agents were used in such concentrations that the products formed could not exceed 5% of the total amount of toluenes initially present, or 20% of the most reactive toluene. Toluene concentrations were adjusted to afford roughly equivalent amounts of products in any single run.

For NBS and NBTFs brominations, pairs of toluenes were used. For all other reactions, increased solubilities of the reagents in benzene allowed larger concentrations of starting materials, and hence of products formed. Judicious selection of substrates allowed simultaneous bromination of three toluenes without affecting the accuracy of product analysis. In every case, one member of the triad was unsubstituted toluene.

Initiation by Ultraviolet Radiation.—For these reactions, run on a 10-ml. scale, an apparatus was designed which allowed maintenance of constant temperature (80 or 19°), reflux of solvent, irradiation with a sunlamp, and introduction of a stream of nitrogen through a gas dispersion tube, serving to introduce bromine and to agitate the solution. Results obtained in this system at 80° did not differ from those obtained with AIBN initiation. At 19°, slower reaction rates and increased solubility of hydrogen bromide in benzene rendered the above method inadequate for molecular bromine reactions (see Table I). At this temperature a large excess of bromine (about 25-fold) was used in a short path length cell and the reaction was halted after a small fraction of the bromine was consumed.

Analytical Method.—Relative reactivities of α -hydrogens of toluenes toward the various free radical brominating agents were determined by the competitive technique, using the integrated rate eq. 8 for the calculation. This necessitates knowledge

$$k_{rel} = \frac{\log((A - X)/A)}{\log((B - Y)/B)} \quad (8)$$

of the amounts of starting materials A and B, and of the respective products derived from them, X and Y (where B refers to the unsubstituted toluene).

At the end of each kinetic run, the solution was tested with starch-iodide paper for completeness of reaction. A weighed amount of phthalide or acenaphthene was added as an internal standard for n.m.r. analysis, and the liquid was concentrated to 1.0–1.5 ml. at 40° (80–120 mm.) on a rotary evaporator.

For the reactions run with excess bromine, the halogen was extracted by shaking the 50-ml. sample with 10 ml. of concentrated sodium thiosulfate solution. After separation of the layers, the organic solution was concentrated on a Rinco rotary evaporator.

As a control to measure the importance of differential loss of products, solutions of known mixtures of benzyl bromides were subjected to the conditions described above; n.m.r. analysis before and after work-up showed no differential loss, by either solvolysis or volatilization, greater than the ±2% accuracy of the analytical method.

Relative concentrations of the internal standard and the product benzyl bromides were determined by integrating the areas of the peaks corresponding to benzylic hydrogens with a Varian Associates Model A-60 nuclear magnetic resonance spectrometer. Analysis of synthetic mixtures of benzyl bromides produced results accurate to within ±2%. At least six integrals were run for every sample, and average deviations seldom exceeded ±1%. Possible effects of saturation were judged negligible by finding invariance of relative peak areas with changing radiofrequency and sweep rates.

Results and Discussion

The rates, relative to toluene, for hydrogen abstraction from substituted toluenes by the various brominating agents at 80 and 19° are accumulated in Table I. The correlations have been calculated by standard statistical methods.¹⁷ In all cases an excellent fit of the

(11) All melting points are corrected. We wish to thank Mr. Oliver Norton, Mr. Richard Johnson, and Mr. Josef Nemeth for microanalytical and spectroscopic data.

(12) (a) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896); (b) C. G. Overberger, P. Huang, and M. B. Berenbaum, *Org. Syn.*, **32**, 16 (1952).

(13) (a) A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, **73**, 1103 (1951); (b) W. F. Zimmer, Jr., Ph.D. Thesis, The Ohio State University, Columbus, 1952.

(14) C. G. Overberger, P. Huang, and M. B. Berenbaum, ref. 12b, p. 48.

(15) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

(16) T. H. Brownlee, B.S. Thesis, University of Illinois, Urbana, Ill., 1957.

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

TABLE I
LOGARITHMS OF BROMINATION RATES OF SUBSTITUTED TOLUENES (RELATIVE TO TOLUENE)

Brom. agent	Substituent (<i>para</i>)							ρ^a	s_p^b	s^c
	CH ₃ O	CH ₃	(CH ₃) ₂ C	H	Cl	<i>m</i> -Br	NC			
1 NBS, 80°	1.093	0.418	0.464	0	-0.145		-0.953	-1.46	0.065	0.069
2 NBTFS, 80°		.500	.457	0	-.081		-.857	-1.45	.073	.054
3 NBTMS, 80°	0.980	.480	.402	0	-.168	-0.616	-.845	-1.36	.050	.058
4 Br ₂ (slow) 80°	.812	.352	.374	0	-.091	-.501	-.620	-1.07	.051	.059
5 Br ₂ (fast) 80°	.956	.383	.393	0	-.138	-.650	-.914	-1.36	.054	.063
6 1, 2, 3, and 5								-1.39	.029	.062
7 NBTMS, 19°	1.108	0.530		0	-0.168	-0.761		-1.79	.077	.039
8 Br ₂ , 19°	0.870 ^d	.507		0	-.116	-.782		-1.36	.181	.164
9 Br ₂ (excess), 19°		.506	0.551	0	-.125	-.703		-1.76	.115	.067
10 7 and 9								-1.78	.060	.047

^a ρ = slope of regression line. ^b s_p = standard deviation of ρ . ^c s = standard deviation of any point from the regression line. ^d Evidence for significant amounts of nuclear bromination justifies omission of this datum, which falls off the regression line, from the statistical calculations.

points to the Hammett correlation is obtained when σ^+ -values¹⁸ are used.

When data for all brominating agents at each temperature are plotted, graphs are obtained for which the standard deviations of the slopes (values of ρ) are less than for any individual series within the set (see Table I and Fig. 1).

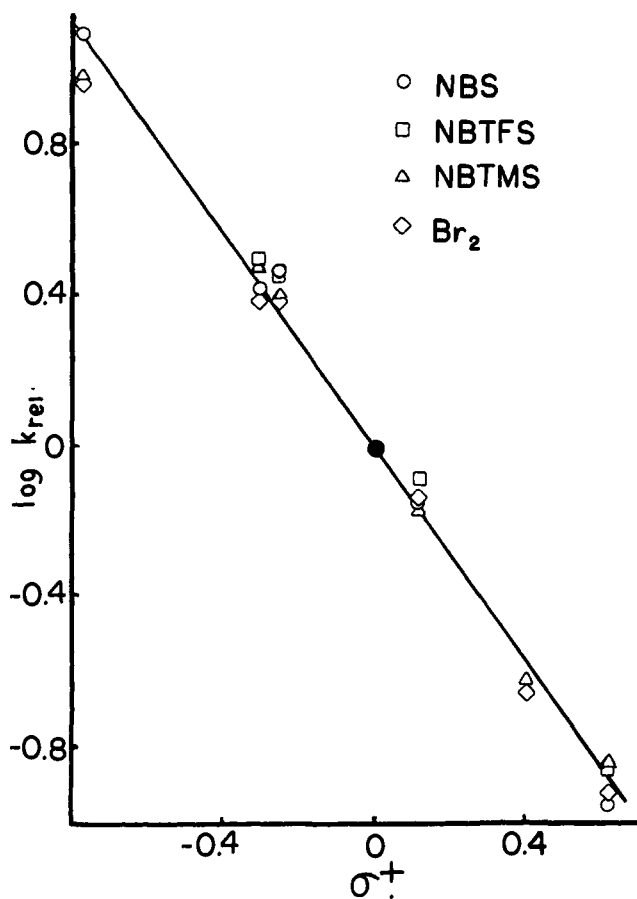


Fig. 1.—Bromination of substituted toluenes with four brominating agents.

One verdict emerges with decisive probability from a consideration of these data: the ρ -values for all four brominating agents are identical under like conditions. For this conclusion, there are two possible explanations: 1. Structural changes in the attacking radicals do not affect their sensitivity to electron availability in the substrate, which is to say that the changes of free energies of activation within a series fortuitously coincide for all attacking species. 2. The hydrogen

(18) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

abstracting species is the same in each reaction series.

Let us consider the first of these alternatives. Although radical reactions at the side chain of toluenes exhibit a small range of ρ -values compared to the range found in ionic reactions, the range is much greater than the small standard deviations of our results. Attack by perbenzoate radicals ($\rho = -0.6$),^{19a} chlorine atoms ($\rho = -0.76$),^{19b} and *t*-butoxy radicals ($\rho = -0.83$)^{19c} show ρ -values far removed from those found in our work. The magnitude of ρ presumably reflects the sensitivity of the attacking radical to the polar effect of the substituent.⁹ Identical selectivities of bromine and succinimidyl radicals would be unexpected, though not impossible. However, failure of the substituents on NBS, especially four strongly electron-withdrawing fluorine atoms, to alter the relative rates is not in accord with expectations based on a similar situation in another system. Comparison of the relative rates of hydrogen abstraction from a series of substituted benzaldehydes by perbenzoate and *p*-chloroperbenzoate radicals reveals²⁰ a value of ρ more than one unit more negative for attack by the more electronegative radical. In this case, three atoms separate the reaction site from the aromatic system. It might be expected that similar differences in ρ -values for the variously substituted succinimidyl radicals might obtain in hydrogen abstractions from toluenes by such species. A comparable degree of insulation of the reaction center from the substituent, with respect to possible electronic effects, is seen in both situations.

The relative rates of reaction of two substances with a given reagent depend on the differences in the free energies of activation for the two reactions ($\delta\Delta F^\ddagger$). If the same compounds in a second reaction series exhibit the same relative rates as in the first, then $\delta\Delta F_1^* = \delta\Delta F_2^*$. In this situation, it is sufficient, but not necessary, that each substrate possess the same value of ΔF^* in each of the two different reactions. The further observation that the change in ρ on going from 80 to 19° is the same (22) for NBTMS and molecular bromine reactions, demands parallel, if not identical, ΔH^* and ΔS^* terms. (A change in $\delta\Delta S^*$ of 0.4 e.u. alters ρ beyond the limits of our experimental error.) Any explanation other than that involving identical activation parameters for all four reactions series seems forbiddingly improbable. We conclude from these results that bromine atoms function as the hydrogen abstracting species in the side-chain reactions of toluenes with NBS and its substituted analogs.

Our data clearly show the sensitivity of the value of ρ to changes in procedure when brominating with

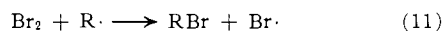
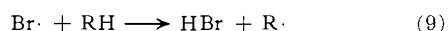
(19) (a) G. A. Russell, *ibid.*, **78**, 1047 (1956); (b) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957); (c) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6116 (1960).

(20) C. Walling and E. A. McElhill, *ibid.*, **73**, 2927 (1951).

molecular bromine. When the bromine was slowly introduced in a stream of nitrogen we obtained a value of ρ equal to that reported by Kooyman. Rapid introduction of bromine (accompanied, in the runs at 80°, by a large increase in the relative amounts of bromine added) effectively increasing the value of the Br₂/HBr ratio, changed the reaction constant from -1.07 to -1.36 at 80° and from -1.36 to -1.76 at 19°. The more negative values are the same as those observed in NBS brominations, where rapid reaction with scavenger NBS prevents accumulation of hydrogen bromide, effectively increases the Br₂/HBr ratio, and minimizes the importance of reaction 7. Wiberg and Slauch²¹ found that measurements of kinetic isotope effects in the bromination of deuterium-substituted toluenes gave results which indicated that reaction 7 could be important. Removal of HBr by rapid sweeping of the systems with nitrogen led to k_H/k_D ratios essentially identical for bromine and NBS brominations. The small differences which were originally interpreted as supporting the mechanism involving succinimide radical seem, in view of our evidence that removal of HBr by sweeping with nitrogen is not always sufficient to prevent a significant occurrence of reaction 7, to be reconciled easily with the postulated Goldfinger mechanism.

The studies of NBS bromination by Dauben and McCoy,⁶ in addition to demonstrating a dependence on environmental conditions typical of radical reactions, detailed the effects of a number of added modifiers on the over-all rate of the reaction. Radical chain inhibitors brought about their expected rate retardation, while the authors classified accelerators into three groups: radical initiators such as AIBN, substances which liberate bromine from NBS, and tertiary amines and their quaternary salts. With the recognition that the last group of compounds also frees bromine from NBS,²² and considering the kinetic analysis described below, these results are compatible with our postulated mechanism of NBS reaction.

More detailed considerations of the reaction schemes of the N-bromoimides require a process whereby bromine may be liberated but kept at a low concentration. Most authors have recognized that hydrogen bromide frees bromine from NBS. As an intermediate ionic step in a radical chain process, it must be very fast. Our experiments show the reaction to occur essentially instantaneously, even at -78° in subdued light. Reactions 9-11 are postulated as the chain-propagating steps. Steps 9 and 11 in this sequence are familiar as the chain-propagating reactions in many gas-phase brominations.²³



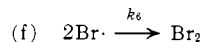
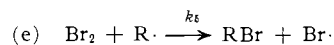
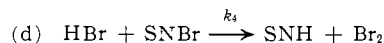
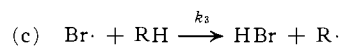
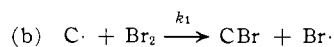
While the NBS bromination may follow different pathways in the benzylic and allylic systems, it is useful to consider whether the proposed chain-propagating steps in the benzylic system can be incorporated into a scheme which fits the experimental rate expressions established by Dauben and Youngman.^{8b,c} Using the reaction steps of Scheme I, for the benzylic system, the derived rate law 12 corresponds to that established by Dauben and Youngman for the allylic system, with AIBN initiation.

(21) K. B. Wiberg and L. H. Slauch, *J. Am. Chem. Soc.*, **80**, 3033 (1958).

(22) E. A. Braude and E. S. Waight, *Nature*, **164**, 241 (1949).

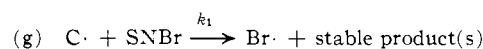
(23) (a) C. Walling, ref. 3, p. 373 ff; (b) H. R. Anderson, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953); S. N. Benson and I. H. Buss, *ibid.*, **28**, 301 (1958).

SCHEME I



$$-d[\text{SNBr}]/dt = (k_3 k_0^{1/2} k_2/k_4^{1/2})(\text{RH})(\text{AIBN})^{1/2} \quad (12)$$

Substitution of (g) for (b) does not significantly alter the resultant expression (13).



$$-d(\text{SNBr})/dt = k_0(\text{AIBN}) + (k_3 k_0^{1/2} / k_4^{1/2})(\text{RH})(\text{AIBN})^{1/2} \quad (13)$$

Evidence is not available to delineate the details of reaction g. Many possible reaction schemes would yield the over-all result of generating a bromine atom from N-bromosuccinimide.

Attack of an initiator fragment at an α -hydrogen of NBS could afford bromine atoms and acrylyl isocyanate in a concerted or stepwise process. A similar reaction between two succinimidyl radicals has been suggested by Dauben and McCoy^{8a} in their search for a chain-terminating reaction. Another possible route would involve the abstraction of bromine from NBS by the 2-cyanopropyl radical, forming an N-bromoketeneimine which then might liberate bromine atoms by spontaneous decomposition or as a result of attack by another radical.

A preliminary investigation, by Curtin and McCarty, of the radical chain reaction of toluene with the N-bromoimine of benzophenone has shown that the products include benzyl bromide, benzophenonimine hydrobromide, and appreciable quantities of diphenyl ketazine.²⁴ The presence of the azine suggests formation of an imine radical which is relatively inactive as a hydrogen abstractor. This, in turn, suggests the accompanying formation of bromine, in a reaction which could have a parallel in NBS brominations.

The fact that Youngman's kinetic results in an allylic system can be explained as well by a pathway involving free bromine as by one incorporating hydrogen abstraction by succinimidyl radicals by no means offers proof that the same mechanism operates in both allylic and benzylic systems. It does make it possible to postulate such an identity of mechanism. Clarification can follow only with further studies.

A rearrangement to yield β -bromopropionyl isocyanate has been detected in NBS brominations²⁵ and has been shown to arise through a free-radical chain mechanism which utilizes a trace of olefin for some necessary function.²⁶ In a solvent containing as little as 1 mole % of an olefin, such as cyclohexene, stilbene, or norbornene, the rearrangement can be almost quantitative, though not proceeding at all in the absence of this olefin. Under these conditions added bromine suppresses the rearrangement. These data suggest that bromine atoms and succinimidyl radicals may exist in equilibrium with NBS. Complexation of bromine atoms by olefin could allow succinimidyl radicals to develop a

(24) C. G. McCarty and D. Y. Curtin, private communication.

(25) (a) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957); (b) H. W. Johnson and D. E. Eubltz, *ibid.*, **79**, 733 (1957).

(26) J. C. Martin, Thomas Brownlee, Leslie Freiburg, and Richard Panich, in preparation.

sufficiently large concentration to make the rearrangement competitive with chain reactions of the bromine atom.

The effect of the removal of bromine atoms from the reaction mixture by complexation with olefin (either as a σ - or π -complex) could shift the mechanism for allylic bromination to one involving a slower chain process with succinimidyl radicals acting as chain carriers.²⁷

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(27) This is consistent with the observation that the addition of 2% of norbornene greatly inhibits the benzylic bromination of a mixture of toluenes in benzene solution; unpublished work of Joseph Incremona.

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Fluorine Nuclear Magnetic Resonance Shielding in *p*-Substituted Fluorobenzenes. The Influence of Structure and Solvent on Resonance Effects¹

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Fluorine n.m.r. intramolecular shielding effects of 63 *p*-substituents in fluorobenzene have been determined at high dilution in a wide variety of solvents. The correlation has been extended between the shielding parameter for a *p*-substituted fluorobenzene relative to its *m*-isomer as internal standard and the reactivity resonance effect parameter, σ_R^0 . The relationship is used both to obtain σ_R^0 values for new substituents and to assess the trends and magnitudes of solvent effects on this parameter. Approximate MO π -electron charge density distributions are also derived. A plot of the shielding parameter for *p*-substituted fluorobenzene relative to internal fluorobenzene, \int_{H^p-X} , vs. the corresponding parameter for the *m*-isomer, \int_{H^m-X} , provides new insight into relationships between the resonance and inductive effects of substituents. Linear σ_R vs. σ_I relationships are shown to be quite special rather than general. A special and well defined class of substituents is recognized by a linear \int_{H^p-X} vs. \int_{H^m-X} plot. These substituents are designated as UAFPD (united atom-like first row pair donor) substituents. The effects of UAFPD substituents on appropriate chemical and physical properties are shown to be quite precisely linear with σ_I in aromatic (or in general, unsaturated) systems, provided that there are essentially no contributing effects of direct charge delocalization interactions between the substituent and the functional group. These remarkably precise relationships, although limited by the number of UAFPD substituents, greatly extend the range of applicability of the relationship $\log(k/k_0) = C_1\sigma_I + C_2$. The effects of polar solvents on fluorine intramolecular shieldings are interpreted as indicating rather distinct categories of solvent dependence on the contributions to the ground electronic state of various types of dipolar resonance forms. Small or undetectable solvent effects are indicated for the contributions of dipolar resonance forms for which at least one of the atomic centers of formal charge is buried within the molecular cavity. On the other hand, with increasing solvent polarity the contributions are generally appreciably increased for those dipolar direct interaction forms in which both of the formal charge centers are on the periphery of the molecule. Some applications to chemical reactivities are considered.

Intramolecular F¹⁹ n.m.r. shielding in the special case of *p*-substituted fluorobenzenes apparently can be directly related, at least approximately, to the π -electron charge density on the fluorine atom^{4,5} or its bonded carbon atom.⁵ Extensive studies⁶ of the solvent effects on the fluorine shielding in *m*-substituted fluorobenzenes suggest that the intramolecular shielding effect of a *p*-substituent in fluorobenzene can be obtained at high dilution in any solvent from the measurement of shielding referred to the standard internal fluorobenzene. The substituted and unsubstituted fluorobenzene present to their environment fluorine atoms which are sufficiently similar that intermolecular shielding cancels with considerable precision in the shielding parameter of the substituted relative to the unsubstituted internal fluorobenzene.

Fluorine shielding is so sensitive to the very small (absolute) intramolecular perturbations in the fluorine atom π -charge density produced by a distant *p*-substituent that this measurement ranks as the most sensitive probe (relative to the experimental error) currently available to investigate such interactions.⁴⁻⁷

Using this distant but very sensitive probe, new and highly instructive investigations of both the effects of substituent structure and of solvent-substituent interactions on the intramolecular shielding effect of *p*-substituents are made possible. In the present paper we report the results of extensive studies of both types.

Solvent-substituent interactions previously investigated by this technique include proton transfer equilibria,⁸ Lewis acid-base equilibria,⁶ hydrogen bonding,⁶ and polar interactions.⁶ This paper reports additional results of the last two kinds, especially the latter. The results can apparently be interpreted in terms of the effects of polar solvents on the relative contributions of various types of dipolar resonance forms to the ground electronic state of the fluorobenzene.

The effects of structure on the intramolecular shielding of $-R$ *p*-substituents have been correlated with the σ_R^0 resonance effect parameter from chemical reactivities.^{7b} The correlation is extended with the present results and is utilized both to obtain σ_R^0 values for new substituent groups and to assess the magnitude of solvent effects on σ_R values. Comparison of the present results with the previously reported corresponding *m*-substituent effect shielding parameters⁶ provides new insight into relationships between the inductive and resonance effects of substituents.

Experimental

Solvents.—Purification of solvents was carried out as previously described.⁹

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