azetidine I. The nmr peaks listed by Kan and Furey (τ 2.88, 6.29, and 7.92–9.40) are satisfactory for the dihydro dimer since the known benzyl analog IV shows a peak for the tertiary benzylic hydrogens as a singlet at τ 6.22.[10] Similarly, the infrared and ultraviolet spectra reported are entirely consistent with this revised structure. Structure II was further established by the identity of its infrared spectrum and undepressed mixture melting point with an authentic sample obtained by the quantitative reduction of VI with aluminum amalgam.[11] Irradiation of a series of related benzaldehyde N-alkylimines also afforded dihydro photodimers (III–V); the infrared, ultraviolet, nmr, and mass spectral properties are entirely analogous to those of II.[12]

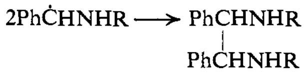
Although the reaction bears analogy to aryl ketone photoreduction, initial experiments indicate that mechanistically the reaction is quite different in that it appears not to involve the excited states of the imine as intermediates in the reduction. While direct irradiation of benzaldehyde N-benzylimine (VII) in 95% ethanol leads to very efficient photoreduction, the imine is *not* photoreduced in 2-propanol, a solvent which is very effective in photoreducing benzophenone.[13] Photoreduction proceeded readily, however, when 2-propanol was diluted with water and led to dihydro dimer IV and acetone. We attribute this behavior to partial hydrolysis of the imine in the aqueous solvent followed by sensitization by small amounts of benzaldehyde which can compete favorably with imine as a light-absorbing component.[14] The N-alkylimine is readily photoreduced when irradiated in 2-propanol in the presence of low concentrations of triplet photosensitizers such as benzaldehyde and benzophenone.

The photoreduction of VII in 2-propanol proceeds in high quantum yield ($\Phi = 0.58$) when benzophenone is used as a sensitizer. It would appear, at first glance, that triplet energy is being transferred from benzophenone to the imine which then undergoes photoreduction. That the triplet state of the imine is not, nonetheless, the active hydrogen-abstracting species is shown by the fact that benzophenone phosphorescence is *not* quenched (EPA at 77°K) by the imine. Also noteworthy is the fact that the imine itself shows no detectable emission and does not quench the small amount of benzaldehyde emission. Although the phosphorescence of benzaldehyde and benzophenone is not quenched, the photoreduction of the latter in 2-propanol is completely inhibited by the imine. In the inhibited reaction, while the imine prevents conversion of benzophenone to benzpinacol, photoreduction of the imine does occur. Examination of the quantum efficiency of a number of triplet sensitizers in effecting imine photoreduction reveals a correlation with the ability of the sensitizer itself to photoreduce in the alcoholic medium. Thus benzophenone, benzaldehyde, acetophenone, and xanthone sensitize in that order of efficiency and are themselves not consumed. High-energy sensitizers, such as dibenzothiophene and triphenylamine, that do not themselves photoreduce in alcohol are ineffective as sensitizers. These observations when taken together suggest that the photoreduction does not involve an excited state of the imine but rather is brought about by one or more of the intermediates of the ketone photoreduction.[15] The photoreaction may be represented by the sequence of reactions 1–4, starting with abstraction of hydrogen from the carbinol carbon by the lowest excited triplet state of the sensitizer. It should be noted that this scheme

$$\mathrm{Ph_2CO^*} + \mathrm{(CH_3)_2CHOH} \longrightarrow \mathrm{(Ph)_2\dot{C}OH} + \mathrm{(CH_3)_2\dot{C}OH} \qquad (1)$$

$$\mathrm{(Ph)_2\dot{C}OH} + \mathrm{PhCH{=}NR} \longrightarrow \mathrm{Ph_2CO} + \mathrm{Ph\dot{C}HNHR} \qquad (2)$$

$$\mathrm{(CH_3)_2\dot{C}OH} + \mathrm{PhCH{=}NR} \longrightarrow \mathrm{CH_3COCH_3} + \mathrm{Ph\dot{C}HNHR} \qquad (3)$$



$$2\mathrm{Ph\dot{C}HNHR} \longrightarrow \begin{array}{c}\mathrm{PhCHNHR}\\ |\\ \mathrm{PhCHNHR}\end{array} \qquad (4)$$

involves radical intermediates similar to those proposed by Cohen in the photoreduction of aromatic ketones using amines as hydrogen sources.[16] For that case the reverse of reaction 2 has been suggested as an important step.

Further investigations to determine the generality of hydrogen atom transfer in imine photochemistry and a more systematic study of the relationship between structure, reaction product, and mechanism will be the subject of future reports.

Acknowledgment. We wish to thank the National Science Foundation (Grant GP-6511) for financial support and Professor Maurice Bursey for obtaining the mass spectra.

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(10) The formation of IV from the photolysis of N-benzylbenzalimine was first reported by A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **89**, 102 (1967).

(11) R. Jaunin, *Helv. Chim. Acta*, **39**, 111 (1956).

(12) Synthetic details and structure proofs will be reported in our full paper. All new compounds were properly characterized and acceptable chemical analyses were obtained.

(13) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

(14) Excitation with 254-mμ light does not result in photoreduction, since most of the light is absorbed by the imine under these conditions.

(15) N. Filipescu and F. L. Minn, *J. Am. Chem. Soc.*, **90**, 1544 (1968).

(16) S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3471 (1967); S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968).

(17) Alfred P. Sloan Fellow, 1968–1970.

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Kinetic Studies in Mass Spectrometry. II. Wide-Range Electron Energy Kinetics. A Novel Transition-State Probe

Sir:

Recently the application of kinetic methods to the analysis of relatively simple mass spectral fragmentation pathways has been developed by McLafferty and Bursey.[1-4] Despite minor criticism,[5] this elegant technique promises to be of extreme value in the study of reactions of gaseous ions in the mass spectrometer, provided that one keeps in mind the approximations and limitations involved in its derivation[1-4] and application.[1-5] We report here a potentially useful ex-

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(1) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

(2) M. M. Bursey and F. W. McLafferty, *ibid.*, **89**, 1 (1967), and subsequent papers in this series.

(3) M. M. Bursey, *Org. Mass Spectrom.*, **1**, 31 (1968).

(4) F. W. McLafferty, *Chem. Commun.*, submitted for publication. We thank Professor McLafferty for helpful discussion and for kindly providing a preprint of his communication.

(5) I. Howe and D. H. Williams, *ibid.*, 220 (1968).

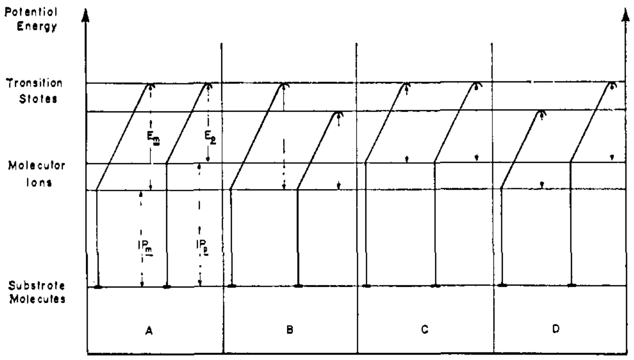

Figure 1. Idealized energy diagrams for reaction rates of *meta*- and *para*-substituted isomer pair molecular ions.

tension of the kinetic technique, designed to distinguish between rate differences due to "ground-state" energy differences as against transition-state energy differences.

A preliminary study[6] of substituent effects on the cleavage of substituted benzyl phenyl ethers $XC_6H_4CH_2OC_6H_5$ to $XC_6H_4CH_2^+$ ions revealed a Hammett linear free energy relationship of relative rate with σ^+ constants (ρ −0.76) at 20 and 70 eV, with each isomeric *m*- and *p*-X pair of substrate molecular ions affording different rates. These data were interpreted[6] in terms of benzylic, rather than tropylium-like,[7] transition states for the formation of $XC_6H_4CH_2^+$ ions in this particular case on the assumption that transition-state energy differences between *m*- and *p*-X pairs of substrates were more important than "ground-state" energy differences for the respective molecular ions.[10]

Table I. Z_p/Z_m Ratios for the Reaction $[XC_6H_4CH_2OC_6H_5]\cdot^+ \rightarrow [XC_6H_4CH_2]^+$ in Benzyl Phenyl Ethers at Various Electron Energies

X	Z_p/Z_m at 70[a]	50[a]	30[a]	25[a]	20[a]	15[a]	12[a]	11[a]	10[a]	9[a]	8[a]
OCH_3	8.95	9.20	9.35	9.50	8.66	8.74	8.82	9.74	10.9	11.5	15.2
CH_3	1.72	1.78	1.98	1.97	1.98	2.07	1.98	1.73	1.89	2.48	2.74
F	2.82	2.70	2.81	2.75	2.59	3.98	4.82	5.99	6.68	7.73	
Cl	2.15	2.25	2.20	2.30	2.45	2.76	3.00	3.04	3.51	3.70	5.62
Br	2.31	2.30	2.25	2.30	2.41	2.44	2.70	2.96	3.27	3.22	4.29
NO_2	0.51	0.48	0.49	0.50	0.58	0.71	0.83	0.87	0.89	0.86	
CF_3	0.97	1.00	0.99	0.98	0.81	0.71	0.56	0.46	0.27	0.06	

[a] Electron volts.

In essence, the problem of differentiating between ground-state and transition-state energy differences[12] for *meta* and *para* isomer pairs of compounds can be visualized in a simplified way as shown in Figure 1. Thus different reaction rates for each *meta*- and *para*-X pair are indicated by energy diagrams A (molecular ion energy difference) and B (transition-state energy difference), and identical rates by diagrams C (same molecular ion and transition-state energy and same "energy of activation") and D (differing molecular ion and transition-state energies but same "energy of activation").[14]

To distinguish between situations A and B (and also between C and D) experimentally, it is proposed here that reaction rates[1] for each *m*- and *p*-X pair (Z_m and Z_p for the same substituent) be compared from 70 eV down to threshold electron energy for the relevant reaction,[15] at convenient energy intervals. For processes with identical transition-state energies (and therefore possibly identical structures) for each isomer (*e.g.*, A and C in the figure) the rate ratio Z_p/Z_m will be effectively constant over the entire electron-energy range[16,17] and will depend on the relative "energies of activation" E_m and E_p.[14] For processes with different transition-state energies (*e.g.*, B and D), the value of Z_p/Z_m will change appreciably as the electron energy is lowered in the vicinity of threshold.[16] This phenomenon arises since the decreasing electron energy approaches the higher appearance potential for the formation of the daughter ion from one molecular ion isomer (*e.g.*, *m*-X) sooner than that of the other isomer (*e.g.*, *p*-X),[18] resulting in rate discrimination against the process of higher transition-state energy.[19]

This new technique has been applied to the investigation of $XC_6H_4CH_2^+$ ion structure from a variety of benzyl substrates, ranging from excellent mass spec-

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[6] P. Brown, *J. Amer. Chem. Soc.*, 90, 2694 (1968).

[7] Previous labeling evidence[8] for the structure of the $C_6H_5CH_2^+$ ions derived from various benzyl systems at 70 eV has suggested a symmetrical tropylium-like species as the transition state for their decomposition to $C_5H_5^+$ ions. Appearance potential determinations[9] have indicated that, in the transition state for formation of $XC_6H_4CH_2^+$ ions from *meta*- and *para*-substituted benzyl halides, the structure is a substituted tropylium ion when X = CH_3, F, and OH, but is of lower symmetry (probably benzylic) when X = OCH_3. We plan to investigate substituted benzyl halides by wide-range electron energy kinetics.

[8] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10, and references cited therein.

[9] J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *J. Amer. Chem. Soc.*, **84**, 4 (1962).

[10] Ionization potentials for *meta*- and *para*-substituted toluenes are the same[11] within experimental error when X = CH_3 and OH.

[11] G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

[12] This problem is a general one in Hammett-type rate studies, but is especially acute in mass spectral kinetics, where the heats of formation of a series of substituted molecular ions are usually unknown, unless precise ionization potential data are available,[13] together with heats of formation of the original neutral molecules.

[13] For example, see ref 11.

[14] The approximation of one transition state and one energy of activation for each reaction only holds at best at threshold. At higher electron energies, a distribution of excited states may each contribute to the over-all rate.[4] Irrespective of the distribution and population of excited states in the *meta*- and *para*-substituted ions having the same substituent, however, the effects of these same substituents (provided that they are not isolated from the reaction site) on transition-state stability for a decomposition reaction are not expected to be identical (due to differing orientation with respect to the reaction site) unless both *meta*- and *para*-substituted ions are proceeding through identical transition states.

[15] With the same limitations already expressed[1-4] in the original application of the kinetic technique to mass spectra.

[16] $Z_p/Z_m \neq 1.0$ for case A and case B, but $Z_p/Z_m = 1.0$ for case C (and also case D at higher voltages).

[17] P. Brown, *J. Amer. Chem. Soc.*, 90, 4461 (1968). In each case, the reaction studied is the major mode of decomposition of the molecular ions.

[18] Implicit in this treatment is the assumption that both isomeric *meta*- and *para*-substituted substrate molecules with the same substituent have the same heats of formation (see Figure 1).

[19] This amounts to kinetic detection of appearance potential differences.

trometric leaving groups (*e.g.*, $\cdot OC_6H_5$) to relatively poor ones (*e.g.*, $\cdot H$).[17] In Table I are listed Z_p/Z_m ratios for substituted benzyl phenyl ether cleavage from 70 eV down to threshold.[20] For all substituents employed (i) each *m*- and *p*-X pair gives a different rate ($Z_p/Z_m \neq 1$), and (ii) Z_p/Z_m ratios are effectively constant in the 70–20-eV range, but vary increasingly in the 15–20-eV to 9–8-eV range,[21] as the electron energy is reduced.

This situation is exemplified by energy diagram B in Figure 1, *i.e.*, transition-state energy differences are significant in the cleavage of *meta*- and *para*-substituted benzyl phenyl ethers. Thus our earlier conclusions concerning this system[6] seem quite justified, and the transition states for formation of $XC_6H_4CH_2^+$ ions from $XC_6H_4CH_2OC_6H_5\cdot^+$ molecular ions are not identical in energy or structure, and therefore most simply are benzylic rather than tropylium-like, when the leaving group is $\cdot OC_6H_5$. By extension,[22] the $XC_6H_4CH_2^+$ ions initially formed in this endothermic process are also expected to be benzylic.

Further studies[17] of the application of wide-range electron energy kinetic substituent effects to the general problems of ion structure and substituent randomization are in progress.

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[20] Experimental conditions have been described in ref 6.

[21] For all substituents used except X = CH_3, the Z_p/Z_m rate ratio changes by at least a factor of 1.5 as threshold is approached. For X = OCH_3, CH_3, F, Cl, and Br, the *meta* isomer must have a higher transition-state energy (Z_p/Z_m increases at low electron voltage) and "energy of activation" ($Z_p > Z_m$ in the 15–70-eV range) than the *para* isomer, and with X = CF_3, the opposite situation obtains. When X = NO_2, the *meta* isomer has the higher transition-state energy, but the lower "energy of activation."

[22] G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

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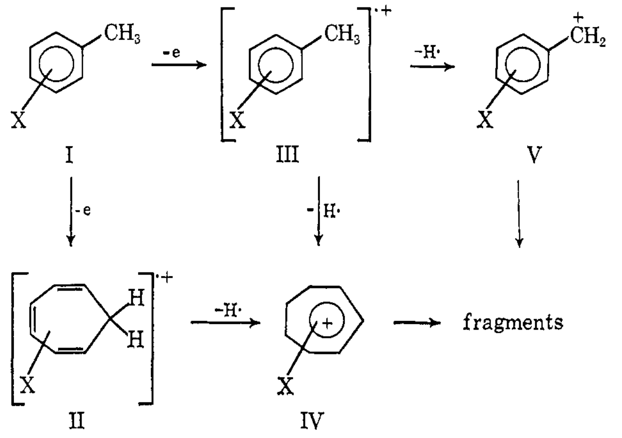
Kinetic Studies in Mass Spectrometry. III. The Nature of the M − H Reaction in Substituted Toluenes

Sir:

In the preceding communication,[1] we propose a simple new kinetic method for determining whether transition-states energies are the same or different for the reaction of *meta*- and *para*-substituted gaseous ions in the mass spectrometer. For *meta*- and *para*-substituted isomeric substrates, this approach amounts to a kinetic evaluation of the difference in appearance potentials for the *meta*- and *para*-substituted daughter ions being produced.[2] Thus the rate[4] ratio Z_p/Z_m well above threshold (typically 20–70 eV) reflects the difference in effective "energies of activation"[3] for the two processes, while variation or constancy of Z_p/Z_m in the electron-energy range approaching threshold (typically 15–12 to 9–8 eV) reflects the nonequivalence or equivalence, respectively, of the energies of the transition states.[1,5]

In continuation of our kinetic studies[1,6,7] on the structure of $XC_6H_4CH_2^+$ ions produced from various substituted benzyl precursors by electron impact induced fragmentation, we report here preliminary results obtained with a series of substituted toluenes[8] (I).



Meyerson has pointed out that decomposing ions of formula $C_7H_7^+$ in the mass spectra of toluene[9,10] and cycloheptatriene[10] are best represented by the symmetrical tropylium ion (IV, X = H). Furthermore, identical heats of formation for $C_7H_7^+$ derived from toluene and cycloheptatriene have been cited[9,11] in favor of a common, rearranged precursor ion such as II, X = H.[9] We have applied the new technique of wide-range electron energy kinetics[1] to the M − H reaction of substituted toluenes (I) as a direct test of its validity and possible scope.

In Table I, the rate data obtained are summarized.[12] The rate ratio Z_p/Z_m remains effectively constant over the energy range 70 eV to threshold for all substituents employed (CH_3, F, Cl, Br, CN) except OCH_3. This result indicates (i) that the transition-state energies for each *m*- and *p*-X substituted pair of isomeric toluenes

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[1] P. Brown, *J. Amer. Chem. Soc.*, 90, 4459 (1968).

[2] Rate processes are controlled by the energy differences ("energies of activation") between parent ions and transition states[3] and the energy available by ionization in the electron beam. Transition-state energies, on the other hand, are coincident with the appearance potential energy barrier.

[3] See footnote 14 in ref 1.

[4] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

[5] It is assumed that the heats of formation of each *meta*- and *para*-substituted pair of substrate molecules are the same for the same substituent.

[6] P. Brown, *J. Amer. Chem. Soc.*, 90, 2694 (1968).

[7] Substituted benzyl phenyl ethers have been studied,[1,6] with the aim of providing an excellent leaving group ($\cdot OC_6H_5$) for $XC_6H_4CH_2^+$ ion formation.

[8] The M − H reaction of substituted toluenes is intended to furnish a poor leaving group ($\cdot H$), and the relatively high appearance potential for this process in toluene[9] itself supports this idea. However, the M − H reaction is still the major fragmentation pathway of the compounds studied.

[9] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

[10] S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 3340 (1963).

[11] S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, 27, 901 (1957).

[12] Mass spectra were secured using an Atlas CH4B instrument, operating under the following conditions: reservoir 150°, source 210°, filament current 2–5 μA. All reported ion abundance measurements were at least duplicated.