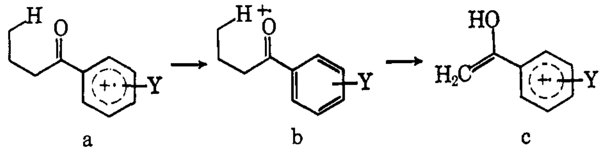
Communications to the Editor

Substituent Effects in Unimolecular Ion Decompositions. IX.[1] Specific Hydrogen Rearrangement in Butyrophenones[2]

Sir:

Of the unimolecular ion reactions observed in mass spectra, the site-specific rearrangement of hydrogen to unsaturated functional groups[3] is probably the most extensively studied class of such reactions known.[4,5] Despite this, there is disagreement on the nature of the driving forces for this rearrangement;[6] it has been proposed that hydrogen migrates as a proton,[5,7] that it migrates as an atom to a radical site,[8,9] and that in particular cases it can migrate to an excited functional group which holds neither a charge nor an unpaired electron.[10]

We report here a study of this problem by the use of substituent effects, a technique employed recently to investigate a variety of mass spectral reactions,[11] including several involving other types of rearrangements.[1,12,13] For *n*-butyrophenones, the effect of Y on the rate of formation of $(M - C_2H_4)\cdot^+$ (reaction 1) is indicated by the log Z/Z_0 values[12] of Table I. Measurements were made at low electron energies to minimize further decomposition of the product ion.



(1)

Electron-withdrawing substituents strongly enhance the formation of the rearranged product; the ρ value[14] of approximately $+2.0$ indicated by these substituents is much larger than any previously reported for the rate of an electron-impact reaction.[13] Thus it appears that the reaction is *enhanced* by an increased positive charge at the reaction site, an effect which is opposite to that expected for the migration of a proton. This could correspond to a lower energy difference between the ground state (a) and the reactive excited state, of which b should represent an important canonical form when Y is an electron-withdrawing group. The ionization potentials of Table I also support this explanation, as the effect of substituents exhibits a negative ρ value and correlates as expected with σ^+_{para} values.[15]

Table I. $CH_3CH_2CH_2COC_6H_4Y\cdot^+ \rightarrow CH_2C(OH)C_6H_4Y\cdot^+ + C_2H_4$

Y	σ	IP, ev[a]	log Z/Z_0[b]
p-NO_2	+0.78	9.86	1.50
m-NO_2	+0.71	9.88	1.39
p-Br	+0.23	8.75	0.91
p-Cl	+0.23	9.03	0.86
p-F	+0.06	9.09	0.41
H	0.0	9.38	0.0
m-NH_2	−0.16	8.06	−0.70
p-CH_3	−0.17	8.75	−0.04
p-C_6H_5	−0.25[c]	8.44	−0.24
p-OCH_3	−0.27	8.33	0.05
p-OC_6H_5	−0.32	8.55	0.07
p-OH	−0.37	8.65	0.14
p-NH_2	−0.66	8.01	−0.16

[a] Ionization potentials, ±0.2 ev, determined by the semilogarithmic plot method. [b] $Z = [M - C_2H_4]/[M]$ (ref 5); determined using electron energies 10 ev above the ionization potential. Log Z/Z_0 values were found to be relatively constant up to 20 ev above the ionization potential, except that *m*-NH_2 rises to −0.41. [c] Reference 11.

The apparent requirement for the presence of the *positive charge* on the carbonyl group is not necessarily inconsistent with our previous postulation that the *radical site* is an important driving force in the McLafferty rearrangement,[8] as the radical site also moves to the carbonyl group in form b. For these compounds Pitts and co-workers[16] have studied the type 2 photochemical rearrangement which is formally analogous to this mass spectral rearrangement, but in which no ionic site is present. These authors also found a positive ρ value for the substituent effect correlation with quantum yield, concluding that the reactivity is due to the n,π^* triplet state. This state contains an unpaired nonbonding electron on oxygen, as does structure b.

However, Z/Z_0 values for many compounds of Table I indicate faster rates than predicted by the Hammett equation using the ρ value of $+2.0$; these compounds are characterized by containing substituents capable of electron donation by resonance. A possible rationalization is that another canonical form, b′, which requires a *negative* ρ value, is also an important contributor to the reactive excited state. Similar electronic structures with a radical site on the oxygen may explain the much higher tendency for the McLafferty rearrangement in the spectra of aliphatic compounds with a heteroatom adjacent to the carbonyl group, such as acids, amides, and esters (d), as compared to aldehydes and ketones

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(2) The generous financial support of the National Institutes of Health, GM 12755 and FR 00354, is gratefully acknowledged. The Hitachi RMU-6D mass spectrometer used was purchased through National Science Foundation Grant GP 4335.

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(8) F. W. McLafferty, *Chem. Commun.*, 78 (1966).

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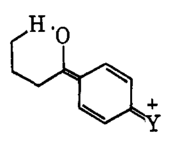
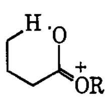
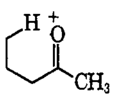


b′



d



e

(e).[8,17] Note that the *m*-NH_2 derivative, in which such resonance donation would be greatly reduced, exhibits a low Z/Z_0 value; the *p*-Ph derivative should have an increased number of canonical forms in which the radical site is removed from the carbonyl group.[18]

Thus for this rearrangement in butyrophenones two substituent effects with ρ values of opposite sign appear to be operative; these effects are consistent with the postulation that the unpaired electron site serves as a driving force for rearrangement.[8]

(17) A similar formulation will rationalize the increased abundance of the (M − C_2H_4) ion in ethyl benzoate compared to that in butyrophenone.

(18) T. Wachs and F. W. McLafferty, *J. Am. Chem. Soc.*, **89**, 5044 (1967).

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The Influence of the Charge and Radical Sites in Unimolecular Ion Decompositions[1]

Sir:

The concept of localized charge[2] as a driving force for unimolecular decomposition reactions induced by electron impact has been used by a number of authors to explain and correlate a large variety of reactions observed in mass spectra.[3] As an extension of this concept, it has been proposed that most decomposition reactions which yield abundant ions can be interpreted as being initiated by the positive charge or the unpaired electron at a particular site.[3c–5] However, for particular cases it has been postulated that the localized charge is not involved in the formation of an abundant ion,[6] and it has been pointed out that the usefulness of such a concept to rationalize decomposition pathways is not proof of its validity.[7]

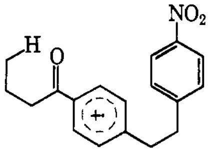
We report here mass spectral data for a series of aromatic ketones in which the characteristic ketone fragmentation pathways are almost completely eliminated in one of the members of the series by a minor structural change; the most logical explanation is that this structural change has moved the site of charge localization to a position isolated from the ketone moiety.

In Table I are listed the ion intensities (based on the molecular ion) of the characteristic fragment ions and the ionization potentials of the molecular ion of a series of *para*-substituted butyrophenones. Previous work[8] on the effect of substituents (Y) on the formation of the YPhCO ion in the spectra of YPhCOR indicates that the intensity of this ion compared to the molecular ion in the latter four compounds in Table I should be approximately the same since the substituent groups present will have nearly identical σ values. In all but one of the spectra of butyrophenones which we have examined, this M − 43 ion is the most abundant in the spectrum. In the spectrum of *p*-[2-(*p*-aminophenyl)ethyl]butyrophenone (III) this decomposition has been virtually eliminated. The same dramatic effect is observed for the M − C_2H_4 rearrangement ion.

Table I. Characteristic Ions in the 75-ev Spectrum of *para*-Substituted Butyrophenones, *p*-$YPhCOCH_2CH_2CH_3$

Y	M	M − 15	M − 28	M − 43	M − 71	IP, ev[a]
H	100	7.9	28.9	470	230	9.38
$PhCH_2$	100	9.0	128	2650	47[b]	8.69
p-$NO_2PhCH_2CH_2$ (I)	100	5[b]	94	3000	2	9.10
p-$C_3H_7COPhCH_2CH_2$ (II)	100	5	99	2600	40	8.91
p-$NH_2PhCH_2CH_2$[c] (III)	100	<1	<1[d]	8	1	8.14

[a] Ionization potentials, ±0.2 ev, determined by previous method.[5] [b] Corrected for isotopic contributions. [c] The most intense ion of this spectrum, *m/e* 106, has an abundance of 975. [d] Value decreased upon lowering the ionizing voltage to a point 10 ev above ionization potential.



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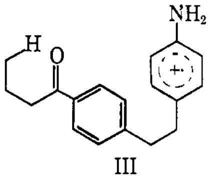

III

Again the substituent effects[5] on this reaction, although not a simple function of σ values, indicate that the *p*-amino substitution should have only a small effect on the abundance of this ion. However, a significant change in the molecular ion caused by the *p*-amino substitution is indicated by the substantial reduction that occurs in the ionization potential. The latter value is similar to the ionization potentials of arylamines[5,9] (8.14 ev for *p*-aminotoluene[9]) and substantially lower than the values for *p*-alkylphenyl alkyl ketones.[5,10] This is consistent with a shift of the charge site to the ring not bearing the keto moiety.[11,12]

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(1) The generous financial support of the National Institutes of Health (GM 12755 and FR 00354) is gratefully acknowledged. The Hitachi RMU 6D mass spectrometer used in this work was purchased through National Science Foundation Grant GP 4335.

(2) F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 93.

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(12) Charge localization offers an explanation for other features of the spectrum of II. Secondary ions whose formation involves reaction at the second ketone moiety after initial decomposition at the first, such