

No Significant Stereoelectronic Effects of Isopropyl Group in Photoaddition of Alkylbenzene Derivatives with 10-Methylacridinium Ion *via* Photoinduced Electron Transfer

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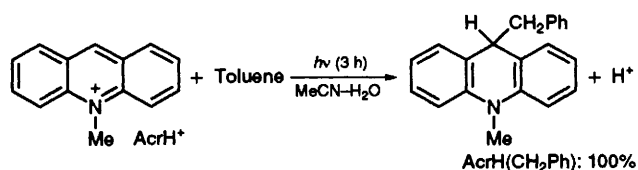
The isopropyl group has no significant stereoelectronic effect on inter- and intra-molecular competition in deprotonation from alkylbenzene radical cations in the photoaddition of alkylbenzene derivatives with 10-methylacridinium ion *via* photoinduced electron transfer from alkylbenzene derivatives to the singlet excited state of 10-methylacridinium ion, followed by the deprotonation of alkylbenzene radical cations.

More than twenty years ago, Schultz *et al.*¹ proposed that a conformation in which the isopropyl group bisects the plane of *p*-cymene would hinder deprotonation from the tertiary centre of the radical cation sparking controversial results on the existence or otherwise of such stereoelectronic effects.²⁻⁴ The role of stereoelectronic effects has been complicated by alternative reaction mechanisms such as direct hydrogen-transfer processes and also by various free radical reaction products, such as, homo- and cross-coupling products and products of further reaction with oxidants or solvents.¹⁻⁴ Thus, unequivocal information has so far been lacking, although stereoelectronic effects in the gas phase have been shown not to exist by Baciocchi *et al.*⁵

Here, we report that efficient photoinduced electron transfer from alkylbenzene derivatives to the singlet excited state of 10-methylacridinium ion (¹AcrH⁺⁺) occurs followed by the deprotonation of alkylbenzene radical cations and the selective radical coupling with acridinyl radical (AcrH[•]) to yield 9-benzyl-substituted 10-methyl-9,10-dihydroacridines exclusively under visible light irradiation. The clean and simple products formed in the photoaddition reactions of alkylbenzene derivatives with AcrH⁺ provide a nice opportunity to gain more comprehensive and confirmative understanding of the existence or nonexistence of the stereoelectronic effects of alkyl groups, particularly isopropyl, on the deprotonation of alkylbenzene radical cations.

Visible light irradiation of the absorption band (λ_{\max} 358 nm) of 10-methylacridinium perchlorate (AcrH⁺ClO₄⁻) in deaerated acetonitrile–water 7:1 vol% solution containing toluene, for 3 h, gave 9-benzyl-10-methyl-9,10-dihydroacridine, Scheme 1. The NMR yield of AcrH(CH₂Ph) was 100% and AcrH(CH₂Ph) was readily isolated as the sole product (the isolated yield was 93%). The AcrH⁺ is also photoreduced by other alkylbenzene derivatives to yield the corresponding adducts. The products were well identified by the ¹H NMR spectra and elemental analysis.[†]

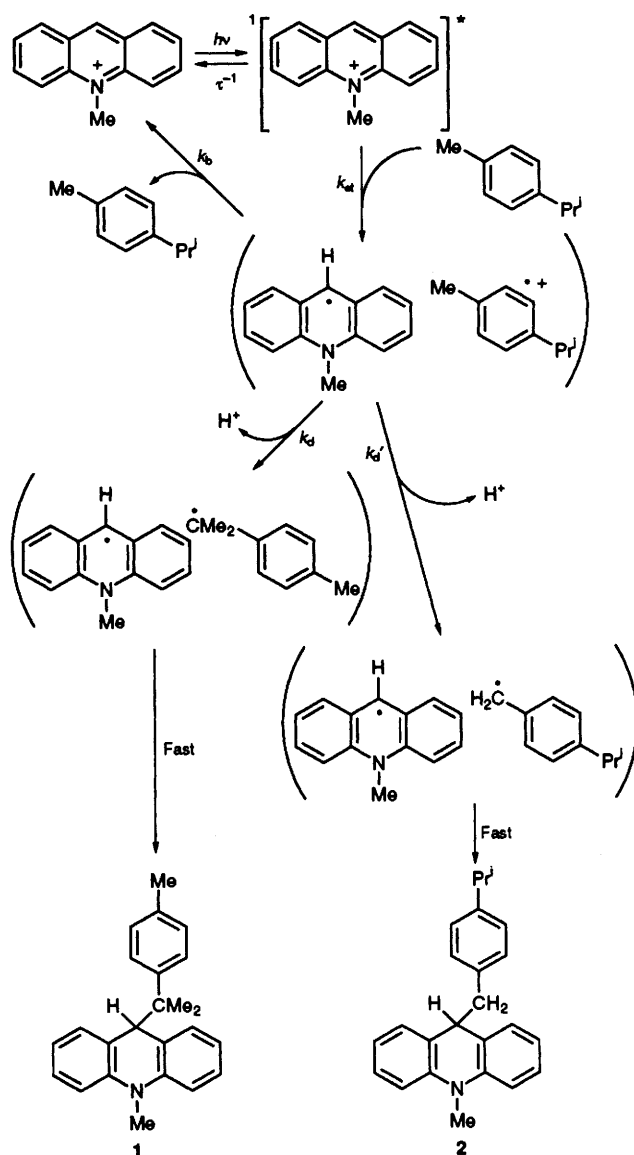
The one-electron oxidation potential (E^0_{red}) of ¹AcrH⁺⁺ has been reported as a highly positive value, 2.32 V (*vs.* saturated calomel electrode)⁶ and thus, the photoinduced electron transfer from most alkylbenzenes to ¹AcrH⁺⁺ is exergonic judging from the less positive one-electron oxidation potentials (E^0_{ox}) of alkylbenzene derivatives.⁷ The



Scheme 1

[†] A representative example for AcrH(CH₂Ph). ¹H NMR (CDCl₃): δ 2.76 (d, 2H, *J* 7.3 Hz), 3.27 (s, 3H), 4.16 (t, 1H, *J* 7.3 Hz), 6.7–7.3 (m, 13H). Satisfactory elemental analysis.

fluorescence of ¹AcrH⁺⁺ is quenched efficiently by monoalkylbenzenes (toluene, ethylbenzene, cumene) and dialkylbenzenes (ethyltoluenes and cymenes) with the quenching rate constants (k_q) in the range of 3.2×10^8 to 4.3×10^8 dm³ mol⁻¹ s⁻¹ and 1.0×10^{10} to 1.3×10^{10} dm³ mol⁻¹ s⁻¹, respectively, which increase with a decrease in the E^0_{ox} value. Thus, the photoaddition reaction may occur *via* photoinduced electron transfer from alkylbenzenes to ¹AcrH⁺⁺ as shown representatively for the reaction with *p*-cymene in Scheme 2.



Scheme 2

The existence of a rate-determining deprotonation step following the photoinduced electron transfer is confirmed by the deuterium isotope effect, which was determined as $\Phi_H/\Phi_D = 3.7$ from the intermolecular competition between toluene and $[^2\text{H}_8]\text{toluene}$. The radical pair in Scheme 2 was detected by EPR spectroscopy [typical triplet signals ($g = 2.0036$ and $g = 4.0$) under visible light irradiation of a deaerated MeCN solution containing cumene ($2.2 \times 10^{-1} \text{ mol dm}^{-3}$) and AcrH^+ ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) at 77 K]. The quantum yields Φ were determined from the disappearance of the absorbance due to AcrH^+ by using a ferrioxalate actinometer⁸ with 358 nm irradiation. According to Scheme 2, the dependence of Φ on the alkylbenzene concentration, $[\text{D}]$ may be expressed by eqn. (1), where k_{et} and k_{b} are the rate constants of photoinduced electron transfer and the back electron transfer,

$$\Phi = [(k_{\text{d}} + k_{\text{d}}')k_{\text{et}}\tau / (k_{\text{d}} + k_{\text{d}}' + k_{\text{b}})] [\text{D}] / (1 + k_{\text{et}}\tau [\text{D}]) \quad (1)$$

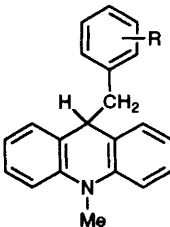
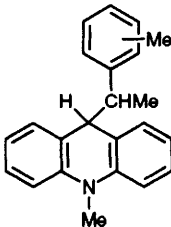
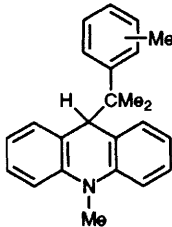
τ is the lifetime of $^1\text{AcrH}^{*+}$ (37 ns), k_{d} and k_{d}' are the rate constants of deprotonation from Pr^i and Me group of the radical cation, respectively. The dependence of Φ on $[\text{D}]$ was confirmed by the linear plots between Φ^{-1} and $[\text{D}]^{-1}$, from which were determined the k_{et} values. The k_{et} values agree well with the k_{q} values determined independently, demonstrating the validity of the electron-transfer mechanism in Scheme 2.

The deprotonation from Pr^i and Me group of *p*-cymene radical cation affords different adducts **1** and **2**, respectively (Scheme 2). In such a case the product ratio 1/2 gives directly the ratio of the deprotonation rate constant $k_{\text{d}}/k_{\text{d}}'$, since the other terms are common in the intramolecular competition. The results of intramolecular competition in the photoaddition of *p*-, *m*- and *o*-ethyltoluenes and -cymenes are summarized in Table 1. The reactivity ratios derived from the intermolecular competition listed also in Table 1 are essentially the same as those in the intramolecular competition. In each instance the significant amount of product *via* the deprotonation from the Pr^i group is observed, in sharp contrast with the previous results,¹ indicating the absence of stereoelectronic effects of the Pr^i group. The relative reactiv-

ity of $\text{Pr}^i:\text{Et}:\text{Me}$ after correction for the statistical factor is 3.7:7.9:1. The heat of formation values of toluene, ethylbenzene, cumene and the corresponding radical cations with various dihedral angles between the benzylic ring plane and the plane of benzene ring were calculated by using the PM3 method.⁹ The calculation indicates that the rotation barriers of Pr^i group are only 1.7 and 1.6 kcal mol⁻¹ (1 cal = 4.184 J) for cumene and the radical cation, respectively, which are not significantly larger than those of Me group (0.1 kcal mol⁻¹ for toluene and the radical cation). The EPR work by Symons¹⁰ has demonstrated that free rotation of the Pr^i group is possible even at 130 K although the rotation is hindered at 77 K. Thus, there may be no preferred conformation of the Pr^i group with respect to the benzene ring at 298 K, in agreement with the absence of the stereoelectronic effects. It should be noted, however, that no adduct *via* the deprotonation from Pr^i is obtained in the case of *o*-cymene. The heat of formation values calculated by the PM3 method⁹ indicate that the deprotonated radical from Pr^i of *o*-cymene radical cation is more stable by 6 kcal mol⁻¹ than that from Me, but that the adduct derived from the former radical is by 14 kcal mol⁻¹ less stable than that from the latter. Thus, no adduct formation *via* the deprotonation from Pr^i in the case of *o*-cymene despite the favourable thermodynamic stability of the deprotonated tertiary radical may be ascribed to the pronounced steric effect operating in the C-C bond forming step between the sterically hindered tertiary radical and AcrH^+ . At present, however, we cannot discard the possibility that such decreased reactivity of Pr^i is due, at least in part, to the stereoelectronic effects in this particular case.

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Table 1 Intramolecular competition of deprotonation from ethyltoluenes ($2.7 \times 10^{-2} \text{ mol dm}^{-3}$) and cymenes ($2.4 \times 10^{-2} \text{ mol dm}^{-3}$) in the photoaddition reactions with AcrH^+ ($8.5 \times 10^{-3} \text{ mol dm}^{-3}$) in deaerated $\text{CD}_3\text{CN}-\text{D}_2\text{O}$ 3/1 v/v% at 298 K

	Product yield (%) ^a (R = Et, Pr ⁱ)		
			
<i>p</i> -Ethyltoluene	16(21)	84(79)	—
<i>m</i> -Ethyltoluene	17	83	—
<i>o</i> -Ethyltoluene	23	77	—
<i>p</i> -Cymene	45(45)	—	55(55)
<i>m</i> -Cymene	50	—	50
<i>o</i> -Cymene	100	—	0

^a The values in parentheses refer to the product yields obtained in the intermolecular competition of ethylbenzene ($1.02 \times 10^{-1} \text{ mol dm}^{-3}$) and cumene ($9.00 \times 10^{-2} \text{ mol dm}^{-3}$) vs. toluene ($1.18 \times 10^{-1} \text{ mol dm}^{-3}$) in the photochemical reactions with AcrH^+ ($8.0 \times 10^{-3} \text{ mol dm}^{-3}$). The difference in the quenching efficiency has been corrected based on the dependence of quantum yields on the quencher concentration.

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