

AN ABSTRACT OF THE THESIS OF

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Title: AN EVALUATION OF CHARGE GENERATION IN HYDROGEN ATOM

ABSTRACTION PROCESSES: THE REACTION OF HOMOARYL AND

HETEROARYLMETHANES WITH T-BUTOXY RADICAL

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Gerald Jay Gleicher

The relative rates of hydrogen atom abstraction from a series of 13 homoaryl and heteroarylmethanes by t-butoxy radical were determined at 70°C. The attacking radical was photochemically generated from di-t-butyl peroxide. A relatively small range of relative rates (factor of seven) has been found among the compounds studied. The relative reactivities of the homoaryl and heteroarylmethanes can be correlated with various calculated energy differences obtained from both HMO and standard semi-empirical SCF-MO methods. Fairly good correlations were obtained using a carbocation model for the transition state (correlation coefficient of 0.92). Much poorer correlations were obtained when either a radical model was used for the transition state (correlation coefficient of 0.46) or when ground state properties, such as charge density, were used (correlation

coefficient of 0.53). This suggests, at best, only partial ground state control for this reaction.

The relative reactivities of all compounds were also studied using empirically derived four parameter equations. A very poor correlation was obtained for that approach which completely neglected charge separation in the transition state. However, good correlations were obtained with those four parameter equations which included cationic character in the transition state. Present use of non-alternant heteroarylmethyl systems strongly suggests the importance of appreciable positive charge development in the transition state of hydrogen atom abstraction processes.

Optimum correlation of the present data was with the relative reactivities for pyrolytic decomposition of corresponding 1-aryl and 1-heteroarylethyl acetates. The coefficient for this correlation was 0.97.

An Evaluation of Charge Generation in Hydrogen Atom
Abstraction Processes: The Reaction of Homoaryl
and Heteroarylmethanes with t-Butoxy Radical

by

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TO MY PARENTS.

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LA FONCTION " QUALITE " EST UNE FONCTION D'ETAT
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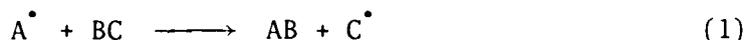
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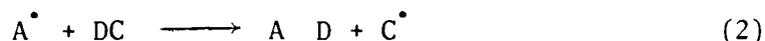
AN EVALUATION OF CHARGE GENERATION IN HYDROGEN ATOM
 ABSTRACTION PROCESSES: THE REACTION OF HOMOARYL
 AND HETEROARYLMETHANES WITH T-BUTOXY RADICAL

INTRODUCTION

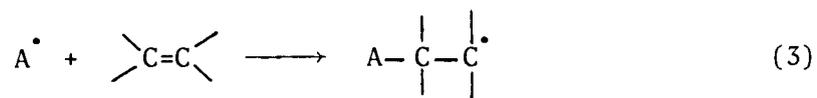
The reactions of free radicals or atoms with organic molecules fall into three broad groups: homolytic substitutions, atom abstractions, and addition reactions. The homolytic substitution can be described by equation 1:



where A^\bullet is the attacking radical (free atom) and B is a polyatomic fragment. The homolytic substitution reaction at carbon centers is rare. It only occurs if there is relief of strain (1). Atom abstraction is described by the following equation:



A^\bullet is the attacking radical (free atom) and D is the transferred atom which must be hydrogen or halogen. Addition is the reaction of a radical (free atom) with an unsaturated substrate. An example is shown in equation 3:



Application of the Hammett equation (2), and more recently, simple molecular orbital calculation (3), have been made to free radical reactions (4). They have been particularly useful in the

investigation of atom transfer reaction paths and determination of the factors which influence these processes. This has been a major goal in the development of free radical chemistry. These studies have led to a better understanding of the effect of substituents on the substrate reactivity and the role of the electron affinity of the attacking radical on the transition state of atom transfer reactions. The pioneering work of Eyring and Polanyi paved the way to an understanding of atom-transfer reactions (5). These workers made the following points:

- a. The transition state can be treated as if it were in equilibrium with the starting material.
- b. In the transition state of atom-transfer reactions, the bond to be broken is only stretched, and the formation of the bond between the attacking radical and the transferred atom provides the driving force for the reaction.

These points have been stressed by Szwarc in his review on the transition state of free radical reactions (6). The Eyring-Polanyi analysis suggests that in atom-transfer reactions, atoms or polyatomic radicals which form the strongest bond with the transferred atom will be the most reactive. This is an over-simplified view which has only a historical importance. We shall return to this point later.

In the case of hydrogen-atom transfer, it has been shown that within a given series of similar organic compounds, tertiary hydrogen atoms are abstracted more easily than secondary hydrogen atoms which, in turn, are more easily removed than primary ones (6,7,8). The relative rates of tertiary, secondary, and primary hydrogen atom abstraction by a common radical reflect the relative ease of breaking the

carbon-hydrogen bond, or the bond dissociation energy (BDE). This is illustrated in Figure 1.

Evans and Polanyi (9) have studied reactions of the type shown in equation 2 where A, D, and C were all small atoms. They found that such reactions could be represented by energy surfaces. Such surfaces can be shown as contours on a two-dimensional plot using the A—D bond distance as one variable, and the D—C bond distance as the other. The progress of the reaction along the reaction coordinate can be plotted using the lowest path along the surfaces as one axis and the potential energy as the other. Graphs such as that shown in Figure 2 can be drawn.

The dotted lines represent the dissociation energy of the A—D or the D—C bond. The transition state is the point of highest potential energy. The energy difference between it and the reactants is the activation energy. Evans and Polanyi have also suggested that there is a relationship between reactivity and the position of the transition state (9). Therefore, if the attacking radicals were changed to a more reactive species, A'^{\bullet} , the transition state would be shifted in a manner which reflects the difference in energy of activation in reactions involving A^{\bullet} and A'^{\bullet} . This leads to the relationship in equation 4 which is the basis for all linear-free energy relationships:

$$\Delta G^{\ddagger} = \alpha + \beta \Delta G \quad (4)$$

The above equation is the mathematical equivalent of the well-known Hammond Postulate (10). The chief value of the postulate has been in its application to highly endothermic or highly exothermic

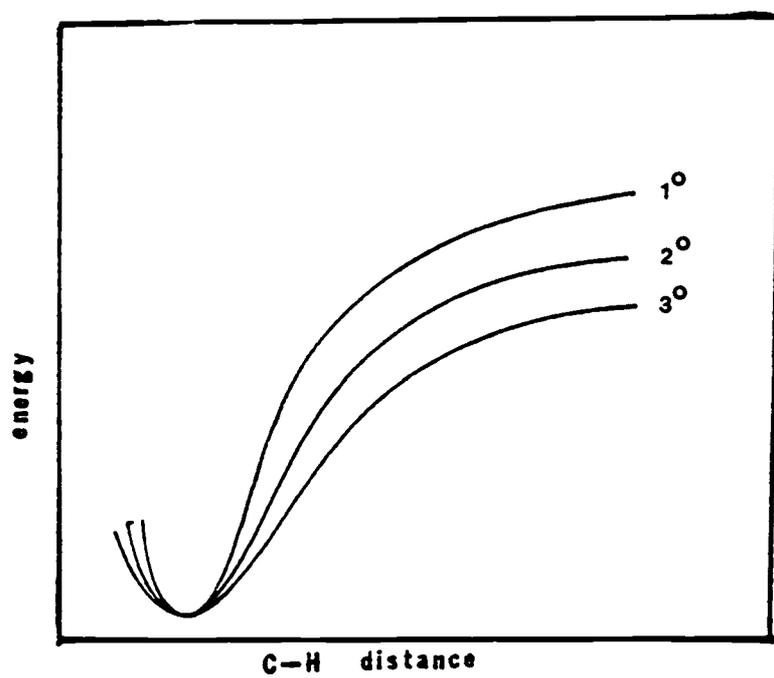


Figure 1. Bond dissociation energy of carbon hydrogen bonds.

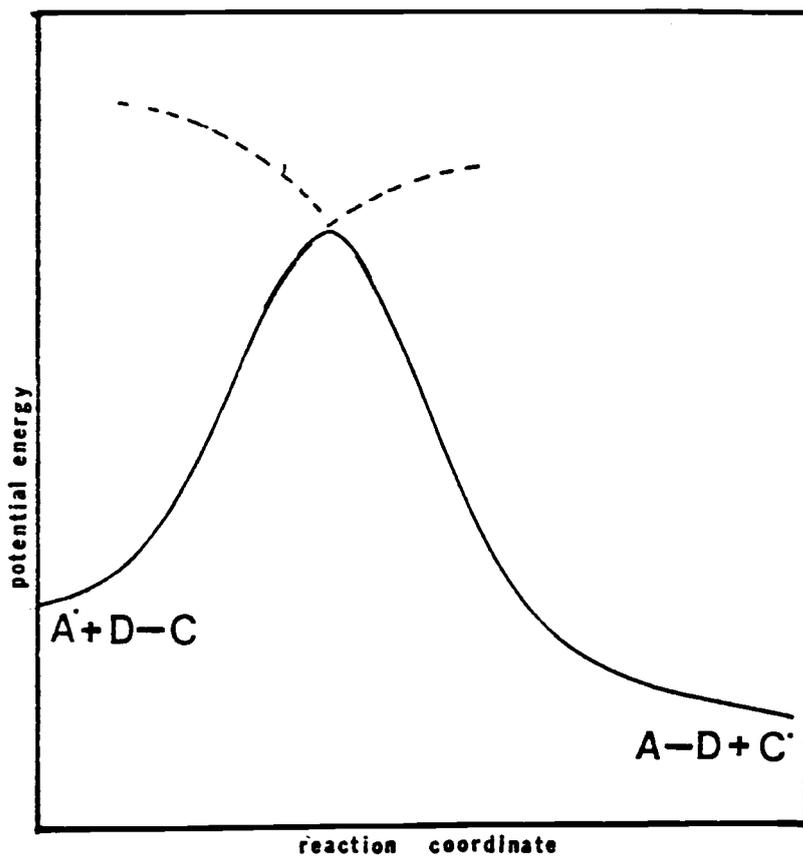


Figure 2. Potential energy diagram for a three atom reaction

processes. In a highly exothermic process, the transition state will resemble the reactants. It is, thus, an early transition state. Conversely, in a highly endothermic process, the transition state will resemble the products and can be considered as a late transition state. There are three general cases, as illustrated in Figure 3.

Curve A represents the conversion of a highly reactive species in an exothermic process. Curve B depicts the formation of an unstable product in an endothermic process. In A, going to the transition state involves little progress along the reaction coordinate, while in B, the transition state resembles products. Curve C represents a thermally balanced reaction.

The typical mechanism for hydrogen atom abstraction from hydrocarbons is shown in Scheme 1:

Scheme 1



The rate-determining step is that wherein the hydrogen atom is actually abstracted. It has been stated earlier, that the stronger is the H—X bond being formed, the lower will be the activation energy required for the hydrogen atom abstraction, therefore, the faster the rate will be. The following example may be considered: the hydrogen chlorine bond dissociation energy is 103 kcal/mole while that of hydrogen bromine is 87 kcal/mole. As expected, the chlorine atom is more reactive and less selective than the bromine atom in hydrogen atom abstraction from a common substrate. In Hammond Postulate terms,

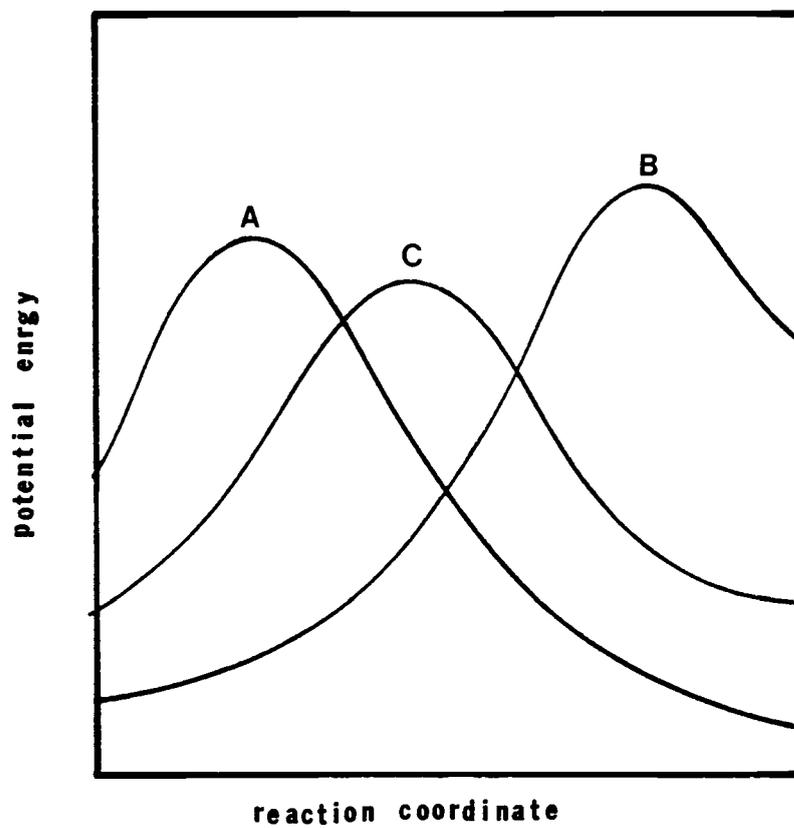
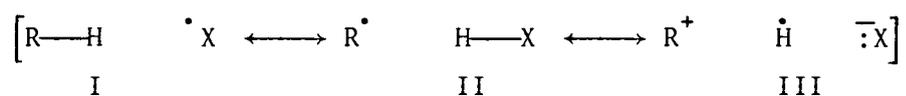


Figure 3. General cases of the Hammond Postulate

the transition state for hydrogen atom abstraction by chlorine atom lies nearer the reactants than that of hydrogen atom abstraction by the bromine atom. As we previously mentioned, Eyring and Polanyi have pointed out that in hydrogen atom abstraction, the carbon-hydrogen bond is only stretched in the transition state (5). However, when the attacking radical has a high electron affinity, polarization of the transition state may occur. This may be important in determining the selectivity of such systems. The result is the description of the transition state by the following resonance forms (6,11):



These canonical structures lower the activation energy for hydrogen atom abstraction (6). The importance of each depends on the nature of the attacking radical. When the attacking radical is extremely reactive, there will be little bond breaking in the transition state. The contribution from Structure I, which resembles the reactant, will be greater than that of Structure II, which resembles the products in this case (12). Because of the predominance of the contribution of Structure I to the transition state, reactivity will depend on the electron density at the reaction site. However, bond breaking in the transition state increases as the reactivity of the attacking radical decreases. In such a case, the contribution of Structure II will be predominant. For a radical of high electron affinity (electrophilic radical), the contribution of Structure III to the transition state is very important. Therefore, the activation energy should decrease as R^{\oplus} becomes more stable. For most hydrogen

atom abstraction reactions, it has been observed that electron donating groups in the substrate enhance the rate of reactions, because of the stabilization of R^{\oplus} (11).

It was mentioned earlier that the ease of carbon-hydrogen bond homolysis is tertiary > secondary > primary (6,7,8). A partial explanation may lie in the resonance stabilization of the incipient radical. This is especially valid when carbon-hydrogen bond breaking is well advanced in the transition state (8). This can be illustrated by the following example. Russell and Brown reported that at 80°C chlorine atom abstracts a hydrogen atom eleven times faster from cyclohexane than from toluene, while bromine atom abstracts hydrogen from cyclohexane 0.017 times faster than from toluene (12). Since chlorine atom is much more reactive, there is little bond breaking in the transition state, therefore, the resonance stabilization of the benzyl radical is unimportant. Thus, chlorine atom prefers to attack the more electron-rich secondary site. On the other hand, bond breaking is well advanced in the transition state when the more selective bromine atom is the attacking radical. Thus, the transition state resembles the intermediate radical, and the resonance stabilization plays a very important role.

We have already introduced the concept of charge separation in the transition state of free radical reactions. This implies that radical hydrogen atom abstraction reactions should be amenable to Hammett studies. Indeed, the Hammett equation has been successfully applied to hydrogen abstraction from substituted alkylbenzenes by a variety of radicals, and rho values gave an indication on the extent of bond breaking in the transition state (13).

Hydrogen atom abstraction from substituted toluenes by several radicals have been fully correlated by the Hammett equation. Some examples are found in Table 1.

In the original analysis of the polar effect found for benzylic hydrogen atom abstraction, it was predicted that for a radical of high electron affinity, ρ should increase in absolute value with the degree of bond breaking. Therefore, the optimum correlation of the Hammett equation should be found using σ^+ rather than σ parameters (22).

The magnitude of ρ for polar benzylic hydrogen atom abstractions has been shown to decrease as the stability of the product benzylic radical increases. For example, absolute ρ value for benzylic hydrogen atom abstractions by bromine atom decreases in going from substituted toluenes (18) to ethylbenzene (24) to cumenes (23). This is shown in Table 2.

Alkoxy radicals have been extensively studied because of their importance in a variety of reactions. Kochi has reviewed the subject (25), and Brun and Waegell have written a critical discussion on the potential use of alkoxy radicals in synthetic organic reactions (26). We will limit our discussion below to the t-butoxy radical and its reactivity in hydrogen atom abstraction reactions.

The t-butoxy radical can be generated by the decomposition of t-butyl hypohalites (16,28,29,30), di-t-butyl peroxalate (14,16), di-t-butyl hyponitrite (16), and di-t-butyl peroxide (27,31,32,33,34).

Hydrogen atom abstraction by the t-butoxy radical has been widely studied. Particular attention has been focussed on substituted toluenes, and correlations with the Hammett equation have been

Table 1. Rho values for hydrogen atom abstraction from substituted toluenes by a variety of attacking radicals

No.	Attacking Radical	T/°C	Optimum ρ	Ref.
1	$(\text{CH}_3)_3\text{CO}^\bullet$ ^a	40.0	-0.345 (σ^+)	16
2	$(\text{CH}_3)_3\text{CO}^\bullet$ ^b	40.0	-0.35 (σ)	14
3	Cl^\bullet	40.0	-0.66 (σ)	11
4	Br^\bullet	80.0	-1.46 (σ^+)	17
5	Br^\bullet	80.0	-1.38 (σ^+)	18
6	$^\bullet\text{CCl}_3$	55.0	-1.50 (σ)	15
7	Ph^\bullet	60.0	-0.10 (σ)	19
8	CH_3^\bullet	100.0	-0.10 (σ)	20
9	$(\text{CH}_3)_3\text{C}^\bullet$	30.0	+0.99 (σ^+)	21

^aFrom di-t-butyl hyponitrite

^bIn Freon-113 as solvent

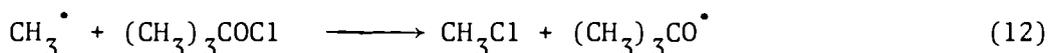
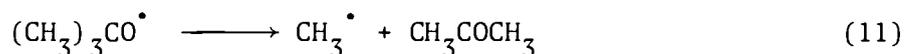
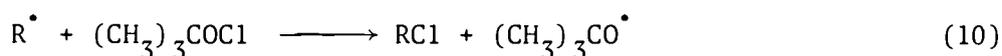
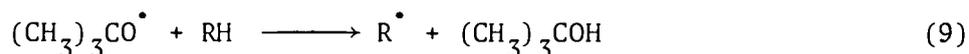
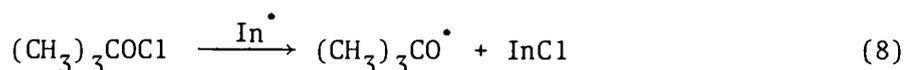
Table 2. Rho values for hydrogen atom abstraction from substituted toluenes, ethylbenzenes and cumenes

System	Temperature	ρ	Ref.
Toluene	80.0	-1.39	18
Ethyl benzene	80.0	-0.69	24
Cumene	70.0	-0.38	23

obtained. Some results of substituted toluenes have been summarized in Table 3. Hydrogen atom abstraction from substituted benzaldehydes (35), and α -heteroatom substituted compounds (36) have also been investigated.

Early attempts to evaluate the rho value for side chain chlorination of substituted toluenes by t-butyl hypochlorite led to controversial results. Scheme 2 shows a radical mechanism for this reaction utilizing t-butoxy radical as the chain-carrying species.

Scheme 2



Reaction 11 competes with reaction 9. However, it has been reported that the activation energy for the decomposition of t-butoxy radical to methyl radical and acetone is relatively high (13 ± 2 kcal/mole) (37). This may be contrasted to the activation energy for hydrogen atoms abstraction from toluene which was estimated to be 2.1 kcal/mole) (28). Walling found less than two percent acetone present in his chlorination of toluenes by t-butyl hypochlorite (28).

Walling and Jacknow, in their work on the photochlorination of substituted toluenes with t-butyl hypochlorite have reported a rho value of -0.38 at 40°C (28). Gilliom and Ward, working at the same temperature, found a value of -0.75 when benzene was used as solvent

Table 3. Rho values for hydrogen atom abstraction from substituted toluenes by t-butoxy radical

Entry	Source of <u>t</u> -Butoxy Radical	T/°C	Optimum ρ	Ref.
1	DTBP	110.0	-0.500 (σ)	27
2	TBHC	40.0	-0.830 (σ^+)	28
3	TBHC	39.6	-0.750 (σ)	29
4	TBHC	40.0	-0.680 (σ^+)	30
5	TBPO	40.0	-0.35 (σ^+)	14
6	TBPO	40.0	-0.32 (σ^+)	14
7	TBPO	40.0	-0.39 (σ^+)	14
8	TBHB	40.0	-0.401 (σ^+)	16
9	TBHN	40.0	-0.345 (σ^+)	16
10	TBPO	40.0	-0.345 (σ^+)	16

DTBP: di-t-butyl peroxide

TBHC: t-butyl hypochlorite

TBPO: di-t-butyl peroxalate

TBHB: t-butyl hypobromite

TBHN: di-t-butyl hyponitrite

(29). Both groups obtained an optimum correlation with sigma rather than sigma-plus parameters, and determined the relative rates of reaction by following the disappearance of starting material by GLC. Kennedy and Ingold challenged Gilliom's and Ward's results on the grounds that they did not investigate substrates which contained substituents which have substantially different sigma and sigma-plus values (30). Hence, Kennedy and Ingold included *p*-methoxytoluene in the list of compounds they examined, and followed the reactions by the appearance of products by means of GLC. They reported a rho value of -0.86 when correlated with sigma, and a value of -0.68 when correlated with sigma-plus. The sigma-plus correlation was somewhat better than that for sigma. Gilliom repeated his work and found a good agreement with his previous results. He argued that Ingold's rate for the *p*-methoxytoluene was fortuitous, since anisole reacts at about the same rate as toluene. Therefore, hydrogen atom abstraction is also taking place at the methoxymethyl of the *p*-methoxytoluene (38).

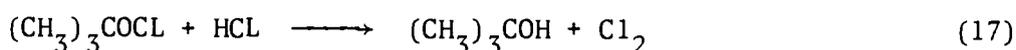
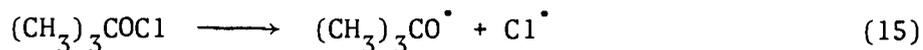
Even though there is some disagreement, the findings presented above are still rather similar. Sakurai, however, has obtained very different results using di-*t*-butyl peroxide as the source of his *t*-butoxy radical. He determined the relative rates of hydrogen atom abstraction from toluenes indirectly by measuring the ratio of *t*-butyl alcohol to acetone formed (14). The ratio of rate constants for abstraction, k_a , to decomposition, k_d , can be determined from equation 14:

$$k_a/k_d = \frac{[\textit{t}\text{-butyl alcohol}]}{[\textit{acetone}]} \times \frac{1}{[\textit{RH}]} \quad (14)$$

Sakurai's results are summarized in Table 5, entries 5, 6 and 7.

The cause for this controversy has been shown to be due to the inclusion of chlorine atom in the chain-carrying process when t-butyl hypochlorite is used (16). Such inclusion is shown in Scheme 3:

Scheme 3



Thus, a stable incipient radical, like benzyl, is selective enough to discriminate between chlorine atom abstraction from molecular chlorine and t-butyl hypochlorite. It has been reported that reactions of benzylic radicals with molecular chlorine are low energy processes, and occur almost at every collision (39). However, reaction with t-butyl hypochlorite is much slower, and requires an appreciable activation energy (28).

The inclusion of chlorine atom in the chain-carrying process is observed only when the incipient radical R^\bullet in equations 9 and 16 is relatively unreactive. Walling found that the addition of trichloroethylene as a chlorine atom trap can effectively stop this competing chain (16). Furthermore, he now obtained a good agreement with the relative rates of Sakurai (16).

It was originally thought that the selectivity of t-butoxy radical in hydrogen atom abstraction was intermediate between those of chlorine and bromine atoms (28). But, in fact, the examination of the rho values for the hydrogen atom abstraction by these radicals (Table

1) indicates that t-butoxy radical is of comparable reactivity to chlorine atom. However, the low rho value might be due to the inherent lower electronegativity of the t-butoxy radical than that of chlorine atom (40), as well as a smaller amount of bond breaking in the transition state. Nevertheless, the t-butoxy radical is more reactive than bromine atom or trichloromethyl radical toward hydrogen atom abstraction. Therefore, the transition state for the hydrogen atom abstraction by this radical should certainly resemble the reactants more than that for hydrogen atom abstraction by bromine atom or trichloromethyl radical.

An additional insight into hydrogen atom abstraction is provided by primary kinetic isotope effects. Wiberg has shown that the kinetic isotope effect can be used to determine the relative amount of carbon-hydrogen bond breaking in the transition state of hydrogen atom abstraction (41,42). In general, the transition state of hydrogen atom abstraction by extremely reactive atoms (radicals) involves little bond breaking and exhibits a low primary deuterium isotope effect. As the reactivity of the radical decreases (activation energy increases), the deuterium isotope effect increases until it reaches a limit ($k_H/k_D = 7$ at approximately room temperature) (4), which corresponds to a symmetrical transition state with fifty percent bond breaking and making. Table 4 illustrates this point.

The transition state of hydrogen atom abstraction from toluene by t-butoxy radical exhibits a moderate amount of bond breaking, based on the relatively small value of k_H/k_D , and the negative rho value. However, the amount of bond breaking is more than that found in the corre-

Table 4. Primary deuterium isotope effect for hydrogen atom abstraction from toluene

Radical	T/°C	k_H/k_D	Ref.
Cl [•]	77	1.3	43
(CH ₃) ₃ CO	40	4.2	45
Ph [•]	60	4.5	19
CH ₃ [•]	164	7.9	44
Br [•]	77	4.9	42

sponding transition state for hydrogen atom abstraction by chlorine atom.

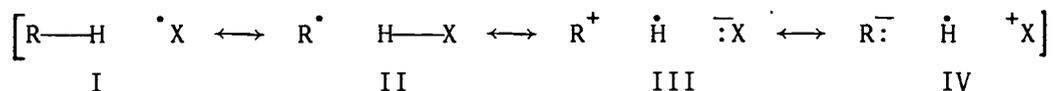
DISCUSSION OF THE PROBLEM

Earlier in the discussion, we have outlined the concept of charge development in the transition state of hydrogen atom abstractions. We have also shown that the rho values obtained for most of the radicals and atoms used were negative, and best correlations were with sigma-plus parameters.

In the early 70's, Zavitsas and Pinto argued that the rho value for hydrogen abstraction from substituted toluenes by t-butoxy radical reflects the differences in bond dissociation energies of the carbon-hydrogen bond in the substrates (46). Electron donating groups were found to weaken carbon-hydrogen bonds. Furthermore, they maintained that the postulation of partial charge separation in the transition state is unnecessary or inconsistent with the experimental observations. Zavitsas's proposal leads to the prediction that only negative rho values can be observed in hydrogen atom abstraction from toluenes by radicals (46). However, Pryor has subsequently shown that positive rho values are observed when alkyl radicals are the hydrogen atom abstracting agents. He obtained a rho value of +0.99 for hydrogen atom abstraction from substituted toluenes by t-butyl radical at 30°C (21,47). Additional examples of positive rho values involving hydrogen abstraction from substituted toluenes by other alkyl radicals have also been reported.

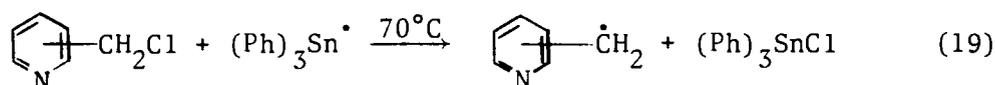
The possibility of having a positive rho value can allow for the presence of another contributing form to the resonance description of the transition state of free radical reactions. In the case of hydrogen atom abstraction, the transition state is now described by the

following:

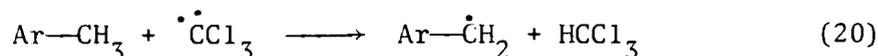


The contribution of Structure III or IV to the transition state depends on the electronic nature of the attacking radical. For electrophilic radicals (atoms), the contribution of Structure III to the transition state is predominant. It is Structure IV that predominates in the case of nucleophilic radicals.

Gleicher and Sophe-Mbang (48,49), in their work on chlorine atom abstraction from arylmethyl and heteroarylmethyl chlorides (equation 19) by triphenyltin radical at 70°C obtained a better correlation using a carbanion model rather than a radical model.

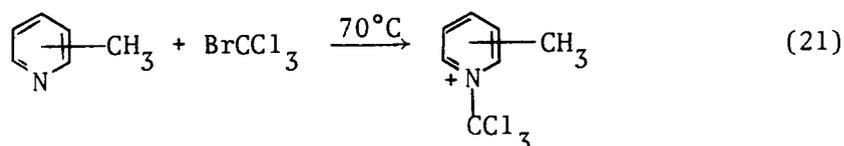


This led them to emphasize the importance of charge separation in the transition state. Earlier work by Gleicher and Unruh on hydrogen atom abstraction from unsubstituted polycyclic arylmethanes by trichloromethyl radical (equation 20) could not be treated in a similar manner (50,51).



The alternant nature of these substrates makes such an evaluation impossible since the relative stability of the arylmethyl radicals, cations and anions are proportional to each other. An attempt to investigate the hydrogen atom abstraction from heteroarylmethanes

under identical conditions was unsuccessful. The electrophilic trichloromethyl radical prefers to react in the ring rather than behaving as a hydrogen atom abstracting agent (52). This is shown in equation 21:



In view of the above results, it would be interesting to study hydrogen atom abstraction from heteroarylmethanes (methylquinolines and methylpyridines) using a radical more prone to react at the exocyclic methyl group than in the ring. The radical of choice is the t-butoxy radical derived from di-t-butyl peroxide for several reasons.

- a. The reaction of t-butoxy radical with the heteroaromatic systems in question should not lead to the quaternization of the ring nitrogen as will the reaction with bromotrichloromethane shown above.
- b. The relative rates can be determined by evaluation of t-butyl alcohol-acetone ratios and not be influenced by extraneous reactions of the substrate molecules.
- c. The t-butoxy radical can be generated from di-t-butyl peroxide rather than t-butyl hypochlorite. This will avoid any inclusion of radical reactions caused by chlorine atom.

Replacement of the CH unit of an arene with an isoelectronic nitrogen atom destroys the uniform pi electron distribution of the parent system and changes the inductive properties of the heteroaryl groups. It would be very interesting to see if simple molecular

orbital calculations can correlate the relative rates of formation of heteroarylmethyl radicals in the hydrogen atom abstraction by t-butoxy radical, and whether optimum correlation is with the carbocation, radical or carbanion model of the transition state.

RESULTS AND DISCUSSION

Reagents

All compounds used in this study were commercially available except for 5-methylquinoline. This compound was prepared from 8-chloro-5-methylquinoline (using the procedure of Yoshikawa (54)) which, in turn, was synthesized by the Skraup reaction described by Gatterman and Kaiser (53). Details on preparation and purification of compounds are found in the experimental section.

Generation of the t-Butoxy Radical

t-Butoxy radical was generated by photochemical decomposition of di-t-butyl peroxide at 70°C.

Rates of Hydrogen Atom Abstraction from

Arylmethanes by t-Butoxy Radical

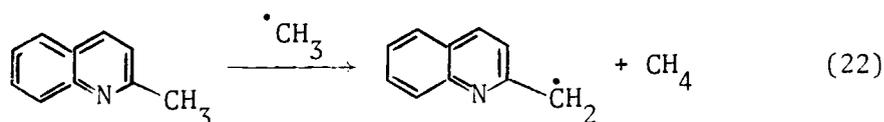
Solutions of arylmethane and di-t-butyl peroxide were prepared in approximate molar ratios of 500:1. The solutions were then equally divided among several ampoules. After being degassed by several freeze-thaw cycles, the ampoules were sealed under a reduced pressure of nitrogen. They were then placed horizontally just below the surface of an oil bath maintained at $70 \pm 1^\circ\text{C}$. Irradiation was carried out with a Ken-Rap 275 W lamp placed 22.5 cm from the surface of the oil. Reaction times varied from 32 to 72 hours which corresponds to 9 to 12 half-lives of di-t-butyl peroxide decomposition at this temperature. Long reaction times were used to have a complete decomposition of the peroxide and avoid any further decomposition during the analysis. GLC was used to determine the amount of reaction as measured by the forma-

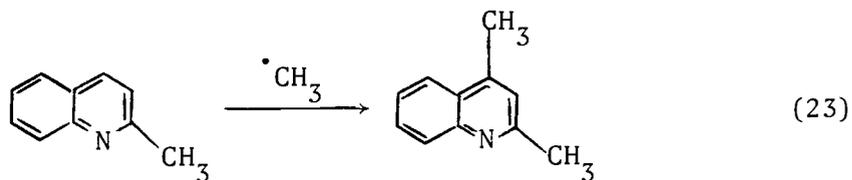
tion of acetone and t-butyl alcohol.

The GLC analysis was carried out as follows: After irradiation for the appropriate reaction time, the reaction was quenched by cooling the ampoules. They were then opened and a fixed amount of a solution of t-butyl benzene in chlorobenzene of known molarity was added. The t-butyl benzene, which acts as an internal standard, was added after photolysis because it has been shown that t-butyl benzene is one-tenth as reactive toward hydrogen atom abstraction as the substrates utilized in this study (56). The analyses were carried out on a H-P 5880A gas chromatograph equipped with a flame ionization detector. A capillary column, 12.5 m x 0.2 mm (ID) of cross-linked dimethyl silicone was employed. Hydrogen gas was used as a carrier and individual samples were analyzed in replicate.

Before the amount of t-butyl alcohol formation can be equated with the rate of hydrogen abstraction, it is necessary to make sure that all the t-butyl alcohol arises from hydrogen atom abstraction from the exocyclic methyl group of the initial substrates and not from any other reaction. Extraneous sources of t-butyl alcohol arise from the reactions of the substrate with methyl radical formed from t-butoxyl radical (equation 11). These processes are shown in Scheme 4 using 2-methylquinoline as a representative substrate.

Scheme 4

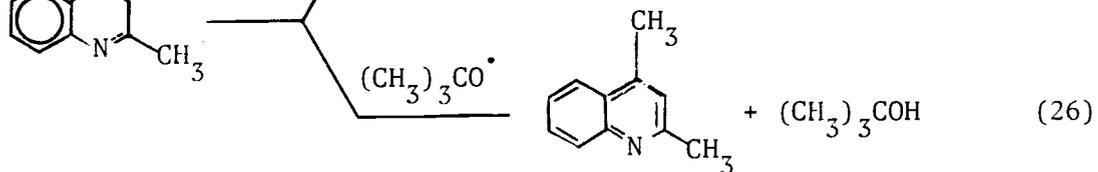
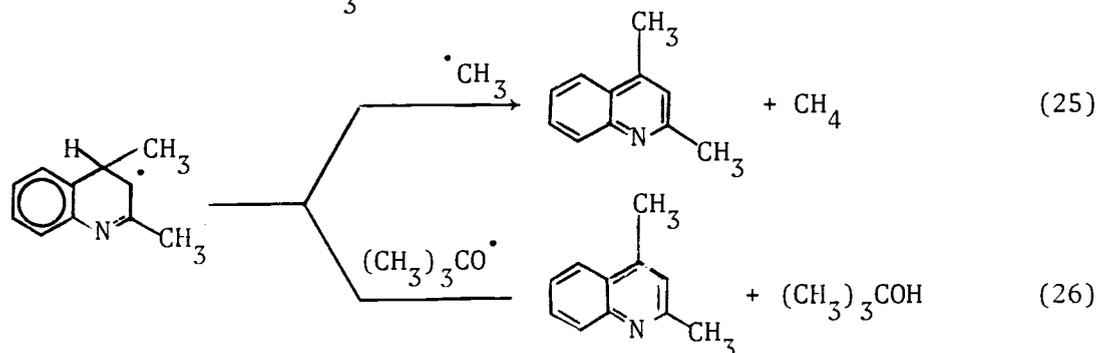
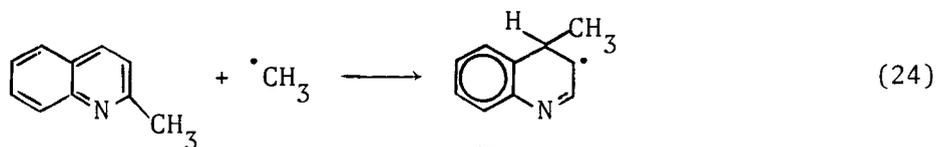




The hydrogen atom abstraction by the methyl radical (equation 22) does not interfere with our analysis since neither of the products which are determined are generated in this process. Methyl radical may also attack the aromatic substrates to produce dimethylated compounds (equation 23). Possible hydrogen atom abstraction by *t*-butoxy radical from these dimethyl compounds should not be of significance since these compounds are present in small concentrations and can never exceed 0.4 percent of the starting substrate.

A side reaction, however, which may affect the amount of *t*-butyl alcohol formed is the hydrogen atom abstraction from the intermediate leading to the formation of the dimethylarene (equation 23) as shown in Scheme 5.

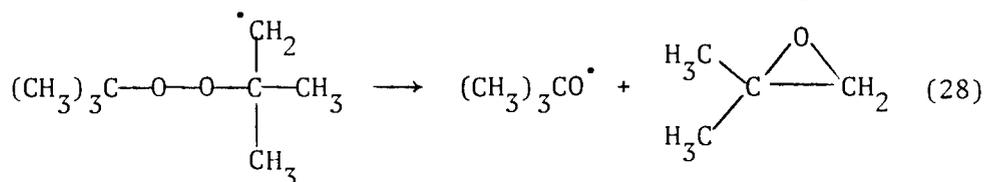
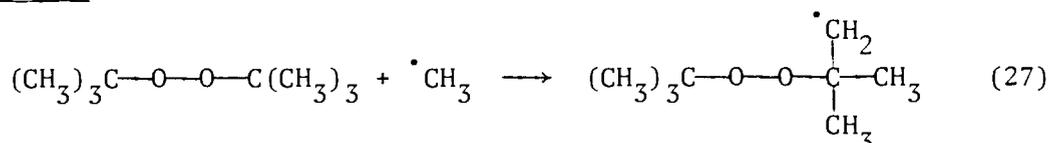
Scheme 5



To estimate an upper limit for the amount of t-butyl alcohol arising from the reaction described by equation 26, the following experiment was carried out. Quinoline was treated with di-t-butyl peroxide under our reaction conditions. This system was chosen because it is the most susceptible of the parent molecules utilized in this study to methylation (55). The ratios of t-butyl alcohol to acetone corresponding to different reaction times were determined by GLC, this is shown in Figure 4. Extrapolation of the plot of the ratios to zero time gave a value of 0.0035 ± 0.0002 for the inherent upper limit of t-butyl alcohol to acetone formed in this side reaction. This value corresponds to less than two percent of the t-butyl alcohol formed in the reaction of the least reactive system we have studied. It is felt that this is not significant.

We observed a relatively poor but constant material balance. For all the runs, the material balance was between 36 to 38 percent, based on the t-butyl alcohol and acetone formed. One of the two possible explanations for this is that potential t-butoxy radical is diverted to isobutylene oxide by an induced decomposition of the di-t-butyl peroxide as shown in Scheme 6.

Scheme 6



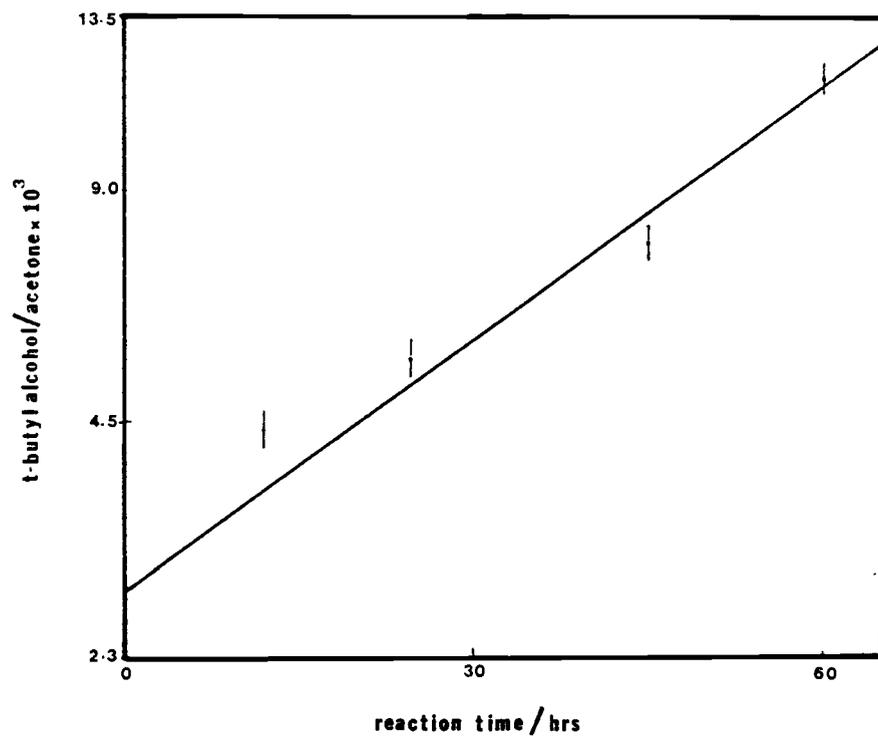
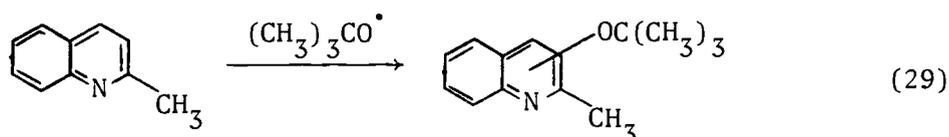


Figure 4. Ratios of t-butyl alcohol to acetone obtained in the reaction of t-butoxy radical with toluene versus time

However, such a reaction is usually observed only in the gas-phase or in neat peroxide. Furthermore, based on statistical arguments, the methyl radical would rather react with the aromatic substrate which is in 500:1 mole excess to the peroxide. The other possible rationale for low material balance is the consumption of t-butoxy radical by t-butoxylation of the aromatic substrate as shown in equation 29. This is illustrated using 2-methylquinoline as an example.



Even though there is no precedent for homolytic t-butoxylation of aromatic compounds in the literature, the hydroxylation is very well documented (25,57,58).

The ratios of t-butyl alcohol to acetone obtained for reaction of aryl and heteroarylmethanes with t-butoxy radical are presented in Table 5. The corresponding relative reactivities are found in Table 6, with toluene taken as the reference compound.

Although the reactivity range between the most and least reactive systems was only a factor of seven, very nice trends were obtained. Some of these parallel the results obtained by earlier workers. Williams and co-workers reported 1-methylnaphthalene to be 1.72 times more reactive than the 2-isomer towards t-butoxy radical at 135°C (56) and 1.67 times as reactive towards t-butoxy radical generated from t-butyl hypochlorite at 70°C (50). In the present work, 1-methylnaphthalene was found to be 1.37 times more reactive than 2-methylnaphthalene.

Table 5. Ratios of t-butyl alcohol to acetone obtained for the reaction of t-homo and heteroarylmethane with t-butoxy radical at 70°C

Compounds	$\frac{\text{t-Butyl Alcohol}}{\text{Acetone}} \times \frac{1^a}{[\text{RH}]}$	Number of Runs
Toluene	0.427 ± 0.012	5
2-Methylpyridine	0.137 ± 0.001	5
3-Methylpyridine	0.271 ± 0.005	5
4-Methylpyridine	0.097 ± 0.001	5
1-Methylnaphthalene	0.702 ± 0.086	5
2-Methylnaphthalene	0.516 ± 0.003	5
2-Methylquinoline	0.124 ± 0.001	5
3-Methylquinoline	0.353 ± 0.005	5
4-Methylquinoline	0.100 ± 0.002	5
5-Methylquinoline	0.504 ± 0.002	5
6-Methylquinoline	0.234 ± 0.020	5
7-Methylquinoline	0.356 ± 0.003	5
8-Methylquinoline	0.395 ± 0.001	5

^a Average standard deviation was less than 2%

Table 6. Relative rates of hydrogen atom abstraction from aryl and heteroarylmethanes by t-butoxy radical generated photochemically at 70°C

Compound	k_{rel}	Number of Runs
Toluene	1.000	5
2-Methylpyridine	0.321 ± 0.003	5
3-Methylpyridine	0.635 ± 0.011	5
4-Methylpyridine	0.228 ± 0.003	5
1-Methylnaphthalene	1.654 ± 0.083	5
2-methylnaphthalene	1.210 ± 0.008	5
2-Methylquinoline	0.290 ± 0.003	5
3-Methylquinoline	0.828 ± 0.012	5
4-Methylquinoline	0.234 ± 0.005	5
5-Methylquinoline	1.182 ± 0.042	5
6-Methylquinoline	0.548 ± 0.042	5
7-Methylquinoline	0.835 ± 0.007	5
8-Methylquinoline	0.927 ± 0.029	5

In the heteroarylmethane systems, the introduction of the electronegative nitrogen atom in the ring destroys the uniform pi electron distributions of the original hydrocarbon. As a result, the hydrogen atom donor ability of these substrates depends on the position of attachment of the methyl group to the ring. The present work shows that 2- and 4-methylpyridine are less reactive than 3-methylpyridine. The actual reactivities are as follows: 3-methylpyridine is 1.98 times more reactive than 2-methylpyridine which, in turn, is 1.41 times more reactive than 4-methylpyridine. Johnston and Williams have reported that 3-methylpyridine is 1.33 times more reactive than 2-methylpyridine towards *t*-butoxy radical at 110°C (27) and 1.1 times more reactive at 127°C (31). Their analysis was based on determining the amounts of coupling products formed from the intermediate pyridylmethyl species. Nababsing has found that the order of reactivities of methylpyridines towards hydrogen atom abstraction by the more nucleophilic benzyl radical was 2 > 3 > 4 (59).

The reactivity order as found in the present work shows the importance of the conjugative destabilization on the rate of formation of the heteroarylmethyl intermediate. This order of reactivities is also observed with the methylquinolines. For the substrates having the methyl group at positions that are in direct conjugation with the nitrogen atom, the order of reactivities found is 5 > 7 > 4. While for the substrates bearing the methyl group in non-conjugated positions, the order of reactivities is 8 > 3 > 6 > 2. These results again emphasize the importance of the conjugative destabilization in the transition state of hydrogen atom abstraction from heteroarylmethanes by *t*-butoxy radical.

It was mentioned earlier that the replacement of a CH unit of an arene with an isoelectronic nitrogen atom destroys the uniform pi electron distribution of the parent system and changes the inductive properties of the heteroaryl group. It would be very interesting to see if simple molecular orbital calculations can correlate the relative rates of formation of heteroarylmethyl radicals.

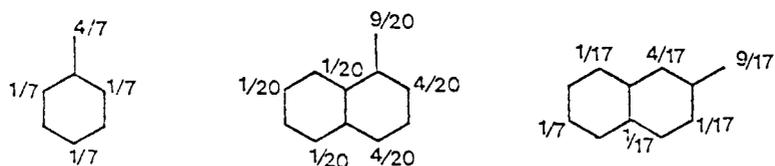
The first correlation attempted was with the PMO theory (60,65). The energy differences were calculated from equation 30 using the basic structures shown in Figure 5.

$$\Delta E_n = \beta N_i - Q_n \delta \alpha_n - \sum_r Q_r \delta \alpha'_c \quad (30)$$

Although this method gave a very poor quantitative correlation (coefficient of 0.83), it predicted the order of reactivities, Ph > 3-P >> 2-P ≈ 4-P. For the α-methylnaphthalene-type systems, the predicted reactivities are 1-N > 5-Q ≈ 8-Q >> 4-Q, and for β-methylnaphthalene-type systems 2-N > 3-Q > 6-Q > 7-Q >> 2-Q. Only in this last case is a discrepancy found with experiment as the 7-methylquinoline is found to be more reactive than its 3- and 6-isomers.

In view of these results, we attempted correlations using a more advanced molecular orbital calculation such as HMO (60) and an SCF-LCAO-MO approach (61,62,63). In the latter, the suggestion of Pople and Nesbit (64) was adopted in keeping separate orbitals for electrons of opposing spins in systems containing an odd number of electrons. The matrix elements for an SCF open shell configuration are shown in equations 31 and 32, for an electron of α-spin.

$$F_{ii} = W_{2p_i} + q_i^a(ii,ii) + \sum_{j \neq i} [(q_j^a - C_j^a)(ii,jj)] \quad (31)$$



$$\Delta E_n = \beta N_i - Q_N \delta \alpha_N - \sum Q_r \delta \alpha'_c$$

$$\alpha_N = -1$$

$$\alpha'_c = -0.35$$

Ph > 3-P >> 2-P ≈ 4-P

2-N > 3-Q ≈ 6-Q > 7-Q >> 2-Q

1-N > 5-Q ≈ 8-Q >> 4-Q

Figure 5. Correlation utilizing Perturbation Molecular Orbital Theory

$$F_{ij}^a = \beta_{ij}^{\text{core}} - P_{ij}^a(ii,jj) \quad (32)$$

The core charge is set equal to 0.5 to account for the fact that we are considering only one-half of the electrons in a given matrix. The traditional one-half has been removed from the second term of the off-diagonal matrix element since all the electron considered in the given matrix can exchange. The resonance integrals were determined at each iteration by a thermocycle suggested by Dewar (62,63). The distances employed in the thermocycle are based on linear bond order bond length relationships.

The energies of the arylmethanes were taken as being essentially those of the parent arenes. The results of the HMO calculations along with the logarithms of relative reactivities are given in Table 7. Correlation of the logarithms of relative rates of hydrogen atom abstraction versus HMO pi energy differences between the parent arenes and the arylmethyl radicals gave a very poor correlation ($r = 0.14$). Utilization of the pi energy changes were calculated by taking the difference between the parent arenes, and the arylmethyl cation was attempted. The use of this model considerably improved the correlation, the correlation coefficient increased to 0.91. This is still a mediocre correlation; however, it is a large improvement over that obtained for the radical model.

Correlations of the logarithms of the relative rates of hydrogen atom abstraction were also attempted using the corresponding energy differences obtained from the more advanced calculations mentioned earlier. The data for carbocation, radical and carbanion systems are respectively found in Tables 8, 9 and 10. The correlation utilizing

Table 7. Relative HMO pi energy^a differences between a series of aryl and heteroaryl intermediates and the parent arenes and heteroarenes along with the logarithms of the relative rates

Parent System		Arylmethyl Intermediate			$\Delta E\pi$			Log krel	
		Cation	Radical	Anion	Cation	Radical	Anion		
Benzene	8.000	8.721	8.721	8.721	0.721	0.721	0.721	0.000	
Naphthalene	13.683	1-	14.495	14.495	14.495	0.812	0.812	0.812	0.216
		2-	14.427	14.427	14.427	0.744	0.744	0.744	0.083
Pyridine	10.549	2-	11.135	11.301	11.467	0.587	0.752	0.918	-0.493
		3-	11.267	11.267	11.267	0.718	0.718	0.718	-0.197
		4-	11.109	11.280	11.450	0.560	0.731	0.901	0.643
Quinoline	16.254	2-	16.775	17.029	17.283	0.521	0.775	1.029	-0.538
		3-	16.991	16.991	16.991	0.737	0.737	0.737	-0.083
		4-	16.836	17.076	17.297	0.582	0.813	1.043	-0.631
		5-	17.013	17.073	17.134	0.759	0.819	0.880	+0.073
		6-	16.995	16.995	16.995	0.741	0.741	0.741	-0.261
		7-	16.941	17.011	17.081	0.687	0.757	0.827	-0.078
		8-	16.941	17.056	17.056	0.802	0.802	0.802	-0.033

^aAll energies in β units

Table 8. Relative SCF energy^a differences between a series of aryl and heteroarylmethyl cations and the parent arenes and heteroarenes along with the logarithms of the relative rates

	Parent Systems			Homo and Heteroarylmethyl Cation					Log k _{rel}	
	E _π	E _σ ^b	E _T	E _π	E _π ^b	E _T	ΔE _T	ΔE _π		
Benzene	8.753	22.029	30.782	11.326	25.889	37.215	6.433	2.573	0.000	
Naphthalene	14.884	40.672	55.556	1-	17.896	44.569	62.465	6.909	3.012	0.216
				2-	17.755	44.522	62.277	6.721	2.871	0.083
Pyridine	9.592	20.998	30.590	2-	11.799	24.867	36.666	6.076	2.207	-0.493
				3-	12.229	24.850	37.079	6.489	2.637	-0.197
				4-	11.504	24.914	36.418	5.828	1.912	-0.643
Quinoline	15.699	39.645	55.644	2-	18.016	43.504	61.520	5.876	2.317	-0.538
				3-	18.601	43.463	62.064	6.420	2.902	-0.082
				4-	18.015	43.554	61.569	5.925	2.316	-0.631
				5-	18.569	43.513	62.082	6.438	2.870	+0.073
				6-	18.692	43.471	62.163	6.519	2.993	-0.261
				7-	18.467	43.493	61.960	6.316	2.768	-0.078
				8-	18.831	43.529	62.360	6.716	3.132	-0.033

^aAll energies in electron volts

Table 9. Relative SCF energy^a differences between a series of aryl and heteroarylmethyl radicals and the parent arenes and heteroarenes along with the logarithms of the relative rates

	Parent Systems			Homo and Heteroarylmethyl Radical					Log k _{rel}	
	E _π	E _o ^b	E _T	E _π	E _o ^b	E _T	ΔE _T	ΔE _π		
Benzene	8.753	22.029	30.782							
Naphthalene	14.884	40.672	55.556	1-	15.484	44.857	60.341	4.785	0.600	0.216
				2-	15.422	44.812	60.234	4.678	0.538	0.083
Pyridine	9.592	20.998	30.590	2-	10.126	25.007	35.133	4.543	0.534	-0.493
				3-	10.137	25.032	35.169	4.579	0.545	-0.197
				4-	10.130	25.019	35.149	4.559	0.538	-0.643
Quinoline	15.699	39.643	55.644	2-	16.242	43.639	59.881	4.237	0.543	-0.538
				3-	16.254	43.720	59.974	4.330	0.555	-0.082
				4-	16.281	43.713	59.994	4.350	0.582	-0.631
				5-	16.313	43.777	60.090	4.446	0.614	+0.073
				6-	16.275	43.737	60.012	4.368	0.576	-0.261
				7-	16.274	43.730	60.004	4.360	0.575	-0.078
				8-	16.313	43.782	60.095	4.451	0.614	-0.033

^aAll energies in electron volts

^bWith bond length variation

Table 10. Relative SCF energy^a differences between a series of homo and heteroarylmethyl anions and the parent arenes and heteroarenes along with the logarithms of the relative rates

	Parent Systems			Homo and Heteroarylmethyl Anion					Log k _{rel}	
	E _π	E _σ ^b	E _T		E _π	E _σ ^b	E _T	ΔE _T		ΔE _π
Benzene	8.753	22.029	30.782		0.196	25.889	26.085	-4.697	-8.557	0.000
Naphthalene	14.884	40.672	55.556	1-	6.770	44.569	51.339	-4.217	-8.114	0.216
				2-	6.627	44.522	51.149	-4.407	-8.257	0.083
Pyridine	9.592	20.998	30.590	2-	1.454	24.756	26.210	-4.380	-8.138	-0.493
				3-	0.969	24.867	25.836	-4.754	-8.623	-0.197
				4-	1.586	24.749	26.335	-4.255	-8.006	-0.643
Quinoline	15.699	39.643	55.644	2-	8.026	43.399	51.425	-4.219	-7.673	-0.538
				3-	7.408	43.544	50.952	-4.692	-8.291	-0.082
				4-	8.202	43.446	51.648	-3.996	-7.497	-0.631
				5-	7.841	43.499	51.340	-4.304	-7.858	+0.073
				6-	7.401	43.508	50.909	-4.735	-8.298	-0.261
				7-	7.670	43.446	51.116	-4.528	-8.029	-0.078
				8-	7.541	43.531	51.072	-4.572	-8.158	-0.033

^aAll energy in electron volts

^bWith variation of bond lengths

the SCF radical transition state yielded a coefficient of 0.47. Although much better than that found in the corresponding HMO calculation, this is still unacceptable. The correlation based on SCF calculations for a carbocation transition state is 0.91. The correlation is illustrated in Figure 6. For both HMO and SCF calculations, correlations based on the carbocation are fairly good and much better than those based on a radical model. This is in agreement with the idea of a substantial positive charge development in the transition state and important contribution of resonance Structure III described earlier to the transition state. All the correlations discussed above are summarized in Table 11.

Correlation based on a carbanion transition state yielded poor results for both HMO and SCF calculations. The coefficients for these correlations are also presented in Table 11. These results reflect the small contribution of the resonance Structure IV to the transition state for this reaction. The fact that the correlation based on carbanion transition state yielded a much poorer correlation than that obtained with a carbocation transition state is an excellent refutation for Zavitsas's arguments that either sigma-minus or sigma-plus parameters may be used to correlate the relative rates of hydrogen atom abstraction from substituted toluenes (46).

In view of the results obtained using energy changes, which imply appreciable progress along the reaction coordinates, a correlation using a ground state parameter was felt to be in order. The charge density on those ring carbons attached to the methyl group was the chosen parameter. This is in keeping with Taylor's suggestion that charge density is the best parameter in correlating relative

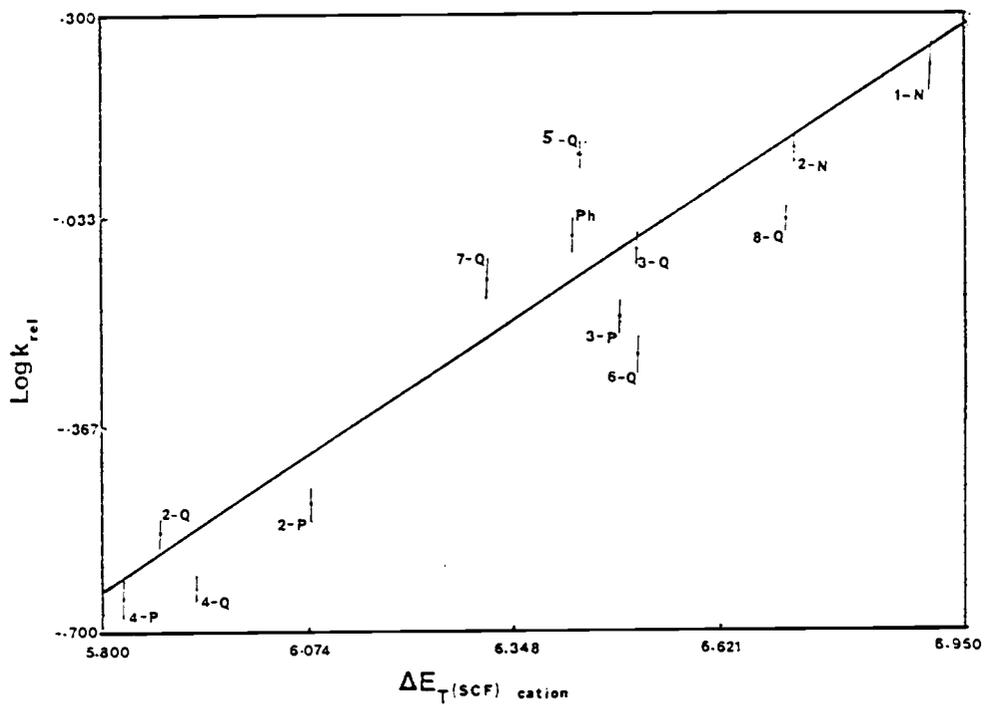


Figure 6. Logarithms of the relative rates of formation of homo and heteroarylmethyl radicals versus SCF calculated energy differences

Table 11. Correlations of the logarithms of the relative rates for hydrogen atom abstraction from homo and heteroarylmethanes by *t*-butoxy radical versus calculated parameters

Parameters	Slope	Correlation Coefficients
HMO Pi energy radical	1.027	0.14
HMO Pi energy carbanion	-1.791	0.69
HMO Pi energy carbocation	2.772	0.91
SCF pi energy radical	4.662	0.46
SCF Pi energy carbanion	-0.435	0.48
SCF total energy radical	0.855	0.49
SCF total energy carbanion	-0.466	0.39
SCF total energy carbocation	0.573	0.92
Charge densities	1.547	0.53
SCF total energy + q carbocation	1.046	0.92
SCF total energy cation + radical	1.051	0.92
SCF total energy ^{13}C chemical shift	1.039	0.92
Taylor's experimental rate data	1.144	0.97

reactivities of heterocyclic systems (66). In the heterocyclic compounds (non-alternant) the charge density at each carbon atom is no longer equal to unity as in the homocyclic compounds (alternant hydrocarbons). The poor correlation ($r = 0.53$) obtained when charge densities were used does not completely exclude partial ground state control of this reaction.

The correlations presented so far seem to indicate that there might be multiple factors which play a significant role in determining the rate of hydrogen atom abstraction. Two approaches are worth consideration. It is known that hydrogen atom abstraction by t-butoxy radical has a relatively early transition state. A correlation including not only energy changes, but also some ground state parameter might, therefore, be in order. In keeping with Taylor's suggestion (66), charge density was again considered to be the best ground state parameter to use. The second possible approach is as follows: It has been shown that hydrogen atom abstraction by t-butoxy radical exhibits polar character. Thus, any treatment of the transition state should reflect this radical-ionic dichotomy. Therefore, it might be instructive to devise an equation similar to that proposed by Yukawa and Tsumo (67) for Hammett correlation which would reflect the transition state sensitivity to both radical and carbocationic factors.

To test the above approaches, four parameter equations of the form shown in equations 33 and 34 were developed by curve-fitting the available data.

$$\text{Log } k_{\text{rel}} = A(\Delta E_T) + B q + C \quad (33)$$

$$\text{Log } k_{\text{rel}} = A(\Delta E_{\text{T}})_{\text{cat}} + B(\Delta E_{\text{T}})_{\text{rad}} + C \quad (34)$$

The values of A, B and C were calculated using the SIPS version 52 program. The final equations are as follows:

$$\text{Log } k_{\text{rel}} = 0.563 (\Delta E_{\text{T}})_{\text{rad}} + 1.893* q - 4.558 \quad (35)$$

$$\text{Log } k_{\text{rel}} = 0.742 (\Delta E_{\text{T}})_{\text{cat}} + 0.167* q - 5.080 \quad (36)$$

$$\text{Log } k_{\text{rel}} = 0.782 (\Delta E_{\text{T}})_{\text{cat}} + 0.031 (\Delta E_{\text{T}})_{\text{rad}} - 5.036 \quad (37)$$

The logarithms of the calculated relative rates from equations 36 and 37 are plotted against the logarithms of the experimental values. This is illustrated in Figures 7 and 8. The correlation utilizing radical total energy differences and charge densities was extremely poor ($r = .075$). It is significant that this is the only approach which completely ignores charge separation in the transition state of the reaction. Equally good, slightly improved correlations were found using the other two-four parameters equations.

A slightly better correlation was found from equation 36. This would correspond to a partial control of the reaction by ground state factors. The transition state, however, exhibits a substantial positive charge development. The use of energy differences-charge density double correlation to treat problems in heterocyclic reactivity has been recommended by Gleicher for systems having a relatively early transition state (68). Pryor has also suggested that radical processes be generally treated by a composite model with significant ground state contribution (21). More recently, the correlation of some extremely rapid thiyl radical addition reactions have been treated by a combined transition state-ground state rationale (69).

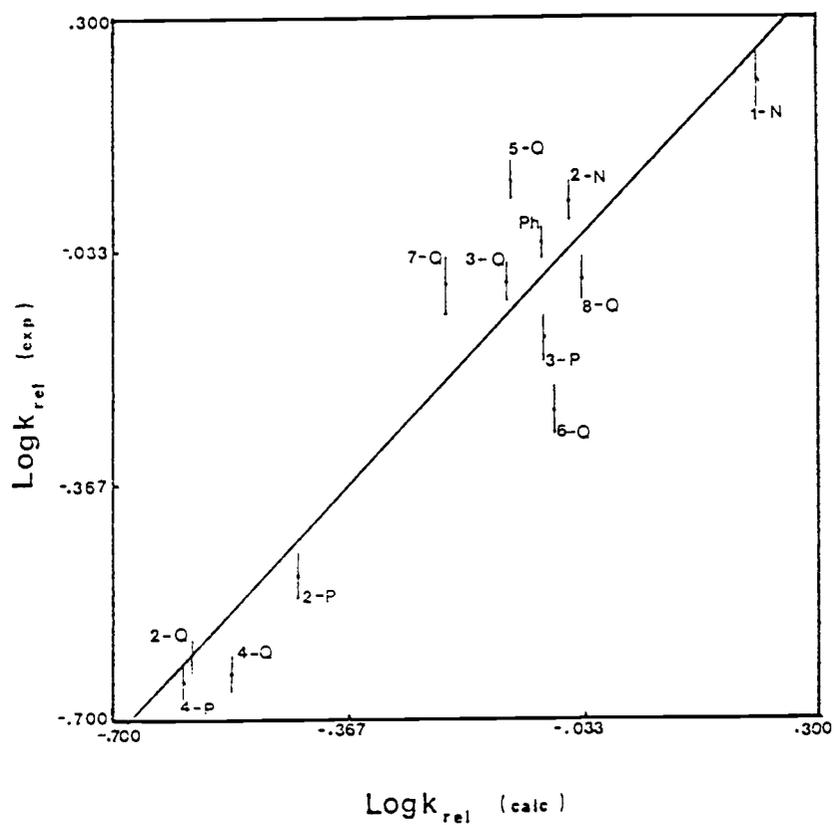


Figure 7. Logarithms of the relative rates of formation of homo and heteroarylmethyl radicals versus logarithms of the calculated relative rates using a four parameter equation

$$\Delta E_{\text{T cat}} \quad \text{and} \quad q$$

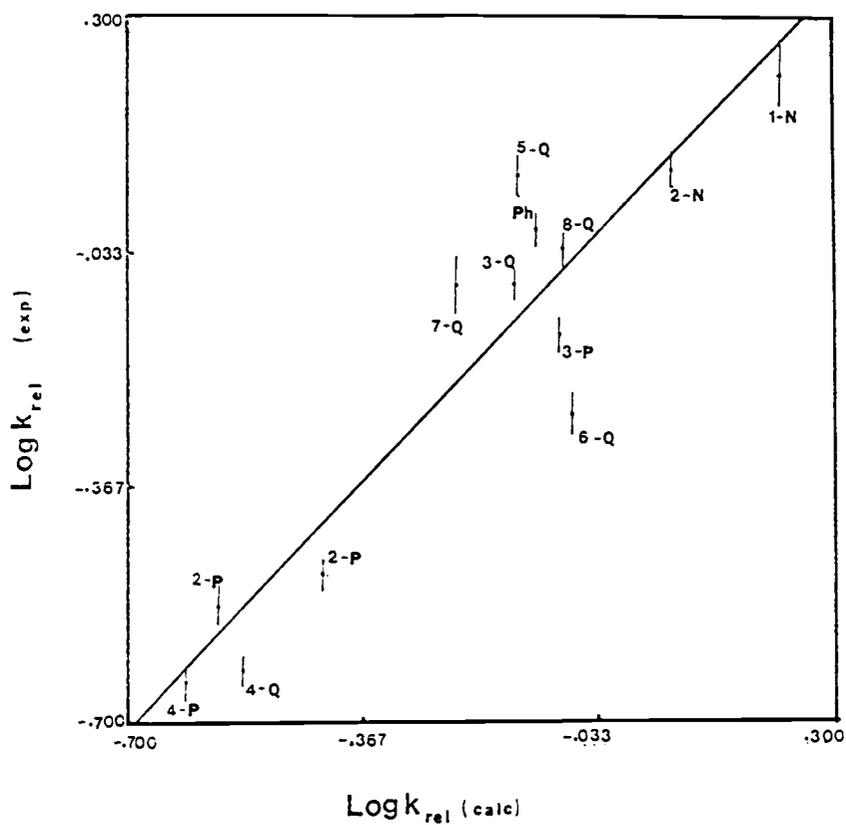


Figure 8. Logarithms of the relative rates of formation of homo and heteroarylmethyl radical versus logarithms of the calculated relative rates using a four parameter equation

$$\Delta E_{T_{cat}} \quad \text{and} \quad \Delta E_{T_{rad}}$$

Although the radical-cation dichotomy discussed above implies sizable contributions by both contributing forms to the transition state hybrid, this need not be the case. Equation 37 indicates a very modest contribution of Structure II relative to Structure III to the transition state hybrid.

A four parameter correlation utilizing a transition state parameter and an experimental ground state parameter was also attempted. The chosen parameters were SCF total energy for a cationic transition state and ^{13}C chemical shift for the ring carbon attached to the methyl group. The equation obtained is shown below.

$$\text{Log } k_{\text{rel}} = 0.712 (\Delta E_{\text{T}})_{\text{cat}} + 0.003 (\delta^{13}\text{C}) - 4.283 \quad (38)$$

Even though a fairly good correlation was obtained ($r = 0.92$), the equation shows a very small dependency of the rate of formation of arylmethyl intermediates on the chosen ground state parameter. The logarithms of the calculated relative rates are plotted against the experimental values. This is shown in Figure 9.

Unfortunately, the amount of pertinent experimental data in the literature dealing with the formation of heteroarylmethyl intermediates is rather limited. Such data would be useful for purposes of comparison with that obtained in the present study. One very good example, however, does exist. Taylor et al. have published a series of papers on the pyrolysis of 1-homoaryl and 1-heteroarylethyl acetates (66,70,71). The transition state for this reaction involves appreciable generation of carbocation character at the benzylic position. This is shown in equation 39.

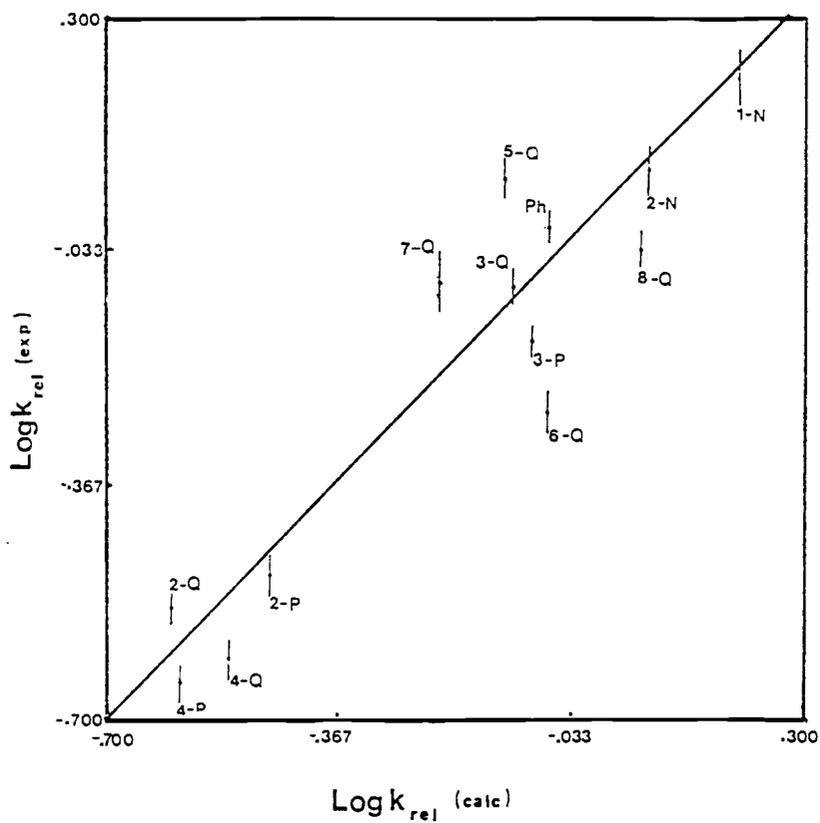
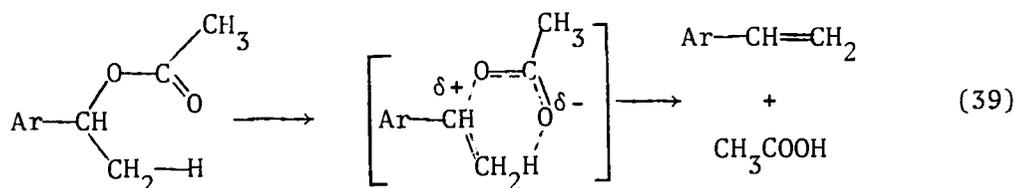


Figure 9. Logarithms of the relative rates of formation of homo and heteroarylmethyl radicals versus logarithms of the calculated relative rates using a four parameter equation

$$\Delta E_{T_{\text{cat}}} \quad \text{and} \quad \delta_{13\text{C}}$$



T.S.

When the logarithms of the relative reactivities for this reaction are correlated with those obtained in the present study, a good correlation is obtained. The value of the correlation coefficient is 0.97. This is the best obtained to date. The logarithms of the relative rates of hydrogen atom abstraction may be plotted against the logarithms of relative rates for the pyrolysis. This is shown in Figure 10. The two sets of relative rates are presented in Table 12. The fact that optimum correlation is obtained when the data for hydrogen atom abstraction is correlated with that for another reaction, rather than some theoretical model, suggests that factors not taken into account by the calculations may be playing some role. These may include peri steric interactions, which could affect the 4, 5 and 8 position in quinoline as well as the 1 position in naphthalene and through space electronic interactions, which would be particularly important for the 2 position in pyridine and the 2 and 8 positions in quinoline. Despite these possible uncertainties, we feel very confident about the results obtained in this study, which for the first time involved a complete series of heteroarylmethanes undergoing a radical reaction. We have also shown that there is an appreciable charge development in the transition state, and the resonance Structure III is the most important contributor to the transition state of hydrogen atom abstraction by t-butoxy radical.

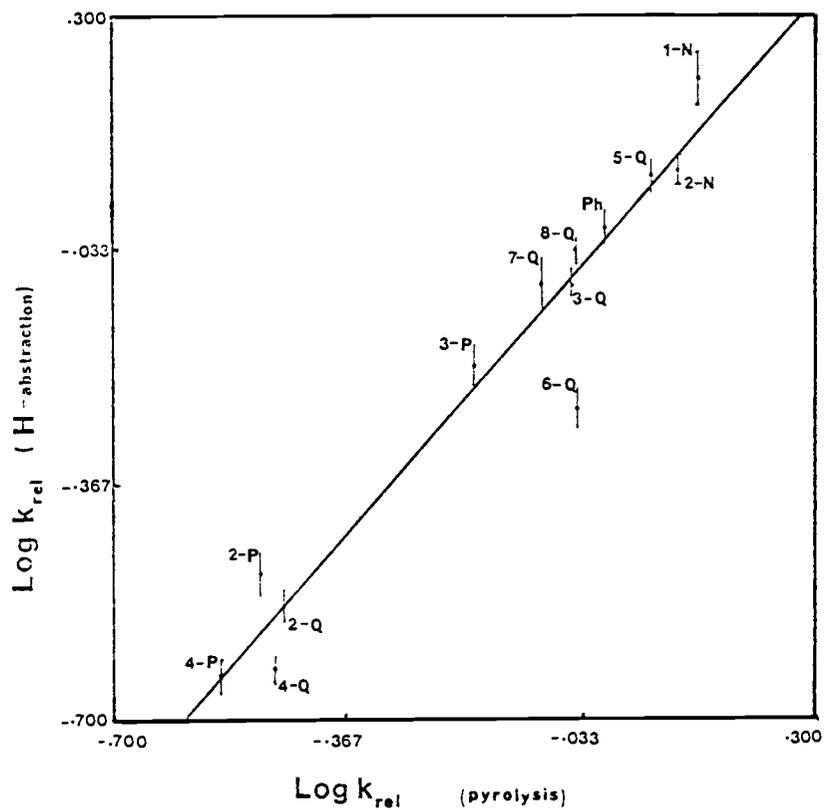


Figure 10. Logarithms of the relative rates of formation of homo and heteroarylmethyl radical versus logarithms of the relative rates of pyrolysis of the corresponding l-arylethyl acetates

Table 12. Logarithms of the relative rates of hydrogen atom abstraction and the logarithms of the relative rates of pyrolysis

Compounds	$\log k_{\text{rel}}^{\text{H-abs}}$	$\text{Log } k_{\text{rel}}^{\text{pyro}}$
Toluene	0.000	0.000
2-methylpyridineene	-0.493	-0.490
3-methylpyridine	-0.197	-0.185
4-methylpyridine	-0.643	-0.545
1-methylnaphthalene	0.216	0.133
2-methylnaphthalene	0.083	0.106
2-methylquinoline	-0.538	-0.460
3-methylquinoline	-0.082	-0.050
4-methylquinoline	-0.631	-0.470
5-methylquinoline	+0.073	+0.068
6-methylquinoline	-0.261	-0.040
7-methylquinoline	-0.078	-0.090
8-methylquinoline	-0.033	-0.040

EXPERIMENTAL

Gas-liquid chromatography analyses were carried out with an H-P 5880A gas chromatograph equipped with a flame ionization detector. The capillary column used in this investigation was a 12 m x 0.2 mm column of dimethyl cross-silicone. The carrier gas was hydrogen. Nuclear magnetic spectra were taken on a Varian FT-80 instrument using tetramethylsilane as a reference and deuteriochloroform as the solvent.

ProceduresPurification of Reagents

The purity of all the reagents was checked by gas chromatography and was greater than 99%.

Purification of di-t-butyl peroxide. Commercial di-t-butyl peroxide (Fluka) was dried over magnesium sulfate (granular). It was then distilled under vacuum, the fraction boiling at 31°C at 67 torr being collected. The di-t-butyl peroxide was kept under dried argon and stored at freezer temperature.

Purification of chlorobenzene. Commercial chlorobenzene (Aldrich) was washed twice with one-tenth of its volume of concentrated sulfuric acid. The temperature was kept below 20°C. It was then washed thoroughly with water and finally, with 10% sodium bicarbonate. After drying over calcium chloride, it was distilled and the fraction boiling at 130-133°C was collected. This fraction was then fractionally distilled under nitrogen and the fraction boiling at 131-132°C was collected and kept under nitrogen.

Purification of t-butylbenzene. t-Butylbenzene from Aldrich was washed twice with one-tenth of its volume of concentrated sulphuric acid. The temperature was kept below 20°C. The t-butylbenzene was then washed with water and 10% sodium bicarbonate. After drying over calcium chloride it was distilled and the fraction boiling at 167-170°C was collected. This fraction was then subjected to a fractional distillation under nitrogen and the fraction boiling at 168-169°C was collected and kept under nitrogen.

Purification of 1-methylnaphthalene. 1-Methylnaphthalene (Milwaukee) was dried over calcium chloride then distilled under vacuum. The fraction boiling at 106-108°C at 10 torr was collected. Then it was fractionally distilled under vacuum and the fraction boiling at 106.5-108°C at 10 torr was collected and stored under nitrogen.

Purification of 2-methylnaphthalene. Commercial 2-methylnaphthalene (Matheson) was recrystallized twice from absolute methanol and dried in an Aberhalden pistol. It was then fractionally distilled under vacuum with the fraction boiling at 103-104°C at 10 torr being collected.

Purification of 2-methylquinoline. 2-Methylquinoline (Aldrich) was refluxed over barium oxide for 24 hours, then was vacuum-distilled from zinc powder. The fraction boiling at 74.5-75°C at 1.5 torr was collected and kept under nitrogen.

Purification of 3-methylquinoline. 3-Methylquinoline from Aldrich was used without further purifications.

Purification of 4-methylquinoline. 4-Methylquinoline (Aldrich) was dried over magnesium sulphate granular overnight. It was then refluxed for 12 hours over barium oxide and finally vacuum-distilled

from zinc powder. The fraction boiling at 93-94°C at 1 torr was collected and kept under nitrogen.

Purification of 6-methylquinoline. 6-Methylquinoline (Aldrich) was refluxed gently over barium oxide for 12 hours. It was then vacuum-distilled from zinc powder. The fraction boiling at 74°C at 0.7 torr was collected and kept under nitrogen.

Purification of 7-methylquinoline. 7-Methylquinoline (Aldrich) was dried over calcium chloride. It was then refluxed for 12 hours over barium oxide and vacuum-distilled from zinc powder. The fraction boiling at 70-71°C at 1.5 torr was collected and stored under nitrogen.

Purification of 8-methylquinoline. 8-Methylquinoline (Aldrich) was dried over calcium chloride. It was then refluxed for 12 hours over barium oxide and vacuum-distilled from zinc powder. The fraction boiling at 70-71°C at 1.5 torr was collected and stored under nitrogen.

Purification of toluene. Commercial toluene (Baker) was washed three times with one-tenth of its volume of concentrated sulphuric acid. The temperature was kept below 30°C. It was then washed thoroughly with water and 10% sodium bicarbonate. After drying over calcium chloride, it was distilled from calcium hydride under nitrogen. The fraction boiling at 110.5-112°C was collected and kept under nitrogen.

Purification of 2-methylpyridine. Commercial 2-methylpyridine (Reilly Tar & Chemical) was fractionally distilled under nitrogen and the fraction boiling at 123-127°C was collected. To this fraction was added 10% of its volume of 20% sulphuric acid. This material was steam distilled to remove hydrocarbons. Approximately 10% of the 2-methylpyridine also distilled over. The remaining material was basified by

adding solid sodium hydroxide and the organic layer separated. The aqueous layer was extracted three times with ether. The ether portions were combined with the organic layer. After evaporation of the ether, the 2-methylpyridine was dried over calcium chloride for two days. It was then refluxed for 24 hours over barium oxide and then distilled under nitrogen. The fraction boiling at 126-127°C was collected and kept under nitrogen.

Purification of 3-methylpyridine. Commercial 3-methylpyridine (Reilly Tar & Chemical) was fractionally distilled and the fraction boiling at 140-145°C was collected. To this fraction was added 10% of its volume of sulphuric acid. This material was distilled to remove hydrocarbons. Approximately 5% of the 3-methylpyridine also distilled over. The remaining material was basified by adding solid sodium hydroxide and the organic layer was separated. The aqueous layer was extracted with three portions of ether, which were then combined with the organic layer and dried over magnesium sulfate for two days. After removal of the ether, the 3-methylpyridine was refluxed for one day over barium oxide and then fractionally distilled under nitrogen. The fraction boiling at 138-139°C was collected and kept under nitrogen.

Purification of 4-methylpyridine. Commercial 4-methylpyridine (Reilly Tar & Chemical) was purified according to the method described for the 2- and 3-methylpyridines. The fraction boiling at 143-144°C was collected and kept under nitrogen.

Purification of quinoline. Commercial quinoline (Aldrich) was dried over sodium sulfate for two days, then refluxed for 12 hours over barium oxide. The dried quinoline was vacuum-distilled from zinc powder and the fraction boiling at 110°C at 16 torr was collected and

kept under nitrogen.

Preparation of 8-chloro-5-methylquinoline. 4-Chloro-3-amino-toluene was converted to 8-chloro-5-methylquinoline by a Skramp reaction described by Gatterman and Kaiser (53). To a mixture of 32 g of glycerol and 10 g of nitrobenzene, 18 g of 4-chloro-3-aminotoluene was added in a dropwise manner. To this well-stirred mixture, 30 g of concentrated sulphuric acid was added dropwise over a period of 90 minutes. The mixture was allowed to stand over night and then heated gently for one hour (after 30 minutes, the dark black color appeared). After additional refluxing for six hours at higher temperature, water was added and the mixture was steam-distilled to remove the unreacted nitrobenzene. The remaining material was basified with 6 N sodium hydroxide and steam-distilled to yield 12.5 g of material. An NMR spectrum showed both product and unreacted starting material in 5:2 ratio.

Preparation of 5-methylquinoline. The 8-chloro-5-methylquinoline was hydrodechlorinated without further purification by the method of Yoshikawa (54). A solution of 4.0 g of 8-chloro-5-methylquinoline in 150 ml of 10% potassium hydroxide in methanol was hydrogenated over 250 g of 10% palladium on carbon for four hours. The mixture was then filtered through celite. The filtrate was then diluted with 300 ml of water and extracted with 150 ml of chloroform. The chloroform layer was thoroughly washed with water and dried over calcium chloride over night. A red-brown oil (3.15 g) was obtained after evaporation of the solvent. This procedure was then repeated twice and a total of 9.27 g of material was collected.

Purification of 5-methylquinoline. The major impurity in the above mixture is m-toluidine which was removed by fractional vacuum distillation (BP 89°C at 7 torr). The remaining material was fractionally vacuum-distilled from zinc dust with the fraction boiling at 114°C at 7 torr being collected. The purity was checked by GLC which showed 98.5% of a single component. The proton NMR consisted of a singlet at 2.64 δ and a very complex multiplet at 7.41 δ , a doublet at 7.93 δ , a doublet at 8.25 δ , and finally, a doublet at 8.86 δ . This agrees with the spectrum reported in the literature.

Determination of Relative Rates of Hydrogen Atom Abstraction Procedure for the Determination of the Relative Rates of Hydrogen Atom Abstraction by t-Butoxy Radical

Solutions of the arylmethanes and di-t-butyl peroxide were prepared in the approximate molar ratio of 500:1. These solutions were equally divided into ampoules. After a series of freeze and thaw cycles, the ampoules were sealed under a reduced pressure of nitrogen. They were then placed horizontally just below the surface of a constant temperature oil bath maintained at $70 \pm 1^\circ\text{C}$. Kinetic runs were initiated photochemically with a Ken-Rap 275 W sunlamp placed 22.5 cm from the surface of the oil. Reaction time varied from 32 to 72 hours, which corresponds to between 9 to 12 half-lives of the di-t-butyl peroxide. After completion of the reaction, the ampoules were cooled and opened. Then, 20 ml of a solution of t-butylbenzene in chlorobenzene of known molarity was added quickly to the open ampoule. The material was then transferred rapidly to a vial equipped with a serum septum. The reaction mixture was analyzed for the formation of

acetone and t-butyl alcohol via GLC using t-butylbenzene as the internal standard. All determinations were run in replicate. The amounts of acetone and t-butyl alcohol formed were determined by equations 40 and 41, respectively. The internal standard is represented by I.S. and the correction factors F_i were determined from solutions of known concentrations under the analytical conditions.

$$\text{moles acetone} = \frac{\% \text{Area acetone peak}}{\% \text{Area I.S. peak}} \times F_{\text{acetone}} \times (\text{moles I.S.}) \quad (40)$$

$$\text{moles } \underline{t}\text{-BuOH} = \frac{\% \text{Area } \underline{t}\text{-BuOH peak}}{\% \text{Area I.S.}} \times F_{\underline{t}\text{-BuOH}} \times (\text{moles I.S.}) \quad (41)$$

The ratio of t-butyl alcohol to acetone can be directly related to the labilities of the hydrogen atoms in the substrates. The detailed experimental data for these reactions are found in the Appendix. The concentrations of the aryl and heteroarylmethanes needed in equations 40 and 41 were determined by measuring the densities of the reaction mixture at 70°C.

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APPENDIX

Table 13. Reaction of toluene with t-butoxy radical at 70°C

GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	<u>t</u> -butanol Acetone	<u>t</u> -butanol Acetone x $\frac{1}{[RH]}$
1a	5.445	1.417	3.842	0.432
1b	5.417	1.497	3.620	0.407
2a	5.637	1.503	3.750	0.422
2b	5.640	1.494	3.776	0.425
3a	5.595	1.511	3.703	0.417
3b	5.671	1.520	3.730	0.420
4a	5.946	1.513	3.930	0.442
4b	6.711	1.680	3.995	0.449
5a	6.014	1.588	3.787	0.426
5b	5.943	1.569	3.788	0.426
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[RH]} = 0.427 \pm 0.012$				

[RH] = 8.891 M

Conditions

di-t-butyl peroxide: 1.334 x 10⁻⁴ moles

70 ± 1°C

48 hours

Table 14. Reaction of 2-methylpyridine with t-butoxy radical at 70°C

[RH] = 9.539 M		Conditions		
di- <u>t</u> -butyl peroxide: 1.402×10^{-4} moles		70 ± 1°C		
		72 hours		
GC run	<u>t</u> -butanol x 10 ⁴ mmoles	Acetone x 10 ⁴ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$
1 ^a	2.170	1.629	1.332	0.140
1 ^b	2.258	1.703	1.326	0.139
2 ^a	2.257	1.739	1.298	0.136
2 ^b	2.211	1.699	1.301	0.136
3 ^a	2.244	1.724	1.302	0.137
3 ^b	2.244	1.867	1.304	0.137
4 ^a	2.137	1.645	1.299	0.136
4 ^b	2.246	1.722	1.304	0.137
5 ^a	2.146	1.649	1.301	0.136
5 ^b	2.202	1.690	1.303	0.137
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]} = 0.137 \pm 0.001$				

Table 15. Reaction of 3-methylpyridine with t-butoxy radical at 70°C

[RH] = 9.735 M		Conditions		
di- <u>t</u> -butyl peroxide: 1.265×10^{-4} moles		70 \pm 1°C		
		72 hours		
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$
1a	5.059	1.923	2.630	0.270
1b	4.849	1.847	2.626	0.270
2a	5.153	1.967	2.620	0.269
2b	5.076	1.934	2.625	0.270
3a	4.550	1.743	2.611	0.268
3b	4.955	1.896	2.613	0.268
4a	4.466	1.720	2.596	0.267
4b	4.761	1.836	2.593	0.266
5a	5.098	1.923	2.651	0.272
5b	5.436	2.057	2.643	0.272
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]} = 0.271 \pm 0.005$				

Table 16. Reaction of 4-methylpyridine with t-butoxy radical at 70°C

[RH] = 9.337 M		Conditions			
di- <u>t</u> -butyl peroxide: 1.338×10^{-4} moles		70 ± 1°C			
		72 hours			
GC run	<u>t</u> -butanol x 10 ⁶ mmoles	Acetone x 10 ⁶ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1 ^a	9.012	9.912	0.909	0.097	
1 ^b	8.066	8.838	0.913	0.098	
2 ^a	8.775	9.543	0.920	0.099	
2 ^b	6.732	7.340	0.917	0.098	
3 ^a	7.081	7.931	0.893	0.096	
3 ^b	7.124	8.015	0.889	0.095	
4 ^a	6.998	7.728	0.906	0.097	
4 ^b	7.115	7.839	0.908	0.097	
5 ^a	8.066	8.933	0.903	0.097	
5 ^b	8.261	9.130	0.905	0.097	
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]} = 0.271 \pm 0.005$					

Table 17. Reaction of 1-methylnaphthalene with t-butoxy radical at 70°C

[RH] = 6.181 M					Conditions
di- <u>t</u> -butyl peroxide: 1.416×10^{-4} moles					70 ± 1°C
					32 hours
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ⁴ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1a	1.897	4.095	4.633	0.680	
1b	1.108	2.474	4.480	0.659	
2a	3.051	5.997	5.086	0.747	
2b	2.597	5.960	4.357	0.705	
3a	1.781	4.123	4.320	0.699	
3b	1.369	2.704	5.625	0.743	
4a	1.287	2.932	4.388	0.710	
4b	1.129	2.639	4.277	0.692	
5a	1.630	3.457	4.717	0.693	
5b	2.012	4.288	4.692	0.689	
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$					= 0.702 ± 0.026

Table 18. Reaction of 2-methylnaphthalene with t-butoxy radical at 70°C

[RH] = 9.725 M					Conditions
di- <u>t</u> -butyl peroxide: 9.369×10^{-5} moles					70 ± 1°C
					48 hours
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ⁴ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1 ^a	3.609	10.304	3.502	0.521	
1 ^b	3.463	9.909	3.495	0.520	
2 ^a	3.540	10.178	3.478	0.517	
2 ^b	3.539	10.133	3.492	0.519	
3 ^a	4.253	12.369	3.438	0.511	
3 ^b	2.996	8.699	3.444	0.512	
4 ^a	2.358	6.786	3.475	0.517	
4 ^b	2.391	6.889	3.470	0.516	
5 ^a	3.457	10.003	3.456	0.514	
5 ^b	3.492	10.100	3.458	0.514	
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$					$= 0.516 \pm 0.003$

Table 19. Reaction of 2-methylquinoline with t-butoxy radical at 70°C

[RH] = 6.922 M		Conditions			
di- <u>t</u> -butyl peroxide: 6.633×10^{-5} moles		70 ± 1°C			
		72 hours			
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1a	2.716	2.223	1.221	0.177	
1b	3.262	2.808	1.162	0.168	
2a	3.111	3.556	0.875	0.126	
2b	3.246	3.728	0.871	0.126	
3a	3.065	3.600	0.851	0.123	
3b	3.319	3.889	0.854	0.123	
4a	3.127	3.640	0.859	0.124	
4b	3.297	3.844	0.858	0.124	
5a	2.936	3.432	0.856	0.124	
5b	3.008	3.521	0.854	0.123	
Average		$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]} = 0.124 \pm 0.001$			

Table 20. Reaction of 3-methylquinoline with t-butoxy radical at 70°C

[RH] = 7.063 M		Conditions			
di- <u>t</u> -butyl peroxide: 5.197×10^{-5} moles		70 ± 1°C			
		72 hours			
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1 ^a	3.763	1.493	2.520	0.357	
1 ^b	3.708	1.489	2.524	0.357	
2 ^a	3.535	1.389	2.546	0.360	
2 ^b	3.543	1.391	2.548	0.361	
3 ^a	3.553	1.434	2.478	0.351	
3 ^b	3.506	1.412	2.483	0.352	
4 ^a	3.572	1.454	2.457	0.348	
4 ^b	3.659	1.486	2.462	0.349	
5 ^a	3.690	1.494	2.471	0.350	
5 ^b	3.611	1.464	2.471	0.349	
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$ = 0.353 ± 0.005					

Table 21. Reaction of 4-methylquinoline with t-butoxy radical at 70°C

[RH] = 7.097 M		Conditions			
di- <u>t</u> -butyl peroxide: 1.012×10^{-4} moles		70 ± 1°C			
		72 hours			
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1a	5.368	7.324	0.733	0.103	
1b	5.334	7.296	0.731	0.103	
2a	7.819	11.548	0.677	0.095	
2b	7.652	11.023	0.694	0.098	
3a	7.276	10.397	0.700	0.099	
3b	7.428	10.450	0.705	0.099	
4a	8.001	11.296	0.708	0.100	
4b	8.313	11.620	0.715	0.101	
5a	7.729	10.912	0.708	0.100	
5b	7.574	10.628	0.713	0.100	
Average		$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]} = 0.100 \pm 0.002$			

Table 22. Reaction of 5-methylquinoline with t-butoxy radical at 70°C

[RH] = 7.170 M					Conditions
di- <u>t</u> -butyl peroxide: 6.975×10^{-5} moles					70 ± 1°C
					72 hours
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ⁴ mmoles	<u>t</u> -butanol Acetone	<u>t</u> -butanol Acetone	x $\frac{1}{[RH]}$
1a	4.719	1.314	3.591		0.501
1b	5.103	1.420	3.594		0.501
2a	3.558	0.982	3.623		0.505
2b	3.960	1.093	3.623		0.505
3a	4.920	1.362	3.613		0.504
3b	5.101	1.410	3.618		0.505
4a	3.936	1.085	3.628		0.506
4b	4.094	1.127	3.633		0.507
5a	4.670	1.299	3.618		0.505
5b	4.719	1.304	3.619		0.505
Average $\frac{\text{t-butanol}}{\text{Acetone}}$ x $\frac{1}{[RH]}$ =					0.504 ± 0.002

Table 23. Reaction of 6-methylquinoline with t-butoxy radical at 70°C

[RH] = 7.106 M		Conditions			
di- <u>t</u> -butyl peroxide: 8.138×10^{-5} moles		70 ± 1°C			
		72 hours			
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1 ^a	2.171	1.236	1.756	0.247	
1 ^b	2.213	1.236	1.790	0.252	
2 ^a	1.982	1.192	1.662	0.234	
2 ^b	2.045	1.232	1.660	0.234	
3 ^a	1.709	1.1629	1.470	0.207	
3 ^b	1.784	1.713	1.521	0.214	
4 ^a	2.064	1.182	1.746	0.246	
4 ^b	1.961	1.129	1.738	0.245	
5 ^a	2.634	1.531	1.721	0.242	
5 ^b	2.934	1.962	1.734	0.244	
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$ = 0.234 ± 0.002					

Table 24. Reaction of 7-methylquinoline with t-butoxy radical at 70°C

[RH] = 7.012 M					Conditions
di- <u>t</u> -butyl peroxide: 7.386×10^{-5} moles					70 ± 1°C
					72 hours
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	<u>t</u> -butanol Acetone	<u>t</u> -butanol Acetone	x $\frac{1}{[RH]}$
1a	3.213	1.269	2.531		0.361
1b	3.686	1.463	2.519		0.359
2a	2.969	1.202	2.470		0.352
2b	3.160	1.265	2.467		0.356
3a	3.230	1.289	2.506		0.357
3b	3.093	1.239	2.496		0.356
4a	3.216	1.301	2.472		0.353
4b	3.240	1.312	2.470		0.352
5a	3.368	1.347	2.500		0.357
5b	3.445	1.377	2.503		0.357
Average $\frac{\text{t-butanol}}{\text{Acetone}}$ x $\frac{1}{[RH]}$ =					0.356 ± 0.003

Table 25. Reaction of 8-methylquinoline with t-butoxy radical at 70°C

[RH] = 7.207 M					Conditions
di- <u>t</u> -butyl peroxide: 6.223×10^{-5} moles					70 ± 1°C
					72 hours
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ⁴ mmoles	<u>t</u> -butanol Acetone	<u>t</u> -butanol Acetone	$\frac{1}{[RH]}$
1a	4.017	1.414	2.840		0.394
1b	4.212	1.482	2.842		0.394
2a	2.925	1.026	2.852		0.395
2b	3.782	1.326	2.852		0.395
3a	6.005	2.1024	2.856		0.396
3b	6.005	2.103	2.855		0.396
4a	5.758	2.107	2.856		0.396
4b	5.743	2.010	2.858		0.396
5a	5.722	2.104	2.842		0.394
5b	5.687	2.002	2.841		0.394
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[RH]}$					$= 0.3953 \pm 0.001$

Table 26. Reaction of quinoline with t-butoxy radical at 70°C for 12 hours

GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$
1a	0.0869	1.7329	0.0502	0.0062
1b	0.0722	1.4993	0.0482	0.0060
2a	0.0868	1.8003	0.0482	0.0060
2b	0.0834	1.7618	0.0474	0.0059
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]} = 0.0060 \pm 0.0001$				

[RH] = 8.027 M

di-t-butyl peroxide: 1.245×10^{-4} moles

Conditions

70 ± 1°C

12 hours

Table 27. Reaction of quinoline with t-butoxy radical at 70°C for 24 hours

[RH] = 8.027 M					Conditions
di- <u>t</u> -butyl peroxide: 1.245×10^{-4} moles					70 ± 1°C
					24 hours
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$	
1a	0.1287	2.3824	0.0540	0.0067	
1b	0.1312	2.4029	0.0546	0.0068	
2a	0.1146	2.1962	0.0522	0.0065	
2b	0.1126	2.0934	0.0538	0.0067	
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$					= 0.0067 ± 0.0001

Table 28. Reaction of quinoline with t-butoxy radical at 70°C for 45 hours

[RH] = 8.027 M		Conditions		
di- <u>t</u> -butyl peroxide: 1.245×10^{-4} moles		70 ± 1°C		
		45 hours		
GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	$\frac{\text{t-butanol}}{\text{Acetone}}$	$\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]}$
1 ^a	0.1501	1.9281	0.0779	0.0097
1 ^b	0.1468	1.8920	0.0776	0.0097
2 ^a	0.1540	2.0192	0.0763	0.0095
2 ^b	0.1874	2.4321	0.0771	0.0096
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[\text{RH}]} = 0.0096 \pm 0.0001$				

Table 29. Reaction of quinoline with t-butoxy radical at 70°C for 60 hours

GC run	<u>t</u> -butanol x 10 ³ mmoles	Acetone x 10 ³ mmoles	<u>t</u> -butanol Acetone	<u>t</u> -butanol Acetone x $\frac{1}{[RH]}$
1 ^a	0.2130	1.9662	0.1083	0.0135
1 ^b	0.2171	2.0187	0.1075	0.0134
2 ^a	0.2174	2.0209	0.1076	0.0134
2 ^b	0.2153	2.0172	0.1068	0.0133
Average $\frac{\text{t-butanol}}{\text{Acetone}} \times \frac{1}{[RH]} = 0.00134 \pm 0.00001$				

[RH] = 8.027 M

Conditions

di-t-butyl peroxide: 1.245 x 10⁻⁴ moles

70 ± 1°C

60 hours