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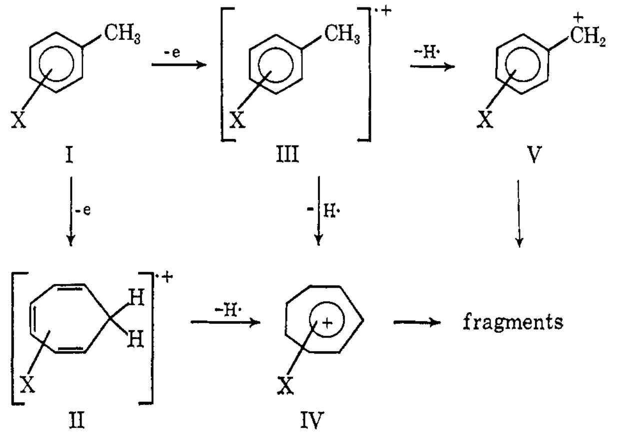
Kinetic Studies in Mass Spectrometry. III. The Nature of the M − H Reaction in Substituted Toluenes

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.

Table I. Relative Rate Ratios Z_p/Z_m for the M − H Reaction of Substituted Toluenes (I)

X[a]	Z_p/Z_m at								
	70[d]	50[d]	30[d]	25[d]	20[d]	15[d]	12[d]	11[d]	10[d]
OCH_3[c]	2.94	2.91	2.83	2.85	2.74	2.65	2.22	1.80	1.1[b]
CH_3	1.04	1.02	1.04	0.99	1.00	0.94	0.91	0.95	0.9[b]
F	0.99	1.03	1.02	1.00	1.02	0.98	1.00	1.00	
Cl	1.47	1.47	1.39	1.40	1.36	1.49	1.5[b]		
Br	1.75	1.85	1.81	1.77	1.70	1.78	1.7[b]		
CN	1.00	1.00	0.98	0.99	0.98	0.97	1.00	1.0[b]	

[a] X = NO_2 and $COCH_3$ did not show M − H peaks. [b] Measurements made from very low rates. [c] M − H measurements made from methoxytoluenes-d_3. [d] Electron volts.

(except for X = OCH_3) are identical, which in turn is most simply interpreted in terms of transition states of the same structure (tropylium-like, II or III → IV) for each *m*- and *p*-X pair (except for X = OCH_3), and (ii) that the distribution and population of reactive excited states over the entire electron energy range must be very similar for each *m*- and *p*-X substituted isomer pairs of molecular ions.

For substituents X = CH_3, F, and CN, the identical rates $Z_p = Z_m$ imply identical "energies of activation"[3] for each *m*- and *p*-X pair (see ref 1, energy diagram C), which in turn suggests either unrearranged[13] (*e.g.*, III) or rearranged[15] (*e.g.*, II) molecular ions of the same energy. For substituents X = Cl, Br, the different rates $Z_p > Z_m$ indicate different energies of activation ($E_m > E_p$) for each *m*- and *p*-X pair (see ref 1, energy diagram A), which in turn argues for unrearranged (III) molecular ions of differing energies. However, as suggested by the voltage independence of Z_p/Z_m, the transition states for the M − H reaction still have the same energy for each *m*- and *p*-X pair, and therefore in all probability, the same tropylium-like structures, leading to M − H ions IV (X = Cl, Br).

For substituents X = OCH_3, Z_p/Z_m decreases with decreasing electron energy as the threshold is approached (Table I), betraying the higher transition-state energy for the *para* isomer. Also $Z_p > Z_m$, and therefore the "energy of activation"[3] is lower for the *para* isomer in this instance. This information permits assignment of unrearranged (benzylic) structures to both transition states and molecular ions (III → V, X = OCH_3).

With all the substituents studied, the nature of the molecular ion and the transition state for the M − H reaction are thus found to be strongly substituent dependent, and it is not surprising that no correlation of over-all rate (log Z/Z_0)[4] with either σ or σ^+ constants is observed.

Table II. Metastable Ion Characteristics for Decomposition Reactions in Substituted Toluenes (I) at 70 eV[18]

X	Transition	Metastable	$\frac{[\text{Metastable}]}{[\text{parent}]} \times 10^3$ *m*-X	*p*-X
OCH_3	$M \rightarrow M - CH_2O$	69.3	1.1	0.33
	$M - 1 \rightarrow M - CH_3O$	68.4	1.3	0.42
CH_3	$M \rightarrow M - CH_3$	78.2	6.3	6.0
	$M - H \rightarrow M - C_2H_3$	59.5	0.80	0.80
F	$M - H \rightarrow M - C_2H_3$	63.2	0.98	0.93
Cl	$M \rightarrow M - Cl$	65.8	4.3	2.3
Br	$M \rightarrow M - Br$	48.2	1.1	1.6
CN	$M \rightarrow M - HCN$	69.2	4.7	4.6
	$M - H \rightarrow M - H_2CN$	68.2	1.6	1.7

Metastable ion characteristics[17] (Table II) have been recorded for decompositions of the molecular ions and the M − H species and are found to be in accord with the kinetic results. Thus identical metastable abundances[18] for decompositions of *m*- and *p*-X pairs of molecular ions when X = CH_3 and CN demonstrate the existence of common, rearranged parent ions (*e.g.*, II), whereas different metastable abundances[18] when X = OCH_3,[19] Cl, and Br militate for unrearranged parent ions (*e.g.*, III). As before,[6] identical metastable abundances for decomposition of *m*- and *p*-X derived M − H ions provide support for the symmetrical tropylium structure (IV) for all substituents except X = OCH_3, when at least the *para* isomer is benzylic (V).[20]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Purchase of the Atlas CH4B mass spectrometer was made possible through Grant No. GB-4939 from the National Science Foundation.

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[13] Ionization potentials of 9.05 and 8.99 eV have been reported[14] for *m*- and *p*-xylene, respectively, but similar data apparently are not presently available for *meta* and *para* isomers of I, X = F or CN.

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

[15] Randomization of hydrogens over the molecule by a series of 1,5-sigmatropic shifts is known to occur in thermally excited cycloheptatriene.[16]

[16] J. A. Berson and M. R. Willcott, *J. Amer. Chem. Soc.*, **88**, 2494 (1966), and references cited therein.

[17] T. W. Shannon and F. W. McLafferty, *ibid.*, **88**, 5021 (1966), and subsequent papers in this series.

[18] Metastable abundances were measured over the energy range 70–12 eV, below which their intensities were too low for accurate measurement.

[19] In I, X = OCH_3, however, identical[18] metastable ion characteristics for the *meta* and *para* isomers for an M − CH_3 process (M − CD_3 in I, X = OCD_3) were observed, which means that at least some molecular ion rearrangement is occurring in this case. Together with the kinetic data, this directly implicates at least two different molecular ions (*e.g.*, II and III, X = OCH_3) in unknown proportions, one rearranged and the other not, for each *m*- and *p*-OCH_3 isomer.

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

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Isolation of Ketone Enolates as Trialkylsilyl Ethers

Sir:

Enolate ions occupy a central place in the chemistry of carbonyl compounds. In connection with our continuing interest in the alkylation of ketones and aldehydes, it became desirable to find a method of trapping