

C—H Bond Energy of the Triphenylene Radical Cation: a Photoionization Mass Spectrometry Study

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Unimolecular fragmentations of the triphenylene radical cation were studied by photoionization mass spectrometry in the vacuum UV region and by RRKM/QET calculations. The vibrational frequencies of the triphenylene neutral and its radical cation were calculated by density functional theory. The major reactions observed were parallel H[•] and H₂ losses. Activation parameters were deduced for the reactions. The H[•] loss reaction is characterized by a loose transition state, whereas the H₂ elimination has a much tighter transition state. The following heats of formation were deduced: $\Delta H_{f,0}^{\circ}([\text{C}_{18}\text{H}_{11}]^{\bullet+}) = 1202.9 \pm 20 \text{ kJ mol}^{-1}$, $\Delta H_{f,0}^{\circ}([\text{C}_{18}\text{H}_{10}]^{\bullet+}) = 1397.7 \pm 20 \text{ kJ mol}^{-1}$. The C—H bond dissociation energy in the triphenylene radical cation is $3.73 \pm 0.2 \text{ eV}$ ($359.9 \pm 20 \text{ kJ mol}^{-1}$). The effect of the triphenylene structure on the C—H bond dissociation energy deduced for the triphenylene radical cation is discussed. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

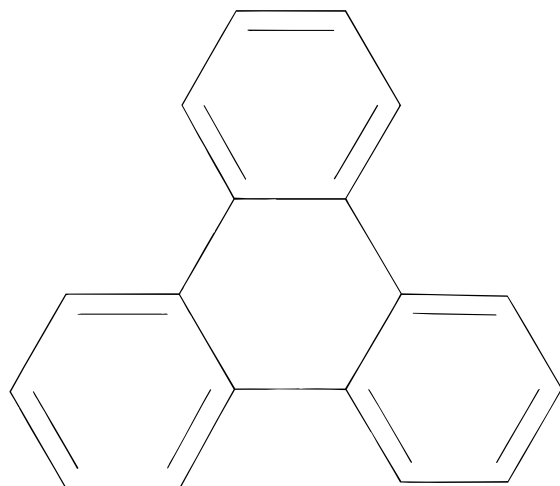
Hydrogen losses from polycyclic aromatic hydrocarbons (PAHs) constitute the major fragmentation reactions for various activation techniques for the isolated ions.^{1–7} The C—H bond strengths of PAH cations are of interest in comparison with each other and also in comparison with the neutral aromatic C—H bonds. The energetics of C—H cleavage of both neutral benzene and benzene radical cation have been thoroughly investigated experimentally.^{8–10} The C—H bond dissociation energy (BDE) of the benzene cation ($3.7 \pm 0.1 \text{ eV} = 357 \pm 10 \text{ kJ mol}^{-1}$) is much lower than that of neutral benzene ($4.7 \pm 0.1 \text{ eV} = 453.5 \pm 10 \text{ kJ mol}^{-1}$). This is due to a bond weakening effect of C—H BDE upon ionization. The C—H BDE of the naphthalene radical cation has been investigated experimentally jointly by time-resolved mass spectrometry¹¹ and by time-resolved photodissociation.¹² A bond weakening effect upon ionization on the C—H BDE has also been observed. The energetics of homolytic C—H bond cleavage in benzenoid hydrocarbons has been studied recently theoretically by density functional calculation.¹³ The reliability of the calculation was supported by the result that the predicted value at 0 K for benzene ($447.3 \text{ kJ mol}^{-1}$) compares well with the experimental

BDE values of 459 ± 3.5 and $468.6 \pm 2.5 \text{ kJ mol}^{-1}$. The calculation shows that the C—H BDEs of neutral PAHs are almost independent of the size of the PAH. Subsequently a PM3 calculation on the PAH molecular cations demonstrated a similar result.¹⁴ The BDEs of C—H bonds were found to be almost independent of the molecular cation size and the environment in the cation and close to those in the neutrals.¹⁴ However, the semiempirical calculation failed to reproduce the available experimental values for benzene⁸ and naphthalene.¹² A series of detailed studies of the vacuum UV (VUV) photoionization and fragmentation of naphthalene,^{3,12} phenanthrene,³ anthracene,⁶ pyrene⁴ and fluoranthene⁵ show that the C—H bond energies in ionic PAHs rise with increasing PAH size and the bond weakening effect upon ionization becomes negligible for anthracene and pyrene.⁷

The aim of the present work was to extend the research on the energetics of PAHs to the triphenylene radical cation (I). It has been mentioned¹ that benzo H—H interactions in phenanthrene and triphenylene may facilitate H-atom loss since the experimental parent ion internal energy at the threshold of H loss reaction is much lower than the calculated value. It has also been observed¹⁵ that the triphenylene radical cation gave the most abundant fragment ion $[\text{M} - 1]^+$ in the unimolecular and collision-induced fragmentations among four isomers with $M = 228$. We demonstrate in this paper that the C—H BDE for the triphenylene radical cation is much smaller than that of the corresponding neutral. This will be explained by triphenylene being made up of a combination of three benzene units.

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(I)

TRIPHENYLENE
Structure I

EXPERIMENTAL

The experimental technique of photoionization mass spectrometry has been described in detail elsewhere,¹⁶ and only a brief description will be given here. Photoionization is induced by a pulsed VUV light source, either the Hinteregger discharge in hydrogen, producing the many-line spectrum, or the Hopfield continuum in He. The effective wavelength resolution employed is 5.0 Å. This corresponds to an energy resolution of ~ 0.025 eV near the ionization threshold of triphenylene (7.8 eV) and of ~ 0.1 eV near the fragmentation onsets.

A simple Knudsen-type molecular beam source for low-volatility compounds constructed earlier³ was used to study triphenylene.

Triphenylene was obtained from Aldrich with a stated minimum purity of 98% and was used without further purification.

RESULTS AND DISCUSSION

Calculation of vibrational frequencies

The vibrational frequencies of the triphenylene neutral and radical cation required in the RRKM calculations were obtained by density functional calculations using the Gaussian 94 package¹⁷ running on a DEC Alpha Turbolaser 8200 3/300 computer at the Hebrew University, Jerusalem. The Becke three-parameter Lee–Yang–Parr (B3LYP) exchange–correlation functional^{18,19} was used throughout, in combination with the 3–21G basis set.^{20,21} We preferred a density functional treatment over a standard Hartree–Fock calculation, since the former is well known²² to be much less sensitive to spin contamination. The very good per-

formance for harmonic frequencies has been well known for some time.^{23–25} The vibrational frequencies of a series of PAHs were investigated by Martin *et al.*²³ with B3LYP/cc-pVDZ and by Langhoff²⁴ with B3LYP/4–31G. It was also shown by Scott and Radom²⁵ that B3LYP/6–31G(d) is one of the most successful procedures for vibrational frequency calculations. It was shown by us⁷ that B3LYP/3–21G frequencies for bromoanthracene are of sufficient quality for RRKM modeling calculations. Expanding to larger basis sets such as cc-pVDZ proved to need an unrealistically long computation time for triphenylene. The geometry of each species was completely optimized at the B3LYP/3–21G level of theory. Vibrational frequencies were computed for all optimized geometries.

The ground state of neutral triphenylene was found to have D_{3h} symmetry. Its cation belongs to the C_{2v} point group because of a Jahn–Teller effect. The computed scaled B3LYP/3–21G vibrational frequencies for neutral triphenylene and its cation are listed in Tables 1 and 2. The E' and E'' vibrations of the neutral (Table 1) are doubly degenerate. The frequencies were scaled by a factor of 0.953 for CH stretching and 0.976 for all other modes. These factors were determined by comparing the computed B3LYP/3–21G harmonics and observed fundamentals for anthracene.⁷

The calculated B3LYP/3–21G frequencies for the triphenylene neutral are compared with the observed data and also the calculated values by a five-parameter force-field approximation.²⁶ Calculated IR intensities > 5 km mol⁻¹ are also given in Table 1. The agreement between the scaled B3LYP/3–21G values and the observed values are better than those between the five-parameter force-field approximation and the observed values. The mean absolute error is 22 cm⁻¹ in the former case compared with 49 cm⁻¹ in the latter.

The calculated IR frequencies and intensities for the triphenylene cation were compared with the calculated B3LYP/4–31G data of Langhoff scaled by his proposed factor of 0.958.²⁴ The difference between our scaled B3LYP/3–21G frequencies are less than 10 cm⁻¹ in most cases and about 20 cm⁻¹ in the worst cases, with a mean absolute error of only 9 cm⁻¹. This confirms the validity of the scaling procedure. It also indicates that the B3LYP/3–21G frequencies are definitely sufficient for the present purpose. The relative intensities are in reasonable agreement with the B3LYP/4–31G results.

Photoionization efficiency curves and appearance energies

Experiment. The total ion photoionization efficiency (PIE) curve for triphenylene was measured over the photon energy range 7.0–21.2 eV and the resultant curve is represented in Fig. 1. Similar resonance peaks to that shown in Fig. 1 were also observed for other PAHs and have been discussed previously.²⁸ They are due to collective plasmon excitations.

The molecular ion PIE curve between 7.70 and 8.70 eV is presented in Fig. 2. The ionization energy, 7.84 ± 0.02 eV, compares favourably with previous determinations: 7.88 ± 0.03 eV from photoionization¹ and 7.84 ± 0.02 eV.²⁹

Table 1. Computed B3LYP/3–21G vibrational frequencies of triphenylene (cm^{-1}) with infrared intensities (km mol^{-1}) in parentheses

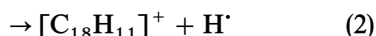
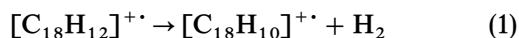
B3LYP/3–21G ^a	NCBC ^b	Expt. ^c	B3LYP/3–21G ^a	BCBC ^b	Expt. ^c
	A_1'			E'	
3096	3035	3055	3093 (34.9)	3041	3085
3061	3030	3040	3077	3035	3070
1555	1599	1550	3058 (30.0)	3032	3038
1450	1530	1458	3045	3030	3024
1308	1434	1341	1599	1656	1611
1227	1185	1230	1566	1590	1579
1209	1106	1180	1514 (14.2)	1535	1500
1068	876	1062	1460 (25.9)	1492	1434
709	675	700	1339	1423	1300
415	332	418	1281	1310	1245
			1269	1169	1167
	A_2'		1211	1120	1144
3072	3041	3062	1118	1005	1110
3044	3032	3030	1064	945	1052
1604	1601	1560	1006	879	1003
1477	1448	1422	786	742	776
1325	1296	1255	643 (5.2)	649	619
1172	1102	1136	408	355	410
1032	1040	1025	261	180	264
627	624	607			
560	506	550			
				E''	
	A_1''		1000	992	980
			949	978	936
995	1081	980	860	903	850
866	978	861	775	843	
770	856		721	766	711
582	595		539	560	570
115	217		429	507	532
			272	312	279
	A_2''		55	141	
960	970	949			
747 (218.3)	755	741			
427 (6.0)	509	422			
119	111	152			

^aThe frequencies are scaled by 0.953 for CH stretching and 0.976 for all other modes. Only IR intensities greater than 5.0 km mol^{-1} are given in parentheses.

^bRef. 26.

^cRef. 27.

We studied two major reaction channels in triphenylene ion, namely, H^\cdot loss and H_2 loss:



The PIE curves for the molecular $[\text{C}_{18}\text{H}_{12}]^{+\cdot}$ and fragment ions $[\text{C}_{18}\text{H}_{11}]^+$ and $[\text{C}_{18}\text{H}_{10}]^{+\cdot}$ are drawn to scale in Fig. 3 for an estimated time of $\sim 24 \mu\text{s}$. The appearance energies (AEs) of the two fragment ions are the same within experimental error ($15.3 \pm 0.2 \text{ eV}$). Values for the AE of C_2H_2 loss have been reported previously.^{1,15} Our own measurement for C_2H_2 loss was not successful because of the low intensity. We found that triphenylene ion intensities were extremely low compared with other PAHs even though these had similar vapor pressures. This may be due to a low ionization efficiency of triphenylene.

RRKM/QET calculations. The PIE curves were modeled by RRKM/QET calculations as described earlier.^{3–6}

The microcanonical rate coefficients $k(E)$ [Eqn (3)] were calculated as a function of energy using an RRKM program.³⁰

$$k(E) = \frac{\sigma G^\ddagger(E - E_0)}{hN(E)} \quad (3)$$

where E_0 is the transition state barrier height, G^\ddagger is the sum of states in the transition state, N is the density of states of the molecular ion and σ is the reaction degeneracy. The scaled B3LYP/3–21G vibrational frequencies of triphenylene cation were adopted as those of the reactant ion. The transition state vibrational frequencies were varied to obtain the best agreement with the experiment. It is widely accepted that the details of the frequency changes in the transition state are not important,³¹ the important factor is the degree of tightness or looseness of the transition state, which is characterized by a single parameter, the activation entropy at 1000 K, $\Delta S_{1000\text{K}}^\ddagger$. The latter is calculated from the vibrational frequencies of the reactant ion and the transition state using standard statistical thermodynamic methods.

Table 2. Computed B3LYP/3-21G vibrational frequencies of triphenylene cation (cm^{-1}) with infrared intensities (km mol^{-1}) in parentheses

B3LYP/3-21G ^a		B3LYP/4-31G ^b		B3LYP/3-21G ^a		B3LYP/4-31G ^b	
Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.
	A_1				B_2		
3118				3117	4.0 (0.01)	3133.7	13.7 (0.04)
3106				3096			
3097				3090			
3081				3080			
3078				3068			
3068				3067			
1575	114.3 (0.41)	1574.6	97.7 (0.31)	1580	4.3 (0.01)	1575.2	10.3 (0.03)
1546		1537.2	14.9 (0.05)	1545	184.6 (0.65)	1538.2	224.3 (0.72)
1524	107.6 (0.38)	1520.1	102.7 (0.33)	1525			
1500	14.2 (0.05)	1485.1	15.5 (0.05)	1472	42.0 (0.15)	1455.0	42.6 (0.14)
1454	43.4 (0.15)	1442.8	37.4 (0.12)	1453	86.2 (0.31)	1433.8	137.1 (0.44)
1442		1434.3	22.8 (0.07)	1383	30.7 (0.11)		
1356	6.8 (0.02)	1357.5	10.6 (0.03)	1332	280.7 (1.00)	1336.0	311.5 (1.00)
1314				1326	16.0 (0.06)	1306.7	18.6 (0.06)
1301	12.2 (0.04)			1281	39.0 (0.14)	1274.0	24.3 (0.08)
1272	35.6 (0.13)	1272.2	51.4 (0.17)	1208	269.9 (0.96)	1189.4	231.4 (0.74)
1248	53.2 (0.19)	1242.0	47.1 (0.15)	1173	18.6 (0.06)		
1225	5.6 (0.02)			1112			
1214	34.8 (0.12)	1192.4	14.6 (0.05)	1074			
1105	9.4 (0.03)			1051	9.5 (0.03)		
1066				1028			
1026				913	125.5 (0.45)	904.2	137.7 (0.44)
980	30.8 (0.11)	973.7	30.5 (0.10)	681	237.2 (0.08)	672.4	242.4 (0.78)
781				614			
691				572			
630	11.5 (0.04)	619.2	10.6 (0.03)	562			
418				309	27.5 (0.10)	306.5	29.4 (0.09)
406				121	160.4 (0.57)	114.3	165.1 (0.53)
260							
	A_2				B_1		
1022				1021			
1017				985			
966				971			
877				870			
861				783	8.5 (0.03)		
779				755	211.1 (0.75)	750.8	180.1 (0.58)
747				695	19.1 (0.07)	686.7	13.3 (0.04)
715				518			
536				423			
492				403			
400				248			
256				116			
94				56			
41							

^a The frequencies are scaled by 0.953 for CH stretching and 0.976 for all other modes. The relative IR intensities are given in parentheses.

^b Ref. 24.

The molecular and fragment ion breakdown curves were calculated from the rate-energy $k(E)$ dependences at 0 K using first-order reaction kinetics for the time appropriate to our experiment. This gives the internal energy dependence of fractional abundances of the ions. Calculated breakdown curves are presented in Fig. 4.

The 0 K breakdown curves were convoluted with the instrumental slit function, with the calculated thermal energy distribution at the temperature of the experiment (473 K) and with the energy deposition function. The photoelectron spectrum of chrysene,³² which is an isomer of triphenylene, was employed as the energy

deposition function because that of triphenylene is not available. The photoelectron spectrum of benz[*a*]anthracene,³³ another isomer, was also tested as an energy deposition function and no effect on the results was observed. The resultant curves following convolution of the 0 K breakdown curves represent the calculated first derivatives of the PIE curves of the ions, provided that the threshold law for photoionization is a step function.³⁴ These curves were integrated to compare them with the experimental PIE curves. The calculated results are compared with the experimental PIE curves in Fig. 3.

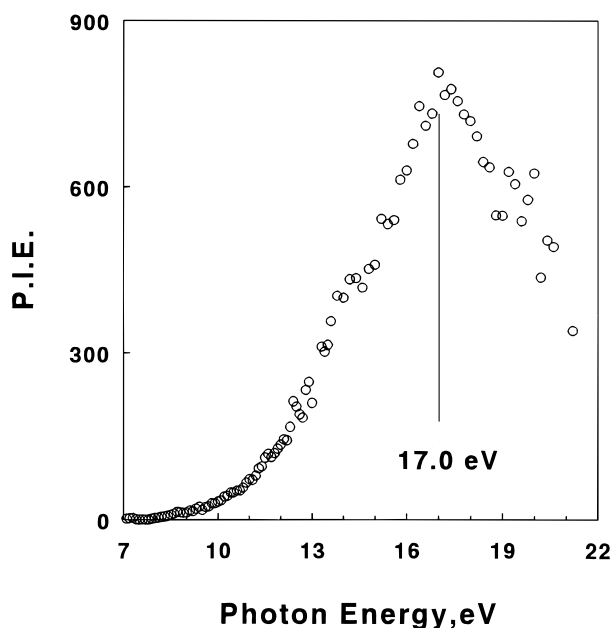


Figure 1. PIE (arbitrary units) for triphenylene ions, without mass selection, in the 7.0–21.2 eV range.

The activation parameters (the critical energies E_0 and activation entropies $\Delta S_{1000\text{K}}^\ddagger$) which best fit the whole set of experimental fragment PIE curves are summarized in Table 3, together with σ values. Figure 5 illustrates our calculated $k(E)$ dependences for the primary parallel reactions in the triphenylene cation.

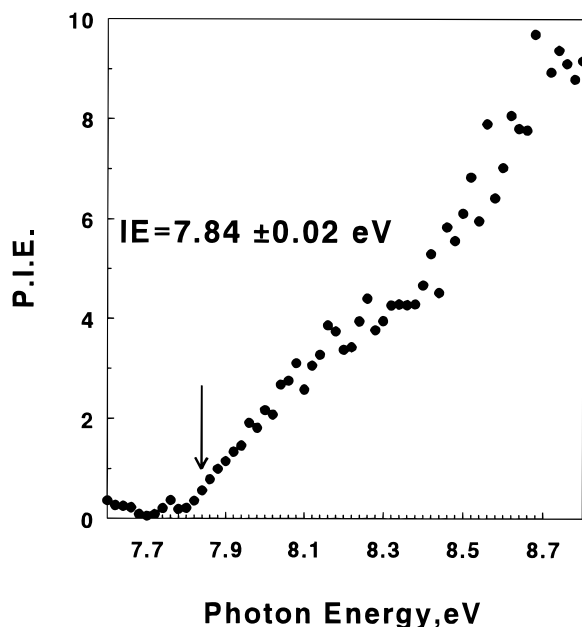


Figure 2. PIE curve for triphenylene molecular ion in the threshold energy range.

Table 3. RRKM/QET parameters for triphenylene cation fragmentations

Reaction	E_0 (eV)	$\Delta S_{1000\text{K}}^\ddagger$ (eu)	σ
H ₂ loss	3.5 ± 0.2	2.0 ± 2.0	9
H loss	3.73 ± 0.2	8.4 ± 2.0	12

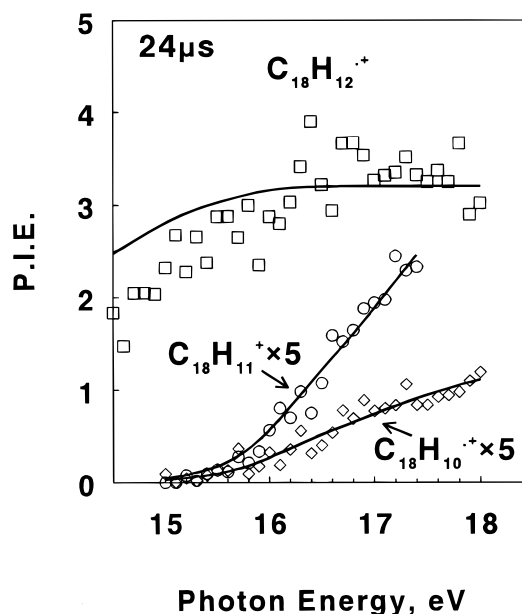


Figure 3. Experimental (\square) $[\text{C}_{18}\text{H}_{12}]^{+\cdot}$; (\circ) $[\text{C}_{18}\text{H}_{11}]^{+\cdot}$; (\diamond) $[\text{C}_{18}\text{H}_{10}]^{+\cdot}$ and calculated PIE curves (lines) for triphenylene in the microsecond range ($\sim 24 \mu\text{s}$).

The experimental appearance energies suffer from large conventional kinetic shifts (CS). It is usually assumed^{3–6} that the CS corresponds to the excess energy required to observe 1% fragmentation on a time-scale of $10 \mu\text{s}$. This corresponds to a rate constant of 10^3 s^{-1} . Our characteristic time is $24 \mu\text{s}$ and 1% fragmentation corresponds to a rate constant of 417 s^{-1} . The AEs and CS values expected for H₂ and H[•] losses can be deduced from the calculated $k(E)$ dependences. They are $\text{AE}(1) = 15.65 \text{ eV}$, $\text{CS}(1) = 4.3 \text{ eV}$ and $\text{AE}(2) = 15.55 \text{ eV}$, $\text{CS}(2) = 4.0 \text{ eV}$, respectively. The experimental AEs ($15.3 \pm 0.2 \text{ eV}$ for both channels) are lower than the predicted values since they are obtained

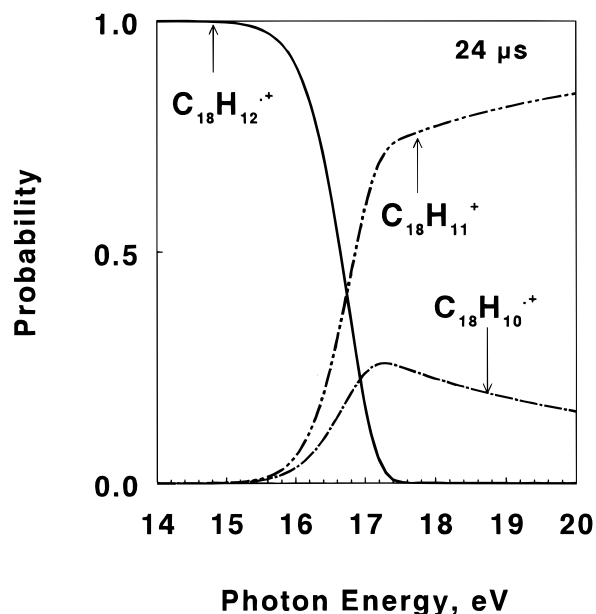


Figure 4. Calculated breakdown curves for triphenylene molecular ($[\text{C}_{18}\text{H}_{12}]^{+\cdot}$) and fragment ions ($[\text{C}_{18}\text{H}_{11}]^{+\cdot}$, $[\text{C}_{18}\text{H}_{10}]^{+\cdot}$) at $24 \mu\text{s}$.

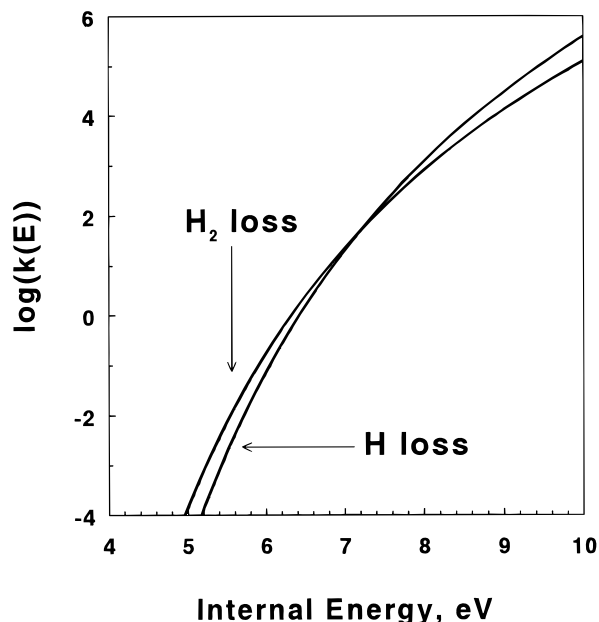


Figure 5. Calculated rate-energy $k(E)$ dependence for triphenylene radical cation dissociation.

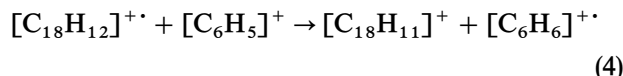
at 473 K and contain a small compensating effect due to the thermal energy of the parent ion.

Thermochemical information and the C—H BDE for the triphenylene radical cation

Reaction (2) is a simple C—H bond cleavage with a loose transition state ($\Delta S_{1000\text{K}}^\ddagger = +8.4$ eu) which is indicative of a negligible reverse activation energy. As a result the critical energy E_2^0 may be equated with the C—H bond dissociation energy of the triphenylene radical cation. This information, combined with additional thermochemical data (Table 4), allows us to calculate the heat of formation of triphenylenyl $[\text{C}_{18}\text{H}_{11}]^+$. The heat of formation of triphenylene at 0 K was calculated from the 298 K value²⁹ and from the

triphenylene neutral frequencies, which are the scaled B3LYP/3-21G values in Table 1, using standard statistical mechanics methods: $\Delta H_{\text{fo}}^\circ(\text{C}_{18}\text{H}_{12}) = 302.5$ kJ mol⁻¹. Employing the ionization energy gives $\Delta H_{\text{fo}}^\circ([\text{C}_{18}\text{H}_{12}]^{+\cdot}) = 1059$ kJ mol⁻¹. Since $\Delta H_{\text{fo}}^\circ(\text{H}^\cdot) = 216.035$ kJ mol⁻¹, we can calculate the heat of formation of $[\text{C}_{18}\text{H}_{11}]^+$: $\Delta H_{\text{fo}}^\circ([\text{C}_{18}\text{H}_{11}]^+) = 1202.9 \pm 20$ kJ mol⁻¹. The heat of formation for $[\text{C}_{18}\text{H}_{10}]^{+\cdot}$ was similarly estimated and is given in Table 4. The C—H bond energy (3.73 ± 0.2 eV = 359.9 ± 20 kJ mol⁻¹) is considerably lower than the value in neutral PAHs (4.7 eV = 453.5 kJ mol⁻¹).¹³ Previous experience⁷ would have led us to the assumption that the bond weakening upon ionization should be negligible for a PAH of the size of triphenylene. The reason for the discrepancy will be discussed.

Although B3LYP/6-311G** is successful in calculating the C—H bond energies of neutral PAHs,¹³ it was found to be unsuccessful in reproducing the C—H bond energies of PAH cations. Different levels of theoretical methods were tried to reproduce the C—H bond energy of the benzene cation, but failed. There is no guarantee for the reliability of PM3 calculations of CH bond dissociation energies of PAH cations.¹⁴ We used the following isodesmic reaction to explore the C—H bond energy of triphenylene radical cation:



The B3LYP/3-21G energies of all the relevant species are given in Table 5. The energy change for reaction (4) at 0 K is -16.3 kJ mol⁻¹. This energy change would be more reliable if higher level calculations were carried out. Nevertheless, the small change indicates that the C—H bond energy of the triphenylene radical cation is close to that of the benzene radical cation. This is probably brought about by the structural similarity of triphenylene and benzene. The triphenylene structure can be viewed as a combination of three benzene rings connected by a six-membered ring, as shown in structure I, rather than a condensed polycyclic aromatic hydrocar-

Table 4. Thermochemical data

Species	$\Delta H_{\text{fo}}^\circ$ (kJ mol ⁻¹)		IE (eV)
	0 K	298.15 K	
$\text{C}_{18}\text{H}_{12}$ (triphenylene)	302.5 ^a	270 ± 1 ^b	7.84 ± 0.02
$[\text{C}_{18}\text{H}_{12}]^{+\cdot}$ (triphenylene)	1059 ^a	1026 ^b	
$[\text{C}_{18}\text{H}_{11}]^+$ (triphenylenyl)	1202.9 ± 20 ^a		
$[\text{C}_{18}\text{H}_{10}]^{+\cdot}$	1397.7 ± 20 ^a		

^a Present results.

^b Ref. 29.

Table 5. B3LYP/3-21G energies (hartree) and zero-point vibrational energies (ZPVE) (kJ mol⁻¹) of relevant species

Species	$\langle S^2 \rangle$	B3LYP/3-21G	ZPVE
Triphenylene, $\text{C}_{18}\text{H}_{12}$, D_{3h} ($^1A_1'$)	0.0000	-689.364 115	639.02
Triphenylene, $[\text{C}_{18}\text{H}_{12}]^{+\cdot}$, C_{2v} (2B_1)	0.7633	-689.089 744	632.83
Triphenylenyl, $[\text{C}_{18}\text{H}_{11}]^+$, C_s ($^3A''$)	2.0262	-688.405 953	599.86
Benzene, $[\text{C}_6\text{H}_6]^{+\cdot}$, D_{2h} ($^2B_{2g}$)	0.7621	-230.643 378	258.65
Phenyl, $[\text{C}_6\text{H}_5]^+$, C_{2v} (3B_1)	2.0169	-229.953 883	227.23

bon. If we take the C—H bond energy of the benzene cation as 357 kJ mol^{-1} , the C—H bond energy of the triphenylene cation calculated from the isodesmic reaction is 341 kJ mol^{-1} . This is $\sim 19 \text{ kJ mol}^{-1}$ lower than our experimental value ($359.9 \text{ kJ mol}^{-1}$), but within the experimental error.

CONCLUSION

Reactions leading to H[•] and H₂ eliminations from the triphenylene radical cation were investigated. The C—H

bond energy of the triphenylene radical cation was determined to be $3.73 \pm 0.2 \text{ eV} = 359.9 \pm 20 \text{ kJ mol}^{-1}$, equal to the benzene value within experimental error. The heats of formation of the key ions have been determined.

Acknowledgements

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REFERENCES

- H. W. Jochims, E. Rühl, H. Baumgärtel, S. Tobita and S. Leach, *Astrophys. J.* **420**, 307 (1994).
- (a) S. J. Pachuta, H. I. Kenttämä, T. M. Sack, R. L. Cerny, K. B. Tomer, M. L. Gross, R. R. Pachuta and R. G. Cooks, *J. Am. Chem. Soc.* **110**, 657 (1988); (b) B. D. Nourse, K. A. Cox, K. L. Morand and R. G. Cooks, *J. Am. Chem. Soc.* **114**, 2010 (1992).
- Y. Gotkis, M. Oleinikova, M. Naor and C. Lifshitz, *J. Phys. Chem.* **97**, 12282 (1993).
- Y. Ling, Y. Gotkis and C. Lifshitz, *Eur. Mass Spectrom.* **1**, 41 (1995).
- Y. Ling and C. Lifshitz, *J. Phys. Chem.* **99**, 11074 (1995).
- Y. Ling and C. Lifshitz, to be published.
- Y. Ling, J. M. L. Martin and C. Lifshitz, *Int. J. Mass Spectrom. Ion Processes* **106**, 39 (1997).
- H. J. Neusser, *J. Phys. Chem.* **93**, 3897 (1989).
- S. J. Klippenstein, J. D. Faulk and R. C. Dunbar, *J. Chem. Phys.* **98**, 243 (1993).
- G. E. Davico, V. M. Bierbaum, C. H. DePuy, G. B. Ellison and R. R. Squires, *J. Am. Chem. Soc.* **117**, 2590 (1995).
- Y. Gotkis, M. Naor, J. Laskin, C. Lifshitz, J. D. Faulk and R. C. Dunbar, *J. Am. Chem. Soc.* **115**, 7402 (1993).
- Y.-P. Ho, C. Dunbar and C. Lifshitz, *J. Am. Chem. Soc.* **117**, 6504 (1995).
- J. Cioslowski, G. Liu, M. Martinov, P. Piskorz and D. Moncrieff, *J. Am. Chem. Soc.* **118**, 5261 (1996).
- K. Fujiwara, A. Harada and J.-I. Aihara, *J. Mass Spectrom.* **31**, 1216 (1996).
- B. Shushan and R. K. Boyd, *Org. Mass Spectrom.* **15**, 445 (1980).
- (a) C. Lifshitz, *Int. J. Mass Spectrom. Ion Processes* **106**, 159 (1991); (b) I. Gotkis and C. Lifshitz, *Org. Mass Spectrom.* **28**, 372 (1993).
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94, Revision C.2*. Gaussian, Pittsburgh, PA (1995).
- A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.* **102**, 939 (1980).
- W. J. Pietro, M. M. Francl, W. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.* **104**, 5039 (1982).
- J. Baker, A. Scheiner and J. Andzelm, *Chem. Phys. Lett.* **216**, 380 (1993).
- J. M. L. Martin, J. El-Yazal and J.-P. François, *J. Phys. Chem.* **100**, 15358 (1996).
- S. R. Langhoff, *J. Phys. Chem.* **100**, 2819 (1996).
- A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).
- G. Neerland, B. N. Cyvin, J. Brunvoll and S. J. Cyvin, *Spectrosc. Lett.* **15**, 137 (1982).
- V. Schettino, *J. Mol. Spectrosc.* **34**, 78 (1970).
- Y. Ling and C. Lifshitz, *Chem. Phys. Lett.* **257**, 587 (1996).
- S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).
- W. L. Hase and D. L. Bunker, *A General RRKM Program*, QCPE No. 234. Chemistry Department, Indiana University, Bloomington, IN.
- C. Lifshitz, *Adv. Mass Spectrom.* **111**, 113 (1988).
- I. Akiyama, R. G. Harvey and P. R. LeBreton, *J. Am. Chem. Soc.* **103**, 6330 (1981).
- M. Shahbaz, I. Akiyama and P. R. LeBreton, *Biochem. Biophys. Res. Commun.* **103**, 25 (1981).
- W. A. Chupka, *J. Chem. Phys.* **30**, 191 (1959).