Theoretical Studies of Aromatic Substitution. Part II.† Gas-phase Protonation of Benzene and Toluene

By **J. T. Gleghorn** * and **F. W. McConkey**, Department of Chemistry, University of Lancaster, Bailrigg, Lancaster LA1 4YA

Complete structure determinations for the Wheland intermediates in the electrophilic substitution of benzene and toluene, as well as for the unprotonated species, have been carried out using the MINDO/2′ method. Studies of the potential energy surfaces about these energy minima afforded the frequencies of vibration (in the harmonic approximation), from which were constructed vibrational partition functions and vibrational contributions to the free energy and enthalpy functions. Thermodynamic functions for the various species are recorded. The results are compared with existing structural and thermodynamic data, and the relationship of the present calculations to the theory of aromatic substitution is discussed.

DATA on gas-phase aromatic substitution reactions are becoming more readily available following the work of (for example) Cacace,[1] Olah,[2] and Rice,[3] using various contrasting techniques. Of considerable theoretical interest is the prototype electrophilic substitution involving the attack of a proton on an aromatic system. Experimental data for similar reactions have been accumulated by Cacace,[4-6] using the helium tritiide cation as the electrophile. The reactions show little intra-molecular or intermolecular selectivity, but the isomer proportions are not those corresponding to simple statistical attack of the electrophile. It is towards an understanding of the isomer distribution that this and subsequent work will be directed.

The essential ideas of activated complex theory as applied to ion–molecule reactions were expounded by Eyring *et al.*[7] in a study of the hydrogen molecule–hydrogen molecule ion reaction, and the following features may be expected to apply to electrophilic aromatic substitution in the gas phase. If the proton and aromatic molecule have no angular momentum about their common centre of gravity there is no activation energy, *i.e.* the barrier is at infinity. The presence of relative angular momentum in the system produces a centrifugal barrier to reaction, the magnitude of which depends on the rotational quantum number. The varying magnitude of this barrier, in opposition to the attractive ion–molecule (rotation free) potential energy surface, causes the structure of the activated complex to be a function of the rotational quantum number.[8]

As a preliminary study attention has been focused on the ionic reaction products; the transition states themselves will be the subjects of further investigations. For the Wheland intermediates and related species the geometric structures have been optimised, and the vibrational frequencies determined. This information allows the partition functions and thermodynamic functions to be evaluated. Of course the implementation of such a scheme presupposes the use of a semi-empirical method (at present), since an *ab initio* study of the system would be somewhat lengthy! (as a general principle it would seem sensible to perform a reliable semi-empirical study before undertaking calculations of a greater theoretical complexity on such large systems). Within this limitation then the MINDO/2′ method[9] was chosen; it has already been shown to give a reasonable vibrational frequency spectrum for benzene,[10] and is parametrised to give good heats of formation. Furthermore it does not suffer from the original defect in MINDO/2 that the C–H bond lengths are predicted to be typically 0.01 nm too long. Calculations have been performed on benzene, toluene, benzenium cation, and the *o*-, *m*- and *p*-protonated toluenes, as well as on the tropylium and benzyl cations (structure and energy optimisations only for these last two species). All species are closed shell molecules.

METHODS

The structures were optimised using a modified version of QCPE Programme 217, developed by McIver and Komornicki.[11] The method used in the programme employs the analytically derived (from the MINDO/2′ energy formulae) forces, or the gradients of the total energy function with respect to cartesian displacements, in the geometry optimisation. This programme requires the specification of two accuracy criteria, one to test when the geometry convergence has been achieved (at equilibrium the forces on the atoms should be zero, so that the closeness to zero of the gradient components may be used as the criterion), and the other to control the exit from the SCF loop. For the work herein reported the former was taken as 10^{-4} hartree bohr^{-1} (no component of the gradient vector was greater than this figure at convergence), and the latter

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† Part I, J. T. Gleghorn, *J.C.S. Perkin II*, 1972, 479.

[1] F. Cacace, *Adv. Phys. Org. Chem.*, 1970, **8**, 79.

[2] R. C. Dunbar, J. Shen, and G. A. Olah, *J. Amer. Chem. Soc.*, 1972, **94**, 6862.

[3] K. Shobatake, Y. T. Lee, and S. A. Rice, *J. Chem. Phys.*, 1973, **59**, 1435.

[4] F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, 1967, **89**, 6848.

[5] F. Cacace and G. Perez, *J. Chem. Soc.* (*B*), 1971, 2086.

[6] F. Cacace, R. Cipollini, and G. Ciranni, *J. Chem. Soc.* (*B*), 1971, 2089.

[7] S. Glasstone, K. J. Laidler, and H. Eyring, ' Theory of Rate Processes,' McGraw-Hill, New York, 1941.

[8] H. Eyring, H. Gershinowitz, and C. E. Sun, *J. Chem. Phys.*, 1935, **3**, 786.

[9] N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1972, **94**, 5303.

[10] J. T. Gleghorn, S. Hadjipavlou, and F. W. McConkey, *J. Mol. Structure*, 1976, **31**, 187.

criterion was set at 10^{-7} hartree. In fact the exit from the SCF loop is also governed by the accuracy of the density matrix, successive iterations satisfying the energy criterion and producing a change in each element of the density matrix of $<10^{-6}$ to define convergence of the SCF cycle.

The force constant and frequency calculations were performed as described by McIver and Komornicki [11] using displacement magnitudes of *ca.* 0.01 nm. These displacements produce accurate force constants, since the gradient changes are large enough to avoid numerical inaccuracies, and since anharmonic effects are not yet important.[12] It should be noted that highly accurate equilibrium geometries coupled with the use of very small displacement magnitudes ($\leqslant$0.01 nm) give force constants which differ little from those found using larger displacements and less accurate geometries.[13a, b]

With a knowledge of the frequencies of vibration and of the structure of each species, the various thermodynamic functions may be evaluated. Note that MINDO/2′ is being used to generate a potential energy surface at 0 K for the calculation of the force constants, and subsequently of the partition functions, although the method is in fact parametrised to give heats of formation at 298 K. This inconsistency is justified by the results, but clearly it would be more satisfactory if the method were parametrised at 0 K.[14] The formulae for the partition functions were taken from the book by Janz,[15] as were the expressions for the thermodynamic functions. Electronic partition functions have been assumed to be unity, but the excited states of the intermediates have not been investigated. Deviations from unity are expected to be small. The symmetry numbers for internal rotation in the toluene series were taken as 6 for toluene and its *p*-protonated form, and as 3 otherwise. Similarly the symmetry numbers for rigid rotation were taken as 2 for benzenium, 12 for benzene, and 1 otherwise (toluene and all the protonated toluenes).[11]

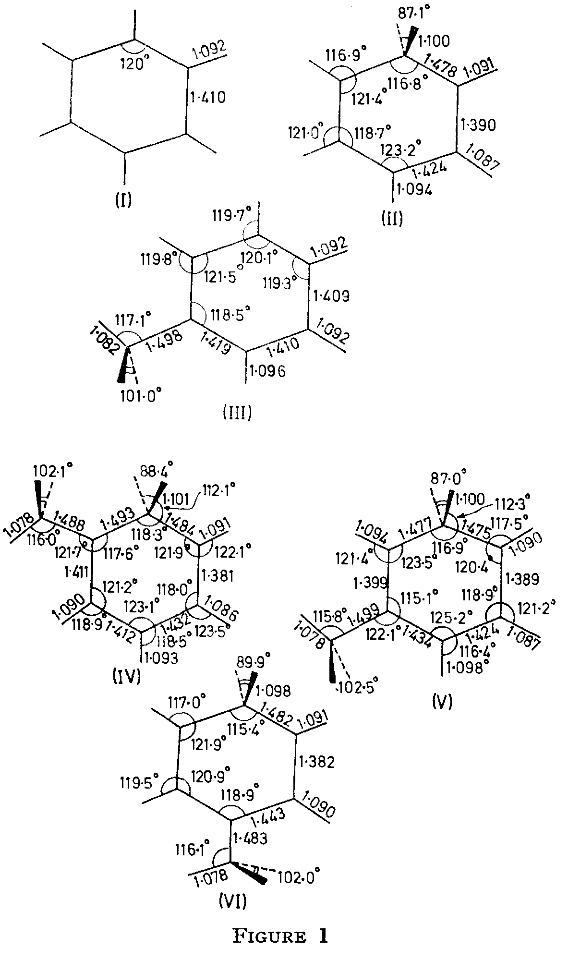

FIGURE 1

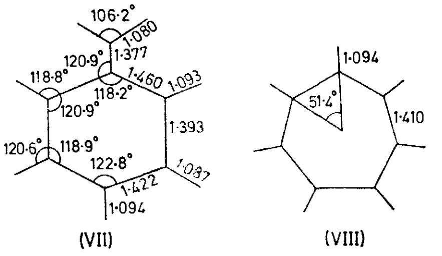

FIGURE 2

RESULTS

The structural parameters of benzene, toluene, benzenium cation, and the *o*-, *m*-, and *p*-toluenium cations are presented as structures (I)—(VI) in Figure 1 (note that the bond lengths and angles relating to the methyl group are averages; small differences may arise for the different rotamers). The additional optimised structures of benzyl cation and tropylium cation are presented as structures (VII) and (VIII) in Figure 2. The calculated heats of formation

TABLE 1

Heats of formation at 298 K (kJmol^{-1})

Species	ΔH_f calculated MINDO/2′	MINDO/2	ΔH_f observed
Benzene	79.0	82.8	80.9 [a,d]
Benzenium	866.2	818.4	848.6 [b]
Toluene	13.4	38.9	49.7 [a,d]
o-Toluenium	784.5	762.0	
m-Toluenium	795.0	777.4	919.6 [c]
p-Toluenium	774.4	750.0	
Tropylium	892.8		907.2 [c]
Benzyl cation	938.0		919.6 [c]

[a] 'Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,' American Petroleum Institute Research Project 44, Carnegie Press, Pittsburg, 1953. [b] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 1969, **73**, 4328. [c] F. H. Field, *J. Amer. Chem. Soc.*, 1967, **89**, 5328. [d] The solution phase proton affinities have been reported as 748 and 767 kJ mol^{-1} for benzene and toluene respectively, S. L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.*, 1972, **94**, 6630.

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[11] J. W. McIver, jun., and A. Komornicki, *J. Amer. Chem. Soc.*, 1972, **94**, 2625.

[12] W. Meyer and P. Pulay, *Theor. Chim. Acta*, 1974, **32**, 253.

[13] (*a*) D. G. Schmidling, *J. Mol. Structure*, 1975, **25**, 313; (*b*) J. T. Gleghorn and F. W. McConkey, *ibid.*, 1975, **29**, 133.

[14] J. W. McIver, jun., and A. Komornicki, *J. Amer. Chem. Soc.*, 1973, **95**, 4512.

[15] G. J. Janz, 'Thermodynamic Properties of Organic Compounds,' Academic Press, London, 1967.

corresponding to the optimised structures are presented in Table 1, and the barriers to internal rotation in Table 2. The calculated partition functions together with the computed zero point energies, are recorded in Table 3. The symmetry numbers used for the evaluation of the rigid rotational, and the free rotational partition functions are those given in the methods section. Finally Table 4 shows the values of the thermodynamic functions $-(G - H_0)/T$, $+(H - H_0)/T$, C_p, and S; the benzene and toluene values may here be compared with experiment.

TABLE 2

Barriers to internal rotation

Species	Conformer energy (hartree) (*a*) *	(b) *	(c) *	Barrier (J mol^{-1})
Toluene	−38.335 69	−38.335 71		50
o-Toluenium	−38.624 97	−38.624 77	−38.625 06	760
m-Toluenium	−38.620 95	−38.620 73	Not calc.	590
p-Tolenium	−38.628 68	−38.628 62		170

* See Figure 3. Conformer (c) is different from (b) only in the non-symmetric *ortho*- and *meta*-cases.

TABLE 3

Computed contributions to the total partition functions at 298 K; zero-point energies

Species	Q_{vib} *	Q_{rot}	$Q_{int. rot}$	Q_{trans} †	Zero-point energy (kJ/mol^{-1})
Benzene	2.61	7.74×10^3		6.65×10^{32}	239.8
Benzenium	4.53	5.03×10^4		6.78×10^{32}	262.0
Toluene	6.17	1.81×10^5	1.82	8.52×10^{32}	305.7
o-Toluenium	12.78	1.92×10^5	3.64	8.66×10^{32}	327.7
m-Toluenium	11.94	1.93×10^5	3.64	8.66×10^{32}	327.6
p-Toluenium	12.06	1.73×10^5	1.82	8.66×10^{32}	328.2

* Relative to the lowest vibrational level. † For a volume of 1 m^3.

TABLE 4

Thermodynamic functions (J K^{-1} mol^{-1})

Species		$-(G° - H°_0)/T$	$+(H° - H°_0)/$T	$C°_p$	$S°$
Benzene	calc	224.5	53.7	95.3	278.2
	obs [a]	222.1	47.7	82.2	268.9
Toluene	calc	264.9	67.8	119.2	332.7
	obs [a]	264.9	60.4	103.5	332.7
Benzenium		244.8	60.3	107.5	305.1
o-Toluenium		277.1	74.4	131.6	351.6
m-Toluenium		276.7	74.8	132.3	351.6
p-Toluenium		271.1	74.0	131.1	345.3

[a] 'Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,' American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, 1953.

The wave-numbers of vibration are not presented here since they would be largely meaningless without extensive commentary on the form of the associated vibrations. The benzene calculation has been reported elsewhere,[10] and the analysis of the other data is under way. Values of the computed wave-numbers and associated data are available on request however.

DISCUSSION

The benzene and toluene ring bond lengths are predicted to be *ca.* 1 pm high, but the agreement with experiment is good.[16,17] Thus the assumption of a regular hexagon perturbed by the methyl group (so that the bonds to the ring carbon joined to the CH_3 group are slightly larger than the hexagon side) made by Rudolph *et al.*,[17] in an attempt to establish the structure of toluene from microwave data, would appear to be a good one. However they are led to reject this structure since it leads to too short an sp^2–sp^3 bond length, which in their view is inconsistent with the electron diffraction results.[18] In the cases of the Wheland intermediates data from both MINDO/2 and MINDO/2′ studies are available. Significant differences in the sp^2–sp^3 bond length are found using the two methods (sp^3 carbon here means that of the CH_2 group); the former method gives a value of *ca.* 145 pm,[19] whilst the latter gives a value of *ca.* 148 pm. Although this latter figure is comparable with that found by Hehre and Pople [20] in their STO-3G study of the benzenium cation, the HCH angle at the sp^3 carbon is predicted by both semiempirical methods to be considerably less than their value of 105°, namely *ca.* 90°. In this respect it may be noted that MINDO/2 has been shown to underestimate HCH bond angles in CH_2XY systems.[13b]

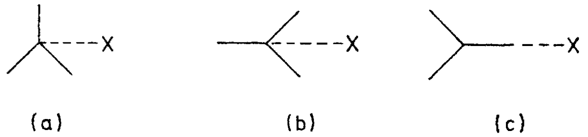

Figure 3 Dispositions of the methyl group with respect to the molecular plane (------) and the CH_2 group (X), where present

The results of Hehre and Pople [20] are in any case not for fully optimised structures, and are estimated by them to be within 25 kJ mol^{-1} of the STO-3G minimum energy configurations for the various molecular symmetries considered. The optimised structures of the toluenium cations may be roughly calculated as perturbed benzenium structures, with the bonds to the methyl snbstituted carbon augmented by 1 pm.

The barriers to internal rotation, calculated by optimising the structures with the methyl group dispositions as shown in Figure 3, and taking the energy difference of the fully optimised structures, were all calculated to be

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[16] A. Langseth and B. P. Stoicheff, *Canad. J. Phys.*, 1956, **34**, 350.

[17] H. D. Rudolph, B. T. Tan, and W. A. Kreiner, *J. Mol. Spectroscopy*, 1973, **48**, 86.

[18] F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, 1956, **25**, 1218.

[19] W. W. Schoeller and G. E. Schenk, *Tetrahedron*, 1973, **29**, 425.

[20] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 6901.

<800 J mol^{-1}. The assumption of free rotation used in the calculation of the internal rotation partition functions is likely to be numerically sound therefore. The *ortho*-cation, as might be expected from the proximity of the CH_2 group, has the largest barrier (800 J mol^{-1}), with *meta*-cation (590), *para*-cation (180), and finally toluene itself (55 J mol^{-1}, or 13 cal mol^{-1}) completing the sequence. The toluene value is in remarkable agreement with the experimental value of 14 cal mol^{-1}.[21] The *ortho*- and *meta*-forms display an asymmetric barrier, with the energies of forms (b) and (c) (see Figure 3) differing in their orientation with respect to the CH_2 group. The minimum energy rotamers of the four species do not have the same dispositions with respect to the ring, but this result may be rather sensitive to the accuracy criteria chosen.

The calculated heats of formation are seen (Table 1) to be in approximate agreement with such experimental data as exists. Note however should be taken of the discrepancy between the value estimated from experimental data [22] and the theoretical values for the toluenium cations; the experimental method would appear to overestimate heats of formation for these species. Evidence for this may be adduced from the compilation of Franklin *et al.*,[23] and from later work by Haney and Franklin [24] using a different technique; the benzenium cation value was earlier reported to be 936 or 982 kJ mol^{-1}, but the later work gave a value of 849 kJ mol^{-1}. Both the 4-31G calculations of Hehre and Pople [20] and the present study support the adoption of the lowest value of the three. If the STO-3G data of Hehre *et al.*[25] for the *p*-protonated toluene species is corrected downwards by *ca.* 165 kJ mol^{-1}, the energy lowering in the benzenium cation case in passing from the STO-3G level to the more accurate 4-31G level,[20] a value for the heat of formation of *ca.* 770 kJ mol^{-1} is obtained, which again is quite consistent with the MINDO results. The values of Hehre *et al.*[25] of course relate to 0 and not to 298 K, as do the MINDO calculations. This agreement then should not be taken at face value, for there are several features of the two methods which distinguish them markedly from each other. In the first place the *ab initio* results [25] have no correlation energy corrections applied to them, whereas the philosophy of the MINDO method is to incorporate correlation effects into the parametrisation of the method.[26] Indeed it does more than that, for in fitting the method to experimental heats of formation MINDO is implicitly correcting for zero-point energy differences as well. Each calculation therefore gives the sum of the Hartree–Fock, the correlation, and the zero-point energies, as well as any contribution due to thermal population of rotational and vibrational levels, so that differences in energy between reactants and products (say) may properly be related to experimental data at ambient temperatures. In the strictly *ab initio* framework the Hartree–Fock potential energy surface is corrected for the correlation energy, and the solution of the rotational–vibrational problem then gives the zero point energy of the system, at 0 K. A simple comparison of the energy difference between the protonated and the unprotonated species at the (approximate) Hartree–Fock level should not simply be comparable with experimental data, although such an energy difference may be accurate to within (say) 50 kJ mol^{-1} as long as the correlation energy difference is small. Although MINDO may be criticised on a theoretical level by the purist, it does, *via* its parametrisation, provide just the sort of energy surface we require. The calculations of the vibrational modes reported herein give zero point energy differences of *ca.* 21 kJ mol^{-1} between benzene and benzenium cation, and between toluene and the toluenium cations. This figure is large because of the extra C–H bond formed in the intermediate, contributing a further $\frac{1}{2}$(3 000 cm^{-1}), or *ca.* 17 kJ mol^{-1}, to the zero point energy of the protonated species. In the light of these reservations about the agreement of the two theoretical methods it is not clear if the theoretical evidence for the rejection of the estimated value for the heat of formation of the toluenium cations is strong enough, but 920 kJ mol^{-1} [22] seems to be too high.

The bending modes are predicted in the neutral species (in the absence of data for comparison with the calculated spectra of the free cations, although the solid-phase benzenium and toluenium ion in i.r. spectra have been reported [27,28]) to be too low,[14] so that the vibrational partition functions are overestimated, and the zero-point energies underestimated. Thus for benzene and toluene the zero-point energies are too low by *ca.* 20 kJ mol^{-1}, compared with the values obtained using the experimental frequencies.[29,30] Whether the method gives similar errors for the cationic species is uncertain; the reported benzenium [27] and toluenium cation [28] spectra are insufficiently detailed to allow meaningful comparison.

The thermodynamic functions $-(G^\circ - H^\circ_0)/T$ and S are (as is well known [15]) dominated by the translational and rotational components, whilst $+(H^\circ - H^\circ_0)/T$ and C_p are more sensitive to the vibrational contribution. For the benzene and toluene molecules the enthalpy and the entropy functions are overestimated by *ca.* 10 J mol^{-1}, whilst the errors in the free energy functions are smaller. The enthalpy values at 298 K for the three

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[21] H. D. Rudolph, H. Dreizler, A. Jaeschke, and P. Wendling, *Z. Naturforsch.*, 1967, **22***a*, 940.

[22] F. H. Field, *J. Amer. Chem. Soc.*, 1967, **89**, 5328.

[23] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 'Ionisation Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' NSRDS–NBS 26, National Bureau of Standards, Washington, 1969.

[24] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 1969, **73**, 4328.

[25] W. J. Hehre, R. T. McIver, jun., J. A. Pople, and P. von. R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 7163.

[26] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 590.

[27] H. H. Perkampus and E. Baumgarten, *Ber. Bunsengesellschaft phys. Chem.*, 1963, **67**, 576.

[28] H. H. Perkampus and E. Baumgarten, *Ber. Bunsengesellschaft phys. Chem.*, 1964, **68**, 70.

[29] S. Brodersen and A. Langseth, *Mat. Fys. Skr. Dan. Vid. Selsk*, 1959, **1**(1), 1.

[30] C. La Lau and R. G. Snyder, *Spectrochim. Acta*, 1971, **27A**, 2073.

toluenium cations reflect accurately the enthalpy differences at 0 K, so that some support for *ab initio* (0 K) comparisons with experimental data (298 K say) may be found. In the light of the near equivalence of the zero-point energies the difference in total energy between the most stable (*para*) isomer and the least stable (*meta*) isomer is only 21 kJ mol^{-1}, with the *ortho*-form having an energy approximately midway between the other two. The free energies of the three forms follow the same pattern at low temperatures, but temperatures above (*ca.*) 1 600 K produce a change in the relative (free energy) stabilities of the *ortho*- and *para*-forms, so that the *ortho*-form becomes more stable. Ultimately, at very high temperatures, the *para*-form becomes the least favoured isomer (due to the greater magnitudes of the temperature dependences of the free energy functions for the *ortho*- and *meta*-forms).

Two types of transition state may be envisaged in these reactions; the former type governs the rate of reaction of the proton with the whole system, and is likely to resemble structurally a slightly perturbed aromatic structure (for low rotational energies), whilst the latter type governs the rate of isomerisation between pairs of isomers. Under the conditions of the highly exothermic reaction studied here the relative energies of the three isomers alone are unlikely to account for the isomer distribution observed. One can envisage essentially statistical attack, followed by isomerisations over the course of several vibrational periods, with final collisional deactivation of the vibrationally excited state. Indeed one could invert the reaction process and consider the unimolecular isomerisations and decompositions of the Wheland intermediates quantitatively, using RRKM theory [31,32] (this is currently under study).

Of course it may not be appropriate to simply consider the vibrationally excited electronic ground state in this scheme; with the highly exothermic reaction we may also have electronically excited states involved. Thus simple PPP calculations [33] show the benzenium cation to have a strongly allowed transition in the near u.v. region of the spectrum (300 kJ mol^{-1} transition energy as opposed to the reaction exothermicity of *ca.* 800 kJ mol^{-1}). Isomerisations could then take place during the lifetime of the lowest excited state before de-excitation occurred, so that a simple treatment based on the properties of the ground state would be invalid. Experimental information on the pressure dependence of the isomer distribution, and on the emitted radiation during the reaction would be valuable in this respect.

The transition state for intramolecular isomerisation has been discussed by Hehre and Pople [20] and by Olah *et al.*,[34] and is depicted in Figure 4. Experimentally [34] it is estimated to lie some 40 kJ mol^{-1} above the benzenium ion energy, whereas MINDO/2′ shows that the symmetric positioning of the hydrogen above the bond corresponds to an intermediate and not to a transition state, differing in this respect from the conclusion of Hehre and Pople.[20] The shallow well has a minimum energy 25 kJ mol^{-1} above the benzenium energy; its appearance may be due to the overestimation of the stability of cyclic systems, commonly found by MINDO when applied to small ring systems.[9] The transition state itself should lie at *ca.* 30 kJ mol^{-1} above benzenium.

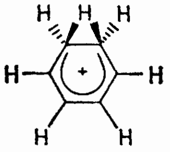

Figure **4**

Finally we mention that the tropyl and benzyl cations have been included in this study since Field [22] indicated that the tropyl and benzyl species had similar heats of formation to his estimated value for the toluenium cations. The values of 893 and 938 kJ mol^{-1} reported here are roughly as indicated by him. As mentioned earlier the toluenium cations are calculated to have substantially different heats of formation from the value of 920 kJ mol^{-1}, so that the near degeneracy is resolved. However the problem of neighbouring potential energy surfaces may become more serious with high vibrational excitation. In passing it is perhaps of interest to note that the uppermost (occupied) MO of tropylium is not of π-symmetry, but that the uppermost π level is only 0.5 kJ mol^{-1} below this σ level (within the MINDO/2′ method).

[5/747 *Received, 21st April*, 1975]

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[31] R. A. Marcus, *J. Chem. Phys.*, 1952, **20**, 359.

[32] M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 94, 927.

[33] J. T. Gleghorn, unpublished results.

[34] G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1972, **94**, 2034.