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Chemistry of the *tert*-Butyl Radical: Polar Character, ρ Value for Reaction with Toluenes, and the Effect of Radical Polarity on the Ratio of Benzylic Hydrogen Abstraction to Addition to Aromatic Rings

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Abstract: We have reexamined the reactions of *tert*-butyl radicals with toluenes and have obtained a ρ value of 0.49 ± 0.04 at 80 °C. The new, independent system involves the quantification of all of the principal products from the reaction of *tert*-butyl radicals with mixtures of toluene and a substituted toluene. Five major products contain benzyl fragments and are formed in significant yields: two symmetrical bibenzyls, the cross bibenzyl, and the two neopentylbenzenes that result from combination of *tert*-butyl and the two benzyl radicals. Attack on the side chain is a major reaction of free *tert*-butyl radicals and is the only significant reaction that they undergo other than cage and termination reactions. *tert*-Butyl radicals do not add to the ring of toluenes. Data on the relative rates of addition to benzenes and hydrogen abstraction from toluenes are collected for a series of radicals including hydrogen atoms; methyl, isopropyl, and *tert*-butyl radicals; and *p*-nitrophenyl, *p*-bromophenyl, and phenyl radicals. The data demonstrate that more electrophilic radicals have a larger tendency to *add* to rings whereas more nucleophilic radicals have a larger tendency to *abstract* benzylic hydrogens.

Introduction

Predictions of radical reactivity often depend on the hypothesis that dipolar resonance structures for the transition states of radical reactions control reactivity.[1-4] This concept is used to rationalize reactivity in virtually every type of radical reaction, including atom transfers, additions, and copolymerizations; the polar character of a radical also has been reported to control the relative rates of *atom abstraction* vs. *addition* by a given radical.[5] Clearly, few concepts can be regarded as more basic to our understanding of radical reactivity than is the polar effect. Recently, however, the existence of dipolar structures in the transition state for hydrogen abstraction from toluenes was questioned by Zavitsas,[6] who proposed that polar effects can be explained by the effects of substituents on bond dissociation energies (BDE's) in the reactants.

We have felt that the study of Hammett correlations of radical reactions provides the theoretically and mechanistically most interesting access to the study of polar effects.[7-12] The Hammett equation is the most useful linear free-energy relationship (LFER) in chemistry, and the very fact that neutral radicals obey this relation, which was originally derived only for ionic species, is interesting in itself. If our explanation of the application of the Hammett equation to radical reactions is wrong, then we surely have important gaps in our understanding of radical reactivity.

The proposal of Zavitsas that the Hammett ρ values observed for radical reactions reflect BDE effects rather than polar effects was based on the hypothesis that electron-withdrawing substituents strengthen the benzylic C–H BDE. Using a kinetic iodination method, we have shown that this hypothesis is correct.[13] The magnitude of the changes in BDE's are not trivial: the BDE of the benzylic bond changes by about 3–4 kcal/mol for a unit change in σ.[13]

Zavitsas' proposal also leads to the prediction that only negative ρ values can be observed in hydrogen-abstraction reactions from toluenes by alkyl radicals.[6] This is a striking and dramatic prediction, and in 1973 we attempted to determine whether positive ρ values could occur. We found that positive ρ values are, in fact, observed for the radical reactions of a number of alkyl radicals.[7-11] However, we also have shown that some reaction systems require the consideration of *both* the BDE effects of substituents and polar effects for a consistent rationalization of reactivity data.[12]

The largest positive ρ value we reported is for the reaction of *tert*-butyl radicals with toluenes;[10] this value has been questioned by Tanner et al.,[14] who have suggested that viscosity effects (due to changing the nature of the toluene substrate) on the cage yields of isobutane are solely responsible for the effects we observed. In view of the critical importance of polar effects with respect to our understanding of radical reactivity, we have studied the chemistry of the *tert*-butyl radical in more detail. We have measured all of the significant products from the reaction of *tert*-butyl radicals with a series of toluenes. (The *tert*-butyl radicals were generated by photolysis of azoisobutane, AIB.) These new data allow us to redetermine the ρ value for the reaction of *tert*-butyl radicals with toluenes by a new and unambiguous method, one that does not involve any correction for viscosity effects. Our our new data demonstrate that *tert*-butyl radicals abstract hydrogens from toluene and substituted toluenes, and do *not* add to the aromatic ring. Since this result is in sharp contrast to statements made in the recent literature,[14,15] we have also examined the effect of the polar character of the radical on the abstraction to addition ratio.

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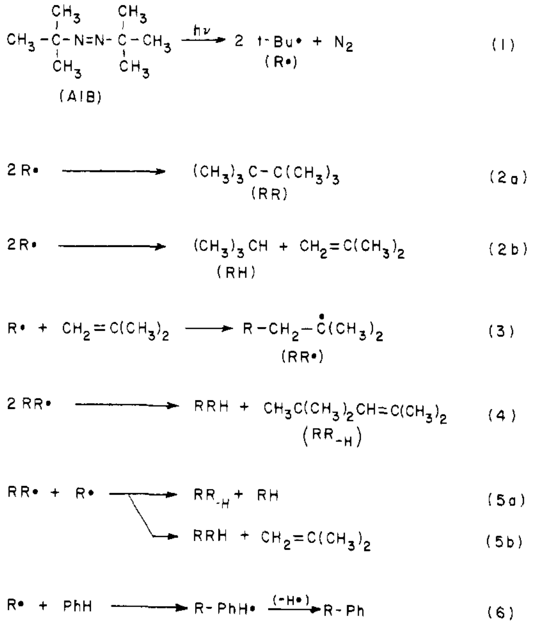
Table I. Photodecomposition of 0.1 M AIB in Neat Benzene

T, °C	t-$C_4H_9Ph^a$
30	0.91
80	0.50
100	0.47

[a] Yield of *tert*-butylbenzene in mol/100 mol of AIB decomposed.

Results and Discussion

Decomposition of AIB in Neat Benzene. The photodecomposition of 0.1 M AIB in neat benzene at 80 °C gives the following major products derived from the *tert*-butyl radical (in mol/100 mol of AIB decomposed): isobutane, 84; isobutylene, 63; hexamethylethane, 18; 2,4,4-trimethyl-2-pentene, 4; 2,2,4-trimethylpentane, 6; *tert*-butylbenzene, 0.5. These products can be accounted for as shown in eq 1–6.



$$\underset{(AIB)}{CH_3-C(CH_3)_2-N{=}N-C(CH_3)_2-CH_3} \xrightarrow{h\nu} 2\ t\text{-Bu}\cdot \underset{(R\cdot)}{} + N_2 \qquad (1)$$

$$2R\cdot \longrightarrow \underset{(RR)}{(CH_3)_3C-C(CH_3)_3} \qquad (2a)$$

$$2R\cdot \longrightarrow \underset{(RH)}{(CH_3)_3CH} + CH_2{=}C(CH_3)_2 \qquad (2b)$$

$$R\cdot + CH_2{=}C(CH_3)_2 \longrightarrow \underset{(RR\cdot)}{R-CH_2-\dot{C}(CH_3)_2} \qquad (3)$$

$$2\,RR\cdot \longrightarrow RRH + \underset{(RR_{-H})}{CH_3C(CH_3)_2CH{=}C(CH_3)_2} \qquad (4)$$

$$RR\cdot + R\cdot \longrightarrow RR_{-H} + RH \qquad (5a)$$

$$\longrightarrow RRH + CH_2{=}C(CH_3)_2 \qquad (5b)$$

$$R\cdot + PhH \longrightarrow R-PhH\cdot \xrightarrow{(-H\cdot)} R-Ph \qquad (6)$$

Table I gives the yields of *tert*-butylbenzene at two other temperatures. These product data clearly show that very few *tert*-butyl radicals add to the benzene ring. It might be argued that R· radicals do add to the ring, but the cyclohexadienyl radicals dimerize or couple with a second R· radical to give products other than *tert*-butylbenzene. However, the products listed above constitute a 102% recovery of *tert*-butyl radicals from AIB, demonstrating that the addition of *tert*-butyl radicals to the benzene ring can be neglected at 80 °C in neat benzene. This very slow addition of *tert*-butyl radicals to aromatic rings contrasts strongly with the well-known addition reactions of the methyl[16] and phenyl[5] radicals and the hydrogen atom (see below).[17]

Products of the Photodecomposition of AIB in Toluene. The photodecomposition of either 0.02 or 0.10 M AIB in neat toluene was allowed to proceed to nearly 100% completion at temperatures from 40 to 100 °C and the products were analyzed by gas chromatography. The data (Table II) show that 100 ± 2% of the theoretical yield of *tert*-butyl radicals is recovered as isobutane (RH), isobutylene, dimer (RR), neopentylbenzene (QR), and a product represented as QR_2 which will be discussed further below. No *tert*-butyltoluene is detected. The only other significant product is the bibenzyl resulting from the coupling reaction. The products containing the benzyl fragment are all characteristic of hydrogen abstraction by the *tert*-butyl radical.

Decomposition of AIB in a Mixture of Substituted Toluenes. The photolysis of AIB in a mixture of toluene and a ring-substituted toluene leads to the formation of five major products that contain benzyl groups: two symmetrical bibenzyls, the cross bibenzyl, and the two neopentylbenzenes that result from combination of *tert*-butyl radicals with the two benzyl radicals. Table III shows these products for mixtures of toluene and a substituted toluene at 80 °C. Again, no *tert*-butyltoluene or substituted *tert*-butyltoluenes were detected. The formation of the five major products is shown in eq 7–13, where QH is toluene itself, Q′H

$$R\cdot + QH \xrightarrow{k} Q\cdot + RH \qquad (7)$$

$$R\cdot + Q'H \xrightarrow{k'} Q'\cdot + RH \qquad (8)$$

$$2Q\cdot \rightarrow Q{-}Q \qquad (9)$$

$$2Q'\cdot \rightarrow Q'{-}Q' \qquad (10)$$

$$Q\cdot + Q'\cdot \rightarrow Q{-}Q' \qquad (11)$$

$$Q\cdot + R\cdot \rightarrow Q{-}R \qquad (12)$$

$$Q'\cdot + R\cdot \rightarrow Q'{-}R \qquad (13)$$

$$Q\cdot + RR\cdot \rightarrow QR_2 \qquad (14)$$

$$Q\cdot' + RR\cdot \rightarrow Q'R_2 \qquad (15)$$

is a substituted toluene, Q· is the benzyl radical, Q′· is a substituted benzyl radical, and R· is the *tert*-butyl radical. The principal product-producing reactions are shown as eq 9–13. One minor process does occur, however, to produce a dimeric radical, symbolized as RR·, and shown in eq 3. The RR· radical combines with Q· and Q′· radicals to give the products symbolized as QR_2 and $Q'R_2$ (eq 14 and 15). (The structural analysis and identification of QR_2 is given in the Experimental Section.) We identified this process after most of the runs reported here were completed and consequently did not quantify the QR_2-type products for every run. However, where we did so, these were minor products that did not change the k'/k ratio within the accuracy of our method. (See the data in Tables VII–IX discussed below.)

The RR· radical is a tertiary radical, like the *tert*-butyl radical itself, and it would be expected to abstract benzylic hydrogens to some extent; however, this reaction should be negligible, since the R·/RR· ratio is large. Furthermore, even if this reaction occurs, it does not influence our analysis of the ratio of Q and Q′ products (to a first approximation) since R· radicals that might have abstracted from QH simply add to isobutylene to give RR· that then abstracts a hydrogen from QH or Q′H (with a selectivity and rate profile similar to that of the R· radical) to give the same Q· and Q′· products that would have been obtained had R· abstracted from QH directly.

As will be discussed below, relative rate constants, k'/k, for attack on the substituted toluenes relative to toluene itself can be obtained directly from the product analyses. It is found that a larger fraction of the *tert*-butyl radicals attack the side chain of toluene at higher temperatures. Most of the work reported here was done at 80 °C; at this temperature approximately 24% of the *tert*-butyl radicals abstract benzylic hydrogens at 0.1 M AIB (the concentration used in most of our runs) and 40% at 0.02 M AIB. Hydrogen abstraction is the only significant reaction that the *tert*-butyl radicals undergo, except for cage and free solution termination processes.

Kinetic Analysis. After escaping from the solvent cage, *tert*-butyl radicals can abstract a hydrogen atom from either toluene or a substituted toluene. A steady-state analysis of eq 7–15 gives eq 16, where PR is the product ratio of molar yields of Q- and

$$PR = \frac{k'}{k}\frac{[Q'H]}{[QH]} \qquad (16)$$

Q′-containing products as shown in eq 17. As we shall show

$$PR = \frac{2[Q'Q'] + [Q'Q] + [Q'R] + [Q'R_2]}{2[QQ] + [Q'Q] + [QR] + [QR_2]} \qquad (17)$$

below, the QR_2 terms in PR can be ignored without effect on the

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[16] Pryor, W. A.; Davis, W. H.; Gleaton, J. H. *J. Org. Chem.* **1975**, *40*, 2099.

[17] Pryor, W. A.; Lin, T. H.; Stanley, J. P.; Henderson, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 6993.

Table II. Products from the Photodecomposition of AIB (RN=NR) in Neat Toluene[a,b] (mol/100 mol of AIB decomposed)

	initial AIB							
	0.0203 M at				0.106 M at			
	40 °C	60 °C	80 °C	100 °C	30 °C	40 °C	60 °C	80 °C
product								
RH	98	111	117	125	89	100	107	110
isobutylene	65	52	42	38	69	65	55	50
RR	11	10	10	10	12	11	10	10
QR	11	13	13	11	11	12	18	17
RRH	0.4	0.5	0.5	0.5	1	1	1	1
isooctene	1	1	1	1	2	2	2	2
QR_2	0.8	0.7	0.5	0.4	2	2	2	2
QQ	11	20	30	39	3	4	11	15
recovery of R groups, %[c]	100	101	98	99	102	105	105	104
Q· formed, %								
from RH yield (in free solution)[d]	17	30	38	44	10	17	26	30
from Q-containing products[e]	17	27	37	45	10	11	21	25

[a] Symbolism: R is *tert*-butyl; Q is benzyl; and Q′ is a substituted benzyl group; RH is isobutane; RR is hexamethylethane; QQ is bibenzyl; RRH is $CMe_3CH_2CHMe_2$ ("isooctane"); QR_2 is $PhCH_2CMe_2CH_2CMe_3$. [b] Toluene is 9.32 M with 0.02 M AIB and 9.19 M with 0.1 M AIB. Reaction time is 20 h in a merry-go-round photochhemical apparatus. Most runs are in duplicate and averages are shown; agreement is generally 1% or better. [c] 0.5[RH + isobutylene + 2(RR) + QR + 2(QR_2) + 2(RRH) + 2(isooctene)]. [d] 0.5[RH − isobutylene]. [e] 0.5[2(QQ) + QR + QR_2].

value of k'/k obtained. Table III gives the product analyses for mixtures of eight substituted toluenes vs. toluene itself.

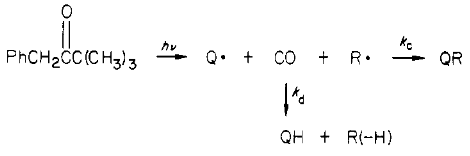
Equation 16 predicts that a plot of PR vs. the solvent ratio [Q′H]/[QH] should give a straight line with slope equal to k'/k with the following conditions. Firstly, Q· cannot abstract hydrogen from Q′H since this would mix the products. Secondly, benzyl radicals cannot revert to toluenes as a result of disproportionation reactions with *tert*-butyl radicals since this would result in our underestimating the amount of hydrogen abstraction that has occurred.

Exchange Reaction (Q· + Q′H → QH + Q′·). Since our kinetic method involves the simultaneous reaction of two toluenes, QH and Q′H, with *tert*-butyl radicals, it is important to show that the exchange reaction, eq 18, is slow relative to the combination of

$$Q\cdot + Q'H \rightarrow QH + Q'\cdot \qquad (18)$$

benzyl radicals, eq 9–15. Control experiments were done in which a degassed solution of *tert*-butyl phenylperacetate (0.1 M) in *p*-chlorotoluene or *p*-xylene was photolyzed at 80 °C for 40 h. Reaction mixtures (in duplicate) were then subjected to analysis by GLPC for toluene, bibenzyl, and *p*-methyl- or *p*-chlorobibenzyl using biphenyl as the internal standard. Table IV shows that only about 1% of the $PhCH_2\cdot$ radicals that become free abstract hydrogen from the substituted toluene (Q′H) solvent; most benzyl radicals couple with other benzyl radicals. (Note that this control neglects the trapping of Q· radicals by R· radicals, which would reduce the fraction of Q· that abstract from Q′H still further.)

Estimation of the Disproportionation to Coupling Ratio (k_d/k_c) between Benzyl Radicals and *tert*-Butyl Radicals. Our method involves measurement of the combination products of the reaction of Q· with R· radicals. However, disproportionation of these radicals also can occur; this disproportionation would re-form the QH and produce isobutylene, a known product, and would lead to an underestimation of the amount of hydrogen abstraction from QH (see eq 19). Fischer et al. have determined these ratios for



$$PhCH_2C(=O)C(CH_3)_3 \xrightarrow{h\nu} Q\cdot + CO + R\cdot \xrightarrow{k_c} QR \qquad (19a)$$

$$\xrightarrow{k_d} QH + R(-H) \qquad (19b)$$

a number of radicals and they are generally quite substantial.[18,19] In a private communication, Professor Fischer indicated that the magnitude of k_d/k_c for *tert*-butyl and benzyl radicals was 0.4 in hydrocarbon solvent at room temperature. We have therefore determined k_d/k_c by the same method, namely, the photodecomposition of benzyl *tert*-butyl ketone (BBK) at 80 °C. Our results are presented in Table V for k_d/k_c determined in chlorobenzene and undecane. These values are somewhat lower than Fischer's, perhaps reflecting the higher temperature in our work. They clearly indicate that a significant fraction of the benzyl radicals are converted back to toluene by the disproportionation reaction. Although the uncertainties involved suggest that the two values obtained in the two different solvents are not significant, a slightly higher value in the hydrocarbon solvent might be due to hydrogen abstraction from the solvent by the benzyl radicals, leading to an anomalously high amount of toluene in the product mixture.

The product ratio given in eq 16 and 17 can be corrected for this disproportionation. The yields of Q′R should be increased by $(1 + k_d/k_c)$, where the k_d/k_c ratio pertains to the particular substituted benzyl radical involved. Thus, eq 17 should be formulated as eq 20. Since both disproportionation and combination

$$PR = \frac{2[Q'Q'] + [Q'Q] + (1 + k_d'/k_c')[Q'R] + [Q'R_2]}{2[QQ] + [Q'Q] + (1 + k_d/k_c)[QR] + [QR_2]} \qquad (20)$$

should be essentially diffusion-controlled processes and therefore should have little dependence on substituents in the benzyl radical, we have assumed that the k_d/k_c ratios are the same for the benzyl radical and for all substituted benzyl radicals. (The contributions of k_d/k_c to the numerator and denominator of eq 20 are so similar that the resulting rate constant ratios are the same, within experimental error, whether the correction for disproportionation is made or not.)

The values of k'/k were calculated from plots of eq 16, using PR's (eq 20) and data in Table III. In all cases, the plots of PR vs. toluene ratio were linear, and correlation coefficients of 0.99 or better were obtained. The resulting k'/k values are shown in Table VI.

Effect of Variation in the AIB Concentration and QR_2-Type Products. In our original work 0.02 M AIB was used, since we were under the erroneous impression from the work of Tanner et al.[14] that *tert*-butyltoluene would be a product, and since the work of Ogata et al.[20] suggested that less addition and more hydrogen abstraction from the side chain occurs for lower initial concentrations of initiator. It developed, however, that 0.02 M is too low a concentration of AIB for convenient, accurate analysis

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Table III. Product Distribution for the Photodecomposition of 0.10 M AIB (RN_2R) in Mixtures of Toluene (QH) and a Substituted Toluene (Q'H) at 80 °C[a]

substituent in Q'H:	[Q'H]	[QH]	products,[b] mol/100 mol of AIB QR	Q'R	QQ	QQ'	Q'Q'
m,m-CH_3	2.72	5.59	7.03	10.4	5.10	13.5	7.93
	2.72	5.59	8.08	11.7	5.79	15.0	8.42
	3.38	4.68	6.01	12.2	3.78	13.8	11.8
	3.38	4.68	5.21	12.7	3.34	13.3	12.0
	4.08	3.80	5.21	17.0	2.62	13.2	16.4
	4.08	3.80	5.30	14.3	2.81	12.9	16.2
	4.66	2.88	4.11	18.4	2.02	12.0	25.4
p-CH_3	3.05	5.63	11.1	10.4	8.18	16.4	9.19
	3.05	5.63	10.5	9.51	6.12	14.9	8.78
	3.86	4.70	8.12	10.75	5.66	14.0	12.0
	3.86	4.70	8.39	11.1	5.56	15.6	15.1
	4.66	3.75	6.09	13.9	5.28	13.5	17.9
m-CH_3	3.03	5.62	9.85	9.98	7.83	13.6	6.72
	3.03	5.62	10.4	10.4	8.32	14.4	7.20
	3.83	4.71	7.90	11.6	6.11	13.7	10.3
	3.83	4.71	7.35	15.4	7.04	14.6	11.0
	4.61	3.84	7.61	14.9	4.80	12.0	13.4
	5.01	3.34	5.42	15.7	3.52	13.3	17.2
p-Cl	3.16	5.63	6.44	3.75	8.34	15.0	2.91
	4.33	4.23	5.88	5.23	5.69	16.6	9.71
	4.33	4.23	5.62	4.99	5.23	15.9	8.08
	4.86	3.76	4.90	5.27	4.47	15.7	10.2
	4.86	3.76	4.69	5.16	4.10	14.6	9.67
m-Cl	2.58	6.47	9.16	5.64	7.58	12.8	1.30
	3.26	5.55	7.29	5.42	5.60	12.6	3.95
	3.26	5.55	7.19	6.02	5.66	13.2	4.23
	3.99	4.69	6.26	7.38	4.27	14.5	6.72
	4.84	3.76	4.35	7.67	2.59	13.2	10.2
m,p-Cl	2.90	5.64	6.31	7.38	5.84	12.1	3.38
	2.90	5.64	6.68	8.15	6.02	11.6	4.31
	3.69	4.68	4.81	7.61	4.39	11.5	8.86
	4.47	3.76	3.31	8.33	3.21	10.5	10.2
p-CN	2.12	6.81	7.46	9.21	7.83	14.9	1.40
	3.05	5.80	5.83	8.41	5.29	13.7	5.63
	3.05	5.80	5.69	6.99	5.03	14.8	6.52
	3.91	4.77	4.01	7.17	3.44	13.2	12.0
	4.83	3.75	2.74	6.59	1.93	9.92	15.8
	4.83	3.75	2.58	6.95	1.77	10.6	15.1
p-*t*-Bu	2.12	5.73	16.3	3.85	10.4	7.19	1.28
	2.75	4.70	14.9	5.16	7.63	8.22	2.20
	3.62	3.79	10.6	5.94	4.43	8.23	3.09
	3.62	3.79	10.2	5.86	4.27	8.32	3.34
	4.21	2.88	5.09	8.74	4.17	8.54	3.67

[a] Reaction time is 20 h. [b] Symbols defined in Table I.

Table IV. Exchange Reaction between the Benzyl Radical and a Substituted Toluene ($Q\cdot + Q'H \rightarrow QH + Q'\cdot$): Results of Control Experiments Using *tert*-Butyl Phenylperacetate at 80 °C

reactants Q'H[a]	reactants $PhCH_2CO_3R$,[b] M	products (mol/100 mol of perester decomposed)[c] $PhCH_3$	$PhCH_2CH_2Ph$	$ArCH_2CH_2Ph$	fraction exchange[d]
p-chlorotoluene	0.1	0.26	11.0	33.2	0.005
p-xylene	0.1	0.96	13.4	35.3	0.015

[a] Neat. [b] *tert*-Butyl phenylperacetate. [c] Average of two runs; runs heated for 40 h. [d] Fraction of the free $PhCH_2\cdot$ radicals that undergo exchange. Calculated as $[PhCH_3]/([PhCH_3] + 2[PhC_2H_4Ph] + [ArC_2H_4Ph])$.

Table V. Estimation of the k_d/k_c Ratio for Benzyl and *tert*-Butyl Radicals at 80 °C

solvent	concn, M BBK_i[b]	BBK_f[b]	product concn, mol/100 mol of perester decomposed[a] $PhCH_3$	$PhCH_2C(CH_3)_3$	k_d/k_c
PhCl	0.108	0.075	6.32	27.4	0.23 ± 0.04
n-$C_{11}H_{24}$	0.134	0.066	0.9	3.0	0.30 ± 0.06

[a] The product concentrations were determined by capillary GC. Uncertainties in the reported concentrations are 8–10%. [b] BBK = benzyl *tert*-butyl ketone; i = initial and f = final concentrations.

Table VI. k'/k Values for the Reaction of *tert*-Butyl Radicals with Substituted Toluenes at 80 °C[a]

substituent in Q'H	n[b]	k'/k[c]	s[f]	CL[g]
m,m-CH_3[d]	7	0.80	0.02	0.02
p-CH_3[e]	6	0.73	0.03	0.03
m-CH_3[e]	6	0.76	0.02	0.02
p-Cl[h]	8	1.03	0.04	0.03
m-Cl	5	1.38	0.01	0.01
m,p-Cl	4	1.55	0.06	0.10
p-CN	6	2.23	0.03	0.03
p-*t*-C_4H_9[i]	5	0.78	0.01	0.02

[a] Data taken from Tables III, VII–IX. k_d/k_c assumed to be 0.23 for all cases. [b] Number of independent runs. [c] Defined in eq 16. [d] A statistical correction of 1/3 was used. [e] A statistical correction of 1/2 was used. [g] Confidence limits at 95% level. [h] Includes data from Tables III and IX. [i] Includes data from Tables III and VII.

Table VII. Product Distribution (mol/100 mol of AIB)[b] for the Photodecomposition of Various Concentrations of AIB in a Mixture of Toluene (QH) and *p*-(*tert*-Butyl)toluene (Q'H) at 80 °C with [Q'H]/[QH] = 0.9[a]

products	$[AIB]_0$, M 0.0219	0.0397	0.0613	0.0827	0.100	av k'/k[d]
QR	6.2	6.5	7.1	7.2	7.4	
Q'R	4.9	5.3	5.7	5.7	5.9	
QR_2	1.5	1.5	1.7	1.9	2.0	
$Q'R_2$	0.5	0.9	1.4	1.6	1.8	
QQ	5.4	4.9	4.3	3.6	3.2	
QQ'	15.2	13.6	10.7	10.6	8.5	
Q'Q'	3.2	3.2	3.0	2.7	2.6	
Including $QR_2 + Q'R_2$						
PR[c]	0.80	0.83	0.85	0.87	0.88	
k'/k[c]	0.86	0.91	0.92	0.94	0.95	0.917 ± 0.035
Excluding $QR_2 + Q'R_2$						
PR	0.82	0.85	0.85	0.87	0.88	
k'/k	0.89	0.92	0.92	0.94	0.96	0.925 ± 0.027

[a] Reaction time is 20 h; [Q'H]/[QH] is constant at 0.922 in all runs except the first column where it is 0.927. [b] Each value is an average of two runs. [c] PR and k'/k defined in eq 16 and 17. [d] Averages taken before data rounded to two significant figures.

when most of our reaction mixtures were analyzed. However, with some pairs we were able to vary the initial concentration of AIB and study the effect on the k'/k ratios. In addition, we discovered that products of the QR_2 type were formed but did not analyze for these in all of the substrate pairs studied. Therefore, we also wished to probe the effect of omitting the yields of these products on the k'/k ratio.

Tables VII, VIII, and IX present data relevant to these points. Table VII shows a study of five concentrations of AIB from 0.02 to 0.1 M at a constant ratio of *p*-*tert*-butyltoluene to toluene of 0.92. The product ratio, PR, is tabulated both when the QR_2-type products are included and when they are neglected. The table shows that the average value of k'/k is 0.92 ± 0.03, whether the QR_2-type products are included or are excluded; however, there may be a trend of the values of k'/k toward slightly higher values as the initial concentration of AIB is increased.

Table VIII shows a similar study of the *p*-chlorotoluene/toluene pair. Again it is clear that the values of k'/k are not affected by the exclusion of the QR_2-type products. For the data in this set, there does not appear to be a trend of k'/k values as the AIB concentration is increased.

Table IX shows data obtained at 0.1 M AIB and at three ratios of *p*-chlorotoluene/toluene. Again, the k'/k values are not affected, within our experimental uncertainty, by the exclusion of the QR_2-type products.[21]

Table VIII. Product Distribution (mol/100 mol of AIB)[b] for the Photodecomposition of Various Concentrations of AIB in a Mixture of Toluene (QH) and *p*-Chlorotoluene (Q'H) at 80 °C with [Q'H]/[QH] = 0.89[a]

	$[AIB]_0$, M				
product	0.0275	0.0573	0.0733	0.103	av k'/k
QR	6.3	6.9	7.2	7.4	
Q'R	4.6	5.2	5.5	5.5	
QQ	8.1	5.9	5.3	4.8	
QQ'	22.3	19.6	17.7	16.1	
Q'Q'	7.3	7.3	5.8	6.4	
QR_2	0.2	0.7	0.9	1.2	
$Q'R_2$	0.7	1.1	1.3	1.8	
	Including QR_2 and $Q'R_2$				
PR[c]	0.94	1.04	0.99	1.06	
k'/k[c]	1.05	1.17	1.11	1.19	1.130 ± 0.063
	Excluding QR_2 and $Q'R_2$				
PR	0.93	1.03	0.98	1.04	
k'/k	1.04	1.15	1.10	1.17	1.115 ± 0.058

[a] Reaction time is 20 h; [Q'H]/[QH] = 0.893 in all runs. [b] Each value is an average of three runs. [c] PR and k'/k defined in eq 16 and 17.

Table IX. Product Distribution (mol/100 mol of AIB)[b] for the Photodecomposition of 0.103 M AIB in Several Ratios of Toluene (QH) to *p*-Chlorotoluene (Q'H) at 80 °C[a]

	[Q'H]/[QH]			
product	0.5810	0.8926	1.305	av k'/k
QR	9.3	7.4	5.9	
Q'R	4.7	5.5	6.4	
QQ	7.1	4.8	3.3	
QQ'	13.2	16.1	14.4	
Q'Q'	3.0	6.4	8.5	
QR_2	1.6	1.2	1.0	
$Q'R_2$	1.4	1.8	2.1	
	Including QR_2 and $Q'R_2$			
PR[c]	0.66	1.06	1.43	
k'/k[c]	1.14	1.19	1.10	1.14 ± 0.045
	Excluding QR_2 and $Q'R_2$			
PR	0.65	1.04	1.41	
k'/k	1.12	1.17	1.08	1.12 ± 0.045

[a] Reaction time was 20 h. [b] Each value is an average of three runs. [c] PR and k'/k defined in eq 16 and 17.

Hammett Correlation and the ρ Value for the *tert*-Butyl Radical. The relative rate constants in Table VI can be correlated against σ values; the plot is shown in Figure 1. The value of ρ is found to be 0.49 ± 0.04 at 80 °C (deviation at the 95% confidence limit is given). It should be noted that this new kinetic system involves the study of the reactions of free *tert*-butyl radicals in solution containing two substrates that react competitively. Therefore, cage-effect corrections and the viscosity of the solutions are not involved in the calculations.

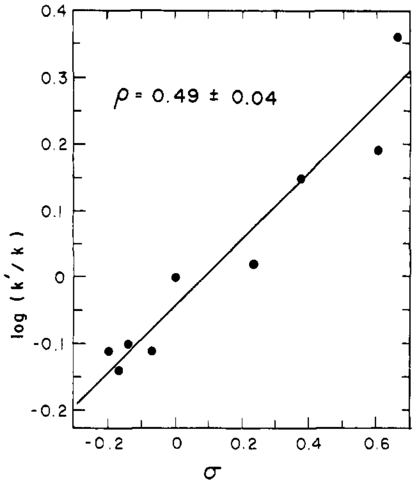

Figure 1. A plot of the relative rate constants for reaction of substituted toluenes with the *tert*-butyl radical at 80 °C vs. Hammett σ values.

After we completed our study, Fischer and his co-workers determined the absolute rate constants for hydrogen abstraction from a number of substituted toluenes by the *tert*-butyl radical using an ESR technique.[22a] They find a ρ value of 0.59 at 48 °C, a result in good agreement with our value.[22b]

Competition between Benzylic Hydrogen Abstraction and Addition to the Aromatic Ring by Various Radicals. Both Tanner et al.[14] and Zavitsas and Hanna[15] have discussed the reaction of alkyl radicals with toluenes in terms of a rapid addition competing with benzylic hydrogen abstraction. Several authors, however, have concluded that more nucleophilic radicals tend to abstract hydrogens, whereas electrophilic radicals tend to add to unsaturated systems;[5,23,24] if this generalization is correct, primary, secondary, and tertiary alkyl radicals might differ appreciably in their addition/hydrogen-abstraction ratios. There are, however, disappointingly few data with which to test this hypothesis, since generally the two competitive rates have not been measured by the same group in the same study. We have compiled the limited data available in Table X.[5,8,13,25-36] The data do indeed suggest that the polar character of the radical determines its abstraction/addition ratio; the table shows the following trend for the rate constant ratio $k_{add}/k_{H\text{-abstract}}$: p-$NO_2Ph\cdot > p$-$BrPh\cdot > CH_3\cdot \simeq Ph\cdot \simeq H\cdot > i$-$Pr\cdot >$ triptyl$\cdot \simeq t$-$Bu\cdot$. Thus, as we stated[5] in 1966, ". . .radicals increasingly favor attack on benzene rings

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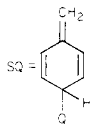
[21] (a) The ratios of bibenzyl products $(QQ')^2/(QQ)(Q'Q')$ often vary significantly from the statistical value of 4.[21b] One suggestion[21c] was that when two benzyl radicals meet they not only couple "head-to-head" to give the expected bibenzyl products, but they also couple "head-to-tail" to give semibenzenes, SQ. Fischer et al.[21c] have studied this alternate coupling process



and find that a substantial number of benzyl radicals (or substituted benzyl radicals that do not have a para substituent) can initially react in this manner. However, not only is semibenzene formation reversible, but semibenzenes can also readily react either with other benzyl radicals to give bibenzyls or with *tert*-butyl radicals to give neopentylbenzenes. Thus, although the product distribution will be altered, the total yield of a given benzyl fragment in the products does not change. Since we are following hydrogen abstraction by measuring all of the benzyl-containing products, our product ratios and, thus, our values for k'/k will be independent of any semibenzene formation. (b) Pryor, W. A., ref 1, p 315. (c) Langhals, H.; Fischer, H. *Chem. Ber.* **1978**, *111*, 543.

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Table X. Comparison of Relative Rates of Addition to Benzene (or Substituted Benzenes) with Rates of Hydrogen Abstraction from Benzylic Positions by Radicals

radical	source	substrate(s)	T, °C	$k_{\text{add}}{}^{a}/k_{\text{H-abst}}$	footnote	ref
hydrogen atom	RSH + light	PhH/$PhCH_3$	40		*b*	25, 26
methyl	various	PhH/$PhCH_3$	65	0.5	*c*	8
methyl	Ac_2O_2	PhH/$PhCH_3$	65	0.2	*c*	27
isopropyl	azoisopropane	$PhCH_3$	30	0.1	*d*	28
isopropyl	azoisopropane	$PhCH_3$	80	0.03	*d*	28
cyclohexyl	*t*-Bu_2O_2 in C_6H_{12}/$PhCH_3$	$PhCH_3$	90	0.2	*e*	26
3-heptyl	*tert*-butyl-2-ethylperoxyhexanoate	$PhCH_3$	80	<0.01	*f*	29
tert-butyl	azoisobutane	PhH	80	~0	*h*	this work
tert-butyl	azoisobutane	$PhCH_3$	80	~0	*g*	this work
triptyl	triptocyl peroxide	$PhCH_3$	60	~0	*g*	30
phenyl	phenylazotriphenylmethane	$PhCH_3/CCl_4$	60	1	*i*	5a
p-bromophenyl	*p*-bromophenylazotriphenylmethane	$PhCH_3/CCl_4$	60	3	*i*	5a
p-nitrophenyl	*p*-nitrophenylazotriphenylmethane	$PhCH_3/CCl_4$	60	10	*i*	5a

[a] Calculated on a per molecule basis; i.e., total k for addition to PhH and or $PhCH_3$ vs. H- abstraction from $PhCH_3$. [b] The hydrogen atom reacts with both benzene and toluenes at rapid rates. [c] The yield of the addition product is approximated by the deficit in the yield of CH_4; the yield of abstraction is obtained from the CH_4 yields. Material balances on the substrate were not obtained. Also see the comment and reference under footnote *h* below. [d] From the product analysis for isopropyltoluene and isobutylbenzene. [e] Based on a partial product analysis for cyclohexyltoluene, phenylcyclohexylmethane, and bibenzyl. [f] Based on analysis for the following products: heptane, 2- and 3-heptene, and 1-(3-heptyl)-3- and 4-methylbenzene. The overall recovery and analysis for compounds containing the 3-heptyl group was 93%. [g] No addition product detected. [h] Less than 1% yield *tert*-butylbenzene; work reported here. [i] Rate of abstraction calculated from k_H/k_{Cl} with CCl_4 as the cosolvent; rate of addition approximated from the deficit in the yield of (ArH + ArCl) products. The assumptions implicit in this method are discussed on p 1197 of ref 5a.

relative to attack on CCl_4 [or benzylic hydrogens] as the radicals become increasingly electrophilic. . .".

Experimental Section

Chemicals. The substituted toluenes were purified[31] before use. Azoisobutane (AIB) was purchased from Fairfield and redistilled under vacuum. 2,2,3,3-Tetramethylbutane was obtained from Aldrich. All of the chemicals were shown to be free of impurities by GLPC. Isobutane and isobutylene (Matheson) were used without further purification.

tert-Butyl phenylperacetate was synthesized by the method of Bartlett et al.[32] except the reaction was carried out at 0 °C. The perester obtained was vacuum dried and further purified by passing down a 20-cm column packed with activated silica gel. The purity of the perester was determined by an improved iodometric method[33] and found to be 80%, as reported by Bartlett and Simons:[32] NMR (δ in CCl_4) 1.17 (s, 9 H), 3.53 (s, 2 H), 7.29 (s, 5 H). Calcd for $C_2H_{16}O_3$: C, 67.31; H, 8.00.

Neopentylbenzenes were synthesized according to the method of Bassindale et al.[34] A solution of 6.25 g (0.05 mol) of benzyl chloride in 50 mL of hexane was kept at 0 °C. To the mixture, 52 mL (0.05 mol) of 1.0 M *tert*-butyllithium in pentane was added dropwise over a period of 30 min under an argon atmosphere. After standing for 2 h at 0 °C, the mixture was refluxed for 30 min and then was treated with saturated aqueous ammonium chloride. The organic layer was dried over anhydrous sodium sulfate and distilled under reduced pressure to give 3 g (0.02 mol) of neopentylbenzene. The substituted neopentylbenzenes were prepared similarly from the corresponding benzyl chlorides. Elemental analyses and NMR spectra were obtained for all compounds synthesized.

Symmetrical bibenzyls were synthesized by the method of Johnston and Williams.[35] A mixture of 10 g of *tert*-butyl peroxide and 100 to 150 g of a substituted toluene was stirred at 140 °C under nitrogen. After 48 h, the low-boiling products (acetone and *tert*-butyl alcohol), the unreacted *tert*-butyl peroxide, and the excess of solvent were removed by vacuum distillation and the homo bibenzyl recrystallized from ethanol.

Cross bibenzyls were obtained by a similar method using a mixture of 25 to 50 g of a substituted toluene, 25 to 50 g of toluene, and 10 g of *tert*-butyl peroxide. After standing at 140 °C for 48 h, the reaction mixture was concentrated to 5 to 10 mL. The cross-bibenzyl was separated and purified by a preparative GLPC (Varian 920) using a 4 ft × 0.25 in. column packed with 20% OV-101 on Chromosorb W.

Synthesis of $PhCH_2C(CH_3)_2CH_2C(CH_3)_3$ (QR_2). 2,4,4-Trimethyl-2-chloropentane was synthesized by bubbling dry HCl into diisobutylene at 0 to 5 °C.[36] After no more HCl was taken up (about 4 h), the mixture was washed with ice water and dried with anhydrous sodium carbonate. The product was isolated by fractional distillation under reduced pressure: bp 55–56 °C (15 mm); NMR (δ in CCl_4) 1.07 (s, 9 H), 1.65 (s, 6 H), 1.85 (s, 2 H). This chloride was allowed to react with the Grignard reagent of benzyl chloride. The product was isolated and purified using preparative GLPC using an OV-101 column (4 ft × 0.25 in.): NMR (δ in CCl_4) 0.95 (s, 6 H), 1.02 (s, 9 H), 1.33 (s, 2 H), 2.51 (s, 2 H), 7.08 (s, 5 H). The mass spectroscopy cracking pattern of this material is given below; it agrees with the QR_2 produced in the toluene–AIB runs.

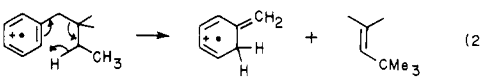
Identification of the Structure of the QR_2-Type Products. Initial GLPC/MS work indicated that the QR_2 product from the decomposition of AIB in neat toluene had the molecular weight and fragmentation pattern appropriate for the compound produced in eq 14 and 15, 2,2,4,4-tetramethyl-1-phenylpentane, (I), as shown in eq 21. However,

$$R\cdot + CH_2{=}CMe_2 \rightarrow RCH_2\dot{C}Me_2 \xrightarrow{Q\cdot} \underset{\text{I}}{(CH_3)_3C{-}CH_2{-}CMe_2{-}CH_2Ph} \quad (21)$$

it also seemed possible that the QR_2 products could result from the process shown in eq 22, giving 3,3,4,4-tetramethyl-1-phenylpentane (II)

$$Q\cdot + CH_2{=}CMe_2 \rightarrow QR\cdot \xrightarrow{R\cdot} \underset{\text{II}}{(CH_3)_3CCMe_2CH_2CH_2Ph} \quad (22)$$

for the AIB–toluene reaction. Therefore, compound I was synthesized (see above) and its GLPC/MS cracking pattern was compared with the unknown. The five largest peaks in the unknown have *m/e* (in order of peak height): 57.1, 92.1, 91.1, 133.1, 112. These data for authentic compound I are: 57.1, 92.1, 91.1, 112, 133. Literature data show that the *m/e* peak at 92 is characteristic of a compound with structure like I and is not given by compounds such as II that have no hydrogens on the γ-carbon atom. (Biemann[37] gives a cyclic mechanism for this rearrangement, eq 23.) Thus $PhCH_2$–CMe_2–CH_2–CMe_3 should give a *m/e* 92 fragment, whereas $PhCH_2$–CH_2–CMe_2–CMe_3 should not.



(23)

General Procedure for Kinetic Runs. For a single kinetic run, reaction solutions of three to six different toluene (QH) to substituted toluene (Q′H) ratios were prepared at the same AIB concentration (usually 0.1 M). The [QH]/[Q′H] ratio varied from 0.3 to 1.5. After placing the reaction mixtures in Pyrex sample tubes and degassing by four freeze–pump–thaw cycles, the ampules were kept in a constant-temperature bath at 80 ± 0.1 °C and photolyzed in a photochemical reactor equipped with eight Rayonet RPR 3500 lamps and a "merry-go-round" device. After 20 h, the reaction mixtures were analyzed by GLPC (Varian 3700 with computer integrator CDS 111) with 10% OV-101 column (10 ft × $^1/_8$ in.).

Quantitative Determination of Photodecomposition Products of AIB in Neat Toluene. A solution of AIB in neat toluene was placed in a 20-mL ampule equipped with a high-vacuum stopcock, degassed by four freeze–pump–thaw cycles, and sealed. The vessel was placed in the photochemical reactor and irradiated for 20 h. Samples of both the gas

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and liquid in the reaction vessel were analyzed by GLPC for isobutane and isobutylene vs. authentic standards (OV-101 column at 25 °C); the total liquid- and gas-phase volumes were measured and the yields of isobutane and isobutylene were then calculated. (Most of the isobutane and isobutylene was found in the liquid phase.) The remaining products in the solution (2,2,3,3-tetramethylbutane, neopentylbenzene, and bibenzyl) were identified and quantitatively determined by GLPC analysis (using biphenyl as an internal standard). No *tert*-butylbenzene was detected. Table I shows the results with both 0.02 and 0.1 M AIB.

Neopentylbenzene and *tert*-butyltoluene can be distinguished by GLPC with temperature programming (50 to 100 °C, program started at 9 min after injection, 50 °C/min) using the OV-101 column. The presence of neopentylbenzene in the reaction mixture was indicated by comparison of its GLPC trace with authentic neopentylbenzene and *tert*-butyltoluene. The presence of neopentylbenzene and not *tert*-butyltoluene was confirmed by comparing the mass cracking patterns (HP 5985 GLPC/MS system with a 6 ft 2% SE-30 column) of the corresponding peak in the reaction mixture with those of authentic compounds.[38] The two have very different MS patterns. For example, the largest four peaks in the spectrum for *tert*-butyltoluene (with % peak height) are: 133.0 (100%), 105.1 (41%), 148.1 (23%), and 93.1 (11%); those for neopentylbenzene are 92.0 (100%), 91.1 (44%), 148.1 (30%), 57.1 (29%).

Acknowledgment. We acknowledge the financial support of the National Science Foundation. We are grateful to Professors Cheves Walling, Hanns Fischer, Dennis Tanner, and Andreas Zavitsas, who read this manuscript in 1980–81 and made helpful suggestions. This work was presented at the Atlanta ACS meeting in March 1981.[39]

Registry No. AIB, 927-83-3; benzene, 71-43-2; toluene, 108-88-3; *m,m*-dimethyltoluene, 108-67-8; *p*-methyltoluene, 106-42-3; *m*-methyltoluene, 108-38-3; *p*-chlorotoluene, 106-43-4; *m*-chlorotoluene, 108-41-8; *m,p*-dichlorotoluene, 95-75-0; *p*-cyanotoluene, 104-85-8; *p-tert*-butyltoluene, 98-51-1; *tert*-butyl radical, 1605-73-8; benzyl radical, 2154-56-5; *tert*-butyl phenylperacetate, 3377-89-7; neopentylbenzene, 1007-26-7; $PhCH_2C(CH_3)_2CH_2C(CH_3)_3$, 81195-34-8.

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Carboxylic Acid Participation in Amide Hydrolysis. Evidence That Separation of a Nonbonded Complex Can Be Rate Determining

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Abstract: Maleamic acids derived from aliphatic amines of a wide range of basicity (compounds **1**–**8**) undergo hydrolysis in solutions of acidity between 10^{-4} M and 1 M hydrogen ion concentration by a mechanism involving participation of the carboxyl group at the adjacent amide. Kinetic analysis of the reaction (50 °C) reveals that the identity of the rate-determining step (or steps) is a function of both the basicity of the leaving group and the acidity of the solution. At pH 4, the rate-determining step is O to N proton transfer to form a zwitterionic intermediate for compounds with weakly basic leaving groups. For compounds with more basic leaving groups, conversion of the zwitterionic intermediate to products is rate determining. In more acidic solutions, where proton transfer is facilitated, diffusion apart from the complex formed from C–N bond breakage of the zwitterionic intermediate is rate determining for compounds with the most basic leaving groups. C–N bond breakage is rate determining for compounds with the least basic leaving groups. This suggests that at pH 4 the breakdown of the zwitterion may also involve rate-determining diffusion. It is concluded that other facile elimination reactions may involve rate-determining diffusion and that changes in the rate-determining step can serve as an indicator of its occurrence and as a means of calibration of rate constants. It is also suggested that since pepsin may catalyze peptide hydrolysis by a carboxyl-participation mechanism, the occurrence of sequential covalent intermediates may exist to permit diffusion of the noncovalently held products.

The transfer of the acyl group of an amide to an oxygen nucleophile may proceed through a tetrahedral intermediate from which a carboxyl group is generated by elimination of the amine derived from the amide.[1] The detailed mechanism of the elimination process is important for arriving at an understanding of catalysis (enzymic and nonenzymic) of these acyl transfer reactions. If the reaction occurs in neutral or acidic water, expulsion of the amine from the intermediate occurs faster than expulsion of water or an alcohol.[1] Thus, the rate-determining step for the overall transfer process occurs during formation of the adduct, and a kinetic study does not provide information that is pertinent to elucidating the mechanism of elimination of amine from the adduct.

If a carboxyl group adds to an amide, that group should leave more readily than the amine from the adduct. However, if the reaction is carried out in water, the carboxyl is such a poor nucleophile that water adds preferentially. If a carboxyl group is adjacent to an amide within a molecule, the addition barrier is greatly reduced.[2] As a result, amine elimination is rate determining in formation of an internal anhydride from a carboxylic acid amide, and kinetic studies of such a reaction bear directly on the elimination reaction.[2] *N*-Alkylmaleamic acids react by such a mechanism,[3] but mechanistic analysis of the elimination process from kinetic data requires a relationship for amine basicity and observed rates. Such a relationship is observed for *N*-arylmaleamic acids but not for the limited number of *N*-alkylmaleamic acids that had been studied.[3,4]

In the case of 2,3-dimethylmaleamic acids, however, we recently showed that some mechanistic complexity results from the fact that the acidity of the medium affects the identity of the rate-

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