gegen die Gyrofrequenz ω_i der Ionen ist. Andernfalls muß die Zentrifugalkraft berücksichtigt werden. In diesem Fall ist eine Begrenzung der radialen Ausdehnung des Bogenstromes nur möglich, solange $|\Omega| < \omega_i/2$ ist.

Herrn H. GORENFLO danke ich für die Programmierung und sorgfältige Durchführung der numerischen Auswertung der Lösungen. Diese Arbeit wurde im Rahmen des Vertrages zwischen dem Max-Planck-Institut für Plasmaphysik und der Europäischen Atomgemeinschaft über die Zusammenarbeit auf dem Gebiet der Plasmaphysik durchgeführt.

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ortho-Effects in Mass Spectra. Alteration of the Molecular-Ion Energy Distribution in Disubstituted Acetanilides

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Simplified quasi-equilibrium calculations performed on the mass spectra of dihalosubstituted phenyl acetates and acetanilides again uncover the same substituent effects on the rise of k with E for the loss of ketene from phenyl acetates as was determined for the monosubstituted phenyl acetates. However, a new effect is found for the disubstituted acetanilides, removal of excitation probability for low-lying energy states of the molecular ion. This effect parallels the removal of transition probability for the lowest excited state of the neutral molecule.

We have been interested in determining the utility of simplified quasi-equilibrium theory in understanding changes wrought by substituents throughout series of aromatic compounds. We have used one of the approximations of WILLIAMS [1] and have argued that, because we deal with a series of very similar compounds, the errors we make in carrying the approximations required in this approach should be almost equally pertinent to each compound studied. Thus, in comparing numerical results for all the members of a closely related set of compounds, trends of substituent effects within a series may be detected and interpreted.

Recently we studied a series of phenyl acetates and acetanilides [2], substituted at the *ortho* or *para* position with fluorine, chlorine, bromine, or iodine, in order to determine the effect on the pre-exponential term A in Equation (1) [3]

$$k(E) = A[(E-E_0)/E]^n \qquad (1)$$

when the substituent is varied. Equation (1) is applicable in the strict sense only to assemblages of harmonic oscillators; however, empirical studies of the effect of the tightness of the activated complex on the value of A required to fit the Equation to spectra where rearrangements occur show that it has utility as a tool for studying activated complexes [4]. In Eq. (1), E is the internal energy of the ion, E_0 is the threshold energy for the process for which k is studied, and n is an effective number of oscillators determined by the best fit.

We argued in this study that the same probability distribution of energies for the molecular ions of each compound studied could be used because of the similarity of structure for the compounds; as an indication of the relative uniformity of the electronic structure of the neutral compounds, we pointed to the very great similarity of their ultraviolet spectra. This might be taken as a likely indication, though not a proof, that the lower states of the molecular ion corresponding to removal of n or π electrons could be of similar energy and accessibility, since

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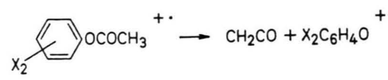
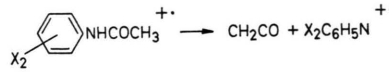
simple promotion of n and π electrons is of similar energy and accessibility in each case.

We now report on our studies of the low-energy spectra of dihalo-substituted phenyl acetates and acetanilides, particularly the effect of *ortho* disubstitution on the preexponential term for Eqs. (2) and (3).



(2)



(3)

Experimental Section

Materials: Tke 2,4- and 2,6-dibromo- and dichlorophenyl acetates were prepared by VOGEL's procedure[5] from the commercially available phenols and purified by vacuum distillation. The difluoro- and diiodophenols were not commercially available; 2,4-difluorphenol was prepared according to a procedure of FINGER and coworkers[6], and 2,6-difluorophenol was supplied by Dr. A. M. ROE[7]. The 2,4-diiodophenol was prepared by BRENANS's procedure[8], and 2,6-diiodophenol was prepared by the procedure of WOOLLETT and coworkers[9]. The acetates were then prepared from these in the same way[5]. Compounds were purified until their melting or boiling points agreed with literature values. Two compounds are new: 2,6-difluorophenyl acetate, b.p. 186 – 188°, m.w. 172.0339, calcd. 172.0334; 2,6-diiodophenyl acetate, m.p. 77 – 79°, m.w. 387.8459, calcd. 387.8454.

The 2,4-difluoro, -dichloro, and -dibromoacetanilides, and the 2,6-dichloro and -dibromoacetanilides, were prepared according to VOGEL's procedure[10] from the commercially available substituted anilines. Dr. A. M. ROE supplied the 2,6-difluoroacetanilide.

Mass spectra, ionization potentials, appearance Potentials, and Calculations: These were obtained or carried out in the same manner as before[2]. The function used for the energy distribution for all compounds was WILLIAMS'[1] $f(E) = \alpha E^{1/2}(E_{\max.} - E)$. The revised function for the 2,6-dihaloacetanilides was finally taken as $f(E) = \alpha E^{3/2}(E_{\max.} - E)$.

Results and Discussion

Ionization and appearance potentials for the ions appearing below 20 eV in the mass spectra of the disubstituted phenyl acetates are given in Table 1.

These ions include the ion of interest formed by Eq. (2) and a competing cleavage to give CH_3CO^+. The data may be compared with similar data for monosubstituted phenyl acetates[2]. No special trends are noted in the comparison of the data, however.

Table 1. Ionization and appearance potentials/eV of ions in mass spectra of disubstituted phenyl acetates[a].

	I.P.	A.P.[M-42]	A.P.-I.P.	A.P.[43]
2,4-F_2	8.60	9.63	1.03	12.00
2,6-F_2	8.88	9.69	0.81	12.24
2,4-Cl_2	8.16	9.37	1.21	12.11
2,6-Cl_2	8.68	9.88	1.20	12.09
2,4-Br_2	8.21	9.45	1.24	12.01
2,6-Br_2	8.42	9.74	1.32	12.36
2,4-I_2	7.90	8.94	1.04	12.15
2,6-I_2	8.07	9.18	1.09	12.02

[a] Average standard deviation of data ±0.03 eV.

The data from Table 1 were then used to calculate spectra between 16 and 20 eV, as Table 2 indicates. In Table 2 the ratio of the intensity of the $[M-42]$ ion to that of the molecular ion is shown

Table 2. Observed and calculated relative intensities for $[M-42]/[M]$.

	eV	Obs.	Calc.	A
2,4-F_2	16	2.38	2.39	6×10^8
	17	3.00	2.90	2×10^8
	18	3.48	3.43	3×10^9
	19	3.91	3.89	8×10^9
	20	4.46	4.43	8×10^9
2,6-F_2	16	0.752	0.724	1×10^7
	17	0.974	0.976	7×10^1
	18	1.13	1.56	2×10^7
	19	1.32	1.13	1×10^7
	20	1.55	1.53	1×10^7
2,4-Cl_2	16	2.48	2.88	1×10^{10}
	17	3.73	3.72	6×10^9
	18	4.34	4.33	2×10^{10}
	19	4.79	4.85	4×10^{10}
	20	5.17	5.12	4×10^{10}
2,6-Cl_2	16	1.47	1.52	2×10^8
	17	1.92	2.04	3×10^8
	18	2.23	2.36	2×10^9
	19	2.47	2.45	4×10^9
	20	2.69	2.63	1×10^9
2,4-Br_2	16	3.16	3.04	1×10^{10}
	17	3.84	3.90	3×10^{10}
	18	4.60	4.62	9×10^{10}
	19	5.18	5.03	1×10^{11}
	20	5.63	5.60	7×10^{10}
2,6-Br_2	16	1.65	1.66	4×10^8
	17	2.00	2.01	3×10^8
	18	2.46	2.41	2×10^8
	19	2.68	2.63	1×10^9
	20	3.11	3.17	6×10^9
2,4-I_2	16	2.15	2.13	3×10^7
	17	2.67	2.65	3×10^8
	18	3.04	3.09	5×10^7
	19	3.38	3.34	5×10^7
	20	3.67	3.66	2×10^8
2,6-I_2	16	1.48	1.53	6×10^7
	17	1.79	1.73	4×10^7
	18	2.12	2.05	4×10^7
	19	2.36	2.35	8×10^7
	20	2.56	2.59	8×10^7

as the observed value and the calculated value for the value of A in Eq. (1) which gives the best fit.

In each of these calculations the value of n is maintained as a constant, so that changes in the rate of rise of k with E are expressed only in the value of A. The variation in A is then a measure of changes in the degree of tightness of the activated complex for Equation (2). According to earlier studies [4], the smaller the value of A, the tighter the activated complex.

Comparing the ratio of A for the 2,6-disubstituted compound and A for the 2,4-disubstituted compound should then yield a picture of the effect of moving the second substituent from the *para* to the *ortho* position. At 20 eV, the voltage where the approximation should give the best fit in the range studied, $A_{2,6}/A_{2,4}$ is about 1×10^{-3} for fluorine, 3×10^{-2} for chlorine, 9×10^{-2} for bromine, and 4×10^{-1} for iodine [11]. It is satisfying to note that the trend of these numbers is in the same direction as the trend of A_{ortho}/A_{para} in the monosubstituted compounds, where the ratio varies from 2×10^{-4} for fluorine to 50 for iodine [2]. This duplication of the trend first of all points out that the result obtained in the first series studied earlier is meaningful, and that the nature of the physical effects causing this trend is the same in both series. It was suggested that the increasing tightness of the complex in the fluorine-substituted compound might be related to a dipolar interaction between the *ortho* substituent and the positive charge residing on the functional group. Such an explanation also explains the effect noted in the present series of compounds. While the change in tightness of the complex has a range of four orders of magnitude in the monosubstituted compounds, it has a range of only two orders of magnitude in the disubstituted compounds. If this difference has a physical significance, it might represent a "saturation" of the effect of dipolar interaction in fluorine; that is, since one *ortho* substituent already interacts with the positive charge, the interaction of the second in the 2,6-disubstituted compounds may not be as great. It should be noted that this is only a tentative explanation, however, since any explanation which can be correlated directly with the electronegativity of the halogens can be used.

We turn now to the dihaloacetanilides and Equation (3). As in the previous case [2], the *ortho* substituent may be lost from the molecular ion in another competing reaction. The ionization and appearance potentials for the difluoro, dichloro, and dibromo compounds are given in Table 3; the diiodo compounds resisted all attempts at synthesis.

Table 3. Ionization and appearance potentials/eV of ions in mass spectra of disubstituted acetanilides [a].

	I.P.	A.P. $[M-42]$	A.P.− I.P.	A.P. $[M-X]$	A.P. [43]
2,4-F_2	8.21	9.70	1.49		13.18
2,6-F_2	8.52	9.52	1.00		13.80
2,4-Cl_2	8.09	10.09	2.00	8.81	13.08
2,6-Cl_2	8.25	9.93	1.68	8.79	13.40
2,4-Br_2	8.08	10.24	2.16	8.84	13.10
2,6-Br_2	8.32	10.02	1.70	8.88	13.21

[a] Average standard deviation 0.03 eV.

No attempt to rationalize the various onset potentials will be made. We note that the ionization potentials for the 2,4-disubstituted compounds are similar to those for the *ortho* and *para* monosubstituted compounds, while the values for the 2,6-disubstituted compounds are higher. Because of the comparative method used [2] for determining onset potentials, the increase in ionization potential could be partially a result of the low intensity of the parent ions of the 2,6-disubstituted compounds in their normal mass spectra at 40 to 70 eV. As in the monosubstituted compounds, the A.P.-I.P. difference for the loss of ketene is lower when the substituent is brought from the *para* to the *ortho* position.

Table 4. Observed and calculated relative intensities for $[M-42]/[M]$.

	eV	Obs.	Calc.	A
2,4-F_2	16	1.49	1.50	2×10^8
	17	1.90	1.85	2×10^8
	18	2.39	2.32	1×10^9
	19	2.43	2.52	4×10^8
	20	2.83	2.97	2×10^8
2,4-Cl_2	16	1.83	1.98	2×10^8
	17	2.45	2.53	2×10^8
	18	2.91	2.68	2×10^8
	19	3.45	3.56	2×10^8
	20	3.94	3.80	2×10^8
2,4-Br_2	16	1.58	1.73	3×10^8
	17	2.09	2.22	3×10^8
	18	2.65	2.46	3×10^8
	19	2.92	3.19	3×10^8
	20	3.52	3.86	4×10^8

Numerical results from fitting the spectra at voltages from 16 to 20 V in the usual fashion are given in Table 4. In order to fit the data it was necessary to choose values of K for the competing loss of halogen in the cases of the chlorine and bromine compounds. The best values in these cases were determined by an iterative procedure and were determined to be 3×10^6 for the dichloro compound and 5×10^6 for the dibromo compound. These values are unexceptional and are comparable to the values obtained for the *para* and *ortho* substituted compounds earlier.

On the other hand, the values for the $[M-42]/[M]$ ratio in the 2,6-disubstituted acetanilides are very high and not easily comparable to those for the 2,4-, *ortho*-, and *para*-compounds: in the case of the difluoro compound the experimental ratio varies from 6 to 10, in the dichloro from 50 to 93, and in the dibromo from 40 to 78. Calculations based on the same model as the other compounds led to very high values of A, in excess of 9×10^{14}. This very high frequency factor is entirely unrealistic, for it corresponds to frequencies greater than the natural vibrational frequencies of chemical bonds by more than an order of magnitude at the very minimum. Consequently, the model must be modified in order to obtain a fit with the experimental facts.

It did not seem reasonable that the exponent should be varied in order to produce a better fit; the number of oscillators in the molecular ion ought to remain the same. Since the ratio indicated an over-production of daughter ions in relation to the molecular ions, it was decided to reduce the fraction of molecular ions by changing the shape of the energy distribution curve. This decision is based on the fact that for the first time among the compounds studied in this series there is a marked difference in the ultraviolet spectra of the 2,6-dihaloacetanilides from the spectra of all the other compounds studied. As a representative example of these data spectra for all the chloro and dichloro compounds are illustrated in Figures 1 and 2. For 2,6-dichloroacetanilide alone, the band at longer wavelength is no longer seen. In analogy with many well known cases[12], this may be a result of serious reduction of the interaction between the acetamido substituent and the aromatic ring. If indeed the substituent is twisted out of the plane of the ring, then just as transitions from the fully conjugated system are no longer seen in the ultraviolet spectrum, so should transitions from this system no longer be seen to states of the molecular ion; the removal of the interaction in the ground state makes the low-energy transitions from it in both the ultraviolet spectrum and the ion excitation spectrum less likely. The same steric factors apply in the different states of the neutral molecule and in the states of the ion because the excitations are all Franck-Condon processes.

Consequently we explored the modification of the assumed probability distribution for energies of the molecular ion $f(\mathrm{E})$ in order to reflect diminished probability of reaching low-energy states of the molecular ion in the actual energy distribution. The function which we had used was that of Williams[1], $f(E) = a E^{1/2}(E_{\max.} - E)$. Our simple modification of this function was to replace it by $f(E) = a E^{3/2}(E_{\max.} - E)$. This has the effect of tilting the energy distribution away from lower to higher energies, as Fig. 3 shows. Many other functions were also generated which accomplished the same redistribution, but no very accurate physical picture can be formulated by attempting to choose between them on the basis of fitting the data. Thus we did not pursue the maximum improvement of the data by changing the $f(E)$ function.

Table 5. Observed and calculated relative intensities for $[M-42]/[M]$.

	eV	Obs.	Calc.	A
2,6-F_2	16	6.58	6.77	2×10^7
	17	7.71	8.67	2×10^7
	18	8.59	6.74	1×10^7
	19	9.40	8.84	1×10^7
	20	10.6	11.2	2×10^7
2,6-Cl_2	16	50.5	50.9	1×10^8
	17	58.8	60.6	8×10^7
	18	73.5	75.0	7×10^7
	19	83.3	85.0	9×10^7
	20	93.3	88.4	5×10^7
2,6-Br_2	16	40.3	35.9	1×10^8
	17	44.7	43.9	9×10^7
	18	59.7	56.8	1×10^8
	19	70.4	70.5	1×10^8
	20	78.1	76.5	7×10^7

When this new function was used in the calculations for the 2,6-disubstituted acetanilides, the values of A for the loss of ketene returned to reasonable values, as shown in Table 5. Again, the chlorine- and bromine-containing compounds have a competing process from the molecular ion, the loss of halogen. The preexponential factors determining the rates of these proceses were again determined by an iterative procedure, and the values giving the best fit to the observed spectra were employed.

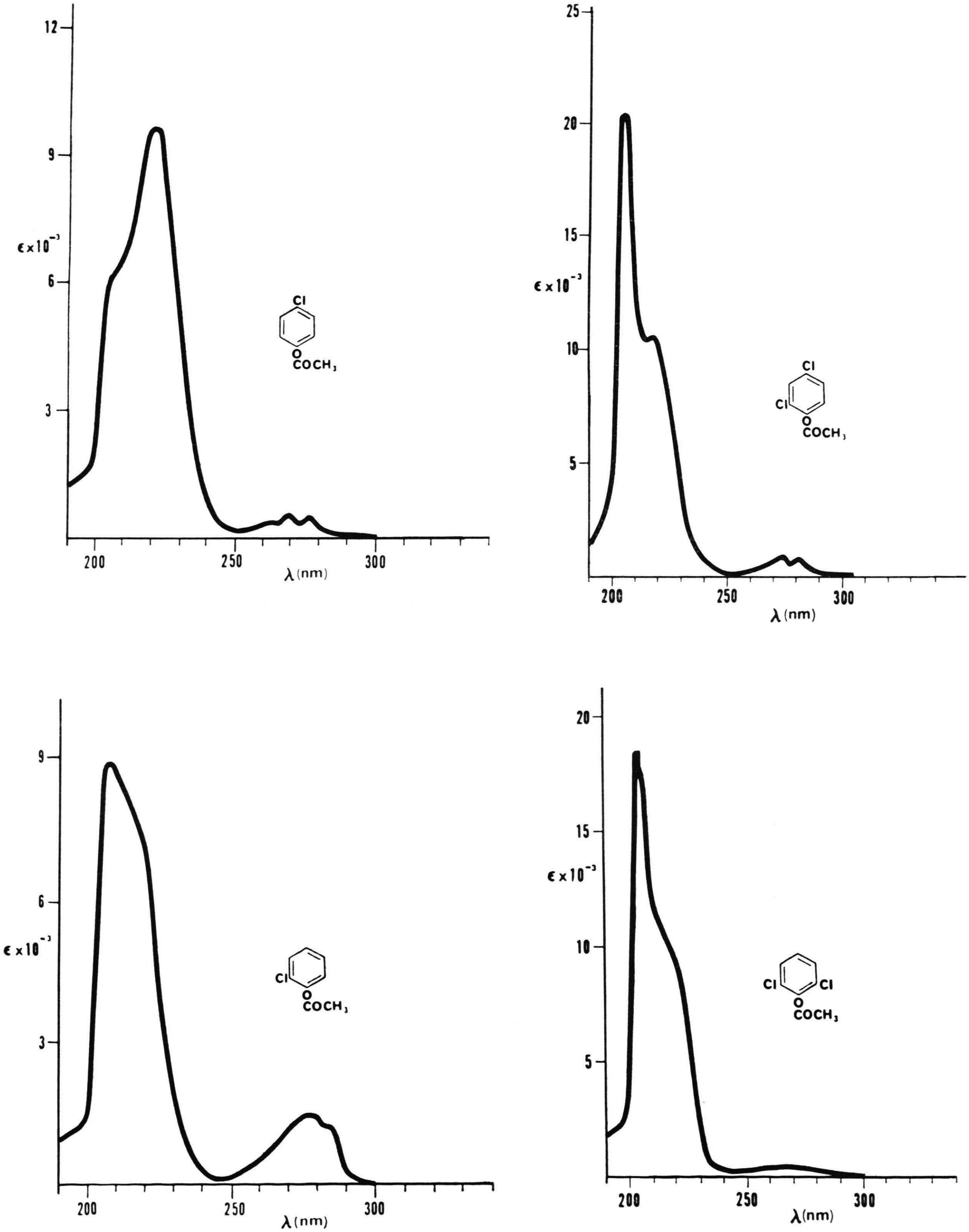


Fig. 1. Ultraviolet spectra of phenyl acetates.

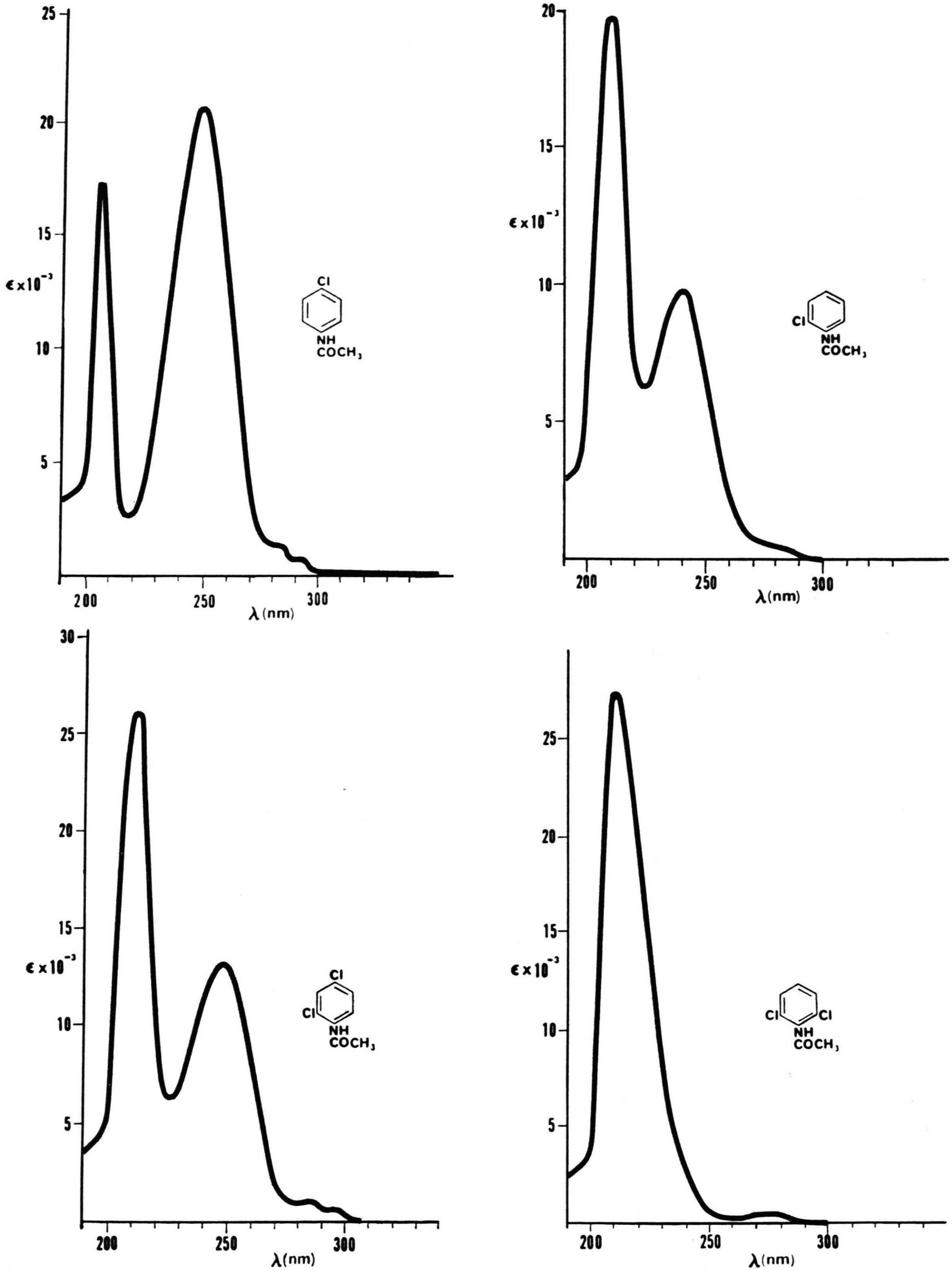


Fig. 2. Ultraviolet spectra of acetanilides. Note the different appearance of the spectrum of the 2,6-disubstituted compound.

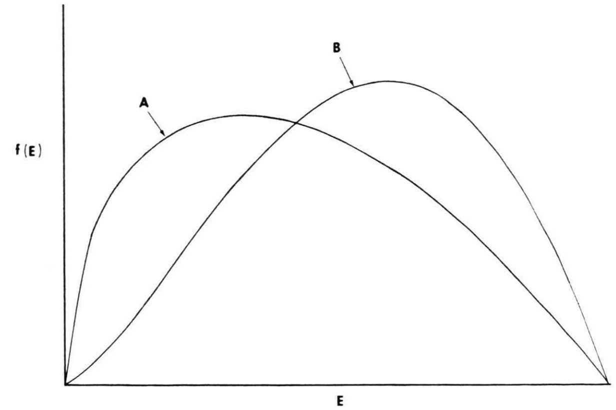


Fig. 3. Energy distribution functions.
A, $f(E)=\alpha E^{1/2}(E_{\text{max.}}-E)$; B, $f(E)=\alpha E^{3/2}(E_{\text{max.}}-E)$.

These are tabulated in the discussion of rates for the loss of halogen, below.

Some question might be raised about the merit of attempting to compare $A_{2,6}/A_{2,4}$ ratios for different substituents, given such discrepancies in the $f(E)$ curves for the 2,6-compounds and the 2,4-compounds. It would appear, however, that since the compounds are closely related in each series, errors brought about by using the assumption would again tend to be canceled when the compounds are compared. At any rate, the ratios for all three substituents are within a factor of three of each other and therefore not significantly different. Apparently, once the acetamide substituent is twisted sufficiently from the plane of the aromatic ring, further differences in interaction between the halogen and the acetamido group are minor for the different halogens.

The competing reaction, loss of halogen, was also studied. Observed and experimental ratios of the $[M-X]$ and molecular ions are given in Table 6. The old distribution function is used for the 2,4-disubstituted compounds and the new function for the 2,6-disubstituted compounds. Once again, as in the *ortho*-substituted compounds studied previously, the activated complex for loss of halogen is even tighter than that for loss of ketene, since the values of A are smaller in Table 6 than in Table 4 or 5, as appropriate. The same conclusions as we drew earlier[2] for the case of the *ortho* substituents apply here, and the same type of mechanism for loss of halogen appears to be occurring here.

Table 6. Observed and calculated relative intensities for $[M-X]/[M]$.

	eV	Obs.	Calc.	A
2,4-Cl_2	16	0.736	0.805	3×10^6
	17	0.756	1.10	3×10^6
	18	0.812	1.41	3×10^6
	19	0.839	1.13	3×10^6
	20	0.871	1.11	3×10^6
2,6-Cl_2	16	31.6	34.4	4×10^6
	17	31.5	37.5	4×10^6
	18	32.6	31.6	3×10^6
	19	32.4	34.7	2×10^6
	20	32.8	34.1	2×10^6
2,4-Br_2	16	1.14	1.32	5×10^6
	17	1.25	1.75	5×10^6
	18	1.35	2.06	5×10^6
	19	1.43	1.85	5×10^6
	20	1.44	1.85	5×10^6
2,6-Br_2	16	49.0	48.0	8×10^6
	17	51.5	48.4	7×10^6
	18	52.9	54.1	4×10^6
	19	51.7	51.9	5×10^6
	20	45.5	49.0	4×10^6

Conclusions

Our purpose in this study as in the previous one is to evaluate a fairly simple approach to mass spectra for its ability to recognize trends of substituent effects in very closely related compounds. This ability appears to be remarkably high. From the present investigation, it may be concluded that the trends found in the first study[2] of the singly substituted phenyl acetates are not an artifice of the method employed, since a very similar trend was observed for the disubstituted phenyl acetates here. Further, the interpretation offered in the first study – dipolar interaction to tighten the activated complex – is consistent with the results obtained in this study as well.

On the other hand, the original model cannot accommodate the results for the 2,6-disubstituted acetanilides, and some distortion of the energy distribution is necessary to make the method fit observed facts. The distortion is also suggested by the unique appearance of the electronic spectra of the 2,6-disubstituted acetanilides. The degree of distortion cannot be gauged accurately by this approximate technique, but it is quite significant that the approximate technique, carefully applied to a long series of closely related compounds, is able to uncover this change. We wish to point out that because this very simple method is capable of detecting trends and new effects which can be confirmed or supported by other studies, it is worthy of examination as a general tool by those interested in uncovering the intramolecular interactions governing the decomposition of organic compounds in the mass spectrometer.

Acknowledgments

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[11] At lower voltages, where the contribution of states of lower energy is more important, the classical harmonic oscillator approximation overestimates the number of states leading to decomposition. Also, it should be pointed out that at lower voltages details of the trend become rougher: at 19 eV, $A_{2,6}/A_{2,4}$ for F is 10^{-3}; Cl, 10^{-1}; Br, 10^{-2}; I, 1.6, for example. The variation of A with voltage would not be expected if the model were truly representative, and the range of values of A represents the range of error introduced by assuming a similar $f(E)$ function of the type chosen for each compound. This range of error is less than the magnitude of the trend from F to I but is great enough to obscure individual steps in the series sometimes, e. g., Cl to Br at 19 eV. More exact $f(E)$ functions would be useful here if they could be obtained.

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