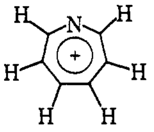
From our data we conclude that, while the C_6H_7N ion is nearly entirely unrearranged, the C_6H_6N ion is largely, at least, rearranged. This result is entirely reasonable since it is, of course, the C_6H_6N ion, an even-electron ion (III),[16] which would correspond to the tropylium ion. The parent ion C_6H_7N is an odd-electron ion[16] which can either lose HCN and C_2H_2 directly or can rearrange to an even-electron ion while losing a hydrogen atom.



III

Acknowledgment. This research was supported by a grant (No. AI 04769) from the National Institute of Allergy and Infectious Diseases. We thank Dr. M. F. Grostic, The Upjohn Co., for assistance in determining the high-resolution mass spectra.

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[16] F. W. McLafferty, in ref 5, p 313 ff. Appropriate symbolism is employed in the present formulas and equations indicating ions as even or odd electron.

[17] National Institutes of Health Predoctoral Fellow, Allied Chemical Co. Fellow.

[18] National Institutes of Health Postdoctoral Trainee in Biophysical Chemistry (Training Grant No. 2TI GM722).

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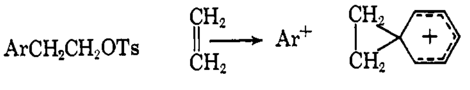
The Solvolysis of Arylethyl *p*-Toluenesulfonates[1]

Sir:

The question of aryl participation[2] has been the subject of recent controversy.[3] We wish to report some studies which have a bearing on this problem, and which also seem to suggest a novel procedure for measuring the nucleophilic activity of nucleophiles.

The idea behind this work was that information can frequently be gained concerning the mechanism of a reaction by comparing the observed relative rates for a number of reactants with those calculated by MO theory, assuming different possible mechanisms. In a study of this kind, it is advisable to use hydrocarbons as reactants, if at all possible, for two reasons: firstly, one avoids in this way the disturbing influence of field and inductive effects which are hard to calculate theoretically, and, secondly, because MO calculations are much easier for hydrocarbons than for molecules containing heteroatoms. This procedure was used very successfully some years ago in studies of aromatic substitution[4] and the solvolysis of arylmethyl chlorides,[5] using a simple perturbational MO approach.

In the case of the assisted solvolysis of a 2-arylethyl tosylate (I), the intermediate ion can be written either as a π complex (II) or a spirocyclopropanoarenonium ion (III).[6] In II the transition state has a structure in which the π MO's of aryl are conjugated with an additional orbital, and which is consequently isoconjugate with the arylmethyl cation, $ArCH_2^+$. The rate of such a reaction should therefore correlate[7] with the difference (δE_π) in π-binding energy between the aryl system Ar and the cation $ArCH_2^+$. In III, one orbital is removed from conjugation, and the rates should correlate with the difference ($\delta E_\pi'$) between Ar and the arenonium ion. Since δE_π and $\delta E_\pi'$ are linearly related, however, the two are indistinguishable by this method. If on the other hand the reaction is not assisted, the rate should be independent of Ar, for Ar is insulated from the reaction center by a methylene group, and any inductive or field effects will be similar for different aryl groups,[8] given that we are concerned only with cases where Ar is a radical derived from a neutral aromatic hydrocarbon.



I II III

A plot of log *k* *vs.* δE_π for such a reaction should therefore be a horizontal straight line if the reactions are all unassisted and a straight line of finite slope if they are all assisted. In the intermediate case, where only the most active aryl groups can participate, the plot should consist of two intersecting straight lines, the value of δE_π at the intersection serving as a measure of the competition between nucleophilic participation by the solvent in a normal SN2-type displacement and participation by aryl in the assisted SN1 reaction.

Winstein and his collaborators[10] have reported an example of the first of these situations: the rates of ethanolysis of 2-phenylethyl (I, Ar = Ph) and 2-(9-anthryl)ethyl (I, Ar = 9-anthryl) tosylates were almost identical. They also showed that in less nucleophilic solvents (acetic and formic acids) the anthryl derivative reacted much faster, implying that the solvolysis must have been assisted. We have now measured the rates of solvolysis of several other 2-arylethyl tosylates[11] in acetic and formic acids, the rate constants being listed in Table I.

Figure 1 shows plots of log *k* *vs.* the NBMO coefficient, a_{0r} (proportional to δE_π),[5] for solvolysis in the two

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[1] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[2] See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] See, *e.g.*, H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

[4] M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

[5] M. J. S. Dewar and R. Sampson, *ibid.*, 2789 (1956); 2946 (1957).

[6] M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1966).

[7] M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 65 (1964).

[8] A referee has claimed that this may be a poor assumption, although it seems to us inherent in the current picture of inductive and field effects. It is generally accepted that the atoms in an alternant hydrocarbon are essentially neutral; such a group could not then exert any field or inductive effects, other than those associated with the polar sp^3–sp^2 bond linking it to an adjacent saturated carbon atom, and these should be similar for different groups of this kind. In any case it is known[9] that an excellent correlation exists between SCF MO delocalization energies and rates of solvolysis for arylmethyl chlorides, a reaction which involves a situation primarily analogous to that in the assisted solvolysis of β-arylethyl derivatives. This result implies very strongly that differential field and/or inductive effects do not interfere with correlations of this kind indicated in the present communication, and also that steric effects due to *peri* hydrogen atoms are likely to be unimportant.

[9] M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965).

[10] S. Winstein, *et al.*, *ibid.*, **87**, 3504 (1965).

[11] All new compounds gave satisfactory analyses, etc.

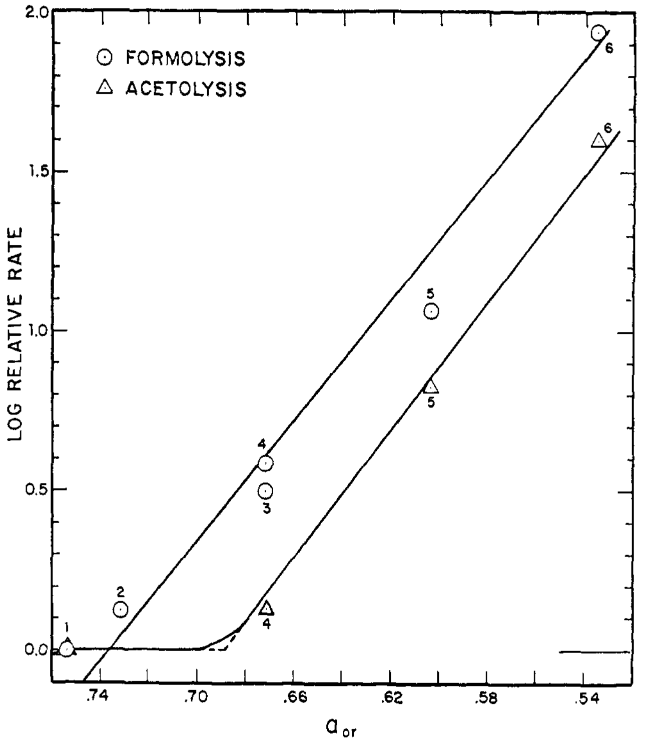

Figure 1.

solvents. The points for formolysis all lie reasonably close to a straight line; the agreement is as good as could be expected, given that the values for a_{or} refer to a system isoconjugate with, but different from, the transition state for assisted solvolysis of I. The plot for acetolysis, on the other hand, consists of two lines intersecting at approximately the point for Ar = α-naphthyl. The general pattern is in complete agreement with our predictions and the results suggest that nucleophilic assistance by the solvent is, as one would expect, less important in formolysis than in acetolysis.

Table I. Rates of Solvolysis of 2-Arylethyl Tosylates (I) at 75°

Tosylate	Acetic acid k, sec^{-1}	k(rel)	Formic acid k, sec^{-1}	k(rel)
2-Phenylethyl (1)	2.88×10^{-7} [a]	1.00	4.56×10^{-5}	1.00
2-(2-Naphthyl)-ethyl (2)			6.03×10^{-5}	1.32
2-(9-Phenanthryl)-ethyl (3)			1.43×10^{-4}	3.14
2-(1-Naphthyl)-ethyl (4)	3.86×10^{-7}	1.34	1.80×10^{-4}	3.95
2-(1-Pyrenyl)-ethyl (5)	1.99×10^{-6}	6.91	5.27×10^{-4}	11.56
2-(9-Anthryl)-ethyl (6)	1.16×10^{-5} [b]	40.28	4.00×10^{-3} [b]	87.72

[a] Data taken from S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **75**, 147 (1953). [b] Data taken from S. Winstein, *et al.*, *ibid.*, **87**, 3504 (1965).

We are continuing these studies to see how well the scale of nucleophilicities defined in this way agrees with that deduced from the method of Dewar and Sampson.[5] We are also investigating the possibility of applying SCF MO to this problem.

(12) NASA Trainee.

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Inductive Effects in Acylsilanes and Acyldisilanes

Sir:

The dominant cause of the abnormally long wavelength absorption of acylsilanes and acylgermanes in both the infrared and $n-\pi^*$[1] ultraviolet regions has been attributed to either inductive effects,[2-5] $\pi(\pi-d)$ bonding between the carbonyl group and the metalloid d orbitals,[6,7] or p–d bonding between the lone pair on oxygen and the silicon "d" orbitals.[8] If $\pi(\pi-d)$ bonding were the major effect involved, the similarity observed in the spectra of acylsilanes and acylgermanes would not have been expected because of dissimilar degrees of π bonding with 3d(silicon) and 4d(germanium) orbitals,[9] and simple calculations of the type carried out by West[6] show that the energies of the 3d-(silicon) orbital and the π^* orbital of a simple carbonyl chromophore differ by about 3.4 eV, a magnitude which would not be expected to lead to extensive overlap. However, no direct experimental evidence has existed to clearly establish which of the effects is the dominant one. We suggest the following data serve to remedy this deficiency.

Studies by Gilman,[10] Kumada,[11] and West[12] have shown that an extended orbital, presumably from overlap of d orbitals, encompasses a polysilane system. It has also been shown that π–d overlap exists in vinylsilane systems.[13] As anticipated, when these two systems are brought together a vinylpolysilane system absorbs at longer wavelength in the ultraviolet than does its monosilane analog ($Me_3SiMe_2SiCH{=}CH_2$ λ_{max} 223 mμ (ε 5200);[14] $Me_3SiCH{=}CH_2$ λ_{max} 202 (1470)), because of the overlap of the disilanyl system with the π-type orbitals of the carbon–carbon double bond. It would then be expected, if $\pi(\pi-d)$ bonding were an important effect in acylsilanes, that an acyldisilane would similarly absorb at longer wavelength

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(1) It is important to recognize that the wavelengths of the $\pi-\pi^*$ transitions of analogous acylcarbon, -silicon, and -germanium compounds differ by no more than a few millimicrons, whereas the $n-\pi^*$ transitions differ by 90–100 mμ.

(2) A. G. Brook, G. E. LeGrow, and R. Kivisikk, *Can. J. Chem.*, **43**, 1175 (1965), and previous publications.

(3) A. G. Brook and J. B. Pierce, *ibid.*, **42**, 298 (1964).

(4) A. G. Brook and G. J. D. Peddle, *ibid.*, **41**, 2351 (1963).

(5) F. Agolini, S. Klemenko, I. G. Csizmadia, and K. Yates, *Acta Spectrochim.*, in press.

(6) D. F. Harnish and R. West, *Inorg. Chem.*, **2**, 1082 (1963).

(7) R. West, *J. Organometal. Chem.* (Amsterdam), **3**, 314 (1963).

(8) A. G. Brook, *et al.*, *J. Am. Chem. Soc.*, **82**, 5102 (1960).

(9) F. Rijkens and G. J. M. Van der Kerk "Organogermanium Chemistry," Germanium Information Center, Midwest Research Institute, Kansas City, Mo., 1964, p 91.

(10) H. Gilman and D Chapman, *J. Organometal. Chem.* (Amsterdam), **5**, 392 (1966).

(11) H. Sakurai, H. Yamamori, and M. Kumada, *Bull. Chem. Soc. Japan*, **38**, 2024 (1965).

(12) G. R. Husk and R. West, *J. Am. Chem. Soc.*, **87**, 3993 (1965).

(13) R. West, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract L-64.

(14) H. Sakurai and M. Kumada, *Bull. Chem. Soc. Japan*, **37**, 1894 (1964).