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RELATIVE REACTIVITIES OF ISOPROPYL, ETHYL AND METHYL GROUPS IN THE GAS-PHASE SIDE-CHAIN DEPROTONATION OF ALKYLAROMATIC RADICAL CATIONS

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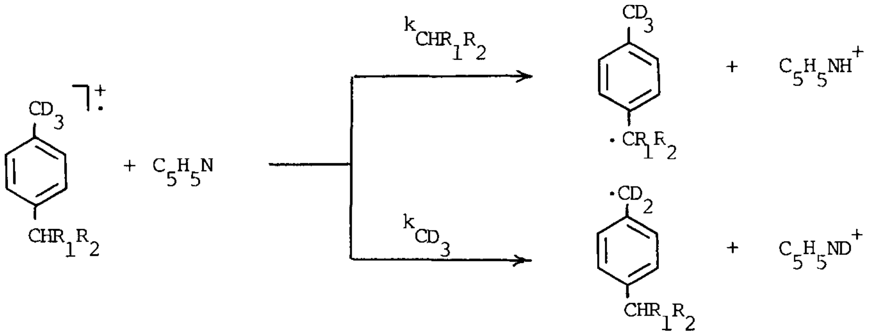
Summary: The relative reactivity of isopropyl, ethyl and methyl groups in the gas-phase side-chain deprotonation of alkylaromatic radical cations by some pyridines has been determined by using Fourier transform mass spectrometry.

The relative reactivities of methyl and isopropyl groups in one-electron side-chain oxidations of *p*-cymene have been used as a mechanistic criterion to distinguish electron transfer from hydrogen atom transfer reactions.[1] It has been suggested that if a *p*-cymene radical cation is formed, it should be much more easily deprotonated at the methyl than at the isopropyl group for stereoelectronic reasons.[1a] Preferential deprotonation at the methyl group should also be observed in *p*-ethyltoluene radical cation. Of course, the converse is expected for a hydrogen atom transfer mechanism. However, serious doubts on this proposal have been raised by recent studies concerning oxidation of alkylaromatics by Ce(IV) salts and $S_2O_8^{=}$.[2]

To throw light upon this problem we now report on the relative reactivity of alkyl groups in the gas-phase deprotonation of *p*-cymene and *p*-ethyltoluene radical cations. Other than for the mechanistic implications, this study is of interest also because it provides us with some fundamental information on the gas-phase chemistry of alkylaromatic radical cations.

Alkylaromatic radical cations **1**-**3** have been generated by electron impact from partially deuterated *p*-xylene, *p*-ethyltoluene, and *p*-cymene in the ion source of a Nicolet FT/MS -1000, equipped with a superconducting magnet charged at 2T, using an electron energy of 9 eV or less.[3] Pyridine (eq. 1), 4-cyanopyridine, and 2,6-dibromopyridine were used as bases for the deprotonation.[5] Typically, the experimental pressure was 1×10^{-6} torr and the alkylaromatic/base ratio about 1.



(1)

1 ($R_1=R_2=H$)
2 ($R_1=H, R_2=Me$)
3 ($R_1=R_2=Me$)

The relative rates of formation of light and deuterated pyridinium ions were measured for each base, thus obtaining the relative reactivity data for the CHR_1R_2 and CD_3 groups ($k_{-CHR_1R_2}/k_{-CD_3}$) which are reported in the Table. In the same Table are displayed the relative reactivities of Me, Et and *i*-Pr groups calculated by correcting the $k_{-CHR_1R_2}/k_{-CD_3}$ values

Table. CHR_1R_2/CD_3 Reactivity Ratios and Relative Reactivities of Alkyl Groups in the Gas-Phase Side-Chain Deprotonation of the Alkylaromatic Radical Cations 1-3 Promoted by Some Pyridines

Base	$k_{-CHR_1R_2}/k_{-CD_3}$ [a]			Relative Reactivities[b]		
	1	2	3	CH_3	CH_2CH_3	$CH(CH_3)_2$
Pyridine	1.6	1.4	0.8	1	1.3	1.5
4-Cyanopyridine	2.0	3.2	1.6	1	2.4	2.4
2,6-Dibromopyridine	2.3	4.2	1.4	1	2.7	1.8

a) The average error is ± 10% ; b) Statistically corrected for the numbers of α-hydrogens. Data calculated from $k_{-CHR_1R_2}/k_{-CD_3}$ ratios after correction for the value of deuterium kinetic isotope effect found for each base (k_{-CH_3}/k_{-CD_3} in the reactions of radical cation 1).

for the statistical factor and for the value of the partition deuterium kinetic isotope effect, which is simply given by the CH_3/CD_3 reactivity ratio found in the reaction of **1**.[6]

The observed relative reactivities span a small range, as expected for a little selective gas-phase exoergonic process. Nevertheless most of differences in the reported data are well outside the experimental error and, therefore, can conveniently be discussed.

The most important finding is that with all bases used isopropyl and ethyl are more reactive than methyl group, which indicates that both *p*-cymene and *p*-ethyltoluene radical cations do not exhibit any intrinsic tendency to be preferentially deprotonated at the Me group. This result is opposite to that previously predicted[1a] and nicely supports the recent caveat against the use of the Me/*i*-Pr reactivity ratio as a mechanistic criterion to distinguish electron transfer from hydrogen atom transfer reactions.[2]

In the deprotonation of an alkylaromatic radical cation reactivity should be influenced by the extent of positive charge delocalized in the alkyl group.[7] In this respect it is interesting to note that a recent ESR study of *p*-cymene radical cation[8] has shown that electron donation from the C-H σ-orbitals into the ring π-orbitals is greater in the *i*-Pr than in the Me group, which is in line with a greater deprotonation rate for the former group.

Two additional comments are possible. First, steric effects appear to be important in the deprotonation process, as shown by the observation that the reactivity order is *i*-Pr > Et > Me when the base is pyridine, but it becomes Et > *i*-Pr > Me, when the base is 2,6-dibromopyridine. Certainly the latter base has larger steric requirements than pyridine and therefore can find it more difficult to approach the sterically crowded α-proton of the isopropyl group. Thus, the reactivity of this group becomes even smaller than of ethyl group.

Second, the increase in the Et/Me ratio on going from pyridine to 4-cyano- and to 2,6-dibromo-pyridine may be accounted for by the lower basicity and therefore greater selectivity of these two bases as compared to pyridine.[9] However, intriguing is the observation that with 4-cyanopyridine Et and *i*-Pr groups exhibit a similar reactivity. At present we have no plausible explanation for this phenomenon.

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3. Under these conditions,ions should not be produced with significant internal energy. See also the recent study by Mautner on the kinetics of gas-phase deprotonation of alkylaromatic radical cations.[4]
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5. These bases have a higher ionization potentials than the examined alkylaromatic compounds. Therefore side processes involving radical cations of the bases are excluded.
6. It is assumed that this value remains approximately constant through the series. To show the substantial correctness of this assumption we have also measured k_H/k_D for the deprotonation of p-$CH_3CH_2C_6H_4CD_2CH_3$ radical cation. The k_H/k_D values obtained were 1.7 (pyridine), 2.2(4-cyanopyridine), 2.5(2.6-dibromopyridine) which are quite close to those observed in the deprotonation of **1**.
7. The transition state for the deprotonation reaction of an alkylaromatic radical cation should be reactant like. See C.J.Schlesener, C.Amatore, and J.Kochi, J.Am.Chem.Soc., 106 7472 (1984).
8. D.N.Ramakrishna Rao, H.Chandra, and M.C.R.Symons, J.Chem.Soc.Perkin Trans.2, 1201 (1984).
9. Proton affinity is 220.4 Kcal/mol for pyridine and 210.6 Kcal/mol for 4-cyanopyridine. Data are not available for 2,6-dibromopyridine, but there is no doubt that it is a much less basic species than pyridine since proton affinity of 2-bromopyridine is 215.6 Kcal/mol.

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