Hydrogen Bonding in Mass Spectral Activated Complexes. A Correction

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A previous hypothesis that hydrogen bonding tightens transition states for loss of keten from *ortho*-substituted acetanilides is found not to be generally supported.

RECENTLY in our study of the application of simplified QET to *ortho*-substituent effects in mass spectra, we examined trends in the *ortho* : *para* ratio of pre-exponential factors for loss of keten from halogeno-acetanilides.[1] The data show the greatest retardation for Cl and Br, and much less for F and I. This trend might be interpreted [1] as a hydrogen-bonding effect on the activated complex, since hydrogen bonds in *ortho*-halogenoacetanilides have strengths in solution which follow this trend.[2]

In order to test the postulate that hydrogen bonding is important enough to cause such substantial changes (more than three orders of magnitude) in the pre-exponential factor, we examined *ortho* : *para* ratios for the hydroxy, amino, and methyl substituents, in which hydrogen bonding involving the acetamido-group ought also to exist in the *ortho*-compounds. We report now that hydrogen bonding in these *ortho*-compounds has little effect on the pre-exponential factor. Hence the role of hydrogen bonding as the cause of the previously

[1] S. A. Benezra and M. M. Bursey, *J. Chem. Soc.* (*B*), 1971, 1515.

[2] L. K. Dyall and J. F. Kemp, *Spectrochim. Acta*, 1966, **22**, 483.

observed change in acetanilides is considerably less, and considerably less general, than we had supposed: it accounts for only a single order of magnitude in the reduction of the pre-exponential factor, even given all the possible hydrogen-bonding arrangements possible in these compounds.

EXPERIMENTAL

Synthesis.—The acetates of *o*- and *p*-cresol, and *o*- and *p*-toluidine were prepared according to Vogel; [3] the monoacetate of catechol was prepared by Green's method [4] and hydroquinone acetate by Olcott's.[5] The *o*-aminoacetanilide was prepared by acetylation of *o*-nitroaniline and catalytic reduction of the nitro-group; the other compounds were commercially available. All had m.p.s in agreement with the literature.

Mass Spectra, Onset Potentials, Calculations.—All of these were obtained or carried out as described previously; [1,6] care was taken to avoid thermolysis of compounds in the source.

RESULTS

Table 1 lists onset potentials for the molecular ion, $[M - CH_2CO]^{+\cdot}$, and CH_3CO^+, the only ions formed below 20 eV in the compounds. These values were treated by our procedure [1,7] to yield average (in the range 16—20 V) values of K, the pre-exponential factor, listed in Table 2. Table 2 also lists the *ortho* : *para* ratios for related pairs of compounds.

The *ortho* : *para* ratio for these five pairs of compounds is always less than one; the variability of K over the range 16—20 V, a measure of poorness of our approximate energy distribution, is on the average half an order of magnitude. Hence these ratios cannot be distinguished from one, in remarkable contrast to the data for the halogenoacetanilides. At the same time, a choice of 3×10^{13} for the simple dissociation to form CH_3CO^+ as a value of K gives a good fit (error $<10\%$) for all of the compounds except the hydroxy-compounds (both *o*- and *p*-) where calculated values are small by a somewhat larger value. Considering that the method is not capable of giving good fits within three to four volts of the A.P., we consider this fact an indication of the high predictive utility of the method.

TABLE 1

Onset potentials [a]

Compound	I.P. (eV)	A.P. ($M - 42$) (eV)	A.P. − I.P. (eV)	A.P. (43) (eV)
o-MeC_6H_4OAc	8·38	9·44	1·06	13·16
p-MeC_6H_4OAc	7·84	9·26	1·42	13·47
o-MeC_6H_4NHAc	8·03	10·05	2·02	13·97
p-MeC_6H_4NHAc	7·75	10·12	2·37	14·21
o-HOC_6H_4OAc	8·16	9·30	1·14	12·54
p-HOC_6H_4OAc	8·12	9·28	1·16	13·83
o-HOC_6H_4NHAc	7·01	9·41	2·40	13·46
p-HOC_6H_4NHAc	7·57	9·82	2·25	13·52
o-$H_2NC_6H_4NHAc$	7·39	10·49	3·10	13·93
p-$H_2NC_6H_4NHAc$	7·12	10·06	2·94	13·72

[a] Average reproducibility for triplicate determinations 0·02 eV; internal consistency of data was estimated as 0·04 eV from previous experience with correlative data.[6]

TABLE 2

Pre-exponential factors

Compound	K	K_o K_p
o-MeC_6H_4OAc	3×10^7	0·1
p-MeC_6H_4OAc	3×10^8	
o-MeC_6H_4NHAc	2×10^8	0·4
p-MeC_6H_4NHAc	5×10^8	
o-HOC_6H_4OAc	1×10^8	0·2
p-HOC_6H_4OAc	6×10^8	
o-HOC_6H_4NHAc	2×10^9	0·5
p-HOC_6H_4NHAc	4×10^9	
o-$H_2NC_6H_4NHAc$	3×10^9	3
p-$H_2NC_6H_4NHAc$	1×10^9	

As noted above, our interpretation of these results is that hydrogen bonding does not play an important role in tightening the activated complex in acetanilides. We therefore must abandon our hypothesis [1] that this is the case in the halogenoacetanilides and seek other explanations of the reduction of the pre-exponential factor in *ortho*-halogenoacetanilides.

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[3] A. I. Vogel, 'Textbook of Practical Organic Chemistry,' 3rd edn., Longmans Green and Co., 1956, pp. 577, 669.
[4] H. Green, *J. Chem. Soc.*, 1927, 500.
[5] H. S. Olcott, *J. Amer. Chem. Soc.*, 1937, **59**, 392.
[6] M. M. Bursey and P. F. Rogerson, *Inorg. Chem.*, 1970, **9**, 676.
[7] S. A. Benezra and M. M. Bursey, *Z. Naturforsch. A*, in the press.