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The Mass Spectral Fragmentation of Halogenated Phenetoles. Absence of an *ortho* Effect

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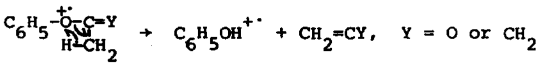
Recently studies on the application of simplified quasi-equilibrium theory to the rearrangement of phenyl acetates have suggested an effect correlated with electronegativity on retardation of the rate for loss of ketene. That is, the "frequency factor" A in the expression

$$k(E) = A\left[\frac{E - E_0}{E}\right]^N$$

is decreased substantially when fluorine is moved from the *para* to the *ortho* position, but not so much when chlorine, bromine, or iodine is moved from the *para* to the *ortho* position.[1] The same trend as one goes down the periodic table is also observed when the 2,6-dihalo- and the 2,4-dihalophenylacetates are compared with each other.[2] It is not clear why this trend should occur, and therefore we have studied the *o*- and *p*-halophenetoles and most of the 2,6- and 2,4-dihalophenetoles as a possible analogy. There is evidence that the loss of ketene from phenyl acetates[3,4] and the loss of ethylene from phenetoles[5-7] proceeds through a four membered activated complex (Eq. 1). Thermochemical evidence for a six-membered complex for phenetole[8] has been



$$C_6H_5\text{-}\overset{+\cdot}{O}\text{-}C{=}Y,\ H\text{-}CH_2 \rightarrow C_6H_5OH^{+\cdot} + CH_2{=}CY, \quad Y = O \text{ or } CH_2 \qquad (1)$$

quoted but is rendered questionable by considerations of contribution of the activation energy of the reverse of the rearrangement reaction.[5,9] Of paramount significance for our discussion, however, is the fact that substituted phenetoles and substituted phenyl acetates lose C_2H_4 and CH_2CO respectively to give ions which decompose in quantitatively similar fashion and therefore are suggested to be of similar structure.[5] The mechanisms for these two processes must therefore be closely related. Comparison of these systems then should shed light on the unusual substituent effect in the phenyl acetates, the behavior of which cannot be correlated with other systems for lack of data.

The same assumptions as before were made:[1,2] an energy distribution is assumed which, if it is in error, will be in error almost equally for all compounds because the compounds are so similar. Further, the energy term is raised to the same power for all members of the series since the compounds have the same number of oscillators and are very closely related structurally.

Data for ionization and appearance potentials collected by our usual method[1,2] are indicated in Table 1; we emphasize that our data are *internally consistent* within 0.03 eV (*cf.* close internal correlations in other data sets[10-12]) but that the absolute values may be in error by somewhat more (the photoionization potential for phenetole is 8.13 ± 0.02 V[13]). Comparison of results obtained with these data within a narrowly defined set then is valid, since errors of method will nearly cancel within the set.

Table 1. Ionization and Appearance Potentials in Phenetoles*

Compound	I.P.	A.P.[M-28]	A.P.-I.P.	Compound	I.P.	A.P.[M-28]	A.P.-I.P.
phenetole	8.05	10.10	2.05				
p-F	8.02	10.49	2.47				
p-Cl	7.87	10.62	2.75	2,4-Cl_2	8.05	10.28	2.23
p-Br	7.87	10.59	2.72	2,4-Br_2	8.00	10.24	2.24
p-I	7.81	10.40	2.59	2,4-I_2	7.91	9.61	1.70
o-F	8.24	10.33	2.09				
o-Cl	8.12	10.19	2.07	2,6-Cl_2	8.46	10.01	1.55
o-Br	8.08	10.18	2.10	2,6-Br_2	8.43	9.98	1.55
o-I	8.02	10.05	2.03	2,6-I_2	8.05	9.58	1.53

*No other processes below 20 V; data are in V

The values of the pre-exponential factor A giving the best fit to the calculated intensities are given in Table 2. The correspondence between observed and calculated intensities is worst (error $\overset{\sim}{<}$ 7%) when the logarithmic step between values tested for the pre-exponential factor ($= 1, 2, 3, \ldots \times 10^n$) is largest, as expected. The ratios A_o/A_p, which we use as a measure of *ortho* substituent interference in the activated complex, are indicated in Table 3. It is immediately obvious that all of the ratios are within an order of magnitude of each other, and therefore are indistinguishable by our estimate of error in the approximations[1,2] involved. We conclude that the influence of *ortho* substituents on the tightness of the activated complex for Eq. 1 in the phenetoles is practically nil. This conclusion stands in spectacular contrast to the interpretation of substituent effects on the analogous reaction in phenyl acetates, in which

Table 2. Optimum Values of A for Fitting Calculated to Observed Values of (M - 28)/M

eV	phenetole A	eV	*p*-F A	eV	*p*-Cl A	eV	*p*-Br A	eV	*p*-I A
16	2×10^8	16	4×10^8	16	2×10^9	16	2×10^9	16	2×10^7
17	2×10^8	17	7×10^8	17	3×10^9	17	2×10^9	17	2×10^7
18	2×10^8	18	8×10^8	18	3×10^9	18	2×10^9	18	1×10^7
19	1×10^8	19	7×10^8	19	3×10^9	19	2×10^9	19	8×10^7
20	1×10^8	20	5×10^8	20	2×10^9	20	9×10^8	20	6×10^7

eV	*o*-F	eV	*o*-Cl	eV	*o*-Br	eV	*o*-I	eV	2,4-Cl_2
16	2×10^8	16	5×10^8	16	3×10^8	16	1×10^8	16	1×10^9
17	2×10^8	17	7×10^8	17	6×10^8	17	8×10^7	17	1×10^9
18	2×10^8	18	8×10^8	18	4×10^8	18	6×10^7	18	1×10^9
19	2×10^8	19	6×10^8	19	4×10^8	19	4×10^7	19	8×10^8
20	1×10^8	20	5×10^8	20	2×10^8	20	3×10^7	20	7×10^8

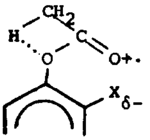
eV	2,4-Br_2	eV	2,4-I_2	eV	2,6-Cl_2	eV	2,6-Br_2	eV	2,6-I_2
16	2×10^9	16	2×10^7	16	2×10^8	16	2×10^8	16	2×10^7
17	2×10^9	17	2×10^7	17	2×10^8	17	1×10^8	17	2×10^7
18	9×10^8	18	1×10^7	18	1×10^8	18	1×10^8	18	1×10^7
19	6×10^8	19	1×10^7	19	8×10^7	19	9×10^7	19	1×10^7
20	5×10^8	20	8×10^6	20	8×10^7	20	6×10^7	20	9×10^6

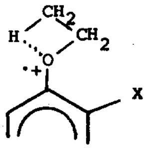
Table 3. A_o/A_p Ratios and $A_{2,6}/A_{2,4}$ Ratios for Halophenetoles*

eV	F	Cl	Br	I
16	0.5	0.2	0.2	0.5
17	0.3	0.2	0.3	0.4
18	0.2	0.3	0.2	0.6
19	0.3	0.2	0.2	0.5
20	0.2	0.2	0.2	0.5
eV		Cl_2	Br_2	I_2
16		0.2	0.1	1.0
17		0.2	0.05	1.0
18		0.1	0.1	1.0
19		0.1	0.2	1.0
20		0.1	0.1	1.1

*Difluorophenetoles were not available.

fluorine exerts a very great tightening effect on the transition state, with a smooth progression in the values of A over five orders of magnitude as one descends to iodine.[1] If the tightening is an internal solvation of the positive charge, as seems reasonable from the close correlation of tightening with electronegativity in the phenyl acetates and from other considerations of such a phenomenon,[14-16] then the charge distribution in ionized phenyl acetates is significantly different from the charge distribution in ionized phenetoles. A hypothesis of ionization of the non-bonding electrons on the carbonyl oxygen in phenyl acetate would at once provide a convenient





geometrical arrangement for internal solvation and also an explanation of the absence of the effect in the phenetoles, where the charge must be located in other orbitals. We are beginning calculations of the electronic distribution in activated complexes for several representative compounds to determine whether this hypothesis can be supported.

The loss of ketene from acetanilides[1,2] cannot be studied by a parallel examination of N-ethyl anilines, since the latter do not decompose by loss of C_2H_4 but lose CH_3 exclusively.[17,18]

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REFERENCES

(1) S. A. Benezra and M. M. Bursey, *J. Chem. Soc., B*, 1515 (1971).
(2) S. A. Benezra and M. M. Bursey, *Z. Naturforsch., A*, in the press.
(3) A. A. Gamble, J. R. Gilbert, and J. G. Tillett, *Org. Mass Spectrom.*, **3**, 1223 (1970).
(4) H. Nakata and A. Tatematsu, *ibid.*, **5**, 1343 (1971).
(5) R. H. Shapiro and K. B. Tomer, *ibid.*, **2**, 579 (1969).
(6) F. W. McLafferty and L. J. Schiff, *ibid.*, **2**, 757 (1969).
(7) I. Howe and D. H. Williams, *Chem. Commun.*, 1195 (1971).
(8) R. G. Gillis, G. J. Long, A. G. Moritz, and J. L. Occolowitz, *Org. Mass Spectrom.*, **1**, 527 (1968).
(9) D. H. Williams, R. G. Cooks, and I. Howe, *J. Amer. Chem. Soc.*, **90**, 6759 (1968).
(10) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *ibid.*, **92**, 519 (1970).
(11) M. M. Bursey and P. F. Rogerson, *Inorg. Chem.*, **9**, 676 (1970).
(12) M. M. Bursey and P. F. Rogerson, *ibid.*, **10**, 1313 (1971).
(13) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).
(14) P. Bommer and K. Biemann, *Ann. Rev. Phys. Chem.*, **16**, 492 (1965).
(15) P. Brown, A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970).
(16) S. Meyerson and L. C. Leitch, *ibid.*, **93**, 2244 (1971).
(17) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p. 323.
(18) R. H. Shapiro and J. Turk, *Org. Mass Spectrom.*, **2**, 1067 (1969).