14. Steric Effects on Reaction Rates. VI. Application of a New MM2 Force-Field for Carbenium Ions to Solvolysis Rates of Secondary *p*-Toluenesulfonates

by **Paul Müller*** and **Jiri Mareda**

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

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An empirical force-field for carbenium ions has been incorporated in *Allinger*'s MM2 programme. Structural parameters of secondary carbenium ions calculated by this method are compared with those obtained with *Schleyer*'s BIGSTRN calculations. The strain changes occurring upon solvolysis of secondary *p*-toluenesulfonates are evaluated by means of this force-field and correlated with the rate constants for solvolysis. The equation for correlation of acetolysis, relative to cyclohexyl *p*-toluenesulfonate, of 28 k_c substrates is $\Delta G^{\ddagger}_{rel} = 0.67\ \Delta E_{st} - 0.20$ ($r = 0.958$).

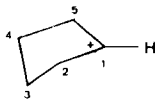
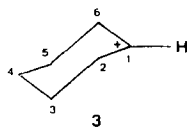
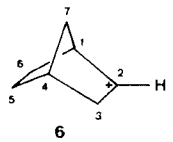
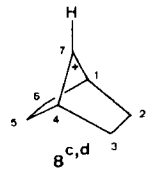
Introduction. – The method of molecular mechanics has been developed to a state that it may be used to calculate with confidence enthalpies of formation, equilibrium geometries and strain energies of hydrocarbons and molecules substituted by a considerable variety of functional groups [1]. Some progress has also been made in application of this method for interpretation of steric effects on reaction rates [2] [3], albeit at much slower pace. The most striking achievement in the field is still *Bingham* and *Schleyer*'s correlation of the rates of solvolysis of tertiary halides and sulfonate esters with the calculated strain changes which are associated with the hybridization change from sp^3 to sp^2 at the reacting center [4]. The success of the calculations with tertiary substrates suggests that an analogous correlation should exist in the secondary series provided that only compounds exhibiting k_c behaviour [5] and exempt of steric inhibition of ionization [5] are considered. The *Foote-Schleyer* correlation for acetolysis of secondary *p*-toluenesulfonates [6] confirms this hypothesis, but the subsequently reported applications of molecular mechanics to the reaction are rather limited in scope [7] so that no conclusion concerning their general validity should be drawn.

The molecular mechanics programmes most widely used today are those of *Schleyer* (BIGSTRN) [8] and *Allinger* (MM1 and MM2) [9]. BIGSTRN is parametrized for saturated hydrocarbons and carbenium ions. In its application to solvolysis the steric requirements of the leaving group are usually approximated with H or CH_3 [4] [7]. MM2 is parametrized for many functional groups, but not for carbenium ions. As a remedy, the carbonyl group has been proposed as a model for estimation of strain in the transition state of *p*-toluenesulfonate solvolysis [3], but the approach fails when highly strained carbenium ions are involved [10].

We describe here a force-field for carbenium ions incorporated into the MM2 programme and its application towards solvolysis of secondary *p*-toluenesulfonates.

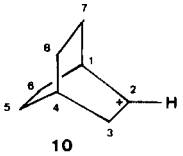
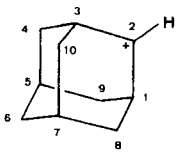
Description and Test of the MM2 Carbenium Ion Force-Field[1]). – The force-field was derived empirically, starting with *Allinger*'s force-field for ketones [9]. Equilibrium distances and force constants for bond stretching were taken from BIGSTRN. For the other parameters, a first set was selected intuitively and then refined until satisfactory agreement in terms of structures and steric energies between both methods was achieved. For the set of parameters *cf.* [11]. *Table 1* shows selected structural data for a series of model compounds for MM2 and BIGSTRN. Some MINDO/3 calculations are also included. Agreement between the molecular mechanics methods is generally satisfactory, while more significant differences appear upon comparison with the semiempirical MINDO/3 method [12].

Table 1. *Selected Structural Data for Carbenium Ions*[a])[b])

Structures		MM2	BIGSTRN	MINDO/3
 2	C(1)–C(2)	1.480	1.478	1.466
	C(1)–H	1.086	1.086	1.106
	C(2)–C(3)	1.540	1.530	1.536
	C(3)–C(4)	1.544	1.533	1.532
	C(2)–*C(1)*–C(5)	117.4	117.8	112.9
	C(2)–*C(1)*–H	121.3	121.1	123.2
	C(1)–*C(5)*–*C(4)*–C(3)	– 28.6	– 28.6	– 3.7
	C(2)–*C(5)*–*C(1)*–H	179.9	179.9	179.6
 3	C(1)–C(2)	1.485	1.485	1.460
	C(1)–H	1.086	1.086	1.110
	C(2)–C(3)	1.535	1.533	1.527
	C(3)–C(4)	1.534	1.534	1.520
	C(2)–*C(1)*–C(6)	119.2	119.7	123.5
	C(2)–*C(1)*–H	120.1	120.2	118.6
	C(1)–*C(2)*–*C(3)*–C(4)	– 51.3	– 51.0	– 30.6
	C(2)–*C(3)*–*C(4)*–C(5)	58.0	57.4	34.9
	C(6)–*C(2)*–*C(1)*–H	177.6	179.8	176.0
 6	C(1)–C(2)	1.480	1.477	1.470
	C(1)–C(7)	1.545	1.524	1.566
	C(2)–C(3)	1.478	1.476	1.489
	C(2)–H	1.085	1.085	1.105
	C(3)–C(4)	1.552	1.539	1.560
	C(4)–C(7)	1.549	1.532	1.566
	C(1)–*C(2)*–C(3)	115.7	116.3	110.4
	C(3)–*C(2)*–H	122.1	121.9	123.9
	C(3)–*C(4)*–*C(1)*–C(6)	113.8	114.7	113.5
	C(3)–*C(4)*–*C(1)*–C(7)	– 123.5	– 122.7	– 122.4
	C(3)–*C(1)*–*C(2)*–H	178.1	179.8	179.6
 8[c,d]	C(1)–C(2)	1.549	1.536	1.562
	C(1)–C(7)	1.466	1.459	1.490
	C(2)–C(3)	1.567	1.553	1.542
	C(7)–H	1.086	1.085	1.106
	C(1)–*C(7)*–C(4)	111.4	112.9	104.0
	C(2)–*C(3)*–H	124.3	123.5	128.1
	C(2)–*C(1)*–*C(4)*–C(5)	114.8	117.6	119.2
	C(2)–*C(1)*–*C(4)*–C(7)	– 122.6	– 121.6	– 120.1
	C(4)–*C(1)*–*C(7)*–H	179.99	– 179.9	– 179.1

[1]) A preliminary report of this work has been published [11].

Table 1 (continued)

Structures		MM2	BIGSTRN	MINDO/3
 **10**	C(1)–C(2)	1.484	1.484	1.469
	C(1)–C(6)	1.539	1.535	1.574
	C(1)–C(7)	1.538	1.535	1.567
	C(2)–C(3)	1.482	1.484	1.476
	C(2)–H	1.086	1.085	1.108
	C(5)–C(6)	1.542	1.542	1.530
	C(1)–*C(2)*–C(3)	118.5	118.5	116.9
	C(1)–*C(2)*–H	120.8	120.7	122.6
	C(3)–*C(4)*–*C(1)*–C(6)	115.6	116.1	118.6
	C(3)–*C(4)*–*C(1)*–C(7)	– 124.2	– 123.3	– 120.1
	C(3)–*C(1)*–*C(2)*–H	179.8	– 179.9	178.8
 **27**	C(1)–C(2)	1.483	1.485	1.478
	C(1)–C(8)	1.537	1.536	1.567
	C(7)–C(8)	1.542	1.541	1.547
	C(7)–C(6)	1.539	1.537	1.552
	C(2)–H	1.086	1.086	1.109
	C(1)–*C(2)*–C(3)	118.5	118.5	119.4
	C(1)–*C(2)*–H	120.8	120.7	120.2
	C(8)–*C(1)*–*C(3)*–C(4)	109.8	109.6	108.8
	C(8)–*C(1)*–*C(3)*–C(2)	– 126.6	– 126.5	– 125.4
	C(1)–*C(9)*–*C(5)*–C(6)	59.9	59.6	58.9
	C(3)–*C(1)*–*C(2)*–H	179.6	179.9	– 179.8

[a]) Bond length C(x)–C(y) in Å; valence angles: C(x)–C(y)–C(z), in degrees; dihedral angles C(w)–*C(x)*–*C(y)*–C(z), in degrees.

[b]) For MINDO/3 calculation of **2** and **6** see [13].

[c]) For MINDO/3 calculations the structure with C_{2v} symmetry was imposed to be compatible with molecular mechanics.

[d]) This structure does not correspond to a global minimum on the MINDO/3 energy surface [14].

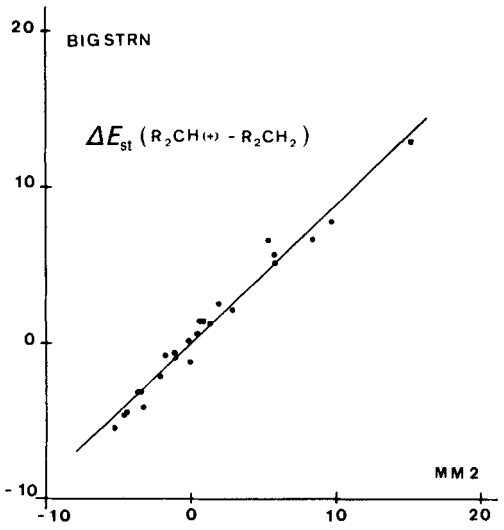


Fig. 1. *Plot of* $\Delta E_{st}(R_2CH\oplus - R_2CH_2)$ *calculated by BIGSTRN* vs. *MM2*. Slope: 0.91, intercept: 0.21, $r = 0.987$.

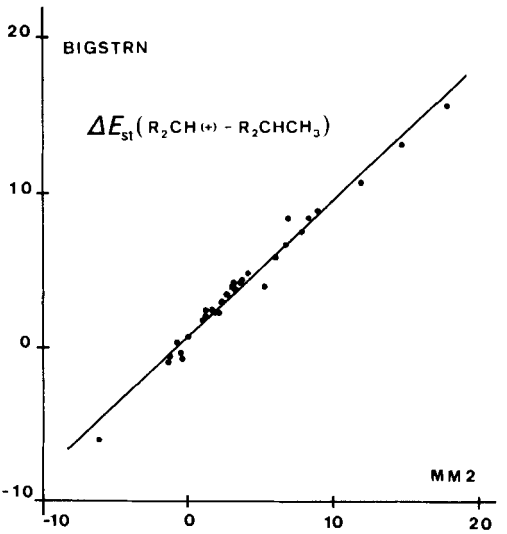


Fig. 2. *Plot of* $\Delta E_{st}(R_2CH\oplus - R_2CHCH_3)$ *calculated by BIGSTRN* vs. *MM2*. Slope: 0.89, intercept: 0.15, $r = 0.989$.

The differences ΔE_{st} for R_CH_2 and $R_2CH\oplus$ calculated with MM2 and BIGSTRN are shown in *Fig. 1*, while *Fig. 2* shows the steric energy differences ΔE_{st} between the methyl derivative R_2CHCH_3 and the corresponding carbenium ion $R_2CH\oplus$. Detailed data are available from the authors upon request. The comparisons show that both methods lead to comparable results. Further, *Harris et al.* [12] have shown that BIGSTRN calculations of tertiary cations are in agreement with their experimentally determined stabilities.

Solvolysis of Secondary *p*-Toluenesulfonates. – Since the MM2 programme is not parametrized for sulfonate groups, we approximated the strain of *p*-toluenesulfonates by that calculated for the corresponding alcohols. This choice is not without pitfalls [3]

Table 2. *Difference of Steric Energies of Carbenium Ions and Alcohols and Acetolysis Rates of Secondary Alkyl* p-*Toluenesulfonates*[a])

Compound	Alkyl	E_{st} (R_2CHOH)	E_{st} ($R_2CH\oplus$)	$-\Delta E_{st}$[b])	$-\Delta G^{\neq}$ (AcOH)[c])	$-\Delta G^{\neq}$ (TFE)[d])
1	Cyclobutyl	30.34	38.70	– 8.36	1.34	
2	Cyclopentyl	12.63	10.95	1.68	2.05	1.90
3	Cyclohexyl	8.22	6.92	1.30	0.00	0.00
4	Bicyclo[2.1.1]hex-2-yl	50.98	57.59	– 6.61	– 0.50	
5	Cycloheptyl	15.56	12.20	3.36	2.42	2.52
6	2-*exo*-Norbornyl(Bicyclo[2.2.1]hept-2-*exo*-yl)	24.46	25.91	– 1.45	3.68	
7	2-*endo*-Norbornyl(Bicyclo[2.2.1]hept-2-*endo*-yl)	24.89	25.91	– 1.02	0.24	0.81
8	7-Norbornyl(Bicyclo[2.2.1]hept-7-yl)	25.40	38.14	– 12.74	– 8.65	
9	Cyclooctyl	20.67	14.79	5.88	3.75	4.80
10	Bicyclo[2.2.2]oct-2-yl	20.99	18.44	2.55	2.51	
11	Bicyclo[3.2.1]oct-2-ax-yl	20.89	19.08	1.81	2.19	
12	Bicyclo[3.2.1]oct-2-eq-yl	20.56	19.08	1.48	0.64	
13	Bicyclo[3.2.1]oct-3-*endo*-yl	22.09	18.06	4.03	2.90	3.82[f])
14	Bicyclo[3.2.1]oct-3-*exo*-yl	20.98	18.06	2.92	1.51	1.99[f])
15	Bicyclo[3.2.1]oct-8-*endo*-yl	21.83	24.95	– 3.12	– 5.58	
16	Bicyclo[3.2.1]oct-8-*exo*-yl	20.92	24.95	– 4.05	– 0.28	
17	2-*endo*-Norbrendyl	45.82	51.51	– 5.69	– 2.73	
18	Cyclononyl	24.56	18.90	5.66	3.67	4.60
19	Bicyclo[3.3.1]non-2-*endo*-yl	19.59	17.10	2.49	0.10[d])	
20	Bicyclo[3.3.1]non-2-*exo*-yl	19.81	17.10	2.71	2.62[d])	
21	Bicyclo[3.3.1]non-3-*endo*-yl	22.78	14.71	8.07	5.53	
22	Bicyclo[3.3.1]non-3-*exo*-yl	19.37	14.71	4.66	4.18	
23	Bicyclo[3.3]nonyl	20.22	18.79	1.43	0.65	
24	2-*ax*-Noradamantyl	31.05	33.24	– 2.19	– 3.19	
25	2-*endo*-Brendyl	34.11	34.45	– 0.34	– 1.62	
26	Cyclodecyl	25.65	19.20	6.45	4.04	4.72
27	2-Adamantyl	18.96	17.74	1.22	– 1.24	– 0.06[f])
28	2-*endo*-Protoadamantyl	30.79	29.13	1.66	– 3.54	
29	Cycloundecyl	27.21	21.82	5.39	2.78	5.35
30	2-*endo*-Homoadamantyl	29.60	26.24	3.36	0.40[d])	
31	2-*exo*-Homoadamantyl	29.58	26.24	3.34	2.00[d])	
32	4-Homoadamantyl	29.24	24.22	5.02	3.32	
33	*endo-exo*-Tetracyclo[6.1.1.^{3,6}0.^{2,7}]dodec-11-syn-yl	55.39	62.46	– 7.07	– 5.34	
34	*exo-exo*-Tetracyclo[6.2.1.1.^{3,6}0.^{2,7}]dodec-11-anti-yl	54.32	60.46	– 6.14	– 3.86	

[a]) Energies in kcal/mol. [b]) $E_{st}(R_2CHOH) - E_{st}(R_2CH\oplus)$. [c]) Relative to cyclohexyl. Data from [3] [6] [7] and [10] and refs. cited therein. [d]) [3]. [e]) Extrapolated from aq. EtOH [17]. [f]) [10].

[15], but we believe from our past experience with secondary substrates [16] that no significant errors are to be expected for the particular series of substrates investigated. Nevertheless, a more detailed study on front strain effects provoked by different leaving groups has been initiated, and it will be published in due course. The rate constants for solvolysis of *p*-toluenesulfonates in AcOH or 97% trifluoroethanol (TFE), summarized in *Table 2*, were retrieved from the literature; they are expressed in terms of free energies of activation ($\Delta G^{\neq}$) relative to cyclohexyl *p*-toluenesulfonate (**2**). For the time being no corrections were applied for polar effects due to different substitution patterns of the substrates at C(β), although such corrections are desirable, particularly for solvents like TFE [18]. However, it was recently found that in rigid molecules the magnitude of the reaction constant ρ depends on the relative orientation of the leaving group and the substituent [17], so that application of the values determined for acyclic substrates [20] appears inappropriate. Since the change in substitution pattern in our series is restricted (only secondary or tertiary C-atoms in β- and β'-positions), we believe that this omission should have no serious consequences.

The *p*-toluenesulfonates selected from *Table 2* are believed to react essentially *via* the k_c mechanism, *i.e.* without significant anchimeric assistance (k_Δ) or leaving group hindrance [5]. This idealized behaviour may not be reached in all cases, but compounds which are clearly not k_c substrates were excluded. *Fig. 3* summarizes the data for solvolysis in AcOH (upper line) and TFE (below, displaced by 10 units in $\Delta G^{\neq}$ for clarity). In both solvents satisfactory correlations are obtained:

$$\Delta G^{\neq}_{rel}\ (\text{AcOH}) = 0.67\ \Delta E_{st} + 0.20\ (r = 0.958)$$

$$\Delta G^{\neq}_{rel}\ (\text{TFE}) = 0.76\ \Delta E_{st} + 0.46\ (r = 0.91)$$

Similar results have been obtained by other investigators. *Smith* and *Harris* [7a] have defined a line characteristic for k_c behaviour based on 6 k_c substrates in the rate range from 7-norbornyl(bicyclo[2.2.1]hept-7-yl) to 2-adamantyl(tricyclo[3.3.1.$1^{3,7}$]dec-

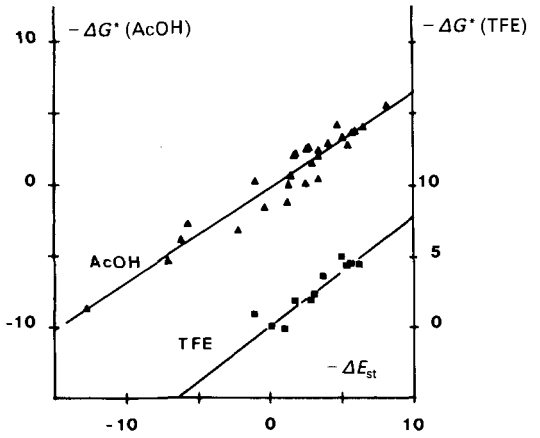


Fig. 3. *Plot of rates of solvolysis ($\Delta G^{\neq}$) in AcOH and TFE* (lower line) vs. ΔE_{st}(*$R_2CHOH-R_2CH\oplus$*). Data from *Table 2*.

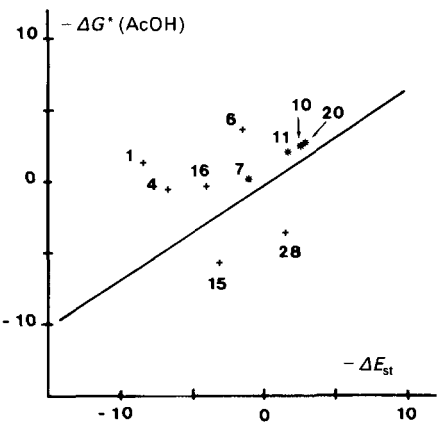


Fig. 4. *Identification of substrates deviating from correlation in AcOH.* * Included in correlation; + excluded.

2-yl) *p*-toluenesulfonates. Their calculations, based on hydrocarbon models, lead to a similar correlation to ours, with a slope of 0.6, if identical units are used. The present calculations extend the rate range by a factor of ~ 2, so that practically the entire range of k_c substrates is covered. We believe that this extension to 28 compounds adds substantial credibility to the k_c line of *Smith* and *Harris* [7a]. The correlations of *Schneider* and *Thomas* [3] correlate strain differences between methylcycloalkanes and the corresponding ketones with the rates of solvolysis of cycloalkyl *p*-toluenesulfonates. We have criticized this work [10] because the carbonyl group rather than the carbenium ion was proposed as model for the solvolysis transition state. However, we now find that within the rate range studied by these authors rather similar results are obtained with both models. The advantage of the carbenium-ion model becomes only evident if solvolysis leads to very strained carbenium ions.

Schneider and *Thomas* [3] proposed solvolysis of cycloalkyl *p*-toluenesulfonates in TFE as representative for k_c behaviour, since in this solvent differential solvent participation (k_s processes) should be negligible. Indeed, they found that solvolysis data from TFE correlate much better with the calculated strain changes of cycloalkyl *p*-toluenesulfonates than data from AcOH. The limited data available for TFE does not allow to generalize this observation to our correlations. Nevertheless, we consider remarkable the fact that even in AcOH monocyclic, bicyclic and polycyclic substrates are correlated by one and the same equation, and this despite of structural differences, polar effects, and possible intervention of k_s and k_Δ terms. The latter are responsible for the scatter in the plot, but the predominant factor is clearly the strain change.

At the origin, the *Foote-Schleyer* correlation was intimately connected with the question of anchimeric assistance in solvolysis, particularly of 2-norbornyl derivatives. The still ongoing controversy concerning the 2-norbornyl cation demonstrates that the principal investigators in the field have not reached agreement. It is not our intention to repeat these arguments here, since they have been presented in a recent symposium [21]. However, we believe that since our strain-reactivity correlation should allow definition of k_c behaviour it may be used to evaluate if a compound is accelerated or retarded. Inspection of the data and of *Fig. 3* shows that 2-*endo*-norbornyl *p*-toluenesulfonate (**7**) fits the k_c line within error limits in both TFE and AcOH. Since k_s contributions are considered weak for this compound [22] even in nucleophilic solvents, its reactivity is adequately described by strain changes, and there appears no need to invoke any combination of other effects. On the other hand the *exo*-isomer **6** reacts faster than expected, not only with respect to the *endo*-compound **7**, but also to all other substrates, particularly the cycloalkyl derivatives. The advantage of the present approach lies precisely in the possibility to compare the steric effects in a particular compound with those of a whole series of reference systems rather than only with its epimer. In our view, an epimer is not necessarily an appropriate point of comparison, and *exo*/*endo* rate ratios alone may always be interpreted in different ways by different authors.

More detailed inspection *(Fig. 4)* reveals that compounds such as **10**, **11**, **16** and **20** which profit from anchimeric assistance during solvolysis [19a] deviate upwards from the plot or fall totally out of the correlation, while their epimers behave normally. Although this comportment corresponds to expectation the scatter in the plot precludes interpretation of deviations in the order of 1 kcal/mol. Large accelerations as in

1, **4** and **6** are, however, clearly recognized. Similarly, one example representative for leaving group hindrance (**28**) [7a] has been included and, as expected, it does not fit the correlation. There remains one point of divergence, namely the low rate of solvolysis of bicyclo[3.2.1]oct-8-*endo*-yl *p*-toluenesulfonate (**15**). While we agree that the *exo*-isomer **16** profits from anchimeric assistance, our calculations show that the rate of **15** may not be described in terms of strain changes alone. The only possible cause for this deviation which we can offer at the present time is leaving-group hindrance, for which there is some, but not conclusive, evidence from model calculations [23]. However, we hope to refine our transition state model in such a way that this effect can be reproduced.

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